STI Roadmap: Revised Annex 2 to deliverable 15.1

Graphene and other 2D materials
Technology and Innovation Roadmap
Version 3

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GRAPHENE FLAGSHIP

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1 Introduction

This is the revised and full version of the updated STI roadmap. The roadmap is a living document and will be further updated and adapted over time.

Although the document is quite extensive, the overall idea is that each major section can be seen as a standalone document having the necessary information to get a good insight into the potentials of graphene and 2D materials. The structure of the document and chapters is further described in chapter 1.4: Reading guide to the report.

This roadmap and assessment document summarizes the insights from desk research, interviews and workshops. Furthermore, the original science and technology roadmap was a major source of information. This internal document will be shared with the whole Flagship, so that the insights can be used for the planning of Core 2. Besides that, comments and remarks will be requested. A tailored version, with the content adjusted to a publishable format, will be prepared for open access publication in the next months.

In order to consolidate and structure the content of this roadmap, we pursue a fusion approach (Figure 1): The technology offer by graphene 2D materials in investigated on the one hand and markets/sectors on the other hand, both meet in “application areas”, which are used as a structure. This classification is neither strict nor systematic but should help the reader to quickly find the area of interest.

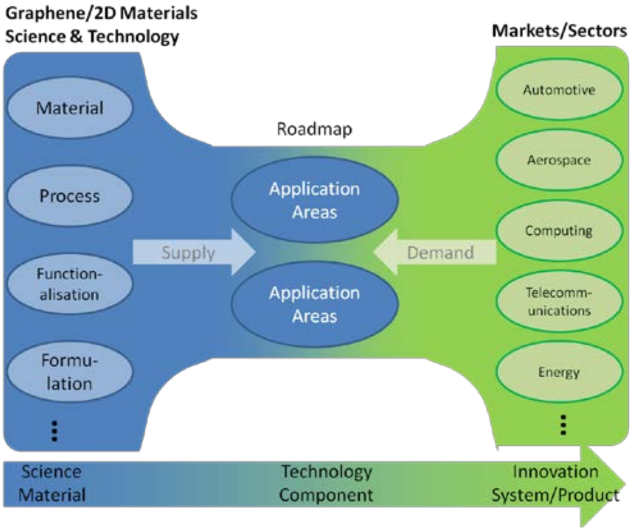

Figure 1: Fusion approach with technology supply on the one hand and markets/sector demand on the other, both meet in application areas that are used to structure the roadmap.

If not otherwise mentioned or referenced, the insights are based on interviews and communication with stakeholders from companies and research.

1.1 Objectives and scope

The Science and Technology Roadmap STR within the Graphene Flagship project aims to guide the community towards the development of products based on Graphene, 2D crystals and hybrid systems (GRM). Accordingly, the STR should outline the principle rules to develop the GRM knowledge base, the means of production and development of new devices, aiming at a final integration of GRM into systems. The updating of the STR has two specific objectives: Firstly, a methodology to update the already existing version of the STR for the first time and on a regular 2-year basis should be developed. Secondly, at the end of the ramp-up phase of the Graphene Flagship a first update should be implemented and the methodology for further updates should be in place.

These objectives address three main target groups. The first one is the internal Graphene Flagship community. The second one comprises the external research communities. Thirdly, industry as a target group should be supported in recognising the potentials of graphene for future applications. Accordingly, the updating of the Graphene STR is expected to create a common few on GRMs and provide guidance for the Graphene research towards market demands. This will also impact future adjustments of the strategic orientation of the Graphene Flagship and respective funding. Finally, guidance for the industry to allow graphene uptake will be provided.

1.2 Approach

In order to meet these objectives, the STR was extended to a Technology and Innovation Roadmap (TIR), taking into account how technology supply could meet industrial demand with a focus on economic aspects and non-technological frame conditions. The approach towards a TIR comprises a combination of the science/technology supply perspective with the market needs perspective. Key questions are what GRM can offer, and what does it need to offer when. The science and technology supply side and the market demand side will merge at the level of different application areas (Figure 1). At this level detailed analyses of the specific market requirements and the contributions of GRM to fulfilling these requirements were carried out. This fusion approach guides the way from science providing GRM material to technology designing GRM-based components to innovation in the form of new systems and products. In accordance with the Flagship management a broad approach was taken for the updating in a way that all promising application areas for GRM were analysed, however at a limited level of detail. Based on this approach the following updates of the TIR will focus on selected application areas and elaborate more detailed specific innovation roadmaps. These activities will be closely coordinated with WP innovation.

Material research is at the core demand of most of the addressed application areas. However, there is no particular purely material driven chapter in this version of the roadmap, as the focus is strongly on applications. This also leads to the fact that there is no particular chapter on production and health and safety although those topics are certainly relevant and very often mentioned as crucial need for further efforts in the application assessments, challenges and potential actions of many application areas.

1.3 Methods

A toolbox of different qualitative and quantitative methods was developed for the elaboration of the Graphene TIR.

1.3.1 Desk research and databases

Desk research focussed on a detailed analysis of the existing STR, additional literature and on market studies. Two types of science and technology indicators were used to analyse and monitor general global trends in GRM-related research and innovation and for positioning the Graphene Flagship activities in the international context: scientific publications reflecting research activities and patent applications referring to technological and market-oriented activities. Publication searches were conducted in the Web of Science (WoS), where Fraunhofer ISI operates an in-house version as relational database searchable by SQL commands. Key word searches for title, abstract, the author key words or the supplementary terms were employed.

Patent analyses also used key word based search strategies. Searches were carried out in the PATSTAT database of the European Patent Office (EPO), covering the patent applications of about 50 patent offices worldwide and in the online database World Patents Index (WPI) which provides better text disclosure since the official abstracts are transformed into useful technical descriptions. The basic definition of the graphene sample was made by WPI and then transferred to PATSTAT where better tools for analyses are available. Patent searches at specific domestic patent offices lead to a so-called domestic advantage of the analysed country. In order to avoid this bias, transnational patents were used which combine either applications at the European Patent Office or international applications according to the Patent Cooperation Treaty (PCT). In both cases the applications aim at several external markets and the cost of applications are substantial (between 20,000 and 70,000 €). Therefore, transnational patents represent a selection of applications with high economic value.

1.3.2 Stakeholder interviews

Expert interviews (face-to-face and by phone) were used for obtaining information on GRM applications. Interviews were carried out with the work package leaders of the Graphene Flagship and industrial representatives within and outside the Flagship. The following topics were covered during the interviews: technology (performance today, performance potential, uniqueness: USP, complexity, ease of use), production (scalability today, scalability potential, integrativeness today, integrativeness potential, cost for production), applications (cost reduction today, cost reduction potential, diversity of applications, product value), market (justified cost/function gain, market volume, market competitiveness), timing (time to market assessment).

A total of 65 interviews (63% with Flagship members (including associates), 71% with industry) have been carried out.

1.3.3 Workshops

A first workshop was organised at the General Assembly of the Graphene Flagship in Berlin on October 13th, 2015. The purpose of the workshop was to provide detailed information about the roadmapping process to the graphene community participating in the General Assembly and to get feedback and new ideas about future GRM application potentials.

Two roadmapping workshops with stakeholders from industry and research were carried. They had the following goals: validation and refinement of results from interviews and desk research, collection of further harmonised information, creation of common views on the use of GRM in main application areas. The workshops were structured into three main sessions. Firstly, a SWOT analysis was carried out (see below). Secondly, a portfolio analysis was used to capture the views of the workshop participants on market attractiveness and technological attractiveness for different graphene applications. Thirdly, a roadmapping section focussed on the estimation of the current technology readiness levels, the timing and development path of GRM for use in application areas and related markets and important challenges and barriers (red brick walls).

Details of the roadmapping workshops are summarised in Table 1.

Feedback from the participants indicates that the workshops were perceived as successful and productive. In particular, the vivid and interesting discussions and the availability of a forum for exchange of ideas were appreciated. For many participants, new perspectives of GRM and new ideas were initiated during the workshop discussions. The mix of participants from research and industry and from different application fields was acknowledged. With respect to the industry perspective it became obvious that for confidentiality reasons some companies are hesitating to provide detailed information about KPIs and their internal GRM related activities.

Table 1: Roadmapping workshops

	Workshop 1	**Workshop 2**	**Total**
Date	January 19th, 2016	February 5th, 2016	
Location	Squaire Conference Centre at Frankfort Airport, Germany		
Number of invitees			254
Invitees from Flagship			128
External invitees			126
Number of participants	47	35	82
Participants from Flagship	29	26	55
External participants	18	9	27
Participants from industry	26	20	46
Participating companies (examples)	Thales, Selex, ABB, BASF, Avanzare, Solaronix, Graphene Batteries AS, Denso Automotive, Fiat, Graphenea, Samsung, Haydale, Italcementi	Companies from first workshop plus ST Microelectronics, Alcatel Lucent, Infineon	

1.3.4 SWOT Analysis

SWOT analysis combine internal strengths and weaknesses of GRM (e.g. existing and potential technological advantages or disadvantages, technological advantages or disadvantages of production processes, maturity) which are directly controllable by R&D activities themselves with external factors, opportunities and threats (e.g. markets and market trends, market needs and specific requirements depending on applications, strengths and weaknesses of competing technologies, the configuration of supply and value chains, regulatory framework conditions), which are not directly controllable by GRM development itself but provide information on the target markets and frame conditions which need to be considered.

Figure 2 summarizes the SWOT analysis.

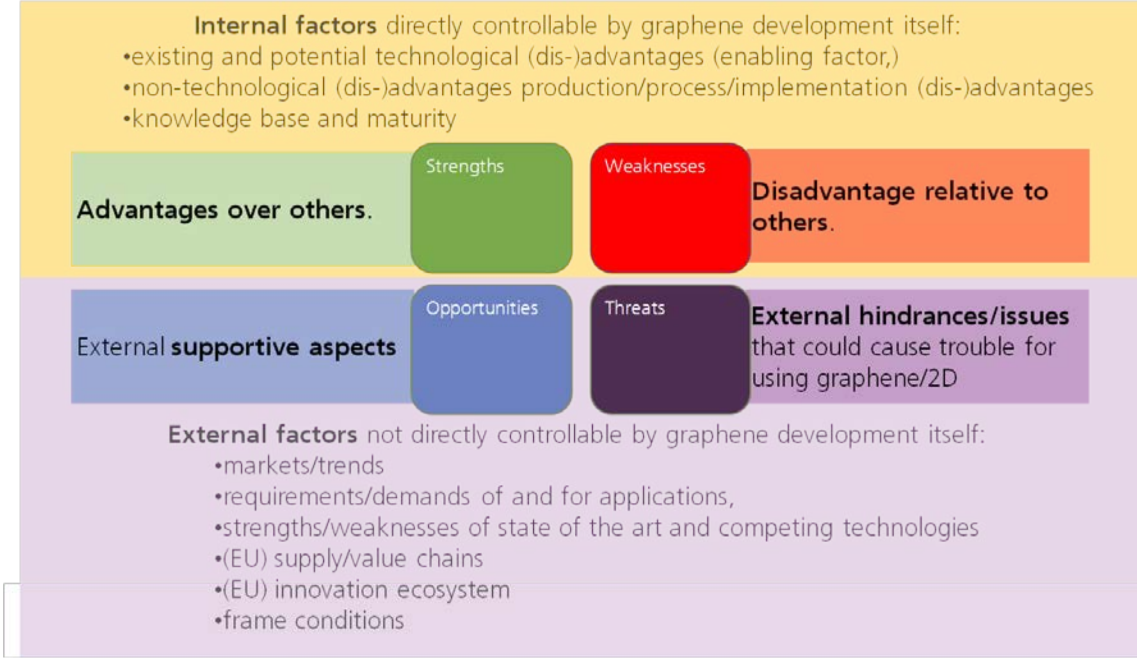

Figure 2: Summary of the SWOT analysis.

1.4 Reading guide to the report

The roadmap is subdivided into four major application areas (level 1):

1. Composites, bulk applications and coatings
2. Energy generation and storage
3. Electronics & Photonics
4. Biomedical applications

Each of these major areas (level 1) has particular application areas that are regarded in more detail (level 2). These application areas are summarized in Figure 3. These chapters are written in a way that they are standalone documents, so that interested readers can focus on their areas of interest.

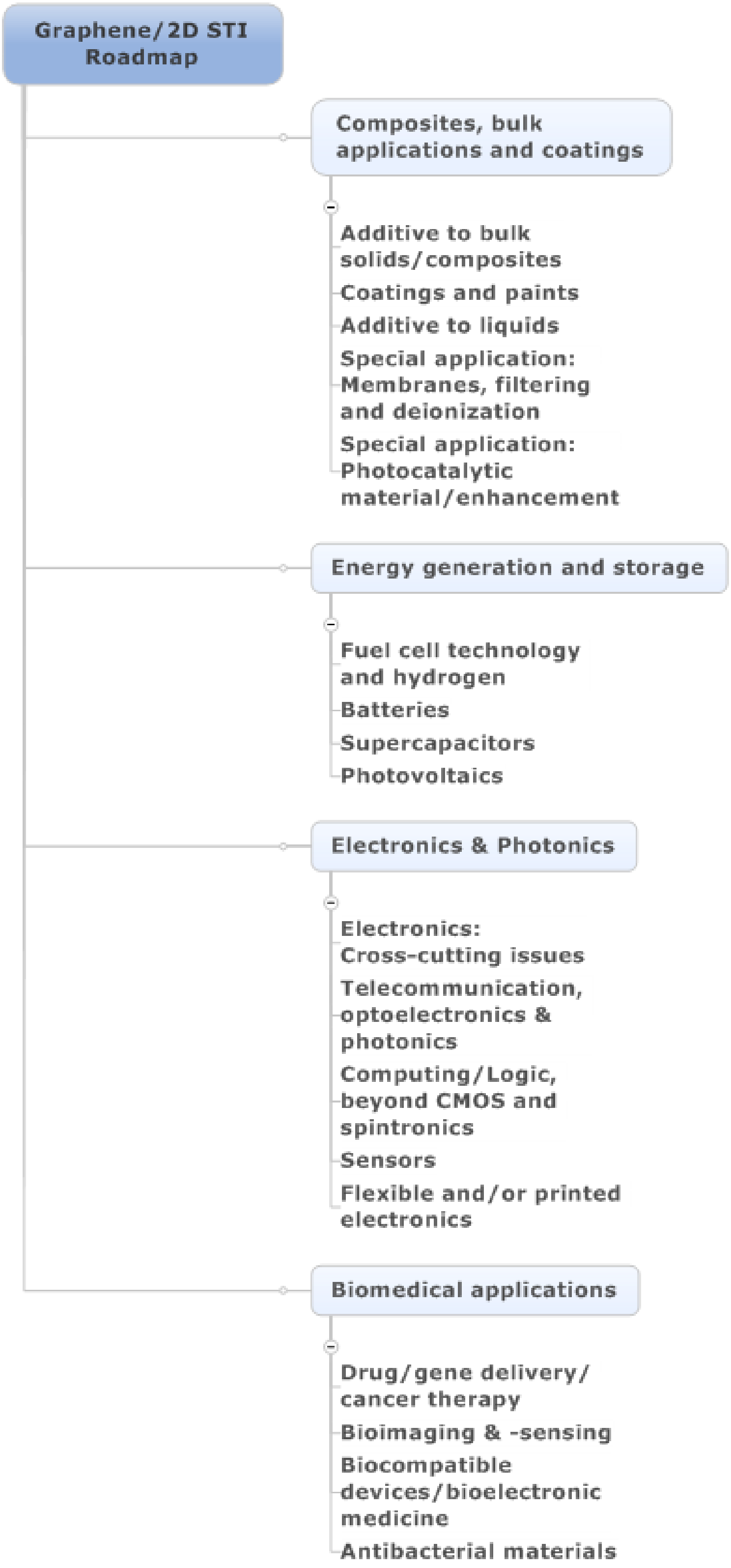

Figure 3: Roadmap structure with major areas (level 1) and application areas (level 2).

The structure of the chapters is as follows: A chapter starts with an overview and delineation on the covered topics within a major area. Then, the application areas are addressed:

1. Introduction to the application area: What is covered (delineation of other application areas), what role do graphene/2D materials play and in which form.
2. Market perspective: What are potential markets of the application area, where graphene/2D materials could play a role. How are the markets distributed locally? What type of markets? If significant, also patent/publication data is presented in this chapter.
    a. Market opportunities: The insights from the SWOT analysis (opportunities) are summarized
    b. Market threats: The insights from the SWOT analysis (threats)
3. Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in the application areas
    a. Current strengths for graphene/2D materials use in the application areas: The insights from the SWOT analysis (strengths) are summarized
    b. Current weaknesses and challenges of graphene/2D materials use in composites: The insights from the SWOT analysis (weaknesses) are summarized
4. KPIs: Important and relevant key performance indicators are summarized qualitatively and if possible quantitatively
5. Roadmap: Time related aspects are presented
    a. Current maturity: An overview of the current maturity of graphene/2D materials in the application is given
    b. Barriers/challenges summarized: The most important barriers/challenges for graphene/2D materials in the application area are summarized as derived from the earlier chapters, the SWOT and further considerations.
    c. Potential actions: potential actions are suggested for further research and development of graphene/2D materials in the application area. These suggested actions are relevant and should be considered, if the application area is further pursued. The actions are derived from the challenges/barriers and SWOT.
    d. Roadmap: Assessments of the potential development in the next years are given. If the maturity is high enough, a roadmap is presented with the anticipated development of different applications for certain sectors. Besides that, important market milestones or market insights are presented. The roadmap uses readiness levels as described in Annex A1 Appendix: Readiness Levels.
6. Conclusions for the application areas: each chapter concludes with some final remarks on the use of graphene/2D materials in the application area.

The conclusion of each application area is finalized with a table analogue to Table 2. Sub topics of an application area are briefly assessed in terms of market and technological potential of graphene/2D materials for this topic. The assessment is to be seen as a **qualitative assessment based on the insights gained for the application area and in comparison to other application areas**.

The current technological potential (USP) takes into account the actual proven and foreseeable technological performance of graphene/2D materials (not the theoretical potential) together with the uniqueness and delineation from emerging competing technologies or the state of the art.

The market potential in particular aims to reflect a **European perspective**, i.e. whether there are companies/Industries that can be enabled by this graphene/2D development in Europe, or whether the strong integrators are rather outside Europe. If there is no dominating industry yet, it is seen as a positive chance for Europe to contribute in building such an industry. Furthermore, it takes into account the overall market potential and market need for solutions offered by graphene/2D materials. If the assessment is negative, it does not mean that a development is not beneficial for Europe at all, but it will rather mean that the applications need to be addressed in global value chains, where most added value will be potentially generated outside of Europe. The assessment is done on a scale - - to ++, also shown in Table 2.

Table 2: Conclusions table for each application area.

Application sub topics	**Current technological potential (USP)**	**Market potential (EU perspective)**
Sub topic 1	- - (rather poor))	- (not good)
Sub topic 2	0 (not promising)	+ (promising)
Sub topic 3	++ (very promising)	? (undecided, not assessable, still open question)

1.5 Definition of graphene and 2D materials

The document follows the definition from Carbon, 2013, Vol 65, 1–6 [1], which is presented in annex A.1 and summarized in Table 3.

Table 3: Definition and nomenclature of graphene.

Number of layers	**Description**
1	Graphene (monolayer)
2-5	Few layer graphene
2-10	Multilayer graphene
>10 but below 100nm	Graphene nanoplates/platelets
Graphene materials	1-10 layers, (reduced) graphene oxide

2 Composites, bulk applications and coatings

2.1 Potential composites, bulk and coatings applications

This chapter covers the use of graphene and other 2D materials as bulk material, as additive to composite materials and as coating. The focus is on structural materials and materials that offer functionalities such as electrical and thermal conductivity, barrier and additional mechanical properties. This chapter covers all bulk applications besides the ones dealing with electronics and energy generation and storage (see chapters 3 Energy generation and storage and 4 Electronics & Photonics). These application areas are summarized in Figure 4.

The basic idea is to use the 2D materials to improve or enhance the properties of the host bulk material, e.g. a polymer, ceramic, or to improve the surface by making use of the interesting properties of graphene as a coating. Besides, graphene and 2D materials can also be used as an additive to fluids to enhance the properties or to fulfil a particular function, e.g. to act as an absorber for unwanted materials (remediation).

In the area of composites, bulk applications and coatings, graphene materials are mostly used as an additive or as a coating in form of bulk powders or flakes: few-/multilayer graphene, graphite nanoplatelets, graphene nanoribbons or (reduced) graphene oxide. For coatings, also films (mostly few layer) are of importance. 2D materials are also investigated to be used as membranes, e.g. for filtering. Often the difference between graphene materials and nano-graphite is blurry.

The potential markets for these application areas are very wide by definition. Essentially, the enhanced composites or coatings can be used in any market that relies on or benefits from material developments. An overview of potential markets will be given in each subsection on the particular application area.

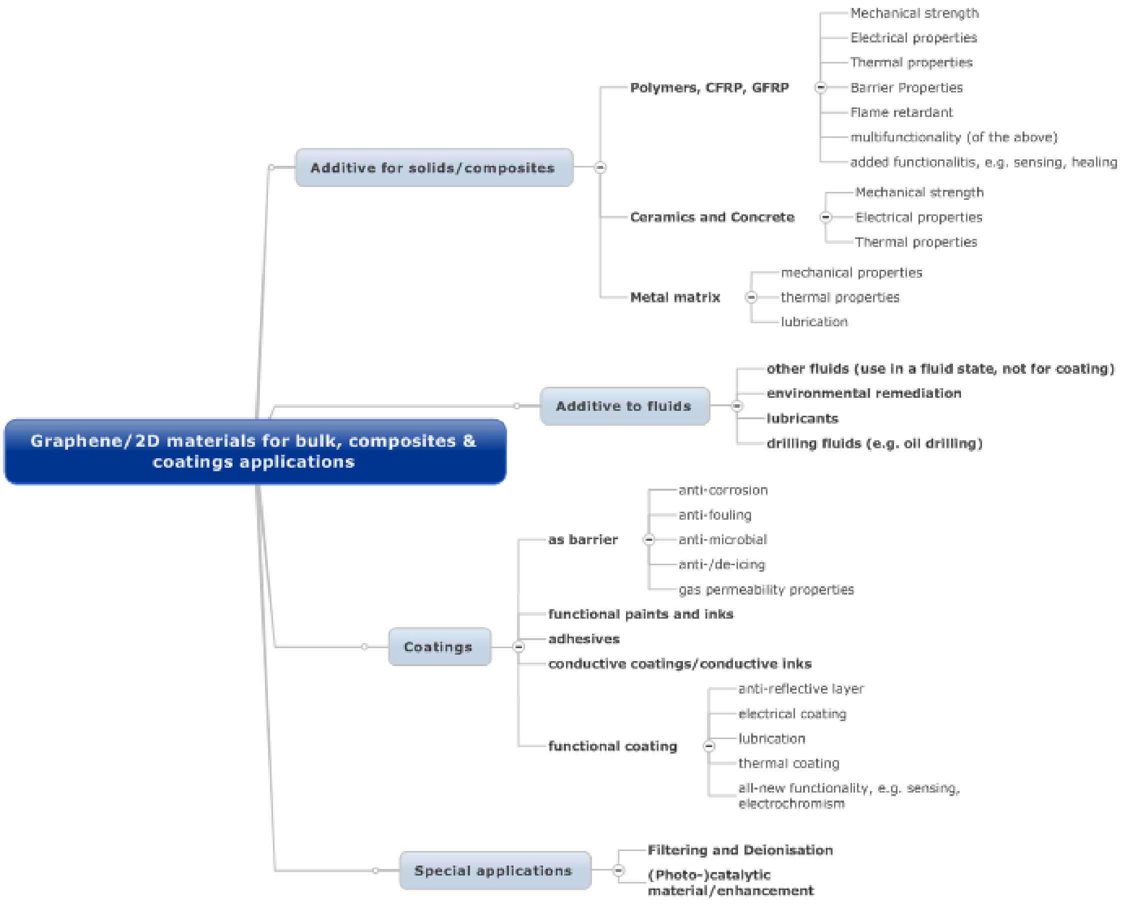

Figure 4: Potential applications of graphene and 2D materials covered in this chapter.

2.2 Additive to bulk solids/composites

Graphene or other 2D materials can be used as an additive or filler for composite materials. The rationale for this application is to improve the properties of the bulk host material by making use of the interesting properties of graphene or other 2D materials (e.g. mechanical strength, electrical or thermal conductivity, etc.), compare Figure 5 and Table 4. Typical host materials are polymers, carbon-reinforced polymers, ceramics, concrete, etc. where the addition of graphene/2D materials shall improve particular mechanical and functional properties usually addressing a weakness of the host material.

Table 5 summarizes potential host materials and the addressed weaknesses. Figure 6 gives an overview of mechanical properties (Young's modulus) of potential host materials. Usually the improvements need to be achieved whilst the original other properties, including the processability of the host material, remain largely unaffected and should not be impaired.

Typically competing technologies/materials are the usually used additives/filler materials, metals, other nanomaterials and other carbon based additives and, such as carbon black, soot, graphite nanoflakes or carbon nanotubes (CNT).

This chapter focuses on bulk materials and their improvements, referring to the use in the body/bulk of a component through dispersion of the additive. This is in contrast to coatings and paints, which are only applied to a surface of a body/bulk material. There are indeed some overlaps with coatings and paints, in particular with respect some potential property improvements and functionality. These can sometimes be achieved in both ways, by using a coating or adding 2d materials to the bulk (properties marked with * in Table 4).

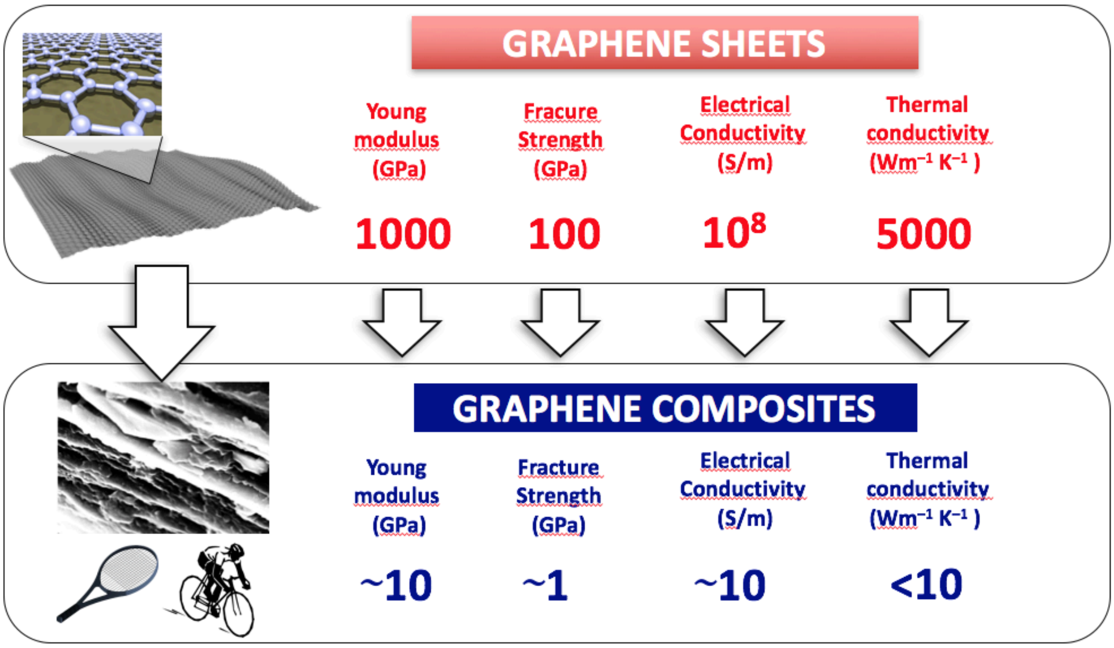

Figure 5: Properties of graphene sheets and current realisation in composites. [2–4]

Table 4: Composite property improvement and application areas. The properties with * can also potentially be achieved with coatings.

Composite property improvement	**Target application areas**
Mechanical properties	Structural applications, improved strength of conventional lightweight materials, improved tensile strength, impact toughness, elasticity, fracture toughness, wear resistance
Electrical conductivity (σ)*	EMI shielding, antistatics, electro-machining, signal/power transmission, functional lightweight materials, field grading materials, electrical toughness/dielectric strength
Thermal conductivity (κ)*	Heat dissipation/heat removal through increased thermal conductivity. Metal replacement for heat exchangers where corrosion resistance and light weight are required.
Barrier properties*	Gas barriers, flame retardancy
Surface area/properties*	Catalysis, tribological properties (lubrication/friction, look & touch & feel, anti-squeak)
Multi-functional property enhancement*, added functionalities	All areas where a combination of the above properties are beneficial, as well as added fucntionalities such as damping, self-healing, damage detection etc.

Table 5: Host materials for composites, weaknesses addressed by graphene/2D material addition and recent reviews on the topic.

Host material	**Sub category**	**Main weakness of host addressed**	**Recent review**
Polymers	Elastomers	Insulating, mechanical strength, fracture toughness, thermal conductivity[a]	[5]
	Thermoplastics		[2, 6]
	Thermosets, fibre-reinforced polymers		
	Adhesives		[7, 8]
Metals	e.g. Al, Cu, metal matrix composites	Weight and/or mechanical strength, functionality (e.g. for batteries)	[9, 10]
Ceramics		Brittle, electr. insulating, fracture toughness	[11]
Concrete/Cement		flexible/tensile strength, strain, brittle/crack formation, electr. insulating	[12]

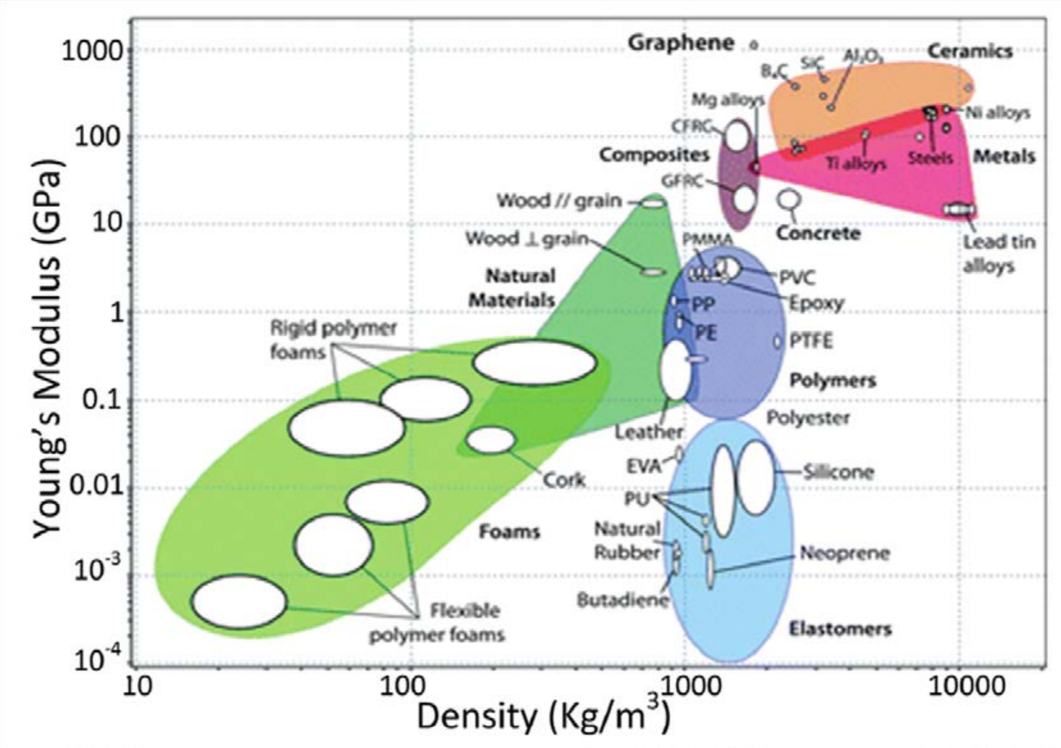

Figure 6: Young's modulus of several potential host materials and of pristine graphene. [13]

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[a] Thermal interface materials are covered in chapter 2.3 Industrial large scale coatings and paints and 4.2 Electronics: Cross-cutting issues.

Other 2D materials, such as two-dimensional Boron Nitride (BN), Magnesium-Hydroxide or Molybdenum Disulfide (MoS2) and other transition metal dichalcogenide (TMD) monolayers also offer interesting functionalities. BN for instance offers barrier properties and thermal conductivity without electrical conductivity.

2.2.1 Market perspective: graphene/2D materials in composites

Solutions, where graphene materials can enter the market are currently mostly addressed by carbon composites. Figure 7 summarizes the global carbon composites market by applications in 2014. Expected yearly growth rates are 10.6%, resulting in carbon composites revenues of 33.6 Billion US$ in 2021. [14]

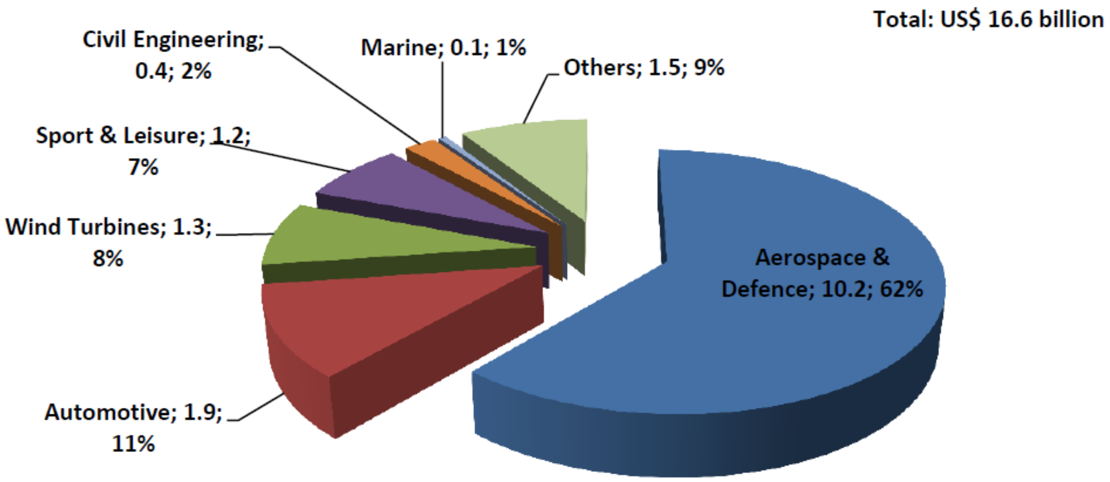

Figure 7: Total global revenues for carbon composites in 2014 were 16,6 Billion US$, of which CRP (Carbon fibre reinforced plastics) accounted for 10,6 Billion US$. [14]

Looking at the wider picture of the composites market in general, global market size in terms of value of end products is expected to reach around $90 billion in 2020 with a CAGR of 7% to 9% between 2015 and 2020. [15] The market for lightweight materials was estimated to be between $88 and $116 billion in 2014 and is expected to grow to $144-188 billion with a CAGR of 8% to 12% until 2020. [16, 17] Looking at high performance polymers in the transport sector, the market is expected to grow by ~5% per year in Europe and North America (2014: $761m).

The functional composites market is still emerging; most of the composites nowadays used are for mechanical strength and low weight. The wider defined conductive polymers market for example is still juvenile and accounts for $3-4 billion by 2020, where filled conductive plastic generates the maximum revenue, contributing more than 4/5 to the conductive polymer market, due to its extensive application in ESD and electromagnetic interference (EMI) [18, 19].

The advanced functional composites market including thermally/electrically conductive/resistive, barrier, optical magnetic and other functional composites was estimated to be $41 billion in 2015 growing at a CAGR of 7.3% to $58.5 billion in 2020. Main markets are in Asia-Pacific (47%), North America (25%) and Europe (19%). Major end users are consumer goods and electronics (25%), building, construction, storage and pipine (23%) and transportation (22%). Main functionalities are thermal (29%), electrical (23%) and barrier (19%). [20]

Major trends served by these applications are for instance (functional, hybrid) lightweight construction, multi-functionality or 3D printing.

In terms of patents, polymer composites are dominating materials where graphene and 2D materials are used followed by metals, ceramics and concrete, see Table 6. The number of graphene/2D material related patents increased over-proportional to the overall area, which can be seen in an increased share of graphene/2D related patents compared to the overall amount of patents in the respective field.

In terms of country distributions (Figure 8), the largest transnational patent activities are found in USA followed by Europe. Europe is particularly strong in polymer composites with graphene/2D materials.

Table 6: Patent analysis of graphene/2D materials in different matrices: Number of graphene related transnational patents in the respective fields in 2009-2011 and 2012-2014. The share gives the ratio of graphene patents from all patents in the area (0.8% of all ceramics patents dealt with graphene/2D materials in 2009-2011.[21]

Composites	**2009-11**	**Share %**	**2012-14**[b]	**Share %**
Ceramics	107	0.8	235	1.7
Polymers	580	0.9	1155	1.7
Metal	147	1.2	322	2.4
Concrete			20[c]	

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[b] 2014 values are projected

[c] Values from 2009-2014

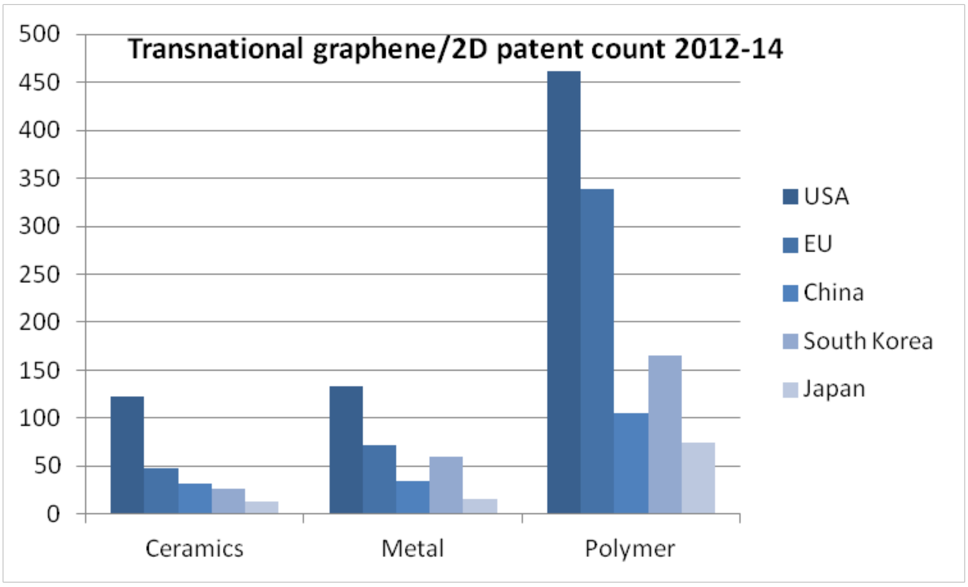


Figure 8: Transnational patent count in the respective area in 2012-2014 for different work regions. 2014 values are projected.[21]

Looking at graphene polymer composites, Europe is second in terms of the transnational patent count after the USA (Figure 9). The relevance of graphene materials, however, is stronger in Korea and China (Figure 10).

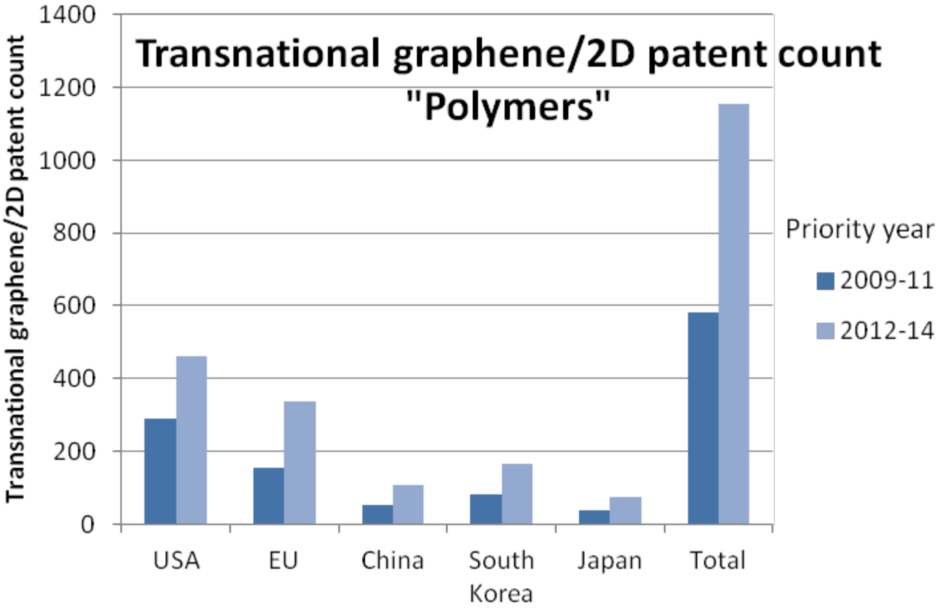


Figure 9: Patent analysis of graphene/2D materials in polymers: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [21]

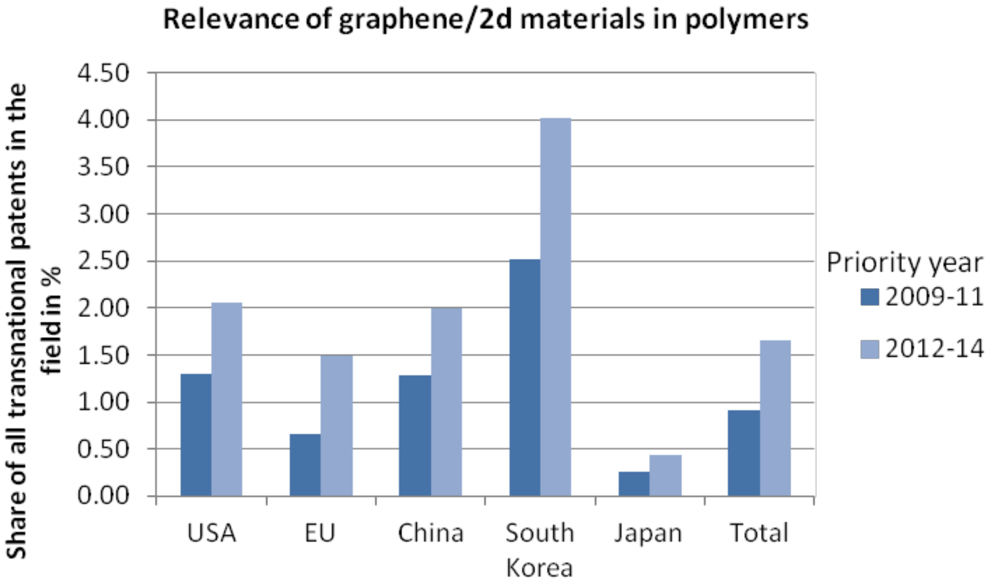
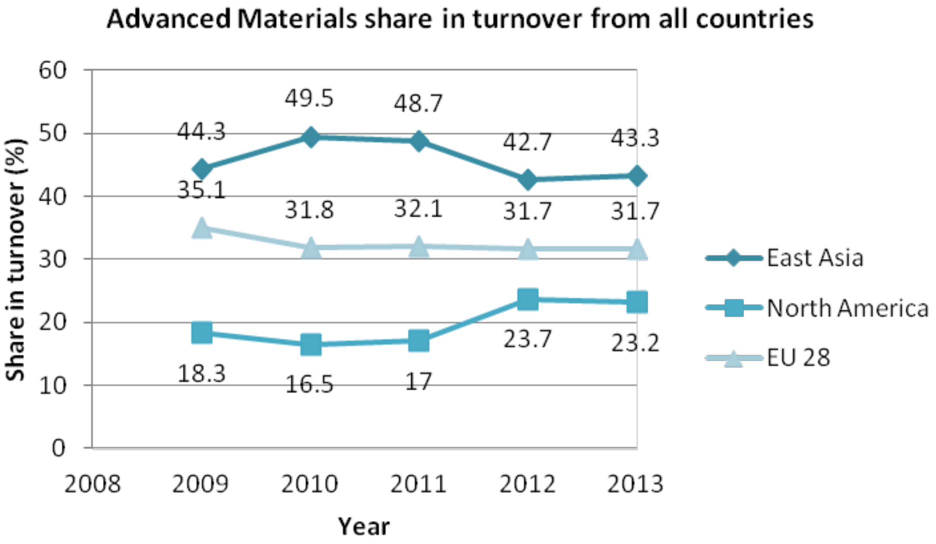


Figure 10: Patent share of graphene/2D related materials with respect to all transnational patents in polymers. 2012-2014 values are projected.[21]

Figure 11 compares the turnover share (worldwide) from EU-28, East Asia and North America for advanced materials and nanotechnology. For advanced materials, Europe is positioned between North America and East Asia, generating roughly a third of all turnover worldwide. In nanotechnology the picture is similar, although North America and Europe are similarly strong behind East Asia.



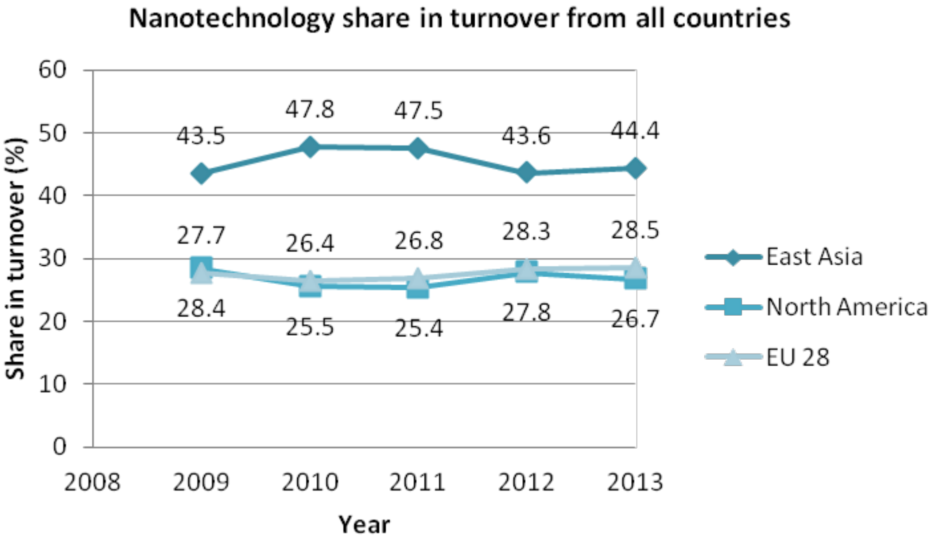


Figure 11: Share in turnover relative to all countries of advanced materials and nanotechnology. [22, 23]

2.2.1.1 Market Opportunities

2.2.1.1.1 European adopters and multiplicity of addressable markets

As composite materials have a great variety and multiple applications, graphene enhanced composites can address, large, growing and strong (European) markets (automotive, aerospace, medical technologies, wind energy, energy transmission, advanced textiles, defence, packaging), compare also Figure 7, Figure 8 and Figure 12. These markets are very versatile and offer many niches and potential early adopters for an early market introduction. Some niche applications also allow higher costs for multi-functionality or increased performances, such as space applications.

Besides, graphene/2D materials enhanced composites address emerging topics such as 3D printing (e.g. conductive 3D printed polymers) or functional textiles. A benefit is that the materials sectors addressed by graphene fillers, such as polymers, are used to working with carbon materials as fillers (e.g. carbon black).

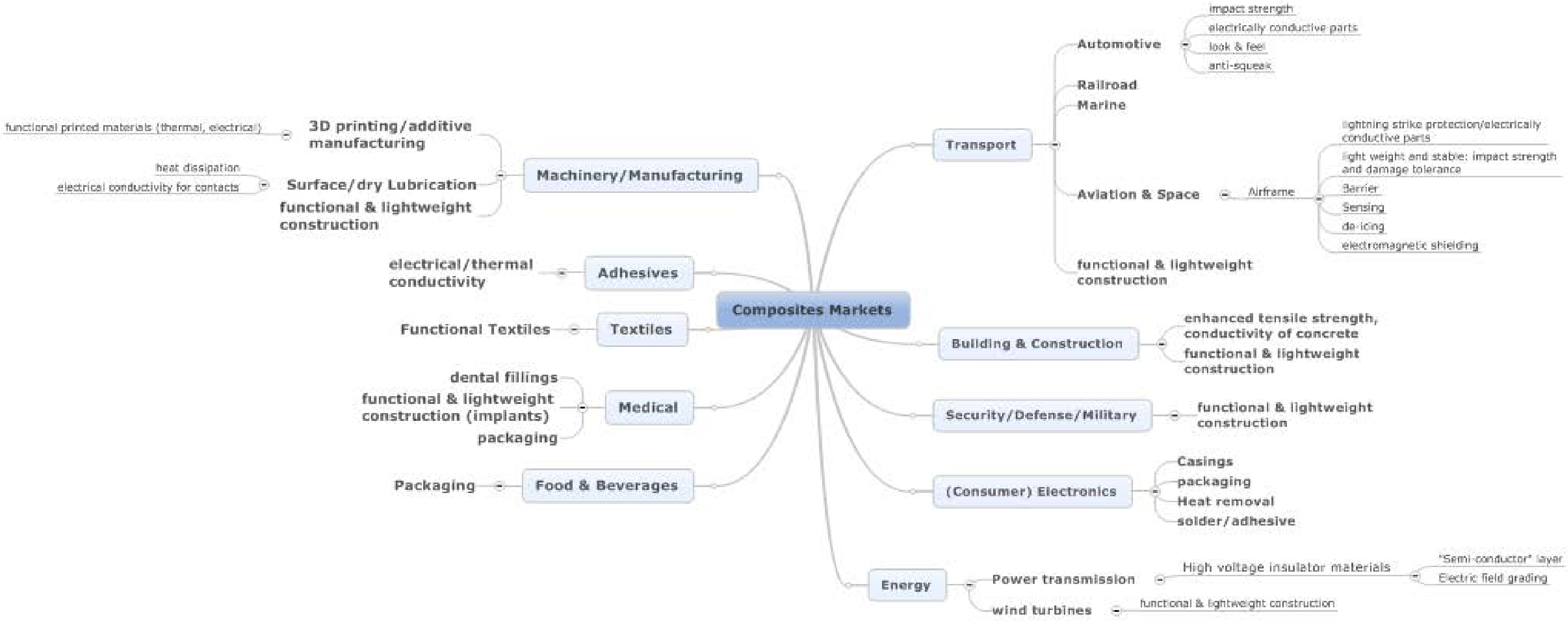


Figure 12: List of potential markets of graphene enhanced composites.

2.2.1.1.2 Trend towards lightweight/functional construction and increasing use of composites in relevant markets

Due to CO_2 reduction efforts, need for improved energy efficiency and regulation, especially in transport related sectors the demand for lightweight and functional construction is high. This trend creates demands for affordable lightweight material solutions and functional integration which maintain and improve strength and safety standards.

It is to a certain extent feasible to increase the cost for a given saved weight (cost/benefit). Estimates of this KPI is given in Table 7. Therefore, although the cost is usually increased when lightweight materials are used, the use of lightweight materials is expected to grow across industries. [24]

Table 7: Allowed added costs per kg saved in most relevant sectors.

Sector	**Allowed added cost per kg saved (roughly)**
Automotive	<3€ (mass market) -8€ (premium market)
Aviation	Few 100€ (depending on aircraft)
Space	Few 1000€ to 10000€

Polymer-based materials and composites are the main type of material used to address lightweighting, where graphene materials can play a role. In the automotive sector, polymer composites are expected to be preferred material by 2030 [25]. This not only accounts for structural components, but also lots of smaller components (e.g. where PEEK is used) in non-structural/non-critical components.

Wind power and aerospace are pioneering the use of novel lightweight materials. In aviation, composites are increasingly used in airplanes (wing and fuselage recommendation by IATA [26], Airbus A350XWB, Boeing 787 Dreamliner) to reach CO_2 reduction goals.

An interesting route to address the cost reduction in composites is to upgrade a low cost polymer by additives to facilitate use of a lower cost matrix for applications where currently higher cost resins/base materials are used. For instance, a bottleneck is the production cost of often used thermoset (epoxy based) reinforced composites due to the cost of structural epoxy resins and also the fibres. Advantages of thermoplastic reinforced composites are the easy processability and the decrease in production cost. Conventional thermoplastics have not achieved the mechanical performance of structural thermosets, which can be addressed by adding graphene materials.

In particular the mechanical enhancement can address interesting needs of several industries such as for example:

- enable lighter materials with similar strength and cost (all)
- Use simpler to process composites with similar performance: Use short fibres and injection moulding (all)
- Replace metals with composites (all)
- increase the mechanical strength i.e. impact performance and toughening of impact absorbing components (aerospace, automotive) for vehicle safety and crashworthiness
- Higher flexibility/elasticity of composites
- Better mechanics at elevated temperatures (or at extremely low temperatures) to extend the temperature window for use of a given material and avoid use of a much more expensive material

Typical early adopters in the sports industry have already taken up graphene materials in their products, see chapter 2.2.4.1 Current Maturity: First niche products are in the market.

Besides, European regulatory laws and agreements require recyclability of materials (e.g. components of vehicles; End of life Vehicle Directive). Important parameters are therefore also regarding the life cycle of composites and their reuse and recycling. One of the bottle necks for the use of thermoset composites in automotive industry is the difficulties of recycling, the best option being waste materials in the cement industry (in the cement kiln route) or just pyrolysis. The use of thermoplastic instead of thermoset materials can be an alternative due to the well stabilised recycling routes.

2.2.1.1.3 Demand for integrated (multi-)functional/smart materials

Functional composites combine various properties in a single material, which allows lightweighting and functionality integration. In particular for this functional integration (functional lightweight construction, hybrid lightweight construction) [27] graphene based additives can play an important role due to their multi-functionality (electrical, thermal conductivity, mechanical reinforcement, barrier properties, anti-friction, flame retardancy).

There is a trend towards this functional integration [28] and multifunctional/smart materials, although actual applications are still not yet widely commercially applied, besides electrical conductivity or barriers to some extent. Therefore, it is expected that the use of functional polymers or other functional lightweight materials will increase in the next years.

In terms of multifunctionality for concrete or cement, the market chances need to be investigated and the market needs to be created/triggered, as there is currently hardly a market for a more conductive concrete or thermally enhanced concrete. The building industry is also very price sensitive and large amounts are needed, even if the loading is low.

The loading of additives to reach multifunctionality is often rather high, which leads to higher cost, different processes and cross-correlation with other properties, such as mechanical strength. A graphene material opportunity is that usually rather low loadings are needed to achieve desired effects.

2.2.1.1.4 3D printing and additive manufacturing as driver

In particular for polymer based 3D printing, 2D material additives can play an enabling role for functional plastics (filaments, photopolymers, e.g. with higher strength or thermal/electrical conductivity). Graphene/2d materials can benefit from the strong growth in this sector (20-30% for consumables [29], ~10% for the 3D printing market [30]). Besides, currently rather large premiums can be charged for 3D printing materials, which reduces the barrier for integration.

2.2.1.1.5 Opportunities in metals and ceramics

Besides the use as coating for metals (see for instance 2.3.1.1.4), also metal and ceramics composites are interesting areas as host material. Both European industries have a large worldwide market share (see 2.2.1.1.8). The worldwide advanced functional composites market is estimated to be $83 billion in 2015, growing at a solid CAGR of 5% in the next 5 years. [20] The metal matrix composites market was estimated at ~$320 million in 2015 growing at a CAGR of 6% in the next 5 years. [31]

Metal matrix composites are used to enhance functionalities, improve certain properties (electrical, thermal) whilst reducing weight, e.g. increased strength of aluminium for transport applications, improve metals for electrical applications such as batteries or supercapacitors or improve the corrosion resistance. Challenges of this technology are high manufacturing costs and limited technological expertise. [32]

Ceramic materials have very valuable properties from the engineering point of view, such as refractoriness (i.e. retaining material strength at T > 600 °C), strength and hardness, but they have an important drawback, their low toughness, which often overcomes their potential benefits. The usual approach to increase toughness is the inclusion of second phase materials that may act as reinforcing agents by producing extrinsic toughening effects. This agent could be nano-additives such as carbon fibres, carbon nanotubes and graphene. An additional benefit to add such additives is to render the ceramic composites electrically conductive, which is also interesting for better machining possibilities (see 2.2.1.2.1).

2.2.1.1.6 Interest for trials from industry

In principle, there is interest in graphene/2D materials in composites and coatings from application industries (e.g. aerospace, automotive, chemical industry, electrical and electronics, construction, defence). Customers/end users demand prepregs, thermoplastics, resin dispersion in paints and thermosets with graphene for testing, so the interest for trials is there.

As for example CNTs are more mature, there might be also synergies/boosting with other (carbon) materials or nano-additives.

In particular when it is not needed to change the production technology, the introduction of a new material can be straight forward and rather easy. For that reason the use of pre-dispersions in solid, liquids or polymers used as nano-intermediates (GRM dispersion in solids for the rubber industry, masterbatch for the thermoplastic industry and prepegs or resin dispersions for thermosets) for test and development of graphene-enabled final products is the way forward, that is also pursued by many suppliers.

2.2.1.1.7 Health concerns about CNT

Occupational health concerns about CNTs are considerably bigger than about graphene. Providing reliable answers that graphene is less problematic than CNT may help graphene to win in applications for which CNTs are presently leading candidates under consideration.

2.2.1.1.8 European value/supply chain

Europe also plays a major role in terms of industrial production of composites or materials. Potential integrators of graphene additives (compound, prepreg, masterbatch producers) are located in Europe. For instance, Europe is the second largest plastics producer after China (20% vs. 26%) with a positive trade balance and a turnover of 350bn€. [33] In 2013, a total global revenue of $14.7 billion was created with carbon composites, of which 34% where generated by US companies and 32% in Europe, followed by Japan (15%) and Asia & Pacific (13%). [34] Furthermore, the demand for carbon composites is also strong in Europe, see Figure 13. Besides, Europe is also rather strong in the patenting of graphene and related transnational patents, especially in the polymer composites area, but also in ceramics, compare Figure 8.

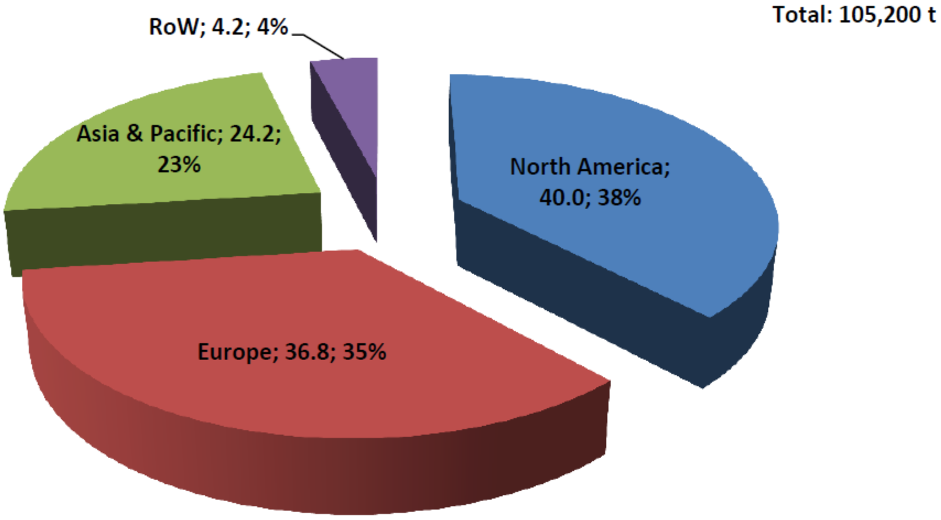


Figure 13: Carbon composites demand in 1,000 tonnes by region (2014). [14]

It is important to involve the prepreg and compound actors in the integration of graphene (e.g. Delta Tech is in the Graphene flagship or Haydale collaborates with SHD Composites Limited [35]). For a broader integration, these collaborations need to be enhanced, see 0., also to figure out whether additional steps are needed in the value chain

The European ceramics industry produced revenues of ~€27 billion in 2014 with a positive trade balance and 25% of global production [36]. The steel industry is the second largest in the world with an output of over 177 million tonnes of steel a year, accounting for 11% of global output. [37] Both industries are under pressure from worldwide competition.

The annual total added value of the European cement and concrete industry was €56 billion in 2013. [38] The production value of ready mixed concrete was 16.1b€ in 2014. [39]

Furthermore, Europe is a naturally strong player in terms of patenting and innovation in the polymer industry. Figure 14 shows that Europe dominates the number of transnational patents dealing with polymers together with the US. It is equally strong in ceramics and metal composites.

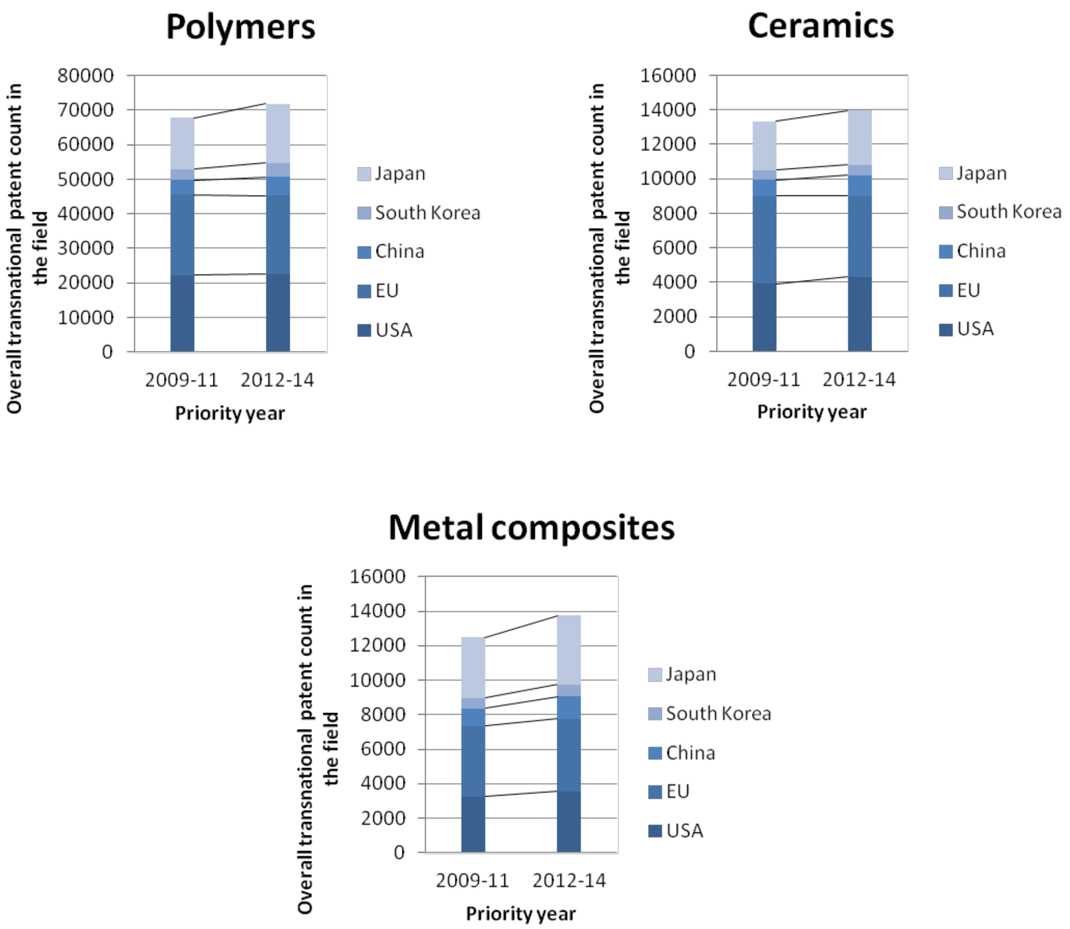


Figure 14: Overall transnational patent count in polymers, ceramics and metal composites. 2012-2014 values are projected.[21]

2.2.1.2 Additional market opportunities: conductivity

2.2.1.2.1 Electrically conductive composites on the rise

Chapter 0 (Besides, European regulatory laws and agreements require recyclability of materials (e.g. components of vehicles; End of life Vehicle Directive). Important parameters are therefore also regarding the life cycle of composites and their reuse and recycling. One of the bottle necks for the use of thermoset composites in automotive industry is the difficulties of recycling, the best option being waste materials in the cement industry (in the cement kiln route) or just pyrolysis. The use of thermoplastic instead of thermoset materials can be an alternative due to the well stabilised recycling routes.

Demand for integrated (multi-)functional/smart materials) highlights the interest for multifunctional/smart materials. Besides the mechanical enhancement, conductivity is an important need from industry for these multifunctional materials and probably already the most pursued approach, as several companies are active in that respect (also with other technologies than graphene):

- Anti-statics, electro-static discharge (ESD)
- allow lighter EMI (electro-magnetic interference) shielding
- lightning strike protection (aerospace)
- functional integration of signal transmission/sensing in lightweight structural parts, i.e. wiring within plastics (automotive, aerospace), e.g. for entertainment in airplanes
- lightweight electrical heating elements (e.g. automotive, de-icing of airplanes)
- electric field (electric stress) grading material in insulation systems for transmission and distribution of power (see box on page 93)

The electrical conductive composites and conductive polymers market is expected to grow with a CAGR of ~8% annually. The overall market of electrically conductive composites is expected to grow at a similar rate.

For ceramics, conductivity can enhance the possibilities of machining by more efficient methods, such as electro-discharge. This benefits from the erosive effect of electrical discharges or sparks (usually ceramic materials are costly to machine into complex shapes).

An ultimate vision would be to achieve a carbon-based lightweight conductor, which might be suitable for particular applications where light weight and corrosion resistance is more important than ultimately high conductivity.

2.2.1.2.2 Harsh environments as interesting opportunities

Electrical conductivity is usually reached by using metal additives. However, in corrosive and harsh environments or hot conditions metals can degrade or use their mechanical properties. These areas are rather niches, but still have a certain demand for corrosion resistant conductive materials.

2.2.1.3 Additional market opportunities: thermal properties

2.2.1.3.1 Need for passive and energy efficient cooling or heating

Similar to the electric conductivity, thermal properties are also important to be integrated into multifunctional composites. Composites can be used to remove or spread heat better than usual polymer materials. Directionality can additionally help to improve the thermal performance. The market for thermally enhanced composites is expected to grow with a CAGR of almost 8.5% in the coming 5 years. [20]

Thermal interface materials are further investigated in chapter 2.3 Industrial large scale coatings and paints.

2.2.1.4 Additional market opportunities: barrier properties

2.2.1.4.1 Water barrier in epoxy resins

Carbon-fibre reinforced composites can suffer from water uptake of the epoxy resin [40]. Additives can help to improve the water barrier and prevent fatigue and at the same time achieve other properties, such as flame retardancy.

2.2.1.4.2 Many potential applications in packaging

Barrier properties are important in many different areas, e.g. in semiconductor, fuel tanks, gas storage, food packaging, beverages and medical applications. These applications are nowadays addressed by multi-layer structures or coatings. Adding a barrier within the primary material/host could simplify the processing.

For food, beverages and medical applications the regulatory (health and safety) constraints are, however, larger than for the other applications.

The use of ESD and conductive films for electronics packaging will increase in the next years. However the use of conductive carbon blacks and CNT are not suitable technologies, due to the rheology and MFI change in the polymer. Still other options are also competing on the market based on other antistatic agents, metal films or conductive polymers.

The market for composites with barrier properties or electrical properties/conductive polymers is expected to grow with a CAGR of around 7% in the next 5 years. Conductive polymers had an estimated world market of ~$3 billion, barrier composites of ~$7.4 billion in 2015. [20]

2.2.1.4.3 Opportunities for flame retardancy in polymers

More restrictive regulatory standards of the European cable industry are emeging, that will be also adopted in China. ATH and MDH filler polymers have difficulties to obtain the requirements, which opens opportunities for new flame retardant additives. Also the tendency of restriction of use of ammonium polyphosphates will be a new opportunity for graphene materials.

Besides, most used flame retarding additives use rather high loadings (20-60%), which can affect properties such as mechanical stability, so that adoption to each polymer is needed, This also has an impact on cost (see 2.2.1.6.2).

2.2.1.5 Market Threats

2.2.1.5.1 Mature markets with many established technologies and complex value chains

Some of the markets targeted by graphene/2D material enhanced composites are already very mature. Additives to all kind of hosts (polymers, ceramics, concrete, etc.) are a mature and well established market. There are also nano-additives addressing similar (separate) enhancements as graphene, such as CNT or nanoparticles of many different materials. In particular for barriers, thermal or structural enhancements, many additives are under investigation. However, the multifunctionality of graphene materials as an additive is rather unique.

In terms of CFRP, the market is still rising and the majority of fibre composites used at the moment is glass fibre based, in particular in the automotive industry (automotive: 93.2% GFRP in 2014). But the CFRP share is expected to increase and the revenue of CFRP is expected to grow globally by CAGR 21% for the automotive industry. Already the introduction of CFRP requires a completely different supply chain compared to metal-based structural components. The current key focus of CFRP manufacturers is the cost reduction. [41] If this can be addressed by graphene, it can be a great opportunity. This could for instance be the case if thermoplastics instead of thermosets can be used while achieving the same properties for lower material and process cost. If costs are increased through graphene usage, it is a threat.

In terms of other nano-additives, one of the main competing materials are CNTs. They are already more mature and better understood (because they are longer studied). So far there is no large roll-out, but it appears that some composites are about to be used for similar applications than graphene. A clear advantage is therefore necessary towards competing technologies. The market is in general very competitive and thus it is hard for a new material to enter the market and outplay competing technologies, even if performance is slightly better. But in case this is successful, a market success can be large, as scaling is usually targeted and desired.

Also graphite powder has interesting properties that might be sufficient for less demanding applications, especially in terms of conductivity. They currently can be obtained much cheaper (0.8€/kg at industrial quantities). However the quality and size covers a broad range (from 200nm to several microns).

Flame retardant additives (even halogen-free) are already known and widely used, however, the halogen and antimony-flame retardant solutions often demand high loading.

In terms of conductivity enhancement, carbon black works quite well for some applications demanding lower conductivities, however, in medium high and high electrical conductivity, conductive carbon blacks are not suitable due to high increase in viscosity of the resin or the thermoplastic. Another drawback of conductive carbon blacks is the brittleness of the composite due to the high loading. But clear advantages need to be proven to replace existing and working conductive additives. For antistatics (e.g. spark protection), which demand rather low conductivities, even more solutions are available so a clear differentiator is needed. On the other hand, most of the antistatic solutions are based on the migration of molecules to the surface of the matrix, rendering it a non-permanent antistatic material. A potential differentiator could be added functionality or low amounts of needed additive.

The composites address complex markets with complex and established value chains with many stakeholders (compounds, master batches…, compare Figure 15). Getting access to these value chains remains a large barrier, especially because they are quite conservative. Depending on the actual target market, these can be very cost sensitive. Due to the variety of potential applications, it demands great efforts to find the right markets and address and prove the needed performances.

There are also strong constraints on the sourcing of materials. Usually a second source/supplier is needed that offers the same quality and standardized testing and quality control are very important.

Last but not least, only if a material can be integrated easily into the existing production processes, a quick uptake is possible. If new equipment is needed, the benefit needs to be much larger and the implementation will take much longer, if it is considered at all.

2.2.1.5.2 Large markets have restrictive requirements on cost, function, health, safety and end of life

Large markets are cost sensitive markets (e.g. automotive), but legislation is a driver to use also more expensive materials. In aeronautical market cost is also becoming a key driver for future aircraft developments. A cost/benefit analysis needs to take into account the system cost and the life cycle cost, which can in some cases justify the initially higher investment for composite parts. However, quite often only immediate costs are recognized and not total system costs. But the total system costs might actually be reduced by adding multifunctionality: Although adding conductivity or thermal sensing to the composite might be more expensive initially, money can be saved in the later process by eliminating the need for a separate system. [42]

However, in the mass markets, composites are at the moment not yet widely used as they are still to a great extent cost prohibitive. In the automotive industry, polymer based composites for structural applications are still not broadly used and mostly reserved for high price luxury segments. Mass markets lightweight strategies are still dominated by cheaper high-strength steels, aluminium or other lightweight metals, partially combined with carbon-fibre or polymer based compounds. [24] Added costs through higher priced materials are still often contrary to many strategies (e.g. in automotive). In almost all potential applications of lightweight materials, cost is still the highest barrier [27]. But aviation and space applications are not so cost prohibitive, so that the integration of higher valued materials is easier.

For CFRP, the current costs are 100€/kg, of which about 1/5 are for materials. So the limiting factor is the processing cost of 4/5. Thus, the highest cost reduction potential comes from the processing and not from the materials. It is therefore unclear how graphene materials can actually contribute effectively to a cost reduction.

The building industry is very price sensitive. The price of concrete is $85-100 per metric tonne, which can limit bulk graphene applications even at low loads. Also the low cost of other building industry materials, for example, ceramic bricks with a medium price of 50 €/m^3 can be a bottle neck. On the other hand, the markets are large (e.g. the flooring market is expected to be 300b€ in 2020. [43]

However, cost is not the only barrier that needs to be overcome or taken into account. There are also many requirements such as health & safety, durability and recyclability that need to be proven before a material can actually be used.

For example, the sustainability and recycling of composites is a major issue for the automotive industry and end of life considerations are essential for graphene materials. Recyclability/biodegradability and influence on life cycle of matrix can thus be a threat but also an opportunity, if it is shown. Anyhow, it needs to be addressed. In terms of durability, standard tests need to be performed (accelerated testing).

Health and safety considerations are particularly needed for the manufacturing and for release in crashes or during recycling. For food and medical applications, the constraints are even higher.

In all cases, just improving the properties of a given material is less relevant for industry; rather the improvement must be achieved at lower cost or other advantages relative to other, already existing materials.

2.2.1.5.3 Awareness and perception of graphene additives

Often nano-carbon additives are not yet on roadmaps (e.g. IATA) or not recognized in market driven (composites) communities. These communities still have a rather observational attitude and do not get engaged heavily. The current situation is still strongly technology push oriented from the graphene community.

Graphene as an additive to composites is often seen in analogy with CNT. For CNT mechanical, electrical and thermal property enhancements were also shown [44]. For CNT composites the mechanical topic was very prominent at the beginning but shifted more and more to functional properties/enhancements. In comparison with CNT, graphene hast several advantages, such as its easier synthesise (no metal catalyst, lower temperature) and better dispersibility.

With respect to the perception of graphene materials, they are quite often compared to CNT with a negative undertone [45]. A problem are the high expectations (stronger than steel, more conductive than copper), that without being properly put into perspective lead to high expectations that will not be fulfilled with composites. Therefore, an honest advertisement is needed to education end users to manage the expectations and highlight the application related actual benefits.

Although the health and safety concerns might be not critical from a scientific point of view, the perception of safety issues in the broader public is also a major barrier and concern (“asbestos” analogy). Therefore, a clear proof and an open discussion is needed.

2.2.1.6 Additional market threats: barrier properties

2.2.1.6.1 Usually rather low cost products

The composites/plastics mass markets demand low cost additives. In particular for the large packaging markets, low cost is a prerequisite, as the products are mostly disposable. Competing technologies are also promising: zeolites, silica or polymers.

2.2.1.6.2 Additional market threats: flame retardant properties

In terms of flame retardancy, the most important issues for polymers are solved (FST: flammability, smoke, toxicity with halogen-free additives). There are several additives available that work well with base level polymers (e.g. TFP Tris(2,2,2-trifluoroethyl)phosphate), ATH Aluminium Trihydrate, MDH Magnesium Hydroxide). Exfoliated graphite is already used and the performance is good as it decreases movement of polymeric chains. However, the loadings for certain polymer compounds need to be high to reach a reasonable flame retardancy (often above 55%), which in turn reduces the mechanical stability. This provides an opportunity for graphene materials as additive (see 2.2.2.1.3, high BET graphene has proven to be interesting) or coating (see 2.3.1.1.5).

In order to be feasible for flame retardancy, the FST test standards of particular applications have to be met (e.g. for airplane interiors, trains, automotive, cable industry). If not via cost or much better performance, graphene or 2D materials have the best chances to enter the market via the multifunctional enhancement, where the flame retardancy is combined with other interesting properties, such as increased strength, electrical and thermal conductivity and/or self-sensing of fire damage.

In terms of cost competition, the average price of a flame retardant additive is \$2.1/kg and loadings are up to or even higher than 55% by weight. For lower percentage of feeding, high performance polyphosphates are the alternative in halogen and antimony free flame retardant materials, however, the price of these materials is 4.0 to 7.2 €/kg with loadings of 35% or 20%, respectively. The overall market for these additives was \$2.07b in 2014 in North America and Europe with a projected CAGR 4.4% in revenue (Europe only: \$1.07b revenue and CAGR 3.7%, being ~10% of the European polymer additives market of \$13b). The demand stems from building and construction, electrical and electronics, automotive, and wires and cables industries. [46]

2.2.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in composites

2.2.2.1 Current strengths for graphene/2D materials use in composites

2.2.2.1.1 Multi-functional property enhancement of host material and improvement potential

The unique selling proposition of graphene materials as an additive in composites is its multi-functional property enhancement. By adding graphene one can not only address a single property such as mechanical enhancement, but also at the same time electrical and thermal conductivity, barrier properties, chemical inertness etc. Also added functionalities such as self-healing capabilities of elastomers can be triggered by graphene materials, which is currently investigated. The presence of graphene materials also allows self-monitoring and self-repair in thermoplastic composites (by the Joule effect), or simple sensing, due to their electrical conductivity.

With these property enhancements, graphene and other 2D materials address common composite challenges of stiffness, strength, fatigue, improvement of crash and impact resistance, environmental resistance, creep, energy management or temperature capability. Ultimately, the functional enhancement can lead to added functionalities such as sensing capabilities or for damage detection. The chemical inertness allows usage in corrosive and harmful environments (sea, chemical plants). It has also a tuneable transparency or absorbance to certain wavelengths of the electromagnetic spectrum (e.g. radar, UV or infra red light) and can thus potentially be used to adjust the interaction of the host material with electromagnetic waves. On top of that, graphene has a potential end of life strengths: it is a carbon based materials, where recyclability, biodegradability or residue-free combustion capability is possible, but clearly needs to be proven. Graphene might not be necessarily better than other technologies for the single parameter enhancements, but the combination is unique. This multi-functionality opens possibilities for new design of components due to integrated functionality and increased strength.

The theoretically high performance improvement potential for these properties is encouraging. Although graphene materials will hardly improve the properties of the host material to the level of pristine monolayer graphene, there is still a large gain possible and room for improvement (see Figure 5). Many potential improvements are shown in the lab (mostly for singular parameters). These “flashes of positivity” now need to be further elaborated to actually prove the benefit in functional environments and the economical feasibility.

Another potential business case is the upgrading of cheap host materials (e.g. polymers PP, PE or chopped fibre-reinforced polymers, using thermoplastic instead of thermosets in structural CFRP) to allow usage in other applications where higher performance is needed for a lower cost. This in turn could enable use of simpler production methods (e.g. use of injection molding/infusion for short-fiber CFRP). In particular for this application it is important to consider the appropriate competing materials i.e. making a cheap polymer better will only be relevant if the improved polymer comes at a price that is lower than that of another material that achieves the properties of concern already without improvement.

While most of the research work has been concentrated on composites of graphene with a polymer matrix, promising results have been obtained more recently also for metal matrix composites (MMC) and ceramic matrix composites (CMC). In literature, only limited researches on metal matrix composites reinforced by graphene are available. Graphene and carbon nanotubes (if processed in the correct way) can give structural reinforcement and self-lubricating properties to metals, influencing as well their microcrystalline structure and reducing the density of the material. [9] In ceramics, better strength and lower brittleness as well as increased conductivity are investigated. [11] Also functional enhancements, for instance for battery electrode, supercapacitors, corrosion or sensing are possible. [10]

2.2.2.1.2 Influence on electrical/thermal conductivity of host

Besides the mechanical enhancement and the multi-functionality, graphene materials are especially promising to improve thermal and electrical conductivity of the host material, which allows “functional lightweighting”.

Carbon black and graphite are already widely used to introduce electrical conductivity, e.g. in ceramics or plastics. However, using graphene materials increases the conductivity further, allowing additional applications to be addressed. For instance, aerographite-PDMS composites are investigated for de-icing purposes and show quite promising results. Further improvement of the conductivity of the composite and thus of its heating behaviour could be achieved by combining the aerographite network with graphene material.

Conducting composites with graphene material as additive are already on the market (e.g. for 3D printing)[d].

Adding conductivity to a composite also allows additional "sensing" properties for degeneration or breakage. A particular strength is the corrosion resistance of graphene, allowing the use in harmful environments, where metals are degenerated. The tuneable transparency or absorbance to certain wavelengths of the electromagnetic spectrum allows also usage where metals are disadvantageous (e.g. for radar dome de-icing).

For conductive applications, graphene material yarns (similar to CNT yarns) could be used as carbon based conductor for electrical signal transmission. In that case graphene is used as a rather pure bulk material and not as an additive. The challenge in that case is to allow higher currents through bulk transport, which calls for a 3D architecture to increase the overall transported power and current. Carbon based power cable constructions, a very visionary application, are not yet possible with material available. However, in high voltage applications graphene materials can be used as the “semicon” in the insulation of power cables and as an electric field grading material both aiming at stress reduction of the insulator.

In case thermal conductivity is needed without electrical conductivity, graphene materials are not viable as the two properties cannot be separated. In that case two-dimensional BN can offer a solution, as it increases the thermal conductivity but is electrically insulating.

Use of low amounts/loading of graphene/2D materials to achieve a good conductivity/good properties might lead to cost advantages eventually.

2.2.2.1.3 Flame retardancy and gas barrier properties in polymers

Graphene and other 2D materials can also increase flame retardancy in polymers. Exfoliated graphite is already used in this respect, and an increased thermal stability of polymers by several tens of degree centigrade were observed, reducing also the LOI (Limiting Oxygen Index).

The chemical stability and layered structure of 2D materials is beneficial for flame retardancy. There are synergistic effects with exfoliated graphite/other retardants to decrease movement of / immobilize the polymeric chains and improve anti-dripping and improving surface char generation as a protection: It has been observed that the use of high BET graphene materials allow to obtain better performance than with exfoliated graphite [47] and it also has synergies in combination with other flame retardant materials such as $Mg(OH)_2$ and phosphates. [48] The flame retarding performance of gra-

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[d] E.g. http://www.graphene3dlab.com/s/home.asp

phene materials and the increase of the thermal stability of the polymers, even at low loading, and its synergetic effect with other low cost flame retardant materials such as ammonium monophosphates (<1€/kg) can allow to have a price competitive alternative to other halogen free flame retardant materials.

Graphene materials thus perform to a certain extent better than other carbon materials and business cases are identified (see paragraph above), but it is still under discussion and debated whether other flame retardants can be outperformed in terms of cost/benefit on large scale. It also needs to be considered that enhanced IR absorption brought into materials by graphene may counteract to an initial benefit due to additional heating. The use as a coating is also possible, which in turn does not affect the mechanical properties of the host at all (see 2.3.1.1.5).

Although most of the problems, such as avoiding the use of halides, antimony or borates are already solved for polymers, still high loadings or higher cost materials such as ammonium polyphosphates and ammonium polyphosphates combined with char promoters are needed. The average price of a flame retardant additive is $2.1/kg for materials demanding high loading (55%) [46] and ~4-7€/kg for materials demanding lower loading (20-35%). In order to compete with that in terms of pricing, the loadings or the additive prices need to be low enough. Graphene materials benefit can be that a much lower loading is needed, which in turn does not change other properties (or even improves them).

Besides, graphene materials can add value when the multi-functionality is desired (e.g. increased strength, electrical and thermal properties).

However, smoke and toxicity need to be investigated for further implementation (application depended: there are differing regulations depending on the use in cars, trains or underground, aircrafts).

The commonly used flame retardant MDH Magnesium Hydroxide (unit shipment share in Europe of 9.2% of all flame retardant additives in 2014 [46]) is also available in a two-dimensional form. This modification could actually lead to improving the performance parameters or to reduce the needed loading of this additive.

Barrier properties can also be enhanced with graphene and other 2D materials, e.g. for gases. When they are well dispersed in the host material and have a reasonably large aspect ratio, the pathway for gases can be enhanced. Barrier properties of graphene nano-sheets are for instance approximately 25 to 130 times superior to those of clay nano-fillers at low concentrations. It remains to be seen how they compete with established coatings.

2.2.2.1.4 Straight forward, scalable preparation, integration and processability for polymers

A benefit for early adoption of graphene materials in composites is that very often multi-layered graphene, graphene nanoplatelets or graphite nanoflakes are sufficient to reach desired improvements. These bulk materials can be rather easily produced from metal-free, low-temperature and scalable wet exfoliation of graphite or reduction of graphene oxide, which is in contrast to carbon nanotubes, that are usually produced in vacuum or dry vapour processes by using catalysts.

There are also potential in-situ methods to produce graphene (e.g. exfoliation in a thermosetting polymer), however, these are currently not feasible due to open questions on how to achieve sufficient quality and control (e.g. distribution of lateral size)

The further integration in the host material is possible in various ways. It is essential for all applications to achieve a uniform dispersion of the added graphene/2D material. In polymers, it can be incorporated in the melt, by a masterbatch or prior to polymerization. Most importantly, the flakes need to be well dispersed.

Using additives in a masterbatch or prior to polymerization is more desireable, as the further processing of the composite requires no change in common standard production methods, i.e. there is no change in the downstream industry needed.

For ceramics it can be added as a powder in a wet mixing process, e.g. in colloidal solutions before sintering. For cement and concrete for example graphene oxide can be added during mixing.

All these processes allow the final composite to be further processed in a usual way, although the additive might influence the process characteristics of the composite (e.g. workability of concrete) positively or negatively. Dispersions or Predispersions of the material could help to further improve the processability.

2.2.2.1.5 Resistance against corrosion and heat

Graphene materials usually withstand high temperatures and corrosive environments due to the chemical inertness. So even if the performance such as mechanical strength or thermal conductivity does not reach certain levels, e.g. of metals, the potential use in these harsh environments and lower degradation can be the USP for particular niches.

2.2.2.1.6 Relatively low implementation barrier in polymers

Due to the somewhat simple integration and the use of graphene nanoplatelets and GO, the use of graphene and 2D materials in composites has a rather low implementation barrier compared to other potential applications. This is further supported by the rather low loadings needed to get an effect. The latter of course depends on the application and host and typically varies from 10^{-2} % to a few percent by weight.

This low implementation barrier has led to the fact that the (so far) only actually marketed applications of graphene materials can be found in the composites area, i.e. in sports equipment. The manufacturers use graphene or graphite platelets to improve the mechanical properties of the compound.

2.2.2.1.7 Value/supply chain for polymers emerging but still open questions

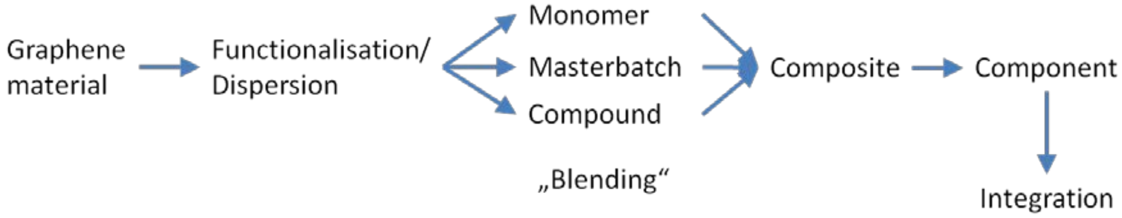

Figure 15: Simplified processing of polymer composites. The steps for other host materials are comparable with different processing techniques when it comes to composite preparation.

As mentioned in the prior subsection, the supply chain for 2D materials based composites presumably requires a change in the typical supply chain for composite materials, due to the low apparent density of the high BET graphene materials and in some case the functionalization (see Figure 15). There are several intermediary companies who specialize on this functionalization and predispersion, such as Haydale in the UK, if this is not done by graphene provides themselves (e.g. Avanzare in Spain or Angstron Materials in USA, are producing predispersion and/or masterbatchs for the reduction of steps in the graphene value chain).

Such intermediate companies or graphene suppliers dedicated to the introduction of the graphene materials in matrixes can sell ready to use masterbatches or predispersions tailored to the correct employment of end users. They can also define working conditions with the prepared masterbatches, because for instance depending on the screw elements, it could be possible to break graphene sheets and lose properties.

Nonetheless, the supply chain is still in its infancy. There are companies of each step of the value chain in Europe and also the graphene material part is covered. Also in terms of the coverage of potential integrators, Europe is well situated (see 2.2.1.1.7).

One issue that is still persistent is the effectively/safe packaging and transport of graphene or 2D materials. This depends on the position in the value chain and is more of a concern for graphene material producers that do not integrate the material in a host (the composite/masterbatch/resin transport and packaging is not a problem). Especially for global value chains this issue can be a problem how to ship tons of graphene materials as powders or dispersions safely and stable.

Massive applications are not competitive in price at the moment, but it is expected that the price of high performance graphene grades will decrease significantly in the next years. The optimization of formulas and performance together with the reduction in price might eventually lead to competitive graphene based materials.

2.2.2.2 Current weaknesses and challenges of graphene/2D materials use in composites

2.2.2.2.1 Variability of supply of graphene materials and missing standardization and knowledge of the needed quality of material

Many different types of graphene are sold on the market for different prices. For composite applications the quality ranges from expensive single to few layer graphene flakes to multilayer flakes and cheap graphene nano platelets or nano-graphite (see Table 3) with different lateral sizes and oxygen contents. The lack of standardization and certification leads to the problem that all these very different materials in terms of performance and price are sold under the name of “graphene”. This leads to a mismatch in expectations and can to a disappointment/disillusionment due to high promises (“stronger than steel”) and first tests with wrong material. The risk is therefore high that the market gets damaged by companies selling carbon based material with 20+ layers as graphene without further clarification. It is important that graphene and 2D material suppliers get their products characterized from an independent institution. The variety and uncertainty of supply makes it complicated for application companies to decide which material to go for. This is already partially tackled by industrial self-regulation on national level, e.g. in Spain the National Association of producers and users of graphene with relevant producers such as Antolin, Avanzare and Graphenea and end users such as AIRBUS and REPSOL have adopted industrial standards for the characterization and labelling of graphene materials. This needs to be enhanced to EU or even worldwide level.

Besides this lack of clarity of the supplied materials, there is also more knowledge needed on the quality of material needed for a particular application. The material properties and its interaction with the host materials is still not comprehensively understood in a way that an application company can easily decide which graphene material to go for. Often it is still unclear which type of material (FLG, graphite flakes…) is best for the application (in terms of cost, quality and performance), e.g. in CFRP the sheets should not be too large in the filler. The needed amount and loading of material needed is also very relevant, especially as it determines cost-competitiveness. The goal should be to use the material that achieves the desired functionality for the lowest added cost, which is determined by quality of the graphene additive (higher quality will lead to higher cost), loading and process of integration.

Due to the lack of standardization there is also no quality assurance and quality control in place, which also hinders market uptake. Application companies need a second source for similar quality material, which is nowadays controllable, possible and not available. A steady, assured and controlled supply is today not yet available.

In order for graphene materials to be broadly applicable also **health and safety** issues have to be addressed based on industry standards (e.g. REACH not conducted yet). This is also depending on a prior standardization. In particular the health and safety aspect needs to be thoroughly addressed as the danger is high that graphene can be perceived as harmful by the broader public, although it might not actually be harmful in the applied form. This is particularly relevant when the material can be exposed due to wear (surface properties/lubrication) or combustion/decomposition.

As soon as a standardisation is available also the important topics such as end of life, environmental compatibility, acceptability from a regulatory point of view for different applications (e.g. in food, medical applications, drinkin water) need to be addressed.

2.2.2.2.2 Cost/benefit often not yet clear

Cost for nano-graphite, graphene nanoplatelets and few layer graphene and can range from \$20/kg to \$2000/g depending on quality and ordered amount. The cost for platelets with 11-100 layers ranges from \$20-\$1000/kg[e] with variable quality (lateral size, oxygen content, BET). The cost of production and of graphene materials is expected to decrease further with target prices for 2020 of €125/kg for high BET few layers and low oxygen content graphene and €25 to €35/kg for platelets with 11-30 layers,, as supplying companies are ramping up and scale to industrial quantities. For low quality graphene, actually an oversupply/overcapacity is claimed [49].

Undoubtedly, adding graphene or 2D materials to a composite will lead to added costs, depending on the loading and quality of used material. It is therefore of utmost importance to objectively clarify the cost/benefit towards competing technologies and the state of the art. The costs are to a certain extend controllable and foreseeable, however, also the actual benefits need to be made clear. This means that it is not enough to compare the composite with the unmodified base material, but there is also a fair comparison with state of the art or competing technologies needed. The goal needs to be to clearly show what added benefit graphene/2D additives can achieve in applications towards the currently used materials or whether it can achieve something that cannot be achieved otherwise.

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[e] Consolidated values from Haydale, Future Markets Inc., Avanzare and Fullerex

Currently, improvements are not enough proven in relevant environments, i.e. often a real proof of principle is missing and tests are only under artificial circumstances. For a further feasibility study, it is important to show the potential in demonstrators relevant for the later application. That also includes testing a set of relevant parameters (e.g. tensile strength and fracture toughness), rather than testing for improvement of single parameters. With that, an objective evaluation of cost/benefit is possible.

There is a feedback from industry stating that lab developments do not go through to products, because not all scientifically interesting effects are commercial viable, although some are encouraging. A problem is the uncertain credibility of some published papers and measured improvements.

The cost and comparison to competing technologies issue becomes even more severe, when the host material is cheap, e.g. PP, PE or engineering polymers, where the polymer on its own costs 1-6€/kg. Adding a graphene material at a loading of 1-3% can easily double or triple the material cost only. It then would need to compete with performance polymers that are typically priced 3-20 times higher than engineering polymers (average 12$/kg [50]). The comparison with other materials achieving similar properties is of highest importance for this case.

Graphene can often replace conductive carbon black in composites to improve conductivity. As lower loadings are needed to get similar or better effects, material is saved. If the loading is reduced by a factor of 10, graphene materials should not cost much more than 10 times the carbon black price (carbon black ~1-2€/kg for carbon black used as filler in the rubber industry, and for conductive carbon black ~16-60€/kg on ton scale). Recently Avanzare and Ashland have introduced in the market an electrically conductive composite based on epoxyvinylester resin (resin alone costs less than 1,5 €/kg)

A next necessity is to also meet the requirements for use in larger markets, e.g. automotive, aviation, packaging (thermal stability, durability, abrasion, qualification, cost). This also includes taking into account life and failure mode prediction and demonstrate lifecycle cost savings. Many commodity products, but also often higher priced products to not allow a higher price point, even when functionalities are improved. Therefore the lifecycle cost savings are essential for a cost/benefit assessment.

Several potential application companies expressed that the current performance improvements are not good enough for the price/effort. In particular for materials that are currently already cost prohibitive to be widely used (e.g. CFRP in automotive despite in high class cars). Prices for graphene materials are expected to go down, which can in turn improve the cost-benefit.

Last but not least, bulk graphene platelets are black in colour, which could have an effect on the applicability of composites due to colour constraints (where a colour coating is not desirable). This particularly applies to applications addressing thermal conductivity or electrical conductivity according to an industrial expert assessment based on market feedback.

The actual achievable tuneability of electromagnetic transmission needs to be communicated more clearly to possible stakeholders before this promise will be accepted in the industry. At the moment, numbers like 3% light absorption per layer of graphene are widely accepted as a universal truth.

2.2.2.2.3 (Potentially negative) Influence on processability of host material and component

For the effectiveness of the additive and reproducibility it is crucial to have the adequate dispersion of the filler depending on the application. Larger platelets of 2D materials are dispersible with the right viscosity, functionalization or dispersing agent. This dispersion is a crucial step and needs to be well designed to reach the desired effects to overcome a lack of solubility/dispersibility (at high loading) and poor blending with host matrix. It is, however, also a process that adds another degree of freedom needing technical expertise and the formulation takes time for each application case. Furthermore, dispersion/functionalization processes need to be available at sufficient scale to not become a bottleneck.

Although graphene or other 2D materials are typically added at relatively low loadings, they can influence the processability of the host material (rheology, e.g. viscosity). This is for example seen in the workability of cement that is exacerbated when GO is added. [12], or in epoxy resins, and most of the thermoplastics when GO, rGO and few layer graphene are used as filler. Changes in the viscosity are also observed in polymers [51], although the changes are smaller than for CNT [52]. This can have positive or negative effects depending on the process (extrusion, molding, …). The addition of a 2D material filler will most probably require at least a change of other processing parameters (sintering, extrusion, assembly). In the worst case, which appears to be the exception, different preparation techniques for components need to be applied (e.g. due to changed process). Additionally, the further processing of the components, such as joining, pressing, could be influenced. This needs to be investigated. The implementation barrier is lowest, where least changes are required. The goal should be to adapt the resin/polymer/host with graphene in a way that the manufacturing does not need to change tremendously, because changing a manufacturing process is very difficult nowadays.

For 3D printing materials graphene materials might be problematic for powder-bed sintering applications due to promotion of crystallization and in photopolymerization techniques due to reduced optical intrusion depth.

The need for safety precautions in production and the related effort for that are is also important and could become a weakness. First good practice protocols do minimize the release in production are available. However, most material production demands a certain degree of safety precautions, so that this is not a severe issue.

2.2.2.2.4 Processing challenges in metals and ceramics and low maturity

Processing GRM in metals or ceramics is more challenging than processing in polymers, due to the high temperatures needed for melting or sintering these materials. Issues such as carbide formation during high temperature processing need to be addressed.

The field of graphene-based metal or ceramic composites is much less mature than the one of polymer composites. However, proving that including GRM in these novel matrices leads to improved properties or cost/performance benefits while addressing the current weaknesses of these technologies (see 2.2.1.1.5), could spur industrial interest, given the large potential market size accessible for ultra-light metals or machinable ceramics.

2.2.2.2.5 Current missing links in supply chain for graphene integration

The value/supply chain of composite materials is currently not well covered in the graphene composites research and the graphene flagship. In particular in terms of prepreg integration and development, there are not many stakeholders involved. This opens up a missing link between material suppliers (e.g. resin and graphene producers) and final integrators (e.g. automotive or aerospace companies). It might be even needed that graphene materials will add another step in the value chain in form of companies doing predispersions mixing, before the materials go to compounders. This step could also be provided by graphene suppliers. Besides, graphene is not yet highly recognized in market driven composites communities.

2.2.3 KPIs for composites

The following chapter summarizes important qualitative and quantitative technical and non-technical KPIs for composite materials.

2.2.3.1 General KPIs

2.2.3.1.1 Recyclability and combustibility

For many applications, recyclability, combustibility (residue free combustion in standard waste treatment) and biocompatibility/biodegradation when released to the environment are needed.

2.2.3.1.2 Cost

Table 8: Allowed added cost per kg saved (same table as Table 7).

Sector	**Allowed added cost per kg saved (roughly)**
Automotive	<3€ (mass market) -8€ (premium market)
Aviation	Few 100€ (depending on aircraft)
Space	Few 1000€ to 10000€

CFRP (automotive): average 100€/kg (material ~20-24€/kg), goal is 30€/kg (processing optimization) [53]

GFRP (automotive): 4.1$/kg (material price) [50]

Flame retardant: average revenue per shipping unit: $2.1/kg [46]

Impact modifier: 2.7$/kg (average) [46]

Engineering polymers: 1-6€/kg

Performance polymers: average 12$/kg [50], up to 100$/kg

Carbon black: 1-2$/kg as filler; conductive carbon blacks 16 €/to to 60 €/kg (on tonne scale)

2.2.3.2 Technical KPIs

For these KPIs it must be clear that just improving the properties of a given material is less relevant for industry; rather the improvement must be achieved at lower cost or other advantages relative to other, already existing materials.

2.2.3.2.1 Mechanical

Youngs modulus: (elastic modulus): increase

Tensile strength: maximum stress that a material can withstand while being stretched or pulled before failing or breaking: increase

Fracture toughness: describes the ability of a material containing a crack to resist fracture, it is the critical value of the stress intensity factor (measured in MPa $m^{1/2}$)Toughness: also toughness modulus: the area under the stress-strain curve and thus the dissipated energy per unit volume; this is much more structural-size dependent and thus less significant than fracture toughness

Look and feel, anti-squeak properties

Tribological properties: Friction, wear rate, (micro-) hardness (wear effects also important for health assessment)

Mechanics at elevated temperatures (and at extremely low temperatures)

Table 9 summarizes a few KPIs of typical composites on the market.

Table 9: Few examples of KPIs of composites for mechanical applications

Composite	**CFRP PPS**	**CFRP TPU**	**GFRP PPS/TPU**	**CFRP Nylon**	**PAN Carbon Fiber**			**Rods: CFRP-EP (unidir.)**
					Standart	**Intermediate**	**High**	
Recyclability and combustibility	"Easily"	"Easily"		"Easily"				
Density [g/cm³]	1.58	1.5	1.8	1.58	~1.8	~1.8	~1.8	1.5
Tensile modulus [GPa]	117 (0° layup) 54 (0°/90° layup)	48 (0°/90° layup)	25 (0°/90° layup)	103 (0° layup)	230-255	275-310	310-600	130
Tensile strength [MPa]	1690 (0° layup) 780 (0°/90° layup)	710 (0°/90° layup)	430 (0°/90° layup)	1620 (0° layup)	3450-5000	4130-6370	1890-4900	1300
Compressive Strength [MPa]	930 (0° layup) 448 (0°/90° layup)			1000 (0° layup)				
Company/Source	Impactcomposites				Vectorply			Carbon-Werke

2.2.3.2.2 Electrical, thermal, barrier, flame retardant

Table 10: KPIs of components for electrical conductivity: [54]

Ω/□	Material	Description
> 10^{13}	Insulative	Insulators and Base Polymers. Not an ESD material
10^{9} to 10^{12}	Anti-Static	Initial charges are suppressed. Typically pink color.
10^{5} to 10^{9}	Dissipative	No or low initial charge. Prevents discharge to or from human contact
10^{3} to 10^{5}	Conductive	No initial charge. Provides path for charge to bleed-off. Typically black color.
1 to 10^{3}	Shielding	EMI
10^{-3} to 1	Carbons	Carbon powders and fiber
< 10^{-3}	Metals	

Bipolar plates for PEMFC: >100 S/cm (and >20 W/mK thermal conductivity)

Bulk graphite in plane: 20-30000 S/m

Competition: metal coated carbon fibre, steel fibres

Thermal conductivity:

e.g.: Smart phone Graphite sheet (effective) d=25 µm, kxy = 400 W/mK, kz = 10 W/mK, Heat capacity 1.520E+06 J/Km³ [55]

Thermally enhanced commercially available polymers have thermal conductivities of 1-20 W/mK, sometimes 30 W/mK (PP or PA6) using organic fillers (e.g. graphite), metallic fillers (e.g. copper) or ceramic fillers (e.g. boron nitride) at high loading (up to 80wt.%). [56]

Barrier: Permeability to gases/liquids/ions, water uptake in epoxies

Flame retardant: flammability, smoke and toxicity tests (FST)

Table 11 and Table 12 show some exemplary KPIs of marketed products.

Table 11: Some KPIs of thermally/electrically conductive or other composites.

Material/Composite	**ECOPHIT**	**CFRC**	**PPS**	**LCP**	**TECACOMP®PA66**	**TECACOMP®PPS**
Type	Graphite in plasterboard	High temp. applications	Therm. & electr. cond.	Therm. & electr cond.	Therm. Cond.	Therm & Electr. conf.
Density [g/cm³]		1.55	1.71	1.84	1.48	2
Tensile modulus [GPa]			17.5	24.3	8	15.1
Tensile strength [MPa]	2.5	400	70	80	55	
Electrical conductivity				1 [Ω/□]	<104 [Ω]	1.42 x 10^4 [S/m]
Thermal conductivity [W/(m•K)] (in plane)	0.52		6	20	11.2	85.8
Thermal diffusivity [cm²/s]			0.0322	0.1	0.051	0.1523
Barrier properties	99.99% absorption of em waves					
Flame retardant				V0 (@1,5mm) [UL 94]	HB [UL 94]	V0 [UL 94]
Company/Source	SGL Carbon		Coolpolymers		Ensinger	Ensinger

Table 12: Some KPIs of thermally/electrically conductive or other composites

Material/Composite	TECACOMP®PA66 ID	TECACOMP®PEEK TRM	TECAPEEK450CF30	Ultrason®
Type	Detectable compound	Tribologically & mechanically optimised compounds	High temperature plastics	GFRP/CFRP with PPS, PES
Density [g/cm³]		1.5	1.41	
Tensile modulus [GPa]		12.5	23	32
Tensile strength [MPa]		155	240	250
Compressive Strength [MPa]		180		
Tribological properties		"very good bearing and wear properties"		Wear and impact resistance
Thermal conductivity [W/(m•K)] (in plane)		0.9		
Barrier properties				Chemical, fuel, and oil resistant
Flame retardant			Melting: 343°C	Excellent FST behavior
Company/Source	Ensinger			BASF Aerospace

2.2.3.2.3 Processing

Compatibility with standard infusion, molding, prepreg, mixing, processes

Influence on viscosity, workability, temperature, curing of composite material during manufacturing

Compatibility with shaping, joining processes

2.2.4 Roadmap for composites

2.2.4.1 Current Maturity: First niche products are in the market

The maturity of graphene based products depends strongly on the application. Potential improvements are shown in the lab, such as increased young’s modulus, improved conductivity and barrier. However, improvements are often shown only for singular parameters. These lab results are often not yet transferred to relevant environments/scales. Additionally, the overall set of parameters in not improved good enough in some cases: For example in some cases although the mechanical strength of a composite increases, the elongation and energy absorption until breaking worsens, which is not good for impact performance. It remains to be investigated which 2D material combination/configuration, loading and host work best together for a targeted applications and how they compare to competing materials in terms of cost-performance.

Only in niche applications (fishing rods, sports equipment) first products advertise the use of graphene. These are areas, where new technologies can be used for advertisement.

In terms of carbon based conductors the maturity is still very low (much lower than for CNT).

Products on the market or close to market:

There are already products commercially available in the sports and leisure sector that advertise their graphene content. As the name graphene is not protected, it is often not clear whether the equipment actually contains graphene materials or rather graphite flakes or carbon black.

Table 13: First available products or products expected to hit the market soon that claim to use graphene in composite materials (as of March 2016).

Company	Product
Head	Tennis racket[57], skis
Vittoria	Bike tires
G-Rods	Fishing rods
Catlike	Cycle helmets
Colmar	Sport clothes
Sher-Wood Hockey	Hockey stick
Graphene 3D Labs	Conductive composite filaments for 3D printing
Angstron Materials	Thermal Foil (k_{xy}=1500-1700W/mK, d=25µm), >12000 S/cm
Ashland Derakane	resin filled with graphene for conductivity

Other product ideas (not exhaustive): Condoms (2 years from now), rubber band with sensing capability, loud speaker cones based on PP+graphene (premium)

2.2.4.2 Barriers/challenges (summarized)

The following challenges summarize the most important issues that are also derived from the chapters on strengths and weaknesses as well as market opportunities and threats.

General challenges:

- Production of right quality (high or low) and functionalization are bottle necks
- Current graphene supply and uncertainty of quality (due to missing material standards), some self-regulatory are in implementation in Spain by graphene producers and some end-users as a first approach to solve it
- Transfer graphene properties to bulk material
- For the integrator or user, it is often unclear which material is best suited for the given purpose (quality, amount, functionalization)
- Show objective and real benefits in relevant environments looking at
- Cost/benefit: crucial, and to a large extent not yet clear or based on “assumptions”, especially important for cost sensitive markets (automotive, consumer).
- System and life cycle cost assessment
- Unclear end of life properties (combustion, recycling, biodegradation)
- Life cycle health and safety (working place, release in operation, end of life)

Process related challenges:

- Lack of technical expertise for applications
- Finding the right formulation takes time
- Reproducibility of large scale homogenization, dispersion and mixing in the respective solvent or matrix throughout the processes (from base material to final part/matrix) to reach and maintain an even distribution, e.g. for CFRP during infusion or prepreg. This was a “killer” for CNT/pellets/buckyballs
- In-situ methods to produce graphene (exfoliation in a thermosetting polymer or other matrix)
- For real electrical conductors, a process needs to be found (yarns?)

Value/supply chain and eco-system:

- Insufficient readily accessible data and design tools (standardized material property database) using performance standards
- The lack of standardization leads to the problem that all these very different materials in terms of performance and price are sold under the name of “graphene”. Due to the lack of standardization there is also no quality assurance and quality control in place, which also hinders market uptake. Standardization as a bottle neck: after that QA/QC, REACH etc can be approached
- Supply/value chain not yet developed, might need to be adapted
- Established and conservative supply chains
- Flagship: value chain not enough covered, e.g. component supplier for automotive missing. End-users/OEMs only do testing, but integration and innovation is done at component or prepreg/masterbatch supplier level (tier 1 and 2).

Thermal and electrical conductive composites:

- Anisotropy: If controllable, the anisotropy of transport can be strength, but until that this induces and additional barrier, as it is more complicated than an isotropic material.
- For higher currents: bulk transport needed, which needs a 3D architecture to increase the overall transported power and current
- Black colour often not desirable

2.2.4.3 Potential actions

If the area of graphene/2D in composites is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

Basic understanding:

- Graphene/matrix interaction deserves further studying (to transfer the properties of graphene to the matrix)
- Study and understand functionalization
- more knowledge needed on the quality of material needed for a particular application (systematic investigation of material) and education for end users to clarify the open question which material needs to be used (1-2 layer, few layer, nano-graphite…) and to manage expectations; this can be supported by predictive modelling
- Study dispersion/aggregation in matrix systems
- How to control isotropy/anisotropy with simple processes (for conductivity)

- Clear proof and an open discussion on Health & Safety is needed
- Is there any intrinsic biodegradability of graphene? Or would graphene rather come out unchanged from biodegradation of the surrounding matrix?
- Investigate actual achievable tuneability of electromagnetic transmission. At the moment, numbers like 3% light absorption per layer of graphene are widely accepted as a universal truth.

Many other actions are related to engineering problems and extensive testing.

Product development:

- “Flashes of positivity”/lab scale developments now need to be further elaborated and transferred to real environments to allow further uptake from industry
- Look at relevant sets of parameters needed for a particular application
- Make use of established standards, characterisation methods and norms for semi finished products, applications and materials where graphene is integrated
- Compare results to competing materials or technologies addressing the same functionality
  - This is particularly relevant for enhancement of host materials, which need to be compared to other materials that achieve a similar property (and not just to the plain host material)
- Address system and life cycle costs instead of only added cost through a new material

Processes:

- Scale up of production of 2D materials with needed quality (be it low or high)
- Develop large scale and mass production compatible functionalization methods
- Understand influence of 2D additives on processing of matrix materials, also in terms of post processing of parts, such as gluing, soldering…
- Investigate 3D printing
- Investigate the potentials for in-situ exfoliation

Testing:

- Durability tests needed (accelerated testing…) to know long term performance
- Test of effective packing and transit and shelf life of intermediates
- Show biodegradability/recyclability or residue free combustion in hosts (is graphene found in exhausts of waste combustion or is it decomposed?)
- Show compatibility with environment (for use in drinking water) to add it t the positive list of allowed materials and make it acceptable from a regulatory point of view
- Study the release of graphene from the host under crash, breaking, heat and other circumstances
- For flame retardant: “FST” Fire smoke toxicity, especially “ST” need to be tested according to targeted applications (cars, planes, trains, underground…)

Value/supply chain and eco-system:

- Enhance interaction with prepreg/compounder and component manufacturers to close the gap between researcher, graphene supplier and final user
- Manage expectations objectively
- Establish material standards and databases
- Bring national initiatives on self-regulation to EU or worldwide level
- Establish standardized methods to determine the quality of produced graphene and other 2D materials (“certification”)

- Create a group of classification criteria in order to evaluate the produced materials to help manufacturers and customers to
    - classify their material quality and customers
    - provide an expectation of the performance of the classified graphene and
    - decide whether or not the graphene or other 2D material quality is potentially suitable for various applications

2.2.4.4 Roadmap

Mechanical, electrical & thermal enhanced composites: broader niche markets will be addressed in the near future. More markets will be addressable in the next 3-5 years and the evolution of the market will be in parallel of the scale up of the graphene materials. Mass markets are expected not before 10 years.

Barrier properties: Marketable solutions are expected within 5-10 years.

Flame retardant: Broader marketable solutions are expected before 5 years, some very positive results has been achieved in thermosets, thermoplastics and even in textile industry. Rather addressed "alongside" with other functionalities as for flame retardancy only many solutions are available.

Further time related aspects depending on addressed sector:

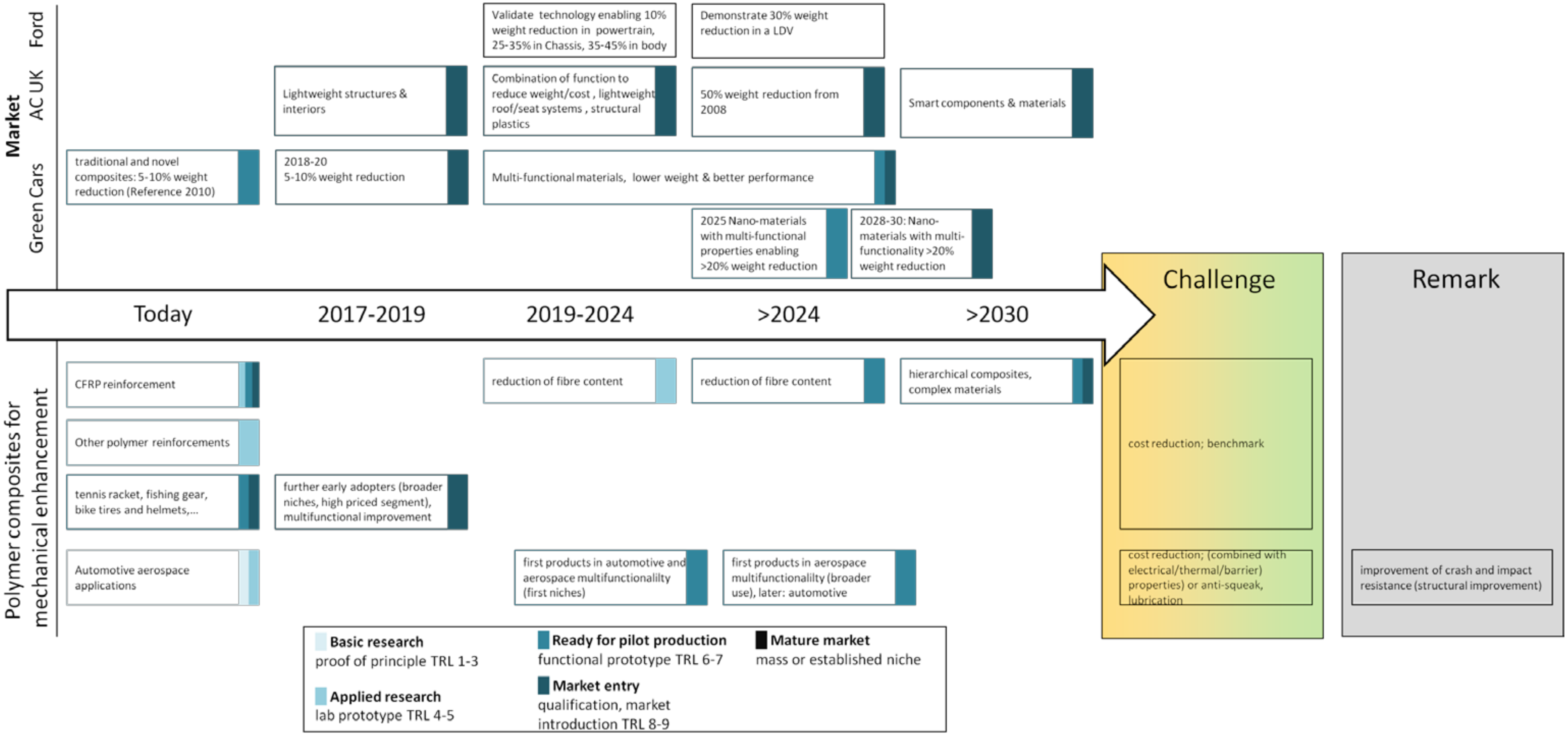
Automotive:

Lead time after "first testing": 4 years until market intro in automotive

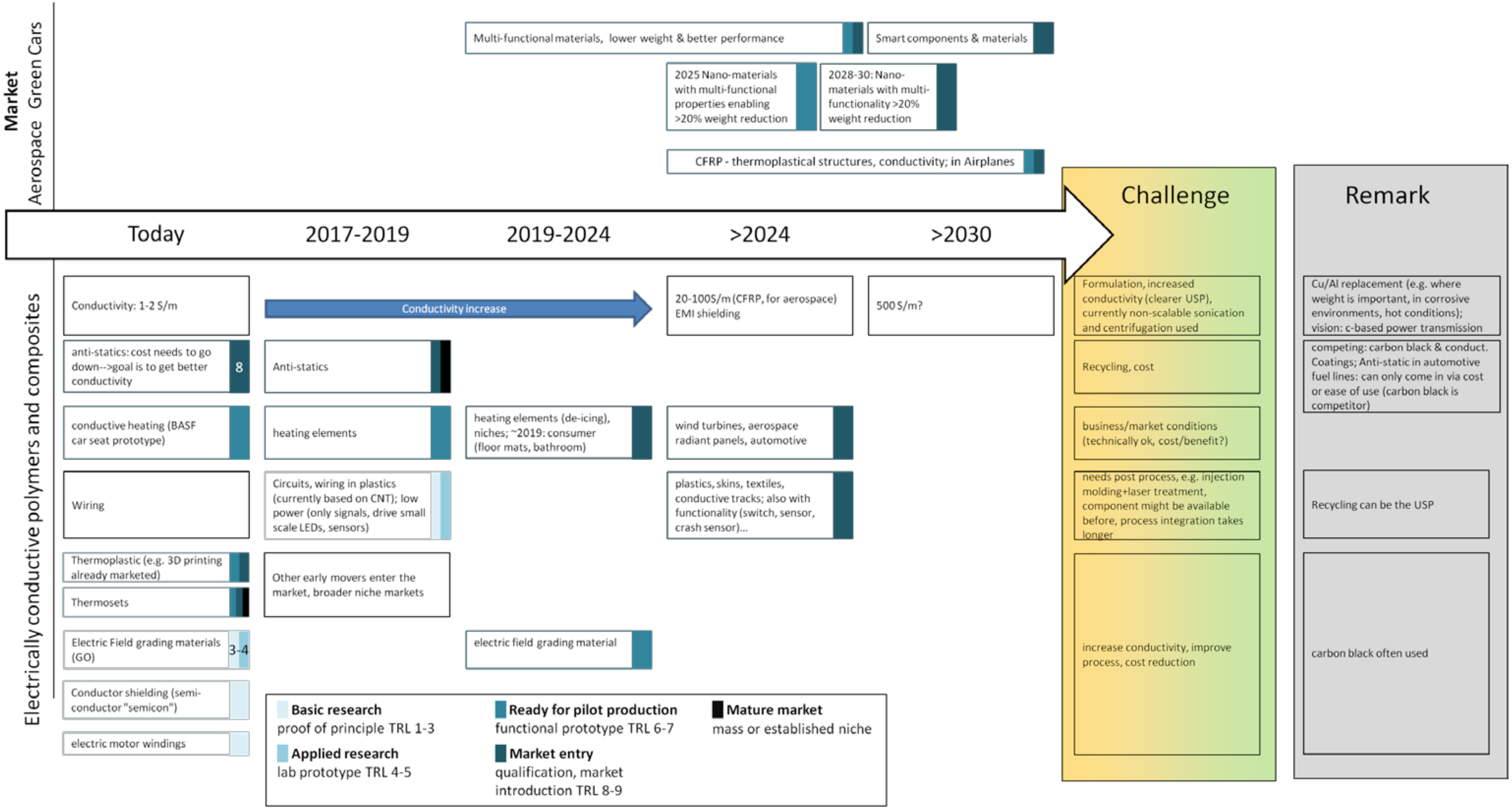
High price point: currently only high value cars (niche)

Aerospace:

It typically takes 10 to 15 years for a new air frame technology from basic principals until operational maturity (speed up is addressed currently).



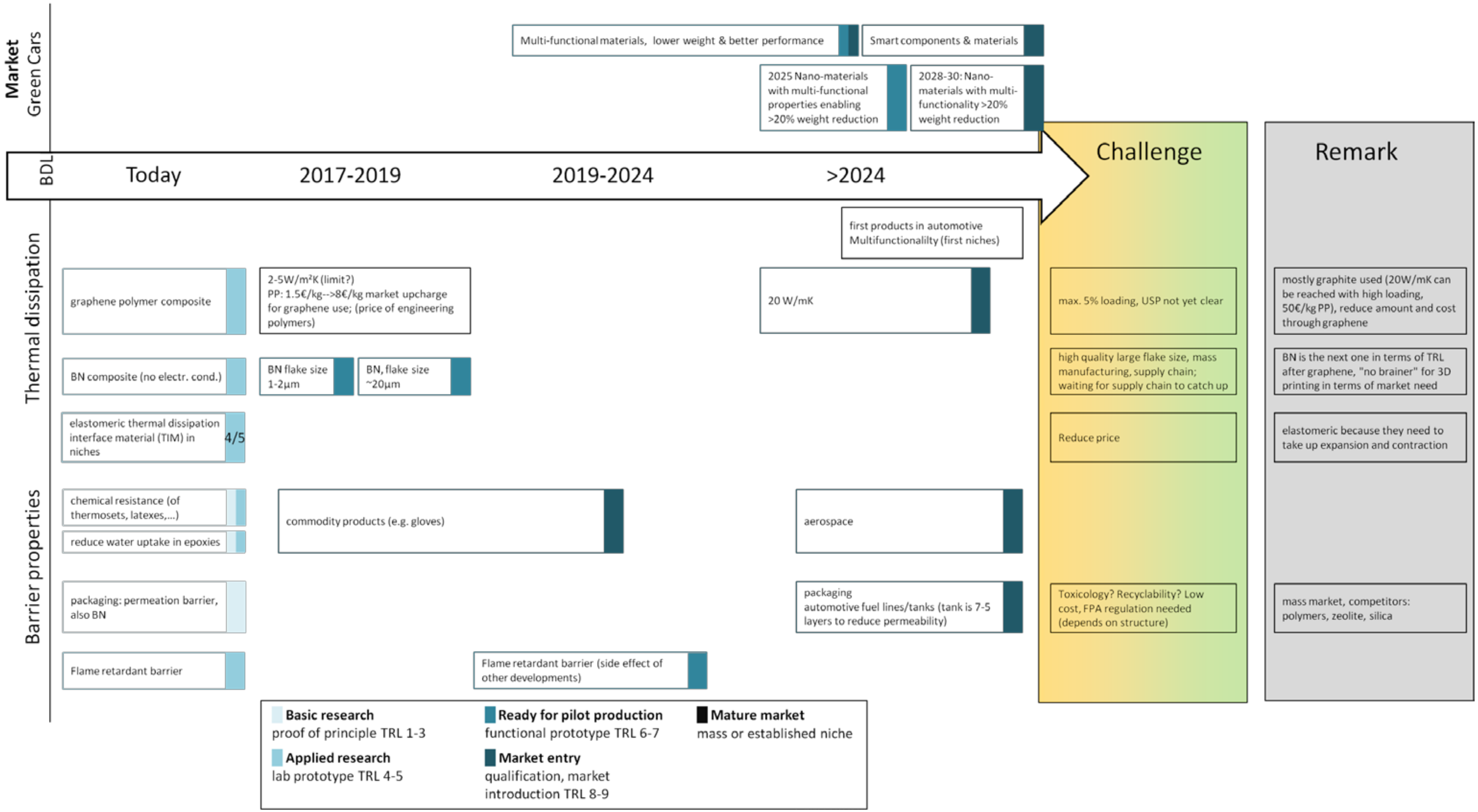
Sources: Ford [58], AC UK [59], Green Cars [60, 61]



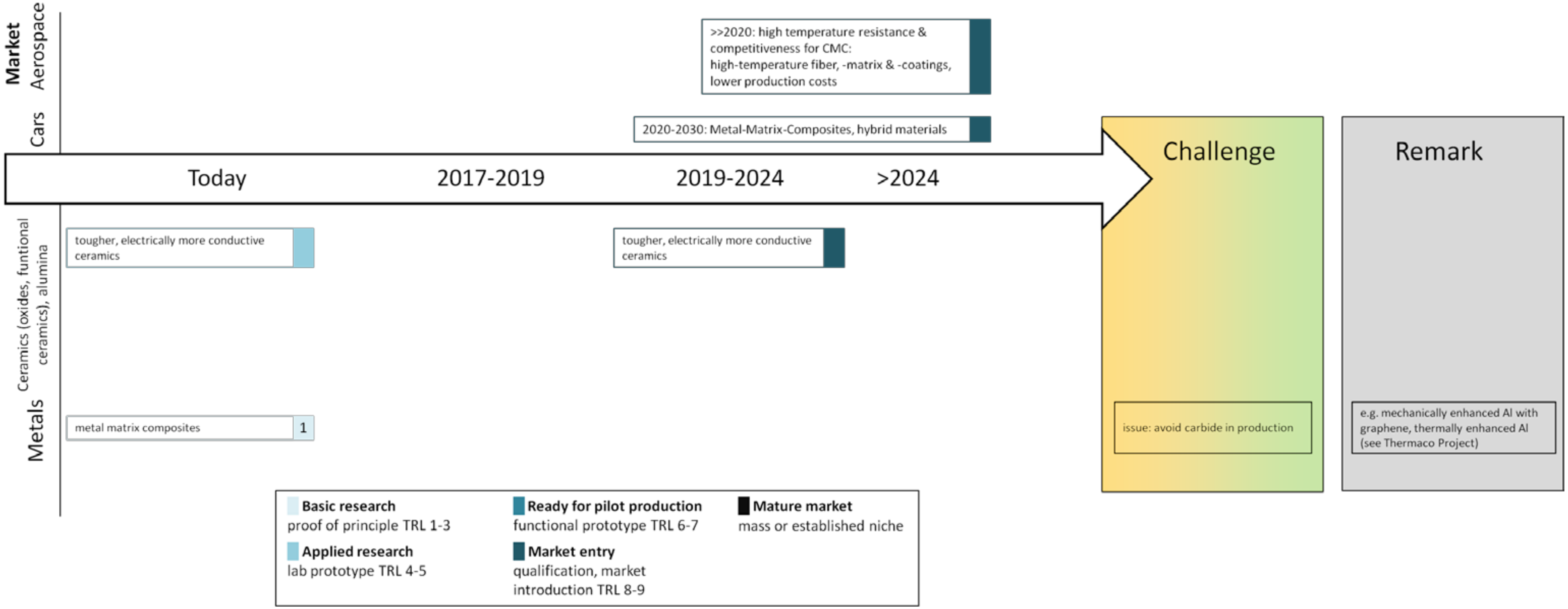
Market	Today	2017-2019	2019-2024	>2024	>2030	Challenge	Remark
Aerospace Green Cars			Multi-functional materials, lower weight & better performance	Multi-functional materials, lower weight & better performance	Smart components & materials		
Aerospace Green Cars				2025 Nano-materials with multi-functional properties enabling >20% weight reduction	2028-30: Nano-materials with multi-functionality >20% weight reduction		
Aerospace Green Cars				CFRP - thermoplastical structures, conductivity; in Airplanes	CFRP - thermoplastical structures, conductivity; in Airplanes		
Electrically conductive polymers and composites	Conductivity: 1-2 S/m	Conductivity increase	Conductivity increase	20-100S/m (CFRP, for aerospace) EMI shielding	500 S/m?	Formulation, increased conductivity (clearer USP), currently non-scalable sonication and centrifugation used	Cu/Al replacement (e.g. where weight is important, in corrosive environments, hot conditions); vision: c-based power transmission
Electrically conductive polymers and composites	anti-statics: cost needs to go down-->goal is to get better conductivity 8	Anti-statics				Recycling, cost	competing: carbon black & conduct. Coatings; Anti-static in automotive fuel lines: can only come in via cost or ease of use (carbon black is competitor)
Electrically conductive polymers and composites	conductive heating (BASF car seat prototype)	heating elements	heating elements (de-icing), niches; ~2019: consumer (floor mats, bathroom)	wind turbines, aerospace radiant panels, automotive		business/market conditions (technically ok, cost/benefit?)	
Electrically conductive polymers and composites	Wiring	Circuits, wiring in plastics (currently based on CNT); low power (only signals, drive small scale LEDs, sensors)		plastics, skins, textiles, conductive tracks; also with functionality (switch, sensor, crash sensor)...		needs post process, e.g. injection molding+laser treatment, component might be available before, process integration takes longer	Recycling can be the USP
Electrically conductive polymers and composites	Thermoplastic (e.g. 3D printing already marketed) Thermosets	Other early movers enter the market, broader niche markets					
Electrically conductive polymers and composites	Electric Field grading materials (GO) 3-4		electric field grading material			increase conductivity, improve process, cost reduction	carbon black often used
Electrically conductive polymers and composites	Conductor shielding (semi-conductor "semicon")						
Electrically conductive polymers and composites	electric motor windings						

- **Basic research** proof of principle TRL 1-3
- **Applied research** lab prototype TRL 4-5
- **Ready for pilot production** functional prototype TRL 6-7
- **Market entry** qualification, market introduction TRL 8-9
- **Mature market** mass or established niche

Sources: Green Cars [60, 61], BDLI [62]



Sources: Green Cars [60, 61]



Sources: AC UK [59], BDLI [62]

Electric field grading material for high voltage insulation

Composites have many different potential applications, sometimes with very special properties and requirements. This box introduces one special applications, i.e. the use as electric field grading material.

The field dependent conductivity (or rather isolation) helps to avoid discharge in isolators for high voltage applications (e.g. in HVDC cable joints), because field peaks and to large field gradients leading to discharge are avoided in the isolation of a cable. This is needed because ever higher voltages and lighter cables are used in power transmission.

GO can be used in a polymer matrix (e.g. 3% in Si-rubber) as a field grading material. It increases the resistance and renders it more field dependent, i.e. having a lower resistance at higher fields. Through that, voltage peaks are avoided. The best case would be a switching behaviour at a certain field threshhold. It has been observed that the conductivity switches by 6 orders of magnitude (from 10^{14} to 10^{11} Ω/m). [63]

The composite competes with SiC or ZnO particles and carbon black in a polymer matrix. Its benefits are that it is stronger and more flexible. Furthermore, it is possible to control and design the electrical properties to a certain extent and allows going to higher fields and thus higher voltage levels. Current issues are the long-term stability. Further understanding and testing, especially of reliability and performance are needed. Another barrier is the conservativeness of customers, e.g. Si-rubber is still a new material and is around since the 90ies. The horizon for commercialisation is on the order of 10 years.

In 2014 4.5b€ revenue was created in Europe with insulated electrical conductors for voltages above 1000V. [39]

2.2.5 Conclusion for composites

The variety of potential applications with early adopters makes composites a very interesting application area. Additionally, the graphene material can be prepared rather simply and cheap and graphene platelets are often sufficient. These platelets are becoming cheaper and with that the barrier for broader use is reduced. Functionalization plays an important role for this area, as the particles have to be well dispersed in the host material to gain the largest effects.

The USP for graphene use in this area is the multifunctionality, because it can increase mechanical strength, electrical and thermal conductivity, barrier properties, surface properties (lubrication) and flame retardancy at the same time.

Although the actual cost-benefit of is not yet known for most applications, the maturity compared to other potential application areas of graphene/2D materials is already quite high and first products are on the market. The sheer number of possible applications on the other hand makes it hard for researchers to address particular products.

Most important for a further market introduction is standardization and testing for health and safety and recycling/end-of-life properties. Besides, the demand oriented communities need to be made aware of the actual benefits and expectations need to be managed. The risk is still high that the expectations are too high (100x stronger than steel), which cannot be reached. Additionally, the perception of “graphene is the next CNT” reduces the interest from many conservative stakeholders.

Table 14: Assessment of market and technological potential of graphene/2D materials use in composites on a scale - -, -, 0, +, ++.

Composite property/host	**Current technological potential (USP)**	**Market potential (EU perspective)**
Mechanical enhancement	+	++
Thermal enhancement (polymers, ceramics)	+	++
Electrical enhancement (polymers, ceramics)	+	++
Barrier (polymers)	+	++
Flame retardant (polymers)	0	+
Multifunctional enhancement, added functionalities	++	++
Metals	0	+
Polymers	+	++
Ceramics	+	++
Cement/concrete	0	+

2.3 Industrial large scale coatings and paints

This chapter deals with graphene or 2D materials coatings or enhanced coatings and paints. The delineation from additive to solids or additive to liquids is the functionality in the final application: In contrast to the use as an additive, the coating covers only the surface of the sample/host. The functionality is thus only effective at the surface. This chapter addresses large scale (square meter) coatings/varnishes/paints for industrial applications. There is some overlap with other chapters. In chapter 4.6 flexible electronics. conductive inks for printed electronics applications and transparent, flexible and conductive films will be discussed in more detail. Coatings dealing with the special application of membranes and filtering are covered in chapter 2.5 Special application: Filtering, desalination/deionization and membrane applications, coatings that deal with photocatalysis are covered in chapter 2.6.

Special application: (Photo-)catalytic material/enhancement and coatings dealing with supercapacitors, batteries, photovoltaics and fuel cells are covered in chapter 3 Energy generation and storage. Films and coatings for electronics, sensing and photonics applications are covered in chapter 4 Electronics & Photonics.

From a technological point of view, coatings can be prepared from bulk graphene/2D platelets (usually used as paints or inks) or from pristine graphene or few layer graphene (usually prepared by chemical vapor deposition and then transferred onto the host). For coatings and inks, 2D materials can be used as additives similar to composites to enhance properties of common coatings. In principle 2D materials are a perfect candidate for coatings due to their sheet character and large lateral size.

There are some overlaps with functionality and application areas of coatings and paints with composites, see entries of Table 4 marked with an asterisk (*). The markets are also to a certain extent similar to the additives for solids, but the technological circumstances and implementation are different and there is a broader range of potential applications. Targeted coatings are summarized in Table 15.

The functionality of coatings is simply speaking independent of the host material, which is why the host material essentially plays no important role and is not extensively discussed here. Of course in reality each coating for a particular application needs to be attached to the host, so that there is indeed some interaction that can also influence the coating’s performance.

Special applications (filtering/desalination and photocatalytic enhancement) that are also partially related to functional coatings are presented in later chapters 2.5 and 0. Thermal interface materials for electronics are also addressed in chapter 4.2 Electronics: Cross-cutting issues.

Table 15: Different coating applications of graphene/2D materials and their functionalities.

Type of coating application	Functionality
All 2D material coatings	• thin and still highly functional • conformable (flexible, stretchable) • chemical inertness (graphene) • (semi-) transparency[f] (depends on number of layers and thickness of coating)
Barrier and protective coatings Recent reviews: Protective: [64–66] Wetting:[67, 68] Fouling/microbial: [69, 70][g] De-icing:[71]	• anti-corrosion • anti-fouling • anti-microbial • biocompatibility coating • hydro/oleo phobic coating (liquid repellant) • anti-/de-icing • reduced gas permeability • flame retardancy
Functional coating Recent reviews: Transparent conductor:[72, 73][i] EMI:[74] Lubrication:[75, 76]	• (anisotropically) electrically or thermally (transparent[i]) conductive layers (e.g. for displays, LED, PV, EMI shielding, anti-statics), thermal interface materials • anti-reflective layers/optical coatings • electrochromic coatings • solid surface lubrication (change of surface properties (lubrication/tribology, wear resistance, anti-squeak)[h] • improved capillary effects (e.g. for heat pipes) • all-new functionalities with e.g. simple sensing properties[i].

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[f] Fully transparent coatings (transparency>90%) (e.g. for transparent conductive films) can currently only be achieved by CVD prepared high quality graphene films.

[g] See also chapter 2.5 Special application: Filtering, desalination/deionization and membrane applications

[h] Graphene can be also used as powder and in liquid lubricants, the latter is covered in chapter 2.4 Additive to liquids

[i] This overlaps with flexible/printed electronics and sensors, please refer to these chapters: 4.5 and 4.6

2.3.1 Market perspective: graphene/2D materials in coatings and paints

The overall market for coatings and paints is estimated to be >$120 billion in 2014 with a growth rate of CAGR ~5% until 2020 where it reaches a projected $160 billion. [77, 78]

Multifunctional smart coatings and surfaces are expected to exceed $1.4 billion by 2021 with the highest share in the construction industry ($625 million) followed by automotive ($450 million) by 2021. [79]

The global automotive coatings market was valued at $14 billion in 2014 and is expected to grow with CAGR 5.5% to ~$19 billion in 2020. [80] The global aerospace coatings market size, in terms of value, was estimated at $2.1 billion in 2013 and is projected to grow at CAGR ~6% to reach $2.9 billion by 2019. [81] For marine applications the coatings market had a size of $7.65 billion in 2013, with a growth of CAGR 6.5% to rise to ~$12 billion by 2020. [82]

Other sources estimate the protective coatings market to be $10 billion today, growing to $14 billion in 2025. A big chance of growth is attributed to coatings that have additional functionality besides protection, e.g. hydrophobicity or other functionalities. These coatings can also come for a higher cost, if the additional investment pays off due to lower maintenance costs or operating cost (e.g. fuel savings for airplanes). [83]

Anti-corrosion is one of the most important functionality addressed by coatings. The overall cost of corrosion is estimated at 3 to 5% of GDP depending on the sources. Undoubtedly it is a large economic challenge. The global market for anti-corrosion coatings was estimated at ~$21 billion in 2014 with a CAGR of 4.5%. The marine industry holds the largest share of the anti-corrosion coatings market. [84] High performance anti-corrosion coatings account for ~$12 billion in 2014 growing at a similar speed. Epoxy coatings are the most important ones accounting for over 55% share. Acrylic coatings are expected to be the fastest-growing product segment. [85]

A smaller, but still important market is the anti-microbial coatings market which is expected to reach >$4 billion by 2020 growing at a CAGR of ~10% from >$2 billion in 2014, with USA being the major market growing at CAGR 10-14%. Most important segments are indoor air quality (~1/4 of the market), mold remediation, medical/healthcare, antimicrobial textiles, construction and food. The European market revenue is expected to reach ~$1 billion by 2020. [86–88]

Functional additives and barrier coatings market for plastic packaging is also a market with potential interest for graphene/2D materials innovations. The global market was estimated to be $2.8bn in 2013 with a CAGR of ~6% (reaching $3.7bn in 2018). Western Europe is the second largest market (~18%) after Asia and before North America (~15%). [89]

IDTechEx Research estimates that the market for flexible barrier films for flexible electronics will grow to $34 million by 2016 and to $240 million by 2023, one third being for display technologies. [90]

The thermal interface material market The thermal interface material market will be $1.3 billion in 2015 growing to $3.5 billion in 2026 (CAGR 9.5%). Applications are ranging from lasers, photovoltaics and LED lighting, to all kinds of electronically driven devices (telecommunication, automotive, industrial, aerospace, medical, consumer), especially related to power electronics. [91, 92] Other sources saw a market of $100 million in 2015 and a growth of CAGR 11% in the next five years. [93]

The global coated fabrics market is also a potentially interesting market with an overall market expected to be $22.6 billion by 2020 and a CAGR of 3-5%. The market share of Europe was roughly 1/5. The coated fabrics market is mainly driven by the transport industry (34% share). [94, 95] Fabrics are for instance coated to make them stronger against wear, change the wettability or increase the flame retardancy.

Optical coatings also depict an important global market (~$10 billion in 2014). However, Europe plays only a smaller role behind North America and the Asia Pacific region, which together account for more than 2/3 of the market. [96]

Transparent conductive films, a widely used optical coating for displays and touch screens, had a market size of ~$2 billion 2013 and is expected to reach $5.9 billion by 2020. Asia dominates this market with more than 50% market share, Europe only has 10%. [97] The market is ITO dominated, but alternative technologies are on the uprise, dominated by silver nanowires and metal mesh which are expected to reach $126m and $191m in 2025, respectively. [98]

Figure 16 and Figure 17 show the transnational patent analysis for graphene/2D materials in coatings and paints. The area is dominated by the USA, followed by Europe. Europe managed to gain a larger share in the patents in recent years, showing that there is a significant interest.

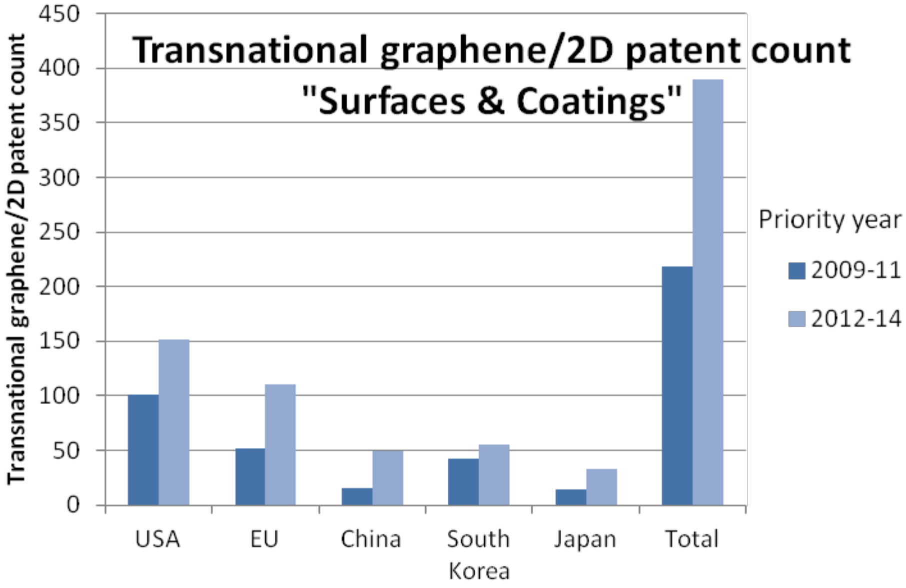

Figure 16: Patent analysis of graphene/2D materials in surfaces and coatings: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [21]

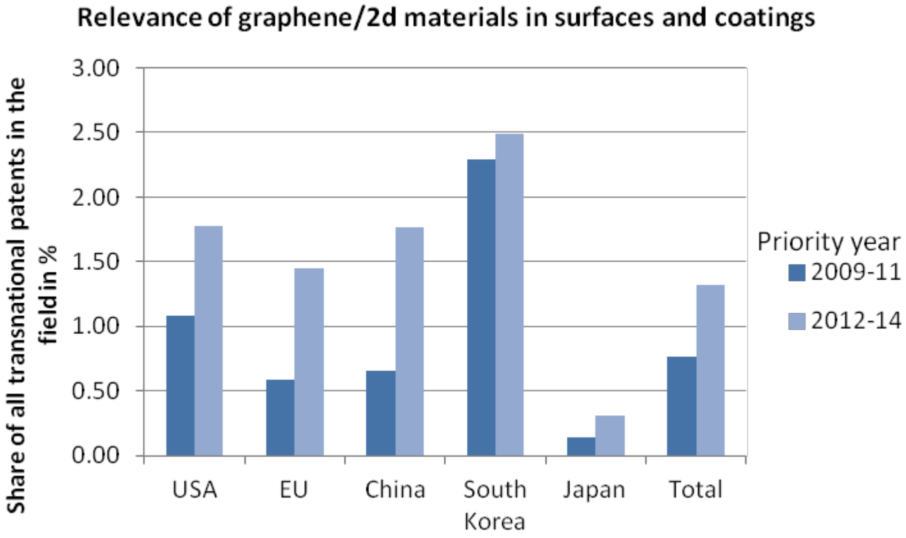

Figure 17: Patent share of graphene/2D related materials with respect to all transnational patents in surfaces and coatings. 2012-2014 values are projected.[21]

2.3.1.1 Market Opportunities

2.3.1.1.1 Many diverse markets with opportunities and niches for potential early adopters

(Functional) coatings are very versatile and can be used in many different markets (see chapter above). There a many potential early adopters, e.g. in high value niche markets such as highly functional textiles in the sports sector. Besides, there are also mass markets addressable, such as food packaging. [66]

Due the versatility, 2D materials can play a role in many of these areas. However, the high diversity of applications also induces a threat, due to the broad sectors addressed making it tricky to find a particular application where the properties lead to a USP.

Potential market opportunities of graphene materials that are already under investigation are summarized in Table 15. With the strong transport industry, Europe also has a large end user of coatings and therefore, the industrial value chain is in Europe to a great extent.

Some of the potential applications address a clear market need, e.g. the de-icing coatings for aircrafts address the economical and ecological need to reduce the use of de-icing agents. There are also particular developments in application sectors that drive needs for coatings, e.g. the change in automotive headlights technology to LEDs, where suddenly a heating film is needed for de-icing of the lamp windows. Also the increasing integration of electronics drives needs for heat dissipation that can be addressed with improved thermal interface materials.

The market opportunity of coatings is strongly connected to the feasibility to apply durable coatings on large area, therefore, most of the opportunities will come from graphene flake based coatings (e.g. through paints). Although the quality of CVD graphene is much higher, the applicability in this area is doubtful from the current perspective.

2.3.1.1.2 Multifunctional paints as opportunity

Opportunities for 2D materials are strongest, where combinations of their properties are needed, such as barrier (corrosion, flame retardancy), conductivity, flexibility and thinness/lightweight. This could for example be realised in multifunctional paints.

2.3.1.1.3 Industrial base in Europe

There is an industrial base in Europe for coatings, varnishes and paints. Relevant production value was on the order of €19 billion in 2014, with a CAGR of 2.3% from 2012 to 2014. [39] Figure 18 also shows that the innovation and patent capacity is high in

Europe in terms of transnational patents. European industry is in on league with USA and Japan.

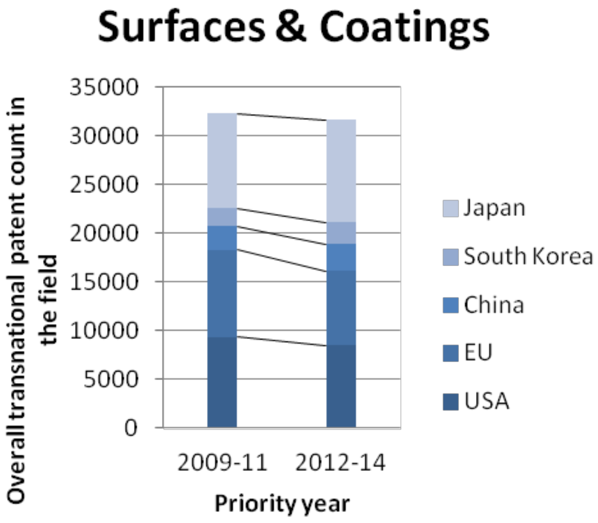

Figure 18: Overall transnational patent count in surfaces and coatings. 2012-2014 values are projected.[21]

2.3.1.1.4 Cost of corrosion as a driver for new coatings

The cost of corrosion is estimated to at 3 to 5% of GDP, which creates a large market need for anti-corrosion coatings. In addition, the chromate-containing system's toxicity adds a need for chromate-free anti-corrosion coatings. In addition, since chromate-containing systems will be banned after the so-called sunset-date (September 21th, 2017) by the European Chemicals Legislation (REACH) due to the toxicity of Cr(VI), applicable alternatives have to be found fast. In typical multi-layer anti-corrosion coatings, the benefit and a cost saving aspect could lie in the reduction of the number or thickness of the layers.

2.3.1.1.5 Flame retardant coatings as alternative to bulk additive solutions

Many problems are solved regarding non-halogenated flame retardant additives to polymers. However, for some polymer compounds the final mechanical properties are poor and barely acceptable due to the high flame retardant load in the bulk. There is an opportunity to address and solve that with coatings.

2.3.1.2 Market Threats

2.3.1.2.1 Mature markets with many established technologies and conservative industries

The opportunity of diverse markets is at the same time a threat for a new technology like graphene, in particular when the preparation techniques are differing from common technologies (e.g. the transfer of CVD graphene), or when the cost/benefit is not explicitly clear.

Due to the multiplicity of possibilities in terms of applications with different needs, it is difficult to define a direction/priority for a material based research. Besides, the diversity of potential end user sectors with many specific but different requirements and diffuse supply chains and niches introduces a barrier. Concrete demonstrations targeted on particular use cases are needed to lower the barrier for particular application areas. This also implies to engage the whole value chain from material supplier, applier of the coating and OEM (which not necessarily come all from Europe).

Another threat connected with a mature market is the availability of mature and established technologies. For most of the markets addressed by graphene or 2D material coatings, there are already technologies/materials on the market that work reasonably well or have similar deployment barriers as graphene (e.g. cost). Besides, the uniqueness of graphene materials only lies in the combination of properties, so that for particular uses where the multifunctionality is not necessarily needed, other coatings might work similarly well, better or might be more cost saving.

Additionally, many industries are conservative (e.g. the TIM industry). Only mature substitutes are considered and only at times when the state of the art has reached its absolute limit. [92]

2.3.1.2.2 Cost sensitivity of application areas

Coatings are mostly mass produced and cost sensitive. Especially for paints, cost/performance place an important role and a too high cost for too low performance increase is a threat for market success.

2.3.1.2.3 Durability requirements

A common threat for new coatings is the requirement for integrity, durability, reliability and low wear. This is important for films on solid substrates, but also for textile coatings, which have to withstand hundreds of washing cycles.

Another threat, in particular for nano-coatings is the perception of environment, health and safety issues, in particular when the surfaces break and the coating is removed/exposed. Although the amount of material released might be low, it still needs to be addressed to avoid bad reputation and wrong perception.

Also in terms of regulatory requirements (exposure, peel off, wear, e.g. when used for lubrication), usually the requirements are rather high and strict. In particular for applications where contact is inevitable and intended health and safety have to be addressed. For biomedical applications, good manufacturing practice (GMP) is inevitable (please also refer to 5.2 Excursus: The specific structures of the health market and 5.6 Biocompatible devices). Also anti-fouling or anti-microbial applications are very sensitive to health and safety and industry might be reluctant to consider nanomaterials (or the barrier will be high).

2.3.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in coatings and paints

2.3.2.1 Current strengths for graphene/2D materials use in coatings and paints

2.3.2.1.1 2D materials as perfect candidate for coatings with multi-functional properties including flexibility

2D materials are by nature perfect candidates for coatings, as they have the thickness of one atomic layer, are flexible, stretchable and have large lateral dimensions to cover surfaces. Nonetheless, 2D materials can be applied as single or few layer large sheets (usually CVD prepared, see chapter 2.3.2.2.3 for further information on implementation issues) or as flakes/platelets in paints or inks usually incorporated into a binder. The former usually achieves better functionalities but the application of the coating is tricky, costly and not yet mass production compatible. The latter is much easier to apply (see 2.3.2.1.2) and reaches also interesting properties, although high transparency is not possible yet.

Graphene materials possess interesting properties for coatings (see Table 15). An important asset is especially the multi-functionality, i.e. combinations of the mentioned functionalities in one coating (e.g. flexibility and thermal/electrical conductivity and barrier against corrosion or for flame retardancy). This (multi-) functionality creates exciting opportunities for customers, also for flexible substrates/host materials and wearable products. Besides this added value through multi-functionality, graphene maintains the interesting properties of carbon materials, e.g. chemical inertness at high temperatures or anisotropy. The latter is interesting for thermal and electrical conductivity. Although in principle a strength, the anisotropic behaviour also poses a barrier, as the material behaves differently to commonly used isotropic materials (e.g. metal based coatings).

Graphene coatings have also interesting electromagnetic properties, e.g. transparency or tuned absorption in certain wavelengths ranges. With the possibility to create multilayer structures of different 2D materials, the versatility becomes even higher. Electroactive coatings, e.g. for electrochromic applications are potential areas of interest, where 2D inks could provide an interesting solution. Also tunable surfaces are possible, e.g. electrically conductive and transparent coatings with tunable wettability. [99]

Lubricating and tribological enhancement has for instance also been shown for 2D material based coatings by increasing lubrication, e.g. in electrical contacts [100] or better pressure properties. [101]

However, due to the multi-functionality it is also tricky for graphene researchers to find suitable applications as the parameter, variable and application space is so large. In general, the flexibility is often seen as a particular asset in combination with the other functionalities.

2.3.2.1.2 Use in harsh environments

Due to the chemical inertness, especially the use as a coating in harsh corrosive or chemical environments can be a USP, where e.g. metal coatings are decomposed and polymer coatings are too permeable.

2.3.2.1.3 Easy processing and application of coatings from pastes, paints and inks

As mentioned above, there are two ways to apply a 2D material based coating to a surface: paints/inks and high quality CVD graphene film transfer. The former has a much lower implementation barrier, although the functionality is essentially lower as for high quality graphene films. These coatings can in principal be applied from solution as inks or paints via printing, spraying, painting or dipping, for fabrics/foams via impregnation or layer-by-layer deposition etc., all well known and widely used scalable processes making the application cheap and mostly depending on material and formulation cost. They also allow rollable continuous production methods (e.g. roll to roll). Due to the nature of the coating, i.e. several layers of graphene flakes with grain boundaries and even voids, the coatings are thicker and typically lower performing compared to graphene films. Still, the cost/benefit ratio can be high enough to become interesting for many applications.

The materials used for these coatings are similar to the ones used as an additive in composites (compare chapter 2.2). The most important step is the formulation of the paste, ink or paint, which needs to be done in a way that the ink/paint/paste is processable and that the final coating reaches the desired functionality/properties with the given process at the substrate/host.

Different ways of functionalization (plasma, surfactant) and binders allow the tuning of the ink/paint/paste formulation and also of the coating. This opportunity of functionalization on the one hand opens room for tailoring and optimization, but also poses a barrier in terms of the manifold of potential solutions and the decision making on optimal routes for a given application. Undoubtedly, functionalization is a critical necessity for the use of graphene or 2D materials in coatings based on pastes and inks, also looking at stability for transport and shelf life. Importantly functionalization processes need to be available at large enough scale.

2.3.2.1.4 Need for relatively small amounts reduces barrier for implementation

The overall material amount needed for a functional coating is relatively low, as only the surface needs to be covered with a thin layer. This means that material cost will most probably not be a prohibitive factor. In this case only the production cost for formulation and application of the coating are more relevant. This will be moderate for paints/coatings/inks as soon as a formulation and process is found for the given application. For high quality graphene films, the process is currently too expensive and not mass-production compatible (see 2.3.2.2.3)

2.3.2.1.5 Value/supply chain emerging but still open questions

For inks/paints/past based coatings, the same arguments apply as in chapter 2.2.2.1.7.

2.3.2.2 Current weaknesses and challenges of graphene/2D materials use in coatings and paints

2.3.2.2.1 Cost/benefit often not yet clear

Similar to composites, the field of coatings is very wide and there are many competing and established technologies. The uniqueness of graphene coatings is not immediately obvious, especially as there are many more mature competing coating technologies available.

The cost/benefit of graphene/2D materials based coatings is often not yet obvious. Often the “same performance or only slightly better than competing technologies” for single functionalities is observed in industrially relevant demonstrations but for (currently) higher cost. Due to the still low maturity of industrialization of graphene materials, the cost comparison with mature and established competing coatings is currently difficult, as processes and formulation still need to be developed. Thus, currently real proof of principles in relevant environments are needed to show the actual benefits (tests only under artificial circumstances). Cost will eventually come down if the benefit is clearly demonstrated and optimal formulations as well as processes are found for the given application, because the material cost for a large are coating will become negligible. However, from the current point of view this knowledge is not yet available for many applications, so that additional testing and time will be needed. In chapter 2.2.2.2.2 further considerations are given to demonstration that also apply for coatings.

In particular for large scale high quality coatings (from CVD or high quality inks/paints) the cost for a mass product and large surfaces might be too high in the future for integration.

A very important factor for the feasibility of coatings is the reproducibility and quality of the coatings to be mass production compatible. In particular for coatings issues as wear and scratch resistance are of utmost importance and need to be addressed from the very beginning, see next chapter.

Furthermore, the potential black colour of graphene material based inks and paints are often not desirable according to an industry expert assessment based on market feedback. This is particularly the case for applications addressing thermal or electrical conductivity.

2.3.2.2.2 Unproven wear resistance, durability and lifetime of coatings

Resistivity against wear and scratching are crucial for essentially all coatings. For graphene based coatings in order to be commercially viable, this mechanical stability under stress and over time needs to be proven. This also has to take into account the environment, where the material is supposed to be used (e.g. humidity, aggressive fluids, biologically active environments…). This property is probably mostly defined by the binder in inks/paints/pastes, but also different substrates need to be taken into account and the interaction of the coating with the substrate to avoid delamination. For coated fabrics, the washability and wear resistance is also important.

2.3.2.2.3 Transfer and preparation problem for high quality coatings from CVD material

High quality graphene and 2D material films are mostly investigated for electronics applications and covered in chapter 4. For large scale (m^2) industrial coatings only a few applications are currently conceivable, such as transparent conductive films, e.g. for windows, or protective coatings. But for high quality very large scale coatings based on CVD single or few layer graphene films the commercial maturity is still rather low because of the problematic preparation method: If not used on a very few substrates directly (SiC, Ge, Ni,..), the graphene layers currently have to be transferred from copper, which is used as substrate and catalyst for CVD (see chapter 4.2 about wafer scale integration). The preparation of graphene on copper is also possible on large scale with role to roll processes. However the transfer process is still critical and not feasible at large scale/roll to roll. So the preparation needs either transfer or is substrate dependent. Besides that, the performance of the coating is also substrate dependent or depends on the quality of the transfer process. This introduces a very high barrier for use of high quality graphene films in large scale coatings, because the transfer processes are hard to control and expensive. Besides, these processes are completely new for standard coatings, which usually are based on inks/paints/pastes, vacuum processes, or wet processes like electroplating. From the current point of view the integratability is thus questionable, as this new process might be needed. CVD graphene is thus currently a rather unlikely candidate for a commercially viable large scale (m²) industrial/protective coating in the near future[j]. One large scale coating application that actually is under discussion is the use as transparent conductive film for touch screens or displays. In that case, the substrates are moderately large and it has been demonstrated (see also chapter 4.6 Flexible and/or printed electronics). However, the commercialization is still pending most probably because it is uneconomic. Besides, other alternatives offer similar or better performance with lower integration barriers, see 2.3.1.2.1.

For thermal and electrical conductivity there is also a limitation for the overall energy transport: Although the thermal and electrical conductivity are high, the overall transport is limited due to the low “cross section” of a 2D material. To achieve this higher transport, a 3D architecture is needed to increase the overall transported (electrical, thermal) power and current.

2.3.2.2.4 Variability of supply of graphene materials and missing standardization and knowledge of the needed quality of material

For inks/paints/past based coatings, the same arguments apply as in chapter 2.2.2.2.1.

2.3.2.2.5 Intrinsic problem for anti-corrosion: conductivity and nobility

Although graphene can be a good barrier for anti-corrosion, it also has some intrinsic drawbacks. Graphite is a very noble material and can lead to galvanic corrosion, so graphite residues can lead to detrimental effects [102]. Therefore, the graphene material used in an anti corrosion coating needs to be well defined and must not have too many layer in order to not promote corrosion, when in direct contact to the metal. Besides, it has been shown that on long term, graphene can enhance corrosion when in direct contact with the metal surface, probably due to its conductivity. [103] However, this may only occur if the surface to be protected is electrically conducted to the graphene species and not insulated by an organic coating as it is typically the case for

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[j] This only applies to the coatings addressed in this chapter and not to coatings for electronics/photonics applications or wafer scale coatings. For the assessment of this type of coating, please refer to chapter 4.

varnishes, inks, etc. Such a multi-layer coating could be feasible, where graphene materials is one of the intermediate layers.

2.3.3 KPIs for coatings and paints

Cost per square meter (e.g. a protective coating anti-scratch and anti debris with hydrophobic functionality can cost ~\$20/m²)

Weight per area (for lightweight applications)

Adhesion and wear tests are important for industrially applicable coatings: e.g. [104]. For textiles, the number of standard wash-cycles are relevant.

Tribological properties: Friction, wear rate, (micro-) hardness

Safety assessment (during production/preparation and use)

In general, many KPIs that are relevant for coatings are also state in chapter 2.2.3 KPIs for composites, e.g. electrical/thermal conductivity and barrier properties. The thermal conductivity of thermal pastes lies in the range of 1-38 W/mK, ~1-9€/g

For barrier properties: corrosion resistance (for anti corrosion)

Table 16: Flexible and transparent barrier KPIs (water vapor and oxygen) for several materials. [90]

Material	**Water vapor transmission rate g/m^2/day (37.8-40 °C)**	**Oxygen transmission rate (standard temperature and pressure) cm^3/m^2/day (20-23 °C)**
PET	3.9-17	1.7-7.7
PEN	7.3	3.0
PE	1.2-5.9	70-550
PP	1.2-5.9	93-300
PES	14	0.04
PI	0.4-21	0.04-17
Polystyrene (PS)	7.9-40	200-540
15 nm Al/PET	0.18	0.2-2.9
SiOx/PET		0.007-0.03

Material	**Water vapor transmission rate g/m^2/day (37.8-40 °C)**	**Oxygen transmission rate (standard temperature and pressure) cm^3/m^2/day (20-23 °C)**
ORMOCER/PET		0.07
LCD requirement	0.1	0.1
Common testing equipment limit	0.0005	0.005
OLED requirement	10^{-6}	10^{-5} to 10^{-3}

For TCF: conductivity (Ω/□), transmission spectrum, patterning/etchability, flexibility, optical properties, roughness.

2.3.4 Roadmap for coatings and paints

2.3.4.1 Current maturity: depends on application

First inks/paints/pastes, especially for electrical and thermal conductivity are already partially marketed.

For instance Angstron thermal paste (10W/mK, 1 3g syringe 18.99$, 5 syringes 69.95$) or Heraeus graphene-based conductive inks.

Other graphene/2D-material based coating technologies (printing, spraying, layer-by-layer, varnishes, multi-layer anti-corrosion) are under investigation and mostly at applied research stage with some companies already active in assessing the potential.

CVD based films are not commercially mature or feasible for large scale coatings at the moment. There are already TCF “marketed” in China (Wuxi), but it is questionable if these are commercially viable.

2.3.4.2 Barriers/Challenges (summarized)

The barriers/challenges for composite materials (chapter 2.2.4.2) also apply for coatings.

Besides, the following barriers/challenges are of additional importance.

- Often real proof of principle missing (tests only under artificial circumstances)
- Cost/benefit unclear
- Reproducibility and quality of the coatings
- Reliability and wear
- Environment, health and safety clarification

- Unclear optimal processes for targeted applications
- Anisotropy of conductivity properties need to be controlled

Ink/paste/paint based coatings:

- Formulation and binders: functionalisation

CVD based coatings:

- Transfer for CVD
- For thermal/electrical conductivity: Overall energy transport limited
- CVD graphene under current circumstances no reasonable candidate for large scale coatings

2.3.4.3 Potential actions

If the area of graphene/2D in coatings is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

The potential actions in the composite chapter (2.2.4.3) also apply for coatings.

Besides, the following potential action relate to coatings:

- Evaluate lifetime under the targeted conditions
- Understand and investigate ink formulation
- Functionalization is critical (also on larger scale)
- Explore different applicabilities for different substrates, e.g. for textiles, foams, multi layered coatings etc.
- Demonstration! Also of wear and scratch resistance of coatings (use cases‼)

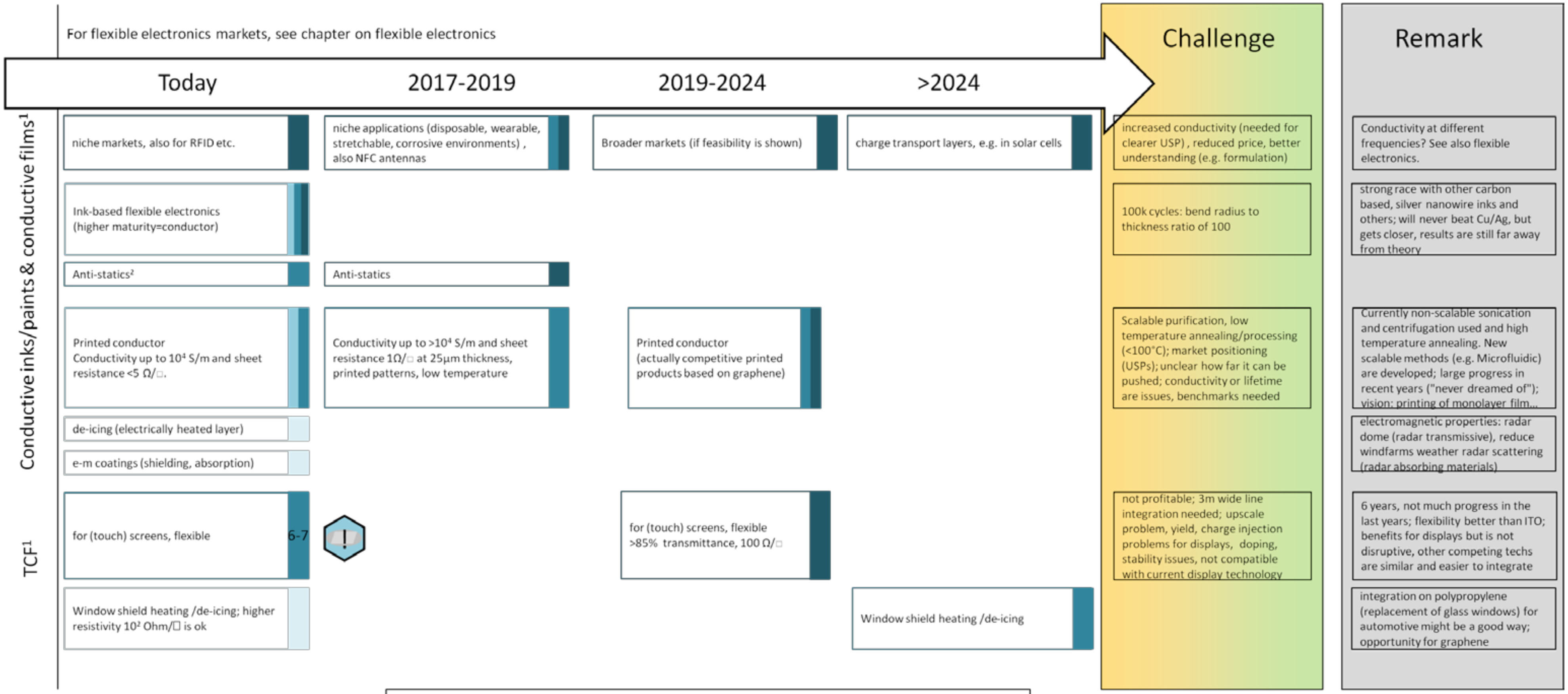
2.3.4.4 Roadmap

Coatings are less mature than composites. Only conductive inks or thermal pastes are already marketed to a certain extent. Their broad commercial success, however, is still pending.

TCFs are to a certain extent marketed, but the broad use in a device is pending. There are rumors that graphene might be used in OLED displays in the next few years.

Anti-corrosion coatings are evaluated and tested. Due to the expected lifetimes of most large scale coatings (e.g. on planes, cars, steel) of 10-30 years, extensive testing needs to be done, which needs time (usually 1 year or more). So even if some applications are under investigation, the time to market is still a few years.

The sector related timing aspects presented in the composites chapter 2.2.4.4 also apply for coatings.



For flexible electronics markets, see chapter on flexible electronics

	Today	2017-2019	2019-2024	>2024	Challenge	Remark
Conductive inks/paints & conductive films[1]	niche markets, also for RFID etc.	niche applications (disposable, wearable, stretchable, corrosive environments) , also NFC antennas	Broader markets (if feasibility is shown)	charge transport layers, e.g. in solar cells	increased conductivity (needed for clearer USP) , reduced price, better understanding (e.g. formulation)	Conductivity at different frequencies? See also flexible electronics.
	Ink-based flexible electronics (higher maturity=conductor)				100k cycles: bend radius to thickness ratio of 100	strong race with other carbon based, silver nanowire inks and others; will never beat Cu/Ag, but gets closer, results are still far away from theory
	Anti-statics[2]	Anti-statics				
	Printed conductor Conductivity up to 10^4 S/m and sheet resistance <5 Ω/□.	Conductivity up to >10^4 S/m and sheet resistance 1Ω/□ at 25µm thickness, printed patterns, low temperature	Printed conductor (actually competitive printed products based on graphene)		Scalable purification, low temperature annealing/processing (<100°C); market positioning (USPs); unclear how far it can be pushed; conductivity or lifetime are issues, benchmarks needed	Currently non-scalable sonication and centrifugation used and high temperature annealing. New scalable methods (e.g. Microfluidic) are developed; large progress in recent years ("never dreamed of"); vision: printing of monolayer film...
	de-icing (electrically heated layer)					electromagnetic properties: radar dome (radar transmissive), reduce windfarms weather radar scattering (radar absorbing materials)
	e-m coatings (shielding, absorption)					
TCF[1]	for (touch) screens, flexible 6-7	!	for (touch) screens, flexible >85% transmittance, 100 Ω/□		not profitable; 3m wide line integration needed; upscale problem, yield, charge injection problems for displays, doping, stability issues, not compatible with current display technology	6 years, not much progress in the last years; flexibility better than ITO; benefits for displays but is not disruptive, other competing techs are similar and easier to integrate
	Window shield heating /de-icing; higher resistivity 10^2 Ohm/☐ is ok			Window shield heating /de-icing		integration on polypropylene (replacement of glass windows) for automotive might be a good way; opportunity for graphene

[1]: see also flexible electronics; [2]: see also composites roadmap

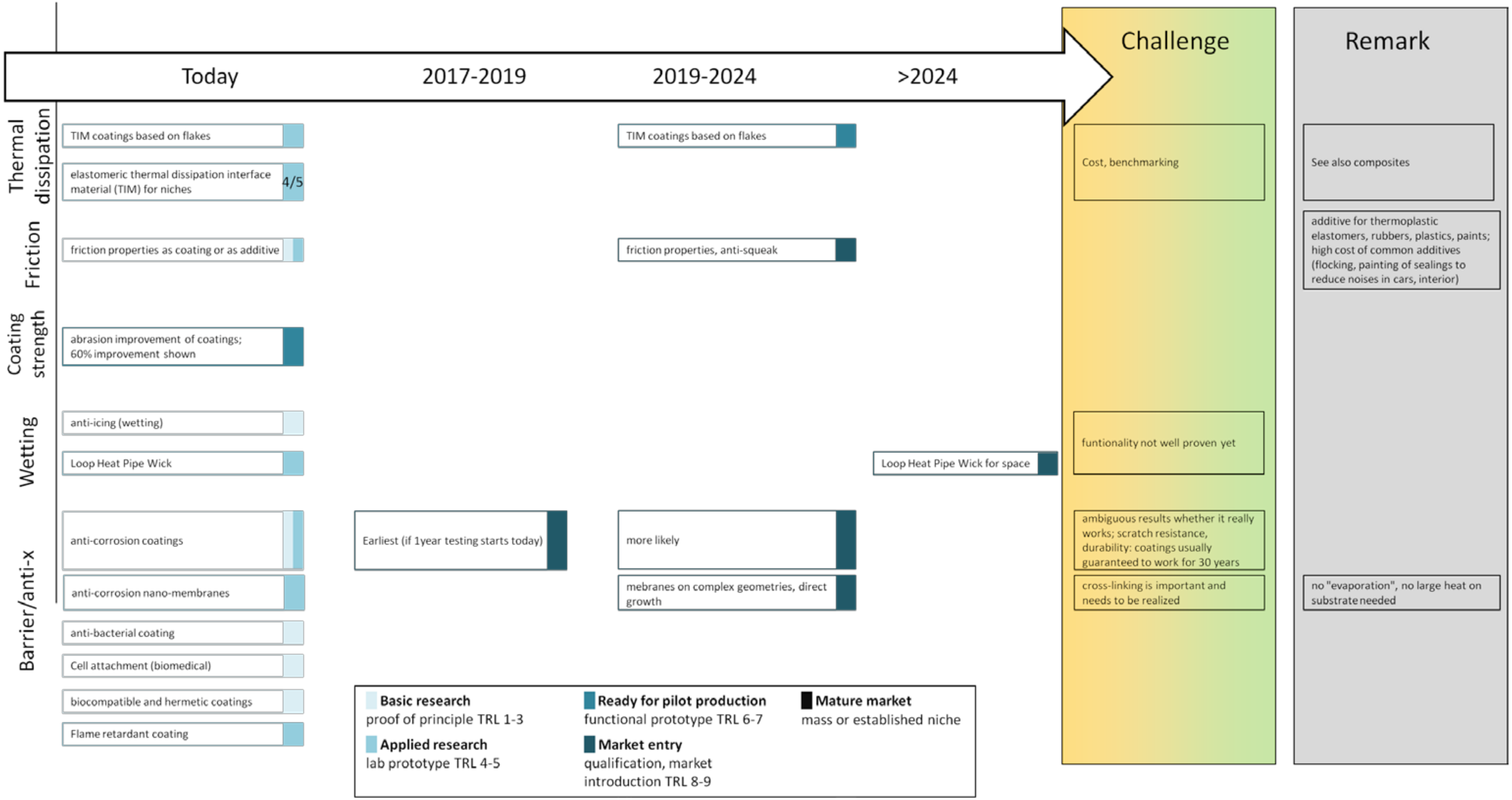
Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche


Today
2017-2019
2019-2024
>2024
Challenge
Remark
Thermal dissipation
TIM coatings based on flakes
elastomeric thermal dissipation interface material (TIM) for niches
4/5
TIM coatings based on flakes
Cost, benchmarking
See also composites
Friction
friction properties as coating or as additive
friction properties, anti-squeak
additive for thermoplastic elastomers, rubbers, plastics, paints; high cost of common additives (flocking, painting of sealings to reduce noises in cars, interior)
Coating strength
abrasion improvement of coatings; 60% improvement shown
Wetting
anti-icing (wetting)
Loop Heat Pipe Wick
Loop Heat Pipe Wick for space
funtionality not well proven yet
Barrier/anti-x
anti-corrosion coatings
Earliest (if 1year testing starts today)
more likely
ambiguous results whether it really works; scratch resistance, durability: coatings usually guaranteed to work for 30 years
anti-corrosion nano-membranes
mebranes on complex geometries, direct growth
cross-linking is important and needs to be realized
no "evaporation", no large heat on substrate needed
anti-bacterial coating
Cell attachment (biomedical)
biocompatible and hermetic coatings
Flame retardant coating
Basic research
proof of principle TRL 1-3
Applied research
lab prototype TRL 4-5
Ready for pilot production
functional prototype TRL 6-7
Market entry
qualification, market introduction TRL 8-9
Mature market
mass or established niche

2.3.5 Conclusion for coatings and paints

Coatings and paints cover a large variety of potential applications. Many potential niches and early adopters offer the chance for integration of graphene or other 2D materials. However, the vast amount of possibilities also induces a barrier for targeted research, as it is largely unclear where 2D materials actually can have a cost/benefit advantage. This is further amplified by the large amount of established coating technologies in the market, which introduce a barrier for new (nano-technology) coatings.

Potential applications under investigation are anti-corrosion, anti-microbial, de-icing, or gas barrier coatings as well as thermally or electrically conductive coatings for electromagnetic shielding or against electromagnetic discharge. Again, the multi-functional properties are a rather unique asset of graphene materials.

2D materials are in principle the perfect coating materials, as they are ultimately thin films. Many potential applications are possible in form of both pastes/inks or as a neat (CVD prepared and transferred) film. The former has a lower implementation barrier, as inks and paints can be much easier applied with common available processes and are largely producible. 2D materials can be even added to common paints to improve properties (similar to composites). The challenges are the ink and paste formulation which needs to be targeted on the application and substrate. Functionalization can play an important role in this respect, but it is also much about choosing the right solvent and binder. Besides, the cost of the raw material is a smaller constraint, as for coatings smaller amount are usually needed. The process cost is therefore the limiting factor.

For CVD based high quality films the barrier is much higher, as a transfer process is currently needed, which seems not feasible for large area applications on square meters. However, the higher quality of those films usually also leads to a better performance. These high quality films will need a much longer time until applied. The only area where they might be used earlier is transparent conductive films (TCFs). However since several years not much progress has been achieved in terms of cost reduction and although first prototypes were presented several years ago, there is no commercial product yet. Besides, other emerging TCF technologies that started out to replace ITO are already quite mature and for instance metal meshes and silver nanowires are perceived as more mature. Beside, Europe only plays a minor role in the TCF business.

For all applications the cost/performance needs to be addressed and durability should be investigated from the beginning. Similar to composite materials, also the environment, health and safety properties and perception have to be considered.

Table 17: Assessment of market and technological potential of graphene/2D materials use in coatings on a scale - -, -, 0, +, ++

Coating	Current technological potential (USP)	Market potential (EU perspective)
Barrier coatings (anti-…)	+	++
Electrical coatings	0	+
Transparent conductive films	0	-
Thermal coatings	0	+
Multifunctional coatings (added functionality)	++	++

2.4 Additive to liquids

This chapter deals with the use of graphene/2D materials in liquids. It deals with the applications where the functionality of the 2D material is exploited in the liquid state. The major goal of these applications is the functionality enhancement of the fluids, e.g. enhanced electrical and/or thermal conductivity, better lubrication, etc. Typical products are lubricants and drilling fluids. In most of these applications, graphene competes with carbon black or other nano-carbons. This chapter does not cover applications where 2d materials are processed in liquid form but after application used in a solid (e.g. conductive inks, paints, coatings). The latter applications are covered in chapter 2.3.

Typical fluid applications where graphene or 2D materials can play a role are summarized in Table 18

Table 18: Fluid applications for graphene or 2D materials

Type of fluid application	Functionality
Lubricants Recent Review: [76]	• Increased lubrication properties, reduced wear • modified electrical conductivity for lubrication of electrical contacts or isolation • thermal conductivity for better heat removal • impede corrosion

Type of fluid application	Functionality
Adsorbent for polluted liquids/water, contaminant adsorber Recent review: [70, 105]	- Oil spill clean-up - Hydrocarbon/pollutant binding and removal - Metal ions and organic compound adsorbent - Photocatalytic, disinfectant and adsorbent with metal oxides [106]
Drilling fluids [107]	- Better lubrication, reduced wear - Better heat removal - Reduce losses of drilling fluid to surrounding rock - Thinner, lighter filter cake - Improved well logging (needs conductivity in the fluid)

This chapter also covers the special case where graphene material powders are used for environmental remediation in fluids, e.g. for oil spills (Directa Plus) as an adsorbent for polluted liquids/water. The graphene materials directly compete with other (carbon-based) materials that can be used for hydrocarbon removal and oil spill clean-up.

2.4.1 Market perspective: graphene/2D in liquids

Depending on the use, the percentage of additives in lubricants varies between 0.5% and 30%, e.g. for steam turbines or compressors 0.5% and 5% or for hydraulic systems 2% to 10%, for engines 10-30% of additives are added. The types of additives are specific for specific applications. [108, 109]

The lubricant additives market is expected to grow at a rate of CAGR 2.7% over the next years to reach $16.2 billion by 2019 (~$14.2 billion in 2014). The growth is attributed to a high demand from major end-use industries such as construction, automotive, and manufacturing. [110, 111] The value of lubricant additives produced in Europe in 2014 was €4.7 billion, growing at a CAGR of 7.9% 2012-2014 (lubricants itself: €2.4 billion, stagnating 2012-2014), with an average unit value of ~2-2.8€/kg in 2014. Thus, European companies have a large and growing share in this additive market.[39]

The overall lubricants market was estimated to $ 144.45 Billion in 2015 and is projected to reach USD 166.59 Billion by 2021, (CAGR of 2.4%). [112] European companies have a small share in this market and are rather suppliers of additives.

The global market for drilling fluids is expected to reach >$14.5 billion by 2020. The global market for drilling fluids was estimated to be ~$8.16 billion in 2013, and is expected to grow at a CAGR of ~7-8%, dominated by America and Asia Pacific.

56% of the total market revenue in 2013 was created with water based fluids, the most consumed drilling fluids. They are also expected to have the fastest growing demand (CAGR of almost 9% from 2014 to 2020). Oil-based fluids are the second most used for drilling, accounting ~30% of the total market 2013. Major companies come from US, only a few multinationals are in Europe (Schlumberger). [113, 114]

The global market for technologies used in the remediation of environmental contamination of surface water, groundwater and soils was estimated at ~$60 billion in 2013. It is expected to grow from ~$61.7 billion in 2014 to ~$80 billion in 2019, (CAGR 5.5%). China is expected to more than double their total market share from 4.7% in 2014 to 10.8% in 2019. The Latin America and Caribbean region could also see stronger growth than average expanding its market share to 7.8% in 2019. The rest of the market is dominated by the most developed economies of North America, Western Europe, Japan and Australia [115]

The global adsorbents market was estimated to be ~$3.1 billion in 2015 and is expected to reach ~$4.3 billion by 2020 (CAGR 6.3%). This growth is fuelled by the increasing global demand for petroleum refining, chemicals/petrochemicals and gas refining industries. A high potential is attributed to molecular sieves and activated carbon. [116]

2.4.1.1 Market Opportunities

2.4.1.1.1 Increased need for high performing and sustainable lubricants

The overall need for lubricants is to increase the lubrication and reduce wear. The increased use of robots and the need for energy efficiency calls for better lubrication and multi-functionality. On the other hand, long term automotive trends (electromobility) will change and decrease the demand for lubricants. In medium term, the demand for reformulated, higher-performing lubricants increases due to downsized powertrains.

Another need is to increase the multi-functionality of lubricants, i.e. to increase the thermal conductivity of lubricants for heat removal or to use lubricants for electrical contacts that support the contact by reducing contact resistance. Similarly, other applications need improved electrical or thermal insulation.

There are also special applications where specialty lubricants need to withstand chemical environments, low temperature, radiation or vacuum. Additives in general are used as friction modifiers, antioxidants, corrosion inhibitor, detergent/dispersant, for anti-wear, anti-foam, alkalinity improvement, demulsification, extreme pressure performance, chemical resistance or viscosity.

A successful integration and increased performance opens up many potential markets, as with additional functionalization many needs could be addressed.

2.4.1.1.2 Strength of European lubricant additive manufacturers

Europe has a competitive and strong lubricant additive supplier industry, which could be further enabled by 2d materials. However, the lubricant manufacturers themselves are rather under-represented in Europe. The competition is moderate, in particular for high performing lubricants.

2.4.1.1.3 Tightened laws on pollution and increased need for remediation

In particular in Europe, but also globally, tightened laws on pollution and clean water increase the need for remediation, e.g. of surface water and waste water from oil production.

2.4.1.2 Market Threats

2.4.1.2.1 High price sensitivity of conventional lubricants

Conventional lubricants are subject to a rather high price sensitivity (~1-2€/L). Lubricant additives cost around 2-3€ on average per kg. Even if the loading can be reduced through the use of graphene/2D materials (typical loadings are between 0.5 and 30%), the price pressure will still be high for mass markets. It is important to address the systemic cost balance (e.g. lower total maintenance and/or energy costs), as a higher performing and more durable lubricant for instance needs to be changed less often, allowing a higher price.

On the other hand, there are also special markets with particular needs for high-performing lubricants or specialty lubricants allowing higher prices.

2.4.1.2.2 Mature and established competing products

The lubrication additives market is well established and many additives exist that allow proper modification of lubricants. Organo-metallic compounds, polymers, phosphorous or sulphur compounds, aromatic compounds, but also MoS_2 and graphite are used. [117]

For remediation and oil spill cleanup, many other (carbon based) sorbent materials are available. The same is true for drilling fluids.

A new additive needs to improve the cost/performance significantly and undoubtedly to allow uptake in industry.

2.4.1.2.3 Environment, health and safety requirements

The need for sustainable lubricants, drilling fluids and adsorbents is increasing. Sustainability is increasingly important and needs to be proven. This includes end-of-life properties (e.g. recyclability), environmental safety as well as health and safety (release of graphene, contact with graphene) considerations. These issues have to be addressed to avoid misperceptions and bad publicity.

Toxicity is seen as a severe problem in additive technology, because real long term biological and ecological effects are mostly not known. [118]

It can be expected that in areas with no tradition of protection against harmful substances, industry will be reluctant to use graphene materials. This is particularly relevant where graphene-based formulations are to be released into the environment or to be used in workplaces (e.g. many lubricant applications). Use of fluids inside closed industrial processes, however, are more probable.

2.4.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in liquids

2.4.2.1 Current strengths of graphene/2D materials use in liquids

2.4.2.1.1 Functionalization and multi-functional property enhancement in lubricants and drilling fluids

Similar to the other applications, again the multi-functional property enhancement is the largest asset for graphene materials as additives to fluids. For lubricants, the combination of electrical/thermal properties and lubrication are of high interest. This also applies to drilling fluids.

Similar to graphite, graphene possesses good intrinsic tribological properties on the nano-scale. When used in oils, graphene platelets and GO show slightly better friction coefficients than graphite and a reduced wear [76].

Also other 2D materials such as MoS_2, WS_2 (and other TMDs) or BN are of interest, in particular because they are already used in lubricants. Recent studies have shown that MoS_2 nanoplatelets increases the performance under pressure and high load conditions compared to other additives. [101] This enhancement of standard lubricant additives by turning them into 2D materials (such as MoS_2) could pose a rather easy implementation and a low barrier, if performance improvements can be shown.

Due to the possibility of functionalization, the properties can be adjusted and the diversity is increased. However, functionalization also has some drawbacks, see 2.4.2.2.1.

2.4.2.1.2 High specific surface area and functionalization for remediation

The high specific surface area of GO allows a high adsorption rate for hydrocarbons in oil spill clean-up. This eventually leads to a higher adsorption capacity and less needed material. A potential uniqueness is also the hydrocarbon removal at low concentration. [119–121]

Due to functionalization, the properties of GO can be tuned so that it becomes hydrophobic and oleophilic, the prerequisite for oil spill cleanup and highly polluted water cleaning (e.g. from oil drilling).

The chemical inertness, thermal and mechanical stability also allows recycling and recovery of sorbent and adsorbent.

2.4.2.1.3 Nano-graphite/graphene platelets and GO are sufficient: Low implementation barrier

For the additive to liquids application, usually graphene/2d platelets, GO or even exfoliated graphite/nano-graphite is used and sufficient. Therefore, the implementation barrier is low, material availability is there and the application has a rather high maturity and expected short time to market (for graphene, not other 2Ds). However commercial viability and cost/benefit still needs to be proven (see 2.4.2.2.2).

Besides, addition to liquids can be seen as a by-product of coatings or composites, where also the graphene/2D platelets need to be dissolved/dispersed. The benefit of a liquid is that it is used as it is and does not need to be applied or dried or further processed. This also reduces the implementation barrier.

2.4.2.2 Current weaknesses and challenges of graphene/2D materials use in liquids

2.4.2.2.1 Unclear influence of surfactant on properties and stability of dispersion

The surfactant or functionalization which is needed to keep the 2D materials dispersed can have negative effects on lubrication or adsorption properties. The most important challenge is to find a functionalization that enables a stable dispersion and long term stability in dispersion (e.g. to survive storage and transport) and at the same time resembles the needed functionality. In that respect functionalization is boon and bane, as it opens up many possibilities, but also constitutes many different approaches and a high degree of freedom with many possibilities, which can also be disadvantageous when looking for the right functionalization. Besides, most functionalization protocols are today available at rather small scale.

In particular for oil spill cleanup applications, the hydrophilicity of (pristine) GO needs to be reversed to hydrophobicity and oleophilicity through functionalization.

2.4.2.2.2 Cost/benefit needs to be proven

Similar to most of the bulk applications of graphene or other 2D materials the cost/benefit is not yet clear and needs to be proven. There are promising lab results which need to be transferred to real applications.

For liquid applications, it needs to be proven whether the benefits outweigh the potentially added costs. For instance it needs to be shown that for oil spill cleanup GO reaches a higher cost efficiency than other sorbents.

For lubricant additives there are no rules up to now to predict additive performances at a given technical application. As a consequence formulations have to be tested and forecast extensively to assure the functionality. Such testing is addressed by international and national regulations. It is further important to look at the lifecycle cost, as a longer lasting lubricant can potentially cost more than a lubricant that degrades earlier. Therefore, added costs can be justified by added functionality if the life cycle costs remain lower (e.g. due to use of lower amount of lubricant, less often change of lubricant, less wear of lubricated parts)

2.4.2.2.3 Clarification of toxicology/biocomaptibility

In particular for use of graphene in open waters, drilling holes and in the environment, the toxicology and biocompatibility of the used form of graphene needs to be broadly tested.

The biocompatibility depends on the type of graphene (e.g. oxygen content, lateral size). For use as oil spill cleanup especially endocytosis needs to be investigated. It appears that current results are "optimistic" in terms of biocompatibility in this respect.

For lubrication applications standard health & safety and regulatory classifications have to be conducted. The eventual fate of graphene and composites used as adsorbent needs to be investigated

2.4.3 KPIs for liquids

2.4.3.1 Lubrication

- Tribological properties: Friction, wear rate (also under pressure/heavy loads, temperature), lubricity
- Viscosity, viscosity index
- Pour point
- Flash/fire/autoignition point
- Chemical stability
- Oxidation and corrosion stability
- Thermal conductivity
- Electrical conductivity
- Cost per volume
- Recyclability/End of life properties

2.4.3.2 Remediation

- Absorption capacity: Absorbed material per g of adsorbent
- Absorption rate
- Absorption rate and capacity, as well as concentration reduction depending on conditions (temperature, concentration of material to be absorbed, type of material absorbed)
- Hydrophobicity (water contact angle)
- Efficiency of recovery/recycling of adsorbent (reusability, effect on other KPIs after cycles)
- Toxicology/environmental sustainability
- Life cycle cost

2.4.4 Roadmap for liquids

2.4.4.1 Current maturity: Drilling fluids on the market, remediation and lubrication under investigation

Additives to liquids have a rather high maturity and expected short time to market, because the integration is rather simple and the application can be seen as a by-product of graphene flake integration into composites.

There are already marketed products (Graphene Nanochem drilling fluid) and plans or concrete investigations to market products (remediation/oil spill cleanup: Directa Plus, lubrication: Puralube [122]). Most of the efforts are technology push driven.

In terms of functional lubricants (e.g. thermally conductive), the maturity is rather low and on lab scale.

2.4.4.2 Barriers/challenges (summarized)

Main challenges are

- actual demonstration of cost/benefit and performance increase towards competing technologies and state of the art
- scalability of processes (e.g. functionalization)
- shelf life of dispersions
- Unclear environmental properties, in particular for oil drilling fluids and remediation
- Functionalization (find the right one and scalable)

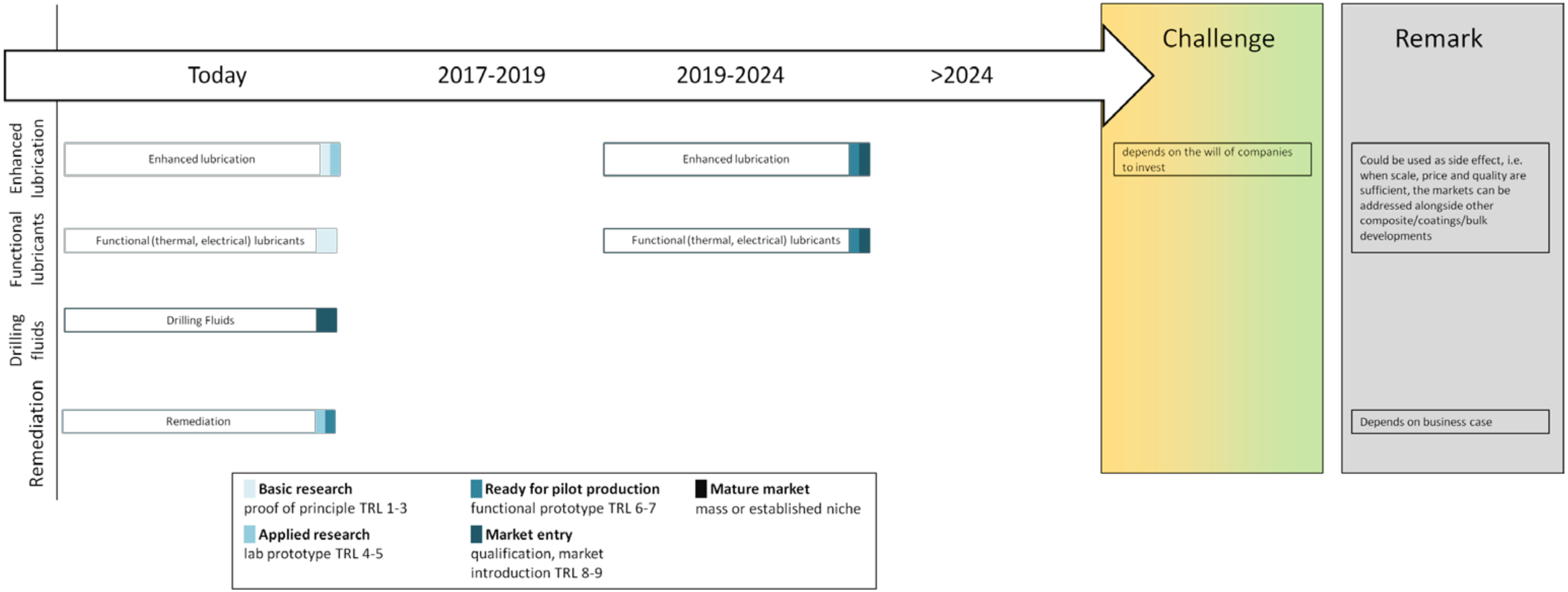
2.4.4.3 Potential actions

If the area of graphene/2D as additives to liquids is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

As additives to liquids can be investigated alongside composites, similar actions are required (such as large scale functionalization). In particular, the application oriented testing needs to be further pursued:

- Application oriented testing under realistic conditions
- Testing of other 2D materials
- Investigate large scale functionalization
- Prove/investigate environmental sustainability
- Investigate end of life properties
- Life cycle cost assessments

2.4.4.4 Roadmap



depends on the will of companies to invest

Could be used as side effect, i.e. when scale, price and quality are sufficient, the markets can be addressed alongside other composite/coatings/bulk developments

Depends on business case

Basic research proof of principle TRL 1-3

Applied research lab prototype TRL 4-5

Ready for pilot production functional prototype TRL 6-7

Market entry qualification, market introduction TRL 8-9

Mature market mass or established niche

2.4.5 Conclusion for liquids

Adding graphene or 2D materials to liquids, such as oils or water is straight forward, as long as the functionalization is right. Essentially, the use in liquids has a lower implementation barrier as coatings or composites, due to the fewer steps needed for implementation. The use in liquids can therefore be seen as a byproduct of coatings or composites. Furthermore, simple to produce graphene varieties can be used, such as GO.

Again, the multifunctional properties are the greatest selling proposition, e.g. electrical and thermal conductivity plus increased lubrication. This is, however, not fully explored yet and the cost/benefit is not clear.

For remediation and oil spill cleanup the high specific surface area is of interest. However, the overall cost/benefit towards other (carbon-based) adsorbents. Besides, for the broader use in the environment, the environmental friendliness needs to be approved.

There are already first graphene-based products on the market, e.g. drilling fluids from Graphene Nanochem and there is the effort of Directa Plus to commercialize their graphene material for oil spill cleanup. There are also first lubricant manufacturers observing the use as an additive (e.g. Puralube).

Table 19: Assessment of market and technological potential of graphene/2D materials use in liquids on a scale - -, -, 0, +, ++

Application in fluids	Current technological potential (USP)	Market potential (EU perspective)
Lubricants (wet)	0	+
Adsorbent for remediation	0	0
Drilling Fluids	0	-

2.5 Special application: Filtering, desalination/deionization and membrane applications

2D materials are the perfect candidates for membranes: ultimately thin, strong and modifiable through functionalization and manipulation. This chapter covers the use of graphene/2D materials as membranes in general and also as a coating or additive to membranes or filter materials for (water) filtering and desalination (membrane and capacitive deionization) [123]. Typical applications are presented in Table 20.

Table 20: Potential applications of graphene and 2D materials in filtering, desalination/deionization and membrane applications.

Type of application	Functionality	2D material
Membrane Review: [70, 124–127]	• Water treatment, filtering (reverse or forward osmosis) • Separation and filtering of liquids or gases • Filtering, size selection of nanomaterials • Sensing, DNA sequencing [128] • See also 3.2 Fuel Cells and hydrogen economy for potential applications	Graphene, rGO, GO
Electrode for capacitive deionization (CDI) [70, 123, 129]	• Replace activated carbon • High surface area, High ion-accessible surface area, high salt adsorption capacity, high adsorption rates and (electro)chemical stability	rGO, GNP
Coating [70, 126, 127] *Also see chapter 2.3*	• Anti-fouling, anti-bacterial, hydrophobic, auto-clean, enhances water permeability of standard (polymer) membranes	GO
Additive to membrane materials [70, 127] *See also chapter 2.2*	• Reinforcement, durability • Functionality (e.g. conductivity, anti-fouling)	GNP, rGO, GO

The graphene-based technologies range from GO-based layered structures as membranes, GO addition to polymeric membranes (as additive or coating) to enhance water permeability and address anti-fouling (G2O [130]), graphene as a perforated membrane itself used like a molecular sieve (Lockheed “Perforene” [131], CNM Technologies [132]). In terms of water desalination, these technologies are investigated for forward or reverse osmosis. But the actual graphene membranes can be also used to size selectively filter, even to separate heavy water (D_2O) from water (H_2O) [133], CO_2 Capture (chemical functionalization needed) [132] or for DNA sequencing, where also the electrical properties are exploited [128].

Besides these functional properties, graphene materials can also be used to increase the mechanical properties of membranes. Here the same considerations apply as presented in chapter 2.2.

Graphene material can be also used in capacitive deionization (CDI) for water desalination, an alternative technology to reverse osmosis. In this technology, the performance depends strongly on the electrode, which in current configurations is made from activated carbon. The general idea is to replace this by graphene to improve the performance and diminish the energy consumption.

2.5.1 Market perspective: graphene/2D in filtering, desalination/deionization and membrane applications

The market needs for the improvement of membrane and filtering technologies are to filter correctly, increase the lifetime and decrease maintenance efforts, improve self cleaning properties and reduce effort for cleaning cycles, reduce energy consumption. Desalination/deionization has the same needs, but in particular increased throughput and reduced energy consumption are crucial aspects. The market needs for the improvement of CDI technology are suitable electrode materials with high electroadsorption capacity and high adsorption rate to improve the performance and reduce the energy consumption.

The global membranes market is projected to grow at a CAGR of ~9.5% from more than USD 20 billion by 2015 to USD 32 Billion by 2020. Asia-Pacific and North America are the key markets for membranes. High growth is expected in Middle East & Africa and Latin America. The market is mainly driven by water & wastewater treatment, pharmaceuticals & medical uses (together 62% market share), food & beverages, and chemical processing sectors. Industrial gas processing segment is projected to witness the highest growth rate due to increasing use of membranes in the oil & gas sector for gas processing, hydrogen production or carbon dioxide removal from natural gas streams.[134]

In terms of the European industrial basis, the revenue created with water and gas filters and filter equipment/machinery was €14.4 billion in 2014 (CAGR 4.6% 2012-2014), of which €2.5 billion where parts for filtering and purifying machinery for liquids or gases (CAGR 4.6% 2012-2014).[39] The global market for the filter industry was $59.1 billion in 2013 and a CAGR of 6.2 percent to $80.0 billion in 2018 is expected.[135]

Looking at transnational patents (Figure 19), the field is dominated by applicants from the US. China is emerging in recent years, but European actors are also at a similar level.

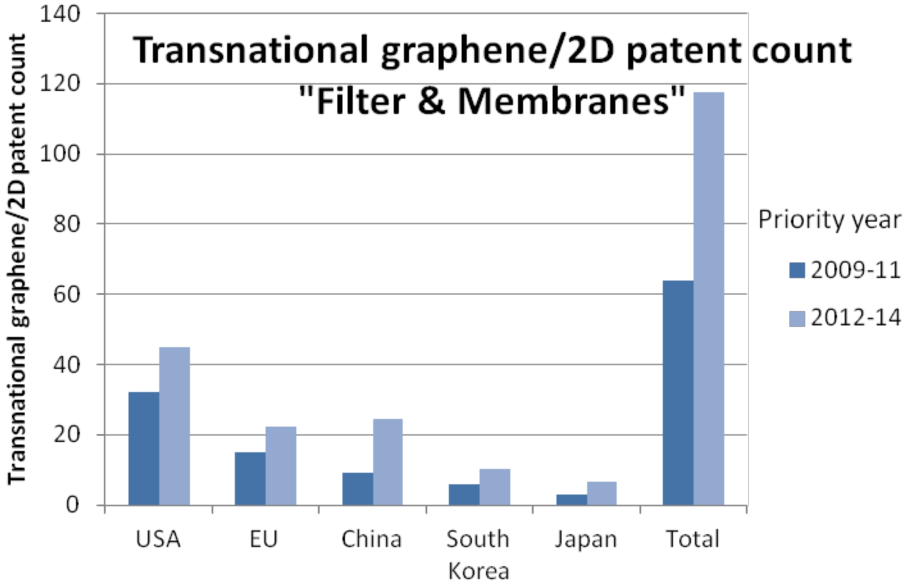


Figure 19: Patent analysis of graphene/2D materials in filter and membranes: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [21]

The relevance of graphene in membranes and filters (the ratio of graphene/2D patents from all patents in the area) is depicted in Figure 20. It is increasing strongly. In particular in China and Korea there is a stronger focus on graphene/2D materials in filters and membranes. Although the total count of patents is higher in Europe and the US.

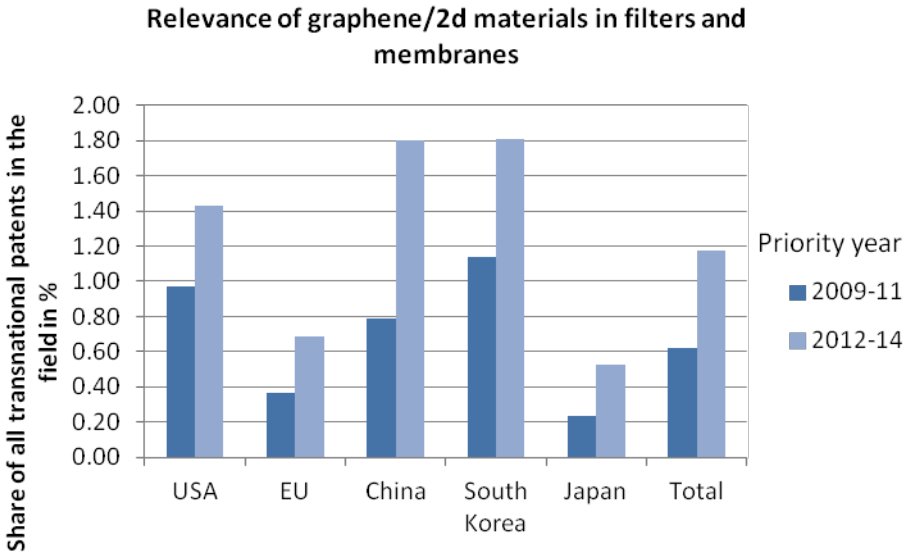


Figure 20: Patent share of graphene/2D related materials with respect to all transnational patents in filters and membranes. 2012-2014 values are projected.[21]

2.5.1.1 Market Opportunities

2.5.1.1.1 Increasing need for fresh water

Global climate change; global warming and increasing population increase the pressure on the water system. Water scarcity and increasing water stress leads to additional demands for fresh water technologies: through 2050, additional 2.3 billion people are expected to be living in areas with severe water stress, especially in North and South Africa and South and Central Asia [136]. The world could face a 40% global water deficit by 2030 under a business-as-usual (BAU) scenario.[137]

On the other hand, the need for portable water will exist due to a lack of infrastructure. Portable or smaller water treatment or desalination equipment could address this problem. This all leads to an increased need for resource efficient water treatment and an increasing need for water desalination with low energy consumption and low maintenance. The past five years has seen a 57% increase in the capacity of desalination plants. [138]

The increasing regulation on water quality in Europe and worldwide also drives the need for more energy efficient treatment technologies. This is not only affecting large scale plants, but also small scale treatment systems, e.g. the increasing need for hospitals water treatment.

Groundwater decontamination in the developing world is also a large market with unmet needs. Besides, applications as resin based water softener replacement or water treatment for cooling towers may also be attractive applications. CDI may very well address those markets.

2.5.1.1.2 Weaknesses of common technologies in desalination

Desalination gains importance but still is very energy intensive, even the most advanced reverse osmosis (RO). The constraints of RO are: low water flux and salt rejection, membrane fouling and regular membrane replacement.[126] Major trends are the reduction of energy consumption and improvement of self cleaning solutions. Additionally, current fresh water and desalination systems are usually large plants because of the economy of scales. Novel technologies can also enable more decentralized and mobile systems that allow a broader and more flexible supply without the need for extensive infrastructures or logistics.

One of the promising, mature but underperforming technologies is capacitive deionisation (CDI). Benefits of this technology is the absence of applied pressure, high rejection of salt, more efficient for low salinity feed water sources (TDS < 15,000 mg/L) and a much higher water recovery (up to 90% or more) than RO, which normally has a recovery rate of 50% or less. Additionally, a polarity reversal results in self cleaning of the electrodes.[125] The overall energy consumption of 0.1–2.03 kWh/m^3 is lower than for RO (3-6 kWh/m^3).[123] CDI in the short term, is expected to be used for low salt concentration water such as underground water (<5,000 ppm TDS) and not for sea water due to high CDI unit costs. The expected cost of desalination using current CDI technology is 0.36 $/barrel for this lower TDS (total dissolved solids) water, which is much less than reverse osmosis (6.11 $/barrel) and membrane electrodialysis (5.5 $/barrel). [139]

However, the efficiency of electrodes for salt separation requires optimization.[125] Standard materials are activated carbon, which is not selective and an optimum electrode was not yet found. The performance strongly depends on the electrode material. There is furthermore only limited data for seawater desalination available.[125] CDI also suffers from the requirement of a considerable external power source and the issue of brine solution disposal of the system. Furthermore, the electrode suffers from self contamination depending on the source water.[123] The market needs for the improvement of CDI technology are suitable electrode materials with high electroadsorption capacity and high adsorption rate. The NaCl adsorption capacity of the currently carbon-based materials is in the range of 0,1–10 mg/g, which is much lower than the theoretical estimations, leading to a too low performance.

2.5.1.1.3 Many other filtering/membrane opportunities

Besides water desalination or purification (waste water treatment, CDI), filter materials and membranes are also important in (exhaust, process) gas cleaning and separation, industrial and pharmaceutical material production/purification processes and analytics. These markets offer highly specialized needs that can be addressed by new technologies. Early adopters are available in this respect, especially for harsh conditions.

Membranes can be seen as a platform technology with a variety of potential end products. If the technology is understood and controllable, more potential markets arise.

2.5.1.1.4 European strength in filter and filtering equipment

With a production value of €14.5 billion in 2014, the European filter industry is rather strong and potential integrators are in Europe. [39]

Furthermore, the competition on the market, especially for high quality products is rather moderate, although the competition increases. Besides, the patent activities (Figure 19) suggest that Europe is not leading this technology strand in terms of graphene and 2D materials, but has a reasonable share of activities. Besides, Europe has the highest overall patent share in this area (independent of graphene/2D), suggesting a strong and innovative industrial backbone (see Figure 21).

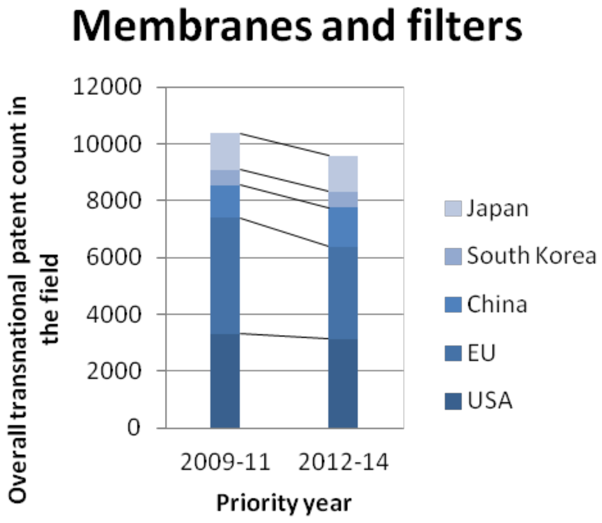


Figure 21: Overall transnational patent count in membranes and filters. 2012-2014 values are projected.[21]

2.5.1.2 Market Threats

2.5.1.2.1 High quality standards and cost sensitivity pose market barriers

Especially the fresh water markets pose barriers due to high standards in terms of durability or health and safety, whilst being cost sensitive. Typically, the markets allow only smaller cost increases for improved functionality or performance on system level. The cost-benefit is usually addressed on system and life cycle level, where the latter eventually needs to be lower. But in terms of added cost for membrane and materials, the room is very limited: The module prices of filter cartridges depend on many different components and membrane materials comprise only a small component of the module price. As they comprise currently a rather small portion of the price, large increase is not possible.

In general, durability needs are high and need to be addressed. A new technology is only feasible, when it is durable and requires low maintenance and down times. A non-negligible issue is that proving durability is rather tricky. Despite accelerated testing, in a conservative industry one will mostly use the technology that actually has shown its durability in commercial applications.

Currently, the need for lower energy consuming technologies is also curbed because of the low fossil fuel prices.

2.5.1.2.2 Competing materials and technologies are diverse

In terms of desalination reverse osmosis is currently the dominant and most economically effective technology. There are also several older plants based on thermal desalination.

In terms of membrane materials, also other emerging materials pose promising properties, such as Zeolites, CNT, Silica, TiO_2 and silver nanoparticles and thin film composites (TFC).[126] Clear benefits in terms of functionality or performance need to be shown towards these technologies and the state of the art.

2.5.2 Graphene/2D materials perspective: Current strengths, weaknesses and challenges for the use in filtering, desalination/deionization and membrane applications

2.5.2.1 Current strengths for graphene/2Ds materials use in filtering, desalination/deionization and membrane applications

2.5.2.1.1 Ultimate membrane: selectivity, mechanical strength and pore size

As a 2D material, graphene has ultimate membrane properties and very small pores are possible. This allows size and ion selective filtering and can be also used for sensors and science (chromatography-like).

Additional functionalization allows tuning of further properties and selectivity. Interest from industry is there (e.g. Lockheed Perforene) and expectations are [131]:

- Tolerance towards harsh conditions (temperature, pH, chemicals)
- Higher permeability (two orders of magnitude)
- Hydrophobicity reduces fouling

For desalination, the expectations are to increase the membrane flux by a factor of five with fewer required elements, which translates in 10-20% energy consumption due to lower needed pressure and 80% fouling reduction and correspondingly enhanced membrane life.

2.5.2.1.2 Laminates as a possible simpler use in membranes

GO graphene laminates (water transport through capillaries) depict a simpler use of graphene materials as membranes. The exhibit good mechanical properties, fast water transport and high rejection capability. The membranes can be tuned to be ion selective. [125] The production and implementation of these membranes is potentially easier as for single layer membranes.

2.5.2.1.3 Interesting enhancements for polymer membranes

Graphene platelets and graphene oxide can be used to enhance the functionality and mechanical strength of polymeric membranes as an additive or as a coating. Added functionalities are hydrophobicity, anti-fouling, anti-bacteria, auto-clean, higher water permeation. The enhanced membranes are ultra-permeable and the GO enhanced membranes show significantly improved membrane performance and anti-fouling. [126, 127]

With the variety and possibility of functionalization the properties can be further tuned. For mechanical enhancement, see chapter 2.2 for further considerations. The goal is to increase the lifetime of filters.

This application poses a rather low barrier, as integration is comparably simple and the state of the art technology is just slightly modified. 2D materials can are used as any other additive and the form factors and outline of the membrane does not change, so the system itself does not to be changed as well.

2.5.2.1.4 CDI: Potential enabler

CDI electrodes need high ion mobility, high adsorption capacity (which is related to the surface area and pore size) and low electrical resistivity, all addressable with graphene. Currently mesoporous (activated) carbon aerogels are used with specific surface areas of 400-1100 m^2/g and electrical resistivity of less than 40 $m\Omega$ cm. [125]

The unique selling proposition of graphene materials is the higher specific surface area combined with the electrical conductivity, chemical properties and the possibility to be functionalized. Currently, reduced graphene oxide is investigated. The chemical properties and potential variety of functionalization could be exploited for better selectivity for ions or molecules due to the much more controlled surface. High surface area and porous electrodes can be achieved by using three-dimensional reduced graphene oxide, with macropores, to enhance the ion mobility and ion accessibility; and micropores for high adsorption capacity. The mobility, capacity and hydrophilicity can be further enhanced by addition of metal oxides nanoparticles. Graphene materials are rather unique material candidates for improving CDI.

Graphene electrodes reach an ion removal efficiency of 18.5 mg (ions)/gram (electrode) [140] while activated carbon electrodes are between 2-5 (ions)/gram (electrode) [129]. It can therefore enable the use of CDI also for higher TDS (total dissolved solids) water.

2.5.2.2 Current weaknesses and challenges for graphene/2D materials use in filtering, desalination/deionization and membrane applications

2.5.2.2.1 Membranes: maturity and unclear actual performance [123, 125, 126]

The current experiences are to a great extent based on lab scale experimental results and modelling/simulation studies. For water desalination, actual tests, e.g. in reverse osmosis configuration, are not yet performed. The membranes need to be optimized to be functional and effective in high pressure configuration under real conditions.

Therefore, important knowledge for an objective application assessment of real-life chances that graphene can be used are missing: recovery range, feed water quality (at least seawater salinity is a must), energy consumption, cost impacts. In terms of energy consumption, expectations are that it will be similar to common RO membranes. Cost will depend on the ability to produce the right quality and quantity of graphene and the integration into membrane structures.

For actual graphene membranes (e.g. perforene), a main weakness is the trade-off between water flow and mechanical stability: a higher flow requires more pores, which reduced the mechanical stability. The optimal pore distribution also needs to be found.

Besides the potentially needed exact membrane nanopore fabrication is a challenge, e.g. for DNA sensing, where pore sizes need to be very precise.

2.5.2.2.2 CDI: Unclear cost/benefit and current maturity in CDI

For the use in CDI, the potential is large. However, the experimental validation is still open. There are only lab scale CDI tests available and no reproducible proof of an improved effect are available yet. The important question is, whether the cost/performance will be good enough to become dominant technology compared to activated carbon. Only if the improvement is considerably high, higher costs are justified. For moderate improvements, the costs for an upgrade from activated carbon to graphene might become too high.

2.5.2.2.3 Health and safety for drinking water needs to be addressed

As graphene is a nano-material, health and safety need to be addressed from the beginning, in order to avoid the threat of health concerns (see 2.5.1.2.1). In particular for desalination and drinking water applications, health and safety needs to be proven. For instance, aging studies can be performed on GO-based CDI electrodes in order to evaluate GO release and thus health and safety.

2.5.3 KPIs for filtering, desalination/deionization and membrane applications

- Compatibility with environment and regulation (no release of graphene)
- Pressure/operating conditions
- Permeate flux
- Rejection and selectivity of filtering
- Durability, reliabilty and contamination/fouling
- Recovery
- Energy consumption
- Cost

2.5.3.1 Desalination: CDI and competing reverse osmosis (RO):

General:

- Pressure
- Water flux (RO: 10 L/m^{2}h)
- Salt rejection
- Selectivity
- Membrane fouling
- Recovery range, feed water recovery (RO: ~40%)
- Feed water quality (total dissolved solids, TDS)
- Treated water quality
- Energy consumption (RO: 3-6kWh/m^3, lowest 1.6 kWh/m^3)
- Cost impacts
- Food/water health & safety regulations

CDI

- high ion mobility, high adsorption capacity (which is related to the surface area and pore size) and low electrical resistivity (NaCl adsorption capacity of the currently carbon-based materials is in the range of 0,1–10 mg/g, new materials need to be much better [126])
- The final and ultimate limit to the pore size is the bare ion size. For example 1.16A for Na and 1.67 A for Cl. These numbers increase for solvated ions with 3.58A for sodium and 3.31A for chloride. Larger pores provide better transport pathways, however, they also decrease the total specific surface area. Besides, the porosity and pore architecture of entire CDI electrodes needs to be considered rather than only the pore characteristics of individual porous particles.

2.5.4 Roadmap for filtering, desalination/deionization and membrane applications

2.5.4.1 Current maturity: applied research towards first applications

First graphene containing membranes are investigated for commercial use: Perforene (Lockheed), CNM Technologies

Also GO enhanced polymeric membranes are investigated: G2O

CDI: No reproducible proof of improved effect of graphene available yet, only lab scale CDI tests done

Sensing membranes are still at the lab stage.

2.5.4.2 Barriers/Challenges (summarized)

2.5.4.2.1 Membranes

- Increased durability
- Selectivity (Functionalization?)
- Prove promising potentials in relevant devices
- Find optimal pore density for optimal stability and permeation (trade off between water flow and mechanical stability)
- Reliable/exact and economically feasible (nano-)pore fabrication
- Scalable manufacturing process
- Compete with Zeolites, CNT, Silica, TiO2 and silver nanoparticles and thin film composites (TFC)
- H&S regulations: approval for use case
- Sensing capabilities: show improved performance towards competing technologies

2.5.4.2.2 Additional challenges for CDI

- Performance of CDI compared to state of the art RO
- Design of module and support for graphene
- Scale up to square meter sized electrodes while keeping electrical drive well connected for high homogeneity of current
- H&S regulations: approval for use with drinking water

2.5.4.3 Potential actions

If the area of graphene/2D as/in membranes is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

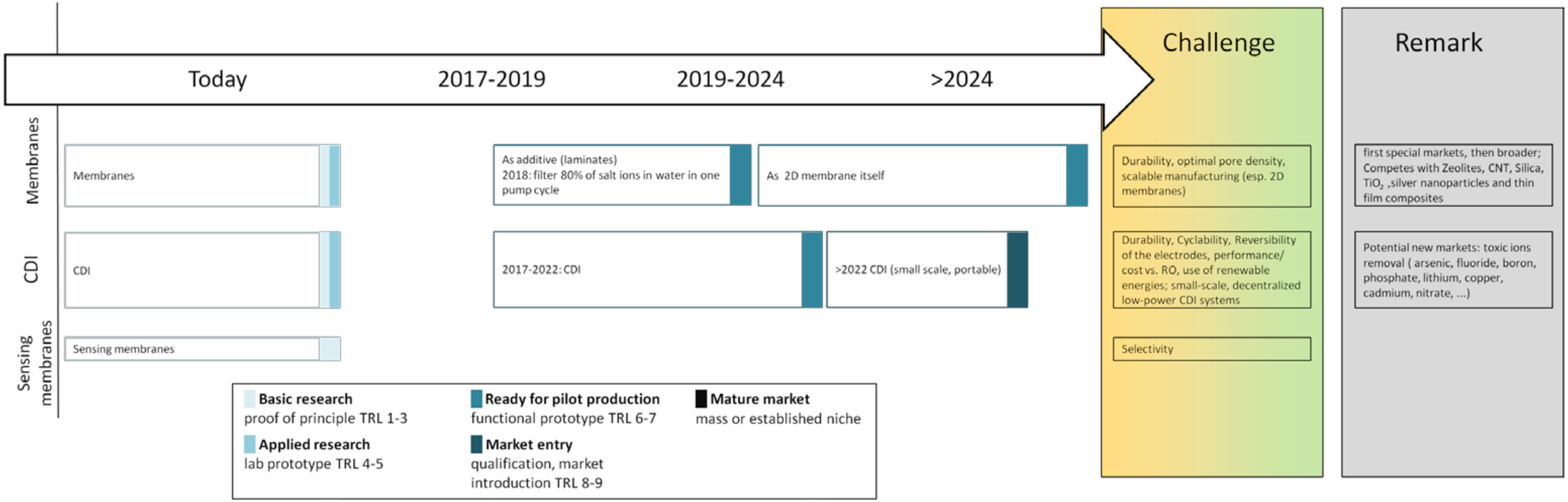
Membranes:

- Experimentally show clear potential and improvement towards SOTA
- Clearly prove performance as close to the application as possible (e.g. in RO configuration)
- Develop scalable manufacturing concepts and compatible form factors
- Address functionalization to improve selectivity
- Address H&S from the earliest developments
- For sensing membranes: address potential concepts for sensing, elaborate clear benefits towards state of the art and competing technologies

CDI:

- Optimize and scale up electrode preparation
- Optimize contacting of electrode
- Transfer from lab scale to actual demonstrator and prove higher performance compared to activated carbon
- Real life testing to allow assessment of cost-benefit and quality of treated water

2.5.4.4 Roadmap



Today | 2017-2019 | 2019-2024 | >2024 | Challenge | Remark

Membranes
- Membranes
- As additive (laminates) 2018: filter 80% of salt ions in water in one pump cycle
- As 2D membrane itself
- Challenge: Durability, optimal pore density, scalable manufacturing (esp. 2D membranes)
- Remark: first special markets, then broader; Competes with Zeolites, CNT, Silica, TiO_2 ,silver nanoparticles and thin film composites

CDI
- CDI
- 2017-2022: CDI
- >2022 CDI (small scale, portable)
- Challenge: Durability, Cyclability, Reversibility of the electrodes, performance/ cost vs. RO, use of renewable energies; small-scale, decentralized low-power CDI systems
- Remark: Potential new markets: toxic ions removal (arsenic, fluoride, boron, phosphate, lithium, copper, cadmium, nitrate, ...)

Sensing membranes
- Sensing membranes
- Challenge: Selectivity

Basic research proof of principle TRL 1-3
Applied research lab prototype TRL 4-5
Ready for pilot production functional prototype TRL 6-7
Market entry qualification, market introduction TRL 8-9
Mature market mass or established niche

2.5.5 Conclusion for filtering, desalination/deionization and membrane applications

Membranes for filtering, deionization and separation are increasingly important for drinking water and purification of gases or liquids. 2D materials can be used for this component in several ways: as a perforated membrane itself, as an additive or coating to common polymer membranes or as an electrode for capacitive deionization (CDI).

In terms of membranes made from 2D material sheets (perforated), the maturity is still rather low, however the theoretical potential is promising. Due to the new kind of material there are still many questions open, in particular how to approach the trade-off between water flow and mechanical stability, but first commercialisation efforts are taken (Lockheed in USA, CNM technologies in Europe). However, the barrier for implementation is still high due to many open questions. As a layered structure membrane (GO laminates) the implementation is potentially easier, but the cost/benefit is also not yet clear

As an additive or coating to existing membranes, graphene materials are easy to integrate and more mature. The additives shall increase mechanical stability, anti-fouling and water permeation. First commercial activities are also approached (e.g. G2O).

As an electrode for CDI, graphene is a promising candidate. CDI is a promising desalination method with reduced energy consumption. Demonstration of an enhanced performance through the use of graphene materials is pending.

Most importantly, for the use in water purification the environment, health and safety concerns need to be addressed and disproven.

In terms of markets it is expected that the need for purification (of gases or liquids) and for drinking water production will increase. Besides, there are potential integrators in Europe.

Table 21: Assessment of market and technological potential of graphene/2D materials use in membranes and filters on a scale - -, -, 0, +, ++.

Applications	**Current technological potential (USP)**	**Market potential (EU perspective)**
Membranes for water filtering/desalination	0	+
Membranes for other filtering	0	+
Membranes with sensing capability	+	0/+
Polymer membrane coating/additive	+	+
CDI electrode	+	+

2.6 Special application: (Photo-)catalytic material/ enhancement

Functionalized or chemically modified graphene flakes and GO can be also used as catalysts to replace for instance precious metals (see also 3.2 Fuel Cells and hydrogen economy). Another specific application area is the use as photocatalytic enhancer for TiO_2, e.g. for air purification or photocatalytically active self cleaning surfaces [141], for treating contaminants and bacteria [142] and for photocatalytic water cleaning [106]. [70] It is such photocatalytic enhancement for decomposition of contaminants and bacteria and, in general, for cleaning applications that is covered in this chapter.

The enhancement of photocatalysts (and catalysts in general, e.g. for oxygen reduction reaction ORR) can also be used in other applications, such as fuel cells or water splitting. These areas are not covered here and can be found in chapter 3.2 Fuel Cells and hydrogen economy.

The general use of 2D materials and their heterostructures as catalysts (also as electrocatalyst and heterogeneous catalyst) is still in its infancy. They have shown considerable potential, but application-orientated research has just started. [143]

2.6.1 Market perspective: graphene/2D as (photo-)catalytic material/enhancement

The global market for photocatalyst products increased from $1.4 billion in 2013 to nearly $1.5 billion in 2014. It is estimated to be valued at nearly $1.6 billion in 2015 further growing at a CAGR of 12.6% until 2020, reaching nearly $2.9 billion. [144]

To get an idea of the European industrial base, the production value of machinery and apparatus for filtering or purifying gases by catalytic process (excluding intake air filters for internal combustion engines, machinery and apparatus for filtering or purifying air) was 3.6b€, for filtering or purifying air (excluding intake filters for internal combustion engines) was 2.1b€ in 2014. Titanium oxides accounted for a production value of 1.2b€ and preparations based on TiO_2 accounted for 2.3b€ in 2014. [39] These categories do not necessarily resemble the industrial base for photocatalytic functionalities, but at least give an impression of the production values in related areas, where photocatalysts are a subset of.

2.6.1.1 Market Opportunities

2.6.1.1.1 Construction sector as main market for photocatalytic material

The photocatalyst products are to a large extent used in the construction sector: construction accounts for ~90% of the market. It is projected to grow with a CAGR of 13% from nearly $1.4 billion in 2015 to $2.6 billion in 2020. [144]

This growing demand comes from increasing urbanization and the need for reduction of increasing air pollution.

Non-refractory surfacing preparations and protective preparations (fire, water) in the building industry account for a production value of €1.8 billion in 2014 in Europe. [39]

The overall market is rather small at the moment, but there is also not much competition on the market.

In terms of European adopters, the annual total added value of the European cement and concrete industry was €56 billion in 2013. [38] The production value of ready mixed concrete was 16.1b€ in 2014. [39]

2.6.1.1.2 State of the art photocatalytic technologies not feasible at the moment

There are already coatings/paints and cements on the market that make use of TiO_2 for photocatalytic self-cleaning and air purification. However, the performance is currently not good enough to allow a broad uptake of the technology for the current price tag.

A major disadvantage of the state of the art technology is the need of strong UV light sources, which makes the application not feasible for inside moderate light conditions.

The performance is good enough for outdoor applications where the UV component of the solar radiations satisfies the TiO_2 band gap. Moderate indoor light conditions and seasonal/diurnal variations of sunlight intensity and clouds, however, create the need for photocatalytically active materials that work with a broad wavelength range and in lower light conditions.

This deficiency creates a need for photocatalytically active materials that work with a broad wavelength range and in lower light conditions. Here, GO could act as an enhancer for the TiO_2 photocatalytic activity.

2.6.1.1.3 European strengths in catalysis in general

Europe is an innovative and strong player in catalysis in general, see Figure 22 on the left. This of course also includes catalysts for chemical reactions, fuel cells, exhaust gas cleaning etc. Also in the field of photocatalysis, Europe is strong, see Figure 22 on the right. This field is gaining importance.

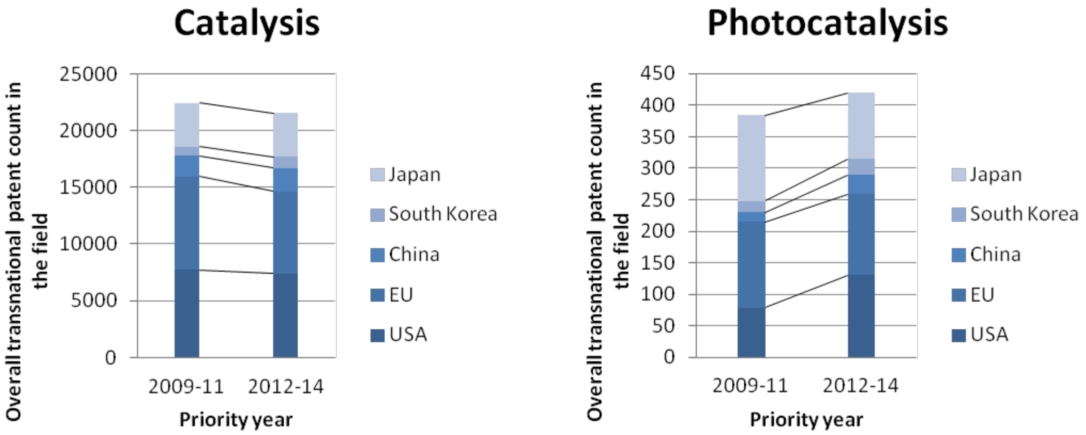


Figure 22: Overall transnational patent count in catalysis and photocatalysis. 2012-2014 values are projected.[21]

At the European Inventor Awards 2014, organized by the European Patent Office (EPO), TX Active, the photocatalytic technology developed by Italcementi, was on the podium at the "Oscar" of innovation.

2.6.1.2 Market Threats

2.6.1.2.1 Price sensitive markets with large volumes

An issue for a successful integration of new technologies in this particular market is the very high price sensitivity of construction materials and the large quantity of material needed. Typical coatings/paints cost on the order of 1 €/kg to 3 €/kg on average, even with functionalities, nevertheless market price is much higher, from 15 to 30€/kg. Paving in photocatalytic blocks costs on average between 10 - 20% more than traditional paving in the materials [145], but only 3-5% adding the cost of manpower. Already this is in parts cost prohibitive in the current market with the current performance.

It appears that the market is not ready for a broad uptake at the moment as the necessity is often not yet seen and the feasibility due to additional costs is not convincing for many decision makers in the buildings industry. There are more or less only lighthouse projects realized with the current technology at the moment. But there is a large potential for the application of this technology to reduce pollution in the cities, provided that their need to be more "green and healthy" is assured by regulations and attention to costs is addressed also at reducing people diseases caused by a polluted environment. A coating a surface area of 1000m^2 with photocatalytic-based products equals eliminating the pollution caused by 30 petro-fueled vehicles or also equals to planting 80 deciduous trees.

2.6.1.2.2 Other emerging technologies under investigation

There are also other strategies pursued and possible, so that the graphene material solution is currently not so unique. Other strategies are doping or dye sensitization. However these technologies are also not commercially feasible yet. [141]

2.6.2 Graphene/2D materials perspective: Current strengths, weaknesses and challenges for the use as photocatalytic material/enhancement

2.6.2.1 Current strengths of graphene/2D materials use as photocatalytic material/enhancement

2.6.2.1.1 Proven photocatalytic enhancement of TiO_2 through graphene materials

Graphene materials enhance the photocatalytic activity of TiO_2, the latter being used for photocatalytic coatings, e.g. for self cleaning or air cleaning. This is proven for composites of graphene material and TiO_2.

In order to tackle more efficiently seasonal/diurnal variations of sunlight intensity and clouds negative effects, new TiO_2-based nanophotocatalysts incorporating graphenic materials have been recently studied and proved to be more effective than titania.

They have better performance under solar radiation and hence are more valid to face variable sunlight intensity over the year and over different latitudes.

The new G-TiO_2 system is expected to be more active under visible light irradiation and to exploit a larger portions of sunlight thereby becoming potentially applicable for indoor cement coatings. Initial experimental results of the research are promising. The TiO_2-graphene nanocomposite absorbs light from the whole visible region, the photocatalytic activity of the hybrid material is proven to be enhanced in the visible region. [146, 147] The potential to use visible light will make functionalised cementitious coatings suitable for indoors.

2.6.2.1.2 Implementation as a paint or filler

The application of such a graphene material enhanced TiO_2 could be done as a paint (see chapter 2.3 for further considerations) or skimcoat. It could be integrated with cement or concrete and coated on large wall areas in cities or streets, also in the form of tiles. Paving of photocatalytic sandwich blocks, with only the upper surface composed of photocatalytic material, is a doable application already on the market for the photocatalysts currently available.

The photocatalytic activity is also influenced by the interaction with the cementitious matrix which is subject to the hydration process and generates new hydrated products (C-S-H, portlandite). It is still open whether this interaction is beneficial or detrimental or has no effect.

The scalability of the processes are not expected to be a major problem.

2.6.2.2 Current weaknesses and challenges of graphene/2D materials use as photocatalytic material/enhancement

2.6.2.2.1 Cost as limiting factor

The applications dealing with air purification and self cleaning are large area applications and require a rather low cost for broad implementation, e.g. in buildings or pavements. Massive application of photocatalytic cement for walls and pillars is not convenient as the photocatalytic action is present only at the exposed surface. Application of photocatalytic paints or skimcoats is a convenient solution to get cost effective results.

However, already a 150€/kg for the graphene material represents an accessible cost for wider use. TiO_2 particles are ~20€/kg. The photocatalytic performances of graphene doped TiO_2 increase also at very low concentration of graphene material. Assuming a 5-10% doping of TiO_2 with graphene materials, it is possible to improve TiO_2 particles with 7,5-15€/Kg.

Considering the case of 1kg of coating and a usual TiO_2 content of less than 5% (50g), a graphene doping of 5-10% of the TiO_2 content (2,5-5g) implies a formula cost increase of 0.38-0.75€ for a kg of photocatalyst coating. Current formula costs are estimated around 1-3€/kg, not considering production cost and earnings. Assuming a price of 15€/kg for the finished product, a broad gap to put in the formula cost increase due to the graphene material is available. But development is needed to limit also the applicative cost on the substrate, which might be reached acting on the composition and the technology.

2.6.2.2.2 Necessity of dispersion and unclear performance in final matrix

In order to have an effective enhancement of the photocatalytical activity, TiO_2 and graphene material need to be in direct proximity and well dispersed in the product. This needs to be achieved in a mass production compatible and simple process. The right functionalization might be a potential solution. The best solution is the preventive preparation of hybrid TiO_2/graphene material that can be dispersed directly in the cementitious matrix, maintaining the contact between the two compounds.

Besides, as the cementitious matrix evolves over the hydration time, it has to be better investigated how the developed micro/nano structure affects the photocatalytic activity. It is still open to investigation whether the potential interaction is beneficial or detrimental or has no effect.

2.6.3 KPIs for photocatalytic material/enhancement

- Photocatalytic activity (wavelength dependence), under artificial light, under sun light, under diffuse light.
- Price (1 €/kg to 3 €/kg on average for building coatings, 20€/kg for TiO_2)

- Decomposition of main pollutants (NOx, …)
  - UNI 11259 standard “Determination of the photocatalytic activity of hydraulic binders. Rhodamine test method
- Large scale production
- How to apply (painting, spraying, tiles, paves, cement, concrete… should be applicable with common building technologies)

2.6.4 Roadmap for photocatalytic material/enhancement

2.6.4.1 Current maturity: statement

Many buildings exhibit the current commercial photocatalytic cement (TX Active©-Italcement) and NOx falls of about 50% were the final proof of the technology (marketed version not containing graphene materials).

Nanocomposites based on graphene material and TiO_2 integrated in a cementitious matrix, were studied with positive results permitting to file a commercial patent and a lab demonstrator was made. Development of new nanocomposites for indoor applications are in progress.

2.6.4.2 Barriers/challenges (summarized)

The main barriers currently are:

Catalysis in general:

- Fundamental understanding of catalytic nature missing [143]
- Actual integration in a product-like environment (moulding, assembly)
- Testing and feasibility study
- Large scale production of adequate quality (not too good, not too bad) with adequate cost

Photocatalyst:

- Maintaining the performance in the final matrix
- Dispersion of graphene/TiO_2 hybrid photocatalyst in the matrix
- Developing technical paint and/or skimcoat
- Reliability and durability against weather and temperature
- Price
- Market uptake of current photocatalytic technology slow at the moment
- Increasing awareness of policy makers/builders towards the advantages of the photocatalytic technology for “healthier” cities to tackle the slow market uptake of the current technology

2.6.4.3 Potential actions

If the area of graphene/2D as photocatalytic material/enhancement is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

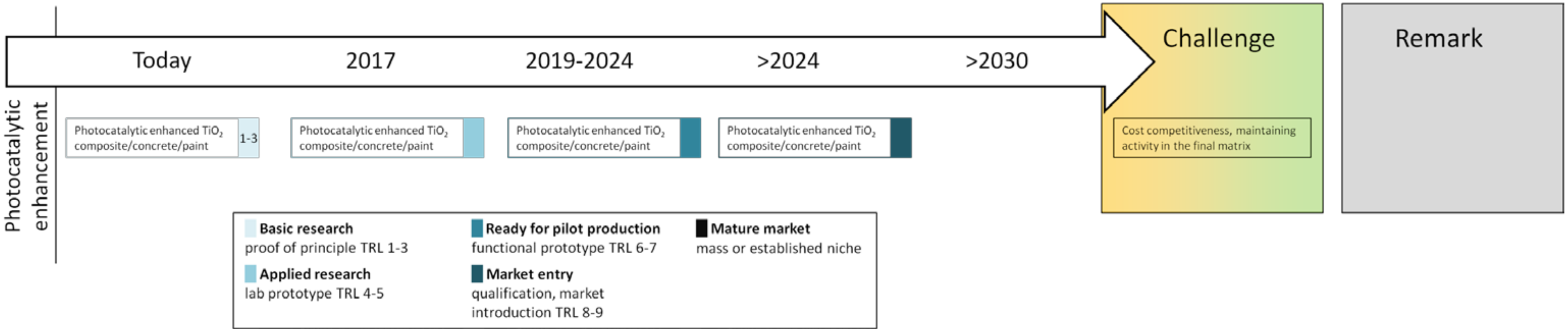
Basic understanding:

- investigate the catalytic nature of these materials by means of in situ characterizations and theoretical simulations [143]
- Understand the underlying physics to better tune the properties

Engineering actions:

- Investigate preparation technologies to meet adequate quality, scale and cost
- find best host(s), assemblies or moulds
- Testing under relevant conditions
- Assess commercial viability
- improve dispersion with TiO_2 (photocatalysis specifically)
- investigate integration into host/matrix material(photocatalysis specifically)
- Develop standards for testing photocatalytic performance

2.6.4.4 Roadmap



2.6.5 Conclusion for photocatalytic material/enhancement

The photocatalytic activity of TiO_2 is enhanced in the presence of graphene material. This is an interesting and rather simple application for photocatalytic paints or coatings for air purification and self-cleaning surfaces. The market is currently not very large but expected to grow. In particular, the greater and greater demand for healthier cities is favorable for the application of the technology. As a drawback the cost seems to be a limiting factor since the construction sector has difficulties to charge it on the customer. The advantages for the urban environment should be better disclosed. It seems likely that the policy makers are not enough sensitized to the technology. Importantly, the competition is not very strong at the moment.

However, the dispersion of the graphene material in the host needs to be better understood to come to a commercially viable process. The actual performance improvement of the material mix of TiO_2 and graphene material also needs to be proven on relevant scale and conditions. The price sensitivity of the potential application as a large scale paint/skimcoat can act as a barrier, which requires low cost base materials to be passed. Nevertheless, the low thickness of the coating, 2-3mm, permits to limit the formulation cost and development is needed to limit also the applicative cost on the substrate.

Table 22: Assessment of market and technological potential of graphene/2D materials use for photocatalytic material/enhancement on a scale - -, -, 0, +, ++.

	Current technological potential (USP)	**Market potential (EU perspective)**
photocatalytic enhancement	++	+

2.7 Summary composites and bulk applications

The application area of composites and coatings is the area which is closest to application (or already there). However, the products on the market address niches, where a new technology can be used for advertisement, such as in sports equipment.

For broader markets, the cost/benefit of graphene/2D materials use is often not clear enough, although companies are more and more interested to investigate the actual potential. A very important issue is that the expectations need to be managed (“100x stronger than steel”), which will never be reached in a composite. For bulk applications and mass markets, often cost and performance need to be improved.

Important assets are functionalisation, biocompatibility/recycling and multi-functionality.

In general, the applications where graphene/2D flakes are used, such as in composites, paints, liquids, have a lower implementation barrier and markets can be easier addressed, compared to e.g. electronics. On the other hand, the technological added value (performance improvement and disruptiveness) is probably smaller for flake based bulk applications compared to high quality films. Coatings or membranes made from high quality (single layer) films will probably only reach markets with rather small surface areas, (e.g. TCFs). The implementation barrier is currently too high. This type of coating can benefit from wafer scale integration in electronics.

Table 23: Summarized assessment table of all composites and coatings application areas primarily sorted by European market potential and secondary sorted by USP.

Composite property/host	**Current technological potential (USP)**	**Market potential (EU perspective)**
Composites: Multifunctional enhancement; added functionalities	++	++
Multifunctional coatings (added functionality)	++	++
Composites: Thermal enhancement (polymers, ceramics)	+	++
Composites: Electrical enhancement (polymers, ceramics)	+	++
Composites: Barrier (polymers)	+	++
Composites: Polymers	+	++
Barrier coatings (anti-…)	+	++
Composites: Mechanical enhancement	+	++
Composites: Ceramics	+	++
photocatalytic enhancement	++	+

Composite property/host	**Current technological potential (USP)**	**Market potential (EU perspective)**
Polymer membrane coating/ additive	+	+
CDI electrode	+	+
Electrical coatings	0/+	+
Composites: Flame retardant (polymers)	0	+
Composites: Metals	0	+
Composites: Cement/concrete	0	+
Thermal coatings	0	+
Membranes for other filtering	0	+
Membranes for water filtering/desalination	0	+
Lubricants (wet)	0	+
Membranes with sensing capability	+	0/+
Adsorbent for remediation	0	0
Transparent conductive films	0	-
Drilling Fluids	0	-

3 Energy generation and storage

3.1 Potential energy applications

This chapter covers energy applications of graphene/2D materials. The application areas are summarized in Figure 23.

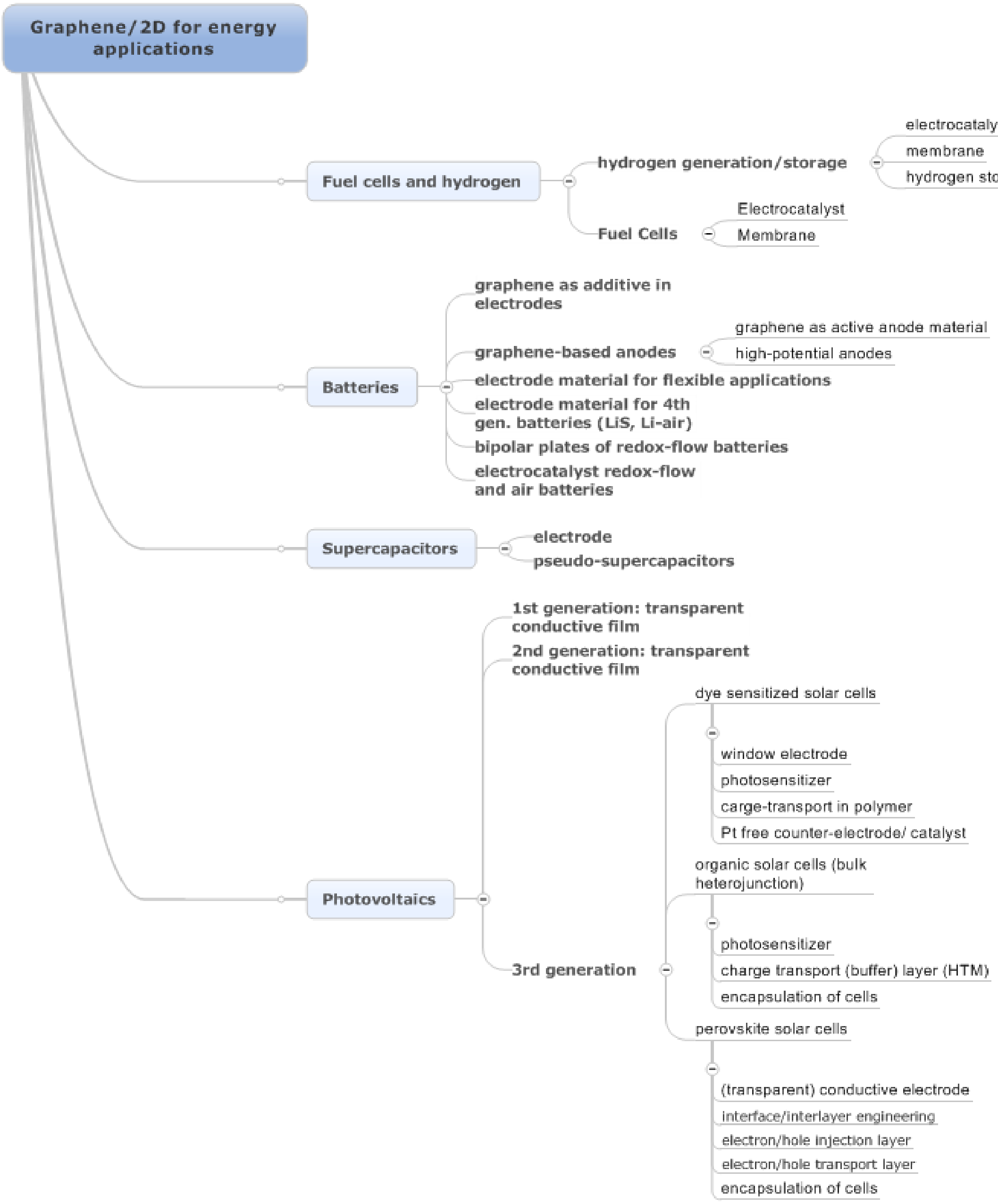


Figure 23: Energy related application areas of graphene/2D materials.

Some other energy related applications are covered in chapters 2 Composites, bulk applications and coatings (electric field grading, electric conductivity) and 4 Electronics & Photonics (nanogenerators/micro-energy harvesters).

3.2 Fuel Cells and hydrogen economy

The following section is particularly focused on Proton Exchange Membrane Fuel Cells (PEM FC). This kind of fuel cells is prevailing in the most relevant application markets, as there are vehicles and stationary storage (s. Figure 24). Moreover, PEM FCs represent the most prominent focus of research. Graphene and other 2D materials are particularly expected to contribute to components for this type of fuel cells. In some special cases Direct Methanol Fuel Cells (DMFC) are also addressed, as graphene and other 2D materials might contribute to improvements in this technology as well. Explicitly excluded are high temperature fuel cells like Solid Oxide Fuel Cells (SOFC).

Fuel cells are energy converters. They transform chemically stored energy in electrical energy. Therefore, fuel cells alone cannot be seen as energy storage solution. But together with fuel tanks they can be used – like batteries and supercapacitors – for energy storage respectively power supply.

The chapter also looks at power to gas applications (electrolysers) in hydrogen generation, as well as hydrogen storage applications for graphene. These applications are assessed separately starting at chapter 3.2.4 Hydrogen generation and storage.

3.2.1 Market perspective: graphene/2D materials in fuel cells

Applications of PEM fuel cells cover a broad spectrum: The technology is used in stationary applications for power generation, particularly in combined heat and power (CHP) generation systems. The related devices are often implemented in residential applications; Fuel cell technology can be used for levelling peak power; and it is used to avoid grid reinforcement. In terms of fuel cells applications, PEMFC is expected to dominate smaller systems with less than 50 kW (relative to other fuel cell technologies), whereas SOFC and MCFC will dominate the high-power output-range (>300 kW). [148] Rather small systems are typically used in residential and small commercial buildings as well as in cell towers for telecommunications. Larger systems are often used in mixed-use buildings such as corporate campuses, hospitals or data centres. Sometimes FC systems are also as backup power.

Another key application-area is transport. In this case particularly bigger vehicles, including those for urban transport and long-distance applications are relevant. A minor part of fuel cell applications are mobile devices and the power supply of portable electronics.

From a global perspective, the market for PEM FC reached $340 million and $460 million in 2010 and 2014, respectively. This number is expected to reach $534 million by 2015 and $1.9 billion by 2020, registering a compound annual growth rate (CAGR) of [149].

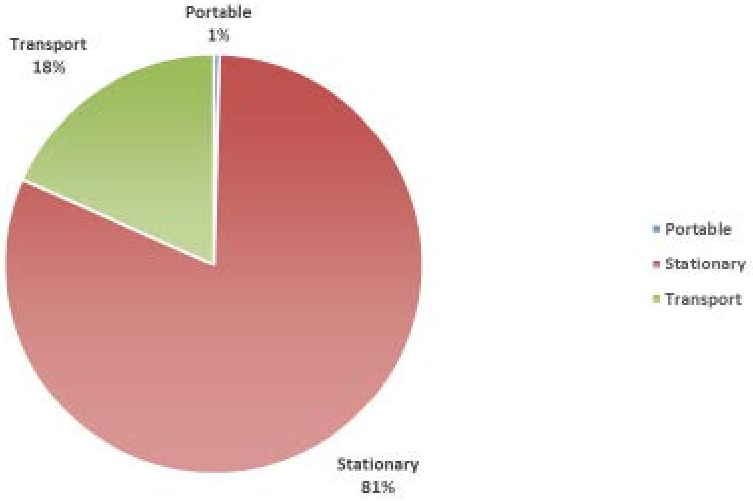


Figure 24: Global fuel cell shipments, broken out by MWS, 2014. Source: [150]

Among these application areas the main advantage of fuel cell technology is that it allows for fast fuelling compared to battery technology. Moreover, for automotive applications, the range of energy delivery is higher due to the higher energy density of 500 Wh/kg (today's lithium-ion batteries have an energy density of 150 Wh/kg). Another advantage is that fuel cell systems show high energy efficiency compared to common combustion technologies. The electric efficiency is up to 60% and the combined efficiency (including heat) reaches even more than 90% [151]. Moreover, it is beneficial for application that fuel cells do not produce poisonous emissions like NOx or SOx, they emit no noise, have no moving parts, the reliability is high, and they can work autonomously [150, 152].

One major technological challenge in fuel cell technology is the oxidant reduction reaction (ORR) at the cathode. The main aim is to increase simultaneously the power density and the durability. The prevalent technology is based on platinum or platinum alloys used as catalyst. An analysis revealed that 15 % of the patents in fuel cell technology are related to platinum based catalysts (s. Figure 25). A drawback of the technology related to PEM FC operation is that the carbon supports degrade during chemically aggressive fuel cycling conditions and that the platinum catalysts can become reduced in activity. For DMFC operations methanol crossover and CO poisoning effects can lead to poorer operational stability and limit lifetime. Moreover the platinum-metal catalysts are expensive and limited in long-term availability and so alternates are under investigation, including graphene-based solutions.

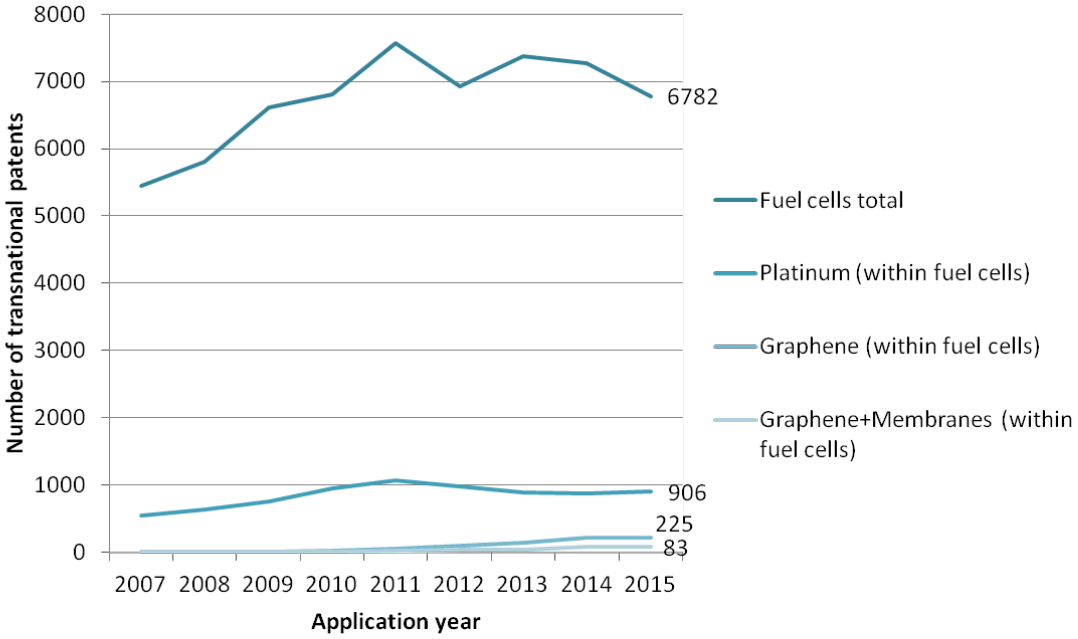


Figure 25: Patents in Fuel Cell technology. [21]

Within the fuel cell domain there is a visible increase of activities in the last few years: The shipping rose about 50% between 2014 and 2015 [150]. With regard to countries, major player in the fuel cell domain is Japan which pursues a vigorous hydrogen policy and intends to create a “hydrogen society” by 2020 [153, 154]. In the US the hydrogen technology gets awareness due to large scale pilot projects [155]. From an economic perspective, Europe already has a relevant role in the fuel cell value chain: 28% of direct jobs on fuel cell system level and even 33% of the companies working in the global fuel cell supply chains are located in Europe [150]. This role of hydrogen-technology is reflected in the research agenda of the European Commission: In Horizon 2020, €1.3 billion are foreseen for related research and demonstration (including the matched industry funding), mostly through the FCH2 initiative. [150]

The major relevance of fuel cell technology and hydrogen power generation is to be seen in a global concept of renewable energy generation. “Green hydrogen”, which means hydrogen generation from surplus peak power from renewables, is certainly not a standard today. But it will be a relevant pillar in the technology mix of a future sustainable energy supply system. Hydrogen technology can play a role with regard to both power supply and energy storage e.g. within power-to-gas concepts. It is assessed that reaching the 20%-CO_2 reduction objective in a global climatic change policy will only be possible with – among others – hydrogen technology.

Even though hydrogen technology will probably play a significant role in the future, today the economic situation is still difficult: In 2014 many fuel cell companies reported higher losses. Only a few were able to reach a growth of revenue [150]. There are still two major barriers for commercial fuel cell applications – even though both are not undisputed: One significant barrier is the hydrogen distribution from highly dispersed sources to the point of need [150, 155, 156]. This appears to generate a dead-lock-situation: Due to technology maturity issues the number of particularly fuel cell vehicles is very limited. Hence the refuelling infrastructure is not widespread. On the other hand, the missing refuelling infrastructure prevents the propagation of fuel cell vehicles, which is the reason for reluctant investments in R&D.

Many governments are tackling this issue with stimulus packages. Japan and South Korea are actively building hydrogen fueling stations. In Europe, UK has approved the Hydrogen Refueling Station Infrastructure Grant Scheme to provide £6.6 million ($9.7 million) in funding over two years for 12 hydrogen infrastructure projects. In Denmark FC vehicles are being encouraged via tax exemption [157]. In Germany, Shell will install a nationwide network of hydrogen fuelling pumps at retail sites [158].As another major barrier for commercial fuel cell applications high costs for the technology are reported. It is repeatedly mentioned that particular high effort for catalysts from platinum and platinum alloys are the reason for these high costs. But also costs for e.g. bipolar plates are playing a relevant role. This barrier, however, is not undisputed, and it is difficult to assess up to which extend this barrier can be overcome by scaling up.

Fuel Cell Vehicles

In vehicle applications, particularly the PEM fuel cell technology is used. Key issues in this area are power density and the reduction of prices [156]. Today, the prices for fuel cell vehicles are similar to battery-based electric vehicles: The price for a Tesla electric vehicles starts at about $57,000; in Japan fuel cell cars are available for about $60,000 [156].

With regard to markets, Japan and Korea are ahead of the US and the EU: In general, Japan focuses on fuel cell based passenger cars, whereas in the EU fuel cells are particularly discussed with regard to range extenders in electric vehicles [156]. Accordingly, in Japan the incentives for fuel cell cars in terms of subsidized bonus are three times higher than for battery-based electric vehicles [156] – Japanese government supports fuel cell vehicles with $20,000 subsidy and the Japanese government equipped its ministries and other offices with fuel cell cars as official vehicles. As leading market, Japan has the power to standardise the related technology. For example the standard for compressed hydrogen filling stations has been defined in Japan. But the Japanese vehicle marketed for fuel cells is more or less a closed-shop and hard to enter for companies from outside Japan [150]. Beside Japan, also Chinese OEMs started significant developments in fuel cell passenger car markets [156], whereas in the US the incentives for fuel cell passenger cars have already started to phase out [156].

From the company's perspective, major OEMs in the sector of fuel cell cars are [156]:

- Toyota (JP)
- Hyundai (KR)
- Honda (JP)
- Daimler (DE)
- BMW (DE)

Key players in the automotive fuel cell technology development are Toyota and Daimler. Daimler recently has announced the launch of a fuel cells based SUV in 2017. Other European car manufacturers appear to pursue rather an on-hold strategy with regard to fuel cell development. In general, the OEMs in the automotive industry often collaborate with fuel cell technology suppliers and do not have significant own R&D activities with regard to this technology. E.g. VW cooperates with the Canadian fuel cell company Ballard. Other leading manufacturers of fuel cells for the automotive sector are [156]:

- Nissan (JP)
- Suzuki (JP)
- Kia (KR)

Another market opportunity for fuel cell technology in the vehicle sector is public transport. Here the major benefit of fuel cells is the issue of non-hazardous emissions. This probably propagates the technology in regions where air pollution is a major issue. Today, already various pilot activities are implemented with hydrogen powered buses. So, it might be that public transport in the future is a relevant market for fuel cells. But with regard to technology development it has no specific relevance as the related technology is the same as in passenger cars – only with cascaded fuel cell stacks. Also in the area of material handling, forklifts, and trucks fuel cell technology has interesting advantages and European companies are involved in related activities. But, in general, these applications can be seen as niches.

The overall picture with regard to fuel cell vehicles can be assessed as follows: even though in 2015 Toyota has already launched the fuel cell based car Mirai and Hyundai the iX35 [156] a significant increase of fuel cell vehicles is not to be expected before 2025 [150].

Stationary Fuel Cells

Another major application for fuel cell technology is stationary systems. The largest share off shipments of fuel cells systems is still in the stationary sector [150]. They are, on the one hand, used for back-up power generation. In large power facilities (>300 kW), the prevailing technologies are SOFC, MCFC and AFC, all not relevant for graphene activities. PEM fuel cells might, however, play a relevant role for smaller scale systems in a decentralised and renewable-based energy system. In this case, electric peak power from renewables can be transferred to gas by electrolysis, the so called power-to-gas approach. The advantage is that the distribution can build on the existing infrastructure of the natural gas grids [152]. In residential PEM fuel cells the gas can then be re-transferred into electric energy and heat. Hence, hydrogen technology, can be used for grid balancing and by this it is a good opportunity to increase the flexibility of renewable-based energy systems [155].

The related stationary systems are used not only for energy generation, but also for co-generation of heat. Here the “waste-energy” can be also exploited and therefore the system reaches a higher efficiency [155]. The related technology is called combined heat and power (CHP) technology. These CHP systems have substantially less CO_2 emissions than boilers or grid power supply [152]. The public and policy is interested in the related technology, as it levers the efficiency of the overall energy system [150]. For this application predominantly PEM fuel cells are used. For residential applications increasingly micro-CHP are implemented with a capacity of 1 kW to 6 kW. Until 2020 the micro-CHP market is expected to be $4.44 bn [159].

A major barrier for the CHP technology is the very high costs for investment [155]. Nevertheless, in Japan, Korea, and the USA stationary fuel cells are already commercialized [152]. The related market is again dominated by Japan, which is about 6-8 years ahead [151]. Japanese government has already heavily and successfully subsidized the market introduction of residential fuel cells [150]. Accordingly, Japan has the lead in stationary applications with more than 120,000 devices [155], and 98% off shipments in the CHP area are in Asia [150].

Also for Europe a large market potential for stationary fuel cells can be assessed [152]. Today, the biggest hurdle is the price and accordingly the reduction of production costs. Only with relevant volumes competitive pricing and acceptable payback periods can be reached [152]. The EU-strategy with regard to stationary fuel cells is implemented in the so-called ene.field project [160], involving nine EU fuel cell system suppliers. This might spread the technology in the end. But, with regard to technology development, the European system suppliers collaborate with Asian fuel cell manufacturers. For example Viessmann (DE) integrates micro-CHP fuel cells from Panasonic (JP) and Vaillant (DE) from Honda (JP). BaxiInnotech (DE), just recently, closed its own technology development and now relies on Toshiba technology (JP). Key vendors of micro-CHP systems are [161]:

- BDR Thermea Group (NL)
- Honda Motors (JP)
- Vaillant (DE)
- Viessmann Group (DE)
- Panasonic (JP)

3.2.1.1 Role of graphene/2D materials in fuel cell technology

Graphene is mainly discussed as electro-catalyst or catalyst support material in e.g. PEM FCs cathodes for oxygen reduction reaction (ORR). Required characteristics of this electro-catalyst include:

- oxidation respectively corrosion resistant and high catalyst durability
- highly conductive
- specifically functionalizable in order to deposit catalysts as well as the ionomer ultra thin layer onto it

Graphene nano platelets (GnPs), in general, show exceptional characteristics of large specific surface area (SSA) combined with extraordinary electric conductivity. Graphene and related derivative 2D materials and nano-composites can be used:

- as catalysts for the electro-catalytic reaction itself
- as functionalised material where active sites are occupied with other active materials
- doped graphene
- graphene / metal or metal oxide composites

Graphene oxide (GO) and related carbon nitrides (gCN) have the advantage that they show many functional groups on their surface. These can act as chemically active sites in catalytic reactions or as anchoring sites for metal-particles. However, functionalized graphene shows decreased electric conductivity.

A major challenge is durability in both the anode and cathode of fuel cells. This is where graphene and related 2D materials have the most potential by providing corrosion resistant catalyst supports [162].

New applications can be envisaged. For example, flexible graphene-based fuel cells could be integrated in smart textiles. An advantage of graphene in this application might be that flexible electrodes for portable fuel cell systems could be realized in the future [163].

From a regional perspective, particularly in China there is an increase of activities on fuel cell catalyst related research with focus on graphene. An analysis of scientific publications revealed that today China is the leading country in this respect (s. Figure 26). But in general, compared to other application areas in energy storage and generation, the scientific activities with regard to graphene in fuel cell technology are rather limited: the total number of publications from 2009-2014 was less than 600, compared to e.g. about 2000 in each of the other application areas: battery technology, photovoltaic and supercapacitors.

Also from a patenting and thus application perspective, graphene and its 2D derivatives appear a little less appealing for fuel cell technology compared to other areas: in the mentioned period of six years worldwide all together 77 transnational patents were filed. For comparison, in photovoltaic application there were almost 400 patent applications with regard to graphene in the same period.

Recent reviews are summarized in Table 24.

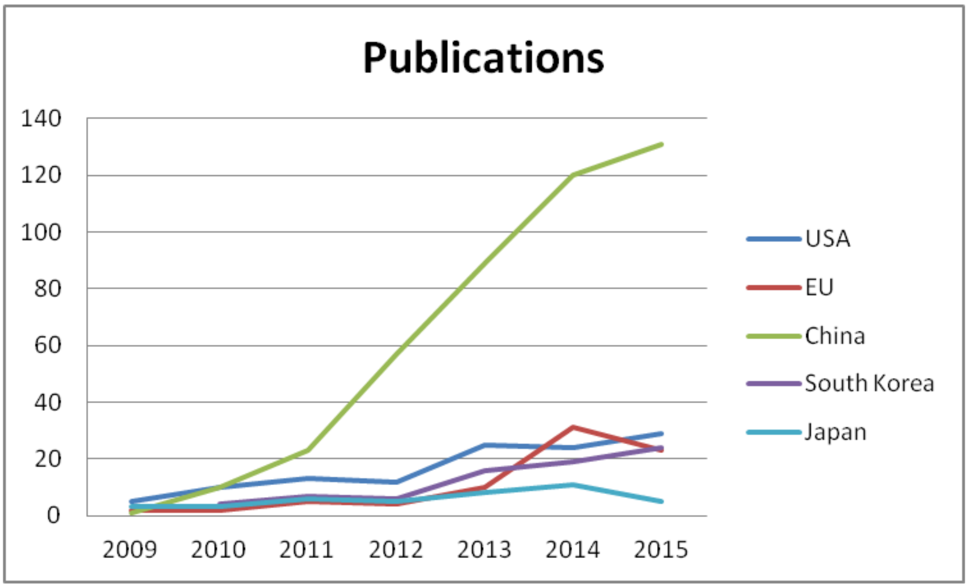


Figure 26: Publications on fuel cell catalyst with regard to graphene. [164]

Table 24: Recent reviews related to fuel cells and hydrogen applications of graphene/2D materials.

Topic	**Reference**
Fuel cell catalysts	[165]
Catalysis with two-dimensional materials and their heterostructures	[143]
Energy applications	[163]

3.2.1.2 Market Opportunities for graphene in fuel cell technology

3.2.1.2.1 Pt-reduction key target of fuel cell development

Today the quantity of platinum used in fuel cells for car applications has already dropped by two thirds [156]. That leads to current costs for noble materials in car fuel cells of 1000-1500 € per system [166]. The reduction of platinum amount is assessed to have a high impact on cost reduction [156]. The US Department of Energy has set the aim of 0.15 g Pt/kW, which means about 500 € for a 100 kW-vehicle or even less. These ambitious targets will require further research and development on noble metal reduced concepts. The key challenge is to maintain a high level of performance and durability compared to fuel cells with a higher platinum loading.

3.2.1.2.2 Pt-free electrocatalyst issue for automotive applications after 2030

Particularly, when/if the fuel cell technology will boom in the automotive sector, costs for platinum will become relevant for the price of the overall system. One expert, consulted for this report, assessed very roughly that platinum costs will cause 25% of the fuel cell system (at a production quantity of 500,000 FC cars). Even though, platinum-free electrocatalyst are expected not to be an issue in the next 10 years – although it might become relevant after 2030. Then it is to be expected, however, that various concepts for noble-metal-free electrocatalysts will be available.

3.2.1.2.3 Carbon species enjoy trust in automotive sector

Scepticism against noble-metal-free electrocatalysts in the automotive sector is high (s. 3.2.1.3.1). But, as one industry expert stated, at least, an advantage for graphene based concepts is that there is a high confidentiality in carbon species with regard to electrode materials, e.g. because of corrosion properties. Therefore, the introduction of graphene might encounter lower barriers, especially when these are offered as "drop-in" replacements for existing Pt/C FC electrodes. Moreover, it is said that there are only a very few materials available to replace activated carbon.

3.2.1.2.4 Different opportunities for graphene in FC technology

A key issue for success of fuel cell technology – particularly in mass applications like vehicles – are power density and costs [156]. Cost drivers for fuel cell technology (PEM FC) are (among others):

- platinum and other noble materials
- membranes
- bipolar plates
- tanks (composites, see also chapter 2.2 Additive to bulk solids/composites)

In all these components graphene or GRM might contribute to an improvement of performance and a cost reduction. Endplates also increase costs in fuel cell technology. But, today it is unclear if graphene can play a role in this area. Another challenge that can be addressed by graphene is durability in both the anode and cathode of fuel cells.

3.2.1.2.5 Fuel cells in automotive sector at a turning point

Currently, the fuel cell technology in the automotive sector is at a critical point: In 2015 two Asian car manufacturers have launched first commercial fuel cell cars (Toyota: Mirai; Hyundai: iX35). The development of the whole technology will decisively dependent on the market success of the new fuel cell series.

Worldwide the discussion on the dominant technology for future transport is still ongoing. Particularly, Japan backs fuel cells. The Japanese policy and society gave a very clear commitment towards hydrogen technology as future backbone of their power system [167]. Nevertheless, not only Toyota but also Daimler as a European company can be seen as technology leader with regard to fuel cells in cars.

3.2.1.3 Market threats affecting graphene in fuel cell sector

3.2.1.3.1 Controversial: Relevance of platinum reduction

The reduction or replacement of platinum in fuel cell electrocatalysts is often discussed in academic publications – not only with regard to graphene. Practically, by 2020 the limit of 15 g platinum per vehicle is expected. And by 2025, when large scale commercialization is implemented, less than 10 g platinum per vehicle should be reached [166]. However, from an application perspective the relevance of platinum reduction is not undisputed:

- Platinum shows a very good recyclability. The US Department of Energy sets the target of 98 % recycling ratio. In case of a significant market increase, recycling might play a relevant role for availability of platinum. Hence, the price for the raw material might decrease some years after a fuel cell technology has been established [150].
- The share of platinum used for fuel cell applications is about 0.1 % of the global demand [150].
- Moreover, it has to be stressed that high overall costs of fuel cell systems are due to various items – like e.g. the compressor, membranes and bipolar plates –, not only due to noble material content of the electrocatalyst [166].
- And last but not least, as crucial barrier for the development of fuel cell technology the insufficient infrastructure for dissemination and hydrogen supply is mentioned – which is not at all related to material costs/costs of fuel cells [150, 155, 168].
- Metal-free catalysts including those based on graphene have not shown equivalent performance. However, Pt-free metal catalysts are entering the market (e.g. Amalyst) and graphene-based GO, gCN nanocomposites could support that by leading to more durable supports.

According to some experts interviewed within this study, platinum-free electrocatalysts will not be an issue for automotive applications before 2030: Particularly, when/if the fuel cell technology will boom in the automotive sector, costs for platinum will become relevant for the price of the overall system. In the midterm and at a given production quantity of 500,000 FC cars, platinum costs will cause 25 % of the fuel cell system. Even though, platinum-free electrocatalysts are expected not to play a role then. After 2030 – when platinum-free electrocatalysts might become relevant – it is to be expected, however, that various concepts for noble-metal-free electrocatalyst will available.

3.2.1.3.2 No relevant European technology development in combined heat and power (CHP)

Micro-combined heat and power (micro-CHP) is an attractive stationary application area for PEM fuel cell technology to use waste heat and to increase overall energy efficiency [152, 155]. Today, in Japan this technology is already widespread for residential applications [155, 169]. There are, however, also relevant system integrators for micro-CHP in Europe (e.g. Viessmann, Vaillant, Bosch, BaxiInnotech, Buderus) [160]. But, as for the related technology development, there is no relevant player in Europe anymore, since also BaxiInnotech has closed down its in-house development. Today, all of the mentioned system integrators use technology from Japan. Some European stakeholders are active in developing FCs for stationary applications, but they need to close the gap to the Japanese manufacturers, which already supply the integrators.

3.2.1.3.3 Niche markets in logistics and transport: weak position for European PEM FC manufacturers

In principle, advantages of fuel cell-based power generation are [150, 152]:

- no hazardous emissions (like NOx or SOx)
- no noise
- high reliability

This suggests the technology for several applications like forklifts for material handling and buses. Indeed, these applications can be seen as attractive and developing niche markets for fuel cells – particularly in Europe [169]. But, though there are some smaller stakeholders in Europe, material handling is already very much dominated by Ballard (Canada). And busses – from a FC technology perspective – cannot be seen as specific field of application, as it is directly linked to the automotive sector: Here, the major strategy of European players is just to redouble automotive fuel cell systems.

3.2.1.3.4 Long lasting development phase threatens reputation

The development phase of fuel cell technology has been on-going for decades. Worldwide, there have been several market incentive programs fostering the technology uptake. In the USA, incentives for fuel cell based passenger cars have been phased out [156]. The number of fuel cell vehicles on the road, however, is not expected to increase substantially before 2025 [150]. It is perceivable that this very long time to market has an impact on the image of the technology in general, threatening the overall reputation. . In one fuel cell expert assessment from 2009 (i.e. 7-8 years ago) it was stated: “For the last 50 years success has always been 10 years away” [170].

3.2.1.3.5 Unclear policy strategy

The fuel cell community complains that in the last years the commitment from European policy makers and industry towards fuel cell technology has been unclear or inconsistent. Compared with the clearly expressed Japanese strategy towards implementation of the “hydrogen society” [150, 156, 167], this impression can be supported. One exception to this is EU measures in research and demonstration: In Horizon 2020 a significant budget will be directed at fuel cell and hydrogen-related energy calls, especially channelled by the FCH2 initiative [150].

3.2.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in fuel cells

3.2.2.1 Current strengths for graphene/2D materials use in fuel cells

3.2.2.1.1 Potential to reduce amount of platinum in fuel cell electrocatalysts

There is a market opportunity to investigate Pt-free catalysts and combinations with graphene-based support systems that offer reduced corrosion and improved durability – especially when these are offered as "drop-in" replacements for existing platinum/carbon FC electrodes. There are several approaches reported where graphene materials contribute to the reduction of platinum as a limited resource key metal used in fuel cell electrocatalysts. Some alternatives based on functionalized graphene derivatives are beginning to show first promising results regarding electrocatalytic activity and robustness or potential cost efficiency – also applications as electrolyzers or in alkaline fuel cells [172, 173].

Reduction of platinum by graphene and graphene related materials can be reached by different means. Graphene related materials are discussed as simple support, active support or active materials. Some examples are:

- Nitrogen-graphene composites have shown promising results as a strategy to reduce platinum in electrocatalysts. E.g. platinum-nano-particles can be encapsulated with a nitrogenated graphene layer [174]
- Today, 70% of the platinum in a fuel cell electrode is not used in the reaction. Graphene can improve the usage of platinum on the electrode [175].
- Graphene oxides (GO) have many functional groups/defects which can be used as chemically active sites on the surface. They can act as anchoring sites for doping with metal nano-particles to foster catalytic reactions. This functionalized graphene can lead to improvements of electrocatalysts in fuel cells [176].
- Graphene can increase resistance of the electrolyte layer against oxidation. This reduces material loss.
- Graphene can increase the efficiency of methanol/ethanol electro-oxidation [177].

3.2.2.1.2 Increased robustness of fuel cells

Graphene can contribute to increase the robustness of fuel cells. Graphene nanoparticle (GnP) based electrocatalysts show a reduced inclination to be poisoned by carbon monoxide [178], which is an often reported problem of fuel cell electrocatalysts. In methanol fuel cells graphene-based electrocatalysts decrease cross-over of methanol, which often reduces efficiency of these systems [179]. Moreover, graphene electrocatalysts are reported to be more resistant against corrosion [180]. Used as a catalyst support in both the anode and cathode of fuel cells, the durability can be enhanced [162]. All this can contribute to the long-term cycle stability of the fuel cell system, which is besides cost and power density still a major challenge.

3.2.2.1.3 Reduce costs of manufacturing due to improved processing

Graphene-based electrocatalytic materials can, on the one hand, contribute to reduce material costs by replacing platinum. But another – maybe even more relevant – contribution of graphene to overall price reduction of fuel cells can be the manufacturing. Graphene is reported to be easier to process compared to platinum-based electrocatalysts. This can lead to a cost reduction in the manufacturing of fuel cell bipolar plates.

3.2.2.1.4 Special applications in functional layers, membranes and flexible fuel cells

Graphene and graphene related materials might play a role in further applications in the hydrogen and fuel cell technology:

- Graphene can be also used on the gas diffusion layers or within the microporous layers to control the water management in operating fuel cells..
- Membranes are another relevant costs factor in fuel cells. Results indicate graphene could improve their properties. Accordingly, the patent analysis revealed an increase in patenting in this area (s. Figure 25). In 2015, about one third of the graphene related patents in fuel cell technology are dealing with membranes.
- Fuel cell technology is establishing as opportunity for power supply in portable electronic applications, e.g. in smart textiles or mobile phones [150, 169]. For these applications graphene might contribute with flexible electrodes.

3.2.2.2 Current weaknesses and challenges for graphene/2D materials use in fuel cells

3.2.2.2.1 Competition with established standards

The introduction of graphene-based materials in fuel cell electrocatalysts are hampered, because the new material has to prove its catalytic advantages, a high durability, and an industry-compatible processability – and all that at the same time. As there are already competing materials on the market, all aspects have to at least reach the state of the art. In general, common platinum/activated carbon electrocatalyst are well established and mastered in the fuel cell technology. The willingness to change electrocatalyst material is limited. Particularly in the automotive industry, concepts have to pass tough accelerated testing, before they are taken into consideration at all.

3.2.2.2.2 Dead-lock situation: production capacity versus attractive orders

Even though graphene appears to have at least some potential for electrocatalyst applications, the industry is reluctant to use it in fuel cells. Repeatedly it is mentioned commercial available graphene materials do not live up to the requirements. That appears to be a result of a typical dead-lock situation: On the one hand, the investment for graphene material and process development is only justified, if relevant market volumes are tangible. On the other hand, realistic market volumes cannot be assessed without data on performance, availability, and prices of the new material – which, however, requires detailed material development and process implementation. The often reported lack of production capacity and insufficient data on the quality of commercial graphene prevent the application industry from commitment towards graphene.

3.2.2.2.3 Graphene-materials not optimized to fuel cell-applications

Graphene-based electrocatalyst structures are often not optimised to fuel cell-applications. In the past, the industry and applied research has purchased commercial available graphene and applied it more or less in their standard processes. The resulting performance with regard to catalytic activities and system’s performance was poor. Therefore, the reputation of graphene suffered. On the other hand, highly specialized graphene is available at best at lab scale.

Besides, functionalized graphene can be used as catalytically active area but at the same time, the electrical conductivity should remain high. This trade off of high catalytic activity (high funtionalisation) with lower conductivity must be managed to maintain the electrochemical performance in FC applications.

3.2.3 KPIs for Fuel Cells

Table 25: Typical KPIs for fuel cells.

	Unit	**Description**	**Literature**
	µA/cm^2	**Specific Activity** Pt on high surface area carbon: 445-535 µA/cm$^2_{PT}$ platinum group metal-free current status: 24mA/cm^2	

	Unit	Description	Literature
		(@0.9V$_{\text{IR-free}}$) 2020 target: >44mA/cm^2 (target is lower due to lower expected cost of platinum group metal free catalyst)	[182]
	A/mg	Mass Activity @ 0.90 V vs RHE for both rotating disk electrode and fuel cells Pt on high surface area carbon 0.43 – 0.52	
		Single-cell polarisation curves (voltage vs current density) along with following KPIs: - **maximum power density** (mW/cm^2) - **current density at 0.8 V** (in mA/cm^2) - voltage at 500 mA/cm^2	
		Pt on high surface area carbon	
810	mW/cm^2	Maximum power density (at 150 kPa)	
240	mA/cm^2	Current density at 0.8V	
	V	Half-wave potential of oxygen reduction (ORR half-wave potential) (E1/2) KPI for the Performance of electrocatalytic activity of catalyst material (for oxygen reduction reaction):	
	Wh/kg	**Specific/gravimetric energy density** characterizes potential capacity of a storage system, weight related	
150	Wh/kg	Today's battery systems	[183]
500	Wh/kg	FC system based on a hydrogen tank at 700 bars (storage capacity around 5% by weight) and an electric yield for the PEMFC system around 60 % http://energy.gov/sites/prod/files/2016/10/f33/fcto_myrdd_fuel_cells.pdf So for a little more than 200 kg and 100 000 kWh, we found 500 Wh/kg	[157]
1100	Wh/kg	Today's Fuel cell systems (including hydrogen storage)	[184]

	Unit	Description	Literature
	Wh/L	**Volumetric energy density** characterizes potential capacity of a storage system, size related	
450-500	Wh/L	Today’s Fuel cell systems (including hydrogen storage)	[184]
	W/L	**Volumetric power density** characterizes maximum power output of a storage system, size related	
>3	kW net/L	Fuel cell for automotive applications	[156]
	€/kW **$/kW**	**Price**	
75	€/kW	in 2023	[185]
150	€/kW	in 2017	[185]
100-200	$/kW	2022 Fuel cell for automotive applications	[156]
200-300	$/kW	2018 Fuel cell for automotive applications	[156]
>500	€/kW	Today	[185]
600-800	$/kW	2014 Fuel cell for automotive applications	[156]
<1500	$/kW	Long term: PEM/SOFC-based fuel cell system	[150]
1500-3800	$/kW	Today’s PEM electrolyser	[155]
2300	$/kW	2014 SOFC-based fuel cell system	[150]
5000	$/kW	2014 MCFC-based fuel cell system	[150]
5000	$/kW	2014 PEM-based fuel cell system	[150]
	€/kWh	Price	
150	€/kWh	Fuel cell system	
450	€/kWh	Battery system	

	Unit	Description	Literature
	€/g	Price material	
34	€/g	Platinum	
		Durability Electrocatalyst stability under dynamic and stationary operation of fuel cells Performance and component degradation via diverse methods and for accelerated degradation, routines have been developed. For instance, operation at open circuit voltage (OCV) Also ex-situ screening of durability, e.g. with rotating disc accelerated testing of catalysts and support [186], is interesting (before going in-situ, does not replace later in-situ testing)	
	h	**Durability**	
5,000 - 6,000	h	Fuel cell for automotive applications	[156]
10,000	h	Fuel cell for automotive applications	Expert

3.2.4 Hydrogen generation and storage

In the field of hydrogen storage, the main field of application regarding graphene is graphene-based hosting material for H_2 fuel storage. Sate of the art of hydrogen storage technology is compressed gas storage, particularly for automotive applications. The gas is stored at a pressure of 700 bar. Disadvantage of the existing technology is that already the compression consumes 12 % of the energy stored in the hydrogen; moreover the fuelling equipment and tanks have to be designed to sustain these high pressures; and last but not least, there are relevant safety concerns.

As for graphene-based storage, already at some 10-100 bar significant absorption of hydrogen on the surface of the graphene sheets can be observed. An increase of pressure makes only sense up to a specific level, i.e. until the whole surface is covered by H_2. Advantage of this so-called absorptive storage is that either a lower storage pressure or an increased capacity is possible, compared to compressed gas storage systems. The lower pressure of the whole system might lead to a higher acceptance of hydrogen fuelling in general, due to safety issues.

Besides, graphene is also discussed to be used as membrane for hydrogen production/filtering. For a more general assessment of the membrane properties, please refer to chapter 2.5 Special application: Filtering, desalination/deionization and membrane applications.

3.2.4.1 Opportunities for graphene in hydrogen storage sector

3.2.4.1.1 Low pressure gas storage might become relevant in the long-term

The high pressures used in today's hydrogen storage require huge investments in infrastructure of the fuelling equipment and have a negative impact on the acceptance of fuel cell technology due to safety reasons. Hence, low pressure solutions are discussed as promising for the long-term perspective. Graphene-based storage systems might play a role, as they can be operated at lower pressure. But this issue is also discussed with regard to other storage concepts like metal hydrated solid storage (s. 3.2.4.2.2).

3.2.4.1.2 Graphene based storage in various applications

Specific advantage of graphene in gas storage is that the material is highly robust and therefore most suitable – not only for transportation applications. Besides applications in the automotive sector, graphene-based hydrogen storage might be interesting for further applications in other sectors, e.g. mobile applications are becoming increasingly attractive, particularly for military applications. Also the electrification of the aerospace sector might be a soaring application area for hydrogen storage and fuel cells. As for hydrogen storage, graphene related activities are not only restricted to PEM fuel cells and DMFCs – like in the area of fuel cell technology as such – but it can also play a role e.g. in SOFC technology which is particularly interesting for all kind of stationary power supply.

Moreover, the further development of hydrogen storage might also enable improved gas storage in general and expand the applications to gases like methane, propane, butane, and even CO_2.

3.2.4.1.3 Hydrogen generation: power to gas

Grid balancing is a relevant issue for the implementation of a power system based on renewables. Hydrogen appears to be an interesting candidate for large-scale energy storage. From a technological perspective, the major issue in this case is the electrolysis with platinum as electrocatalyst. The very high voltages, typical for these application, require highest robustness against corrosion. Graphene related materials

(MoS2/WS2) are reported to be used to foster the hydrogen evolution reaction (HER) by delivering active catalytic sites [187, 188].

3.2.4.2 Threats to graphene in hydrogen storage sector

3.2.4.2.1 700 bar standard locked in for coming years

Today in the automotive sector the operating pressure for compressed gas hydrogen storage systems is standardised at 700 bar. This settled standard is a high barrier for new storage concepts as all the equipment is now designed to come up to these requirements. Currently, particularly in Asia relevant investments are made to install fuelling infrastructure, based on 700 bar standard. A parallel standard with lower pressure is not probable. Hence, experts underline, the hydrogen storage technology in mobile applications is more or less locked in for the coming years. A potential matter of discussion, however, is to keep the 700 bar standard for fuelling infrastructure but at least reduce pressure in the mobile tanks of the vehicles. By doing this, the costs and weight for the tanks might be reduced and safety might be increased.

3.2.4.2.2 Alternative technologies discussed for hydrogen storage

To increase the capacity by using highly porous materials is exploited not only in graphene based storage technology, but also in others like graphite- or metal hydrate-based storage systems. Currently, there are some technologies strongly discussed for hydrogen storage – even though, they are, like graphene-based approaches, still in a research stage:

- Particularly for solid storage, **metal hydride-based** storage systems are researched. These systems are particularly dedicated for stationary applications due to their high weight. Advantage of metal hydride storage systems are safety issues, as the process of hydrogen dissolution stops immediately after an incident. Disadvantages are the high effort required for charge/discharge, the relatively low capacity of 2-3 % W at low pressure (could be increased up to 6-8 % W at high pressure), and high costs for the system.
- **Graphite or carbon nanotubes** can also be used for hydrogen storage. As for graphite flakes, a specific surface area of up to 3000 m^2/g is reported. Advantage of these systems is a theoretical increase of capacity up to 3-5 % W. But a problem can be the required cryogenic temperatures of 50-80 K, respectively high pressures. Another problem can be the fast dissolution of the hydrogen with related safety concerns [189].
- Best figures ever reached for absorption-based storage systems were based on **metal-organic frameworks**. They are particularly interesting, as they have both a huge internal surfaces area and many active sites. The capacity reached about 6-7 % W. The metal organic frameworks were integrated in pressure tanks. The activities were pursued e.g. by GM and partially financed by the US DoD. Until now the maturity has reached a level of about TRL 3-4.
- An expert reported **polymer-based** storage systems with polyanilin and polypyrrol already reaches 8 % W.

3.2.4.3 Strength of graphene in hydrogen storage sector

3.2.4.3.1 High specific surface area of graphene increase capacity of gas storage

The advantage of graphene for gas storage in general, respectively hydrogen storage in particular, is the high specific surface area of the material. Theoretically, this allows, first and foremost, an increased storage capacity. The related figure of merit is percentage by weight (% W) which is a measure for the weight of hydrogen in relation to the material or whole system. In principle, 6-7 % W is possible for the pure material, resulting in 3-4 % W for the whole storage system.

The aim of the Graphene Flagship activities is to lower the required pressures for hydrogen tanks (120-300 bar) at same capacity and to increase capacity in general. Reference point for the activities is the hydrogen storage system of Toyota, which reaches 0.04 kg/L at 700 bar. The dedicated research focus of the flagship is on material design to increase the surface area and porous networks.

3.2.4.3.2 More design opportunities as chemi- and physisorption possible

Gases can be absorbed on the surface of solids by physisorption or chemisorption. As for graphene, both ways of binding are possible.

In case of physisorption the gas molecules are attached at the surface by e.g. van der Waals forces. The binding energy in this case is low. That allows the fast loading, respectively fuelling of the storage system. Moreover, theoretically the high surface area leads to high gravimetric density of the storage system, whereas in the related systems the volumetric density is rather low. That means the final systems are relatively light but rather large-sized. As for graphene, the volume depends decisively on compacting of the material.

In case of chemisorption, the gas is bound on the surface of the storage material by atomic bonding. For release the bonding has to be dissociated by additional energy effort. Advantage is that the storage is quite stable. The chemisorption based storage material is expected to reach highest gravimetric density of up to 8.3 % W if the graphene sheet is completely saturated with hydrogen molecules [190]. That means by using graphene, lighter hydrogen storage systems might be viable.

- Within the Graphene Flagship improvements of the gravimetric density are intended for both: chemisorptions (0.8% W are reached in an experimental stage) and physisorption (1% W @ room temperature and 120 bar). Also research is aiming at reducing the sorption and desorption activation energy by doping with Nb_2O_2.
- A new approach for hydrogen storage based on graphene tries to combine the advantages of the physisorption and chemisorption: the local curvature of the graphene sheet determines which kind of carbon hydrogen bonding prevails. As the graphene

sheets are mechanically flexible and the curvature can be manipulated, this characteristic can be exploited to implement new charging respectively discharging strategies – also at room temperature [191].

- Another focus of research is porous mesostructures with irreversible amine linkages between the graphene layers. This leads to a functionalization which allows dynamic change, specific distances and the change of curvature under light irradiation (WP12).

3.2.4.3.3 Graphene to increase volumetric energy density of high-pressure tanks

Before a transition phase from high to low pressure storage, graphene might be used to enhance high-pressure storage systems. A high pressure tank could be filled with graphene to enhance the tank-system, make it more stable and increase capacity. The approach has a couple of benefits: It has the potential to increase the volumetric energy density of the system (even if it might not decrease the weight related storage capacity greatly H_2/kg of the system). By this, it would decrease the volume of the tank, which is very valuable for the automotive industry. And finally, the system is less explosive. Hence, an option for graphene in the mid-term might be to use it within existing storage concepts as high-surface-area material to increase storage density.

3.2.4.3.4 Graphene (membranes) for hydrogen generation

Graphene is impermeable for gases and liquids, but not for protons. This property can be used for hydrogen generation. By employing these highly selective graphene-based membranes, hydrogen can be extracted from air and used in fuel cell applications, as demonstrated by the Manchester University [192, 193]. This approach, however, is in a very early stage as today the required single-layer graphene sheets can be produced just in the size of some millimetres. For further membrane applications please refer to chapter 2.5 Special application: Filtering, desalination/deionization and membrane applications.

Besides and as mentioned above, Graphene related materials (MoS_2/WS_2) are reported to be used to foster the hydrogen evolution reaction (HER) by delivering active catalytic sites [187, 188].

3.2.5 KPIs for hydrogen generation

Gravimetric density GD, mass percent, percentage by weight [% W; w/w]: to compare weight of hydrogen storage systems (percentage of the weight of the hydrogen related to the weight of the storage system)

The figure of merit in the hydrogen storage is the gravimetric density. It can be related to the pure material or the storage system. Even though, the weight of the storage system is unclear until it is finally developed, an average estimation is: the system will have half of the gravimetric density the material has.

Table 26: KPIs for hydrogen storage.

	Unit	Description	Literature
	% W, (also w/w)	**Gravimetric density GD, mass percent, percentage by weight**	
3	% W	Solid storage of hybrids	
5.5	% W	System @ room temperature Definition of Department of Energy DoE of the USA of a “good” storage system	
7	% W	gasoline system	[194]
8.3	% W	chemisorption based storage with graphene material (if graphene sheet is completely saturated with H_2	[190]
8.8	% W	pure gasoline	[194]
	kWh/kg	**Gravimetric/specific energy density** to compare weight of energy storage systems	
1.8	kWh/kg	System, Definition of Department of Energy DoE of the USA of a “good” storage system	
1.8	kWh/kg	System, State of the art of hydrogen storage (Compressed gas storage [GH2] @ 700 bar)	[194]
8	kWh/kg	System, gasoline	[194]
11.5	kWh/kg	Pure material, gasoline	[194]
33.3	kWh/kg	Pure material, State of the art of hydrogen storage (Compressed gas storage [GH2] @ 700 bar))	[194]
	kWh/L	**Volumetric energy density** to compare size of energy storage systems, indicator for the range of an energy storage system	
0.9	kWh/L	System, state of the art of hydrogen storage (Compressed gas storage [GH2] @ 700 bar)	[194]
1.3	kWh/L	Pure material, state of the art of hydrogen storage (Compressed gas storage [GH2] @ 700 bar))	[194]

	Unit	Description	Literature
7	kWh/L	System, gasoline	[194]
8.8	kWh/L	Pure material, gasoline	[194]
	m²/g	**Specific surface area SSA** KPI for porous materials	
540-650	m²/g	Commercial Graphite	[195]
500-1000	m²/g	Commercial Graphene	[195]

3.2.6 Roadmap for Fuel Cells and hydrogen storage

3.2.6.1 Current maturity: ‘Mostly lab scale’

Most of the developments are currently at lab scale and low TRL levels. Electrocatalyst (Pt reduction) are at a higher TRL level (TRL2-3), whereas membrane related and other fuel cell related technologies are rather at TRL1/2. Storage applications are at best at applied research stage, but the optimized configurations are not fully known yet. Therefore, the overall rating of graphene in fuel cells and hydrogen production is rather at lower TRL.

3.2.6.2 Barriers/challenges (summarized)

Fuel Cells

- Most PEM fuel cell technology integrators are not based in Europe, especially for CHP
- Fuel cell technology itself is at a turning point and the future direction in Europe is not yet clear; also the policy is not clear enough.
- Reputation of non-metallic catalysts is not good; platinum could work and cost reduction potential when avoiding platinum is only limited
- Competition with established standards (low willingness to change)
- Low maturity at the moment (test in actual fuel cells needed)
- Graphene supply: dead-lock situation between demand and supply (investment is only justified through larger markets, markets only start existing if larger scale testing and assessment is possible)
- Commercially available graphene materials not tailored to fuel cell use (as electrocatalyst). Existing materials perform not well enough with existing processes.
- Some promises/ideas (e.g. for end plates, flexible fuel cells) are still only ideas or theoretical

Hydrogen storage and production

- Membrane technology is only at fundamental research level
- 700 bar technology locked-in for coming years, no change foreseeable
- Benchmarking with alternative technologies missing

- Viability of some storage solutions based on graphene are interesting, but need to be proven in application (e.g. combination of physisorption and chemisorptions)

3.2.6.3 Potential actions

If the area of graphene/2D in fuel cells and/or hydrogen storage is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

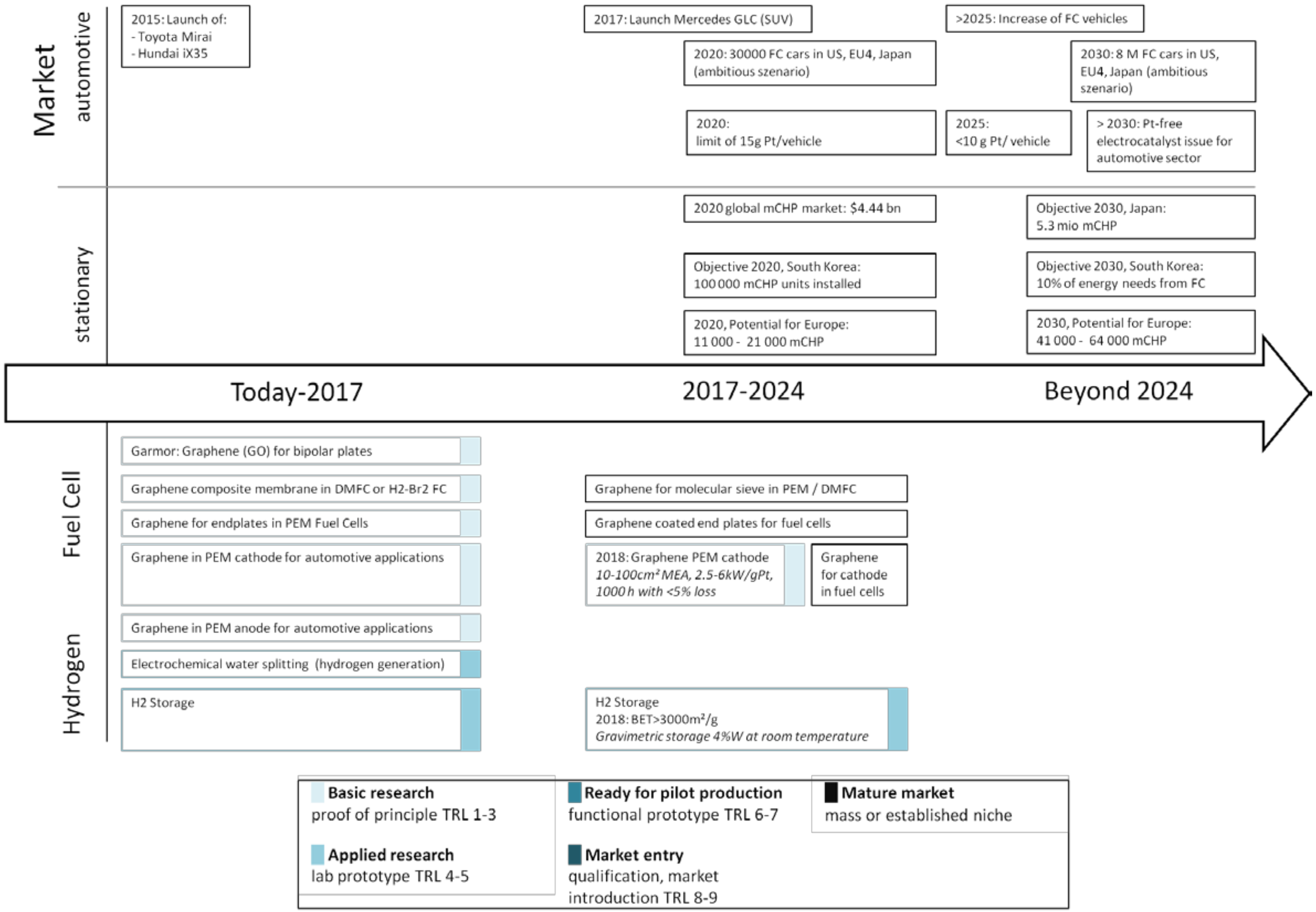
Fuel Cells

- Engage with fuel cell research community to allow realistic testing and benchmarking with competing technologies and metal catalysts
- Further investigate functionalization (with e.g. metals)
- Investigate standard processes compatible with existing ones for integration into fuel cells
- Large scale functionalization and preparation of porous networks/curved graphene
- Repeatability and degradation
- Live up to very high performance expectations and fulfil industrial standards with regard to quality and quantity to reach at least the level of well established platinum

Hydrogen storage and production

- Explore possibilities to improve storage at 700 bar
- Check if low pressure tanks in vehicles are feasible despite 700 bar standard
- Explore market opportunities for storage of other gases
- Benchmark with competing technologies
- Increase surface area and porosity
- Further investigate physisorption and chemisorptions to optimize sorption and desorption (e.g. with functionalization)

3.2.6.4 Roadmap



3.2.7 Conclusion fuel cells and hydrogen economy

Graphene shows a potential to reduce or even replace noble metals in fuel cell electrocatalysts. Moreover, it has beneficial properties regarding durability of electrocatalysts. It can be in principal used as a simple drop in for conventional catalyst support, as active catalyst support, or even as an active material (when functionalized). But the relevance of particularly platinum reduction is disputed in the fuel cell community: on the one hand it contributes to costs; on the other hand it has a very good recyclability and platinum-free fuel cells are sometimes even assessed to be not viable. In any case, all kinds of new concepts have to come up to very high performance expectations and fulfil industrial standards with regard to quality and quantity to reach at least the level of well established platinum. In general, platinum-free electrocatalyst is rather an issue for fuel cells beyond 2030. Besides electrocatalyst applications, in the future graphene might be interesting for membranes, functional layers, or portable applications. Even fully new fuel cell architectures are thinkable e.g. based on printed circuit boards (PCB).

For hydrogen storage, graphene has the advantage to be highly efficient due to its large specific surface area which allows low pressure and higher volumetric capacity. When it comes to applications, a decrease of pressure in the storage system is no short term opportunity, as high pressure tanks are already an established standard. But a short to medium term opportunity could be to exploit it to decrease tank volume of 700 bar systems.

As for the fuel cell market, residential technology is increasingly dominated by Japanese companies. In automotive applications fuel cell technology is at a turning point: the future role of the technology will be decided shortly, because soon strategic decisions of relevant car manufacturers are expected. Europe, however, has given no clear commitment towards fuel cells anyhow. For graphene, it appears reasonable to primarily observe the strategic decisions in the fuel cell market very properly and to assess if there is further technology development in Europe to be expected.

Table 27: Assessment of market and technological potential of graphene/2D materials use in fuel cells and hydrogen storage and generation on a scale - -, -, 0, +, ++.

Role of graphene	**Current technological potential (USP)**	**Market potential (EU perspective)**
Reduction of noble metals in electrocatalysts	+	-
Replacement of noble metals in electrocatalysts	+	0 (long-term)

Role of graphene	**Current technological potential (USP)**	**Market potential (EU perspective)**
Membrane	+	0
Endplate	?	?
Increased volumetric capacity of high pressure tanks	+	+
Low pressure tanks	+	+ (automotive: long-term ?)
Hydrogen generation (membrane)	+ ?	0 ?
Hydrogen generation (electrocatalyst)	+ ?	++ ?

3.3 Batteries

This chapter deals with the use of graphene in batteries. The focus is on (rechargeable) lithium ion batteries and post lithium ion batteries. Flexible batteries are particularly investigated in chapter 4.6 Flexible and/or printed electronics

3.3.1 Market perspective: graphene/2D materials in batteries

Today, the $-60-billion global battery market is still dominated by lead-acid batteries [196]. The lithium-ion battery market accounts just for $ 13.6 billion, but with a significant higher growth rate of 14 % per year [196]. The global lithium-ion battery market is further expected to increase with a relevant growth rate of more than 20 % per year. That will lead to an estimated global market of $ 65 billion in 2020 and $ 130 billion in 2025 [197]. The following chapter will focus particularly on lithium-ion batteries, as it is the predominantly discussed technology in most of the relevant energy storage applications.

Today, the predominant application of lithium-ion batteries is **portable electronic devices** [198]. In this sector, according to a pivotal Japanese roadmap of NEDO [199, 200], the reached properties of the batteries are more or less sufficient. Accordingly, in this field specific research is not urgently required. In some cases, improvements might be interesting regarding higher capability and a longer lifetime. Until 2025, the related market sector will grow particularly in Asia and ROW-regions, as cell phones are becoming commonly widespread there; in the USA and Europe there is no growth expected for this sector [196]. A specific part of the portable electronics market is flexible, printed thin-film batteries. In 2015, this market accounted for $ 70 million, expected to reach $300-600 million by 2020 [201, 202]. Related applications are RFID-tags, smart-cards, skin patches, and wireless sensor networks. The related issues will be addressed in chapter 4.6 Flexible and/or printed electronics. Other early adopter applications of lithium-ion batteries are e-bikes, power tools, and mechanical devices [196].

For lithium-ion batteries, however, predominant growth will be based on **automotive** and **industrial applications** [196]. The demand for battery technology will particularly rise due to applications in the transport sector. In 2014, this sector comprised of just $ 5.5 billion [196]. Today, the market particularly for hybrid electronic vehicles is dominated by Japanese companies: in 2014 Toyota had a share of sold units of 70 % and Honda of 15 % [196]. The market forecast for all kind of electronic vehicles (xEV) is 7 million cars in 2025 with a related lithium-ion battery market of $ 16 billion [196].

Another major application area for battery technology will be cheap **energy storage for grid balancing**. Also, local storage e.g. as residential storage battery will become more widespread as an addition to photovoltaic systems and will play a role in micro-grids [203]. In these applications technology concepts will establish which are optimized with regard to cost efficiency, whereas weight and energy density will be less an issue. Moreover, storage systems to improve the reliability of electricity will become more relevant. Beside lithium-ion batteries, e.g. redox-flow batteries or sodium-ion batteries might play a role in these application areas.

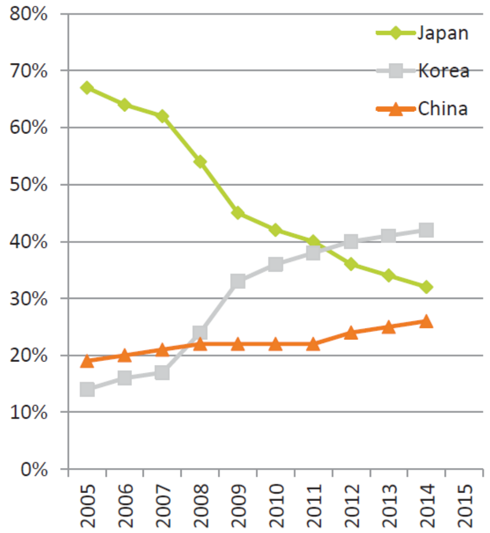


Figure 27: Lithium-ion battery market by country. Source: [196]

Today, the production of lithium-ion batteries is dominated by Asian companies. The major manufactures of lithium ion batteries are [196]:

- Samsung (KR)
- Sanyo-Panasonic (JP)
- LG Chem (KR)
- Sony (JP)
- ATL (HK)

- Lishen (CN)
- BAK (CN)
- BYD (CN)
- Maxell (JP)

In recent years, Japan is significantly losing market shares, whereas China is catching up (s. Figure 40). The two major stakeholder countries are following very diverse strategies with regard to lithium-ion battery technology: China has significantly increased research in the last few years, whereas in Japan the focus is still very much on patenting. Compared to these two countries, however, the other regions show significantly lower engagement in lithium-ion battery technology (s. Figure 35).

Table 28 gives an idea of the European industrial basis. The European actors are still focused on lead-acid batteries. Other batteries play only a minor role and the worldwide market share is below 5% in Lithium batteries.

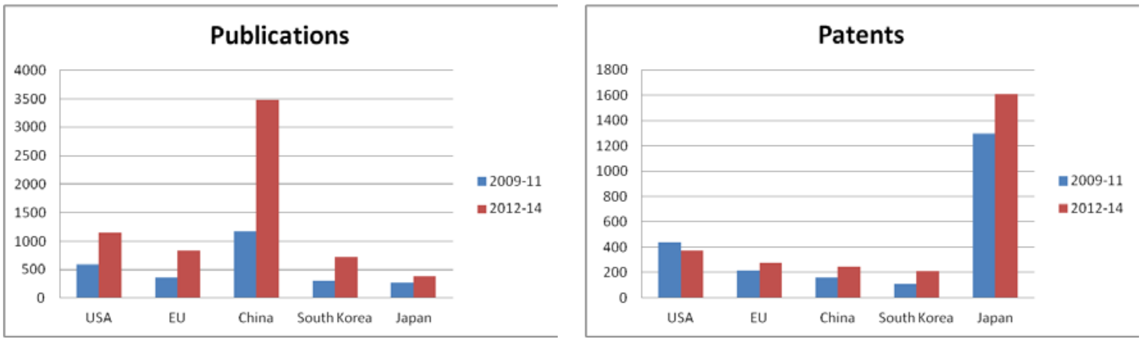


Figure 28: Publications and transnational patents on lithium-ion batteries. [21, 164]

Table 28: Production values in EU-28 of batteries and accumulators. [39]

EU 28 Production Value in b€	2012	2013	2014	CAGR 2012-2014
Primary cells and primary batteries	0.66	0.76	0.83	12%
Lead-acid accumulators	4.29	4.59	4.45	2%
Nickel-cadmium, nickel metal hydride, lithium-ion, lithium polymer, nickel-iron and other electric accumulators	0.70	0.74	0.86	11%
Parts of electric accumulators including separators	0.31	0.34	0.31	-1%

3.3.1.1 Role of graphene in batteries

Graphene is primarily discussed for anode material in various battery technology concepts. It can be used as pure anode material to increase the capacity of the battery. In this case, particularly, for lithium insertion the high specific surface area (SSA) of 2630 m^2/g of graphene is beneficial, compared to standard anode materials – depending on granularity, graphite has an SSA of down to 15 m^2/g. Particularly, defects and edges of the material increase the lithium insertion [204].

As additive, graphene can be used for both anodes and cathodes. In these applications the main purpose is to increase conductivity to reach quicker charge and discharge and to reduce thermal runaway for safety reasons. Samsung is said to apply graphene already for this purpose.

In high-capacity anodes and cathodes graphene can be used as structuring material particularly to additionally increase mechanical properties of the electrodes [205]. Specifically in cathodes, the state-of-the-art lithium-cobalt-oxide might be replaced by graphene-lithium compounds [204]. Samsung is also said to integrate a Si-cathode with high-crystalline graphene in its coming mobile phone generation [206]. Hybrid structures, however, are primarily discussed for anode concepts.

In general, graphene appears suitable for battery electrodes due to its high electric conductivity, the high specific surface area, many active sites for specific functionalization, and short lithium-ion diffusion distances [204].

Based on these properties, graphene-based batteries promise to have [207]:

- high-capacity for energy storage
- short charging times
- high durability
- light-weight
- extended lifetime
- flexible applications
- tailoring possible due to printing

Research in graphene related lithium-ion battery activities is, according to the number of publications, very much dominated by China. In general, there is a very high scientific engagement in lithium-ion technology in the country (s. 3.3.1.2) – and about one third of it is related to graphene. With regard to industrial application, particularly the USA is very engaged – what can be deduced from the number of patent applications. Here it might play a role that several of the frontrunner companies, combining graphene and battery technology, are located in the USA (Angstron Materials, Graphene3DLab, Vorbeck Materials, and XG Sciences). Recent scientific reviews are summarized in Table 29.

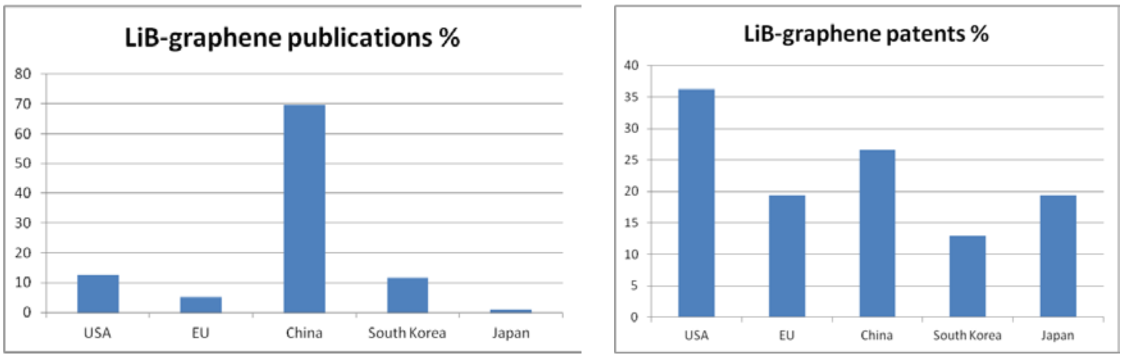


Figure 29: Percentage of publication and patent activities in selected countries

Table 29: Recent reviews of graphene/2D materials in energy storage and batteries.

Topic	Reference
Graphene-Based Nanomaterials and their Applications in Energy-Related Areas	[208]
Energy applications	[163, 204]
Graphene-based electrode materials for rechargeable lithium batteries	[209]
Graphene/metal oxide composite electrode materials for energy storage	[210]

3.3.1.2 Market Opportunities

3.3.1.2.1 Battery technology urgently requires new material concepts

A major problem for the current generation of lithium-ion batteries is the need of further cost reductions and an increase of capacity. In all kind of electric vehicles the major task for further development is the increase of capacity of the battery, in order to extend the range of the vehicles. In this case, particularly, high energy cells are required [198]. Moreover, quick charging is important. For stationary lithium-ion batteries major issues for further propagation are costs and lifetime. In this case, electrode materials shall allow low cost concepts and high stability [198].

In general, the lithium-ion battery technology is relatively expensive compared to other cell concepts. In the lithium-ion battery cells, 50 % - 60 % of the costs are related to materials. Therefore, a major aim is to implement low-cost material concepts with high lithium storage capacity and sustainable availability in the long run – to overcome the risk of shortages [211]. With the current material concepts, lithium-ion batteries are stretched to their limits regarding all the relevant parameters [212]. To overcome these fundamental barriers, graphene might contribute in different material and cell concepts. But it has to be underlined that particularly in Europe the related value creation is probably very limited (s. 3.3.1.3.1 and 3.3.1.3.3).

3.3.1.2.2 4th generation battery technologies good chance for graphene

Lithium-ion batteries are state of the art, but for storage in transportation and grid balancing new concepts are needed to live up to the requirements of the applications [203]. Accordingly, for transportation and smart storage, relevant breakthroughs are not expected from lithium-ion technology any more [212]. In the automotive sector it is assessed that for mass market development the costs have to be one fifth of today's costs. These significant cost reductions have to come along with substantial expansion of range up to some hundred kilometres [203]. The International Energy Agency (iea) underlines in its technology roadmap for energy storage as a key action: "Support investments in research and development for early stage energy storage technologies" [213]. Conceptual innovations like lithium-sulphur, lithium-air, or redox-flow-batteries are discussed heavily as a fourth generation of battery technology [203]. The prerequisite for these new high-energy batteries are concepts with [214]:

- high voltages (high potential differences between anode and cathode)
- high-capacity
- low mass

Graphene is repeatedly discussed as material component for fourth generation battery technology. Particularly, lithium-sulphur (LiS) and lithium-air (Li_2O_2) battery concepts are discussed as promising candidates for long-term battery solutions in transportation and grid balancing. As for lithium-sulphur batteries, particularly the degradation of electrolytes due to reactions at the cathode is a major barrier for this technology. Graphene might contribute to overcome this problem as the sulphur can be covered with a graphene film and avoid the direct contact between electrolyte and cathode [207]. For this application it is necessary to have a high conductivity at the surface and a high pore volume. First testing of graphene based LiS-electrodes was not very successful, but the early stage of both graphene and LiS-battery technology suggest drawing no final conclusion on this. Accordingly, e.g. the American company Vorbeck, Pacific Northwest National Lab, and Princeton University are still working on a LiS-cathode with a reversible capacity of more than 800 mAh/g. [197]

As for lithium-air batteries, porous graphene might contribute to new electrode concepts [215] or new graphene based catalysts can increase the lifespan of the batteries [216]. Another contribution of graphene in future battery concepts can be composite bipolar plates of redox-flow batteries.

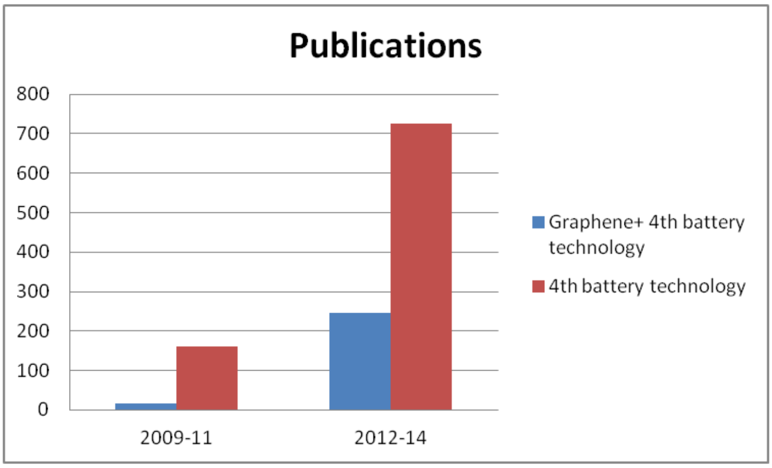


Figure 30: Publications in 4th generation battery technology in general and with regard to graphene. [164]

According to the number of publications, there are already some scientific activities on graphene in 4th generation battery technology. About one third of research in the related battery technology is dealing with graphene (s. Figure 30). Again, China is very present in this area with more than 160 publications in between 2012-14 whereas European researchers did almost not contribute at all to the related research (12 publications, not shown here).

Even though the current position of Europe is weak, the related technology might have a potential in the future: Indeed, an expert assessed that not until the dawn of a 4th generation battery-technology Europe has a chance to contribute significantly to the global battery production. But the related new battery concepts are expected to be commercialized not before 2030. That means Europe would have some time to reach a competitive level, on the one hand, from scientific perspective. On the other hand, it is essential for a future exploitation of the value creation potential to establish a European battery cell production, which requires a broad and orchestrated approach of all relevant stakeholders in Europe.

3.3.1.3 Market Threats

3.3.1.3.1 Macroeconomic revenue of graphene-based anode material negligible

40 % - 60 % of the costs of a lithium-ion cell are related to materials [198] and about half of that are related to electrodes [196]. Certainly, that means that material costs are relevant for cell producers. But the macro-economic role of electrode production should not be over estimated. In 2014 the global revenue for cathodes was $ 2.5 billion and for anodes only $ 0.8 billion [196] – in an overall battery market of $ 60 billion [196]. The major part of value creation is generated in the downstream industry.

To make things worse, graphene-based anodes are assessed to contribute in the best case to only 15-20 % of the overall anode market [197]. That leads to a potential share of graphene-based materials to the total value added of lithium-ion batteries of 0.5% (calculation based on [217]). From a macro-economic perspective, the related revenue does not justify relevant public research investments.

This is even more the case for Europe, as even though there are a few European anode suppliers, the major players are located in Asia [196]:

- Shenzhen BTR
- Hitachi
- Nippon Carbon
- Kureha

That means for European research funding: The investment in graphene-based material research is not to be justified with economic impact due to electrode production. It only makes sense if (particularly) European downstream revenue is enabled, respectively hampered without the related materials. However, this requires a relevant cell production in Europe in any case (s. 3.3.1.3.3 and 3.3.1.2.2).

3.3.1.3.2 For real life electrodes mastering of various parameters required

The development of battery cells requires the concertation of various interrelated specifications [218]. Always with regard to specific applications, the following major tasks have to be balanced:

- capacity
- power
- safety
- durability

Moreover, the battery development has to be aware of prices, weight and power of the final battery, cyclability, calendar lifetime, and last but not least the producibility and scaling up issues. For the concrete applications, e.g. for xEV, also issues like temperature range up to extremes, vibration and shock behaviour have to be checked.

The demand of battery driven electric vehicles is indeed to extend the range from today 150 km to 650 km. That requires an increase of specific energy on material level from 400 Wh/kg to 750 Wh/kg. And this has to be reached with lower system costs than today [219] – and by meeting all the other specifications. Only when all the related aspects are respected, a material concept is relevant for real life applications. The graphene community is said to be not aware enough of all these requirements of application – particularly to meet the demand of the automotive industry.

3.3.1.3.3 Weak position of Europe in lithium-ion cell manufacturing

Today, there are only a very few battery cell manufacturers in Europe. The European Union cell manufacturers are:

- BatScap (only lithium-metal polymer batteries)
- SAFT
- Varta Microbattery
- Gaia (holding company: Lithium Technology Corporation, USA)

Or to say it in other words, none of the major global players of lithium-ion cell production is located in Europe (s. 3.3.1) and European actors have a negligible market share. As a consequence, it is difficult to implement technology improvements in Europe, even if there should be promising results from research.

So the question remains what kind of impact graphene development might have in Europe with regard to battery technology. In general, it can be assumed that graphene will play a role in lithium-ion technology, as all main lithium-ion cell manufacturers are said to have graphene-activities. Indirectly, indeed the European OEMs which are active in the field of xEV might benefit from this development – as they strongly rely on and are strategically linked to Asian cell producers like LG Chem, SDI, and Panasonic. But there will be no competitive advantage for the European industry, because the related companies will also sell their batteries to other OEMs.

This situation will remain as it is, because in the nearer future particularly for electric vehicles there will be no relevant lithium-ion battery cell industry in Europe, as a lithium ion battery expert assessed. Even if there were relevant advancements in graphene technology from European research that will most probably have no impact on that situation. For a successful cell production in the automotive industry there are manifold tasks to be mastered, besides (anode) technology.

Nevertheless, minor developments are perceivable from an upstream perspective: Some graphene-producing companies are also working on lithium-ion technology. In this field there are also at least two companies in the EU [220].

- Angstron Materials (US)
- Grafoid (CA)
- Graphene Nanochem (UK)
- Graphene3DLab (US)
- Vorbeck Materials (US)
- XG Sciences (US)

But until now these companies are not established in the application markets and still have to prove success in fostering graphene-based systems in target markets. That means, even if graphene will play a role in lithium-ion technology in the nearer future, a relevant part of the value chain will most probably not be implemented in Europe. This underlines the relevance of 4th generation battery research embedded in an overall European initiative (s. 3.3.1.2.2).

3.3.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in batteries

3.3.2.1 Current strengths for graphene/2D materials use in batteries

3.3.2.1.1 Functionalization and composite structures broaden field of opportunities for electrode materials

The major advantage of graphene appears to be the expansion of the materials-toolbox for battery electrodes, while still using a carbon-species – which is a beneficial aspect for acceptance, as graphite is standard today. On the one hand, the physical properties of graphene, like conductivity and high surface area, can be exploited as such, but an even broader spectrum of opportunities is gained by combination of material species by functionalization or composite-structures. However, it has to be mentioned that there is a trade-off: improved properties of the product might entail increased complexity of the production process. Moreover, related formulations cannot only cause progresses in one significant characteristic but also drawbacks for other relevant parameters.

Graphene can be **functionalized** and used as substrate for electro-chemically active materials like vanadium oxide or lithium ion phosphate [207]. The vast number of active sides of graphene materials can be doped with non-conducting nano-particles. This allows hybridization and exploitation of beneficial properties of the different material species. In the end, this can facilitate quicker charge/discharge, higher capacity, more charging cycles or lighter battery solutions [204].

An even more relevant advantage of graphene in electrode applications is the opportunity to use it as **structural component in nano-composite materials**. In this case the whole toolbox of nano-tailoring can be exploited. Often, the combination of conductivity properties with increased chemically or mechanically stability is of interest. In addition to that, the processability of nanoparticles can be improved by avoiding aggregation [204]. To improve processability of nanoparticles is a major task of today’s nanotechnology as a whole.

Some examples for graphene-based nano-composites for batteries are:

- Often graphene is investigated with regard to mechanical reinforcement of silicon anodes. In this case, the graphene coating of silicon-nanoparticles prevents swelling of the anode during charging – a major barrier of the Si-anode technology [204, 221, 221–223]. A solution for this problem is highly required, as it would allow the exploitation of the tremendous lithium storage capacity of silicon [212] at reasonable cycling performance of the battery system.

- Also, in sodium batteries graphene can provide a spherical stabilization of the anode material [224]. Swelling of the anode in this technology approach is even more significant and a related solution would facilitate the use of cheap Na for electrode production.
- Also MnO_2-Graphene nanoribbons can be wrapped with graphene (GMG). These cost-effectively producible, hierarchical nano-composites enable higher specific capacities and higher cycle stabilities. [217]
- High-energy electrodes can be implemented based on 3D crumpled graphene, encapsulating nickel sulphide [207].

3.3.2.1.2 Graphene as additive can contribute to incremental improvements

Graphene can be used as additive in electrodes for lithium-ion batteries. Particularly, lithium-ion batteries are suffering from thermal stability. This causes safety concerns. Small amounts of graphene additives are supportive to reduce thermal runaway. Samsung already uses graphene for this purpose. Also, high conductivity of graphene is expected to improve charge/discharge properties of the battery. The conductivity of both anode and cathode can be enhanced.

As there are only relatively small quantities of graphene available on the market today, it is advantageous that for the related application area in principle only low quantities are required. Even though, the industry reports of rejecting using graphene for this purpose, due to insufficient availability of commercial material. Additionally, the technological benefit of graphene-additives compared to state-of-the-art additives like carbon black is not very high.

3.3.2.1.3 An additional approach for printing of flexible batteries

In general, graphene fits to all kind of flexible applications, due to its excellent mechanical flexibility. This supports the idea of using graphene in flexible batteries. For example, graphene-oxide flakes (GO) can be used as conducting scaffold, loaded with silicon nano-particles in flexible and stretchable applications [204]. The American company Vorbeck Materials already introduced the first graphene-enhanced flexible and light-weight battery for mobile charging [220].

Moreover, production processes have been developed, which allow industry friendly printing processes for related products. Today, graphene-inks are suitable for roll-to-roll processes. E. g. US Graphene3DLabs demonstrated printability of batteries for various shapes and sizes [207]. Also, Manchester Metropolitan University works on this issue [225].

But printable and flexible thin-film battery concepts are already implemented without graphene [170, 201]. And at least today, the market volume is limited with $ 70 million

[202], compared to the $ 60 billion battery market worldwide [196]. Additional information on that issue is to be found in section 4.6 Flexible and/or printed electronics.

3.3.2.2 Current weaknesses and challenges for graphene/2D materials use in batteries

3.3.2.2.1 High-potential anodes are missing their counterpart electrolytes and cathodes

Besides the use as additive, for hybridization, and in composite formulations, graphene is discussed as pure active material in battery anodes [209]. Due to its high specific surface area of 2630 m²/g, there is a significant higher intercalation of lithium-ions possible than in graphite with 15 m²/g, i.e. today's-standard. [204]. Beside the high capacity, the relatively fast insertion and re-insertion of ions during charge and discharge is an advantage, because charging time is one of the most relevant issues in the battery market.

But the high specific surface area of graphene leads to a high reactivity of the material. On the one hand, the advantage is basically a high electric potential of related battery concepts – with resulting high-power batteries. On the other hand, today, the high reactivity and potential causes a significant irreversible capacity lost already at the first charging cycle, because all lithium-ions are immobilized at the anode. This means, a high-power concept is viable only in a system approach: as long as both high-voltage electrolytes and cathodes are not available, a stand-alone high-voltage graphene based anode is pointless.

But as the problem of capacity loss in high-potential batteries is already an issue for many years now, there have been relevant research efforts to develop related electrolytes [199]. E.g. currently, BASF develops a high-voltage-electrolyte for up to 4.7 V. Hence, it can be expected that this barrier might be passed. But this shows that the main research effort for high-power batteries is not related to or depending on graphene development.

3.3.2.2.2 Material quality, price, and processability insufficient

Pure graphene, in the form of graphene nano-platelets (GNP), might theoretically increase the effectiveness of lithium-ion battery electrodes. However, the graphene material, currently available on the market, became apparent to be not suitable for pure-graphene electrode concepts. The delivered material was rather graphene oxide particles or quasi-graphene than graphene nano-platelets. Moreover, the particles are often coagulated and rather in micrometer- than in nanometer-size. Accordingly, it is reported that the normal graphene processing leads to aggregation and, as a result, to reduction of surface area [207]. Moreover, in the post-processing the graphene powder turned out to be difficult to handle. Processing of graphene-suspension appears easier – even though it is more difficult to weigh out.

In general, high-capacity graphene anode materials are not manufacturable today in mass-production processes: randomly organised graphene nano-sheets are derived from graphene oxides by reduction (rGO). The related processing methods like hydrogen reduction, low-temperature pyrolysis, rapid expansion, or electron beam irradiation is not compatible to mass-production. Hence, commercially available graphene is said to be rather expensive. However, as long as the potential market for graphene-based anodes is not attractive for Europe or not viable due to maturity issues of the technology (high-power batteries, 4th generation batteries) process development is not a predominant issue.

3.3.2.2.3 Problems of reputation and exchange

Even though, graphene shows – at least theoretically – potential for battery applications and provides new opportunities for electrode materials, it can be observed that graphene materials appear only very occasionally and not as a dominant topic on battery material related conferences. Also, battery experts and industry associations appear to be not very much interested in graphene. Unfortunately, it appears that initial high prices, poor quality, and low quantity of commercially available graphene has spoilt the image of the material in the battery community. At first, superficial testing was apparently disappointing, so that the image of graphene has changed in the battery industry from a “promising” to an “overestimated” candidate. If – occasionally – graphene is mentioned in the battery community as an option with some prospects, particularly for automotive and electric vehicle applications, the material is assessed to be far away from meeting the requirements of the sector [226].

Repeatedly, it is mentioned that the exchange between the graphene-community and the application community and industry is very poor. The requirements, specifications, key performance indicators, and standards appear to be only rarely a matter of discussion in graphene-focused academia. What makes the situation particularly difficult for European researchers is that they have only very few counterparts in the industry available as all relevant cell manufacturers are located in other regions of the world.

In addition to that, it has been generally stated that the different stakeholders in academia and industry pursue not the same targets, as the ones are already satisfied if they can issue their results in a paper and the others are just expecting tailor-made, qualified materials without own research efforts. Especially, the requirements of applications have to be discussed in common activities.

3.3.3 KPIs for batteries

The most often used key performance indicator for battery electrodes is the specific or gravimetric capacity [mA/g]. An expert assessed every material concept reaching 1000 mAh/g and above can be seen as interesting.

The specific energy density [Wh/kg] is one of the most important figures of merit to compare battery systems. It quantifies the range of a storage system with regard to weight. Even though graphene will probably contribute only to specific components of the battery, the assessment of a material concept can only be done in the context of the cell design. Battery experts from the industry emphasized this issue vigorously.

Table 30: Battery KPIs.

Value	Unit	Description	Literature
	mAh/g	**Specific/gravimetric capacity** To compare electrode technologies	
170	mAh/g	LiFePO4-graphene battery (pure graphene anode)	[204]
250	mAh/g	Amorphous carbon (theoretically)	[204]
250	mAh/g	Graphene-cathode (wrapping of active material with rGO)	[204]
150-350	mAh/g	Cathodes others	[204]
372	mAh/g	Graphite (theoretically)	[204]
540	mAh/g	rGO-based andode @ 1C	[204]
700	mAh/g	Benchmark: Si-anode	Expert assessment
730	mAh/g	rGO-CNT andode @ 1C	[204]
744	mAh/g	Graphene based battery	[204]
750	mAh/g	High SSA graphene-anode	[204]
784	mAh/g	rGO-C60 hybrid structure anode @ 1C	[204]
800	mAh/g	High-capacity anodes (Si-graphene)	[204]
900	mAh/g	Cathode sulfuric at low potential ~2.5 V	[204]

Value	Unit	Description	Literature
~1000	mAh/g	High-capacity anodes (SnO_2-graphene)	[227]
>1000	mAh/g	Benchmark for interesting material concept	Expert assessment
1100	mAh/g	GO-Si-nanoparticle (flexible)	[197]
Up to 1500	mAh/g	Si-based anode	[204]
2500	mAh/g	SiNode Systems, USA Graphene composites anode	[228]
4200	mAh/g	Silicon (theoretically)	[197]
	A/g		
~1600	A/g	Lithium-sulfuric battery (Li_2S) at 2 V	[229]
~1600	A/g	Lithium-air battery (Li_2O_2) at 4 V	[197]
	Wh/kg	**specific energy density**	
60-100	Wh/kg	Batteries for electric vehicles (2011)	[200]
110	Wh/kg	Batteries for electric vehicles (2011)	[200]
190	Wh/kg	$LiFePO_4$/graphene	[228]
250	Wh/kg	Batteries for electric vehicles (2011)	[200]
250	Wh/kg	Gold standard: lithium-ion battery	[197]
387	Wh/kg	Lithium-ion battery (theoretically)	[197]
500	Wh/kg	Batteries for electric vehicles (2020)	[200]
700	Wh/kg	Batteries for electric vehicles (2030)	[200]
1000 @2.3 V	Wh/kg	Claimed by graphenano/Grabat battery	[197]
	V	**Specific energy**	
2.5-4.5 @> 250 Ah/kg @ < 750 Wh/kg	V	Lithium-ion battery	[204]
~3.7	V	STOA battery (2010), LiCoO-	[204]

Value	Unit	Description	Literature
		cathode+graphite andode	
5	V	High-energy batteries	[199]
	€/kWh	**Costs battery storage**	
150-400	€/kWh	Battery cell for electric vehicles (2016)	
200	€/kWh	Lithium-ion battery 2020, LG chem	
<200	€/kWh	Batteries for electric vehicles (2020)	[200]
~100	€/kWh	Batteries for electric vehicles (2030)	[200]
~50	€/kWh	Batteries for electric vehicles (>2030)	[200]
40-80	€/kWh	Lead acid (today)	
		Other KPIs	
		Depth of Discharge (DoD) @ 80 % power capacity	
		Discharge, C-rate (1C= discharge in 1h, discharge relative to maximal capacity)	[204]
		Cyclability (time related durability) Number of charge/discharge before capacity < 60 % (nominal value)	[199]

3.3.4 Roadmap for batteries

3.3.4.1 Current maturity: ‘Use as additive already close to market’

Today graphene is used as additive against thermal runaway. Samsung already has commercially implemented related anode concepts. Also other additive-related applications are almost mature for first commercialisation.

CalBattery has announced a nano-silicone/graphene-based composite anode, using graphene nanoparticles (GnP). Target applications for the electrode have shifted from electronic vehicles to consumer products, as probably scaling up and testing for automotive has been too demanding.

In November 2015, Graphenano announced the launch of a graphene-based battery manufacturing in Spain. It remains to be seen whether promises of timeline and performance can be met.

XG Sciences and Boston-Power are collaborating in silicon-based anode development based on graphene.

The high-power electrode concepts based on silicon-graphene composite are currently a matter of first commercial activities.

3.3.4.2 Barriers/challenges (summarized)

Value chain, industry and frame conditions

- There is no significant lithium-ion battery cell production in Europe and the major players are not in Europe.
- Thus, a relevant part of the value chain is and will be outside of Europe.
- Initially poor graphene supply and value chain, low production quantity, no tailored quality, high price and limited processability
- The reputation of graphene in the battery community ("spoilt expectations") is poor, there is a poor acknowledgement in/exchange with the battery community
- The graphene community is said to be not aware enough of all requirements of applications – particularly to meet the demand of the automotive industry
- Deviating targets from academia and industry, clashing of expectations (publishing versus expectations to deliver tailor-made, qualified materials to industry and be outsourced research)

Technology and production

- Goal is to increase specific energy with lower costs
- Improve batteries without increasing complexity of production process
- Prove success in fostering graphene-based systems in target markets
- Improve cell concept to exploit benefit of anode high surface area (improved electrolyte, cathode)
- Implement targeted functionalization and approach scale up
- Swelling of anode (especially for Si-enhanced anodes)
- Missing electrolytes and cathodes for high potential graphene anodes (capacity loss at first charge with common electrolytes)

3.3.4.3 Potential actions

If the area of graphene/2D in battery technology is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

The following potential actions can be derived from the barriers.

- Connect with battery technology community
- Further activities in lithium ion battery technology only if relevant common activities with European industry are given
- Address full set of relevant parameters
- Focus on 4th generation batteries as a European opportunity (in a common European initiative)
- Explore flexible batteries as a potential opportunity and USP of graphene

3.3.4.4 Roadmap

2020

In 2020 there global lithium-ion battery production is expected to be 95,500 MWh. Until then, batteries have to fulfill the following specifications:

- 1,500 W/kg
- 600 Wh/L
- 250 Wh/kg
- 10 to 15 years life-cycle

4th generation batteries (post-lithium-ion batteries) like lithium-sulfur batteries are expected to be commercialised not before 2020. Then, however, there are is a grounded hope that Europe will play a role as manufacturer, also with a relevant cell production.

In battery industry it requires 10 to 20 years to implement new material concepts. Subsequently, in the automotive sector, it needs more than another 4 to 5 years to launch a new battery technology based on the new material.

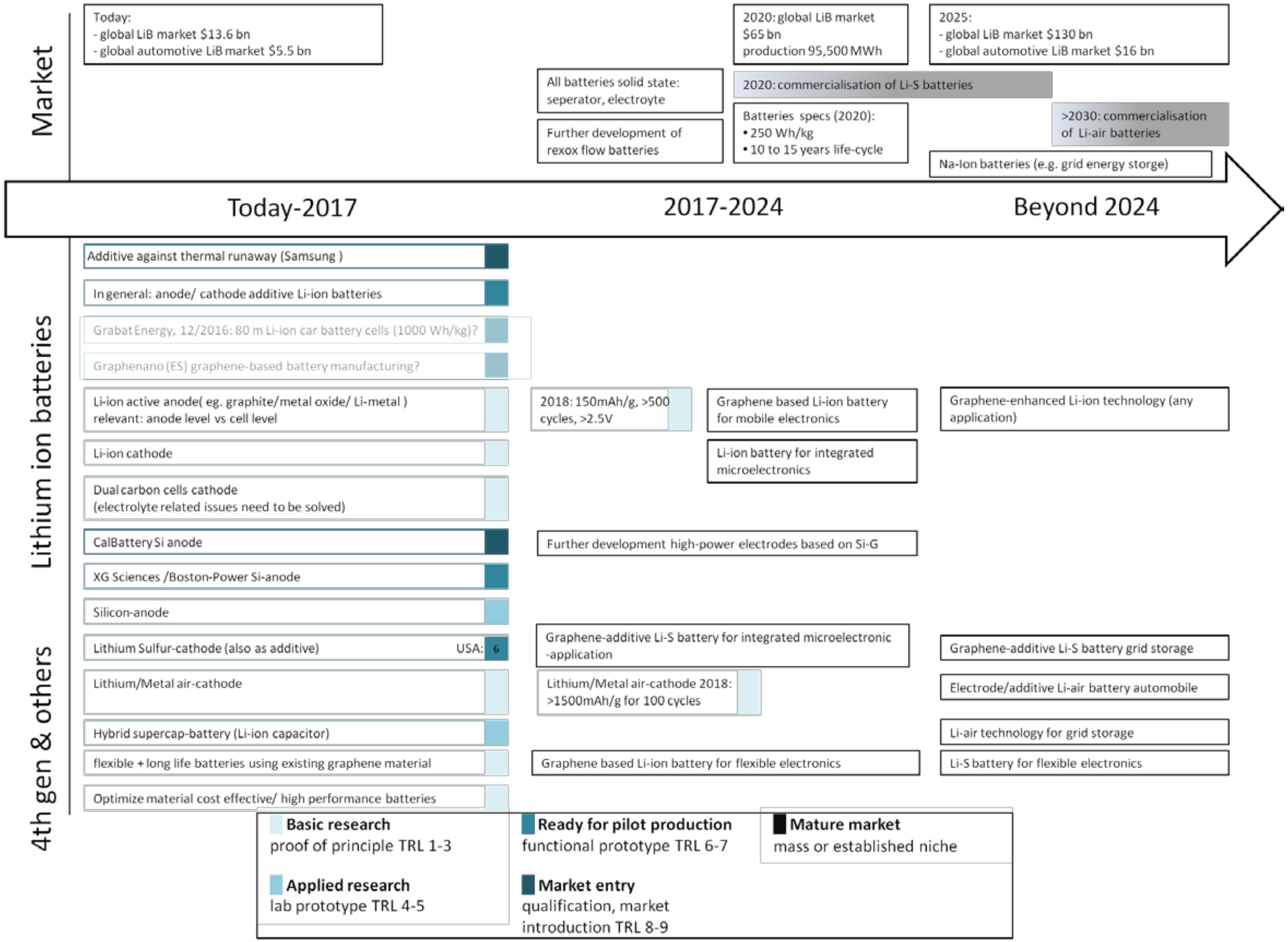
Another assessment calculates for the first testing of a production sample in the automotive sector more than one year. The subsequent production development, testing in automotive applications, and passing of standards for electric vehicles requires at least another 8 years.

2030

Lithium-air batteries in general are expected to be commercialised not before 2030.

Innovative battery concepts might be standard beyond 2030.

Graphene will play a role in automotive applications not before 2030.



Market

Today:
- global LiB market $13.6 bn
- global automotive LiB market $5.5 bn

All batteries solid state: seperator, electroyte

Further development of rexox flow batteries

2020: global LiB market $65 bn production 95,500 MWh

2020: commercialisation of Li-S batteries

Batteries specs (2020):
- 250 Wh/kg
- 10 to 15 years life-cycle

2025:
- global LiB market $130 bn
- global automotive LiB market $16 bn

>2030: commercialisation of Li-air batteries

Na-Ion batteries (e.g. grid energy storge)

Today-2017 | 2017-2024 | Beyond 2024

Lithium ion batteries

Additive against thermal runaway (Samsung)

In general: anode/ cathode additive Li-ion batteries

Grabat Energy, 12/2016: 80 m Li-ion car battery cells (1000 Wh/kg)?

Graphenano (ES) graphene-based battery manufacturing?

Li-ion active anode(eg. graphite/metal oxide/ Li-metal) relevant: anode level vs cell level

2018: 150mAh/g, >500 cycles, >2.5V

Graphene based Li-ion battery for mobile electronics

Graphene-enhanced Li-ion technology (any application)

Li-ion cathode

Li-ion battery for integrated microelectronics

Dual carbon cells cathode (electrolyte related issues need to be solved)

CalBattery Si anode

Further development high-power electrodes based on Si-G

XG Sciences /Boston-Power Si-anode

Silicon-anode

4th gen & others

Lithium Sulfur-cathode (also as additive) USA: 6

Graphene-additive Li-S battery for integrated microelectronic -application

Graphene-additive Li-S battery grid storage

Lithium/Metal air-cathode

Lithium/Metal air-cathode 2018: >1500mAh/g for 100 cycles

Electrode/additive Li-air battery automobile

Hybrid supercap-battery (Li-ion capacitor)

Li-air technology for grid storage

flexible + long life batteries using existing graphene material

Graphene based Li-ion battery for flexible electronics

Li-S battery for flexible electronics

Optimize material cost effective/ high performance batteries

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

3.3.5 Conclusion Batteries

Graphene is investigated as an additive to lithium-ion battery electrodes. The technological barriers for current generation lithium-ion batteries are rather low despite only limited performance enhancements. The market is dominated by Japanese and Chinese companies, Europe’s position is negligible and a relevant cell production for lithium-ion batteries is not to be expected in Europe in the coming years. Accordingly, from a European perspective the current generation of lithium-ion batteries is less attractive for graphene development.

Most promising market developments are expected in automotive and micro-grid applications. Currently prevailing lithium-ion battery technology will not come up to the needs of these new sectors. New material concepts are required to allow significant improvements regarding performance and costs. Graphene offers additional opportunities for new electrode material concepts. Particularly, functionalized, hybridized graphene materials and composites can be tailored for new electrode solutions.

Therefore, graphene appears particularly promising for future cell generations and could contribute to 4^{th} generation batteries (lithium-sulphur, lithium-air, and redox-flow batteries) enabling their feasibility. For these battery concepts manufacturing potential in Europe is expected beyond 2030. Another interesting area for Europe is flexible batteries. Currently, the major threat for graphene in battery technology is a negative image in the battery community due to exaggerated and not kept announcements. A dialogue with the related battery community about actual potentials and limits is needed.

Table 31: Assessment of market and technological potential of graphene/2D materials use in batteries on a scale - -, -, 0, +, ++.

Role of graphene in batteries	**Current technological potential (USP)**	**Market potential (EU perspective)**
additive in electrodes	+	-
active anode material	0	--
high-potential anodes	+	+
electrode material for 4th generation batteries (e.g. LiS, Li-air)	++	++
bipolar plates of redox-flow batteries	+	?

3.4 Supercapacitors

This chapter covers the use of graphene/2D materials in supercapacitors (also: ultra-capaci-tors, electrochemical double layer capacitor EDLC), pseudo-capacitors and hybrid capacitors. In supercapacitors power storage is based on electrostatic interactions. In contrast to batteries, simply speaking, no electrochemical reactions are used for energy storage. Pseudo-capacitors are based on charge transfer from the electrolyte to the electrode, but without reduction or oxidation of the electrode. And hybrid capacitors use both, electrochemical and electrostatic energy storage.

In supercapacitors (also: ultracapacitors, electrochemical double layer capacitor EDLC) power storage is based on electrostatic interactions. In contrast to batteries, simply speaking, no electrochemical reactions are used for energy storage. Pseudo-supercapacitors use both, electrochemical and electrostatic energy storage.

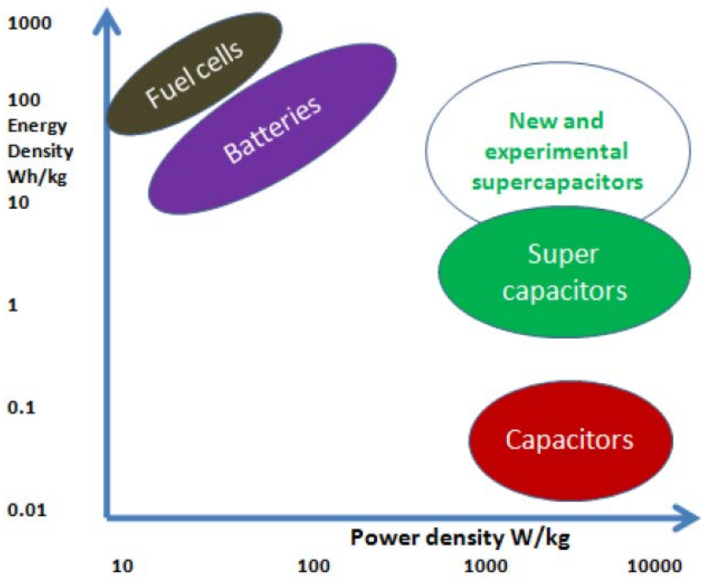


Figure 31: Energy density vs. power density for storage devices [230]

As the storage in supercapacitors is not based on redox reactions, the storage systems can be charged and discharged in seconds. This recommends the technology for all kinds of fast capturing and delivery of power. Moreover, it has the effect that these systems show a very high lifetime and boast many charging cycles. Another advantage of supercapacitors compared to batteries, is that they can be used in rougher environments and have a higher temperature tolerance [197]. Moreover, the systems have no thermal heating issues [230], so that there is no risk of overcharging and catching fire. That means, supercapacitors are distinguished by higher safety and reliability, long lifetime of about 20 years and, deduced from that, very low maintenance costs [230]. The disadvantage of supercapacitors is, first of all, the significantly lower energy density, leading to an about 20 times lower storage capacity than in batteries [197, 230, 231]. Therefore, today the systems are bulky. Moreover there is a higher inclination to self-discharge [230].

3.4.1 Market perspective: graphene/2D materials in supercapacitors

The ability of fast capturing and delivery of power (pulse power) makes supercapacitors ideal for higher power and highly dynamic applications. Today, supercapacitors are standard particularly for motor start up in large engine tanks, submarines, missiles, diesel trucks, and railroad locomotives. So, the predominant markets are heavy engineering, automotive, and military [230]. Supercapacitors are also interesting also for specific applications where fast delivery of stored energy is required, like electroforming of metals. Moreover, peak power for robotics and actuators are relevant areas and supercapacitors might play a role for back-up power in electric utilities and factories. Hence, relevant drivers for supercapacitor technology are industrial machinery and transportation [197]. In transportation, applications like mass transit and load cranes are relevant [204]. In the professional sector, additional drivers for supercapacitors are electronic instruments like power tools and communication devices [197].

The characteristics of fast capturing and delivery of power puts supercapacitors also forward for electro-mobility applications, as they might solve the problem of fast fuelling of electric cars. But as the energy density is still significantly too low, this application is not viable today. In the short term, applications like energy recuperation from braking processes are rather probable. This can contribute to a decrease of fuel consumption from 15 % up to 20 % [232, 233]. Moreover, supercapacitors might be used in the electric vehicle market for acceleration and extra boost on hills. In the long run, transportation is expected to be the largest market and it is sometimes speculated that supercapacitors might even completely replace batteries [234]. But today the systems are not competitive with regard to both energy density and price. In fuel cell technology they might be used for augmentation in order to increase dynamic of the system.

An advantage of supercapacitors is that they do not necessarily contain hazardous substances, the only exception being the electrolyte, which can be hazardous. It is possible to fully implement supercapacitors without hazardous substance. Moreover, they show a good recyclability.

In general, supercapacitors can be used as bridge power for uninterrupted power supply (UPS) [230]. Particularly in the renewable energy sector, supercapacitors might be interesting for short term grid stabilization of voltage. Both bridging and peak power can be provided [235]. The “energy smoothing” and momentary-load devices might generate a totally new market [230].

Another main growth driver for supercapacitors is consumer electronics [197]. Today, in these applications supercapacitors are suffering from being too bulky, due to low volumetric density [197]. But, in principle, they can be used for flashlights, PC cards, digital cameras, portable media players, automated meter reading, and remote transmitting devices [230]. Also, in the long-term, they might be used in combination with energy harvesting, e.g. to be used in wireless sensors systems for monitoring purposes [230].

The market size of supercapacitors in 2016 is estimated > $ 850 million. In 2020, it is expected to be > $ 3 billion [197]. Suppliers of supercapacitors are:

- Maxwell Technologies (USA)
- Panasonic (JP)
- LS Mtron (KR)
- Vina Technology (KR)
- Supreme Power Solutions (CN)
- Man Yue Technology Holding (SAMXON) (CN)
- Yunasko/Solvay (UA)
- ELIT (RU)
- ESMA (RU)
- NessCap Ltd (KR)
- Cap-XX (AU)

Today, the market size of supercapacitors is just about five percent of the battery energy storage market size [197]. But the growth rates are higher. It is interesting that the market appears less consolidated and the dominance of Asian companies is far less pronounced than in other energy related application areas. Accordingly, the number of patents in supercapacitor technology shows that the USA is in the lead position and Europe on the second place (s. Figure 32).

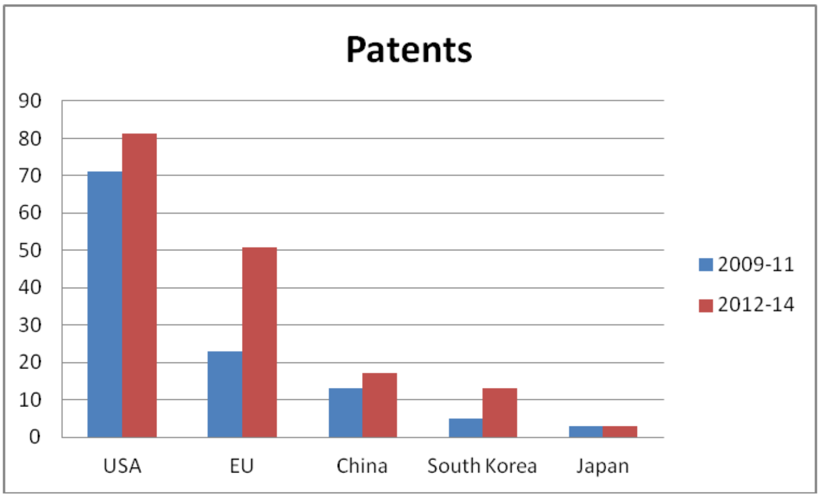


Figure 32: Number of transnational patents in supercapacitor technology. [21]

As for **graphene-based supercapacitors**, Future Markets estimate a potential market size of \$500 m up to \$1 bn [197]. Today, there are some supercapacitors based on graphene available on the market. Some companies engaged in the development and manufacturing of graphene-based supercapacitors are [197]:

- Sunvault Energy (USA)
- Skeleton Technologies (EST)
- Graphenex (UK)
- Graphene ESD (USA)
- AdvEN Solutions (CA)
- Angstron Materials (USA)
- BASF (printable supercaps) (DE)
- Bluevine Graphene (roll-to-roll) (USA)
- Zapgocharger (UK)

Only two of the European companies (Skeleton Technologies, Zapgocharger) are really producing supercapacitors [234].

3.4.1.1 Role of graphene in supercapacitors

Graphene materials are used in supercapacitors for electrodes. The huge advantage of the material is the high accessible specific surface area (SSA) of 2630 m²/g. Indeed, state-of-the-art material activated carbon has even a higher theoretical SSA (3000 m²/g), but the usable surface for the electrolyte is lower due to unfavourable mesoporous properties [234]. Moreover, the conductivity of graphene is higher [229]. Another advantage of graphene-based supercapacitor compared to existing concepts is the higher mechanical and thermal stability of the electrodes [163].

Currently, there are different kinds of graphene used for supercapacitor electrodes. Some examples are:

- Reduced graphene oxide (RGO) [163, 204]
- Graphene-based platelets (GnP) with different spacer materials CNT [204, 234]
- Aerosol spray dried Graphene Oxide with a hierarchical 3D structure (GO) [163]
- GO decorated with chemicals, e.g. KOH [163]
- Microwave expanded graphite oxide (a-MEGrO) [163]
- Skeleton technologies uses curved graphene for their ultracapacitor electrodes (CDC) [233].
- Angstron Materials use graphene as additive in supercapacitor-electrodes [197]

To decrease the size of the supercapacitor systems, research activities aim at raising the fill factor and by that improving packaging density [204]. This leads to storage systems with higher power density.

The power density determines speed of charging and discharging. A limiting factor for the charging speed of a supercapacitor system, however, is the ionic conductivity of the electrolyte, which is not influenced by graphene electrodes. Also, the number of charge and discharge cycles depends significantly on the electrolyte and less on graphene-related components. And last but not least, the energy storage capacity is among others determined by the operating voltage, which is again limited by the stability of the electrolyte.

Another concept of graphene based storage technology are pseudo-supercapacitors, which combine the principles of supercapacitors with redox reactions, common in battery technology – like e.g. lithium-ion hybrid supercapacitors [204, 229]. The aim is to combine high storage capacities with fast charge/discharge cycles and high life time. But the related concepts are still in an early research stage.

Comprehensive overview on the role of graphene in supercapacitors is provided in the review articles summarized in Table 32.

Table 32: Summary articles for graphene in supercapacitors.

Topic	Reference
Graphene/2D materials for energy conversion and storage	[163, 204, 208, 210]
Graphene-based materials for supercapacitor electrodes	[236, 237]

3.4.1.2 Market Opportunities

3.4.1.2.1 State-of-the-art electrode material activated carbon has poor porosity characteristics

State-of-the-art of supercapacitors is activated carbon for both electrodes. The activated carbon has a specific surface area SSA of 3000 m^2/g. On the one hand it is important for electrode materials to have a high specific surface area. But moreover, it is important to have a meso- to nano-porous structure in order to ensure access of the electrolyte to the surface of the solid material [204]. The activated carbon is, indeed, designed as a nano-porous material [238]. But, the distribution of the pores is insufficient [197]. As a result, a major problem with activated carbon in supercapacitors is particularly low energy density [197]. Hence, one of the major objectives in supercapacitor development is the electrode material improvement to overcome this problem. And graphene has the potential to be a key technology for this task [197].

3.4.1.2.2 Potential for new supercapacitor applications due to higher energy density

Today, supercapacitors are often not used in energy storage applications due to the low energy density of the devices. E.g. for grid balancing supercapacitors have relevant benefits, as they show high dynamic properties. But, the storage capacity is too low for these applications. In many other energy storage concepts, supercapacitors are just used as an auxiliary power source for batteries and fuel cells to allow a higher dynamic of the overall system. But, the major energy is delivered by the other storage technologies. By using graphene, the energy density of supercapacitors might be increased significantly, which opens up a huge potential for various applications.

3.4.1.2.3 New attempt for energy storage cell production in Europe

Energy storage is certainly a most relevant area in the energy system development. Currently, the field of battery cell production is very much dominated by Asian companies (s. 0

Batteries), whereas in Europe a major cell production for the automotive sector is still missing. To win ground in the field, e.g. of lithium ion batteries, will require a very high effort. The supercapacitor technology still bears a lot of potential and is less covered/dominated from other regions – even though China, Korea, Japan, and Taiwan are already in a starting position [234].

Due to performance restrictions, initially the supercapacitor production will not be for the automotive sector. But, there are various high-value applications viable for (graphene-based) supercapacitors, like in cranes, forklifts, and other kinds of load levering applications, which might allow the creation of business opportunities in the nearer future.

A joint European effort towards next-generation energy storage might lead to a specific ecosystem, entailing the creation of regional manufacturing capacities. To achieve that, it is necessary that the related competences enclose not only technology development, but also integration, scale up, commercialization and market expansion activities. It has to be stressed that the set up of a new production and subsequent market expansion requires huge investments. Private investors will reject from financing an activity which is isolated and just based on material related competences. Beside material research, demonstration is crucial. The development of a whole value chain with orchestrated innovation activities will be necessary to stir a cell production in Europe.

3.4.1.2.4 Chance for graphene supercapacitor deployment from advances in nanotechnology

Graphene based supercapacitor development can benefit from graphene material sciences as such. But, in addition to that, the graphene deployment can profit from further development in nanotechnology – as it certainly is a nanotechnology as such. E.g. the mastering of processes, equipment and nano-architecturing of the materials might contribute to improvements in graphene deployment. Therefore, a systematic collaboration between and within the subjects might be beneficial. This is probably not only related to supercapacitor development, but it might be particularly beneficial in this area as it might increase opportunities on the further way towards commercialization.

3.4.1.3 Market Threats

3.4.1.3.1 Strong focus on battery technology in energy storage technology

In the last couple of years, the battery technology has been a more visible research focus in the field of energy storage than the supercapacitor technology. Even though supercapacitors show a reasonable potential, the technology was less matter of public research and industrial research and development [231, 239]. Publication analysis reveals that particularly in Europe and the USA the engagement in battery technology was significantly higher (Figure 33). Even though, some companies like Skeleton Technologies were quite successful in acquiring funding for graphene-based ultracapacitor development and ramp-up [240, 241], patent intensity in supercapacitor technology suggest low interest of industry in this area (s. Figure 33). Certainly, this is due to the fact that batteries have a broader application spectrum and a significant higher level of maturity. But supercapacitors might provide attractive solutions for high-value niche applications, what is particularly interesting for US and European economy. And in the long run they might even become an alternative to batteries – or the two technologies merge.

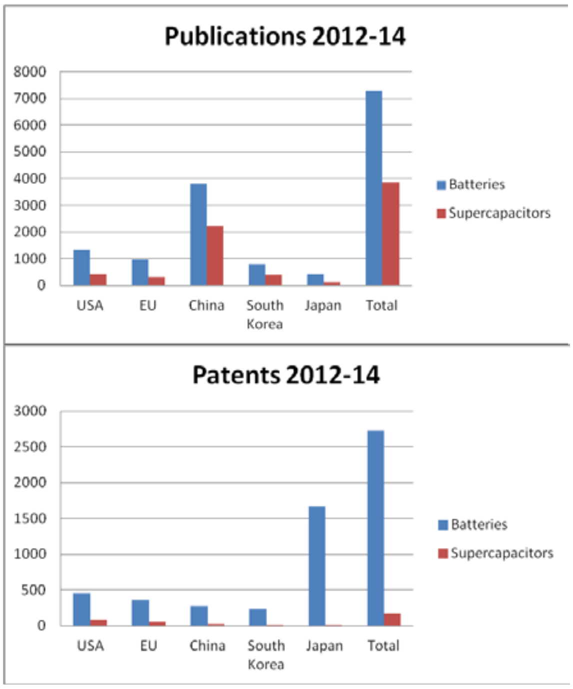


Figure 33: Publications and transnational patents in battery and supercapacitor technology (2012-2014). [21, 164]

3.4.1.3.2 Relevant macroeconomic value added starts with cell production

At least in the high volume automotive market, for both batteries and supercapacitors there is no major cell manufacturer located in Europe. But lower steps of the value chain will most certainly not generate relevant macroeconomic value added for Europe (s. 3.3.1.3.1 “Macroeconomic revenue of graphene-based anode material negligible”). Moreover, both materials and electrodes have to be seen as commodities, suffering from high price competition. Only in case of high volume applications, companies can generate relevant revenue by materials. But, even then, the macroeconomic role will be negligible compared to the revenues created with systems and from OEMs. That leads to the conclusion that the economic impact of graphene research in the area of energy storage depends decisively on the creation of a European cell manufacturing – which does not depend on success in electrode technology but particularly on economic and political considerations and will (s. 3.4.1.2.3).

3.4.1.3.3 Research to improve producibility

Today, supercapacitors are still relatively costly in production [197]. That entails high costs per energy – even though it is repeatedly emphasized that the high durability leads to a relatively lower price with regard to the cycle time and total cost of ownership. However, a critical barrier is < 0.01 $ per Farad: Just below this threshold, supercapacitors are competitive – particularly for automotive applications. It is expected that this can be reached with a production volume of more than one million cells per year as, beside material costs, production quantity is a major factor having an impact on the price. This emphasizes the relevance of both low material costs – a potentially critical issue for graphene-based supercapacitors – and improvements in the scaling up of the production processes. Graphene related research funding should therefore not only focus on improvement of electrode materials and systems but also on producibility of the electrodes.

3.4.1.3.4 Research for high-voltage electrolytes

Supercapacitors are distinguished by a very high number of charging cycles of more than one million [204]. The charging cycle performance can be even increased by using graphene. But, in the end, the durability and the number of charge and discharge cycles is not limited by the graphene electrode but by the stability of the electrolyte. Moreover, the operating voltage, and by that the speed of charge and discharge, depends decisively on the stability of the electrolyte. That means to exploit the performance increase of a supercapacitor, caused by graphene, a significant effort is necessary to further develop the electrolyte.

3.4.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in supercapacitors

3.4.2.1 Current strengths for graphene/2D materials use in supercapacitors

3.4.2.1.1 First steps towards commercialization

In energy related application areas graphene based supercapacitors appear to be the most mature application. Currently, there are already several demonstrators launched:

- Skeleton Technologies presented an unmanned ground vehicle [242] and establishes a small series production for truck applications [233]
- In 2015, Sunvault Energy and Edison Power presented a 10,000 F graphene-supercapacitor [243]
- Graphene-based lithium-ion capacitors are implemented in electric bicycles [244]

Even some first products are commercialized in Europe:

- Zapgocharger launches a supercapacitor phone charger based on graphene [197]
- Skeleton Technologies launched an ultracapacitor [197]
- Lomiko announced the launch of a kickstarter in-wall charging device [245]

Launching these first products on the market has a high signal effect. They proof applicability of graphene in commercial energy applications. The related products are addressing particularly the consumer electronics market. In the nearer future, particularly high value/low volume applications in premium segments like load levering or avionics is to be expected.

3.4.2.1.2 High accessible surface area due to designable porosity

Graphene development for supercapacitor electrodes has initially two interconnected advantages which can be used to improve the storage capacity: Theoretically, graphene has a specific surface area of 2630 m^2/g, with doubled amount if both sides of the graphene-sheet are used. Now, one major issue is to exploit this and increase the measurable specific surface area. The other issue is to ensure the benefit of this high specific surface area by making it accessible to the electrolyte [204]. Here, the significant advantage of graphene is that it can be specifically tailored and the porosity can be designed and controlled. Accordingly, graphene-foam has been tested and has shown an increased performance [246]. Also graphene-aerogels used as electrode material have shown doubled performance compared to commercial carbon-based electrodes – not only with regard to specific surface area, but also with regard to electric conductivity, chemical inertness, and long-term cycling stability [247]. Another approach to ensure electrolyte access is to use graphene-platelets with carbon nanotubes as spacer material [204].

3.4.2.1.3 Hybridization allows exploitation of different strengths

Supercapacitors show specific advantages regarding dynamics of charging and discharging, lifetime/cyclability, safety and environmental issues, and temperature range; whereas batteries are superior with regard to storage capacity and operating voltage [228]. A hybridization of both technology concepts is very interesting in order to get an energy storage solution which allows fast charging and discharging, shows a higher range for vehicle applications then supercapacitors-based storage systems, and has a higher efficiency [248]. In principle, graphene is suitable for such hybrid concepts, e.g. the surface can be modified with electroactive materials and by this a hybrid of pseudo-supercapacitors and supercapacitors can be reached. Pseudo-supercapacitors are based on an electro-chemical reaction – like batteries –, but this reaction takes place just on the very surface of the electro-active materials. High-performance pseudo-capacitors based on graphene reach a specific capacitance of 922 F/g @ 3 A/g [249]. Currently there are different approaches to develop electrode improvements for pseudo-capacitors [249, 250]. For future hybrids of supercapacitors and batteries a power density of > 8 kW/kg and an energy density of more than 60 Wh/kg is targeted [228].

3.4.2.1.4 Flexible applications possible

In addition to high energy density, graphene-based supercapacitors show further beneficial properties: The related energy storage systems can be designed light-weight and flexible and elastic solutions are possible [197, 251] (s. also 4.6 Flexible and/or printed electronics). As for flexible supercapacitors, graphene is the only material which makes related concepts feasible. In the future, portable and even wearable solutions are possible. In the very long-term even disposable supercapacitors are conceivable.

3.4.2.1.5 Industry friendly processes applicable

In the first production testing it has become apparent that there are no principle problems with graphene-based materials in processing. Also some industry friendly processes appear feasible for graphene processing like spray gun deposition and 3-D printing. These processes are standard, easy to handle and very versatile [251].

- BASF is developing a printable supercapacitor with specific capacity of 269 F/g [197].
- A 3-D printed supercapacitor uses graphene-composite aerogels for electrodes [251].
- Another development approach is to use laser induced graphene (LIG) to improve the production process [252].

3.4.2.2 Current weaknesses and challenges for graphene/2D materials use in supercapacitors

3.4.2.2.1 Today's commercially available material does not always fit to industrial requirements

Today, commercially available graphene materials with sufficient properties are still quite expensive (>200 $/kg) compared to carbon black, activated carbon (<15 $/kg), and other nano-materials (CNT: 50 $/kg). Indeed, there are very small quantities of graphene necessary in process materials like inks, and based on this, already relevant improvement in supercapacitor applications can be reached. But, if the whole electrode consists of graphene, the total amount of material becomes more substantial. The commercially available volume of graphene-based materials, however, is not undisputed: even though there is already a delivery capacity of tons per year [197], representatives from the industry complain of insufficient reliable production volumes. Moreover, it appears the manner of provision does not come up to the typical purchase standards in manufacturing industry.

Also the quality of the delivered material, especially from batch to batch and supplier to supplier, appears improvable. An advantage, indeed, is that for supercapacitor applications there is not such a high purity of material necessary as it is e.g. in electronics. To the contrary, low quality multi-layered materials have even shown a better performance regarding conductivity. But, today, the available material is said to be particularly usable for research. The processing of graphene powder is still very difficult. Due to strong van der Waals forces, aggregation occurs, which affects both the surface area and the number of electrochemically active sides [197]. Graphene in dissolved forms like in inks is easier to process.

3.4.3 KPIs for supercapacitors

Within the supercapacitor technology the most often used key performance indicator is the specific capacitance [F/g].

In order to compare the capability of different storage technologies, particularly specific energy density [Wh/kg] is relevant which provides information on storage capacity of a system with regard to weight. Particularly for comparison of battery and supercapacitor technology specific power density [W/kg] is relevant. This figure determines the speed of loading respectively power provision of a storage system – what is the decisive advantage of supercapacitors.

For comparison of supercapacitor electrode materials the most important figure of merit is specific surface area (SSA) [m^2/g], as it determines storage capacity.

Table 33: KPIs for supercapacitors.

Value	Unit	Description	Literature
	F/g	**Specific capacitance** characterizes performance of capacitors, weight related (V @ mAh/g)	
3-4	µF/g	Pristine graphene	[228]
120	F/g	Reduced graphene oxide RGO + organic electrolytes	[204]
140	F/g	Benchmark (2.5 V @ 30 mAh/g)	[228]
190	F/g	Reduced graphene oxide RGO + aqueous electrolytes	[204]
200	F/g	Realistic/good performance for graphene based SC	
269	F/g	BASF printable supercapacitor specific (target)	[197]
284.5	F/g	supercapacitors (@131 Wh/kg) (lab stage)	[229]
550	F/g	Single layer graphene (theoretical surface area)	[197]
922	F/g	Psydo-capacitors based on graphene @ 3 A/g	[249]
	F	**Capacitance** Typical descriptive parameter for a capacitor	
2,000	F	20210: EDLC of Maxwell Technologies Inc. (@2.7 V DC)	
4,500	F	High-power ultracapacitors of Skeleton Technologies	[233]
10,000	F	Sanvault Energy/Edison Power Company graphene-based supercapacitor	[197]
	Wh/kg	**Specific energy density** characterizes potential capacity of a storage system, weight related	

Value	**Unit**	**Description**	**Literature**
5	Wh/kg	Current supercapacitor for acceleration support of trucks (2kWh, 400kg)	[231]
4-7	Wh/kg	Commercially available supercapacitors	
> 6	Wh/kg	Supercapacitor @95% efficiency (2009)	[230]
> 10	Wh/kg	Minimum performance level for graphene based SC	[204]
20	Wh/kg	Realistic/good performance for graphene based SC	
20	Wh/kg	Skeleton Technologies, graphene-enhanced SC (target 2020)	[234]
10-14	Wh/kg	Supercap-hybrid: graphite Li-ion anode + activated carbon SC-cathode (commercially available)	[204]
50	Wh/kg	Graphene-based supercapacitor (today)	[197]
60	Wh/kg	Trend high-energy supercapacitors	
60	Wh/kg	Future hybrids of supercapacitors and batteries	[228]
80	Wh/kg	Supercapacitor of Angstron Materials (lab-level) (@1 kW/kg)	[197]
100	Wh/kg	Batteries for battery electric vehicles (today)	[183, 199]
131	Wh/kg	supercapacitors (@ 284.5 F/g) (lab stage)	[229]
150	Wh/kg	Graphene-based supercapacitor (target)	[197]
250	Wh/kg	Batteries for electric vehicles (2020)	[199]
>500	Wh/kg	Electric vehicles (target)	
	W/kg	**Specific power density**	

Value	Unit	Description	Literature
		characterizes potential dynamic of a storage system	
10	W/kg	Graphene-based supercapacitor (today)	[197]
1,000-2,000	W/kg	Lithium-ion batteries for hybrid electric vehicle (2015)	[183]
2,000	W/kg	Batteries for dynamic high-power applications (forklift, power tools) (today)	[199]
2,500	W/kg	Batteries for dynamic high-power applications (forklift, power tools) (2020)	[199]
5,000-8,000	W/kg	Current commercial packaged EDLC supercapacitors (@2.7V and 7-10Wh/L)	[204]
2,000-,8000	W/kg	Target of future supercaps (@energy density <10 Wh/kg)	[228]
1,000	W/kg	Supercapacitor of Angstron Materials (@80 Wh/kg) (lab-level)	[197]
> 1,000	W/kg	Electric vehicles (target)	
6,000-7,000	W/kg	Commercially available supercaps	
> 8000	W/kg	Future hybrids of supercapacitors and batteries	[228]
>10,000	W/kg	Applications where supercapacitors have advantage over batteries	[204]
10,000-14,000	W/kg	Current commercial lithium-hybrid supercapacitors (18-25 Wh/L)	[204]
100,000	W/kg	Record: commercially available supercapacitors	
	m^2/g	**Specific surface area SSA** material related, relevant for energy capacity	
<700	m^2/g	RGO used in graphene-based	[204]

Value	Unit	Description	Literature
		supercapacitors	
1810	m^2/g	Graphene (measured)	[204]
2630	m^2/g	Graphene (theoretically)	
3000	m^2/g	Activated Carbon	[197]
3100	m^2/g	Microwave expanded graphite => highly curved single-layer sheets (CDC)	[204]
3523	m^2/g	Organic material dispersed with GO => 3D structure with nanopores	[204]
	V	**Operating voltage** characterizes operating potential of a storage system, impact on charging speed and power	
~2.5	V	Today	[228]
3.0	V	Barrier, difficult to overcome	[228]
3.3	V	Future, (1.5 fold energy density)	[228]
3.5	V	Today	[197]
	cycles	**Lifetime**	
500,000-1 m	cycles	Common supercapacitor	
1 m	cycles	Potential performance of graphene based SC	[204]
>1 m	cycles	Skeleton Technologies, graphene-enhanced SC	[234]
		Costs	
<0.01	$/F	Classical figure of merit for supercapacitors (e.g. 20$ / 3000 F cell @ production quantity >1m/a)	
200	$/kWh	Today: Li-ion battery	[197]
		Material costs	
~18	$/kg	actviated carbon (2013) (cell of 500g requires ~ 200g activated	

Value	Unit	Description	Literature
		carbon)	
<15	$/kg	activated carbon (today)	
50	$/kg	carbon nanotubes used in supercapacitors	[197]
>200	$/kg	graphene species, relevant for supercapacitors	[197]

3.4.4 Roadmap for supercapacitors

3.4.4.1 Current maturity: ‘Pilot scale and commercialization’

For graphene applications in energy, supercapacitors appear to be the most advanced and mature technology with a clear USP. First commercial activities, also in Europe, can be observed and graphene is an enabler to allow addressing new applications for supercapacitors. Besides that, the integration is rather simple, so that this indeed can be seen as a “low hanging fruit”.

3.4.4.2 Barriers/challenges (summarized)

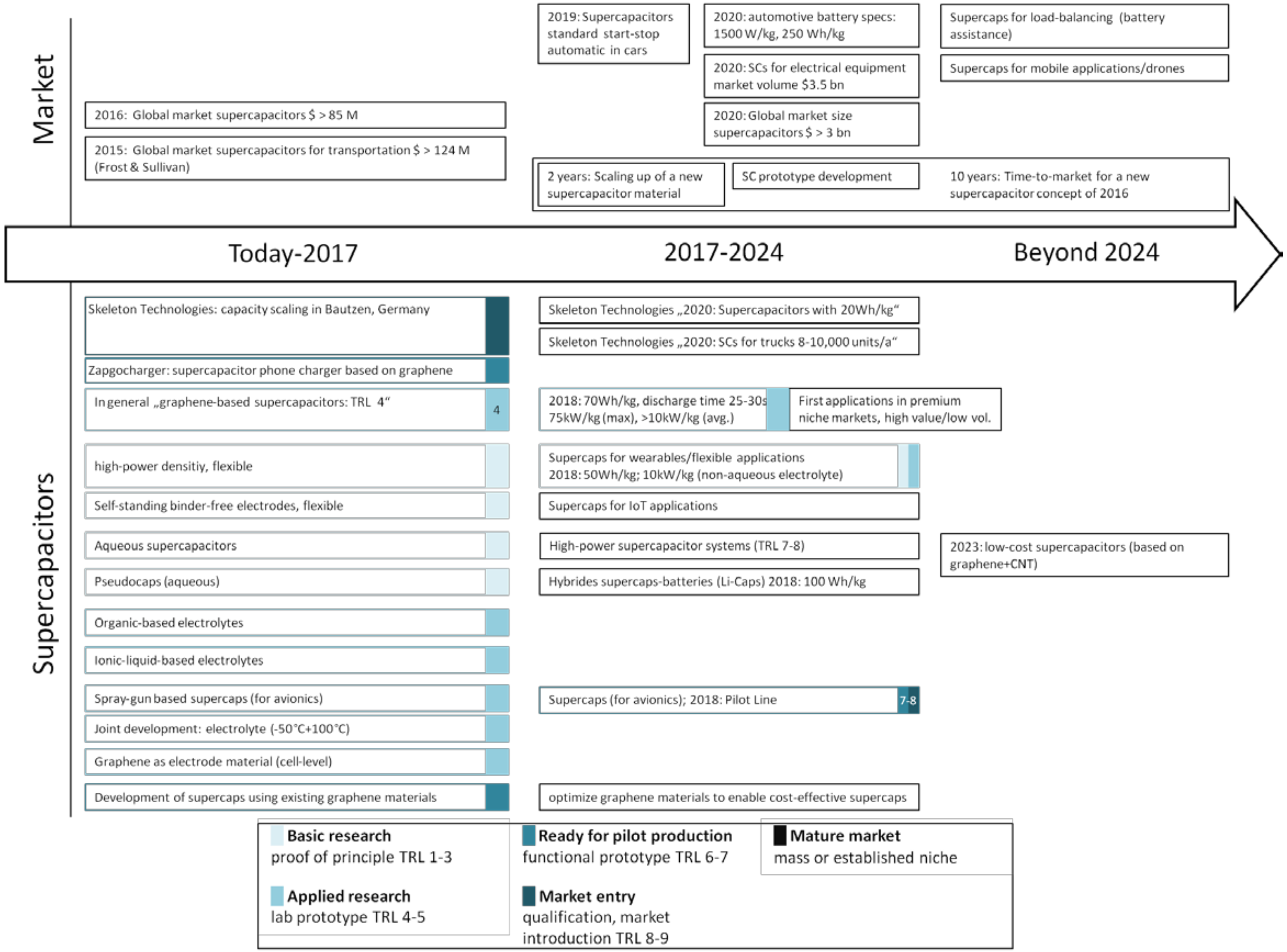
- Graphene supply chain not established and materials with diverse qualities
- Tailored quality for supercapacitors is still too expensive to reach competitiveness for mass markets
- Graphene quality itself is not needed to be high (multi layers sufficient), but this needs to be supplied with constant and reliable quality at reasonable quantity and price
- Durability, number of charge cycles and voltage limited by electrolyte

3.4.4.3 Potential actions

If the area of graphene/2D in supercapacitors is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

- Address tailoring and specific design of porosity to improve performance (e.g. graphene foams, aerogels, composites with nanotubes)
- Explore hybrid capacitors with functionalized graphene (using electroactive materials for functionalization)
- Explore flexible supercapacitors
- Stronger focus on processability (especially inks)
- Address tailored graphene preparation techniques with reduced cost (not such a high quality needed, multi-layer flakes sufficient, but those need to have a reliable quality from batch to batch and supplier to supplier)
- Also address electrolytes that match graphene and allow fast and many charge/discharge cycles.
- Support value chain generation, also looking at “cell” production

3.4.4.4 Roadmap



Market

2016: Global market supercapacitors $ > 85 M

2015: Global market supercapacitors for transportation $ > 124 M (Frost & Sullivan)

2019: Supercapacitors standard start-stop automatic in cars

2020: automotive battery specs: 1500 W/kg, 250 Wh/kg

2020: SCs for electrical equipment market volume $3.5 bn

2020: Global market size supercapacitors $ > 3 bn

Supercaps for load-balancing (battery assistance)

Supercaps for mobile applications/drones

2 years: Scaling up of a new supercapacitor material

SC prototype development

10 years: Time-to-market for a new supercapacitor concept of 2016

Today-2017

2017-2024

Beyond 2024

Supercapacitors

Skeleton Technologies: capacity scaling in Bautzen, Germany

Zapgocharger: supercapacitor phone charger based on graphene

In general „graphene-based supercapacitors: TRL 4“ 4

high-power densitiy, flexible

Self-standing binder-free electrodes, flexible

Aqueous supercapacitors

Pseudocaps (aqueous)

Organic-based electrolytes

Ionic-liquid-based electrolytes

Spray-gun based supercaps (for avionics)

Joint development: electrolyte (-50°C+100°C)

Graphene as electrode material (cell-level)

Development of supercaps using existing graphene materials

Skeleton Technologies „2020: Supercapacitors with 20Wh/kg“

Skeleton Technologies „2020: SCs for trucks 8-10,000 units/a“

2018: 70Wh/kg, discharge time 25-30s 75kW/kg (max), >10kW/kg (avg.)

First applications in premium niche markets, high value/low vol.

Supercaps for wearables/flexible applications 2018: 50Wh/kg; 10kW/kg (non-aqueous electrolyte)

Supercaps for IoT applications

High-power supercapacitor systems (TRL 7-8)

Hybrides supercaps-batteries (Li-Caps) 2018: 100 Wh/kg

2023: low-cost supercapacitors (based on graphene+CNT)

Supercaps (for avionics); 2018: Pilot Line 7-8

optimize graphene materials to enable cost-effective supercaps

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

3.4.5 Conclusion supercapacitors

Supercapacitors have the significant advantage – compared to batteries – that they have a distinctive higher power density. That allows the implementation of more dynamic storage systems and in real live faster “fuelling” respectively charging and discharging. But, one of the major barriers for supercapacitor propagation is the significantly lower energy density, which for example determines the range of electric vehicles. This is an important chance for graphene as graphene-based electrodes can increase the energy density of supercapacitors. This is not only due to the high specific surface area of the material – which state-of-the-art activated carbon also has –, but due to a high surface area accessible for electrolyte.

Today, there are already first graphene-based supercapacitor products commercially available. And from the technical perspective, there is still manifold potential for improvements: graphene can be engineered and porous structures can be designed according to the requirements. Therefore, the whole nanotechnology toolbox can be exploited. Furthermore, graphene can be functionalised with other molecules due to many active sides. Hence, many different hybridization approaches or pseudo-supercapacitors are possible.

Currently, there is no major supercapacitor manufacturer located in Europe. There is a risk for Europe of missing the opportunity and slide into a situation like in other energy application technologies, where the technology value chain is already very much settled particularly in Asia, and partially in North America. There are, however, first supercapacitor manufacturers and related material producers in Europe. It appears highly necessary to support the development of a European eco-system and value chain in order to seize the opportunity of this less established technology.

Table 34: Assessment of market and technological potential of graphene/2D materials use in batteries on a scale - -, -, 0, +, ++.

Role of graphene	**Current technological potential (USP)**	**Market potential (EU perspective)**
Supercapacitor electrodes	++	++
Pseudo-supercapacitor electrodes	++	++

3.5 Photovoltaics

The photovoltaics (PV) technology is divided in three different technology generations:

1st generation is particularly based on crystalline-silicon (c-Si) solar cells. This technology generation dominates the photovoltaics market with about 90% market share [253]. One of the most relevant key figures of PV technology is energy conversion efficiency. Today, 1st generation solar cells reach the highest efficiencies with 25 % of all the three technology generations [254]. In 2014, the costs for the related PV systems were < € 1/Wp [255]. Even costs of $ 0.59/Wp are reported [253]. Even though the prices have already dropped significantly, the trend in the PV market towards reduction of costs continues. But it is not only about module and system related costs, also cost drivers like installation and maintenance play a significant role [256]. This has to be taken into account when the different technologies are compared.

2nd generation photovoltaics is based on thin-film technologies. Particularly, CdTe solar cells represent this technology with an overall market share of 5-15 % [253, 257]. The aim of 2nd generation solar technology is the reduction of material costs, because smaller amounts of materials are needed. Moreover, the technology aims at decreasing the production costs. Low cost deposition techniques like printing and electro deposition are feasible. Today, CIGS, a specific 2nd generation technology, reaches already a production cost level of < € 0.5/Wp. A drawback of 2nd generation technology is a lower efficiency than 1st generation, reaching about 22 % [258]. The long term perspective of 2nd generation PV is unclear as the International Energy Agency reported the market share shrank from 15 % in 2009 to 10 % in 2013 [253]. But besides today's classical roof-top applications, 2nd generations might play a role for flexible and light weight solutions as well as in building integrated PV.

3rd generation photovoltaic encompass:

- dye sensitised solar cells (DSSC)
- organic photovoltaics (OPV)
- quantum dot photovoltaics (QDPV)
- perovskite photovoltaics

3rd generation photovoltaics is driven by further cost reduction trends and use of more abundant materials. Production processes should be industry friendly and materials should be low cost. In addition to that, new applications are possible as e.g. some 3rd generation technologies allow flexible devices. Moreover, dim lighting and indoor applications can be implemented as these types of solar cells usually perform better under indirect/diffuse and low light conditions. That recommends 3rd generation for consumer electronics. A promising new field of applications are off-grid applications, e.g. in the internet of things (IoT). As most 3rd generation solar cells can be made (semi-) transparent, also new building integrated photovoltaic concepts might be realised in the future [259]. Today, 3rd generation photovoltaic technologies are in an early stage and still show low efficiencies with <15 %. Only perovskite PV has reached efficiencies of > 20 % [254]. But this young technology is far from being used commercially.

3.5.1 Market perspective: graphene/2D materials in photovoltaics

In 2013, the global photovoltaic market was about $ 96 billion [253]. A further increase up to $ 137 billion is expected for 2020 [256]. Frost & Sullivan even calculates for 2020 with $ 179 billion [260]. Until then, there will be a two digit annual growth rate for this sector [256]. Even though Europe still represents one fifth of the global photovoltaic market (s. Figure 34), for the future it is expected that lead markets will be in China and India due to beneficial solar irradiation in these regions [255, 256].

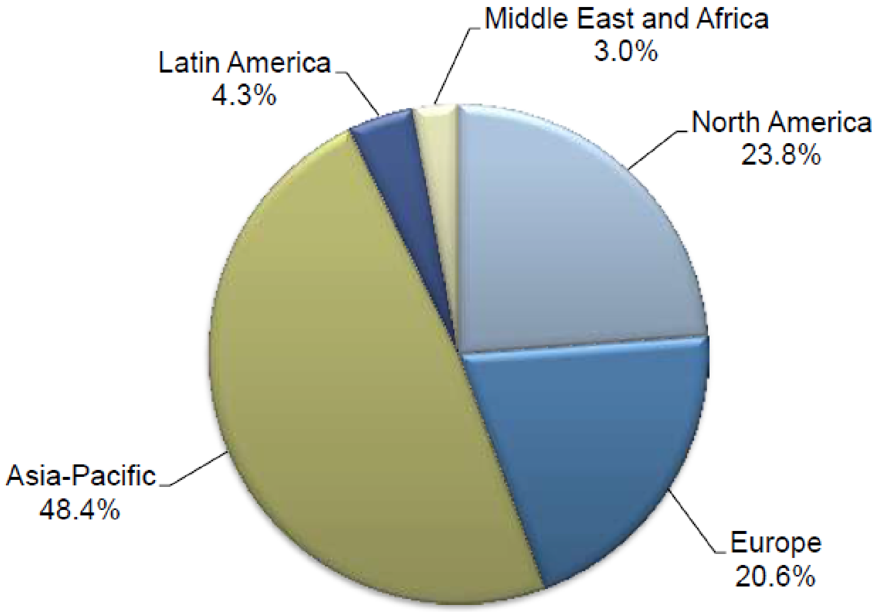


Figure 34: Total Solar Power Market: Per Cent of Revenue by Region, Global, 2015 (source: [260])

In addition to that, manufacturing has already shifted towards China, due to lower production costs and also unfair pricing advantages of Chinese companies. Therefore, between 2008 and 2014 several US and European manufacturers have declared bankruptcy [261]. Today, according to analysts, all of the top ten PV manufacturers are located in China or Taiwan [262]. Frost & Sullivan also mentions for the major market participants of the solar power market some companies from other regions [260]:

- Trina Solar (CN)
- Canadian Solar (CA)
- Jinko Solar (CN)
- JA Solar Holdings (CN)
- Hanwha Q Cells (KR)
- First Solar (USA)

- Sharp Solar (JP)
- Yingli Green Energy (CN)

Even though major industrial players are located in China, the engagement in transnational patenting of next generation solar technologies is low in that region (s. Figure 35 and Figure 36). The data underpins the conclusion that China challenges the field by increasing scientific activities: The number of Chinese publications has more than doubled in recent years and today the country shows the worldwide highest amount of publications for 3rd generation PV.

Patent and publication data allow another relevant clue with regard to the interest of industry in 2nd and 3rd generation PV: Initially, the technologies stirred a lot of attention in the industry, indicated by an extraordinary high transnational patenting activity – in Japan and the USA the number of transnational patents even exceeded significantly the number of publications. This is no surprise as the related technologies particularly aim at cost reduction, a very relevant issue for industry. But the high engagement of industry and the patenting has dropped significantly. This is particularly the case for 2nd generation PV in the USA and Japan (Figure 35). A reason for that might be the decreasing economic engagement in solar technology in these countries.

Despite the decreasing engagement of industry-oriented stakeholders, the academic attention on the issue of next generation solar technology is still unabated – not only in China. With more than 25,000 publications between 2012 and 2014 the amount has surged by 55 % compared to the period before.

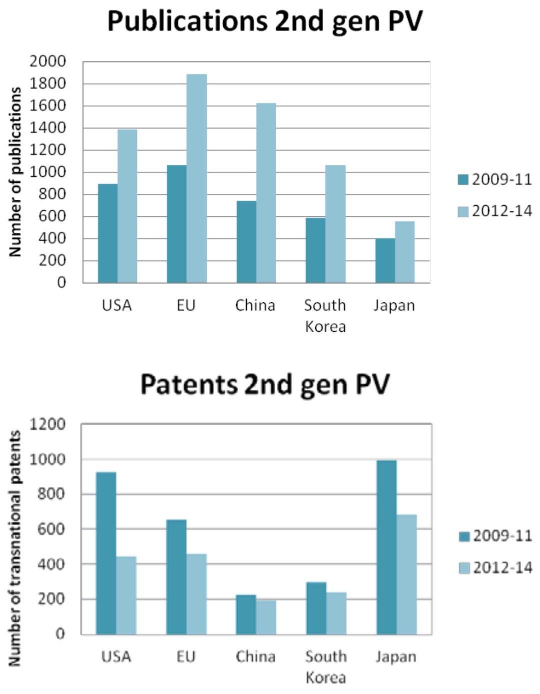


Figure 35: Publications and transnational patents in 2nd generation solar technology. [21, 164]

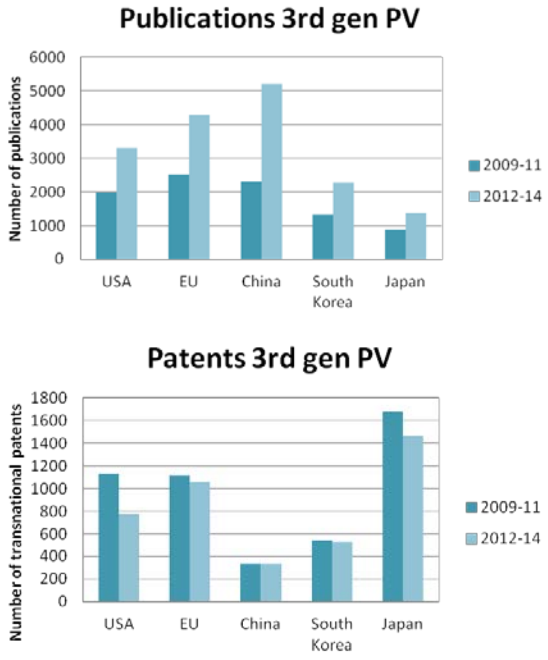


Figure 36: Publications and transnational patents in 3rd generation solar technology. [21, 164]

3.5.1.1 Role of graphene/2D materials in photovoltaics

The theoretical advantages of graphene for solar cells are particularly the transparency and high conductivity , combined with its universal applicability, originating from the tuning of the optoelectronic properties through functionalization. Hence, in all generations of solar cells graphene might be taken into consideration as transparent conductive electrode. For building integrated solar cell applications, (semi-) transparency is relevant for both electrodes. Hence, it can be also used as platinum free counter-electrode in 2nd and 3rd generation solar cells. Perovskite solar cells, integrating transparent conductive electrodes based on graphene, reached an efficiency of 12 % [263].

In dye sensitized solar cells and organic PV graphene can play a role as photosensitizer for light harvesting. Graphene with tunable work function can be used as a universal buffer layer in OPVs [264] and perovskite solar cells (PeSCs) [265] for charge transport. and can replace e.g. PEDOT:PSS [266]. In perovskite solar cells it can be used for charge collection and transport. Related graphene-based perovskite solar cells reach an efficiency of >18% at lab scale [267], and 12.6% on 50cm^2 active area, [268] and are produced by low temperature processing (< 150 °C). This allows cost reduction in the manufacturing process [269].

- In dye sensitized solar cells graphene can be used as counter-electrode instead of platinum. In this case the high specific surface area (SSA) of graphene is beneficial.
- Moreover, graphene can build a barrier for moisture. As for perovskite solar cells, a monolayer of graphene might be used for encapsulation.

- Even though the scientific community is very much engaged in next generation PV (s. 3.5.1), graphene is not in the centre of research interest: In 2nd generation PV graphene plays a role in 4 % of the publications; in 3rd generation PV it is almost 7 %, after all (for comparison: in supercapacitor technology about 50 % of all publications are related to graphene).
- The use as power bars/connectors in 1st generation PV (conductive inks) is highly debatable, as the used inks already perform well and graphene inks currently do not perform well enough. For further considerations on conductive inks please refer to chapter 4.6 Flexible and/or printed electronics.

Table 35: Recent reviews related to photovoltaics applications of graphene/2D materials.

Topic	Reference
Graphene/2D materials for energy conversion and storage	[204]
Graphene/2D materials for dye sensitized solar cells	[270]
Graphene/2D materials for solution processed solar cells	[266]

3.5.1.2 Market Opportunities

3.5.1.2.1 Potential of price reduction by 2nd and 3rd generation PV

The prices for PV power generation are expected to decrease continually. Frost & Sullivan expect a price of $ 0.5/kW [262] in 2020. This steady price fall will support technology concepts with potential for cost reduction. Both 2nd and 3rd generation solar cells are particularly developed to decrease module costs. Beside material costs and material consumption – as for 2nd generation PV –, the production process is vital for the overall costs. Therefore, for 2nd and 3rd generation PV it is crucial that the production process is industry friendly. Making e.g. easy roll-to-roll processes available for PV manufacturing is an attractive advantage of 3rd-generation PV. Graphene might contribute to these improvements.

3.5.1.2.2 Perovskite solar cells with high efficiency and new properties

Because of high efficiency, perovskite solar cells enjoy a high attention recently. Within the family of 3rd generation solar cells, in 2014 this new technology concept has caused a leap in efficiency up to 22.1% [258] – and there is still room for advancements. These cell efficiencies are already comparable to 2nd generation photovoltaics. The high-efficiency can be reached despite cheap materials and manufacturing processes [257]. The perovskite solar cells can be produced in wet chemistry processes and at low temperature, therefore they are usable for roll-to-roll processes. The final costs, announced for semi-transparent perovskite solar cells are $ 0.06/W, which is 50 % lower than the one for Si solar cells [271]. Moreover, the cells allow new application areas, similarly to other 3rd generation cells, due to [257]:

- flexibility
- semi-transparency
- tailored form factors
- thin-film
- light-weight

3.5.1.2.3 New application areas for PV beyond classical roof-top modules

2nd and particularly 3rd generation PV is suitable for light weight, wearable, and flexible solutions. This opens the field for new off-grid applications. Moreover, 3rd generation PV allows the exploitation of dim lighting and indoor conditions, because these cells do not lose power dramatically under shade and variable light conditions [272]. These characteristics are making 3rd generation PV suitable for consumer applications and new Internet-of-things (IoT) related tasks (see also chapter 4.6 Flexible and/or printed electronics for further considerations on flexible applications).

3.5.1.2.4 Building integrated PV

The 2nd and 3rd generation of solar cells allows new ways of adapted integration of PV technology in buildings. This so-called building integrated photovoltaic (BIPV) is different to c-Si-based photovoltaics. With the modified modules it is possible to integrate photovoltaics in the facade, the roof tiles [273] and even in windows – as semi-transparent solar cells are concerned. Even though, the efficiency today does not reach the level of Si-based solar cells, the BIPV approach promises a relevant contribution to European energy supply. The boom of BIPV has been expected for a while but still has not taken off [274]. However, the BIPV concept might open up an opportunity for relevant revenues in Europe [275]: It allows new architectural design concepts, which require customisation. That offers new opportunities for different parts of the value chain and it can be expected that relevant parts of value creation will remain near the point of use.

3.5.1.3 Market Threats

3.5.1.3.1 Potential cool down of perovskite PV-hype

The technology readiness level of particularly the perovskite technology is still very low, as it is still very young. The technology is expected to be commercialised not before 2020. The current hype, based on the very promising properties of the perovskite cells, is in danger to cool down when major implementation problems occur. Already now, major issues are under investigation on larger scale: Perovskite solar cells are criticized due to their lead contend; the long-term stability is an issue; and scaling up shows significant problems [257]. In the worst case graphene activities might be affected, regarding both lost research investments and image. However, the recent developments in terms of stability of perovskite cells are promising and these advancements mitigate this threat. [276, 277]

As graphene addresses several of these issues (e.g. stability and manufacturability), it can become an enabler and mitigate this threat or even turn it into an opportunity for graphene as a potential large scale application. But there are also other technologies/materials addressing these issues, such as in above mentioned references (e.g. fluoropolmers and rubidium cations).

3.5.1.3.2 Continuous cost reduction in 1st generation PV

Costs are the most relevant issue for 1st generation solar cell market. The global market share is more or less directly related to costs. The price of c-Si-based PV has experienced a significant decrease in the recent years. And it is expected that this crumbling of prices will continue in the coming years – not particularly because of 2nd and 3rd generation PV, but because of improvements in c-Si-based PV. Hence, the price advantage of second and third generation solar cells – with and without graphene – shrinks. Therefore, a purely price driven approach will not be feasible but applications need to be targeted where the USPs towards c-Si are high.

3.5.1.3.3 Scepticism against solar technology investment due to the "trauma" of lost Si-PV production

From 2009 to 2014, 1st generation PV has experienced a rapid shift of manufacturing capacities from Europe and the US to particularly China [262]. Today, the manufacturing is highly dominated by Chinese and Taiwanese companies [253]. This devastating loss of production capacity in the area of solar cells has caused scepticism against supporting next generations of photovoltaic technologies. To make bad things worse, particularly China and India are the most promising markets for photovoltaics due to beneficial solar irradiation [256] – and it is often reported, that production follows markets.

3.5.1.3.4 Low efficiencies of dye sensitized solar cells and organic PV

Dye sensitised solar cells (DSSC) and organic PV (OPV) are suffering from low efficiencies (OPV: 11.1 %; DSSC: 11.9 % [254]). As for dye sensitised solar cells, it is expected that the figures will not improve significantly any more. The low efficiency combined with the disadvantage of liquid electrolytes turned relevant industry stakeholders to abandon the technology and recently change over to particularly perovskite technology.

Better low light efficiency and building integrated PV, however, is still a valid business case for this technology, which might be even pushed by internet of things developments.

3.5.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in photovoltaics

3.5.2.1 Current strengths for graphene/2D materials use in photovoltaics

3.5.2.1.1 Transparent conductive electrode for flexible PV

Basically, graphene can be used in transparent conductive electrodes (TCE) of solar cells in all three generations. Today, fluorinated tin oxide (FTO) or indium tin oxide (ITO) are state of the art for the related applications. But, because the former is brittle and the latter is based on rare materials, potentially expensive in the future and also not very mechanically flexible, there is pretty much research done to replace them [278]. Graphene is discussed as one candidate among others – like metal meshes and silver nano-wires – for future transparent conductive electrodes. In the end also combinations of graphene and silver nano-wires might replace ITO [279]. In general, graphene-based TCEs have some generic advantages:

- A particular advantage of graphene as TCE is that the material can be used in flexible applications – in contrast to FTO.
- Graphene based TCEs show good optical transmission properties. Hence, they might be used in (semi-) transparent solar cells.
- Particularly, for 2nd-generation PV, graphene based TCEs are interesting because they can be implemented in high temperature thin-film processes.
- As for dye sensitised solar cells, graphene might be an interesting alternative to silver nano-wires as TCE because it is resistant against corrosion caused by halides, commonly used in the technology approach.

For further information on transparent conductive films, please refer also to chapter 2.3 Industrial large scale coatings and paints and for flexible TCFs particularly to chapter 4.6 Flexible and/or printed electronics.

3.5.2.1.2 Good results for charge collection layers in perovskite solar cells

Graphene shows very good charge collecting properties in perovskite solar cells. Graphene nanoparticles (GnP) can increase the efficiency of related solar cells [269]. Also, few-layer graphene (FLG) flakes incorporated in titanium dioxide-nanoparticles can be used as electron collection layer [204]. The related perovskite solar cells show – for 3rd generation PV – a remarkable efficiency of 19.5% [280]. Graphene oxide exhibits an even better performance regarding charge collection and is more transparent than graphene, but it is less conductive [278]. Interface engineering performed with Graphene and 2D related materials shows a viable role in improving both the performance and stability of perovskite solar cells. In particular, n-rGO was demonstrated as additive into the perovskite layer of perovskite solar cells (reaching PCE of 18.7%). [281] rGO was demonstrated as an additive in the PCBM electron transport layer of planar inverted perovskite cells, resulting in a PCE of 14.5% [282]. rGO also showed improvements in the TiO_2 of mesoscopic perovskite cells resulting in PCE of 19.5% [280].

As graphene addresses some of the current issues of perovskite solar cells, it can be seen as a potential enabler of this technology, making it more feasible for commercialisation. In proof of that, GRMs were used to “on-demand” tune the interface properties of perovskite solar cells, enabling the realization of large area (active area 50.6 cm^2) perovskite-based solar modules achieving the highest efficiency PCE of 12.6% for a perovskite solar module with >30 cm^2 active area to date. [268]

3.5.2.1.3 Hole transport layer in OPV with tolerance to moisture and good processability

As hole transport material (HTM) in organic photovoltaics graphene can replace PEDOT:PSS. Compared with PEDOT:PSS, graphene is not hygroscopic [204]. Like PEDOT:PSS, graphene-based materials are compatible to roll-to-roll processes and do not require vacuum techniques for deposition, as inorganic hole transport layers do. Graphene can also be deployed as electron transport layer (ETL).

However, best film qualities are only realized with high quality films, which need to be transferred to the substrate. Thus, the assessment of wafer scale integration applies (4.2 Electronics: Cross-cutting issues), although the requirements are potentially lower.

3.5.2.1.4 Increased durability of perovskite solar cells by graphene/2D materials

Due to the inert properties, graphene/2D materials are distinguished by a high resistance against corrosion. This together with the tunable work function recommends the material for being a universal and protecting buffer-layer. In perovskite solar cells graphene and other 2D materials and composites thereof have been used for this purpose increasing stability and efficiency of the cell [267, 283, 284]. This prevents the entrance of moisture and reduces internal degradation through heating and, by this, increases the durability of the system. Therefore graphene and 2D materials can enable a better stability as one of a few potential options, addressing a major barrier of perovskite technology.

3.5.2.1.5 Industry friendly processability of graphene-based materials

The processability of graphene materials fits to standard processes used in 2nd and 3rd generation PV. The materials are processable in cheap procedures, no cleanroom is necessary and rather simple wet chemistry technologies can be used. Also it is suitable for roll-to-roll processes. Solution-based techniques or vapour-deposition, suitable for graphene-based materials, have the advantage that they are more or less easy to scale up. Printed and graphene flake based processes are easier to scale up as higher quality CVD films that need to be transferred. Indeed, the development of graphene-based PV is in a very early stage, but until now, the available graphene quality appears high enough.

3.5.2.2 Current weaknesses and challenges for graphene/2D materials use in photovoltaics

3.5.2.2.1 High resistivity of graphene-based transparent conductive electrodes

Even though some properties of graphene as transparent conductive electrode are superstitious than the incumbent ITO (see also chapters 3.5.2.1.1 and 4.6), and graphene materials have the advantage of being highly transparent, the insufficient conductivity of the today’s graphene materials is a relevant drawback. The sheet resistance of ITO is <20 Ω/m^2 and solution processable graphene material are said to be far from that (at similar transparency). Even if the conductivity is increased by using more graphene layers, this would have a negative effect on the transmission. Other alternative approaches, for instance doping, need to be controlled and endurable. Hence, it is disputed if the conductivity and transparency, combined with manufacturability, stability, economical feasibility and compatibility can in principle reach required levels.

Moreover, silver nanowires and metal meshes are discussed as current technologies of choice for ITO-replacement. The related technologies already show high technology readiness levels. The only drawback for silver nano-wires is applications where halides are used, like in dye sensitised solar cells, as they are inclined to corrode.

3.5.2.2.2 Very early stage of 3rd generation PV: weaknesses still veiled

3rd generation PV development is still partially in an early stage – particularly in the perovskite solar cell technology. Even though graphene materials have shown interesting properties for related technology concepts, the production implementation – or even the commercialization – is not broadly addressed yet. Therefore relevant weaknesses are still unclear and might come up during the implementation phase. For example, in process developments of second-generation PV, the production of large surfaces with graphene materials has caused degradation of electric properties. It is to be expected that comparable problems might occur in 3rd generation process development too, when they are transferred to pilot production and mass manufacturing.

3.5.2.2.3 R&D focus on other issues than graphene

As mentioned, the basic technologies with regard to 3rd generation PV are in an early stage of development. The main research effort is put in basic problems of the technology as such, e.g. in dye sensitised solar cells rather the redox couple is a fundamental issue of industrial research. If any, these fundamental tasks are in the focus of the research budgets of companies engaged in the 3rd generation technology deployment. Graphene related research appears to have a low priority in PV industry. Accordingly, less than 4 % of transnational patents in 2nd and 3rd generation PV are related to graphene.

3.5.3 KPIs for photovoltaics

Most often used KPI for photovoltaics technologies is the energy conversion efficiency [%]. Moreover the price per peak power [$/Wp] plays a relevant role.

For indoor energy harvesting or at low light conditions (application areas like Internet of Things (IoT) or Wireless Sensor Networks (WSN)) – additional criteria are relevant for the performance assessment of photovoltaic technologies:

- life-time
- size in relation to performance (form factor advantage)
- flexible, wearable
- light weight

Table 36: Typical KPIs for photovoltaics applications.

	Unit	Description	Literature
	Ω/□	**Sheet resistance (R_s)** KPI for transparent conductive electrodes Always with regard to transmittance (TR)	
< 10	Ω/□	Requirement for transparent conductive window in PV systems	[204]
~30	Ω/□	Graphene-based TCE (via doping) (@TR ~90%)	[204]
~20	Ω/□	Graphene-metal grid TCE (@TR ~90%)	[204]
	%	**Transmittance (TR)**	

	Unit	**Description**	**Literature**
		KPI for transparent conductive electrodes Always with regard to sheet resistance (R_s)	
> 90	%	Requirement for transparent conductive window in PV systems	[204]
	%	**Energy conversion efficiency** KPI to compare photovoltaic technologies	
~25	%	1st generation PV (c-Si)	[258]
22-23	%	2rd generation PV (CdTe, CIGS)	[258]
		3rd generation PV	[258]
11.5	%	Organic PV (OPV)	
11.9	%	Dye sensitized solar cells (DSSC)	
22.1	%	Perovskite solar cells	
12	%	Perovskite solar cells with graphene based TCE	[263]
13.5	%	2nd generation (CIGS, 45 mm² cell with graphene TCE)	[285]
18.2-19.5	%	Perovskite solar cells with graphene material interlayer and/or doping	[267, 280]
	$/$W_{DC}$	**Costs**	
		CIGS (@14% module efficiency)	[286]
0.56	$/$W_{DC}$	Manufacturing costs	
0.72	$/$W_{DC}$	Sustainable price	
< 0.4	$/$W_{DC}$	Potential for cost reduction (long term)	
	$/$W_p$ €/W_p		
0.59	$/$W_p$	PV system	[253]
0.48–0.56	$/$W_p$	silicon heterojunction (SHJ) solar cells	[287]

	Unit	Description	Literature
0.50	$\$/W_p$	conventional c-Si module	[287]
< 0.5	€/W_p	2nd generation solar cells (CIGS) (= < 0.55 $\$/W_p$)	
0.38	$\$/W_p$	Target for solar PV modules (according to Frost&Sullivan)	[260]

3.5.4 Roadmap for photovoltaics

3.5.4.1 Current maturity: ‘Mostly lab stage research’

Graphene use in photovoltaics is currently mostly at the lab stage. Some applications already are in the applied research stage, such as transparent conductive electrodes. However, despite the advancements in recent years, there is still no actual application close to market and not much advancement has been reported in recent years. As regards to 3rd generation photovoltaics, graphene has some advantages when it comes to corrosion resistance and flexibility. However these types of solar cells are themselves not yet commercialized or are currently at the pilot production scale. In the most commercially advanced 3rd generation PV applications, graphene plays no role so far. The focus is rather on improving existing and already used materials. Still chances are there that graphene might play a role in 3rd generation PV in the future, especially as some lab scale demonstrations are promising (e.g. use in perovskite cells). Moreover, graphene and 2D materials could enable or support hybridization of various 3rd generation PV (especially OPVs with perovskite PV) in tandem and integrated structures.

3.5.4.2 Barriers/challenges (summarized)

2nd generation PV

- Drastically downturn in 2nd generation PV production
- Integration as TCE and elaboration of actual USP compared to other upcoming technologies and the incumbent ITO
- Cost reduction as major argument for 2nd and 3rd generation PV while cost of 1st generation PV decreases continuously and is hardly beatable

3rd generation PV

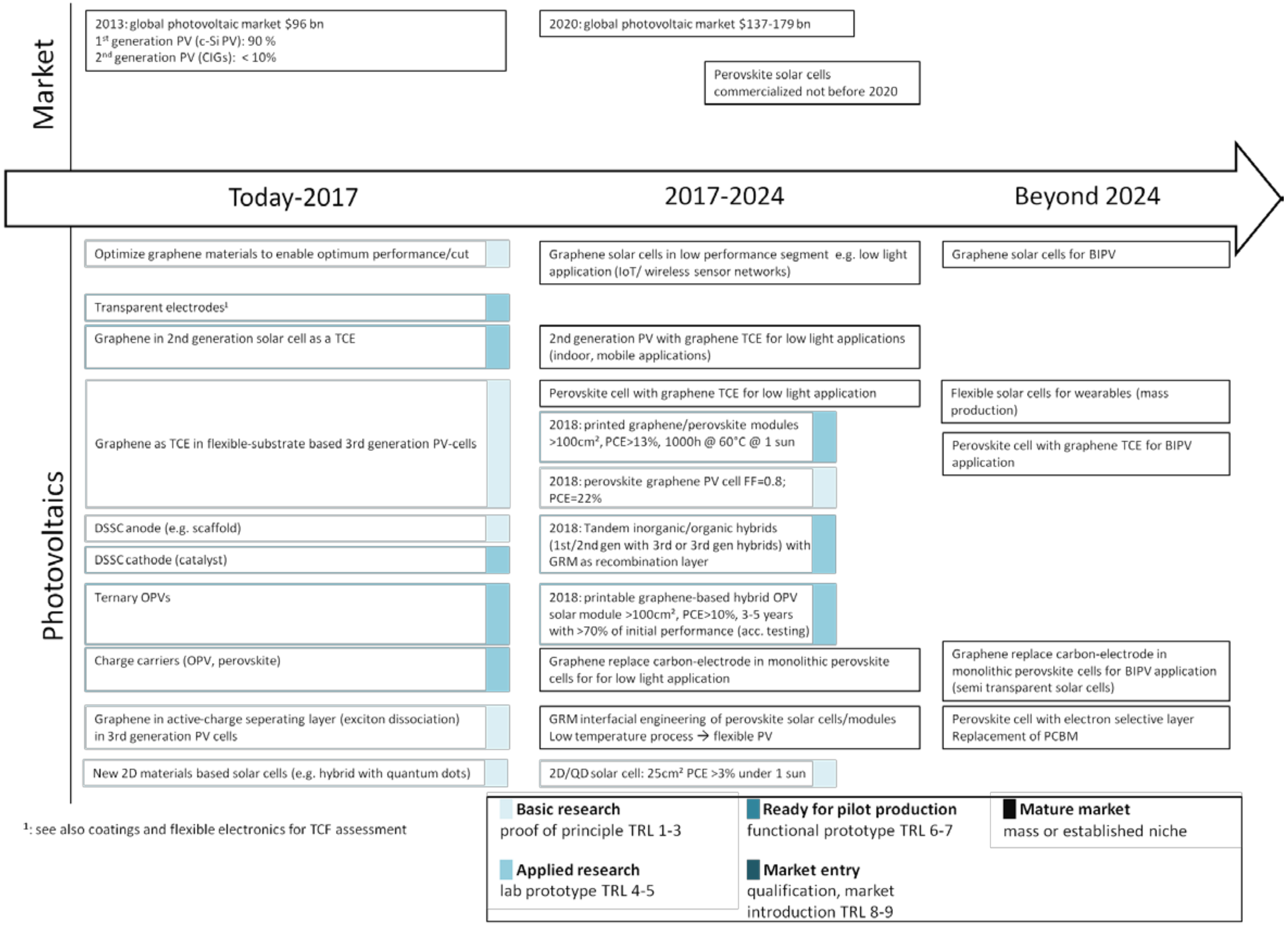
- Reduce cost to compete with 1st and 2nd generation
- Low power conversion efficiency or reliability/long term stability
- USPs compared to 1st generation PV
- Actually industry friendly and scalable processes
- European value chain?

3.5.4.3 Potential actions

If the area of graphene/2D in PV applications is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

- Continuous monitoring of European economic potential and role in photovoltaics manufacturing
- Continuous monitoring of performance in alternative technologies (e.g. silver nanowires, metal mesh)
- Engage with PV community and test under industrially relevant conditions
- Elaborate value added and USPs of 2nd and 3rd generation photovoltaic solutions compared to 1st generation PV (new application areas, building integrated PV)
- Address feasible processes for integration compatible with common production techniques
- Investigate graphene's influence on long terms stability and other deficiencies of 3rd generation PV
- Upscaling of 3rd generation PVs, utilizing GRM inks for large area/throughput, when feasible
- Explore GRM as cross-linking layer (intermediate recombination layer) for hybrid tandem and integrated structures to reach higher efficiencies

3.5.4.4 Roadmap



Market

2013: global photovoltaic market $96 bn
1st generation PV (c-Si PV): 90 %
2nd generation PV (CIGs): < 10%

2020: global photovoltaic market $137-179 bn

Perovskite solar cells commercialized not before 2020

Today-2017

2017-2024

Beyond 2024

Photovoltaics

Optimize graphene materials to enable optimum performance/cut

Transparent electrodes[1]

Graphene in 2nd generation solar cell as a TCE

Graphene as TCE in flexible-substrate based 3rd generation PV-cells

DSSC anode (e.g. scaffold)

DSSC cathode (catalyst)

Ternary OPVs

Charge carriers (OPV, perovskite)

Graphene in active-charge seperating layer (exciton dissociation) in 3rd generation PV cells

New 2D materials based solar cells (e.g. hybrid with quantum dots)

Graphene solar cells in low performance segment e.g. low light application (IoT/ wireless sensor networks)

2nd generation PV with graphene TCE for low light applications (indoor, mobile applications)

Perovskite cell with graphene TCE for low light application

2018: printed graphene/perovskite modules >100cm², PCE>13%, 1000h @ 60°C @ 1 sun

2018: perovskite graphene PV cell FF=0.8; PCE=22%

2018: Tandem inorganic/organic hybrids (1st/2nd gen with 3rd or 3rd gen hybrids) with GRM as recombination layer

2018: printable graphene-based hybrid OPV solar module >100cm², PCE>10%, 3-5 years with >70% of initial performance (acc. testing)

Graphene replace carbon-electrode in monolithic perovskite cells for for low light application

GRM interfacial engineering of perovskite solar cells/modules
Low temperature process → flexible PV

2D/QD solar cell: 25cm² PCE >3% under 1 sun

Graphene solar cells for BIPV

Flexible solar cells for wearables (mass production)

Perovskite cell with graphene TCE for BIPV application

Graphene replace carbon-electrode in monolithic perovskite cells for BIPV application (semi transparent solar cells)

Perovskite cell with electron selective layer
Replacement of PCBM

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

[1]: see also coatings and flexible electronics for TCF assessment

3.5.5 Conclusion photovoltaics

Graphene is discussed as transparent conductive electrode TCE for all generations of photovoltaics (see also 2.3 Industrial large scale coatings and paints for further considerations regarding TCF) as alternative to fluorine tin oxide (FTO) or indium tin oxide (ITO). The assessment of graphene-based TCE is ambiguous: Either the conductivity or the transmittance has shown to be not sufficient. Moreover, there are more mature alternative candidates like metal meshes and silver nano-wires to replace ITO. Only with regard to robustness graphene shows a better performance than silver nanowires. Graphene-based TCE, however, might be advantageous in niches like flexible and semi-transparent photovoltaics.

Today, the major players for the production of 1st generation photovoltaics (silicon-technology) are located in China. Graphene is not expected to cause a technological step change in this technology. That means neither from an economic nor from a technological perspective strong engagement in this area make sense. 2nd and 3rd generation photovoltaics are particularly developed to lower module prices by decreasing production costs. In some tasks graphene can make a difference in these technologies. But the market perspective of the younger PV technology generations is still unclear: the price distance to 1st generation PV shrinks. Hence, particularly, 2nd generation has lately shown a step backwards with regard to market shares. Moreover, particularly western industry rather back down from the next generation PV technologies. In academia, 3rd generation perovskite solar cells are highly valued as future photovoltaic technology, due to promising results regarding efficiency. As for market attractiveness, the related technology might be used in the future for building integrated PV, wearable and moblile applications, windscreens for automotive industry, self-powered devices for IoT, etc.. It is important to focus on the USPs of the technology and not only claim that it will be cheaper than Silicon photovoltaics. The latter can be doubted anyways, especially for a new technology, and interesting areas are the ones where Silicon cannot be used. This might bear an industrial potential for Europe, as some of the main academic and industrial actors on perovskite solar cell and 3rd generation PV commercialisation are located here.

From a technological perspective, graphene shows promising properties for charge collection in perovskite modules. Accordingly the concentration on 3rd generation, and particularly perovskite solar cells appears reasonable.

Table 37: Assessment of market and technological potential of graphene/2D materials used in photovoltaics on a scale - -, -, 0, +, ++.

Role of graphene	Current technological potential (USP)	Market potential (EU perspective)
Transparent conductive electrode	-	-
2nd generation	0	-
organic solar cells (bulk heterojunction)	+	0/+
dye sensitized solar cells	+	--
perovskite solar cells interface engineering and protection	+	+

3.6 Summary Energy

Graphene applications in energy vary from fuel cells, hydrogen generation and (gas) storage, batteries, supercapacitors to photovoltaics.

The fuel cell market is dominated by Japanese companies and the future role of fuel cells in Europe, be it stationary or mobile, is not clear yet. One of the main barriers for fuel cells for transportation is the missing fuelling infrastructure. This unclear market situation for Europe and the missing integrators reduces the macroeconomic potential of graphene research for fuel cells. Graphene can be used to reduce the Pt catalyst content, e.g. as catalyst support or as active material. It is also discussed as membrane, but this technology is still at early the lab stage and less mature as the use as catalyst support. From a European innovation perspective it is not the most interesting energy application. Hydrogen storage and generation on the other hand are more interesting, as the integration into storage systems is more promising and the market prospects and vision for a Europe with an energy system based on renewables is clearer.

The current lithium ion battery cell production, i.e. potential integrators of graphene technologies, is dominated by non-European companies. The European perspective on graphene innovation for this type of batteries is not so attractive, as European actors are only active in niche markets. Although the European automotive industry will need batteries and can benefit from graphene innovation, the graphene integration occurs in the battery cell production. In lithium ion batteries, graphene can be for instance used as an additive to electrodes. The usage of graphene in that area poses a low technological barrier, but also no large improvements. It appears that graphene has a somewhat negative image in the European battery community. A more promising field for European graphene innovation is in 4th generation batteries (lithium-sulphur, lithium-air, and redox-flow batteries) and flexible batteries, which are expected to enter the market beyond 2030. Because these markets and the related battery production is not yet existing on large scale or dominated by a country, there is still a chance to enter.

The area of supercapacitors is the energy application area where graphene enabled innovations are closest to the market. It is one of the most interesting fields for graphene innovation for energy due to the strong added value and ease of integration. The results are promising and there is still room for improvement. However, the mass market for supercapacitors does not exist yet, because the technology is not competitive with batteries in terms of storage capacity. There are some special applications and first markets in special areas. From the integrator perspective, there is no dominating industry yet and Europe is still in the race. Therefore, further research, development and ecosystem development is highly recommendable. This could also become a real success case and advertisement for graphene.

The area of photovoltaics is strongly dominated by silicon-based 1st generation PV from China, with low and still declining prices. The 2nd generation PV market share is declining, although the technology never really took off. From a European macroeconomic perspective it is less favourable to address 1st and 2nd generation PV with graphene developments. The 3rd generation is currently entering the market (e.g. OPV) in niche markets with some European players. Perovskites are currently under strong investigation and appear to be promising. The market perspective for 3rd generation PV is still unclear and despite the expectations of large building integrated PV markets, it has not reached beyond large scale demonstration and niche applications yet. It is important to strengthen the USPs of 3rd generation PV with graphene developments in applications where Si cannot be used. Cost reduction alone is no argument for 3rd generation PV, because cost only will become competitive (if ever) with 1st generation PV after a large scale production is established. Potential graphene applications for all PV generations are graphene as transparent electrode but other solutions appear to be better. Only in flexible areas some advantages are possible. Besides the use as TCE, for perovskite and other 3rd generation PV, graphene can address some of the current drawbacks and appears therefore particularly interesting, e.g by interfacial engineering in hybrid and perovskite solar cells to improve efficiency and stability.

In summary, the most interesting application areas from a European innovation perspective for graphene innovation are supercapacitors and 4th generation batteries. Hydrogen production and storage are further interesting areas. In terms of photovoltaics, 3rd generation PV is more likely to become interesting on European level, with perovskites being the most promising application area for graphene.

Table 38: Summarized assessment table of all energy application areas primarily sorted by European market potential and secondary sorted by USP.

Role of graphene	**Current technological potential (USP)**	**Market potential (EU perspective)**
Supercapacitor electrodes	++	++
Pseudo-supercapacitor electrodes	++	++
Battery: electrode material for 4th generation batteries (e.g. LiS, Li-air)	++	++
Hydrogen/gas: Hydrogen generation (electrocatalyst)	+ ?	++ ?
Hydrogen/gas: Increased volumetric capacity of high pressure tanks	+	+
Battery: high-potential anodes	+	+
PV: perovskite solar cells interface engineering and protection	+	+
Hydrogen/gas: Low pressure tanks	+	+ (automotive: long-term ?)
PV: organic solar cells (bulk heterojunction)	+	0/+
Fuel Cells: Membrane	+	0
Fuel Cells: Replacement of noble metals in electrocatalysts	+	0 (long-term)
Hydrogen/gas: Hydrogen generation (membrane)	+ ?	0 ?

Role of graphene	**Current technological potential (USP)**	**Market potential (EU perspective)**
Fuel Cells: Reduction of noble metals in electrocatalysts	+	-
Battery: additive in electrodes	+	-
PV: 2nd generation	0	-
PV: Transparent conductive electrode	-	-
PV: dye sensitized solar cells	+	--
Battery: active anode material	0	--
Battery: bipolar plates of redox-flow batteries	+	?
Fuel Cells: Endplate	?	?

4 Electronics & Photonics

4.1 Potential Electronic & Photonics applications

Graphene and 2D materials have interesting electronic applications:

- Varying electronic band structures as metal, semi-metal, semiconductor and insulator
- Varying optical and optoelectronic properties
- strongly nonlinear optical properties in the whole electromagnetic wave spectrum, from RF to optical frequencies
- High electron mobilities
- Two-dimensional character being optimal for layered devices
- Large surface area and strong influence of surrounding on electronic properties are good for sensing applications
- Flexibility for flexible electronics
- Interesting properties for spintronics (e.g. long spin diffusion length)

The electronics and semiconductor industry currently sees two major directions, i.e. “More Moore” (miniaturisation) and “More than Moore” (diversification), see Figure 37. Graphene and 2D materials can play a role in both areas and in the combination of both, although a higher potential is currently seen in the More than Moore path. The various potential application areas of graphene/2D materials are summarized in Figure 38. The several application areas are covered in separate chapters. The assessment starts with a few cross-cutting topics and issues that are to a certain extent relevant for all electronics applications.

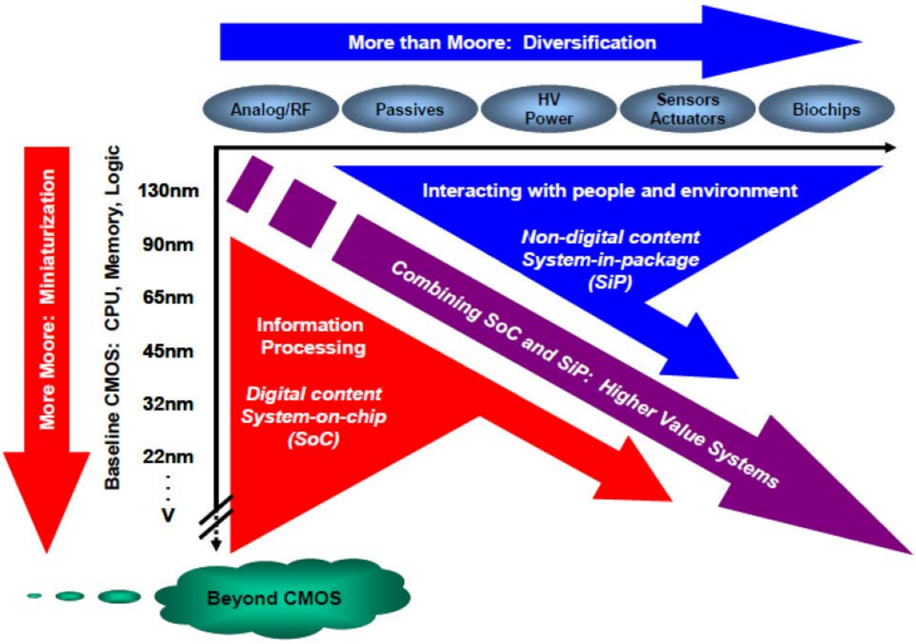


Figure 37: The major developments in the semiconductor industry towards miniaturisation and diversification as well as their combination in heterogeneous integration. [288]

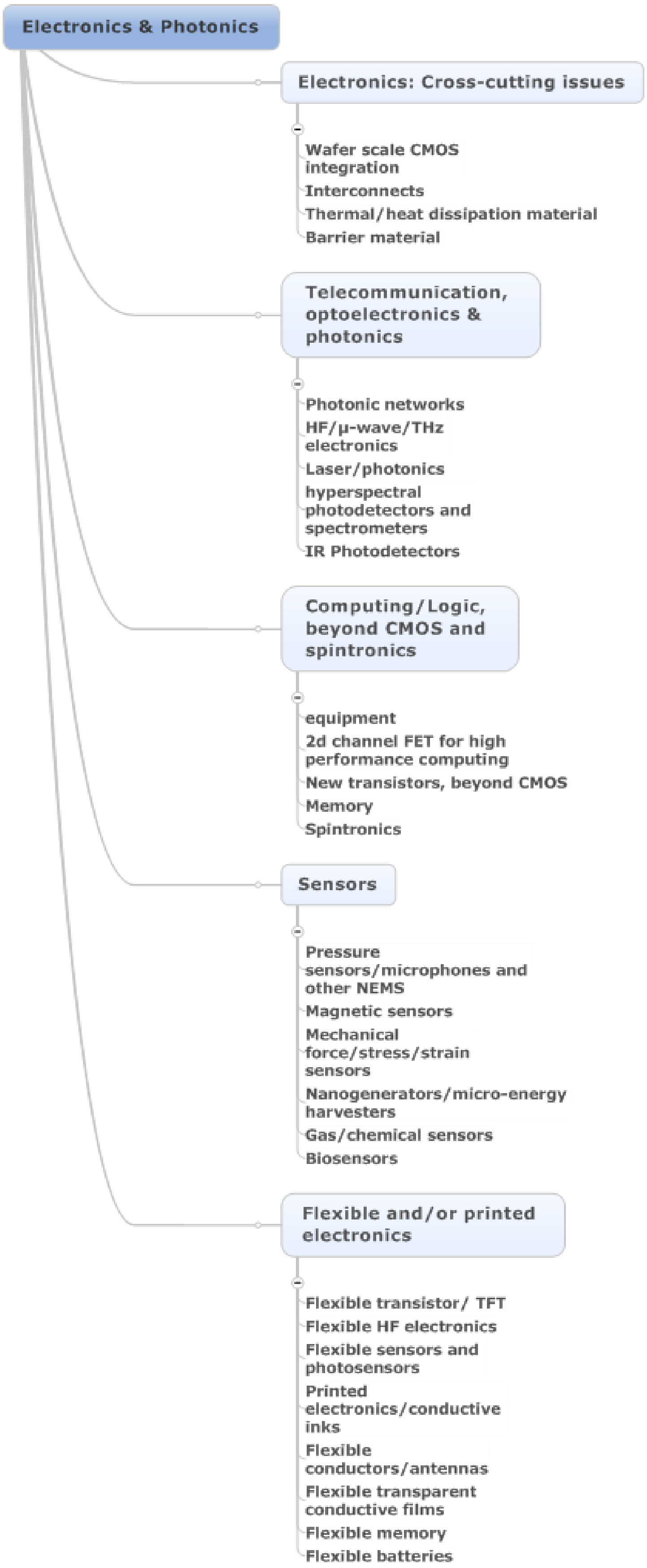


Figure 38: Application areas in the electronics and photonics domain.

4.2 Electronics: Cross-cutting issues

In the broad (Opto-)Electronics, Photonics and (Bio-)Sensing area several common issues with respect to the use of graphene/2D materials exist. This section covers the following identified common issues:

- General and common issues, i.e. issue related to the use of graphene/2D materials as (semi-)conductors and in the electronics industry in general.
- Wafer scale CMOS integration, i.e. integration of graphene/2D materials in standard CMOS processes, a prerequisite for many applications in the electronics industry.
- Interconnects, i.e. the use of graphene/2D materials in the back-end-of line for contacting between various semiconductor devices on a chip.
- Thermal material, i.e. use of graphene/2D materials as a thermal materials for heat removal and dissipation.
- Use as a barrier in electronics, i.e. to avoid diffusion of harmful substances into the semiconductors, e.g. metals from contacting.

The issues, opportunities etc. related to particular application areas will be presented in later chapters.

Table 39: Different cross-cutting electronics issues of graphene/2D materials and their functionalities.

Type of cross-cutting issue	Functionality
Wafer scale CMOS integration	• Laminate graphene on CMOS for specific functions, e.g. in optoelectronic transceivers, optical interconnects to reduce power consumption & increase speed • How to integrate graphene into MNE industry, large area, large scale
Interconnects	• Graphene as interconnects on chip and on package level
Barrier materials	• Graphene/2D materials as barrier material between different materials (e.g. via/interconnect and chip), probably combined with heat dissipation, interconnect or other active functionalities.
Heat dissipation material	• Graphene/2D materials as heat dissipation material for passive cooling, probably combined with other features such as barrier or interconnect or other active functionalities.

4.2.1 Market perspective: graphene/2D materials in the semiconductor and electronics industry

Worldwide semiconductor sales were $335.2 billion in 2015, expected to increase to $341 billion in 2016 and $352 billion in 2017 (CAGR of 2.5% 2015-2017). [289]

The product value generated in Europe with Micro- and Nano-electronics components was €17.8 billion in 2014 with a CAGR of –7.2% from 2012-2014. [39] In this area Europe is behind Asia and North America in terms of turnover (see Figure 39). European producers have roughly 10% of the global market share (USA 50%). [289] Looking at the broader picture of electrical and electronic engineering industries, including radio and telecommunications industries as well as wireless communication industries, the European gross output in 2012 was €703.3 billion, approximately 9.6% of all manufacturing gross output, and the industry produced €212.4 billion in 2012. It is recognized as one of the most competitive manufacturing industries in Europe by the European Commission. [290]

It is a goal of the European Commission to double the economic value of the semiconductor component production in Europe by 2020-2025. Europe has a strength in More than Moore technologies and special logic applications, e.g. for automotive and low power. It furthermore is strong in material, equipment, chip design and fabless activities, and system integration. 20% of the production of equipment and material is currently done in Europe and there is growth potential. [291] Only a very small share of classical PC and mobile phone processors and high performance processors are currently manufactured in Europe (Intel in Ireland and Globalfoundries in Germany, there are also some state of the art fabs in Israel), similar to storage media (RAM).

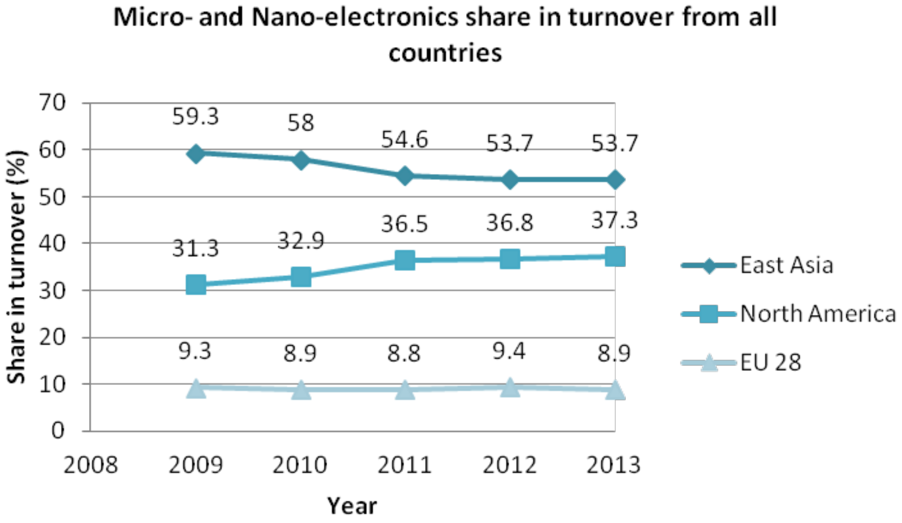


Figure 39: Share in turnover relative to all countries of micro- and nano-electronic goods. [292]

The value chains for semiconductor industry are truly global, which can be seen in Figure 40. The value creation is largest at the systems level. Graphene will be integrated at the semiconductor and material level, although it can have effects and enabling character along the value chain, see Figure 41. Europe is strong in vertically integrated markets, such as automotive, energy, security and smartcards. There are also certain strengths in industrial electronics and data processing electronics. [293] It possesses leading positions in sensors and MEMS markets (see 4.5.1 Market perspective: graphene/2D in sensors). Besides that, it has strengths in virtual components and low power processors, and in the supply of equipment, materials and IP (Intellectual Property) into the value chain. [291]

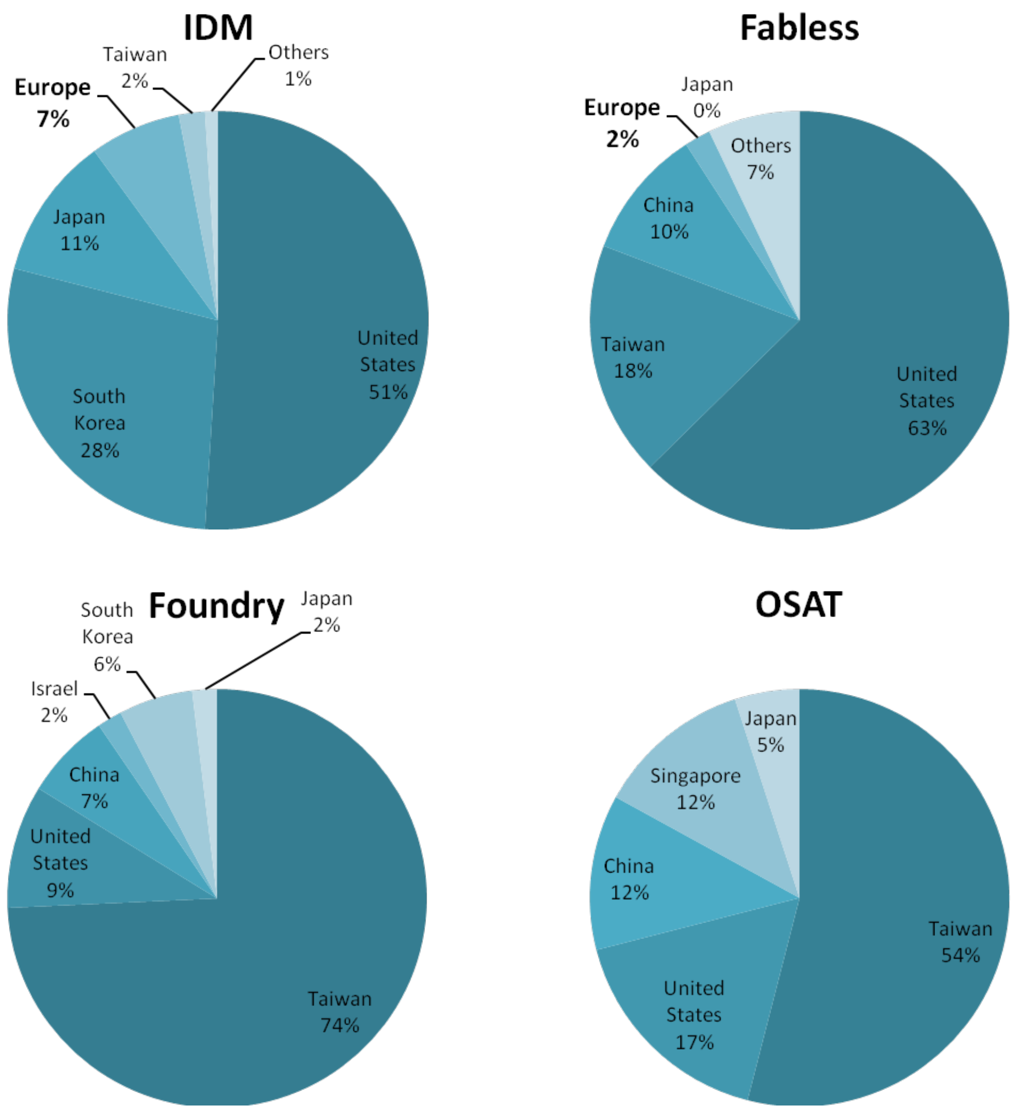
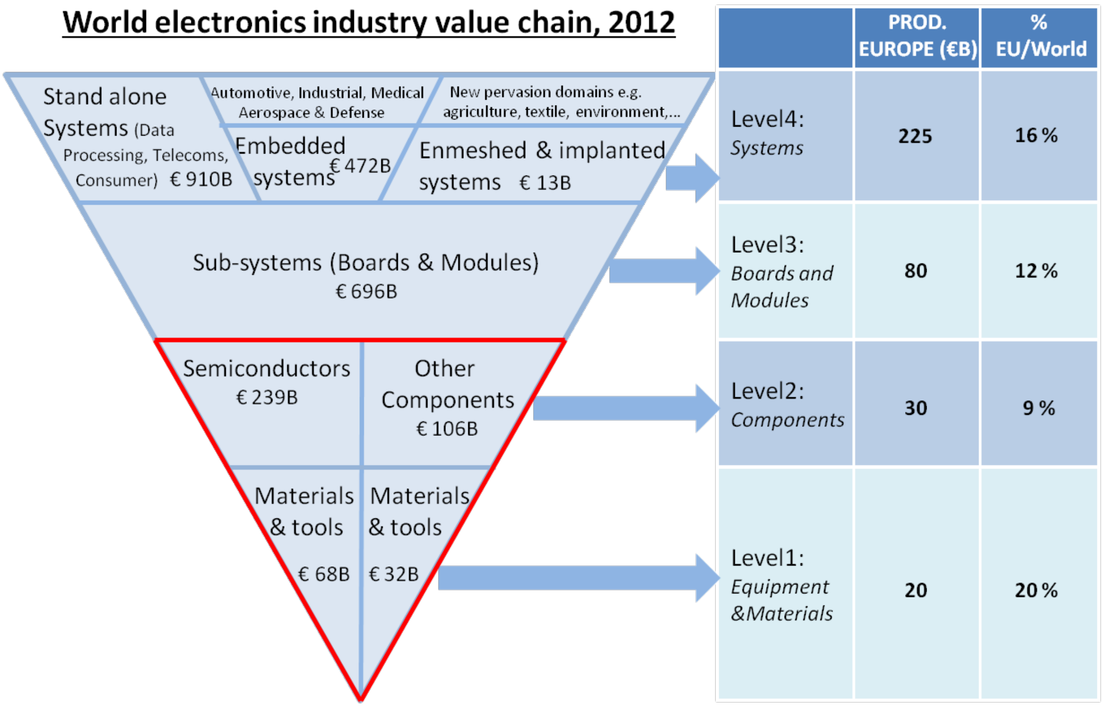


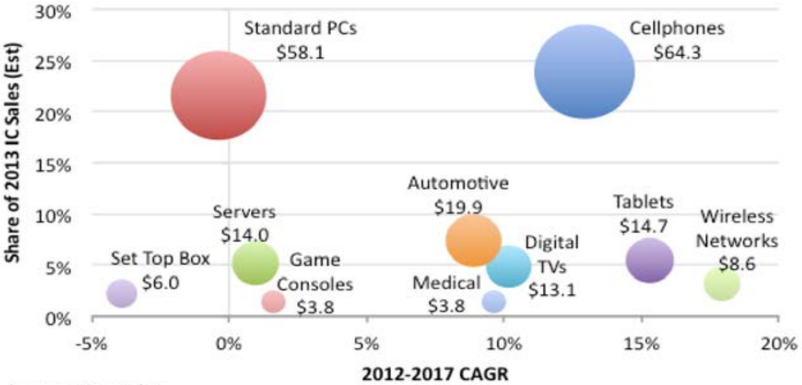
Figure 40: Percentage of global revenue. Europe plays a role in the semiconductor components industry with integrated device manufacturers (IDMs) and a few fabless companies. Outsourced semiconductor assembly and test (OSAT) and foundries play a negligible role. [294]

Figure 42 gives an overview, which in which end use markets ICs generate the greatest sales and growth rates. Automotive is the third largest market after computers and phones. Figure 43 highlights the type of semiconductor products sold in 2015. Logic and memory are the strongest products ("more Moore"), followed by analogue, MPU and opto components. The largest growth was observed for opto components and sensors. The semiconductor industry is among the most research intensive industries with expenditures reaching almost 20% of sales. [289]



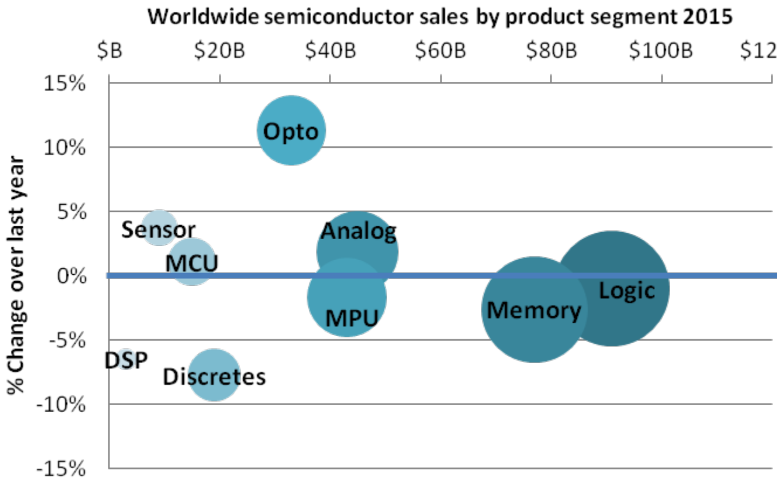
	PROD. EUROPE (€B)	% EU/World
Level4: *Systems*	225	16 %
Level3: *Boards and Modules*	80	12 %
Level2: *Components*	30	9 %
Level1: *Equipment &Materials*	20	20 %

Figure 41: Value chain in the electronics industry and European share. Graphene can be integrated and used to the greatest extent in the highlighted areas, although it can enable downstream innovations and improvements. [291]



Source: IC Insights

Figure 42: Global sales of ICs in end use markets in billion $ and growth rates 2013 [291]



Product	Sales	Growth
Logic	$91B	-1.0%
Memory	$77B	-2.6%
Analog	$45B	1.9%
MPU	$43B	-1.7%
Opto	$33B	11.3%
Discretes	$19B	-7.7%
MCU	$15B	1.1%
Sensor	$9B	3.7%
DSP	$3B	-6.5%

Figure 43: Global semiconductor sales by type of product sold in 2015. [289]

4.2.1.1 Market Opportunities

4.2.1.1.1 Electronics and hybrid approaches with Si as an entry point for commercialisation

Purely graphene or 2D materials based electronics as well as “graphene as the new silicon” is not expected by most actors in the electronics field. However, there are opportunities to use graphene and 2D materials in hybrid approaches integrated with silicon (“more than Moore”). This can add active and passive functionalities (e.g. optoelectronic, sensor, analogue interconnect, nonlinear elements) whilst the benefits of the well known and understood Silicon platform can be used. Therefore, hybrid approaches with graphene/2D on Si (Si-on-Insulator, SiN, etc.) are probably the most promising and the most reasonable first entry point for commercialisation in electronics. Such an integration can enable further use of the technology and allows a proper industry assessment. But there are still major barriers to overcome until such a scenario becomes reality.

Moore’s law (higher transistor density and lower cost per transistor), as a self-fulfilling prophecy will at some point come to an end (some time between 2020 and 2025 according to most experts in the field [295]). However, this rather opens up the diversification of applications, as the field is already now becomes more and more diversified and at the same time many functions converge (software, SoC, SiP, networks, new architectures, etc.). The planability will decrease and the ITRS is already reacting with the initiative ITRS 2.0 [296]. Still, materials will remain at the core of new hardware developments in semiconductor industry and electronics. As such, new concepts and materials will be always sought.

4.2.1.1.2 Back-end-of-line and back end demand cost-effective technologies

The back-end-of-line (where individual devices produced in front-end-of-line get interconnected with wiring on the wafer) and the back-end (packaging and connectors of finished chip) are nowadays often more expensive and work intensive steps than the front-end-of-line. Therefore, these steps have a high pressure to become cheaper and any solution that delivers a performance increase whilst not increasing cost or process effort is welcome. Furthermore, back-end processes have less stringent constraints on integration compared to front-end-of-line. At the core of devices (front end), there are many constraints on quality, but if a material is added on top of something as added functionality, constraints are not so high, and the chance is higher for integration.

Especially for MEMS devices, the back end is very important and packaging is part of the innovation in MEMS. Therefore graphene use in MEMS technologies opens interesting opportunities, especially as Europe is strong in MEMS technologies and specialized medium sized companies are active in that field.

If a technology can be easily integrated into an existing line, it can lower the barrier for a new material tremendously. In that case, even the expectations on performance or cost advantage are reduced (not the 10x, see below) and integration can be feasible even for niche applications. The simplicity of integration alone can justify the incorporation of a new material in the back-end-of-line.

It might eventually become a great chance for graphene to play a role in these back end steps.

4.2.1.2 Additional market opportunities: wafer scale integration

4.2.1.2.1 When the technology and production is demonstrated, many doors are opened

Industry demands a (simple) demonstrator made with actually compatible CMOS processes and reasonable yield. If this is successfully shown, spill-over to other applications is possible and broad adoption can begin. Only if wafer scale integration works, many applications will be possible to realize on commercial scale.

Especially if it is shown that graphene/2D materials can be incorporated into existing foundries with good material control and are compatible with the existing tools, there is a great opportunity that it will be used for variety of applications.

At some point later in time, other very cost sensitive applications might also become feasible when the price of integration declines.

Currently, there are a few promising applications that already demonstrate the “10x” potential experimentally, e.g. in hall sensors, photodetectors or optical modulators. However, the integration challenge is still too high, that a single company takes over the integration challenge.

4.2.1.2.2 First implementation possible without foundries

The diffusion of the technology to foundries can trigger broader implementation, as many fabless companies could also implement graphene and many downstream industries (such as automotive, datacomm and telecomm) can benefit on a broader basis. However, European strength lies in IDM companies (see Figure 40) and integration could be possible there, especially for know-how sensitive products (in the beginning). So some applications do not need foundries, even for broader implementation.

4.2.1.2.3 Spill over effects to other 2D materials

Graphene is a good entry to pave the way for further 2D materials. It is the pioneering 2D material and if an integration scheme works, other 2D materials can follow easier in the slipstream. TMDs are more complicated, as stoichiometry is an additional degree of freedom playing a role for the properties, so in principle they are trickier to integrate. On the other hand, if graphene integration does not succeed, other 2D materials can be in discredit.

The same logic is true for spill-over effects of TMDs: If you can make one TMD, others follow the same principle and the whole class of materials might be accessible.

4.2.1.3 Additional market opportunities: interconnects

4.2.1.3.1 Limits of current Cu-based technology

Interconnects are a major bottleneck and there is an opportunity for new materials and systems, such as high quality repeaters. Below 20nm Cu interconnects suffer from strong increase of resistance and electromigration. Novel materials are needed to overcome this limitation. The need arises starting from 2020 and increases to 2028. [297] RC of interconnects started to dominate the delay and power dissipation already from 10 nm CMOS. Already today interconnects account for >60% power dissipation and 20% of circuit delay and are thus an ever growing challenge. [298, 299]

Interconnects become more and more important for heterogeneous integration as systems on chip (SoC) and (3D) systems in package (SiP), especially for 3D integration. Multilayer graphene might be a valid alternative for interconnects and could be worth exploring further from the technological point of view.

4.2.1.3.2 Opportunities when graphene integration works feasibly

For technologies where graphene is used anyway (e.g. as active material), graphene can be easier integrated as interconnect. Graphene becomes furthermore very important as interconnect, the day other 2D materials are used, but this is far out in the future, if it occurs at all.

4.2.1.4 Additional market opportunities: Barrier materials

4.2.1.4.1 Need for ultrathin and conductive Cu barrier layers

As long as Cu interconnects are used (possibly beyond 2028), a barrier layer is needed between interconnect and transistor. This layer conducts the charges but prevents Cu from diffusing into the active device. It further acts as an oxidation and corrosion resistant layer. The barrier layers need to become ultrathin and conductive, so that graphene is one of the potential candidates to replace barrier metals such as Ta(N) and Mn(N). [297]

4.2.1.5 Additional market opportunities: Heat dissipation material

4.2.1.5.1 Thermal management is an important issue

Thermal management is a general issue, from film/chip-level to system-level solutions. System level materials are also covered in chapter 2.2 Additive to bulk solids/composites and 2.3 Industrial large scale coatings and paints. Power dissipation and heat removal of components are important challenges for energy efficiency. For current chip technologies temperatures <100°C are the limit and <65°C are the desire. This should be achieved with compact and lightweight solutions. Passive cooling is therefore the desired solution, however passive cooling is a problem as it may be not efficient enough.

Already a slightly better performance than incumbents or competing solutions could well be sufficient for a stronger market interest, as 10% lower temperatures results in 10% higher efficiency and double the lifetime of electronic components. A better cooling can help to push existing technologies further due to smaller footprints, higher possible currents and harder driving. On transistor level local thermal issues are becoming more and more a limiting factor, especially when going to power density increases in ever smaller scales and higher integration.

On system level, a better and more expensive thermal management can probably lead to an overall cost reduction as the core technology can be further exploited (though harder driving, larger currents…).

Cooling is crucial for all ICs and active components including high power electronics. If graphene/2D based solutions are demonstrated to work and an integration scheme is feasible, it can be used for many different products, from low cost to high value. A first entry would probably be advanced packaging for high value products.

4.2.1.5.2 Active cooling disadvantageous and not desired

Active cooling is maintenance intensive, consumes energy, has usually a larger footprint and some solutions have moving parts (fans). This is not desirable and therefore passive solutions are more appealing.

4.2.1.6 Market Threats

4.2.1.6.1 Conservatism regarding new materials: expectations for new materials in terms of cost/benefit are enormously high

The conservatism to stick to known technologies and materials and fully exploit them leads to unwillingness to bring new technologies/materials into a fab, following the idea of: If it works today, why change?

The experience with Silicon, CMOS and other bulk semiconductor technologies is very strong and everything that can be done with further improvement of existing technologies will be done with them.

The market demands either much cheaper solution with same performance or much better performance (very good cost/benefit). Therefore new materials/technologies have to present benefits of 10x better performance or 10x cost advantage (or something in between both cost and performance advantage) to be regarded as interesting. If this is not met on a demonstrator level, it is likely that a technology is disregarded. This results in a hesitation to include new machinery and processes presenting a barrier for new material systems. If a 100x increase in performance or power consumption is achieved for transistors or basic platform technologies, industry will solve the integration almost independent of the related challenges.

The effort/cost for qualification of a new material is tremendous and therefore, not many materials will be able to change the electronics industry on broader basis. New materials therefore see large barriers and need a long time until they are recognized and implemented in a fab (incubation time is 12-15 years [288]). However, the semiconductor industry faces challenges due to ever higher integration and the mantra of Moore’s law, so that the will to go for new computing and beyond CMOS technologies, as well as to go for new materials within CMOS was never as high as today.

4.2.1.6.2 Paradigm shift from 3D to 2D materials

It requires a paradigm shift in the semiconductor industry when going from 3D materials to 2D materials. Whereas the bulk material determines the properties in 3D materials, properties of 2D materials are determined by their surface. Therefore, every process step can have consequences on the 2D material properties and the cross-correlation of different process steps is much higher than with 3D materials today.

4.2.1.6.3 Overarching expectations that will hardly be met: threat of disappointment

The industry has high expectations on research results coming from fundamental research, especially in terms of timing of advances. If after a discovery no further improvements are seen and a technology/material does not live up to its expectations after 2-3 years, the industry becomes uneasy regarding the new technology. Graphene was strongly researched in recent years (e.g. IBM, Samsung, Texas Instruments) but it got quiet around that. This either points towards the fact that the research was unsuccessful and the interest is fading or that first real applications are under development in secrecy.

The impression at the moment is rather that the confidence in graphene is fading, especially from the application side and as the barriers for integration and production are still high and killer applications everybody sought for have not been found so far. The theoretical expectations were very high initially (“replace silicon”). This turned to the opposite effect when they were not met within recent years (trough of disillusionment in the hype cycle), leading to the perception of a “wonder material” that does not do anything. It is important to temper these attitudes and honestly and realistically manage the expectations for the material. This demands for instance analyzing the material holistically, i.e. in terms of electronics applications for low power, high performance and good reliability instead of studying one attribute at the time.

Furthermore, standardization becomes important to make sure what are we talking about, when talking about graphene.

If graphene is not successful in any application, it can be a threat for the application of other 2D materials, as they might also be in discredit.

4.2.1.6.4 Patent thickets

The initial strong interest of companies such as IBM[11] and Samsung lead to a patent thicket, especially in the electronic applications. This is particularly tricky for other ac-

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[11] IBM patents are now with Globalfoundries since the acquision of IBM’s microelectronics business in 2015

tors and smaller companies, as it is hard to keep an overview of all patents. Especially for smaller players, negotiating license agreements can be very complex and expensive, creating a huge barrier particularly for small players.

4.2.1.7 Additional market threats: wafer scale integration

4.2.1.7.1 Wafer scale integration as key bottle neck for a variety of applications: if it does not work, many applications will be doomed

Wafer scale integration is key for many electronics related applications. If wafer scale integration does not work, many applications will be impossible to realize on commercial scale. It is the dominant bottle neck for: logic, RF/µ-wave, optoelectronics, telecommunication and partially for sensors and flexible electronics.

Wafer scale (CMOS) processes are based on films, coating technologies, patterning, etching and post processing. Graphene and other 2D materials are in principle compatible with these technologies, as it is a two-dimensional sheet. Graphene integration is comparable with MEMs production, where also many different materials are added to the semiconductor. Despite this compatibility, it is a long way to go and many open questions on the feasibility remain. One already perceives some scepticism in the industry regarding whether GRM integration will work properly at all (and in an economically feasible way).

No matter how the GRM integration will succeed, scalability and demand need to be matched, i.e. depending on the demand for particular applications, different scales (e.g. wafer sizes) might be sufficient. This might at some point lead to imbalance, as demand will come with scalability and further demonstrators. Still, it is most important that the economically feasible integration can be shown for interesting applications, where graphene delivers an actual technological USP.

4.2.1.7.2 Conservative semiconductor companies and reluctance to use new materials needing new processes

Semiconductor companies are conservative and shy away from new materials and tools. This is especially true for fabs and foundries: a new material in a fab is usually equivalent to huge costs, which introduces a huge barrier. Many innovations are done with existing tools to the extreme. As soon as new processes/tools are needed this induces a large acceptance barrier. The incubation time for new technologies and materials is usually 12-15 years [288]. Expectations are to either provide 10x performance increase and/or 10x better cost efficiency.

4.2.1.7.3 Expectations on new processes and materials are high

Due to the usually high costs to bring a new material into a fab, very clear cost/performance advantages are needed in an application to justify large investments in new machinery or materials. This also applies to graphene and 2D materials, although some of the processes are compatible or used semiconductor processes (especially in MEMs manufacturing).

Further barriers are related to expectations from industry on reliability and very high yields (typically >90%). Additionally, a semiconductor fab needs to have a high degree of capacity utilization (usually >90%) to be economically feasible. This also implements a barrier for low volume applications and highlights the demand for a critical mass of applications.

Incumbent materials (Si, Ge, III-V, etc.) are always a threat for new materials, as the processes are well understood and under control. Qualification of new processes and materials can take 1-4 years, which adds an additional barrier towards materials that are already used today.

4.2.1.7.4 Foundries needed to address large mass markets

To become relevant for fabless companies, foundries need to be involved and machinery needs to be developed together with foundries. This only works for large volumes, as foundries only address processes with high enough throughput and volume. It seems that large foundries currently do not work on graphene (only on basic research level). If new tools are needed, it is less interesting for foundries and the demand needs to be even higher. It is an open question, who pays the cost for graphene integration when a new tool is needed in a foundry.

4.2.1.7.5 Competition with US and Korea

Strong players in US and Korea patent graphene, especially with respect to electronics applications (Samsung, IBM, Apple). This creates a patent thicket (see 4.2.1.6.4 Patent thickets). It is yet unclear, whether the big players, who might be capable of graphene integration are still following this path (Samsung, Texas Instruments, TSMC).

4.2.1.7.6 Ecosystem development needed

The full integration of graphene/2D materials needs to be done by industry. Academia and research institutes can only push the integration and demonstrator development to a certain point, from which industry has to take the lead. It is indeed a problem, that the question when and how this point will/can be reached remains unsolved. Especially the currently high integration challenges and open questions together with the demonstrators that are not yet promising enough, are too much of a risk for a semiconductor company to stronger focus on graphene integration. Along with that, the new material needs a modified ecosystem and supply chain, open up another risk. The endeavour to reach a point where industry can take up the development, the demonstrators need to be further developed, also looking at scientifically less interesting parameters such as reliability, (temperature) stability as well as the holistic and full set of relevant parameters for the performance, so that a benchmark with other technologies is fair and possible. Equally important, processes need to be further developed and scaled for reliable and feasible production. This demands a lot of engineering knowledge and work. Furthermore, the whole value chain and eco system needs to be developed at the same time. This demands standards and joint efforts from research and industry.

4.2.1.8 Additional market threats: interconnects

4.2.1.8.1 Incumbent and competing materials

Besides the existing Cu conductors, other technologies are under investigation, e.g. Silicides, CNTs or CNT-Cu composites or in general making use of collective excitations in the conductors. [297] Furthermore, the thinness of 2D materials is not necessarily a big advantage, as the lateral dimensions are more important for further integration. The Cu layers are also already quite thin.

4.2.1.9 Additional market threats: Barrier materials

4.2.1.9.1 Incumbent and competing materials

The incumbent materials (Ta(N) and Mn(N)) are still sufficient for the next 10 years or so. Other researched material classes are for instance self-assembled monolayers. [297]

4.2.1.10 Additional market threats: Heat dissipation material

4.2.1.10.1 Existing technologies

On system level, metal and carbon pastes or bulk materials (Cu) work fine, although they have a typically large footprint. 30-40 other concepts are under investigation and to a certain extent similarly promising as graphene based heat dissipation materials.

4.2.1.10.2 Packaging as a cost driver

Packaging is a cost driver and costs usually need to go down. Only if on system level a price reduction through a better package is possible it will be worth it. For specialised applications, some added costs might be feasible, but only for small and high valued markets.

4.2.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in electronics: cross-cutting issues

4.2.2.1 Current strengths for graphene/2D materials use in electronics: cross-cutting issues

4.2.2.1.1 Multifunctionality

The combination of electrical, mechanical, barrier and thermal properties is a USP of graphene. Especially for interconnects and in the back-end-of-line and back-end, these properties can be very interesting. Furthermore, it offers transparency and flexibility, interesting properties for flexible electronics (4.6 Flexible and/or printed electronics) and wearables.

4.2.2.1.2 Combination with other 2D materials

There is a high potential in combination with other 2d materials, e.g. using BN as passivating layer for graphene. These devices offer currently the best performances. 2D material stacks and all-2D material electronics can be interesting in the future, although the fabrication challenge increases tremendously.

4.2.2.2 Additional strengths: wafer scale integration

4.2.2.2.1 Monolithic 3D integration (BEOL or FEOL) is in principle technically possible

Monolithic 3D integration of graphene and 2D materials is in principle possible. This is one of the reasons, why graphene has been hyped as an interesting material for electronics (besides its electrical properties). The processes for fabrication of graphene layers are in principle CMOS process compatible and a co-integration with Si and other existing solutions is possible. 2D materials even have a better compatibility with SiN electronics/photonics than Ge and III-V semiconductors. However, there are still many open questions regarding quality of the prepared films, transfer, reliability, yield, etc. (see current weaknesses further below).

A CVD production tool is available for graphene on Cu foil for wafers [300] and roll-to-roll processes [301], capable of making large sheets available. There has been a huge progress in terms of quality in recent years; however, the quality is not yet high enough (e.g. due to grain boundaries). Furthermore, the transfer process is yet to be optimized in a scalable way.

For epitaxially grown graphene on SiC substrates, the quality of graphene is already reasonably high [302], however, this way of production is only economically feasible at the moment for products that need to be made on SiC anyways, due to the currently somewhat high cost of SiC wafers (~30x cost of a silicon wafer) [303]. This could be interesting for RF/HF applications (MMICs), LEDs or power electronics. However, the current processes for graphene growth on SiC are not compatible with common devices based on SiC due to the high temperatures needed. Therefore, it is not possible to grow graphene on SiC ICs without destroying the ICs. Epitaxial growth has also been shown on sapphire [304, 305] and germanium [306, 307]. The quality of the graphene grown on germanium and sapphire, however, is still inferior to the CVD methods on SiC and copper and thus not good enough for high performing devices.

A dissolution/precipitation sequence facilitating Ni films on SiO_2 has also been demonstrated, but this process is currently not reproducible enough, does not reach sufficient quality and has issues with the layer number control. [308]

A transfer-free CMOS compatible process would make graphene integration much more likely, although it is currently not foreseeable. For other 2D materials it is probably possible (direct growth on dielectrics).

4.2.2.3 Additional strengths: interconnects

4.2.2.3.1 Performance results are promising

The laboratory results so far to use multilayer graphene as interconnect are promising. 10nm wide MLG was shown to have lower resistivity than Cu at the same scale [309]. However, this also needs to be shown with larger scale integration schemes.

4.2.2.3.2 Not only high quality film possible to use (depending on application)

For larger interconnects, especially on flexible substrates, also the use as an ink could be possible. (see also chapter 4.6 Flexible and/or printed electronics).

4.2.2.4 Additional strengths: thermal interface materials

4.2.2.4.1 Ink or high quality film usage

The use of graphene or other 2D materials (BN) can be interesting on system/device level (“painting” of box/package) in the back end or even at higher levels of assembly or on transistor level in the back-end-of-line. (high quality CVD). The use as an ink after packaging is also covered in chapter 2 Composites, bulk applications and coatings (thermal interface materials). Also for flexible electronics, the opportunities exist, especially in terms of electronics that incorporate graphene or 2D materials anyway.

4.2.2.4.2 Anisotropy

The heat transfer in 2D materials is directed and anisotropic. This can be beneficial to direct the heat transfer, where it should go. On the other hand, coupling of the heater (chip) to the dissipation material might be an issue. Furthermore, currently used materials conduct the heat isotropically, so a rethinking of conventional approaches would be needed.

4.2.2.4.3 Volume/footprint and mass benefit

Due to the 2D nature, potentially less space is needed than for common heat dissipation solutions, e.g. based on Cu. A lower mass per overall conducted heat is also possible. This is interesting due to ever smaller integration and the need to smaller footprints and space savings (e.g. in mobile phones, wearables).

4.2.2.4.4 First applications are expected on the market soon

Recently, functionalized graphene-graphene oxide films from flakes showed interesting properties in heat dissipation on package level [310]. There are also first products announced making use of graphene as heat dissipation and thermal interface material.

4.2.2.5 Additional strengths: barrier material

4.2.2.5.1 Use as barrier material for interconnects in back-end-of-line

High quality SLG or MLG graphene can be used as an ultimately thin and conductive barrier layer to replace barrier metals between Cu interconnects and transistors to avoid Cu diffusion into the active layers. It could also be generally used as barrier "metal" for other metals in the back end of line as well as for oxidation and corrosion resistance [297]. The performance is promising as barrier layer for Cu interconnects [311]. Flexibility as conformal coating are additional added values.

4.2.2.5.2 Graphene Oxide as material for packaging in back end

Graphene oxide based coatings and paints could be used as barrier layers in the packaging back-end. This would be a special application of paints and coatings or composites as barrier material, see chapter 2 Composites, bulk applications and coatings.

4.2.2.6 Current weaknesses and challenges for graphene/2D materials use in electronics: cross-cutting issues

4.2.2.6.1 Mobility vs. bandgap in 2D materials

Most advanced and high speed semiconductor applications require a bandgap and high charge carrier mobility. In this respect, GRM offer no better performance than bulk materials (see Figure 44) and graphene cannot escape from this mobility-bandgap trend. It is an intrinsical disadvantage against 3D semiconductors (e.g. III-V), which have higher mobilities and a bandgap. Applications for graphene are particularly interesting if one can make use of the gapless and tunable nature and benefit from it, e.g. in non-linear applications. However, there might be 2D materials out there, which can compete (such as Germanane, MoS_2), but they have to be investigated further especially in terms of the manufacturability. Recent results on MoS2 as channel material appear promising for further developments. [312, 313]

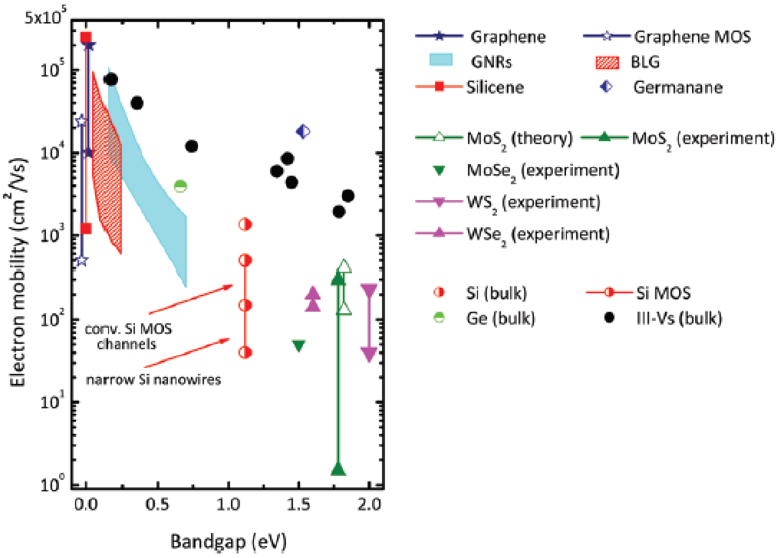

Figure 44: Electron mobility vs. Bandgap from several 2D and bulk materials. [314]

4.2.2.6.2 Performance lags behind initial expectations

For most electronics applications, the theoretically high promised performances are not yet shown experimentally (or only on basic lab level or with lab methods). This is a major disadvantage for the argumentation towards industry as too many risks and uncertainties currently exist. The lab-based demonstrators need to be prepared with more industrially relevant methods, or the methods have to be further developed to become industrially relevant to achieve breakthrough demonstrators.

As for all new kinds of nanomaterials, 2D materials in general receive a lot of attention and promise, but also have a lot of challenges. The integration and commercialisation is not straight forward.

4.2.2.6.3 Challenges in quality, reliability and degradation

Reliability is a very important factor for the semiconductor industry. Reliability models are crucial and necessary for a broader commercialisation. For 2D materials, these reliability models are unclear and need to be addressed at some point. For silicon, it needed 20 years until today's reliability models.

Therefore, degradation processes need to be understood. So far, it is seen that the graphene quality strongly depends on encapsulation. So more knowledge on encapsulation is needed.

4.2.2.7 Additional current weaknesses and challenges: wafer scale integration

4.2.2.7.1 Too low quality or yield of current high quality film methods

High mobility in graphene is a key factor to outperform the competition (e.g. in optoelectronics Si-modulators and Ge detectors). Therefore, a high quality, high purity, larger area production of GRM is needed and a prerequisite for many application areas.

There are several possibilities to grow high quality graphene films, examples are:

1. CVD on Copper
2. CVD on Ge (or Ge on Si)
3. CVD on catalytic material combinations at low temperatures (e.g Au-Ni) [315]
4. "Epitaxial" growth on SiC
5. dissolution/precipitation sequence facilitating Ni films on SiO_2

Usually and depending on the application, a transfer process is needed to get the graphene layer on the device substrate (e.g. SiO_2, etc.), see next subsection on the transfer process.

The quality of graphene on the substrates is at the moment not good enough to outperform competing technologies. For the most often used Cu CVD process only mm domains are synthesized due to thermal mismatch, resulting in a too high defect density. It is very important to find a suitable substrate (e.g. single crystal Cu or Ge), where the mismatch is better. The current process has issues with defects, wrinkles and metal impurities in graphene.

For graphene on SiC, the wafers are currently too expensive and the process is only economically feasible when components are made of SiC anyway.

At the moment, there is no existing high quality and low cost synthesis on dielectrics available. The Ni film route has problems with layer number control and poor reproducibility due to grain boundary effects. [308]

In some applications (e.g. modulators, sensors) bilayer graphene or two graphene layers with a spacer (e.g. of aluminium oxide) perform better due to interesting properties (tunable bandgap with an electric field). However, a controlled way of producing bilayer graphene on larger industrial scale does not exist yet, although some promising results have been achieved very recently. [316]

Another disadvantage is that there are large variations of graphene quality from supplier to supplier, which calls for standardized characterisation and labelling. This is a problem and barrier for the future ecosystem, as the second source principle could at the moment be not fulfilled.

The ultimate goal and Holy Grail for graphene integration would be a transfer free direct growth on Si or dielectric, but this is currently not in sight and rather unlikely to exist. Lattice matching would be very important for the quality; this also applies to TMDs growth.

4.2.2.7.2 Transfer process

As there is currently no high quality direct growth (transfer-less) process on Si or dielectrics in sight for graphene, the integration can only work with an upscalable transfer process to be compatible with various substrates. This transfer process is currently seen as the major barrier for integration and the hardest part, as it can strongly influence the quality of the graphene film.

The transfer process is not easy to control and scale up. Large area dry transfers create wrinkles, cracks, cleanliness, adhesion and flatness are issues influencing graphene quality tremendously and leading to lower mobilities. Furthermore, the CVD on metal processes introduce metal contamination, which is detrimental for CMOS processes and for the graphene itself (see 4.2.2.7.6 Contamination). Other transfer processes, such as in-situ transfer with a Cu wet etch process followed by adhesion to a dielectric through capillary forces creates less defects due to self alignment, but has long etch times [317], see also Table 40. Transfer processes are desirably dry, quick and on wafer scale to allow more efficient processing. Chip-scale transfer is probably easier but usually needs more effort and leads to higher cost, as the chips have to be processed one by one.

Table 40: Comparison of three common wet transfer methods. Credits to M. Lemme.

Etching method	Bubble method	Capillary method
Chemical process	Electrochemical method	Physical Process (capillary effect)
Cu is etched/dissolved Etchant: $FeCl_3$, Sodiumper-sulfate	Cu is removal by bubbles created at the interface Electrolyte: NaOH	Cu removal by water at the interface Reactant: DI water
Duration: 1.5h	Duration: 30s	Duration: 8h

If a transfer process is controllable and scalable, it also bears some advantages, e.g. the freedom of process parameters to achieve highest quality material during the growth process independent from final substrate or its constraints; it allows additional interface engineering and can be transferred on basically any substrate.

A transfer process could be compatible to MEMS transfer processes, so that the tools for such a transfer are partially standard back-end-of-line MEMs tools (e.g. for wafer transfer). But this is depending on the actual process and new tools might be eventually needed. This potential need for new tools with new working principles is a barrier for integration into fabs. It is most desirable that a process can be facilitated with existing tools, or the graphene films can be bought on the desired substrate with the needed quality (in case this is compatible with the component design).

4.2.2.7.3 Substrate interaction, encapsulation or self-passivation

The substrate material and surface treatment has a strong effect on graphene properties. This originates from the interaction with the substrate, from roughness, doping by dangling bonds or local charge inhomogeneities (see Table 41). Especially the atomic flatness of graphene seems to be a key factor to achieve extreme mobilities [318] needed to compete with existing technologies in many high performance applications. This atomic flatness most probably cannot be achieved on substrates where graphene corrugates, like on SiO_2. It might even be that defective graphene with fewer corrugations can achieve better mobilities than defect-free graphene with more corrugations, as corrugations might be key for mobility.

Best performances are achieved when using self-passivated layers, e.g a hBN-G-hBN stack embedded in dielectrics. As hBN is still at the exfoliation stage and production on larger scale is not possible at the moment, it is an even bigger challenge for upscaling but could contribute to the actual performance gain needed to outperform competing technologies. The economical feasibility for such a process is not yet assessable, as an industrially compatible process does not even exist on lab scale yet. The bottle neck in this case is the hBN production and the assembly of the stacks.

But different applications also demand different substrates, e.g. Si, Si/SiO_2, SiN, SiGe, quartz or AlN as well as flexible substrates (polymers, foils). In that case the mobility will be most probably limited, if graphene cannot be embedded in a passivating layer as hBN.

Table 41: Charge carrier mobilities of graphene on different substrates. [319–322]

Substrate	**Mobility [cm²/Vs]**
SiO2	4400…25000
h-BN	25000…140000
SiC	27000

Furthermore, encapsulation is also important to protect graphene from adsorption of contaminants. It is a challenge, that the encapsulation materials also effects the performance. For such an encapsulation it would be interesting if those encapsulating materials could be directly grown on graphene, e.g. through ALD. So far the nucleation of ALD materials on graphene, however, seems to be difficult. There are, however, ways to encapsulate graphene with a system of materials, such as Parylene, on which Al_2O_3 can be grown with ALD easily. This is particularly interesting for chemical sensors and biomedical applications.

4.2.2.7.4 Delamination, reliability and yield

Delamination is one of the most important challenges for graphene integration. It can appear during process steps, for instance due to temperature differences, stress in a stack, chemical-mechanical planarization or during wet processes. Already 1% of delamination is a problem in a pilot line, where delamination can lead to contamination of equipment eventually reducing the cycle time and yield. Irregular adhesion/delamination is also a problem in operation of a graphene-based device, as it can lead to failures and malfunctions reducing durability.

There is also an intrinsic tradeoff: On the one hand, weak adhesion forces are needed due to the required minimal graphene/substrate interactions, which can influence the graphene performance. On the other hand, a stronger adhesion bears a lower risk of delamination. So a balance between adhesion and substrate interactions needs to be found and an adequate and suitable integration scheme.

Most of the basic processes leading to delamination are unknown, so a better understanding of the adhesion limitations is needed (size and substrate dependent). This needs to be investigated for each process step and in operation, leading to more confidence in the window of stability and thus to a better process control and more reliable operation. Depending on the application, knowledge is needed for different substrates (Si, Si/SiO2, quartz, SiN, AlN, even polymer or foils for flexible applications) and wafer and sheet sizes.

However, the generic question and challenge remains currently still open, whether large scale high quality graphene be grown and laminated on top of a wafer with controlled defects. It is still unclear how to achieve reliable and constant quality over the wafer and batch/wafer to batch/wafer.

Related to the delamination in operation as well as other potential defects is the reliability failure model of a new material and technology, which is unclear for graphene. Device reliability failure models were important for silicon semiconductor success as they can be used in design factors and testing to improve the reliability of integrated circuits. Reaching this high standard and level of understanding needed 20 years for silicon. For reliability of graphene/2D materials based devices, other processes, such as delamination or encapsulation might play a role. For future mass production it is important to consider these effects for a reliability model during scale-up to avoid missing the high standards of the semiconductor industry.

Last but not least, the yield of wafer scale graphene processes needs to be considered, as yield expectations are very high in CMOS processes. It is to be investigated how high this yield can be pushed for graphene and if the needed yields can be achieved at all.

All these processes (delamination, reliability and yield) demand intensive engineering efforts and knowledge (what are the parameters, process control, impurities, etc.), which probably will not lead to highest ranked publications. Still this knowledge is essential for industrially compatible wafer scale integration.

4.2.2.7.5 Contacting

Reliable and low resistive contacting of 2D sheets is another important challenge. A reproducible and production compatible electric contacting with low resistance is not available to date. Classical and rather simple top contact shows resistance degradation due to work function mismatch, chemisorption of the contact metal [323], doping by the contact metals, induced stress or a contaminated interface. A possible solution are one-dimensional side contacts or combined architectures [324]. Here, reproducibility (top vs. edge) and scalability are major challenges. Most importantly, the metals used need to be compatible with the existing processes and used materials, compare Figure 45.

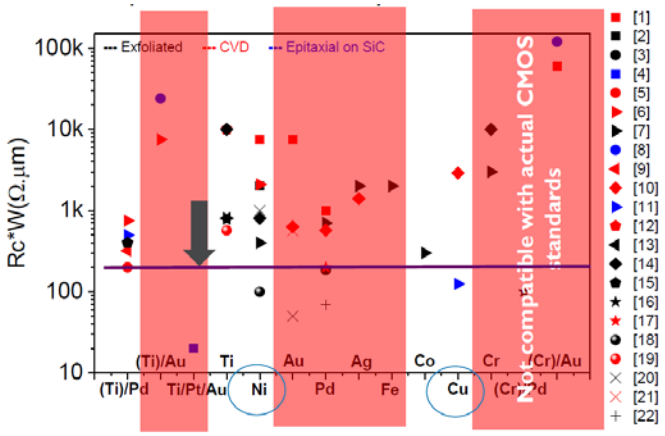

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Figure 45: Graphene/Metal contact resistivity values – state of the art. Different results for contacting of graphene depending on metal and type of graphene used. Several metals are not compatible with CMOS processes (red). Credits to C. Huyghebaert, IMEC 2016.

4.2.2.7.6 Contamination

Contamination problems through metals or polymers exist for graphene itself (e.g. unwanted/uncontrolled doping) and for CMOS processes in general. Metal contamination in CMOS processes is undesirable (CMOS specification: <10^9 at/cm^2 metal contamination). This is particularly important for font-end-of-line processes. High metal contaminations of >10^{13} at/cm^2 of Fe and Cu have been observed in CVD prepared graphene [325]. This demands optimized cleaning processes or growth on non-metallic substrates. Furthermore, delamination during a process can also lead to contamination of equipment.

4.2.2.7.7 Deeper basic understanding needed

From the above mentioned challenges it becomes obvious, that a deeper understanding and better control of the interfaces is very crucial. This applies for interfaces and grain boundaries of graphene sheets, but also the interfaces with substrates or encapsulation. A fundamental understanding of grain boundaries is absolutely necessary for further process and device optimization: This includes the investigation of the influence of grain boundaries on electrical and mechanical properties as well as reproducibility.

4.2.2.7.8 Post process compatibility

Due to the 2D nature of graphene and the danger of delamination, all processes taking place after graphene deposition can influence the device performance and reliability. Thus, it is currently unclear how compatible and robust graphene devices are towards post-processes (patterning, litho, encapsulation, thermal treatment, packaging…). Graphene is sensitive to O_2 at high temperature, O_2 and H_2 plasma and prone to carbide formation with other elements at high temperatures. So it needs to be investigated whether it can survive the post process steps in typical integration schemes.

4.2.2.7.9 Design tools

Graphene-based components are new materials and concepts in the semiconductor area. As for all new materials and concepts, design tools are needed to allow system design and later foundry processes. The design tool are important at the interface between system planners and manufacturing. The development of design tools for graphene based components is an ongoing challenge and needed as another step towards CMOS integration.

4.2.2.7.10 In-line quality control and monitoring and standardisation

An industrial manufacturing compatible metrology is needed for process monitoring, reproducibility and quality control of graphene/2D films. As graphene is currently at a scientific metrology stage, new or adapted methods are required for industry compatibility. Some techniques are already investigated, e.g. based on raman scattering, ellipsometry, THz or eddy current. Industrial measurement techniques need to provide the desired measure (e.g. graphene quality, number of layers…), whilst being non-destructive, working on large area (full wafers up to 300mm), being high-throughput (inline compatible) and in best case being substrate independent.

Furthermore, if graphene wafers are sourced from a supplier, it is inevitable to exactly know the quality of the graphene product. Therefore, a certain degree of standardisation is necessary to ensure product quality and allow comparison between different graphene products and manufacturers and second sourcing. This especially requires standardised characterisation methods and measures. Therefore standardisation is required to a certain extent to drive the commercialisation of graphene.

4.2.2.7.11 Open question: Is it worth the effort?

Looking at the open challenges of graphene integration, the missing process demonstration for industrial manufacturing and the needed effort and uncertainties to resolve this, the barrier and risk for industry to take up the development seems to be still too high. This is especially the case, as there is currently no trustworthy realized opportunity (functional demonstrator, proof of concept application) on the horizon that justifies this whole risky endeavour for a single company. The benefits for different application areas in electronics appear to be just not yet clear enough. The incentives in terms of performance and cost are currently not high enough to justify the risks of successful integration.

Furthermore, a crude assessment of potential cost leads to the notion that prices for graphene/2D based/enhanced technologies might not come down enough or be competitive.

It remains an open challenge how far research needs to go until big industries will pick up the development to bring graphene electronics to the market. There are two major parameters influencing that:

1. Show benefits and potentials of the technology against competing and existing technologies to justify the investment
2. Reduce the risk for process integration by demonstrating the feasibility on a R&D level

Both issues need to be addressed to bring graphene/2D materials closer to the market. If the potential of demonstrators is high enough and the risk for integration at the same time is lowered, the point will come where industry will take up the development. It is, however, not known yet, whether and when this point can/will be reached.

4.2.2.8 Additional current weaknesses and challenges: interconnects

4.2.2.8.1 Integration scheme and worthiness of effort

Although multilayer graphene based interconnects already show some potential, the difference to state of the art Cu interconnects currently appears too low to justify a system change. The actual competitiveness with Cu has not yet been fully demonstrated. Cu and other incumbent metals have an integration scheme and are in fabs, whereas graphene has neither a solid integration scheme for interconnects nor currently shows the benefit to justify the evolution to this new material. Expert assessments currently say that in silicon-based electronics graphene will probably never be used as interconnect. However, it is still considered as potential candidate in ITRS publications. [297] Currently, there is no feasible method available to produce and implement multilayer graphene. If (multilayer) graphene integration works for other applications in CMOS back-end-of-line processes, the interconnect use case could get a revival and be developed based on the other developments (or vice versa).

4.2.2.8.2 Potential pollutant at interconnect interface

Due to the high pollution with metal [325], graphene may be a pollutant at an interconnect interface, which would require a barrier layer, similar to Cu. The advantage of getting rid of a barrier layer would in that case be cancelled out.

4.2.2.9 Additional current weaknesses and challenges: thermal interface materials

4.2.2.9.1 Total heat removal scaling

The total heat removal of single layer graphene might be too small, as the total heat transfer is limited by the small volume. Thicker layers do not scale up the thermal conductivity so well, so the challenge remains how the overall heat flow can be increased. (FLG, multiple separated layers, how are they attached,…). A functionalization approach for GO seems to be interesting and has been demonstrated on lab scale. [310]

4.2.2.9.2 Unknown reliability

The functional benefit of graphene-based heat spreader have been shown and are promising. [310] But the reliability and heat radiation properties in the application remain to be tested further. It is clear that for system level, the influence of surfactant, functionalization or binder on properties are important and need to be studied.

4.2.2.9.3 Unknown substrate interaction and contact improvement

Thermal heat spreaders need to have a good contact to the heat source. It is unknown, how graphene interacts with substrate/matrix and how the phonon-coupling can be extended. It is important to study how to establish good contact between the material and the heat source/heat exchanger.

4.2.2.9.4 Anisotropy and implementation differ from state of the art materials

Today isotropic materials are used (e.g. Cu or Al). For an anisotropic material a paradimg shift and a rethinking is needed. The anisotropy can be both beneficial or detrimental. As soon as the handling/implementation is different compared to state of the art, an additional barrier is introduced. The simpler the implementation is, the better.

4.2.2.9.5 Wafer scale integration needed on transistor level and unknown contamination issues

For transistor level heat spreaders, CMOS integration or at least CMOS compatibility is needed (back-end-of-line). Poisoning of graphene and the transistors below from metal catalyst residues similarly applies to this application as to all wafer scale applications. Also for heat spreader materials, the question remains how to attach the material on transistor level so that a good thermal conductivity between the materials is guaranteed and long lasting. Is physical adhesion sufficient or some kind of bonding or functionalization needed?

4.2.2.9.6 Application dependent: Electrical conductivity of graphene

The inherent combination of thermal conductivity with electrical conductivity in graphene is not always needed or might even be detrimental. It thus cannot be used universally for all applications. hBN or other insulating 2D materials might be an opportunity for applications where thermal conductivity without electrical conductivity is needed.

4.2.2.10 Additional current weaknesses and challenges: barrier material

4.2.2.10.1 Differences to competing materials in integration

At the moment graphene is not so much better as a barrier than some other materials that can be integrated with lower temperature at interconnect scale, e.g. self-assembled monolayers. At the moment integration of graphene is not compatible with standard integration at back-end-of-line, whereas other materials are. But as soon as graphene integration at BEOL is available, maybe due to other applications that are driving the integration scheme, also the use as barrier can become feasible.

4.2.3 KPIs for electronics: cross-cutting issues

4.2.3.1 Wafer-scale integration:

Table 42: KPIs for wafer-scale integration

Specification	Required for CMOS
Wafer size	200/300mm
Charge carrier mobility / cm²/Vs	>25000 to compete in most applications, the higher the better
Yield	$\gg$90%
Impurities (metals)	< 10^9 at/cm^2
Contamination (e.g.PMMA)	< 0.1 %
Mechanical defects	< 0.1 %
Inclusions (e.g.water)	< 0.1 %
Uniformity along 300 mm wafer (with acceptable edge exclusion)	< 0.1 %
Scattering time	1 ps
Contacting	CMOS or process/material compatible metal, RcW as low as possible, parasitics should be <10 % of transistor channel resistance

4.2.3.2 Use as barrier

- Resistivity of interconnect (Cu) over barrier: ~10 u ohm cm (depending on line width, usually ~10-100nm) (as low as possible)
- Capacitance (as low as possible)
- EM reliability
- O2 barrier, Cu diffusion barrier properties
- cumulative failure probability vs. Time to failure (TTF)

Some KPIs are taken from [326]

4.2.3.3 Use as interconnect

- CU resistivity: 1.7 µOhm cm (bulk)
- Dimension (critical dimension CD<20nm)
- Line resistance RL=ρL/Wt (as low as possible)
- Voltage drop (IRL/V) (as low as possible)
- Line response time (RLC) (as low as possible)
- Line current density (I/A) (as high as possible)
- Resistivity ~10µOhm cm for line width ~10nm
- EM reliability
- Electron mean free path (<10nm)

Some KPIs taken from [326], For further KPIs, please refer to ITRS 2013:Interconnect Tables via www.itrs2.net or directly: [327]

4.2.3.4 Use as thermal material:

easy integration, good TIM pastes (silver) get 40W/mK for 10€/g; bulk Cu 400W/mK, Silver 430W/mK, graphite sheet in smartphones, e.g. 400W/mK (xy), 10W/mK (z)

4.2.3.5 Design tools

Compatibility with CMOS design tools

4.2.4 Roadmap for electronics: cross-cutting issues

4.2.4.1 Current maturity: ‘Labscale demonstrators available, wafer scale integration R&D has started’

Promising lab scale demonstrators are available, although benchmarking needs to be intensified and the material quality needs to be increased to become competitive.

For SiC based graphene “epitaxially” grown graphene processes reach sufficient quality, but wafers are expensive and limiting the applicability. 3” wafers are quite uniform (99.9% coverage), 6” is also possible.

Wafer scale processes for other substrates (Si, SiO_2, etc.) are under investigation and often demonstrated, sometimes already on larger scale. However, the quality is still not good enough. Especially the quality of the growth process and the transfer processes are bottlenecks. Also the preparation of other semiconducting 2D materials (e.g. TMDs) and bilayer graphene (as a low bandgap material) is under development but much more juvenile than high quality SLG technologies. For graphene, especially hBN could play a decisive role, as best performances are achieved in combination with hBN.

TMD devices are currently still dominated by material quality (impurities, defects). hBN is currently still at the exfoliation stage and large scale high quality preparation methods are not yet known. Thin film growth processes yield either only small crystals or polycrystalline films.

The potential as interconnect and barrier material has been shown. Manufacturability is currently the biggest issue.

For thermal material slightly better performances are observed compared to state of the art TIM. However, experts are slightly critical about experimental published results, which seem to be not easily reproducible and sound.

4.2.4.2 Barriers/challenges (summarized)

Fundamental understanding

- High quality transfer and growth processes
- Grain boundaries and their influence on performance
- Interplay of doping, contamination, flatness, substrate, interfaces and performance

Application:

- For which applications is the SiC process feasible? How far do prices of SiC wafers have to go down for further applications?
- High prerequisites of industry before they take up the development: 10x performance increase and/or 10x lower cost demonstrated and lowered manufacturing risk needed or 100x performance increase demonstrated for platform technology (e.g. transistor)
- Realized mobility for most applications not high enough (performance lacks behind expectations)
- Unclear reliability/degradation in operation (e.g. due to delamination, influence of package or heat)
- Wafer scale feasibility as key barrier

General manufacturing technology and graphene:

- Wafer scale: very large challenge to implement wafer scale integration within 2 years time. Almost impossible? Time expectation for a new material usually ~10 years.
- Manufacturability not proven yet for a simple device
- Transfer process
- Large area single crystals preparation method for needed substrate not yet available
- Mobility of large scale films way behind expectations and need
- Unclear quality, reliability, degradation
- Delamination problems and unclear optimal parameter space
- Yield
- Doping and defect control, defect density

- Interface control
- Stacking/lateral alignment (control)
- Contacting, contact resistance
- metal contamination (especially Cu)
- Post process compatibility
- Quality control and monitoring
- Missing design tools
- Substrate and encapsulation with hBN on industrial scale
- missing estimate of a cost for process integration + unclear prospects of a missing “killer application” that can be feasibly produced keeps semiconductor companies from taking graphene into the fab and making larger investments

hBN substrate/encapsulation:

- Thin film growth processes yield either small crystals or polycrystalline films: better ways are needed
- Precursors
- Growth mechanism
- Layer number control
- Grain size
- Can single crystals of a significant size be grown –controlled?

TMDs:

- Material quality (defects, impurities)
- growth on large scale, multi-layer
- Substrate selection: lattice matching, extended defect control, grain size control
- Growth technique selection: CVD, ALD, MBE, VPE, etc
- Precursor selection
- Contamination
- Nucleation and growth
- Point Defect Control: intrinsic doping (vacancies, extrinsic doping

Ecosystem:

- Companies seem to wait, because there are still too many questions: Is it worth the effort? This is not clear enough yet!
- How much does it cost to integrate graphene into a fab and what is the benefit? As long as this is unclear, a company will not go for it
- For larger company: 1-2 million pieces per year are interesting, but is that enough for a completely new material?
- Not only technologists need to be convinced, but also marketing
- Open manufacturing challenges and demonstration with adequate parameters, missing actual prospect for “killer app” & uncertainty of cost keeps semiconductor companies from taking graphene into the fab and making larger investments
- Scalability and demand need to be matched (currently ok)
- Challenge: how far does research need to go until pick up through big industries?
- Even if the KPIs are met for wafer scale it is yet unclear who will take it up in Europe (→hypothetical device)
- Single customer/single source issue: for a supplier a single customer is not interesting; for an end user a single supplier is not ok: whole ecosystem is needed, whole environment needs to develop at the same time

- Start ups can cover low volume production, but for industrialisation/mass production a whole infrastructure needed. Start with start-up to get first demonstrators (who will finance them?) on a smaller scale for low volume niche applications to show the potential. Getting the whole ecosystem for mass production forward will take much more effort and is probably not feasible at the moment.
- Patent thicket

4.2.4.3 Potential actions

If the area of graphene/2D in electronics and cross-cutting applications is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

Fundamental understanding

- Grain boundary and interface investigations
- Investigate new growth processes and substrates
- Further investigations on interplay between material (doping, substrate, interfaces, contamination) and performance

Applications:

- Benchmark with existing technologies and other researched technologies in terms of functionality and figure of merit
- Focus on applications that promise to fulfil the 10x performance and/or 10x cost challenge

Manufacturing:

- SiC: engage with power electronics and PV who know how to work with SiC
- Lab-level and fab-level collaboration to address challenges
- Address the relevant process parameters and challenges in wafer scale integration (engineering knowledge), e.g. yield, contamination, etc.
- Demonstrate the process for a simple but convincing application, allowing cost assessments
- Elaborate design tools for integration
- Intensify hBN manufacturing research

Ecosystem:

- Develop a way how the innovation eco system can go ahead together (what is needed, in terms of customers and orders for a semiconductor company to do the investment); make an exercise/case study: how and if at all can that be achieved? What role can be taken by start ups/large enterprises? Even engage with marketing/management to get to know clearer prerequisites for uptake by (European) industry.
- Establish standardized methods to determine the quality of produced graphene and other 2D materials (“certification”)
- Create a group of classification criteria in order to evaluate the produced materials to help manufacturers and customers to
    - classify their material quality and customers
    - provide an expectation of the performance of the classified graphene and
    - decide whether or not the graphene or other 2D material quality is potentially suitable for various applications

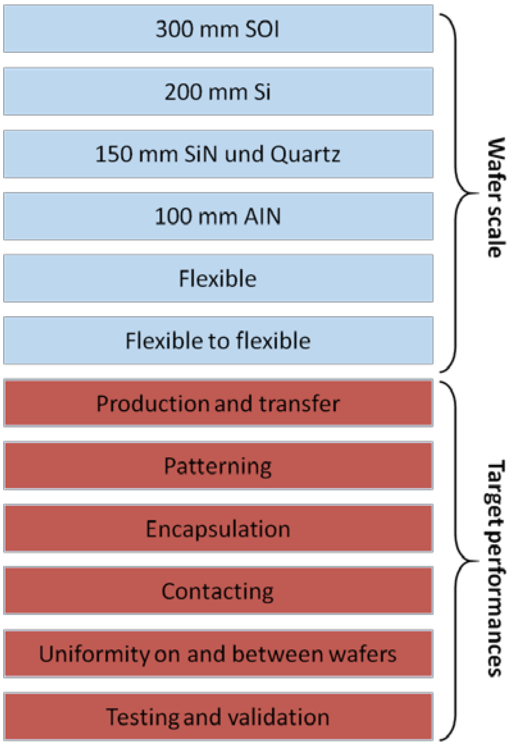
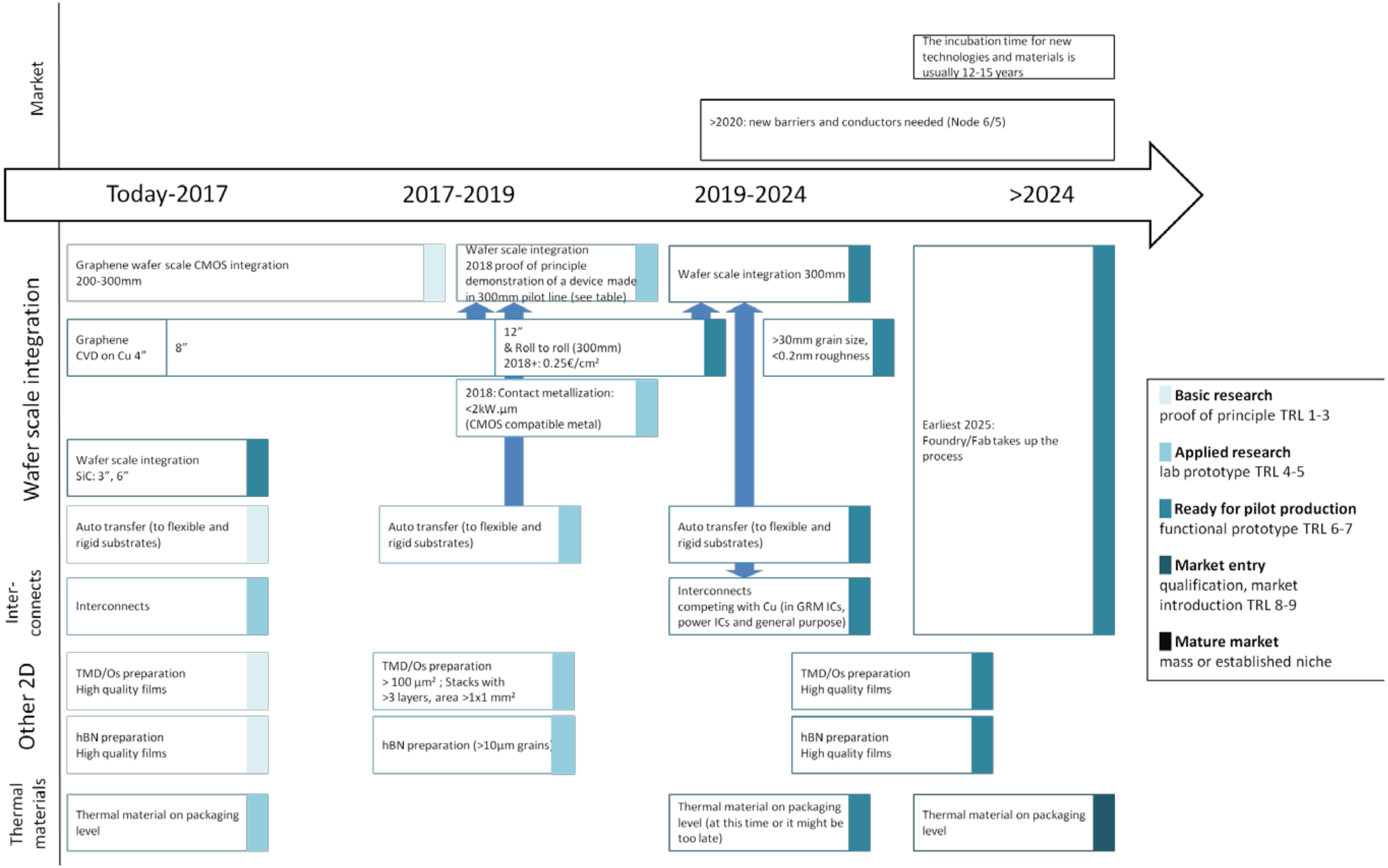


Figure 46: Areas of actions for wafer scale integration in the Graphene Flagship. Credits to C. Huyghebaert, IMEC 2016

4.2.4.4 Roadmap

The incubation time for new technologies and materials is usually 12-15 years [288]



Sources: [288, 297]

Table 43: Wafer scale parameters

Specifications	**Target 2018 (prototype)**	**Required for product**
Impurities	< 10^{12} at/cm2	< 10^{11} at/cm2
Contamination (e.g.PMMA)	< 10%	< 0.1 %
Mechanical defects	< 10%	< 0.1 %
Inclusions (e.g.water)	< 10%	< 0.1 %
Uniformity along 300 mm wafer (with acceptable edge exclusion)	< 10%	< 0.1 %
Scattering time*	100 fs	1 ps
Prototypes	Photodetector array, optical transceiver, …	

4.2.5 Conclusion electronics: cross-cutting issues

Cross-cutting electronics issues address common technology areas relevant for all electronics applications, e.g. common production related issues (wafer scale integration) or common technological issues such as electrical connection (interconnects) or thermal heat dissipation or barrier layers.

These areas typically address front-end-of-line and back-end-of-line as well as packaging in the chip/semiconductor fabrication. In this industry, Europe is behind East Asia and North America with a turnover share of 9.4% in 2012.

In particular the wafer scale integration is currently a bottleneck for many applications of graphene/2D materials in electronics. Positively seen, accomplishing a commercially viable wafer scale process opens up a wide area of applications and paves the way for a broad integration of 2D materials. On the other hand, if commercially viable wafer scale integration is not feasible, many applications will be not possible to be realized with 2D materials on a broader scale commercially. As these applications demand high quality films (mostly single or double layer), the integration will take more time as in composites or areas where flakes are sufficient. In order to justify the investment into new production technologies and 2D material integration, a clear and trustworthy demonstration is needed for a particular application, where the actual potential of graphene/2D materials is obvious in the device and the production.

For the back-end-of-line and packaging applications (interconnect, thermal and barrier material), the multi-functionality of electrical, mechanical, barrier and thermal properties as well as flexibility is again rather unique. There are definitely needs for new solutions, as this part of electronics manufacturing has a high cost pressure and physical boundaries are soon to be reached with the common materials. On the other hand there is a high barrier for materials needing a new process (conservative industry, higher investments needed).

For thermal heat dissipation applications on packaging level there are first products approaching the market, which make use of graphene flakes.

It is obvious that in general demonstrators are needed that show the potential in functioning devices prepared by production-compatible methods. Due to the long history of silicon and related materials and the strong experience, everything that can be done with Si, will be done with Si or incumbent materials, which introduces another barrier for uptake of new technologies.

Table 44: Assessment of market and technological potential of graphene/2D materials use in cross-cutting electronics issues on a scale - -, -, 0, +, ++

Cross-cutting electronics	**Current technological potential (USP)**	**Market potential (EU perspective)**
Electronics in general	+	+
Wafer scale CMOS integration	+	+
Interconnects	+	0
Thermal material	+	0
Barrier	+	0

4.3 Telecommunication, optoelectronics & photonics

This area deals with the broad application area of telecommunication, but also covers photodetectors and light sources/lasers for various applications. It essentially covers all technologies that deal with electromagnetic wave interaction and processing and analogue electronics. Figure 47 gives an overview of the electromagnetic spectrum and the spectral regions where 2D materials can play a role.

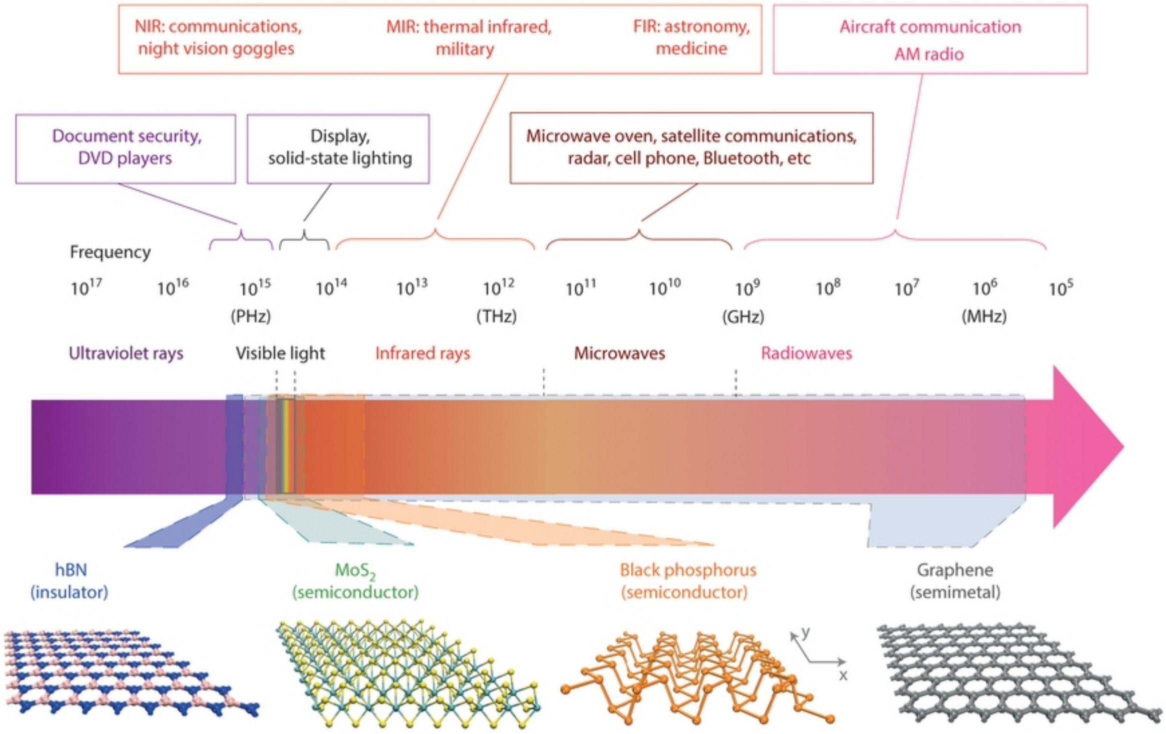


Figure 47: Optical spectrum and interaction with 2D materials. [328]

Telecommunication and networking covers all technologies that deal with high speed and low power data transmission and processing, ranging from optical networks, wireless networks, mobile applications/terminals to RF electronics. Graphene/2D materials are investigated due to their interesting optoelectronic and high frequency properties. Typical application areas are:

- **High frequency electronics deals with generation, acquisition and manipulation of high-frequency signals**, including RF, **microwave (MMICs) and THz/sub-mm waves** through analogue transistors, e.g. for amplification or signal processing. Radar/Telecom signal sampling/downconversion
  - **THz/sub-mm wave detection, imaging**
  - **Antennas and resonators**, i.e. passive HF electronics, e.g. for filtering (resonators) and reception (antennas), antennas for near-field enhancements for detectors.
- **Optical switches and modulators**, i.e. the manipulation of optical signals through electronic devices for high speed optical networks/optical fiber communications, e.g. (de-)multiplexing, modulation, switching. Together with photodetectors these components are important for photonic networks and optical data transmission, combined in optical transceivers and photonic ICs.
- **Photodetectors** for several uses, including high speed, high bandwidth detectors for optical networking, broad wavelength range (UV-VIS-IR) detectors for hyperspectral imaging/detection, x-ray detection, THz detectors.
- **Laser/photonics** for several uses and light sources, such as tuneable lasers, ultrafast lasers, THz light source.

The markets besides telecommunication (backbone network, radio cells for mobile communications, distribution network, terminals and end user devices) are in security, production/manufacturing (control and monitoring), biomedical applications and fundamental science. Table 45 highlights a few potential applications and scientific reviews dealing with the topics.

Table 45: Potential applications for graphene and 2D materials in telecommunication, optoelectronics and photonics as well as recent reviews.

Application area	**Use of graphene/2D materials as**	**Important markets**
High frequency components, analogue electronics (RF, µ-wave, THz, mm-wave) [163, 329–332]	Transistors, diodes, varactors and microwave-photonic devices for use in amplifiers, oscillators, frequency multipliers, mixers, receivers, transducers, MMICs, spin torque nano-oscillators as tunable µ-wave source	Telecommunication (incl. mobile), monitoring (industry, security), research
Resonators	electrode in BAW resonators	Mobile communications
Antennas [331]	Unobtrusive antennas, flexible RFID/NFC antennas, antenna for increased sensitivity (near field) of detectors	Mobile communications, RFID
Photodetectors for imaging and ultrafast detection [328, 333–338]	Electro-optically active material in imaging sensors and photonic ICs (VIS-IR)	Telecommunication, photonic networks, industrial monitoring and inspection, security, health, research
Optical modulators for optical networks [333, 339, 340]	Electro-optically active material for modulation of optical signals (VIS-IR)	Telecommunication, photonic networks
Laser/LED components [336, 341, 342]	Photonic component for ultrafast lasers/fibre lasers (e.g. saturable absorber); transparent conductive layer for LEDs	Telecommunication, photonic networks, research, industrial production, health

4.3.1 Market perspective: graphene/2D materials in telecommunication, optoelectronics & photonics

Various markets can be addressed by radio/high frequency, optoelectronic and/or photonic components, ranging from security applications such as radar, via the broad field of telecommunication and data transfer to inspection/monitoring methods and lasers.

In terms of telecommunication applications (optical and RF/HF/THz), mobile networks, network data centers, video broadcasting networks play important roles in driving the need for faster and more efficient solutions.

Optical network components

The overall optical transport network market was estimated to be ~$11.4 billion in 2014 and growing to ~$23.6 billion by 2019 at CAGR of close to 16%. [343]

Optical transceivers are at the core of optical network components. The datacom optical transceiver market is expected to grow to over $2.1 billion by 2019. 10-, 40- and 100-Gigabit optical transceivers for enterprise and data center markets created an estimated revenue of $1.4 billion in 2014 (growth of 21% that year), whereas worldwide revenue for client 10G modules stagnated. [344, 345] Other sources suggest even larger markets of $3.2 billion in 2013 growing to $9.9 billion by 2020 (CAGR 17.5%) driven by the availability and cost effectiveness of 40 Gbps, 100 Gbps, and 400 Gbps devices. [346] Optical modulators are part of these markets and the revenues for those are in the few hundred million $ range (~$230m in 2013). [347]

Looking at the photonic ICs market, the silicon photonics market is estimated at ~$330m in 2016 and expected to reach ~$1 Billion by 2022 (CAGR 22.1%). Highest CAGR is expected for active components, including optical modulators, photo detectors, wavelength-division multiplexing filters, switches, and lasers integrated within a single device, providing a smaller form factor with the help of silicon photonics. [348]

Photodetectors and imaging

Optical sensors are part of optical transceivers but also find applications beyond telecommunication, e.g. in imaging, inspection and all kinds of sensors facilitating light to measure a particular parameter (e.g. pulse sensors, proximity). Optical sensors go into many different areas ranging from consumer electronics, health to industrial monitoring and security, addressing low cost to high value products

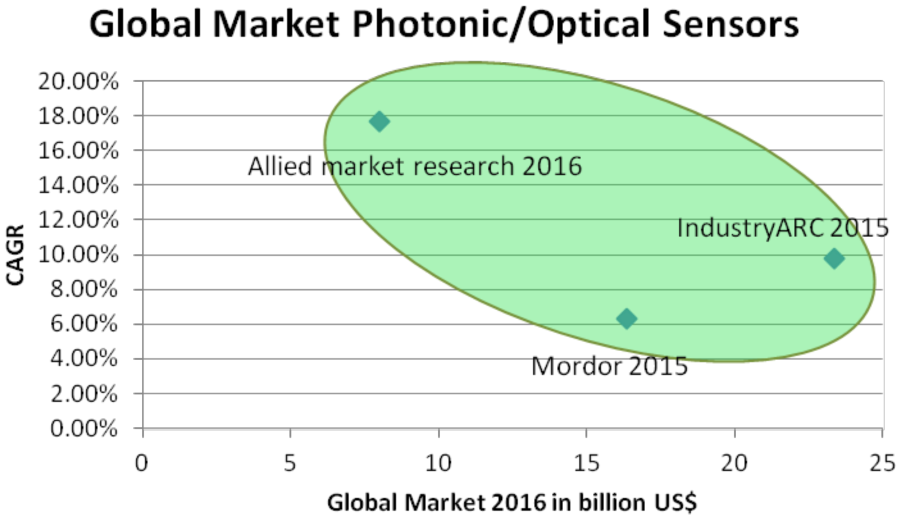


Figure 48: Global market overview 2016 for optical sensors from several sources. [349–352]. Another source estimated the optical sensor market at $5.3 billion in 2015. [353]

The market figures vary, which depends on the definition of the area of optical sensors and photodetectors and the uncertainty of such market expectations. Figure 48 summarizes three sources. Nonetheless it is a fast growing market expected to grow with rates between close to 10 and above 20% from $10-20b in 2016. [349–352, 354].

The global image sensor market, a subset of optical sensors, accounts for the largest share of optical sensors. Figure 49 summarizes several sources. This market accounted for revenues of around $10b in 2015 with expected growth rates between 4% and 8%. [355–358] CMOS sensors occupy more than 90% of the market. IR sensors were expected to have created revenues around $180m in 2013 growing to around $410m by 2018. [355] European based companies were responsible for about 10% of the worldwide production of image sensors. [359] For a more general sensor overview and to put it into perspective with other sensors, please refer to chapter 4.5.1 Market perspective: graphene/2D in sensors.

IR spectroscopy markets are today estimated to be valued close to ~$1 billion, expected to grow to $1.25 billion by 2020 (CAGR ~7%). [360]

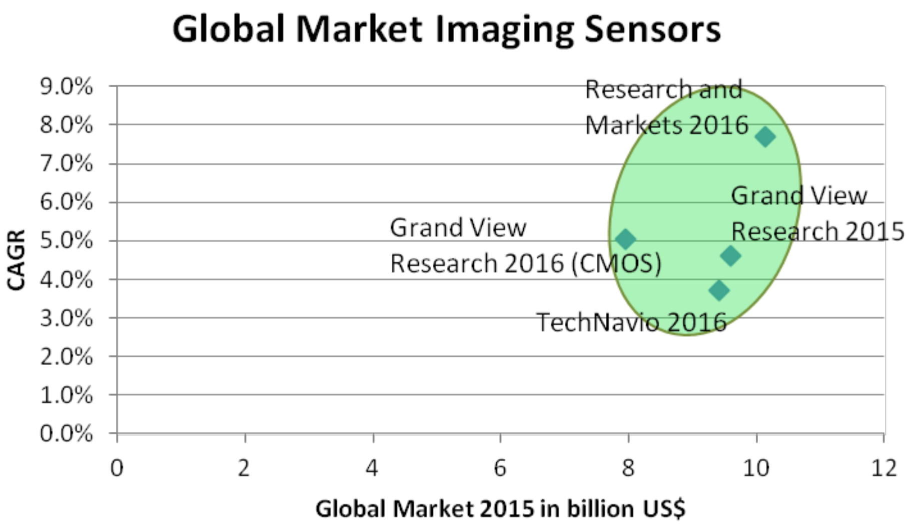


Figure 49: Global market overview 2015 for imaging sensors from several sources. [355–358]. Another source estimates the market to $10.6 billion in 2015. [353]

Optoelectronic semiconductors are the fastest growing semiconductor segment (11.3% growth in 2015) accounting for $33 billion. [289]

HF/RF/THz/sub-mm wave markets

RF power semiconductors revenues are estimated to grow heavily from USD 10-11 Billion in 2015 to USD >31 Billion by 2022 (CAGR 15.4% 2016-2022). In the last few years, new improved materials such as gallium nitride (GaN) are increasingly being used in RF power semiconductor devices [361] Of the RF Power revenues 2014 the main applications were: 65.9% cellular, 20% wireless communications, 4.7% military, 3.7% fibre-optic communications, 3.9% consumer, 1.8% automotive. [362]

The global Wi-Fi market is also expected to grow heavily with a CAGR of 17.8% until 2020 from USD 14.8 Billion in 2015 to USD 33.6 Billion by 2020. [363] Antennas, as an important part of its backbone accounted for a market of $15.1 billion in 2014, expected to grow to $19.9 billion in 2019 (CAGR of 5.7%) [364] The antenna, transducer, and radome (ATR) market for defense, aerospace, and homeland security was estimated to be close to USD 8 Billion in 2015. It is expected to reach USD 12.5 Billion by 2020 (CAGR of 9.53%). [365]

The market estimates for THz technologies are summarized in Figure 50. THz technologies are emerging and high growth rates are expected (>20% CAGR), although the market itself is not yet very large (~$100m in 2016). The high growth rates are attributed to a high adoption rate of THz technology-based products for laboratory research applications, as well as a growing demand from the defence/homeland security and medical sectors. THz imaging systems accounted for the largest market share of the

THz market in 2015. The market for THz communication systems is expected to exhibit the highest growth in the years to come. [366] THz spectroscopy is projected to reach a $50 million market by 2020 market growing from ~$25 million today at a CAGR of ~20%. [360]

The millimetre wave technology market accounted for revenues of $208.1 Million in 2014 and is expected to grow at a high rate of 42.70% in the near future. [367]

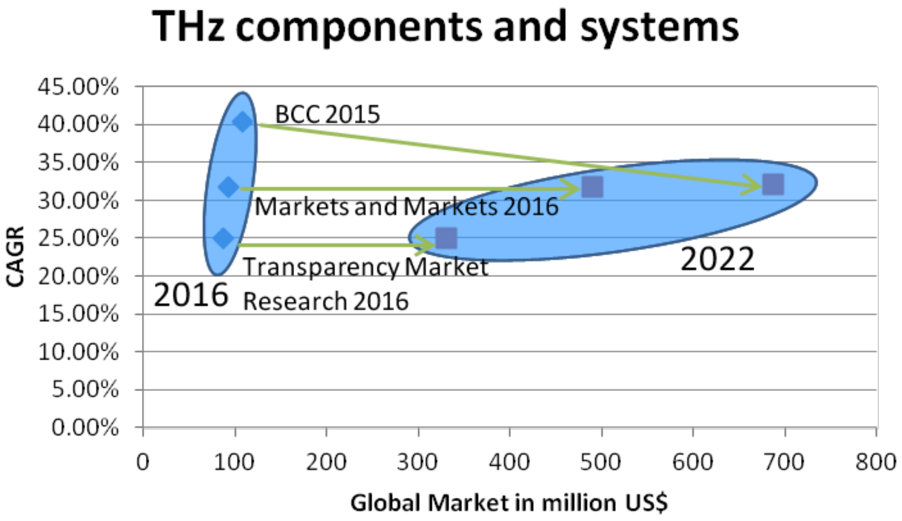


Figure 50: THz components and systems market overview from different sources. [366, 368, 369]

Analogue semiconductors accounted for a market of $45 billion in 2015, growing about 1.9%. [289]

The global signal generator market is projected to grow at CAGR 8-9% until 2022. It was estimated at ~$0.8 billion in 2014 growing to ~$1.2 billion in 2020. Signal generators are used for pre-production processes, e.g. designing, and post manufacturing, e.g. to check the conformance and accuracy of electronic devices. More and more “smart” devices enter the market and more and more industries are affected by digitalisation and sensor implementation, which drives the market need for signal generators. [370, 371]

Radar apparatus and parts product value in Europe was ~€4.5 billion in 2014 with slight downwards trend since 2012 (-2.5% CAGR). [39]

Laser/photonics:

The global market for lasers was on the order of $10 billion in 2014/15 with a split of 55% non-diode and 45% diode lasers. With annual growth rates of more than 6% the market is expected to reach $16b in 2020. Lasers for processing accounted for roughly over 50% of the market growing at CAGR of 6%. [372] Fiber lasers are expected to grow at a strong 16%.[373, 374]. The ultrafast laser market (15 picoseconds or less) is expected to climb past $1.4B by 2019. [374] Another study looking at titanium-sapphire lasers, diode-pumped lasers, fiber lasers and mode-locked diode lasers estimated a $2 billion market in 2014 expected to grow to nearly $5.5 billion in 2019 with a CAGR of 23.7%. [375]

Optoelectronics & photonics patents:

In terms of the innovative basis of the R&D and industry, some evidence can be gathered from the comparison of transnational patents between countries as depicted in Figure 51. The EU is behind the US and Japan and especially China is advancing. Figure 52 looks at the graphene/2D patents in optoelectronics, where Korea and US are leading followed by Europe. Japanese patent applications play only a minor role. The graphene share is increasing (see Figure 53) and particularly strong for Korea.

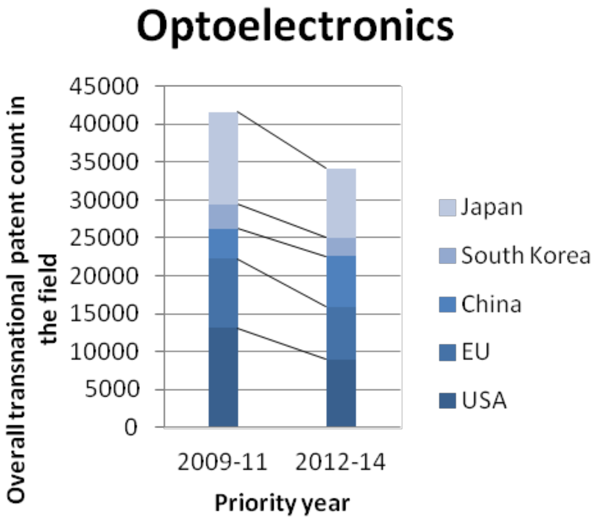


Figure 51: Overall transnational patent count in optoelectronics. 2012-2014 values are projected.[21]

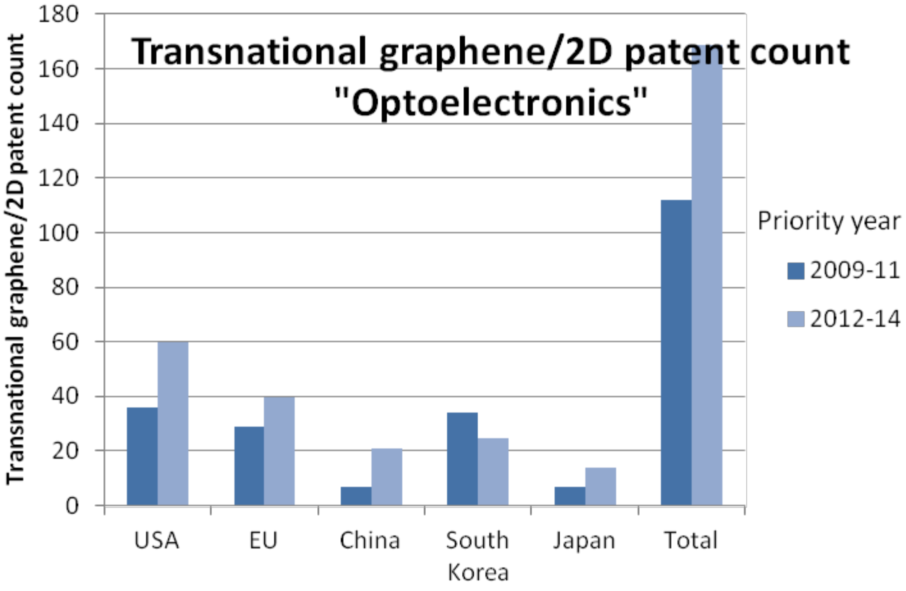


Figure 52: Patent analysis of graphene/2D materials in optoelectronics: Number of graphene related transnational patents in 2009-2011 and 2012-2014. 2012-2014 values are projected. [21]

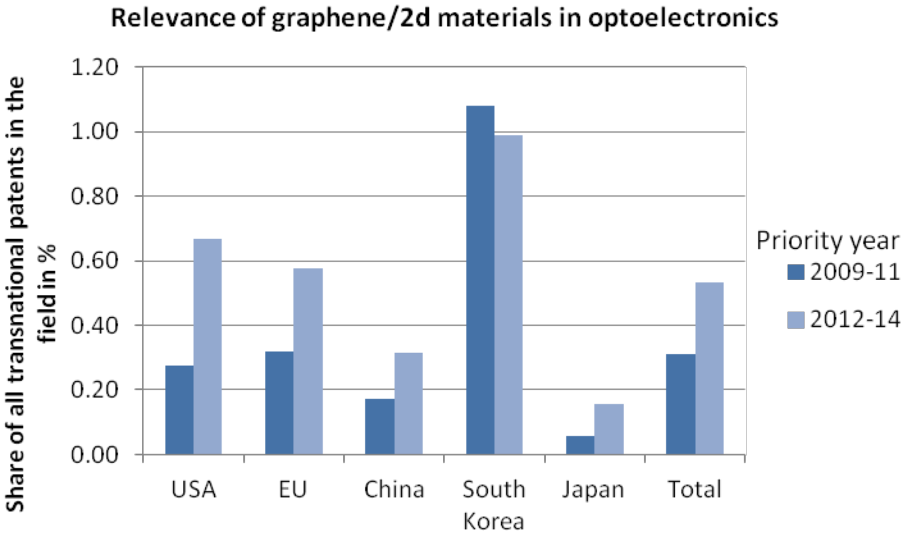


Figure 53: Patent share of graphene/2D related materials with respect to all transnational patents in optoelectronics. 2012-2014 values are projected.[21]

European industrial basis:

Table 46 gives an overview of product values produced in Europe in 2014 that are related to telecommunication, optoelectronics and photonics. Other sources claim that European based companies were responsible for about 10% of the worldwide production of image sensors, accounting for roughly 1b€ in 2016. [359]

Table 46: Production of manufactured goods value in EU-28 in 2014 and growth since 2012. [39]

Product	Product Value EU-28 2014 in billion €	CAGR 2012-2014
Logic/HF transistors, components and ICs	15.78	-1.7%
Telecommunication equipment	12.50	-22.6%
Photodetectors (incl. solar cells), spectrometers	3.37	-23.3%
Other Optoelectronics (Optical instruments, UV/IR for medical, optical fibre cables)	2.87	3.6%
Antennas	1.37	-1.5%
Light sources (semiconductor) & Lasers	1.20	4.1%
Signal measurement devices	1.01	-8.2%
Mounted piezo-electric crystals (including quartz, oscillator and resonators)	0.21	12.8%

The overall European photonics industry (including light sources, optical systems, solar cells, optoelectronics, etc.) has a global market share of [376]

- 55% in production technology
- 40% in optical components & systems
- 35% in measurement & automated vision
- 30% in medical technology & life sciences
- 30% in safety & defence systems

However, depending in the sources, the overall turnover share of EU-28 is smaller than for East Asia and North America, compare Figure 54.

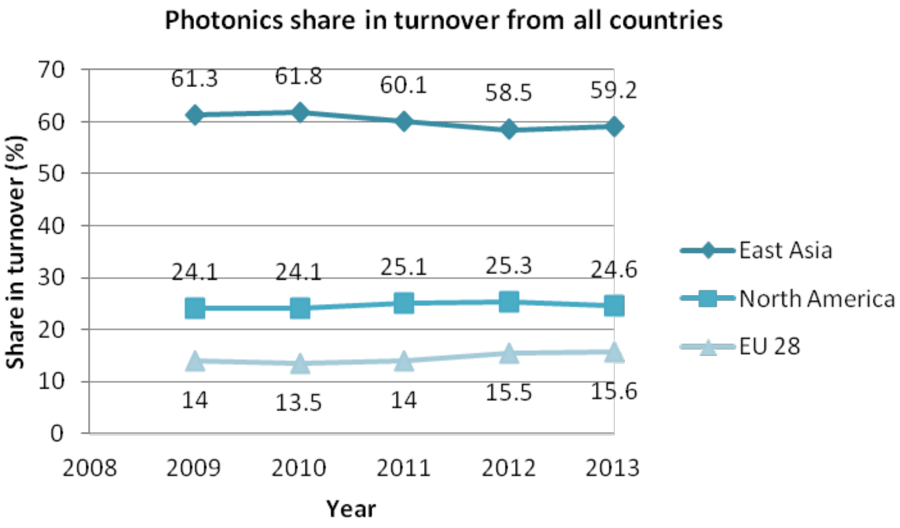


Figure 54: Share in turnover relative to all countries of photonics-related products. [377]

4.3.1.1 Market Opportunities

4.3.1.1.1 Strong and ambitious plan for 5G and beyond creates pull for new technological solutions

The internet of things and consumer markets drive needs for low cost, high volume wireless solutions. 33 billion devices are expected to be connected to the Internet in 2020 [362], almost 40 billion connected mobile devices are expected by 2024 [378]. The increasing use of cloud services and big data call for connectivity with high bandwidth and low latency everywhere.

The evolution of the mobile network standards to address these demands is ongoing and the next generation mobile network 5G is under full development. Key differentiators from earlier networks are: faster and higher-capacity broadband internet (100x-1000x capacity of 4G), lower (real time) latency, multi-access, multi-layered. [378] Although most of the 5G developments will be driven by software [379], there are also hardware related challenges: especially the backhaul (optical networks) and higher frequency (above 6GHz) wireless communication require new technologies or the heavy exploitation of existing ones (such as CMOS, SoI, SoS, GaN, SiGe, InP, Ge on Si, Si photonics). 5G plans involve developing networks at frequency bands of 5 GHz to 86 GHz [362], or even towards 300GHz waves for data transmission and backhaul. Besides, the power consumption challenge creates a need for new technologies: the increased bit rate must come without increasing power consumption (although bit rate is proportional to power consumption) and without increasing cost.

5G therefore generates needs in terms of hardware technologies for ever higher integration of functions and chips, low energy consuming small radio cells and terminals or photonic ICs beyond 600Gbit/s for backbone. To accommodate the new frequencies and higher number of bands, a better linearity and a lower R_{on} x C_{off} is needed for terminal RF power amplifiers and switches besides a better efficiency (currently realized with GaAs, RF-SOI or RF-CMOS). But for higher frequencies a big jump in improvement is needed at some point (most probably beyond 5G). [380]

5G Network development is already happening, but deployments may not be until 2020. Still, most technologies are already settled today. But after 5G there will be some sort of “6G” or at least further incremental developments for lower power consumption and higher bandwidth at lower cost necessary beyond 2020.

4.3.1.1.2 Broad market available (from high to low cost, low to high volume)

The telecommunication equipment market offers a broad variety of applications of RF and optoelectronic components. There are high cost components, e.g. in the backbone/main network with lower cost constraints but high constraints on durability and performance, as well as low cost components with shorter life cycles, high integration, increasing performance needs for user equipment, terminals and (optical) network units. The market competition is very high.

Besides the potential telecommunication markets, there are also high valued applications for RF/HF electronics, e.g. in defense and safety applications, so higher performance for some low cost increase is possible (but will only serve niche markets). For these markets, competition is moderate.

4.3.1.1.3 Race is still open for new technologies in and beyond 5G

5G hardware technologies and materials are not yet fixed, especially when it comes to wireless transmission beyond 6GHz and optical networks for the backbone. Beyond 2024 (“6G” or 5G evolution) it is to a great extent unclear which technologies can meet the needs. So even if 5G specifications are not met in time, there will be further future needs opening up another window of opportunity.

In terms of wireless transmission beyond 6GHz, technologies (e.g. CMOS) living up to the expectations are already demonstrated and quite mature. However, above 80GHz, there are not many technologies capable and feasible.

In terms of optical networks, ultra-low energy (optical) transceivers are required. Competing new technologies in development are either costly or do not live up to the needs yet. As such, crystalline Ge and III-V semiconductors are (currently) rather exotic and too expensive for massive integration, Si-based photonics are juvenile but emerging and expected to be cheap, Ge on Si is already mature and rather cheap and a main competitor. There is a particular need for new wavelengths beyond 1.3 and 1.55µm, e.g. 9xx nm, which could allow cheaper lasers to be used as light sources. Furthermore, current optical network components are not highly integrated and still quite bulky. There is a clear need for higher integration, e.g. an optical transceiver on one chip (including laser, modulator, multiplexer, demultiplexer photodiodes, ADC and digital signal processing). In this respect, there might be potential synergies with the rise silicon photonics, where graphene could be used as active material. [381]

Large players in the telecommunication/optoelectronics area are looking at graphene as one potential technology. It has the potential to be a special differentiator in optoelectronics creating a competitive advantage (at least it is partially seen like this).

4.3.1.1.4 Importance of optical networks steadily increasing

As mentioned above, optical networks are gaining more and more importance and also the markets are growing with annual rates beyond 15%. Optical high bandwidth communication is playing an important role also for server farms, on chip communication, etc. Also for the last mile in telecommunication networks, passive optical networks (PONs) are increasingly interesting with demands for 1530-1560/65nm variable light source and resonators. The latter application addresses a high quantity, low cost application (last mile).

4.3.1.1.5 European strength in photonics technologies

Europe is a strong international player in photonics technologies with a broad industrial basis. The focus, however, is more on production related technologies, on optical system level, in measurement & automated vision, in medical technology & life sciences and in safety & defence systems. [376]

4.3.1.2 Additional market opportunities: optical switches and modulators

4.3.1.2.1 Optical switches and modulators one of the key components of advanced optical networks

Fast and efficient optical switches and modulators are one of the key components and issues for mobile networks optical backbones, besides photodetectors. There is a strong need for broadband optical modulators with low switching voltage and high bandwidth. These components are high up in networks and high valued products with prerequisites of high switching speed ($\gg$50Gbaud), low power consumption, low driving voltages and low loss. Addressing new wavelength ranges comes as an additional opportunity.

4.3.1.2.2 Lack of alternatives for high speed switches and modulators

In terms of optical modulators there is a gap between future demands and technological offers. There are not many competing technologies with similar potential as graphene/2D materials: Si, SiGe and III-V semiconductors need higher switching voltages. LiNbO modulators have a size of 10cm or more, need high switching voltages and are expensive. InP performs well but is expensive and currently has no integration scheme on Silicon. It is yet unclear which technology can help to meet the ambitious market demands beyond 2024. No competitor has a solution at the moment for modulators that are economically feasible and meet the demands. This is a great opportunity for graphene-based modulators beyond 2024.

For optical switches, free-space MEMS and liquid crystal switches are competitors, but an integrated and compact switch with low-cost and high reliability is not available at the moment.

4.3.1.3 Additional market opportunities: Photodetectors

4.3.1.3.1 Need for high bandwidth optical detectors for communication

Optical networks demand high bandwidth and broadband optical transceivers and one key component of these transceivers are photodetectors. Most important properties are sensitivity, speed, reliability and cost. However, for optical long distance transmission, components can cost up to several thousand dollars, so performance and reliability is more important. The shorter the distance, the cheaper the products need to get, because volume increases. The opportunity for a first entry in higher valued products is possible, followed by a later entry in end user components (low cost).

4.3.1.3.2 High cost of competing technologies and SOTA

Although performance and reliability are more important for early adopting applications, cost can be an advantage on the long run. Depending on the integration scheme and further development of graphene/2D materials, costs are probably better than the established and rather expensive Ge and III-V crystals. Cost reduction could actually become a USP towards other, similar or better performing technologies.

4.3.1.3.3 Need for cheap and broadband NIR and hyperspectral (fast) imaging

Photodetectors are not only relevant for telecommunication applications, but also for photosensing and imaging. In particular hyperspectral imaging/sensing is an interesting field, as the cheap Si based technologies usually cut off at about 1100nm due to silicon’s bandgap and other technologies are more expensive.

There is a clear need for VIS+NIR/IR imaging, e.g. for industrial inspection and monitoring, e.g. in the food sector, but also in the health market and for wearables. Large and diverse markets are addressable with hyperspectral sensors, consisting of many available niche markets for early adoption:

- Consumer market: digital imaging, surveillance, remote sensing
- Wearable devices: pulse oxymetry and other health monitoring
- Biomedical industry: biomedical imaging and diagnostics
- Automotive industry: thermal, passive night vision
- Environmental monitoring: x-ray, infrared, UV and hyperspectral imaging
- Safety: imaging, explosives and threat detection
- Metrology: scientific metrology, space applications
- Process monitoring: agro/food, product inspection
- Machine vision: industrial manufacturing, autonomous vehicles

For competing technologies price is a major issue, which either comes from the production cost of materials or from the need for cooling. For instance, InGaAs is too expensive and sensitive (600-2000nm) for certain applications, such as food quality inspection. In that case a lower sensitivity for lower cost would be sufficient and allow a broader market uptake. In particular cheaper and uncooled solutions are interesting, as often InGaAs solutions are price prohibitive. A lower functionality is often justifiable with lower price. Such lower performing but cheaper products could open up new and diverse areas of application/markets (particularly when lower cost is combined with a broader spectral range). The NIR analysis already accounted for 9.6% of the total analytical instrumentation market in food testing in 2014, which corresponds to $175 million. [382]

European based companies were responsible for about 10% of the worldwide production of image sensors (~$1b), so there is an industrial basis. [359] In particular in the hyperspectral range competition is moderate.

4.3.1.4 Additional market opportunities: laser technologies

4.3.1.4.1 Early adopters with lower cost-sensitivity

Many specialised laser technologies address low volume, high value niche applications, such as science and health. These are important early adopters for new technologies and can be addressed by new laser technologies. For these high performance lasers, cost is not so prohibitive. However, when it comes to industrial applications (laser machining), telecommunication (optical networks) or consumer products, cost sensitivity increases.

UV-LED transparent film and substrate, Crayonano [383]:

Further applications are possible in special areas such as deep UV LEDs. Here graphene can be used as a combined epitaxial substrate and transparent electrode to make AlGaN nanostructured UV LEDs. These types of deep UV LEDs can be used for e.g. water and air disinfection purposes. The current LED technology is struggling with low performance and high cost, e.g. due to expensive AlN substrates (commercial graphene transferred wafers are already 10 times cheaper today). ITO is not an option as transparent contact as it is not transparent in deep UV. Furthermore, AlGaN nanostructures on graphene are dislocation free, whereas conventional deep UV LED are growing AlGaN thin films with very high dislocation densities resulting in low performance. Current barriers are availability of graphene wafers and Cu contamination to comply with AlGaN MOCVD requirements.

4.3.1.4.2 Need for tuneable sources in telecommunication

Optical networks demand photonic-assisted signal processing technologies (e.g. optical modulators, switches and photodetectors) or directly modulated light sources, currently provided by diode lasers. Tunable lasers are needed in telecommunication for WDM and passive optical networks (PON) in the NIR range: C-Band (1530 – 1565nm) / O-Band (1260 – 1360nm) 15-20nm tuning range. But these technologies are typically high volume, low cost, so for these products a high volume production method (e.g. wafer scale integration) is necessary.

4.3.1.5 Additional market opportunities: HF/microwave/THz generation, detection and processing

4.3.1.5.1 Market needs and opportunities for improved resonators

In terms of RF resonators for filters, there are market needs to increased the Q factor, reduce losses and increase energy efficiency. Besides, another important need is to downsize the package and reduce the total height by increasing the package density. The latter is especially important for mobile applications such as smartphones. For 5G and beyond there is also the need to increase frequencies and make higher frequencies available, whilst not increasing or even reducing cost (some added costs allowed for added value/functionality). Resonators address broad application areas in mobile communication from mobile handset to stations. For broad market diffusion, high volume is needed (billions).

4.3.1.5.2 Market needs and opportunities for antennas

Antennas are another passive element important for any wireless data transmission. There is a need/wish for unobtrusive (transparent) antennas in the frequency range 2-

5GHz for mobile broadband communication to increase acceptance, especially when more and more small cells are established. Conformal antennas are another important field, also for RFID and NFC (see 4.6 Flexible and/or printed electronics). Miniaturized and integrated antennas are important for mobile devices (e.g. integratable with SiGe RF components).

4.3.1.5.3 THz opportunities in imaging, detection and data transmission

THz-frequencies and sub-mm waves are a more a more exploited frequency range that previously has been neglected in terms of electromagnetic radiation. THz band communication is seen as one of the possibilities addressing the spectrum scarcity and capacity limitations of current wireless systems. [366] It is discussed for high speed communication at low distances (dense environment, buildings with many terminals and users, on-board of aircrafts, ships) or in pico cells with big bit rates and spatially constraint information.

Furthermore, THz radiation can be used in imaging, detection, remote sensing, e.g. for explosives, in security and defence applications but also in industrial quality control and monitoring or diagnostics.

There are markets that allow higher costs for better functionality (e.g. defense, security), but also consumer markets are possible at a low enough cost (telecommunication). The diversity of such a technology can be quite high.

4.3.1.5.4 Existing THz technologies rather expensive and/or over-performing

THz applications are currently not possible with Si. GaN and SiC are typically used, but those materials are quite expensive and at the moment not feasible for mass integration. Furthermore, the performance of these technologies is also partially too high, making it too expensive and over-performing for many mass applications. If graphene turns out to be integratable and economically feasible, THz applications could be interesting even if the performance is lower.

For instance, some current THz detectors (bolometers) are expensive because they need heavy cooling. The cooling also leads to a poor usability. There is thus the need for new lower or un-cooled technologies (room temperature device or 70K standard IR cooler compatible) device needed. A 10x lower sensitivity (NEP) than bolometer would be acceptable. Such a technology would be more compact, less energy demanding and cheaper, leading to a broader implementation and new application possibilities. On the other hand, Schottky diode based detectors are operating well at room temperature.

Other candidates to address this demand are based on semiconductors, but also still difficult to make. The cost of the current systems is so high that even single chip fabrication may be feasible. Additionally, the competition for THz components is not so high at the moment.

4.3.1.5.5 THz modulation and polarization insufficient with existing technologies

Besides THz detection, also modulation techniques are interesting. Intensity modulation is interesting to enhance, via a lock-in detection, the sensitivity and eventually the speed in mainstream THz applications, such as material characterization/quality control, medical diagnostics, remote sensing and security [384] as well as in THz wireless communications [385]. Polarization modulation is an approach for measuring the linear and the circular dichroism. The linear dichroism can be used, for example, for the evaluation of the homogeneity and internal strains of plastic films and papers. The circular dichroism is a key to distinguish absolute configurations of organic chiral molecules and as such is an important analytical tool in biology, chemistry, medicine and pharmacy. [386, 387]

One of the obstacles for advancing various THz applications (especially between 1-5 THz) is the lack of efficient and fast intensity and polarization modulators. Mechanical and thermal modulation techniques are possible in the THz range [388] but intrinsically slow (< a few kHz). The use of all-optical modulation is limited by the cost of ultrafast lasers. Many conventional techniques, used in the visible, near infrared and microwave ranges are difficult to apply in the THz due to the lack of proper materials. As a result, measurements of both types of dichroism that require such modulators are rare and not commercialized in the THz range.

The market is currently rather small but has high growth rates and a new development which makes the applications simpler or cheaper could even further push this growth. There are also a few companies active on THz spectroscopy in Europe (e.g. Menlo Systems, Toptica Photonics, EKSPLA, Hübner and others).

4.3.1.6 Market Threats

4.3.1.6.1 Highly competitive and international telecommunication market with high price pressure but performance focus

The large telecommunication equipment market is a highly competitive and international market. Competition and price pressure is high on system (networks) and operator level, and even higher on terminal/consumer level. This is price pressure is passed on to the components and parts of the systems.

But, for new technologies, performance comes before price: not performing better but being cheaper is no successful entry point. A potential cost advantage is only secondary, as material cost is less of a concern for data centres, high speed links and high power computing. There are also applications in defence or special applications with low volume that accept higher prices.

So the market has its space for high quality, high performing and high priced products, but especially in the backbone, the price pressure is high. As soon as it comes to high volume end-user equipment, terminals or optical network units (ONUs) low cost is even crucial and decisive.

4.3.1.6.2 Value/supply chain for telecommunication equipment exists and emerges in Europe but with a weak link and strong competition

Companies from each part of the value chain are in Europe. Telecommunication equipment manufacturers (such as Ericsson, Nokia including Alcatel Lucent) are mostly multinational companies within a strong international competition (Huawei, Cisco,…). Although the value of telecommunication equipment in Europe declined by 22.6% per year from 2012-2014, still a value of €12.5 billion has been created in 2014. [39] These companies can be enabled by graphene development. However, these companies will most probably not directly integrate graphene themselves, as they buy the components from their suppliers. On this supplier level, graphene integration needs to take place technologically. This is where the value chain is possibly weakest in Europe: The majority of component producers and fabs for optical communication are not in Europe, however, there are a few actors active (mostly integrators or fabs, e.g. ST Microelectronics, BAE Systems, NXP in Si photonics). For HF components the European position is better, as larger companies like Infineon, ST Microelectronics, NXP and medium sized companies such as AMS, X-Fab and others produce semiconductor components for RF/sub-mm applications. However, if graphene can make a difference, these manufacturers can be enabled and get a competitive advantage.

But there are several barriers to be taken and prerequisites that can hinder the uptake of a new material in this industry:

1. Sourcing: The sourcing of graphene materials on wafers need to be clear. Second sources need to be available.
2. The supply chain for the integration into a functional system needs to be clear
3. Single user/single customer conundrum: a supplier will say that a single customer is not interesting; the end user/customer will say: a single supplier is not ok. Therefore, a whole ecosystem and a whole environment is needed for successful and broad integration.
4. Larger companies need at least markets of 1-2 million pieces per year
5. For a broad use, foundries need to be involved. Currently, foundries do not investigate graphene for optoelectronics. Unless a mass market is addressed, foundries will not react.
6. Not only technologists need to be convinced, but also marketing

The possible early market entry scenario is via start-ups and researchers showing the actual potential in close-to-reality devices on low volume and smaller scale in niche applications. For industrialisation/mass production: a whole infrastructure needed, which will only be established when the added value is large enough (“10 times”). Getting the whole ecosystem for mass production forward will take much more effort and is probably not feasible at the moment, especially taking into account the second supplier, second source issue.

If this mass market is established for one applications, others will follow. It was assessed that optical switches and modulators for long range, high value market will most probably be available later, after a first mass market is established.

4.3.1.6.3 Stringent market requirements for reliability and durability

Reliability and durability are always major problems for a new and not established technology. The durability/stability needs for network infrastructure are 5-20 years, -40-70°C, depending on applications. The operational lifetime in telecommunication systems for instance can reach 30 years guarantied life time. There is a high demand for reproducibility and quality standards. Thermal stability is also very important, especially as thermal changes might induce changes in 2D materials. If the requirements are met, it is a huge opportunity for 2D materials.

4.3.1.6.4 Medium-term success unlikely as the window of opportunity is closing

As the graphene-based technology is still too young and especially the large scale production is not yet solved, it is very unlikely that graphene can play a role in the first generation of 5G components. The 5G window of opportunity is closing, standardisation is happening now and until ~2020. Solutions need to be there soon to be fully recognized for 5G. However, even if first technologies are fixed for 5G now and until 2020, there will be an evolution of 5G or 6G will follow afterwards, demanding higher bandwidth with lower power consumption and lower cost.

Besides, competing technologies and common technologies can be still used through optimization and higher level of processing. Additionally, Si-photonics is arising as a competing technology and bears large potentials. Graphene on the other hand could also find its way into Si-photonics and use this new technology as an enabler. [381] Si-photonics is capable of 100 Gb/s optical transceivers without graphene, using four laser wavelengths, each operating as an independent 25 Gb/s optical channel at low cost. [389]

The typical timeframe for new technologies in this area are >10 years from initial experiments to full market entry. For instance, Si photonics needed >10 years from early stages demonstration to maturity in a foundry (which is not yet reached).

4.3.1.6.5 Without wafer scale integration no success

For a broader market roll out of graphene-enabled technologies in telecommunication and optoelectronics, especially for larger markets and lower cost products, wafer scalability and CMOS integration is a prerequisite. A convergence of graphene technology and semiconductor technology is needed for most products (e.g. graphene on read-out of focal plane arrays for imaging sensors). Without economically feasible integration, graphene based technologies in this overall area will only be available for small niches and special very high valued products where other production schemes can be used, e.g. in lasers or simple photodetectors, if at all.

Refer to 4.2 Electronics: Cross-cutting issues for the SWOT analysis of wafer scale integration.

4.3.1.7 Additional market threats: optical switches and modulators

4.3.1.7.1 Competing technologies catch up rapidly

Although graphene is very promising and incumbent technologies currently do not meet the future demands (see 4.3.1.2.2 Lack of alternatives for high speed switches and modulators), the incumbent technologies still have further potentials for development and also other competing technologies catch up rapidly. The race therefore is still open.

4.3.1.8 Additional market threats: Photodetectors

4.3.1.8.1 Competing technologies for photodetectors

For high speed photodetectors, III-V, quantum well and resonant tunnel diodes are competing technologies with interesting performances. Those technologies are more mature in terms of production.

For NIR/IR imaging, many different technologies exist and are established, such as III-V semiconductors, Ge, PbS/PbSe, InSb, InGaAs, InAsSb, Mercury Cadmium Telluride (MCT) or other ternary compounds. III-V is well compatible with Si technology. These technologies mostly have proven to be reliable and have an adequate operational lifetime. The major drawback of those incumbent technologies is that they all are quite expensive, need cooling or are rather slow. Furthermore, the resolution is usually not good for given wavelength regions.

There are even already LWIR applications available for consumer electronics, such as the un-cooled VOx microbolometer Lepton® from FLIR, which is used in a CAT smartphone. [390]

4.3.1.8.2 Some markets require low cost

High cost markets are already served by other technologies, e.g. NIR in health addresses a high value, but rather specialised niche market with only few end products and high competition from competing and mature technologies. For these markets, the performance advantage must be rather large and be needed or the prices should be considerably lower for the same performance.

Applications with stronger cost constraints present interesting opportunities, e.g. food safety or consumer markets. But if the lower cost targets are not met, these markets are not an option. The first smart phone with LWIR imaging is already available on the market, see chapter 4.3.1.8.1 Competing technologies for photodetectors.

4.3.1.9 Additional market threats: Laser technologies

4.3.1.9.1 For large markets: cost constraints

Larger markets usually served by laser diodes and integrated lasers have strong cost constraints. For example, in telecommunication passive optical networks (PONs), high volumes are needed at a low costs of ~1$ per piece. For these high volume markets, laser applications needs efficient wafer scale integration.

4.3.1.10 Additional market threats: HF/microwave/THz generation, detection and processing

4.3.1.10.1 Mature competing incumbent technologies

MMIC technologies (GaAs, SiGe, GaN, SiC) are mature and established for 4G and first 5G applications. GaAs is currently the dominant technology. CMOS/SOI-based amplifiers and switches capture market share from GaAs. [362] Highest performing material is InP (with the highest f_{max}), but InP is very expensive and currently not integratable easily. Only SiGe has an integration scheme on silicon at the moment. For RF switching MEMS solutions are also possible and might replace RF SOI in the future.

For THz detection, Schottky diode based detectors are operating well at room temperature and are the reference and most important established competitor.

All in all, there are several advancing technologies which also build on a longer history that can technically outperform current graphene/2D based demonstrators. However if graphene is integratable and if it can be shown that the performance can be even better, this might turn into an advantage.

4.3.1.10.2 THz disillusionment

THz technologies were hyped in the 2000s and are now approaching something like the slope of enlightenment. Back in 2000 the technology was oversold and now expectations are low and interest vanished. However, it is again discussed nowadays for small cells and short range communication in 5G. Also for imaging and inspection (e.g. for production monitoring), it is still very interesting.

Although the growth rates of THz markets are strong, the overall market is still relatively small.

4.3.1.10.3 Resonators: Process/application addressed by graphene is very cost sensitive

In particular the use as an electrode in BAW resonators is a very cost-sensitive process, as it is nowadays realized with rather simple metal evaporation (SOTA: metal/alloy sheets of 200-300nm). The addressed products are prone to high competition and address large volume market (billions).

4.3.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in telecommunication, optoelectronics & photonics

4.3.2.1 Current strengths for graphene/2D materials use in telecommunication, optoelectronics & photonics

4.3.2.1.1 Outstanding potential of graphene for optoelectronic applications

Due to the missing/tunable bandgap and high charge carrier mobility, graphene is an interesting candidate for optoelectronic applications as active material for light-matter interaction. Other 2D materials with varying band gaps and mobilities could also play a role in this area.

Graphene absorbs broadband light ranging from visible to IR to THz. The combination with the high speed (bandwidth), tunability, low noise and flexibility make it a quite unique candidate for optoelectronic applications. In principle, it can be also integrated on waveguides and on fibres and thus be used for fibre communications. It is also compatible with typical optical communications bands in the 1200-1700nm range, like the C-band and beyond.

The broad optical absorption and tunability (band gap engineering) render it further interesting for hyperspectral detection and imaging. For most applications more or less integrated lab scale demonstrations are available showing the potential. The high charge carrier mobility (electrons) make it an interesting candidate for high bandwidth fast photodetectors used in optical networks.

Besides this technological substitution, graphene and 2D materials can also be enablers for new optoelectronic devices, e.g. mixers at high frequency and microwave. Due to the linear energy dispersion of electrons and holes graphene demonstrates a strongly nonlinear electromagnetic response in a broad frequency range from microwaves to visible light. Resonance frequencies and the nonlinear response can be controlled by the electron density, i.e. the gate voltage. This can be used in different nonlinear electric-field controlled optoelectronic and photonic devices, including saturable absorbers, fast and compact electro-optic modulators, optical switches, frequency multipliers and mixers, parametric amplifiers, etc. If wafer scale integration work economically, all these nonlinear graphene devices could be implemented on silicon-based chips, thus opening up new opportunities for the realization of nonlinear integrated Si-based photonic circuits.

The multifunctionality, performance, flexibility for conformal electronics and potential integratability therefore make graphene and 2D materials rather unique candidates with that potential. Only few other materials have similar optoelectronic potentials, depending on applications (e.g. some III-V sc's).

Besides the technological performance, the probability that it can be even cheaper than competing technologies is there, although this remains to be proven. In that case, a cost advantage towards other technologies, such as Ge could become a USP (but this is still not clear). The technological potential is already there, but in particular for cost effectiveness an integration scheme is crucial. Devices could also be made simpler by using graphene for instance because less complex circuits or less transistors are needed (e.g. for demodulators), also leading to a potential cost reduction.

At the moment, optoelectronic applications are seen as a realistic and feasible application of graphene/2D materials, also from industrial point of view.

4.3.2.1.2 Compatibility with Si/SiO2, SiGe and SiN platforms

Wafer scale integration would allow adding active functionality though graphene on passive Si-photonics, Si/SiO2, SiN platforms. It would make it possible to integrate graphene on SiGe or Si CMOS (VLSI) as optical modulator. The convergence of graphene technology and semiconductor technology is still possible and might be feasible (see wafer scale integratiion in chapter 4.2 Electronics: Cross-cutting issues).

4.3.2.1.3 Possibility for fully integrated optoelectronic devices

The evolution of the prior integration potential is to integrate different active components made with graphene with similar processes to allow preparation of fully integrated optoelectronic devices on Si or other semiconductor materials. For instance to integrate a photodetector, switch and modulator on a VLSI chip to make an all-integrated optical transceiver.

4.3.2.1.4 Mechanical flexibility and conformability

2D materials are naturally flexible. This opens up interesting applications such as flexible RF electronics (see also 4.6 Flexible and/or printed electronics).

4.3.2.1.5 New types of spin-based data communication might become possible in the future

Graphene’s long spin diffusion length (see chapter 4.4.2.2 Additional strengths: spintronics) offers a potential to be used within completely new data communications scheme in the future which relies on the modulation of the electrons’ spin polarization [391]. If spins are used to encode information, then the charge current is used to drive the information instead of to carry it. This spin based scheme is expected to be free of transmission line effects, electromigration problems, and the need for wire shielding. Graphene could offer better performances in this type of data communication towards other semiconductors. This may open ways for spintronic applications beyond information storage.

Furthermore, the long spin coherence length in graphene could be used to drive spintronic nano-oscillators at microwave frequencies. This would be a new and economically interesting way how wideband (1-100 GHz) microwave signals can be generated, modulated and detected in future graphene based microwave devices. [392]

4.3.2.2 Additional strengths: optical switches and modulators

4.3.2.2.1 Electro-optical properties of graphene well suited for optical switching and modulation

Graphene exhibits interesting optical switching/modulation capabilities, especially a theoretically low switching voltage, low loss and high speed. It can be used for integrated switches and modulators with smaller package size compared to Mach-Zehnder type modulators. The experimental demonstrations have not yet reached these high levels, but are promising. The design of graphene-based optical modulators is available. It has been shown that the devices exhibit reasonable speed, are optically broadband and temperature insensitive. The switching voltage is already acceptable and lower than for SiGe-based modulators.

Besides reproducibility, lower insertion loss and higher extinction ratios are needed as well as higher speeds, leaving still room for improvement. Only few other materials have a comparable potential for optical switching and modulation (some III-V sc’s or the large footprint Mach-Zehnder modulators). So graphene is quite unique and promising for this application.

4.3.2.3 Additional strengths: Photodetectors

4.3.2.3.1 Broad optical absorption has a huge potential

Graphene absorbs electromagnetic waves from the UV to THz. Furthermore, the material can be optically tuned with plasmonic effects. This broad optical absorption has a huge potential for hyperspectral applications and tailored applications for any wavelength range.

Furthermore, graphene can be used as very thin antennas strongly focusing radiation in small near-field areas (the thinner the conducting layer, the larger is the field amplification factor, see also 4.3.2.5.3 Potential to be used as transparent antenna or absorber for certain wavelength ranges and 4.3.2.10.4 Antenna performance still too low). This can be used in detectors and mixers.

4.3.2.3.2 Potential for high bandwidth detectors and first lab results are promising

For high bandwidth photodetectors, simulations suggest a much higher possible speed (>600GHz) than existing technologies (roughly double the speed as III-V, Ge) [393]. Experimentally shown frequencies in the laboratory are close to III-V based frequencies (~262 GHz, III-V are >300GHz) [337] and performances of laboratory scale integrated photodetectors on Silicon (SoI) show a promising of 50Gbit/s. Up to 100 Gbps (at 850 nm and 1310 nm optical wavelengths) should be possible. [394] Furthermore, an improvement of 1-1000x bit/power (lower energy consumption) seems possible. The bandwidth and detection speed is already superb (in simple lab prototype) and the wavelength flexibility is very interesting. Sensitivity/responsivity is a current challenge, but there are concepts addressing this issue. [395]

Another key advantage is that graphene based ultrafast photodetectors can operate without the power-hungry transimpedance amplifier, which reduces power consumption of the system.

There is no specific intrinsic disadvantage. However, as the high potential needs to be actually demonstrated to show the actual technological benefit, it does not mean that graphene will evidently be the “winner” concept.

Another advantage is that the process for photodetectors is compatible with graphene modulator processes. The latter have similar promising characteristics, so that important parts of optical transceivers could be available and integratable from graphene with similar processes.

The combined properties of graphene for photodetection are quite unique (it is one out of a few candidates for future detectors). Other concepts are III-V semiconductors, quantum well or resonant tunnel diodes. The competing technologies are also quite costly, so if integration works and turns out to be rather cheap, graphene based detectors could become cheaper and easier to handle. Thus, cost can become a USP for photodetectors based on graphene.

4.3.2.3.3 Potential flexible detector solutions allow simpler optics

Graphene photodetectors can be made flexible on conformal substrates. This is an added value and quite unique (one out of a few candidates), especially for simple photodetectors (e.g. for fitness wrist bands pulse measurement, proximity sensors or imaging). Furthermore, the robustness is higher compared to e.g. InGaAs, which is brittle.

Flexibility and conformability can be important depending on the targeted market. For imaging it can for example simplify the optics leading to cheaper optics or smaller packages.

4.3.2.3.4 IR imaging allows higher resolution

IR imaging is an important application area for graphene. Graphene based IR imaging sensors can in principle lead to a better spatial resolution than InGaAs possible (resolution somewhere between InGaAs and Si). The overall performance of graphene based NIR/IR sensors today is already close to Si and InGaAs and there is still room for improvement. There are at the moment no specific or intrinsic disadvantages of graphene based sensors, besides the CMOS integration issues, which does not mean that it would evidently be the “winner” concept. But there are still many challenges to be addressed and an economically feasible wafer scale integration would be very beneficial. This in the end could lead to even cheaper sensors, especially as the competition is rather expensive. There is a market for poorer performing but cheaper IR/NIR sensors.

4.3.2.3.5 For non-integrated photodetectors and single pixel wafer scale integration is not necessarily needed

For very simple (single pixel) not-integrated detectors or flexible detectors, wafer-scale integration is not necessarily needed and roll to roll or sheet to sheet direct transfer is sufficient. This might still be cost competitive (probably already today), as many existing solutions in the IR are quite expensive. With working and feasible wafer scale integration, the cost reduction potential for these simple detectors would be very high potentially opening up wide markets.

4.3.2.4 Additional strengths: laser technologies

4.3.2.4.1 Saturable absorber and non-linear properties of graphene

Ultrafast carrier dynamics combined with large, spectrally broad and fluence dependent absorption due to Pauli blocking make graphene an interesting ultrabroadband wavelength independent and fast saturable absorber (SA) for ultrafast lasers (typically nano to sub-ps pulses). [163] The dominant SA technology for commercial (fibre) lasers is based on semiconductor SA mirrors (SESAMs), suffering from narrow tuning ranges and complex fabrication and packaging. Graphene SAs are an alternative to low-temperature grown GaAs (LT-GaAs).

Graphene based SAs enable broad tunability and can be realized with LPE and CVD graphene and the fabrication is relatively easy. They have been demonstrated for the important telecommunication wavelengths (e.g. ~1.5µm) but can be also used for mid-IR photonics.

Furthermore graphene exhibits higher order nonlinearities ($\chi^{(3)}$) for frequency conversion. In general, it should be possible to reach small form factors for graphene based photonics, e.g. in ultra short pulse laser diodes, especially if wafer scale integration technology is available.

Other nonlinear optical properties of graphene, such as second harmonic generation, difference frequency generation, four-wave mixing have been predicted and experimentally observed. It has been found that the nonlinear graphene parameters are substantially larger than in many other nonlinear materials and graphene might be more practical/robust to be used in applications. This opens new opportunities for design and development of different nonlinear graphene-based optoelectronic and photonic devices, controlled/tunable by the gate voltage.

4.3.2.5 Additional strengths: HF/microwave/THz generation, detection and processing

4.3.2.5.1 Physical properties are beneficial for HF/microwave/THz electronics transistors and realized advances are promising

The main motivation to use graphene for high frequency and analogue electronics is the ultra high carrier mobility, which allows high speed. Additional benefits are the very short life time of the photo-carriers, and the availability of 2D gas of electrons (plasma properties, plasmonics). This leads to realised graphene transistors with promising cut-off frequency f_T of 427 GHz (for a 67nm channel) [396] already reaching cut-off frequencies of competing technologies at similar wavelengths (e.g. GaAs, Si MOSFET). Furthermore, devices exhibit a low noise and allow for ambipolar electronics, leading to lower amount of needed transistors, leading to less chip area and lower energy consumption. f_{max} of competitive 200GHz at 60nm gate length have been demonstrated, which is not yet enough to outperform incumbent technologies but further shows the potential. [397] However, voltage gain A_v still lags behind. For a comparison of f_T and f_{max} with other technologies see Figure 55.

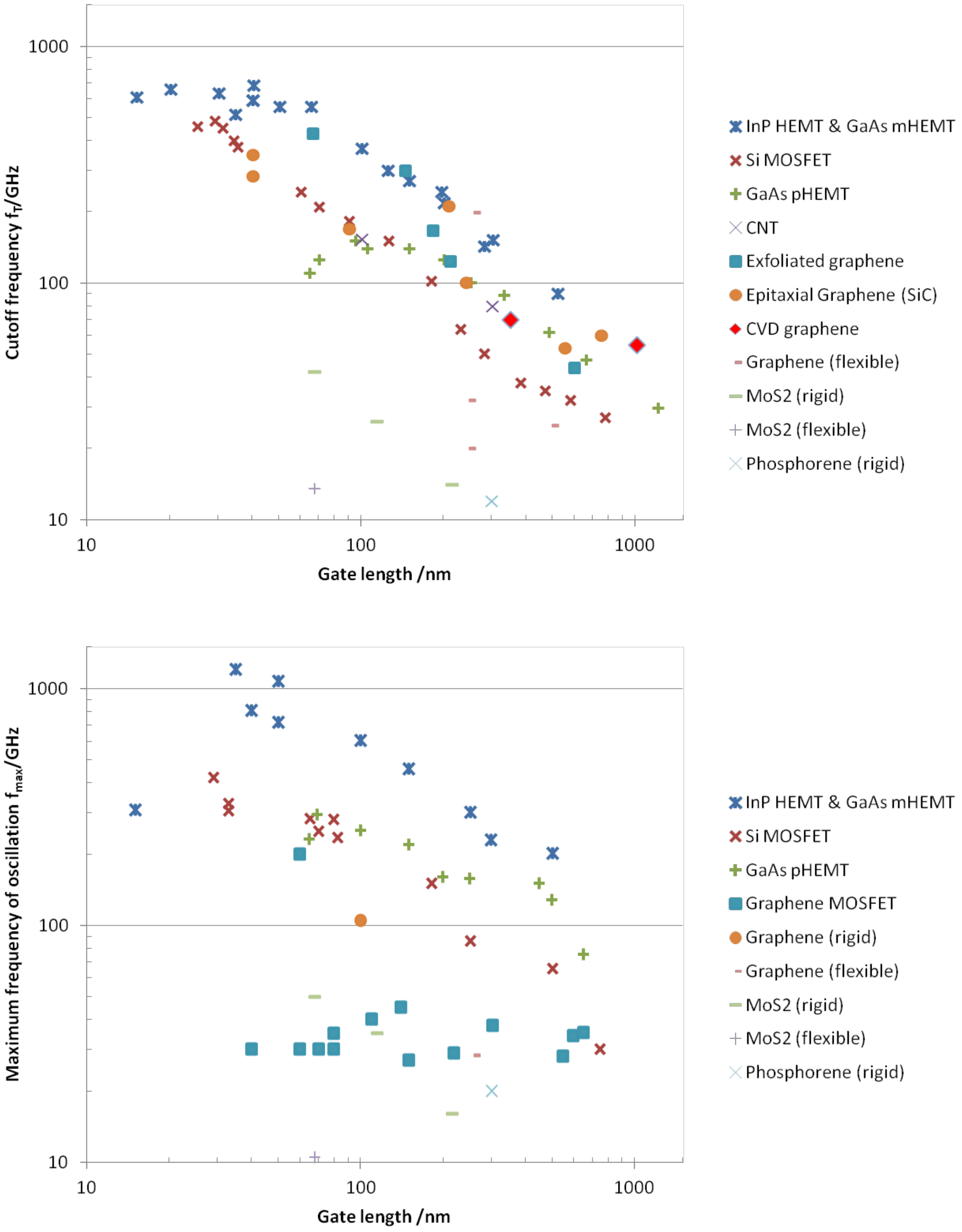


Figure 55: Comparison of cutoff frequency and maximum oscillation frequency depending on gate length for incumbent technologies, graphene and other 2D materials. Adapted from [314, 397, 398]

Graphene based modulators, demodulators, mixers and power detectors, key components for microwave and millimetre wave (wireless) applications, have extraordinary high linearity, possibly better than other semiconductors. First proof-of-concept measurements show a great potential for spectral efficient, very high data rate wireless communication interesting for systems for 5G and beyond for backhaul communication.

A larger mobility is also interesting because the larger the gate can be for a given frequency, which makes coupling easier, as the gate length gets closer to an antenna. Furthermore, optoelectronic functions and optoelectronic mixing can be addressed at the same time leading to an interesting multifunctionality. This is even further interesting due to the tunable optical properties. Tunability can even be achieved through stretching.

In principle, the technology is scalable and integratable with existing technology on wafer scale (see chapter 4.2 Electronics: Cross-cutting issues). It is also possible to integrate graphene in MMICs.

Also large arrays can be made for THz detection or radar application and flexibility is also interesting for RF applications. Due to the heat transfer properties, power dissipation can also be addressed at the same time.

An interesting novel transistor type is also the hot electron graphene base transistor, which uses gapless graphene and has some promising properties, although it is currently still difficult to seriously assess its potential for logic applications.

4.3.2.5.2 Graphene is the ultimately light and conductive electrode for BAW resonators

Graphene could be used as an ultimately light conductive electrode to replace metal/alloy sheets of 200-300nm on BAW resonators. The perfect electrode has low weight (very thin) and high electrical conductivity to allow a high q factor and low energy consumption. The theoretically calculated q-factor of graphene resonator is not achievable with other materials. However, the experimental validation of potential performance is still open (high risk, can also be a complete failure).

4.3.2.5.3 Potential to be used as transparent antenna or absorber for certain wavelength ranges

Graphene can be made tunable and optically transparent. At the same time it can have absorbing characteristics in the RF or microwave range. [399] Therefore it is potentially usable as a transparent and unobtrusive antenna, potentially in buildings or wearables. It can be also used as optically transparent radar absorbing material. On the other hand, it could be possible to tune it so that it is RF transparent and DC conductive, e.g. for radomes.

Graphene and GRM can serve as efficient micro-antennas of RF, MW, THz and IR radiation. The local AC electric field near sharp edges of thin conducting layers can be orders of magnitude larger than the field of the incident wave, with the field enhancement factor being stronger for thinner layers. Since the mono- or bi-atomic graphene layers are one or two orders of magnitude thinner than typical metallic layers, the graphene-based antennas can much more efficiently focus the incident wave field in very small areas. To reach that, higher mobility samples need to be available (with the scattering time of longer than ~ 1ps) with industry compatible manufacturing techniques. For this scattering time, the surface resistance is ~36 Ω/□. Thus, monolayers of graphene with the electron density ~$3x10^{12}$ cm^{-2} and the scattering time ~ 1ps could serve as very thin antennas and replace metals.

Such antennas can be also used in RF, THz, IR detectors strongly focusing radiation in small areas and hence increasing the detector sensitivity.

4.3.2.5.4 Potential in low cost room temperature THz detection (also for RF, MW, IR)

Due to the plasmonic effects, the absorption of THz, RF, MW and IR radiation can be much higher than 2.3%, especially allowing access to these frequency domains for detection and manipulation. There are investigations towards the potential for low-cost room-temperature THz imaging/detection and ultrafast THz detection. Although the sensitivity may not be as good as with other techniques (at least with the current graphene quality), the speed is high. This has potential for ultrafast THz detection, even for quantum information applications, covering a broad frequency range from 3 THz to1 GHz. Un-cooled THz detectors are already demonstrated at lab scale with NEP and fast speed approaching competing technologies [332, 400–402]. With wafer scale integration, also the cost could become competitive or even better for room-temperature THz imaging. Currently, the complexity of integration is more tricky than for semiconductors, which are prepared by MBE, but easier than for CNT. If room temperature performances are reached, which are comparable with cooled solutions, the indirect cost reduction potential is high, because the cooling system is not needed any more or can be weaker and at the same time power consumption can be reduced.

Other strength could lie in THz modulation, where graphene-based mixers were demonstrated up to 600 GHz.

Further investigations address MW, RF and IR detection based on plasmonic enhanced detectors.

4.3.2.5.5 Graphene interesting for THz modulation

Graphene allows an ultrafast modulation of its optical properties (absorption, reflection, transmission) by applying a periodic electric potential to the gate in a field-effect transistor (FET) configuration. Maximum cutoff frequencies of 100 GHz and higher in graphene-based FETs were shown. In the THz frequency range the modulation can be especially strong, due to graphene's high Drude conductivity, the dominant mechanism of electromagnetic absorption in this frequency range. As compared to its already high intrinsic value, the Drude absorption can be further enhanced by using plasmonic effects, external Fabry-Perot cavities and applying magnetic field.

It could be used as free-standing modulator, in the THz source or in the detector. In quantum cascade lasers (QCL) as THz sources, graphene showed promising properties and achieved 100% modulation on the lab scale (concentric-ring QCL) [403]. For THz detectors, it could be used with bolometers and/or semiconductor photodetectors (e.g. InAs, GeGa etc.), where the amount of THz radiation impinging on the detector could potentially be modulated by electrically gated graphene. In this case, the small detector size allows using small area (and therefore high-mobility) graphene.

A unique feature of graphene is a strong magnetic circular dichroism (MCD) and the Faraday rotation (FR) in the THz range [404, 405]. It appears that the MCD is especially significant (30% and higher) and that it can be inverted electrostatically by the gate at a fixed magnetic field. This feature allows switching between the LHC and RHC polarizations electrically with the maximum modulation speed allowed by a given GFET. The magnetic field intensity generated by compact and cheap permanent magnets and thus suitable for practical applications is limited to about 1.2 T. Preliminary estimates show that for high-mobility graphene this field can be sufficient to achieve a significant MCD, required for a proper modulator functioning.

4.3.2.6 Current weaknesses and challenges for graphene/2D materials use in telecommunication, optoelectronics & photonics

4.3.2.6.1 Quality and maturity of demonstrators

Many lab demonstrators show proofs of principles/concepts and the technological potential, but not on industrial scale. The graphene/2D material based technology is still rather young and thus a concise and solid business assessment is not possible at the moment. However, the potential is there and further investigations, especially in terms of actual demonstrators used in relevant environments and benchmarking with other technologies will help to reduce the uncertainties and assess the actual technological potential and unique selling propositions.

Besides that, the manufacturability is the most important topic, where especially reproducibility and the reduction of the scattering of the performance need to be addressed, as those issues are crucial for manufacturability and broader usage (see below).

Current key limitations are therefore a reliable large scale production, contacting of the material, energy efficiency and the overall performance in relevant systems and its benchmarking.

4.3.2.6.2 Integration challenge (wafer scale)

Undoubtedly, wafer scale integration is a crucial challenge for most telecommunication, optoelectronics and RF electronics applications. For some areas, such as simple photodetectors, laser applications and flexible applications wafer scale processes and integration with existing electronics is not needed and the already quite mature roll to roll or sheet to sheet transfer might be sufficient in quality. Using graphene and 2D materials as optoelectronically active material on Silicon or other substrates is very promising but also very demanding. If this is not feasible, many applications will not be able to address broader markets and will be relegated to a niche existence, if at all. For more information on wafer scale integration see chapter 4.2 Electronics: Cross-cutting issues.

In the following, the most important aspects of wafer scale integration for telecommunication, optoelectronics, photonics and RF electronics are addressed. Reliable large scale production is a key concern of many interested companies. The best case and desire would of course be a transferless process.

These applications mostly demand and benefit from the high charge carrier mobility in graphene films. Further needs are related to tuning the graphene homogeneously over the whole substrate (e.g. to introduce a bandgap, increase light interaction, etc.). Production of films exhibiting the needed electrical properties over the whole substrate is not yet possible. For instance, there is currently no reliable large scale technology to fabricate devices integrating a graphene film exhibiting carrier mobilities above 20000cm^2/Vs and strong carrier velocity saturation (using e.g. dry transfer, BN/Graphene/BN structures,…) over the whole substrate.

Besides the films itself, also the contacting and post-processing are key challenges not yet resolved: Contacting limits the performance of many devices due to parasitic effects such as capacitances and/or resistances. New concepts are needed to address these issues on wafer scale. This is not a physically limited challenge, but effort is needed to resolve that by proper engineering.

Independent of the actual challenge, the production reliability and yield play important roles in a fab and for the final price of a product. Especially as graphene exhibits a high sensitivity of properties to defects, so that small defects can have large effects. This calls for very stringent and precise processes. To address that, a stronger focus of research on process understanding and metrology is needed.

Furthermore, the substrate and encapsulation can influence the devices and long term reliability. Currently, there is knowledge missing about the most suitable substrates and the need, potential and influence of encapsulation.

The package of the unresolved integration scheme and limitations in current demonstrators (actual device-like demonstrations are needed) limits the overall advantage and will for companies to get stronger engaged and interested in the topic. Obviously, the unclear cost and effort of the production process can become a killer for broader graphene use. This applies to more or less all integrated solutions (laser, detector, …).

The remaining question is how much investment is needed to improve prototypes and manufacturing to a level that industry takes up the development. It is believed that especially for the manufacturing larger investments and patience are still needed.

4.3.2.6.3 Unproven long-term stability and robustness

Long term stability and robustness (2-5-10-20 years qualification period depending on application) are crucial for market acceptance. Although it is clear that this topic cannot be in the focus from the early beginnings of a technology, especially when the actual performance gain is not yet fully proven, it needs to be addressed as soon as the technological potential is seen. Especially when it comes to manufacturing and large scale production methods, long term stability/behavior need to be investigated and proven.

4.3.2.6.4 Graphene most probably too late for 5G, but there will be further evolutions

It is not realistic that graphene or other 2D materials will play a significant role in the beginning of 5G. High enough maturity and qualified graphene-based 5G solutions might come too late (needed before ~2020). Still the demand for efficient and fast data transmission components will increase after the launch of 5G creating the need for new solutions in further evolutions of the standard. To go further down this path, more industrially relevant and still better performing proof of principle/concepts are needed.

4.3.2.7 Additional current weaknesses and challenges: optical switches and modulators

4.3.2.7.1 Need for high doping and speed-drive voltage trade-off

Current demonstrators need a high and homogeneous doping to reach the performances. It is yet unclear how this doping can be implemented in a feasible and large scale process. Furthermore, the trade-off between speed and drive/switching voltage (influencing the energy efficiency) could be an intrinsic disadvantage of graphene and needs to be addressed and balanced, as both parameters are important for the application.

4.3.2.8 Additional current weaknesses and challenges: photodetectors

4.3.2.8.1 Imaging hardly possible without wafer scale integration

For imaging application a convergence of graphene technology and semiconductor technology is needed, e.g. to provide the read-out of focal plane array. Especially for imaging the production yield is crucial to avoid pixel defects and higher rejection rates which can drive the costs although initial savings are possible in the production due to for instance lower temperatures or faster and simpler processing steps.

For flexible and lower performing applications, already established roll to roll or sheet to sheet transfer might be sufficient, if it becomes cost competitive.

4.3.2.8.2 Still rather juvenile technology with open questions on sensitivity, reliability, stability and device linearity

As the technology is still rather juvenile and only lab type first proof of principles demonstrators are available, several next steps need to be addressed. A major challenge of ultrafast photodetectors for telecommunication is the poor sensitivity. A heterogeneously integrated graphene on Si detector for instance exhibits very fast speed, but a poor sensitivity due to the setup. The IQE is in principal good enough and it is an engineering task to increase the overall sensitivity. [394]

Further key issues are increasing and proving the combined performance in terms of insertion loss, sensitivity and speed as well as contacting and energy efficiency. At the moment, it is still unclear whether the realizable advantages are sufficient for broad use and to justify the investment in the production challenge.

4.3.2.9 Additional current weaknesses and challenges: laser technologies

4.3.2.9.1 Still unclear where graphene provides a winning application

Winning applications have not been clearly identified yet, although some results are promising. There are still open questions in terms of actual USPs and benchmarking with existing technologies. In this respect it is not sufficient to compare with graphene-based laser but to compare with actually competing technologies (incumbent and under development), which are mostly not based on graphene.

4.3.2.10 Additional current weaknesses and challenges: HF/microwave/THz generation, detection and processing

4.3.2.10.1 Currently experimentally realized benefits for telecommunication and high performance applications do not yet justify the needed risk and effort for integration

In order to be interesting enough, a one order of magnitude improvement needs to be offered by graphene towards integratable/mass manufacturable competing technologies to justify the needed investment to solve the manufacturing problem. Alternatively, it needs to be shown that integration is easy and does not require large efforts and costs. This is currently not fully obvious, particularly for high performance and telecommunication applications, and needs to be further investigated. Therefore, the current promising but not good enough performance is a major barrier, especially in the HF and microwave field. A similar efficiency, speed, etc. as, for instance, SiGe or Si will not justify the use of graphene.

Major disadvantages for RF transistors are at the moment the poor output power, voltage gain. The maximum oscillation frequency f_{max} is already competitive with Si and GaAs, but to justify the integration effort, it needs to be higher. (see Figure 55).

First proof-of-concept measurements of Graphene based modulators, demodulators, mixers and power detectors, key components for microwave and millimeterwave applications, have extraordinary high linearity, possibly better than other semiconductors. This, however, needs to be further investigated to actually proof the added value.

Alternative approaches than the GFET might lead to additional benefits for RF/microwave transistor, e.g. the barristor or graphene base transistor (GBT).

For other applications, e.g. THz technologies, a lower performance can be acceptable if total system cost is reduced. In terms of THz technologies, for sources the output power is an issue and for detectors the sensitivity might be too low compared to other room temperature technologies, but speed is already an important advantage.

4.3.2.10.2 BAW resonator electrode: Current processes more complex than metal electrodes

The processes for the preparation of the graphene based electrode are definitely more complex process than for metal electrodes, which are just evaporated. Furthermore, the RF conductivity in experimentally realized sheets is still too low. The industrial scale deposition on substrate is not available yet. With current transfer processes, it will be hard to reach the utmost spatial precision that is needed for BAW electrodes. The cost of the final product will be most probably higher (as the metal electrodes are very cheap), so that the benefit needs to be reasonably high in order to be feasible.

4.3.2.10.3 Missing basic understanding of (micro-)acoustic properties of graphene for BAW resonators

At the moment, there is no BAW resonator adequately experimentally realized yet. Furthermore, a basic understanding of (micro-)acoustic data of graphene (stiffness, density, mechanical tensor) and how to influence that is not yet experimentally confirmed, currently only theoretically estimated data is available. This is a challenge that needs to be addressed in order to gain further basic understanding of graphene in the device (to optimize, design and simulate the performance).

Further open questions are related to the unclear behaviour at higher power, e.g. in terms of delamination. This is strongly related to the question of how well it attaches to the piezo (AlN, quartz).

Last but not least, after first potentially successful experimental tests in simplified structures, a realization and investigation in optimized resonators with state of the art geometries is needed. Therefore this application is rather high potential, but also high risk with the chance to become a complete failure.

4.3.2.10.4 Antenna performance still too low

For the use as RF antenna , the antenna performance is still too low. Only for NFC and RFID the antenna performances are currently sufficient from printed materials, which are not transparent.

For better antenna performance, the resistivity at RF of graphene is too high. If this applications area is further investigated, it needs to be researched to which extent this RF resistivity can be influenced, e.g. through structuring, defect-healing, doping or other modifications.

For the use as micro-antenna instead of metals, the mobility and quality of industrial manufacturing compatible graphene is not good enough. To be a good plane "two dimensional" antenna, the surface static resistance of graphene/GRM should be (much) smaller than the free space impedance of ~376 Ω. Surface resistance of <50Ω/□ would be sufficient to reach that. For graphene layers with an electron density of ~$3x10^{12}$ cm^{-2} and relatively low mobility, as reached from todays industrially compatible processes (with the effective scattering time ~100 fs), the surface resistance is ~360 Ω/□, which is not sufficient. If higher mobility samples are available (with the scattering time ~ 1ps), this changes, and graphene becomes interesting for RF, THz, IR detectors strongly focusing radiation in small areas and hence increasing the detector sensitivity.

4.3.2.10.5 Realized gain in HF circuits is not good enough at the moment

As mentioned above, there are still limitations of graphene use in RF applications, especially as GFETs, such as the low voltage gain A_V which lags behind incumbents. This is mostly due to the poor conduction band of graphene and the missing bandgap, so that there is essentially no “OFF” state available through a gate electrode bias. Furthermore, for RF power applications, although the current density is highest among all semiconductors, the total power is low due to the low voltage. But recent demonstrations of high f_{max} [397] appear promising for low power HF applications.

Doping is needed to address the bandgap issue and the doping possibilities of graphene available today are not so good.

In terms of ultrafast DAC/ADC and LNAs with high bandwidth, good resolution and operation efficiency, low power losses there is currently no economically feasible graphene-based solution on the horizon, because these devices require wafer scale integration.

4.3.2.10.6 Other 2D materials not yet promising enough

Other 2D materials are still too immature to do a proper assessment. However, the results so far suggest that there is no 2D material based film/ribbon with a proper bandgap and high carrier mobility. However, as the amount of potential 2D materials is very large, it cannot be excluded that a better performing material can be found.

4.3.2.10.7 Mobility vs. bandgap trade-off

Especially for RF and high frequency applications, a high mobility and a bandgap is needed. Chapter 4.2.2.6.1 Mobility vs. bandgap in 2D materials elucidates, that these parameters are intrinsically not better than for 3D materials, such as III-V semiconductors. There is an intrinsic cleft between band gap and charge carrier mobility, as opening of bandgap reduces the mobility in graphene and the mobilites of 2D materials with a bandgap are not very high compared to bulk semiconductors. In contrast, CNTs have the combination of high mobility and reasonable bandgap, whereas bulk graphene and GNR have issues with that.

4.3.2.10.8 Substrate dependence of performance

The performance of graphene based electronic devices is heavily depending on the used substrate layers. Best performing devices usually use 2D boron nitride as substrate layer to encapsulate the graphene. So far, there is no industrially scalable process for graphene-BN stacks available, so all applications that perform only well with BN layers will have a very long time to market, if the integration challenges can be solved at all.

4.3.2.10.9 THz applications need high mobility

To develop graphene-based intensity and polarization electrically driven modulators for THz applications, large-area high-mobility graphene (>20.000 cm^2/Vs) is preferred, since this increases the peak intensity of the electromagnetic absorption and consequently enhances the modulation depth and speed. Depending on the integration level, this quality is needed on >3mm (free space propagation modulation), ~500µm (waveguide modulator) or <100-200 µm (modulator integrated into small THz sources or detectors). The latter is easiest to be achieved currently.

4.3.3 KPIs for telecommunication, optoelectronics & photonics

In this chapter several important key performance indicators for applications are highlighted. In some cases specification of competing technologies (state of the art or under development) are presented for comparison. This chapter shall simplify and motivate benchmarking of graphene/2D material based technologies with competing technologies by means of functions and not technological principles.

4.3.3.1 Telecommunication in general

- General: 5G: 100x-1000x capacity of 4G, standardization until 2016-2020
- Terminals 1Gbps – 10Gbps, Small (Micro) Cells 100 Gbps
- General specs: 1-1000x lower bit/power
- Reliability and durability (qualification period): 2 years (consumer) – 20 years (backbone)

4.3.3.2 Antennas and resonators:

Antenna:

Unobtrusive, transparent

- 50Ω/□ at mm-wave and µwave-frequencies needed

For micro-antennas and detectors (focusing radiation in small areas and hence increasing the detector sensitivity):

- Mobility good enough to allow a scattering time >1ps (at electron density of ~$3x10^{12}$ cm^{-2} to reach ~36 Ω/□

Resonator: (G as electrode on piezo BAW)

- Q-factor/insertion loss (≤1dB?), small footprint, frequency (2-40GHz?), temperature stability
- Electrodes: <0.1Ω/□

4.3.3.3 HF & microwave:,

For analogue HF transistors high mobility and I_{ON}/I_{OFF} ~10-100 needed.

Table 47: Desirable properties of ideal high performance RF FET channel materials. From [314].

Property	Desireable
Bandgap	sizeable, probably lower limit below 0.4 eV and optimum above 0.17 eV
Carrier effective mass	very light, $m_{eff} < 0.05\ m_e$
Mobility	very high, > 10 000 $cm^2\ V^{-1}\ s^{-1}$
Peak/saturation velocity	very high, ≥3 × 10^7 cm s^{-1}
Heat transport	Thermal conductivity: High Thermal boundary resistance: Low
Contact resistance	Low ≤0.03 Ω mm
Scale length, channel thickness	Small

mmWave **transceiver** MMICs/TMICs (30-40dBm)/analogue transistors, modulator, demodulator with high bandwidth

Low Noise Amplification

use of a broader spectrum up to mm (30-300GHz) waves for data transmission and backhaul

See Figure 55 for f_{max} and f_t values.

For further KPIs please refer to the ITRS 2013 tables www.itrs2.net or directly via [327] (RFAMS2013tables).

4.3.3.4 Optical Switches/modulators

Important figures of merit: Optical Insertion loss, switching speed, responsivity and switching voltage

Needed KPIs for optical backbone communications devices are:

- Optical Wavelength: 1530 nm ... 1610 nm
- On/Off Switching Voltage: Vπ ≤ 0.5 V (Ge-based EA modulator: 2V, LiNbO3: >2V; VπL>0.2Vcm)
- Low energy consumption (currently < 0.4 pJ/bit)
- Input Impedance: 50 Ohm
- Optical Input Power: ≥ 10dBm
- Insertion Loss: ≤ 5 dB (Fiber to Fiber) (Ge-based EA modulator: 4.1 dB, LiNbO3: >2.6 dB)
- Extinction Ratio: ≥ 20 dB
- Bandwidth: ≥ 30/35 GHz (Ge-based EA modulator: 50 GHz, LiNbO3: 10s of GHz)
- Chirp Free
- Small form factor (cf. today‘s LiNbO3 Modulator ~ 10cm)

Si-photonics capable of 100 Gb/s transceivers without graphene (4x 25Gb/s) [389]

Table 48: KPIs of electro-optical modulators. [406]

Modulator Type	**Footprint [µm^2]**	**Drive voltage [V]**	**Optical BW [nm]**	**Temp. Range [°C]**	**ER [dB]**	**IL [dB]**	**Dyn. Power [fJ/bit]**	**3 dB freq. [GHz]**	**Bit Rate [Gb/s]**	**Ref.**
Si Mach-Zehnder	~3000x5000	1.5	> 80°	> 80°	3.4	7.1	450	30	50	[407]
Si Ring	~10x10	0.5	< 0.1	< 1	6.4	1.2	~1	21	44	[408]
SiGe EAM	~55x10	2.8	35 5	< 1 < 40	~5	~4	60	> 30	28	[409]
Graphene-Si EAM	~40x10	3	>180	n/a	2.4	n/a	n/a	1.2	n/a	[410]
Graphene-Si EAM	~50x10	2.5	>80	> 29	2.5	< 4	350	2.6 - 5.9	10	[406]

4.3.3.5 Photodetectors (high speed)

Needed KPIs are:

- Fast speed (100GHz) (current semicon based tech >50Ghz) (met already for material, not component, rest is integration)
- 100Gbit/s are necessary; photonic ICs capable to reach 600Gbit/s
- High Efficiency
- Responsivity of >0.5 A/W
- Low Noise
- Robustness→valid for all components (integration)

Handling different wavelengths: nice to have to span to other wavelengths ranges besides standard wavelengths (bands). (met already); beyond 1.3 and 1.55µm, e.g. 9xx nm

Graphene needs to achieve a contact resistance of <50Ohm µm, mobility 10000Vs/m² (µ) on wafer, then KPIs will be met (currently µ=7000Vs/m²)

Table 49: Parameters of some fast photodetectors. Credits to D. Neumaier.

	Data Rate	**Sensitivity**	**Wafer-Scale Integration on Si**
Graphene [394]	50 Gbit/s	0.1 A/W	in principle possible
Graphene [411]	42 Gbit/s	0.36 A/W	in principle possible
Ge [412]	40 Gbit/s	0.8…1A/W	OK
Ge-APD [413]	10 Gbit/s	~10 A/W	OK
InP [414]	160 Gbit/s	0.6 A/W	NO
Phosphorene [415]	3 Gbit/s	0.7 A/W	Not yet

4.3.3.6 Broadband photodetectors and broadband hyperspectral Imaging

Needed KPIs are:

- High Detectivity (Jones D*) (depends on noise, typical values for competing technologies: @1-1.7µm: 10^{12} cm$\sqrt{\mathrm{Hz}}$/W @1.7-10µm 10^{10} cm$\sqrt{\mathrm{Hz}}$/W, ultra high sensitive InGaAs detectors reach 10^{13} cm$\sqrt{\mathrm{Hz}}$/W) but cut off at 1.7µm;
- High speed (fast response); Standard mid-IR detectors have D*=3x10^{8} cm$\sqrt{\mathrm{Hz}}$/W with a speed of ~1 kHz (non tuneable)
- High resolution (256x320 available for IR)
- Price: InGaAs 2k€/sensor for 256x320 pixels; with high spatial resolution for imaging: 15-50k€, “lower quality, better price” could facilitate new markets, e.g. food quality sensing: InGaAs has too high sensitivity (600-2000nm; 256x320 pix) and is too expen-

sive (2k€) →compromise needed/possible; LWIR bolometers 10-100€ (e.g. FLIR detector for mobile phones)

- Hyperspectrality (wavelength range covered)
- Low dark current (for ultra-sensitive applications and single photon counting: <nA (InGaAs)), or high gain, as e.g. realizable in graphene-QD phototransistors
- Flexibility

Table 50: Comparison of THz detectors taken from [332].

Detector Type	**Temperatur [K]**	**Response Speed**	**Integration**	**Responsivity [V/W]**	**NEP [pW/\sqrt(Hz)]**	**Frequency**	**Remarks**
PC LT-GaAs	300	Slow (ms-s)		-	~10	Broad band	Indirect
EO GaAs	300	Slow (ms-s)		-	~100	Broad band	Indirect
EO DAST	300	Slow (ms-s)		-	~10	Broad band	Indirect
Golay Cell	300	Slow (~50ms)		10^4-10^5	100-1000	Broad band	
DLATGS	300	Slow (~10ms)		~10^5	1000-3000	Broad band	
Si Bolometer	0.3-4.2	Slow (~1ms)	320 x240	~10^4/~10^8	0.01 @0.3 K	Broad band	
QW	4.2	Fast (50ps)		-	$7x10^{-8}$	0.5~3 THz	
QD	0.07-4.2	Slow (20 µs)		-	10^{-10} @70mK	0.5~3 THz	
NbN STJ	0.3-9	Fast	36-1000	~10^9	10^{-4} @0.3 K	Nb: <700 THz	
TES	0.3	Slow (~50 ms)	1024	-	10^{-5}	Broad band	

Detector Type	Temperatur [K]	Response Speed	Integration (pixel size)	Responsivity [V/W]	NEP [pW/sqrt(Hz)]	Frequency	Remarks
Nb HEB	4.5 K	Fast (~50ps)	64	-	~50	<30 THz	
SBD GaAs	300	Fast (~20ps)		0.3~1K @150-400 GH	5 ~ 20	~900 GHz	
SBD ErAs/InAlAs	300	Fast (~20ps)		6.8 K @100 GHz	1.4 at 100 GHz	~2.6 THz	
SBD In-GaAs/InP	300	Fast (~20ps)		~1K @300 GHz	0.4 at 100 GHz	<1 THz	
Graphene FET (NR-Plasmon)	300	Fast		14 @0.6 THz	515 @0.6 THz	Broad band	
Graphene (PV/PTE)	300	Fast		700 @10-100 GHz	16 @10~100 GHz	Broad band	pulsed meas.
Graphene Bolometer	0.1-4.2	Slow (~1ms)			$5*10^{-8}$ @0.1 K @1 THz	Broad band	
Si-CMOS (NR-Plasmon)	300	Fast	32^2	57k @0.9 THz	470 @0.9 THz	0.3~3 THz	amp. Inte-grated
InP HEMT (NR-Plasmon)	300	Fast (~10ps)		23k @0.2 THz	0.5 @0.2 THz	~5 THz	

4.3.3.7 Optical transceiver system

Competing typical systems are:

- Luxtera Blazar 4x10 Gb/s QFSP+
- Avago MicroPOD 12x10Gb/s
- Cisco: All modules 100GE (CFP4, CPAK, QSFP28)

4.3.3.8 Passive and Active Lasers

Saturable absorber (SESAMs) for ultrabroadband tuneable mode-locked lasers and Integrated fibre, semiconductor, waveguide and solid-state lasers. Conventional technology KPIs:

- Wavelength tuning range: 680-1080 nm (Kerr-lens mode-locking)
- Output power: ~300 W (SESAM)
- Repetition rate: 1.2 THz (NPR)

Tunable light source for communication for passive optical networks (PONs):

- Wave Length: C-Band (1530 – 1565nm) / O-Band (1260 – 1360nm)
- Tuning Range: 15 - 20nm
- SMSR (side mode suppression ratio): >30dB
- Optical Output Power: > 1mW (0 - 5dBm)
- Electrical Input Power: < 1W
- Bitrate: ≥ 1.25Gb/s (bis zu 10Gb/s)
- BER (bit error ratio): < 10-10 (ITU)/10-12 (IEEE)
- Extinction Ratio: > 6dB (IEEE)/10dB (ITU)
- Good Noise Performance
- High Volumes, lowest Cost! (Mpcs, 1$ range)

4.3.3.9 Components for THz applications

Detector (KPIs of competing technologies)

- Uncooled or 70K THz detector, 10x lower sensitivity than bolometer is ok (typical NEP are ~2pW/Hz1/2 and few kV/W)
- Response speed of conventional high-speed THz detectors on the order of 10-100kHz
- THz arrays of 1024 pixels
- Bolometers (aSi or Vox): TCR: 2%/K-1; Response time 20 ms, Absorption: > 80 % broadband)

Modulator:

- Mobility >20.000 cm^2/Vs; depending on the integration level, this quality is needed on >3mm (free space propagation modulation), ~500µm (waveguide modulator) or <100-200 µm (modulator integrated into small THz sources or detectors)

4.3.4 Roadmap for telecommunication, optoelectronics & photonics

4.3.4.1 Current maturity: 'Lab demonstrators'

For this applications area, most research is currently at the lab demonstrator stage when it comes to graphene. Other 2D materials are less mature. The lab demonstrators usually show some promising parameters, but the overall benefit and proof in a relevant environment is not yet there. A major obstacle for further maturity improvements is related to the manufacturability. Wafer scale integration is necessary for most applications in this area to gain a higher relevance for industry. However, the current overall demonstrated performances appear to be not good enough so that industry would easily pick up the lead for solving the integration problems.

4.3.4.2 Barriers/challenges (summarized)

A major challenge is wafer scale integration, as it is a must have for most applications. The barriers highlighted in chapter 4.2.4.2 apply similarly. For the integration challenge related to telecommunication, optoelectronics and photonics applications, the following challenges are of particular relevance:

Demonstrators and technology

- Performance gain (or less likely: cost reduction) must justify wafer scale efforts (seems to be not yet the case), quality and maturity of demonstrators and how they are produced do not yet provide the needed certainty to profoundly assess that
- Benchmarking with technologies that address the same applications in terms of functionality (and not within graphene or with a device concept that is also far away from the incumbent or competing application-addressing technology)
- Reliability, energy efficiency and durability requirements (delamination)
- Contacting
- Substrate and package interactions, understanding of properties of graphene in MMICs, opto-electronic and acusto-electronic devices (for proper design and simulation)
- Other 2D materials even too early to assess

Ecosystem development:

- Dead-lock situation: OEMs are interested in the technology (such as Nokia, Ericsson). This is important, but they buy components and the integration of graphene is done elsewhere.
- Missing link at least in Europe? Who will integrate graphene into components? Developments are currently mostly done in the (public) labs, nobody is capable or willing to take it up at the moment.
- Foundry/integrated device manufacturers (the ones who have own fabs) need to be convinced of the potential of graphene via realistic demonstrators to act as a middleman between OEMs and labs. To achieve that, convincing KPIs need to be reached to justify the probably high investment needed.
- Single user/single customer conundrum: A supplier will not change for a single customer, a customer will not by from someone who is the only supplier (second source principle)

Antennas & Resonators:

In terms of antennas and resonators, the following challenges are particularly relevant:

- Unclear RF conductivity of (transparent) graphene films for efficient antennas, especially 2-10-20GHz and how this can be influenced through manipulation (tunability, doping, …)
- Highly precise, yet economically feasible (and thus not complex) transfer on dielectrics (piezos)
- Missing basic understanding of (micro-)acoustic properties of graphene

Optical Switches/modulators:

Major challenges related to optical switches and modulators are:

- Open question: Who will integrate the technology into components in Europe (from the current partners in the flagship)? Or is integration in Europe actually needed? Should it be licensed?

Technological challenges

- Trade-off speed vs. drive voltage (depends on quality)
- Homogeneous doping over large substrates
- Bilayer or double-layer graphene with a spacer (e.g. aluminium oxide)
- Need lower insertion loss –Higher extinction ratio
- Better quality large area graphene with mobility >10.000 cm^2/Vs (performance limited by graphene quality after processing)
- Need higher speed (28GBit/s, 56 Gbit/s …)
- More compact devices: shorter devices need higher interaction with graphene film
- Lower contact resistance (speed limited by RC-constant)
- Better reproducibility, need reliable and reproducible integration process
- Demonstration of full transceivers (multi-channel devices, also detectors)

Photodetectors (fast speed):

Technological challenges:

- Sensitivity needs to be improved (while insertion loss and speed remain or improve)
- Current speed of graphene based components limited by contacts and assembly (65GHz overall performance vs. >200GHz for material)
- Limits of the system integration/ assembly
- Key limitations: Reliable large scale production, performance, contacts

Imaging:

Major challenges related to photodetectors for imaging/high sensitivity are

- High priced, high performance market is already existing and an actual added value must be shown through working demonstrators
- Medium to lower priced markets are very interesting, but price and performance competitiveness must be shown
- Integration with silicon on wafer scale for highly integrated sensors needed (e.g. to combine with read-out focal plane arrays). But: single pixel and flexible do not necessarily need wafer scale
- Contacting of the graphene
- Sensitizing/plasmonic enhancement to increase sensitivity without sacrificing hyperspectrality

Laser:

For laser applications the integration issue is important for low cost/laser diode applications. For fibre lasers and high performance ultrafast lasers, especially benchmarking with existing well performing technologies is needed.

HF/microwave/THz electronics:

For microwave/RF/sub-mm applications

- Current realized RF performance in transistors not good enough (does not justify the effort): especially voltage gain A_V
- Promising proof of concepts need to be further developed to be able to benchmark with competing technologies
- Bandgap issue in graphene not good for transistors, but can be also exploited for other interesting applications and also seen as a benefit
- Reliable large scale production, requirement of high mobility, contacts are key issues

Major barriers for THz applications

- Missing proof of principle of potentially (and theoretically) good THz performance in devices
    - Proof of principle for actual THz detector and THz mixer
    - Proof of principle of detector arrays for THz detection
- For bolometer: proof of principle and improvement of temperature coefficient of resistance TCR response time and absorption

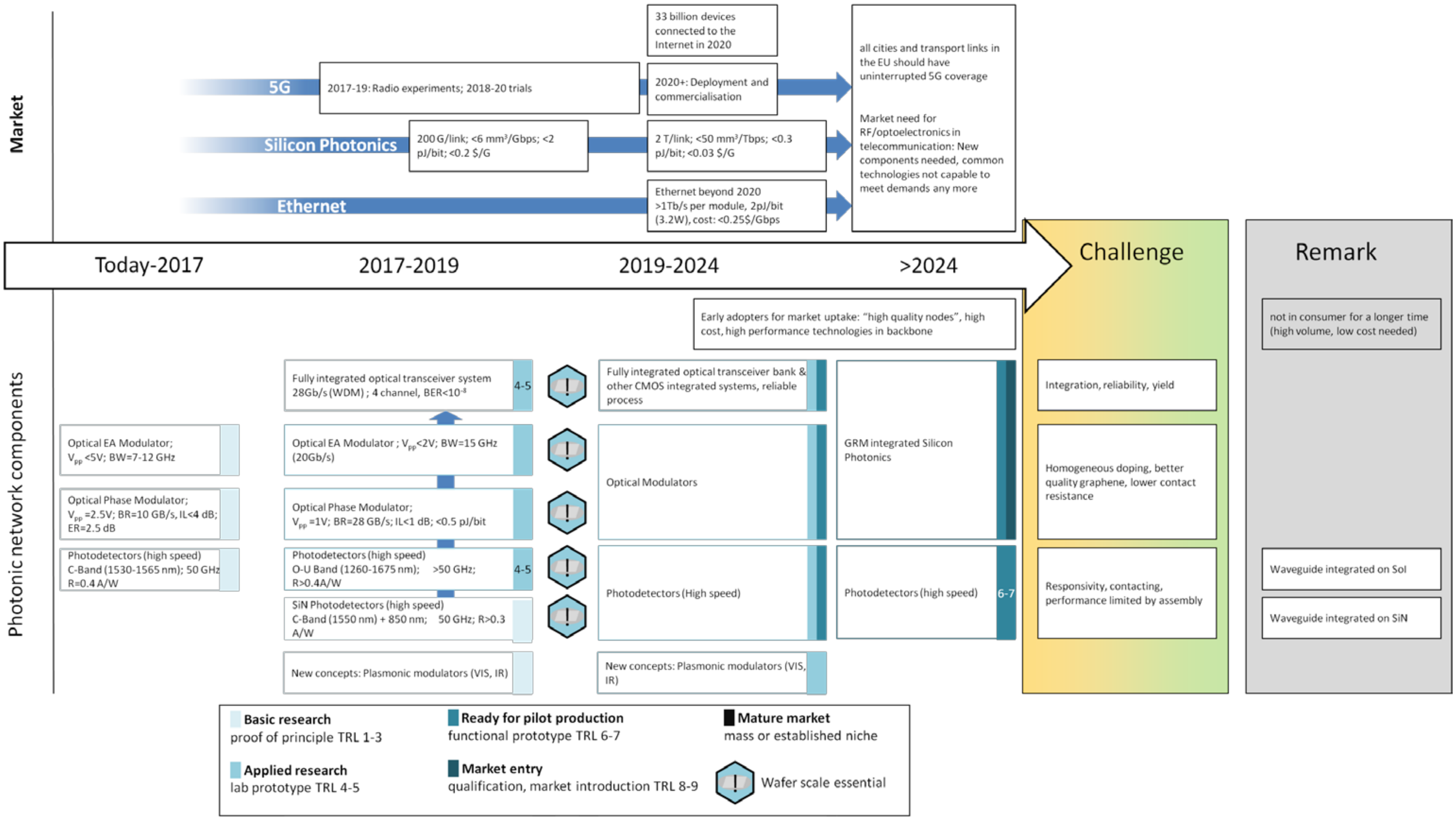
4.3.4.3 Potential actions

If the area of graphene/2D in telecommunication, optoelectronics and photonics is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

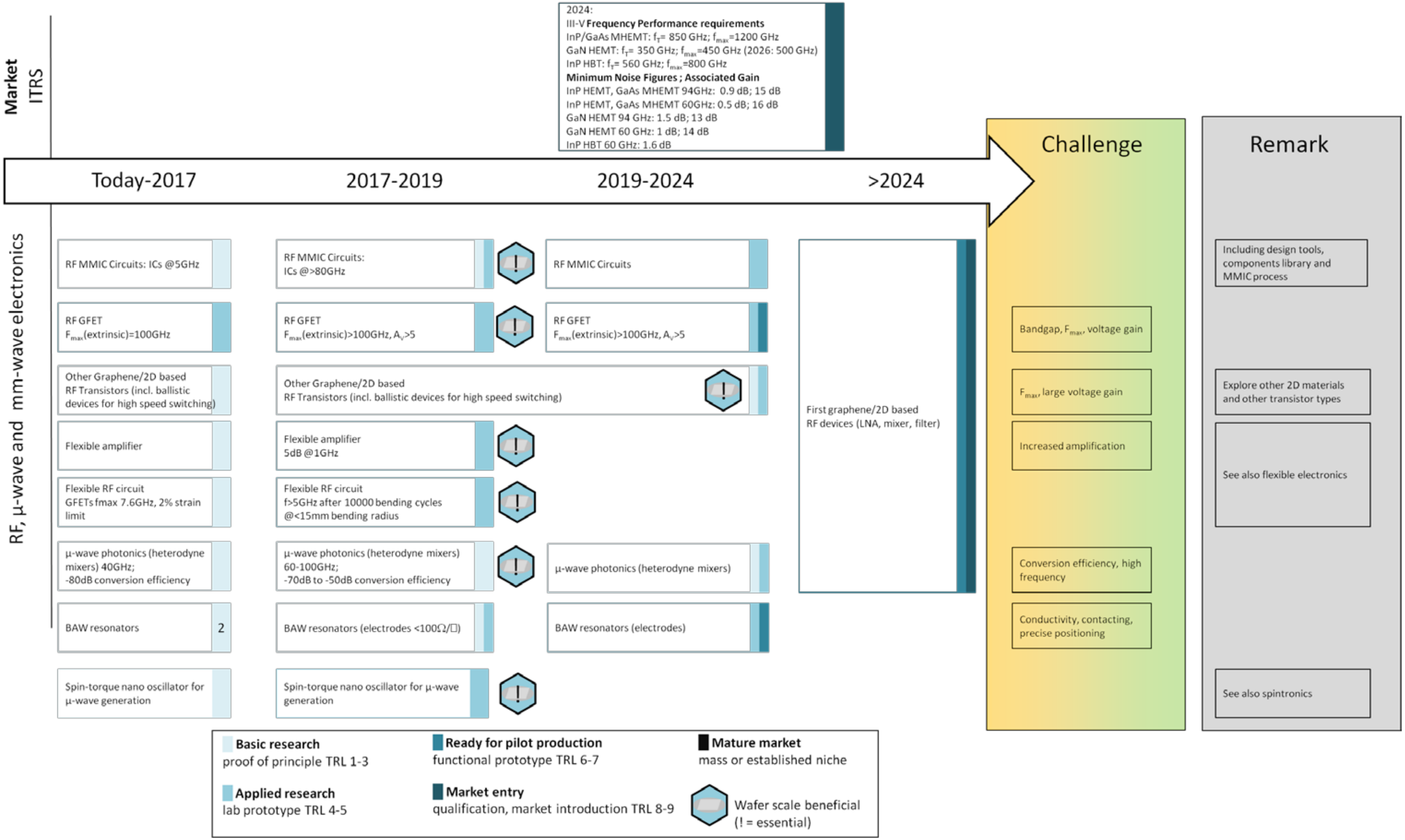
The following potential actions are identified as addressing common issues:

- Go from idealised or simplified proof of principle demonstrators with promising performance to actually relevant designs and demonstrators for actual benchmarking (create “engineering knowledge”)
- Explore other 2D materials
- Look at full relevant set of parameters when comparing to other technologies (including reliability, temperature stability, long term performance, energy efficiency)
- Explore and intensify the ecosystem to get ideas on how to overcome the dead-lock situation when the time is ripe.
- Explore alternative approaches tailored to graphene (GBT, etc.)
- Explore substrates, lamination and passivating layers for the applications
    - With AlOx(wafer scale devices)
    - With HBN (exploratory, small scale devices)
    - Towards double layer graphene devices (allows shortening of optoelectronic devices)
    - On silicon or silicon nitride waveguide

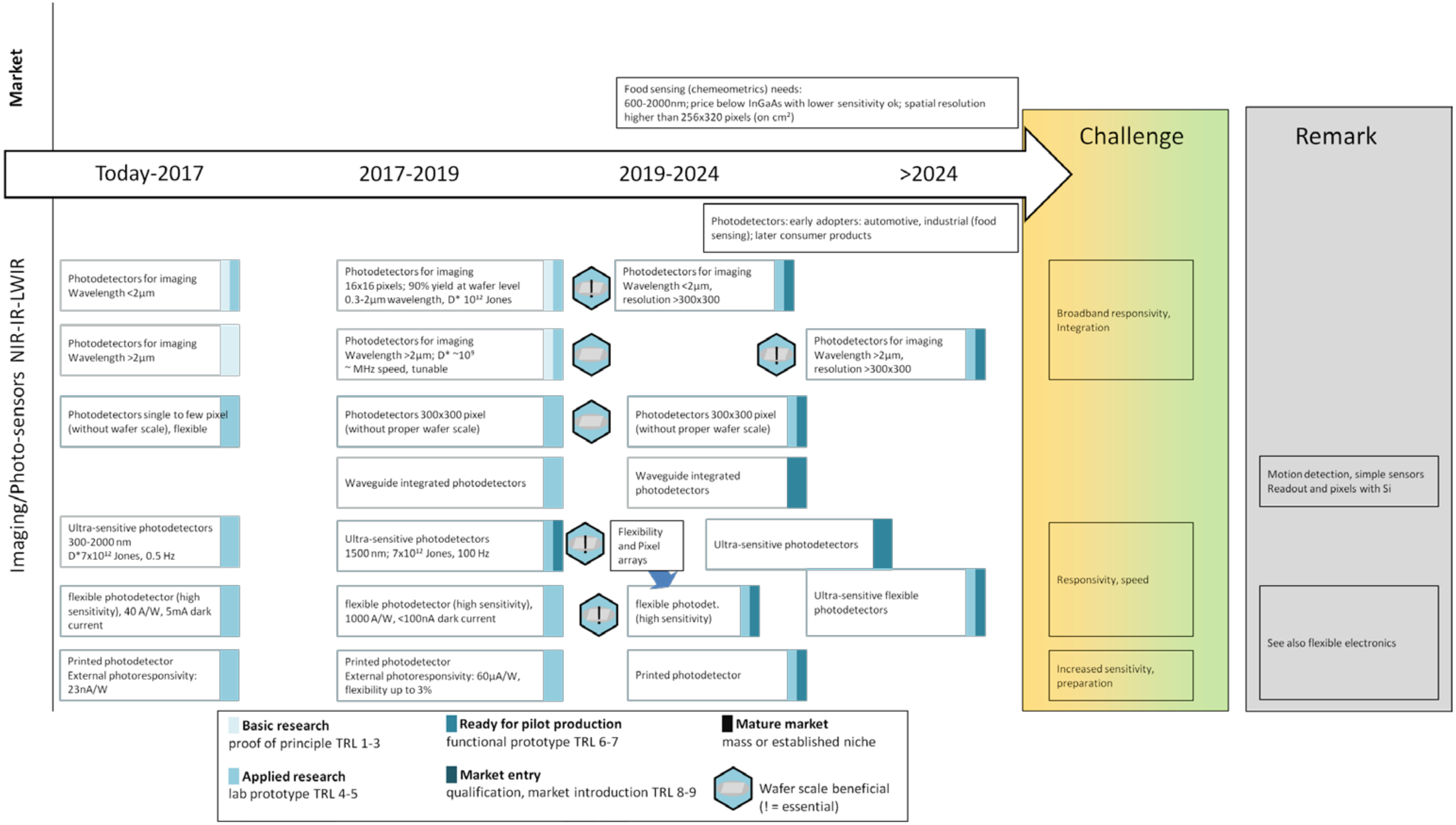
4.3.4.4 Roadmap



Sources: 5G [379], Ethernet [416], Si Photonics [417, 418]



Sources: ITRS [419]



Market

Food sensing (chemeometrics) needs:
600-2000nm; price below InGaAs with lower sensitivity ok; spatial resolution higher than 256x320 pixels (on cm²)

Today-2017

2017-2019

2019-2024

>2024

Photodetectors: early adopters: automotive, industrial (food sensing); later consumer products

Imaging/Photo-sensors NIR-IR-LWIR

Photodetectors for imaging
Wavelength <2µm

Photodetectors for imaging
16x16 pixels; 90% yield at wafer level
0.3-2µm wavelength, D* 10^{12} Jones

Photodetectors for imaging
Wavelength <2µm,
resolution >300x300

Photodetectors for imaging
Wavelength >2µm

Photodetectors for imaging
Wavelength >2µm; D* ~10^9
~ MHz speed, tunable

Photodetectors for imaging
Wavelength >2µm,
resolution >300x300

Photodetectors single to few pixel
(without wafer scale), flexible

Photodetectors 300x300 pixel
(without proper wafer scale)

Photodetectors 300x300 pixel
(without proper wafer scale)

Waveguide integrated photodetectors

Waveguide integrated
photodetectors

Ultra-sensitive photodetectors
300-2000 nm
D*7x10^{12} Jones, 0.5 Hz

Ultra-sensitive photodetectors
1500 nm; 7x10^{12} Jones, 100 Hz

Flexibility
and Pixel
arrays

Ultra-sensitive photodetectors

flexible photodetector (high sensitivity), 40 A/W, 5mA dark current

flexible photodetector (high sensitivity),
1000 A/W, <100nA dark current

flexible photodet.
(high sensitivity)

Ultra-sensitive flexible
photodetectors

Printed photodetector
External photoresponsivity:
23nA/W

Printed photodetector
External photoresponsivity: 60µA/W,
flexibility up to 3%

Printed photodetector

Challenge

Broadband responsivity,
Integration

Responsivity, speed

Increased sensitivity,
preparation

Remark

Motion detection, simple sensors
Readout and pixels with Si

See also flexible electronics

Basic research
proof of principle TRL 1-3

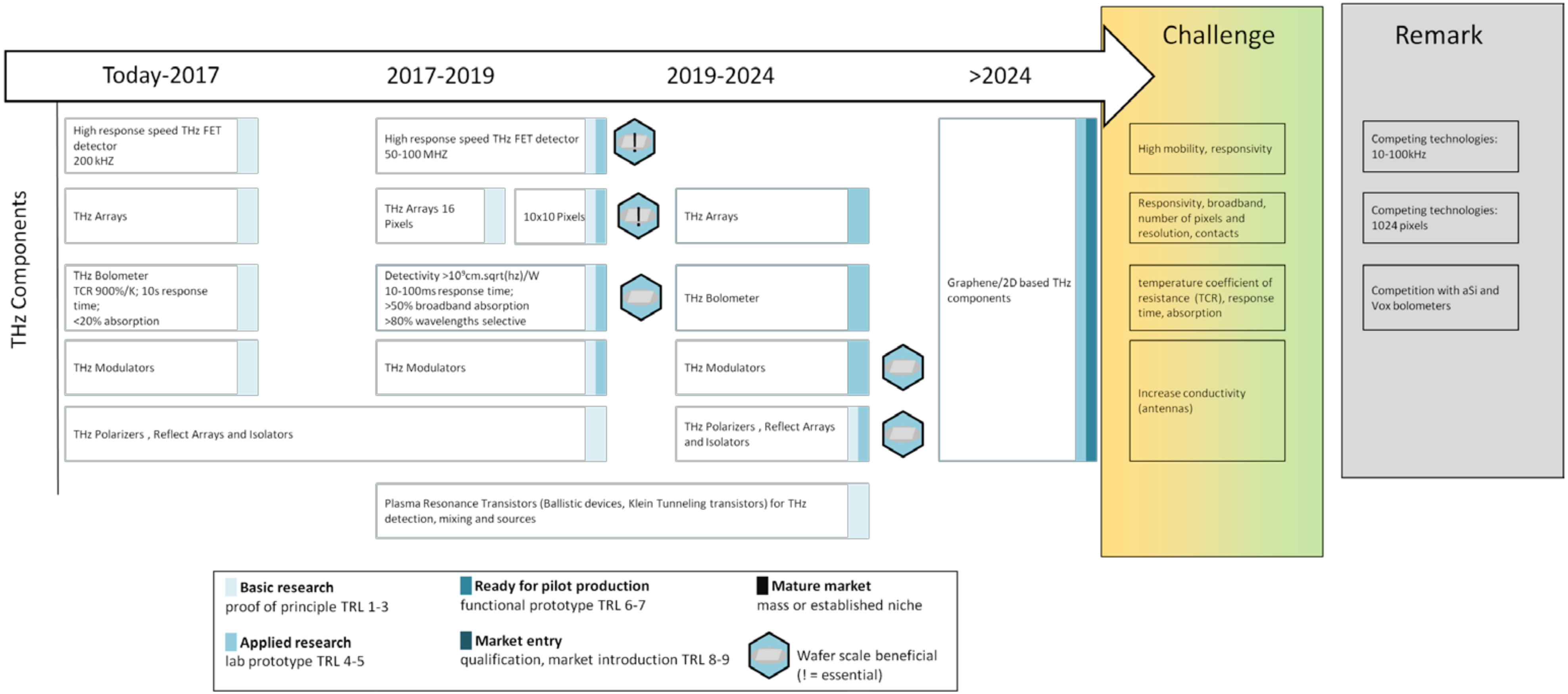
Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale beneficial
(! = essential)



THz Components

Today-2017

2017-2019

2019-2024

>2024

High response speed THz FET detector
200 kHZ

High response speed THz FET detector
50-100 MHZ

THz Arrays

THz Arrays 16 Pixels

10x10 Pixels

THz Arrays

THz Bolometer
TCR 900%/K; 10s response time;
<20% absorption

Detectivity >10^9cm.sqrt(hz)/W
10-100ms response time;
>50% broadband absorption
>80% wavelengths selective

THz Bolometer

THz Modulators

THz Modulators

THz Modulators

THz Polarizers , Reflect Arrays and Isolators

THz Polarizers , Reflect Arrays and Isolators

Plasma Resonance Transistors (Ballistic devices, Klein Tunneling transistors) for THz detection, mixing and sources

Graphene/2D based THz components

Challenge

High mobility, responsivity

Responsivity, broadband, number of pixels and resolution, contacts

temperature coefficient of resistance (TCR), response time, absorption

Increase conductivity (antennas)

Remark

Competing technologies: 10-100kHz

Competing technologies: 1024 pixels

Competition with aSi and Vox bolometers

Basic research
proof of principle TRL 1-3

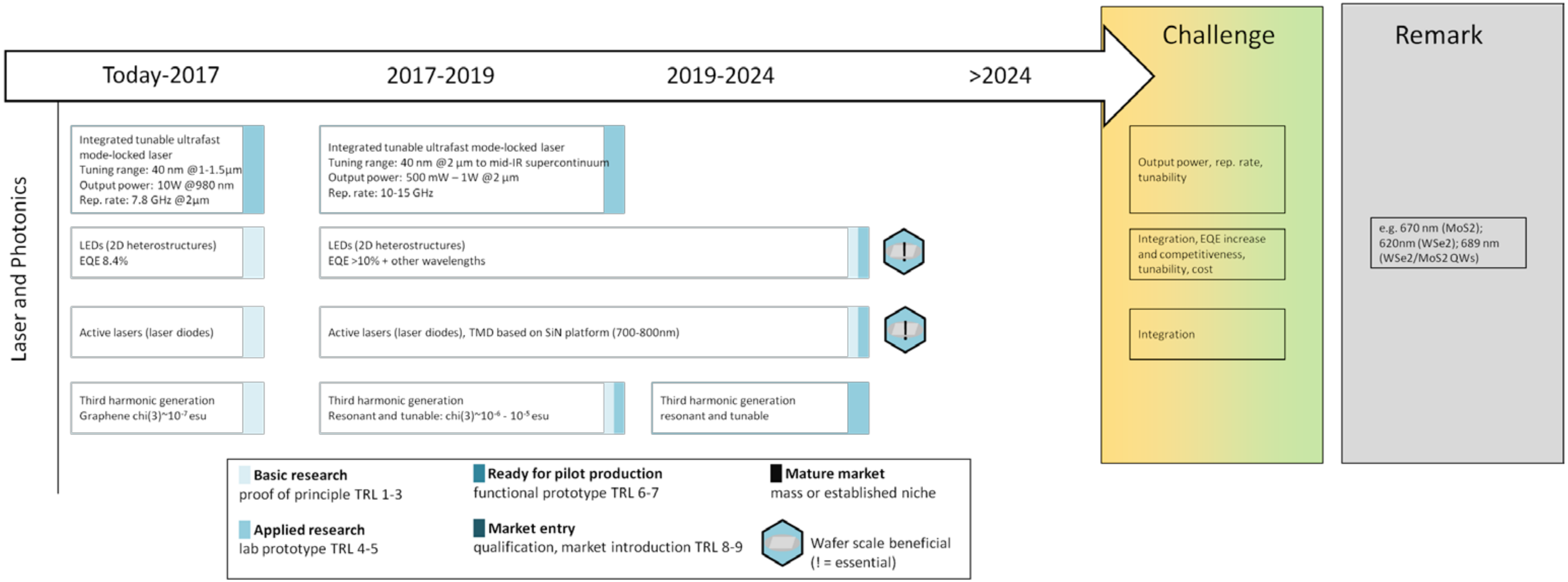
Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale beneficial
(! = essential)



Laser and Photonics

Today-2017 | 2017-2019 | 2019-2024 | >2024

Challenge

Remark

Today-2017:
Integrated tunable ultrafast mode-locked laser
Tuning range: 40 nm @1-1.5µm
Output power: 10W @980 nm
Rep. rate: 7.8 GHz @2µm

2017-2019:
Integrated tunable ultrafast mode-locked laser
Tuning range: 40 nm @2 µm to mid-IR supercontinuum
Output power: 500 mW – 1W @2 µm
Rep. rate: 10-15 GHz

Challenge: Output power, rep. rate, tunability

Today-2017:
LEDs (2D heterostructures)
EQE 8.4%

2017-2019 to 2019-2024:
LEDs (2D heterostructures)
EQE >10% + other wavelengths

!

Challenge: Integration, EQE increase and competitiveness, tunability, cost

Remark: e.g. 670 nm (MoS2); 620nm (WSe2); 689 nm (WSe2/MoS2 QWs)

Today-2017:
Active lasers (laser diodes)

2017-2019 to 2019-2024:
Active lasers (laser diodes), TMD based on SiN platform (700-800nm)

!

Challenge: Integration

Today-2017:
Third harmonic generation
Graphene chi(3)~10^{-7} esu

2017-2019:
Third harmonic generation
Resonant and tunable: chi(3)~10^{-6} - 10^{-5} esu

2019-2024:
Third harmonic generation
resonant and tunable

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale beneficial
(! = essential)

4.3.5 Conclusion telecommunication, optoelectronics & photonics

With the increase of data traffic (5G and beyond), there is a strong need for new technologies and innovations to reach higher bandwidth and energy efficiencies. The telecommunications equipment market is globalized, and driven by large commercial markets. With Ericsson and Nokia Networks/Alcatel-Lucent, two of the largest telecommunication equipment suppliers are European companies.

Optoelectronic, in particular photodetector applications, also address other larger markets with growth opportunities, e.g. (IR/hyperspectral) imaging, spectrometers and optical sensors in general.

Other potential applications also address reasonable markets or markets with large growth opportunities, e.g. optical or THz imaging, lasers for scientific, communication and machining purposes or radar applications. These also offer niche markets for early adoption (e.g. ultrafast lasers for fundamental science).

Due to the high electron mobility, graphene can play a role in high frequency electronics. The optoelectronic properties of graphene are very promising for optoelectronic applications (optical switches, modulators; optical detectors), ranging from high speed communication applications to hyperspectral imaging (due to its broad optical absorption). In principle, graphene can be also integrated in Si-photonics and integrated photonics. Additionally, graphene can help to reduce form factors or introduce flexibility. The optical properties render it also interesting as wavelength-independent saturable absorbers for lasers.

Although laboratory demonstrators are promising, wafer scale integration is the bottle neck and commercial manufacturing compatible processes are needed. Besides, the demonstrators have to be tested against state-of-the-art and other emerging technologies in systems to show their actual potential. After that, the reliability has to be addressed, as depending on the application, the needed durability can be between 2 years (consumer) and 20 years (network backbone). It is important to also involve the parts of the value chain that actually implement the graphene materials, e.g. the component manufacturers (e.g. of optical transceivers) or chip producers. Implementing a new technology or material in this industry is an effort of the whole (global) ecosystem.

Currently, the not specified performance in devices and the unclear commercially feasible production method impede the uptake in commercial applications. This is not a fundamental problem, as many questions are still open and under investigation, due to the novelty of the 2D material technology.

Table 51: Assessment of market and technological potential of graphene/2D materials use in telecommunication, optoelectronics & photonics on a scale - -, -, 0, +, ++

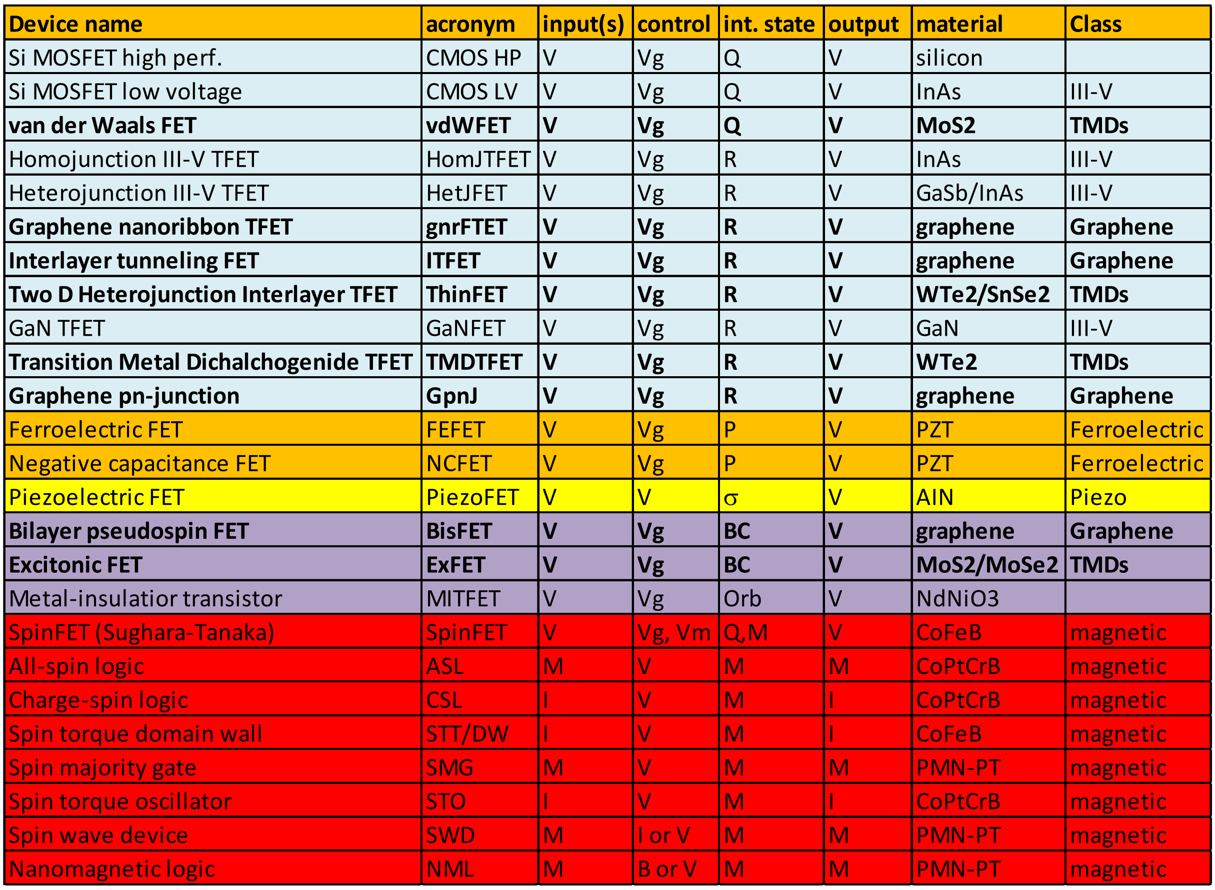
Application area	Current technological potential (USP)	Market potential (EU perspective)
Photonic networks	++	++
Wireless communication	+	++
RF transistors	0/+	+
Optical switches and modulators	++	+
Photodetectors/Imaging systems/Spectrometers	++	+
Resonators	+	0/+
Antennas (large area, unobtrusive)	-	0/+
THz/sub-mm wave	+	0
Laser/photonics	+	+

4.4 Computing/Logic, beyond CMOS and spintronics

This area deals with digital/logic electronics applications, i.e. high performance computing, the progress of miniaturization of integrated logic circuits (“more Moore”), in contrast to the “more than Moore” path, where improved functionality is key (covered in the other application areas within the electronics and photonics chapter). This area focuses on the use of graphene/2D materials as active semiconductor material and passive channel in or beyond Si electronics/CMOS.

Logic computing can be subdivided in three major areas: high performance computing, low power computing and memory. Beyond CMOS technologies generally address computing with new architectures or principles of computing.

A special focus is attributed to spintronics, an emerging type of beyond-CMOS computing in which information is carried, stored and processed by spin instead of charge. Graphene has some interesting properties for spintronics, which will be further elaborated in this chapter. Graphene based spintronics promise to address some of the major challenges in spintronics technology and can also enable new applications, e.g. in magnetic sensing and microwave generation in nano oscillators.



Device name	acronym	input(s)	control	int. state	output	material	Class
Si MOSFET high perf.	CMOS HP	V	Vg	Q	V	silicon	
Si MOSFET low voltage	CMOS LV	V	Vg	Q	V	InAs	III-V
van der Waals FET	**vdWFET**	**V**	**Vg**	**Q**	**V**	**MoS2**	**TMDs**
Homojunction III-V TFET	HomJTFET	V	Vg	R	V	InAs	III-V
Heterojunction III-V TFET	HetJFET	V	Vg	R	V	GaSb/InAs	III-V
Graphene nanoribbon TFET	**gnrFTET**	**V**	**Vg**	**R**	**V**	**graphene**	**Graphene**
Interlayer tunneling FET	**ITFET**	**V**	**Vg**	**R**	**V**	**graphene**	**Graphene**
Two D Heterojunction Interlayer TFET	**ThinFET**	**V**	**Vg**	**R**	**V**	**WTe2/SnSe2**	**TMDs**
GaN TFET	GaNFET	V	Vg	R	V	GaN	III-V
Transition Metal Dichalchogenide TFET	**TMDTFET**	**V**	**Vg**	**R**	**V**	**WTe2**	**TMDs**
Graphene pn-junction	**GpnJ**	**V**	**Vg**	**R**	**V**	**graphene**	**Graphene**
Ferroelectric FET	FEFET	V	Vg	P	V	PZT	Ferroelectric
Negative capacitance FET	NCFET	V	Vg	P	V	PZT	Ferroelectric
Piezoelectric FET	PiezoFET	V	V	σ	V	AlN	Piezo
Bilayer pseudospin FET	**BisFET**	**V**	**Vg**	**BC**	**V**	**graphene**	**Graphene**
Excitonic FET	**ExFET**	**V**	**Vg**	**BC**	**V**	**MoS2/MoSe2**	**TMDs**
Metal-insulatior transistor	MITFET	V	Vg	Orb	V	NdNiO3	
SpinFET (Sughara-Tanaka)	SpinFET	V	Vg, Vm	Q,M	V	CoFeB	magnetic
All-spin logic	ASL	M	V	M	M	CoPtCrB	magnetic
Charge-spin logic	CSL	I	V	M	I	CoPtCrB	magnetic
Spin torque domain wall	STT/DW	I	V	M	I	CoFeB	magnetic
Spin majority gate	SMG	M	V	M	M	PMN-PT	magnetic
Spin torque oscillator	STO	I	V	M	I	CoPtCrB	magnetic
Spin wave device	SWD	M	I or V	M	M	PMN-PT	magnetic
Nanomagnetic logic	NML	M	B or V	M	M	PMN-PT	magnetic

Figure 56: List of beyond CMOS devices under consideration. B=magnetic field, Vg=gate voltage, Vm=magnetic switching voltage, BC=Bose condensate. The cell color designates the computational variable (from top to bottom): blue=electronic, orange=ferroelectric, yellow=straintronic, purple=orbitronic, red=spintronic devices. Key materials are listed and 2D-materials-based solutions are bold. [420]

4.4.1 Market perspective: graphene/2D materials in computing/logic, beyond CMOS and spintronics

An overview of the overall semiconductor market is presented in chapter 4.2.1 Market perspective: graphene/2D materials in the semiconductor and electronics industry. The logic and memory markets account for the largest share of sales in the semiconductor industry (~50%, ~$168 billion in 2015), see Figure 43.

In logic, Europe has a strength in special applications, e.g. for automotive and low power, and is strong in material, equipment, chip design (fabless activities) and system integration. 20% of the production of equipment and material is currently done in Europe and there is growth potential. [291] Only a very small share of classical PC and mobile phone processors and high performance processors are currently manufactured in Europe, similar to storage media (RAM).

The spintronics market exists nowadays mostly in memory in the form of magnetic hard drives (read heads) facilitating based on the giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) effect. There are also GMR sensors for magnetic fields and GMR-based signal isolators/couplers/transceivers. Other applications besides that, e.g. MRAM, magnetic junctions, and spin-based logic are still in a nascent stage, but they offer advantages over the traditional electronics such as low power consumption, economic viability, and compactness, high data transfer speed. The spintronics market, especially MRAM is seen as important with strong growth opportunities reaching potentially $50-70 billion in the future [421]. MRAM are expected to contribute with more than $ 1billion in 2021 (current sales are ~$50 million to few hundred million, depending on the source). [422, 423]

4.4.1.1 Market Opportunities

4.4.1.1.1 Limitations of Si and More Moore: search for new technologies

For digital CMOS/Von Neumann computing, there is little room for improvement after the next nodes in some 5-10 years. FinFETs will probably take CMOS to the 5nm node. As the classical Moore’s Law approaches a phase out due to limitations in CMOS technology scaling, and the demands for new chips is diversifying (more and more chips have tailor made functionalities and there is no “one fits all”-solution), the semiconductor industry will also diversify. This can be already seen in the re-booting of ITRS in terms of diversification. [296]

This trend opens up new opportunities for novel architectures, ways of computing (NP-hard problems, non Von Neumann computing, optimization problems like probabilistic computing, machine learning, cellular neural networks etc.) and new materials that add functionality. Moore’s Law in that sense can be newly interpreted as doubling the user value every two years. [424]

There is a clear need to especially find new solutions to overcome Si physical limits, such as the transistor density, performance, but most importantly the energy efficiency. The need for reduced power consumption is evident as more and more devices are mobile and remotely powered. Furthermore, as more and more computer power is installed, the need for lower energy consumptions per bit is rising.

In the latest ITRS/IRDS discussions, TMDs, graphene and graphene nanoribbons have still been in the discussion to deliver some solutions, also in the realm of logic transistors.

Furthermore, there are also limitations in the overall system besides the classical transistor, e.g. interconnects (see 4.2 Electronics: Cross-cutting issues) or added functionalities through materials/components that can be integrated in the standard (CMOS) fabrication processes (FEOL, BEOL) achieving better performance and higher energy efficiency, as well as lower cost (see chapters 4.2 Electronics: Cross-cutting issues for wafer scale integration and 0

Telecommunication, optoelectronics & photonics, 4.5 Sensors, 4.6 Flexible and/or printed electronics for the respective topics).

Looking at theoretical benchmarking of beyond CMOS devices (Figure 57), it becomes obvious that spin based devices have benefits in energy efficiency (especially in terms of standby and active power), whereas tunnelling devices (including GNR TFET and graphene pn junctions) have advantages in switching speed (lower delay), where spin-based devices are suffering from the low magnetization speeds. [420]

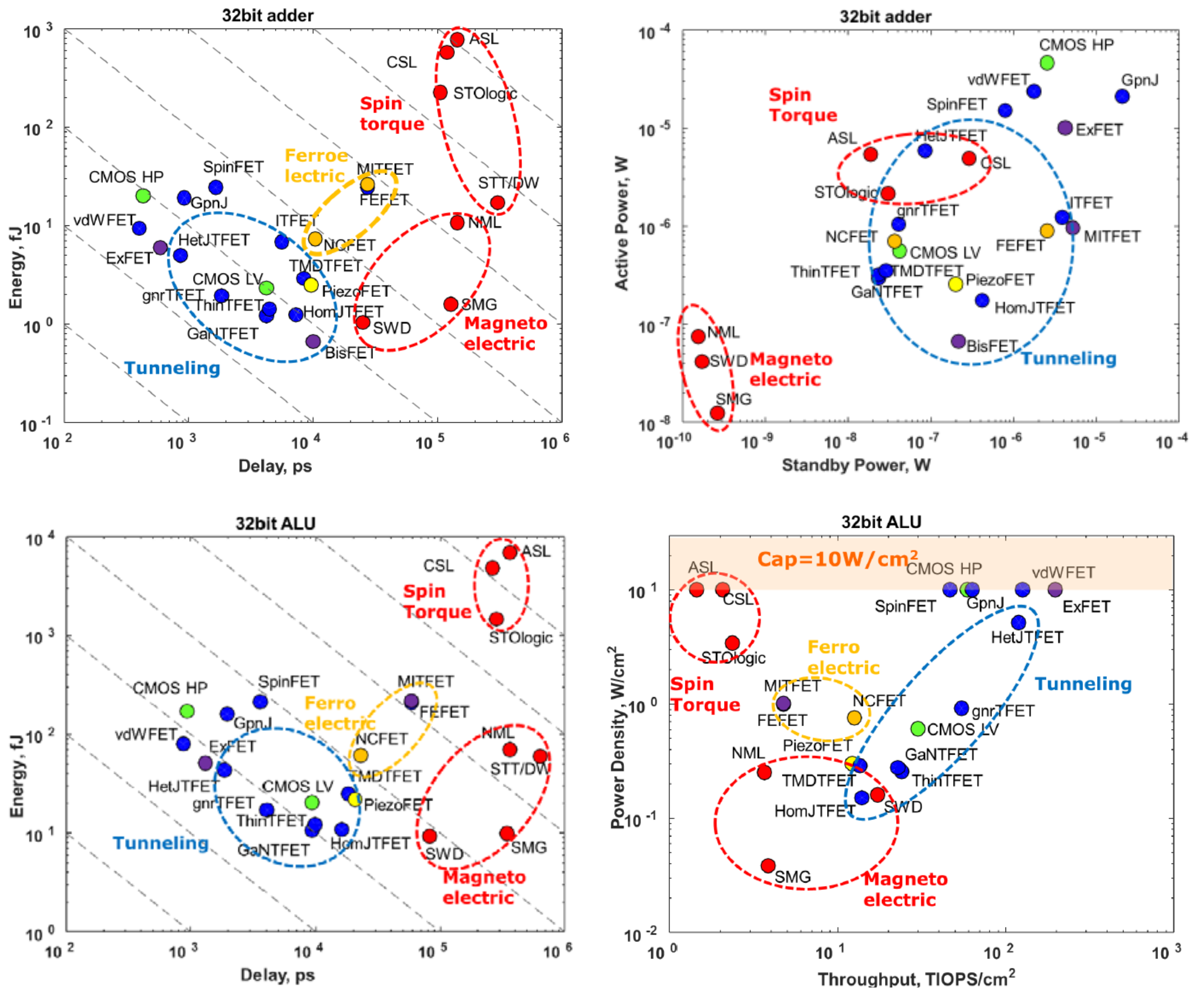


Figure 57: Simulated benchmarking of beyond CMOS devices in a 32bit adder and ALU. [420]

4.4.1.1.2 Non von Neumann, beyond CMOS

Novel architectures beyond von Neumann are currently investigated for special applications, such as cellular automata, co-located memory-logic (e.g., processor-in-memory, memory-in-logic, computational memory, non-volatile logic), reconfigurable computing, cognitive computing (e.g., neuromorphics, machine learning), statistical and stochastic computing (e.g., statistical inference, approximate computing for pattern recognition), collective-effect computing (e.g., coupled oscillator network), etc. [425]

These new concepts demand new technologies and materials, e.g. for tunnel FETs or spin/magnetic logic or other principles (see Figure 56).

4.4.1.1.3 Thin film low power applications

Within the diversification there are opportunities for transistors which do not perform at highest performance, but consume much less power. This is especially interesting for internet of things, portable and flexible electronics in general and more than Moore applications. For these applications low power consumption is a key demand. They are also employed in displays and other large area applications. For flexible electronics please refer to chapter 4.6 Flexible and/or printed electronics.

4.4.1.1.4 European strength in equipment and materials

Europe plays an important role in material and equipment for cutting edge electronics (20% of the production of equipment and material is currently done in Europe). But besides that, Europe is not strong in cutting edge More Moore technologies, see 4.4.1.3.1.

4.4.1.1.5 Memory: carbon based memory and spintronics in STT-MRAM as potential non-volatile memories with high speed and density

New memory technologies are also investigated by the semiconductor community. Electrically accessible non-volatile memories with high speed and high density are major demands from the industry, as they could initiate a revolution in computer architecture. [426]

MRAMs play an important role in that respect and are heavily researched and already marketed. The disadvantages of classic field switching MRAMs offer an opportunity for spin-torque transfer (STT) MRAMs, which are currently introduced to the market for special applications where high speed and endurance is needed. STT-MRAMS are also seen as the most promising emerging memory device, see Figure 58. STT-MRAMS are spintronics based memories [427], where graphene could play a role in a magnetic tunnel junction (see next subsection).

Ongoing efforts on MRAM involve several non-European companies including Sony, Toshiba, IBM, Samsung, TDK. Everspin recently announced that it is shipping 256Mb spin torque technology (ST-MRAM) chips, now the highest commercial density on the market, aimed at applications requiring persistent memory in storage devices and servers using DDR3 and DDR4 interfaces. The company is expected to deliver further density increases for its MRAM-based storage class memory and plans to sample a 1Gb product based on its proprietary perpendicular magnetic tunnel junction (pMTJ) ST-MRAM by late 2016. [428]

They currently use conventional insulating materials within the tunnel barriers, such as MgO. Unfortunately, further reduction of the cross-sectional area of the junction, as density increases, is expected to lead to prohibitively high junction resistances. The industry already envisions the replacement of the insulating materials, or its complete elimination, using standard giant magnetoresistance structures. The latter, however, leads to a very significant reduction of the magnetoresistance, and therefore a material like graphene can help overcome the future challenges.

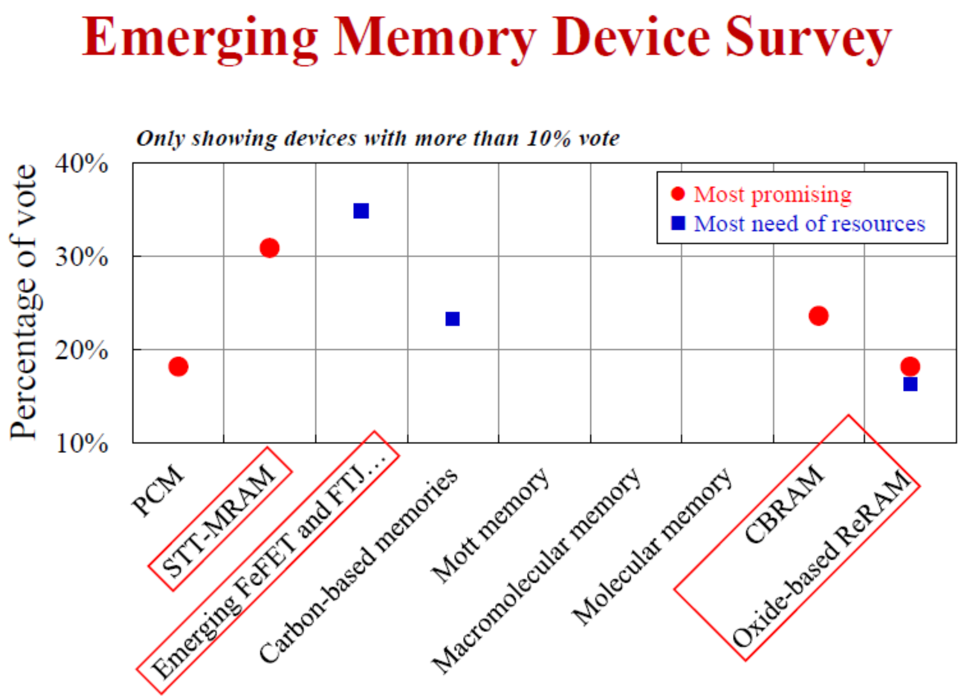
STT-MRAM have further issue with cost/bit, as there is currently no strategy how to realize multi-level cell structures or 3D integration. Furthermore, there is limited demonstration of high temperature data storage and retention. [429]

Carbon based memory is investigated for three material systems: nanotubes, graphene and amorphous carbon based resistive memory. Besides resistive memory, many possible mechanisms can be employed for data storage in these material systems (e.g. carbon nanotube based NRAM). [429]

4.4.1.2 Additional market opportunities: spintronics

4.4.1.2.1 Need for new and optimized magnetic tunnel junctions and tunnel barriers for TMR devices

Tunnel barriers are main building blocks of magnetic tunnel junctions (MTJs), which are part of for instance read heads of hard drives, sensors, MRAMs etc. For many of these applications, it is crucial to achieve sufficiently high tunnel magnetoresistance (TMR) signals with optimal junction resistances. This demands for controlling the thickness of metal oxide tunnel barriers with atomic level precession, a challenge for the production of these MTJs. [430] Graphene and other 2D Materials,such as BN and TMDs, can play a role in these MTJs addressing this challenge.


Emerging Memory Device Survey

Only showing devices with more than 10% vote

Source: ERD Emerging Memory Device Assessment Workshop, Albuquerque NM, Aug. 2014

Figure 58: Emerging memory device survey for most promising devices and devices in most need of resources. Graphene can play a role in carbon-based memories, as well as in STT-MRAM and ReRAM. [425]

4.4.1.2.2 Magnetic sensors and nano oscillators as a market opportunity for TMR devices

Graphene-based magnetic tunnel junctions (MTJs), where graphene is used as a tunnel barrier, can be used in magnetic sensors, e.g. in fast and accurate position and motion sensing and automotive sensors, refer to 4.5.1.2 Additional market opportunities: Magnetic sensors. Furthermore, the spin torque nano-oscillators can be used as a source for microwave signals for telecommunication, refer to 4.3.1.5 Additional market opportunities: HF/microwave/THz generation, detection and processing for further opportunities in telecommunication and 4.3.1 Market perspective: graphene/2D materials in telecommunication, optoelectronics & photonics for further market insights.

4.4.1.2.3 Beyond CMOS: All-spin logic devices (ASLD) and spin-based interconnects

All-spin logic devices (ASLD) have attracted increasing interests as one of the promising candidates for post-CMOS technology thanks to their low power consumption, non-volatility and logic-in-memory structure. ALSDs are also amongst the promising candidates to overcome the power dissipation issues, particularly relevant for high density computational circuits and one of the main road block for future downsizing of CMOS technology. ASLD with perpendicular magnetic anisotropy nanomagnets is anticipated to reduce the critical current, while spin transport efficiency can be enhanced by optimizing the device structure, dimension, contact resistance as well as the material parameters. Some benchmarking models [431] of ASLD opens up new prospects for design and implementation of future spintronics applications, which can be based on graphene and 2D materials [432]. Unlike the all-magnetic logic, which require magnetic fields, the ASLD uses spin currents, which may lead to a significant increase in both scalability and versatility.

The expected key feature of the ASLD are its compactness, completeness and simplicity because no CMOS transistor is needed for logic operations and all the logic functions can be constructed with a minimal set of Boolean logic gates [433].

Power dissipation is an additional factor that should be taken into account One of the most critical challenges for ASLD is to find a suited material for the spin-coherent channels. Metals, semiconductors and graphene are the main candidates for fabricating these channels, exhibiting long spin diffusion lengths. The main disadvantage of using semiconductors is the very low efficiency in the spin injection due to the mismatch in the conductivities of a ferromagnetic metal and a semiconductor (so called “conductivity mismatch” problem). Graphene exhibits the longest spin diffusion length reported to date.

4.4.1.3 Market Threats

4.4.1.3.1 Highly competitive and conservative market and major players not in Europe

The logic devices and memory market is a highly competitive market. The major IDM and foundry players are in the USA and East Asia. There is no major cutting edge high performance logic chip producer or memory producer headquartered in Europe at the moment (despite fabless ones). Intel operates a fab in Ireland with 14nm technology and Globalfoundries operates a state-of-the-art fab in Dresden. Therefore, in contrast to more than Moore technology, it is unlikely that an existing European company would integrate high performance logic or memory advancements realised with graphene or 2D materials. In cutting edge semiconductor “more Moore” technologies Europe still plays an important role in the machinery and equipment, as well as material area. Thus, the benefit would be only indirect for the European downstream economy and the equipment and material suppliers could benefit upstream. But the integration for high performance logic itself would probably not be done by a European company. This of course does not exclude the initiation of spin-offs for niche markets or fabs in Europe from international companies that build on the European IP and research infrastructure.

Major logic graphene activities have been at Samsung, IBM (most patents now moved to Globalfroundries) and Sandisk (now Western Digital).

Furthermore, the four major players in the semiconductor industry remain to date very conservative with new materials.

4.4.1.3.2 New types of logic and memory: graphene/2Ds one out of many

It is in principle anticipated that FinFET or Nanowire technology will be capable to go to 5nm with materials already used in fabs (classical semiconductors, e.g. Ge, III-V,…) continuing the von-Neumann architecture. SWCNTs are also still in the race due to better intrinsic properties for digital electronics compared to graphene (e.g. intrinsic bandgap, compatibility with Nanowire FET structures). Recent advances in that area have proven that one major challenges related to use CNTs is controllable, namely the scalable contacting [434]. But other challenges such as the separation of semiconducting and metallic CNTs as well as reliable, non-lithographic ways to place billions of nanotubes exactly where they are needed on a chip remain open. [435]

There is a common perception by many semiconductor producers that the GFET has no chance for broad uses in high performance logic and will not replace the CMOS FET in the conventional charge based transistor. This is further supported by the notion that the majority of high performance chip producers do not touch graphene at the moment beyond research level (only on research level for new device architectures, e.g. spintronics).

Other 2D materials (TMDs) on the other hand have a better perception and are still considered as viable options.

In terms on carbon base memory, CNT is more studied. With Nantero, there is already a US based company commercializing CNT based NRAM.

4.4.1.3.3 Window of opportunity: 5 years from now, the decisions will be made

No matter where graphene or 2D materials will be used in high performance logic and more Moore (beyond CMOS/non van Neumann or further scaling of CMOS), the window of opportunity lies in the next 10-15 years. To be recognized in time, important breakthroughs are needed within the next 5 years, because 5-10 years are needed for scale up and decisions will be made then. If these breakthroughs are not achieved by then, other technologies will be most probable more promising and it might be too late to be still recognized as a valid alternative.

4.4.1.4 Additional market threats: spintronics

4.4.1.4.1 Competing materials, technologies and worldwide competition

Graphene competes in spintronics with established materials like silicon and metals. It has benefits towards these materials (see 4.4.2.2 Additional strengths: spintronics). Current STT-MRAMs work without graphene and 2D materials and it remains to be tested to which extent graphene and 2D materials can add value or enable the technology.

Spintronic based on MRAM technologies is a quite mature branch of ICT, although they so far only address niche markets due to limited storage density and competitiveness with standard volatile RAM technolgy. There is strong effort of implementation/production of non-volatile very large scale integration (VLSI) of spintronics, notably in Japan with a strong academic/industrial bond. Industrial companies such as Toshiba, Samsung, Qualcomm and Intel are involved in spintronics. Hence graphene spintronics co-integration will strongly rely on graphene’s ability to be integrated. Integration of graphene has been demonstrated on lab scale in CMOS-technology through existing graphene-interconnects [436].

Furthermore, some applications can also be realized with the more mature GMR effect. And in terms of sensors and microwave sources, it competes with other well established concepts, e.g. hall sensors or GMR sensors for magnetic sensing (see 4.5.1.7 Additional market threats: Magnetic sensors).

It is noted that a coordinated effort is undergoing in Europe, America, whereas Spintronics activities in Japan and Korea are also identified. Further progress will require convincing operational demonstrators and further demonstration of wafer-scale graphene device integration (see 4.2 Electronics: Cross-cutting issues). This issue not only derails spintronics but all electronic and optoelectronic applications, which require fast processing of high-quality graphene over large areas.

4.4.1.4.2 Limitations of ASLDs

ASLD provides the stage for majority logic operations since the output magnet state can be controlled by the sum of the spin-currents from all input magnets. As a trade-off, by increasing the number of input devices in a majority gate, the uncorrelated thermal noise of these devices adds up and impacts the transient magnetization output. This phenomenon sets a practical limit on the number of input devices to a majority gate.

4.4.1.4.3 Connectivity of ASLD to CMOS, design tools and library needed

Whatever the logic macro, at some point one has to interact. outside the chip, between units (where the spin diffusion length is exceeded) or within a System-on-Chip (SoC).

Circuits are needed to generate (on/off) currents at the inputs of some logics macros and others, for readout and conversion of the magnetic data in electrical signals (currents, voltages) to drive a copper line or a chip I/O. The magnetoresistance is not infinite and requires a well-designed amplifier, applied currents (drivers) might need regulation, to avoid overdrive of the macro for instance. Up to now, standard CMOS is the best choice for those developments, but CMOS technology has some drawbacks in term of leakage, scalability, power and the use standard interconnects. To maximize the efficiency, it is mandatory to have as few as possible interfaces, meaning that all-graphene ASLD need to perform a "quite complex" calculation (inversion is not good enough for instance). Part of the challenge is therefore to define the minimal subset of functions/macros (or the minimal size, complexity) allowing the description of standards digitals with a minimum number for electrical/magnetic interfaces.

Digital designers use HDL (Hardware Description Language) to describe digital functions and a synthesis tool generates the circuit thanks to a library of CMOS "standard cells" (inverter, nand, nor…). At the macro level (all-graphene ASLD), it is mandatory to define a library of magnetic "standard cells" and find a way to connect the HDL description to the ASLD generation through an update of the synthesis tool. At the chip or system level, one needs to combine the standard CMOS approach (interfaces management…) and the all-graphene ASLD blocks in order to generate an efficient and usable digital product. The generation of complex digital functions using this technology plus the CMOS interaction will require a specific software development in term of design automation going from pure Electronic Design Automation (EDA) to (Spintronic (+Electronic) Design Automation).

4.4.1.4.4 Weak European industrial base and engagement

In Europe, the graphene flagship spintronics WP is exploring how graphene and other 2D materials can be harnessed for spintronics applications in both vertical and lateral geometry and trying to solve several challenges. The C-SPIN consortium in USA is a world-leading center that brings together top researchers from across the nation to develop technologies for spin-based computing and memory systems. Sponsors of the network activities include organizations and companies such as DARPA, GLOBALFOUNDRIES, IBM, Intel Corporation, Micron Technology, Raytheon, Texas Instruments, United Technologies. Specifically, Intel Corporation is exploring the use of graphene and other 2D materials having high spin-orbit coupling for developing spintronics beyond-CMOS technology. There is also a strong commitment in Japan with Tohoku University (own a 300mm line) working on spintronics VLSI and several industrial companies such as Toshiba or Canon-Anelva. Therefore, the international competition is high and especially non-European companies and bigger players address the field and generate IP (see also 4.4.1.3.1 Highly competitive and conservative market and major players not in Europe)

4.4.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in computing/logic

4.4.2.1 Current strengths for graphene/2D materials use in computing/logic

4.4.2.1.1 Combination of graphene and other 2D materials are still in the race for beyond CMOS

Graphene and other 2D materials are still considered as a valid candidate for beyond CMOS technologies in the ITRS discussions, see Figure 59. TMDs are (theoretically) more promising due to the intrinsic bandgap. Also GNRs are still considered. The role of graphene FETs and graphene as a channel material in standard CMOS is no option anymore (conventional charge based transistors), as CNT and other technologies are more promising and advanced. But GNRs can potentially be uses as nano ribbon in tunnel-FET (conventional charge based). Furthermore, 2D materials can play a role in charge-based as well as non-charge based novel structures, such as the 2D transistors or in spintronic devices (see below). For instance, there is a potential in combining and stacking TMDs to 2D transistors, a novel type of a charge based transistor.

Figure 60 shows a result of an ITRS workshop from August 2014. Here, TFET, nanowire FET and CNT FET were assessed as the most promising devices for beyond CMOS. 2D channel FET was one of the topics assessed to be in most need of resources. This topic addresses 2D materials as germanene, MoS_2, WSe_2 as a 2D channel. Open questions are related to scaling: it is still unclear whether dielectric thickness/gate control or body thickness is more relevant for scaling. In case the dielectric is the issue, it would call for a nanowire or fin structure solution, which is probably not so well suitable for 2D materials. [437]

Overall, the strengths of 2D materials for high performance logic transistors are reduced short channel effects and reasonably good I_{On}/I_{Off} performances. Strengths of low power transistors (tunnel FETs) are the lower power supply (<0.5V) and the good control of the gate over the tunnel barrier combined with a subthreshold swing of $\ll$60mV/dec and large I_{On} currents of $>10^3$µA/µm. 2D materials provide a fully terminated surface, free of dangling bonds. [438]. Very recently, new experiments clearly demonstrate the potential of MoS_2 for ultimately scaled devices. [312, 313, 439]

Independent of the high performance solutions, 2D materials have also chances in TFT (lower constraints, less scaling) in the medium term, as well as in flexible solutions. [314, 440] For the latter please also refer to chapter 4.6 Flexible and/or printed electronics.

In summary, for high performance logic transistors, 2D materials will most probably only play a role beyond CMOS after the end of the ITRS 2013, as also outlined in the scenario presented in reference [314], see Figure 61.

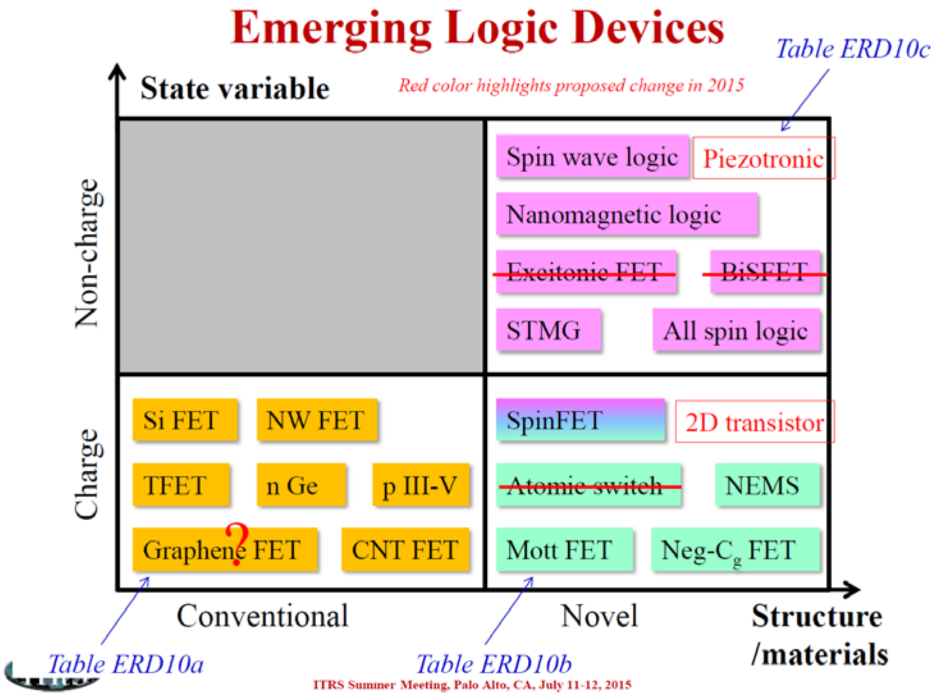
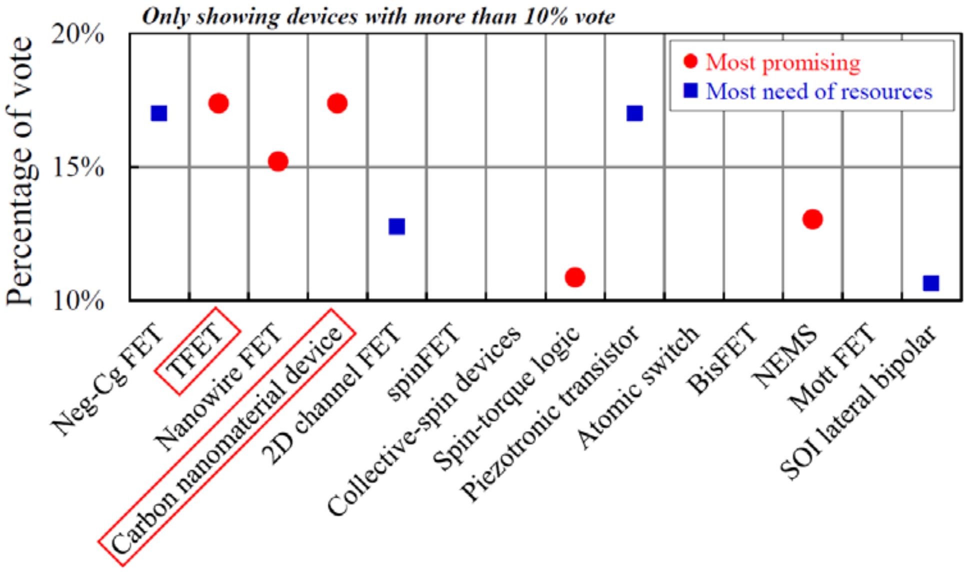


Figure 59: New concepts for beyond CMOS. STMG: Spin Torque majority gate. From [425].



Source: ERD Emerging Logic Device Assessment Workshop, Albuquerque NM, Aug. 2014

Figure 60: Results of an ITRS ERD Emerging Logic Device Assessment Workshop, Albuquerque NM, Aug. 2014. Carbon nanomaterials device relates to CNT or GNR. Taken from [425]

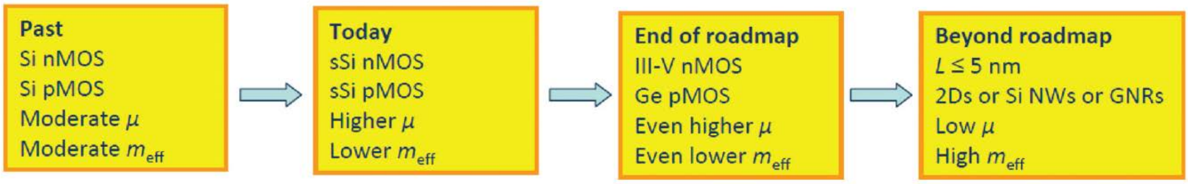


Figure 61: Selection of the channel materials for logic MOSFETs, a scenario from [314]. sSi means strained Si, μ is the carrier mobility, m_{eff} is the carrier effective mass, and 2Ds means semiconducting 2D materials. Roadmap refers to the ITRS 2013 roadmap.

4.4.2.1.2 Promising results for TMDs

Recent experiments show that MoS2 can be use in FinFETs contributing to very short gate lengths. These breakthroughs push TMDs at the forefront of logic developments and scaling for low power, high performance technologies. [312, 313, 439]

4.4.2.1.3 New and unconventional logic as potential application area

In terms of high performance logic, 2D materials are not only a candidate as a gate/FET channel material, but there are also potentials in post-Si spintronics or unconventional switching. Several realisations of beyond CMOS transistor types under consideration are based on graphene or 2D materials, see Figure 56. In case there is a new concept, e.g. a new type of logic or device, which is not realizable with other materials, it might actually create an important uniqueness for 2D materials. However these solutions need to outperform other solutions targeting the same functionality.

It might also become interesting once wafer scale integration becomes economically feasible and competitive, which could be driven by the more than Moore path. As soon as this is possible, the barrier to also look at logic or spintronics applications of graphene and 2D materials becomes lower and an entry scenario could be via cost reduction (e.g. compared to compound semiconductors), for instance when a complex device is made simpler with graphene.

4.4.2.2 Additional strengths: spintronics

4.4.2.2.1 Spin filtering properties

Advantages of graphene/2D materials for magnetic tunnel junctions-based memory and nano-oscillator applications are its spin filtering properties, passivation properties for new process development such as ALD, its relatively low barrier resistance, a low enough density of defects and the capability of sustaining large applied currents.

Graphene (including multilayers and graphite), h-BN and their heterostructures, have a strong potential for vertical geometry spintronic devices and MTJs to increase tunnel spin polarisation. It has been demonstrated that graphene/ferromagnet and graphene/h-BN/ferromagnet interfaces can efficiently filter spin channels. [441] [442, 443]

Other 2D materials beyond graphene are also investigated for magnetic tunnel junctions, especially those that can be directly grown by CVD on ferromagnets. [444] This could improve interfacial spin polarization giving rise to high tunnel magnetoresistance values, similarly to the case or better than epitaxial MgO.

Graphene can also alter the magnetic properties at ferromagnet|graphene interfaces, e.g. by increasing the perpendicular magnetocrystalline anisotropy, an important direction to pursue for the downscaling of spintronic devices to improve energy efficiency [445].

4.4.2.2.2 Long spin diffusion length

Graphene is a promising material candidate for spin communication and transport due to its weak spin-orbit coupling. The measured spin lifetime of graphene at room temperatures is about 10 ns and the spin diffusion lengths is up to 30 µm, the longest of any metal or semiconductors.

The long spin lifetime and high electron velocity make graphene a suitable candidate for future emerging and proposed spintronics transistors (Datta-Das device), magnetologic gates and spin coherent interconnects for ASLD. Furthermore graphene could be used in new spin-based data communication devices (see 4.3.2.1.5 New types of spin-based data communication)

4.4.2.2.3 Direct CMOS compatible growth (without transfer) on Nickel

Vertical 2D MTJ technology requires in-situ growth of ferromagnetic materials and large area CVD graphene/h-BN heterostructures with clean interfaces without air exposure. Within the Graphene Flagship, experimental demonstration of this effect has been obtained using CMOS-compatible processes (<450°C large scale CVD processes developed by Spintronics WP in collaboration with Materials WP) for the direct integration of graphene in devices [446]. For this process, no transfer was needed as the graphene was directly grown on Nickel (which is the ferromagnetic material used). Already these novel electrodes have been proven to be oxidation-resistant and allowed to unlock low-cost processes for the fabrication of Magnetic Tunnel Junctions (MTJ) such as ALD. [447]

4.4.2.2.4 Graphene magnetologic gates and spin-coherent channels/interconnects for ASLD

One possible building block of graphene spin logic is a magnetologic gate (MLG) consisting of a graphene sheet contacted by five ferromagnetic electrodes [448]. By integrating memory and logic within the MLG device, i.e. all-spin logic device, spintronic circuits could produce substantial gains in data-intensive applications by alleviating the von Neumann bottleneck, i.e. the computational overhead involved in transferring data between memory and CPU. A proof of concept has been recently reported by the US consortium C-SPIN [449], see “XOR Operation in Graphene Magnetologic Gates at Room Temperature” [450].

Functionalization of graphene by proximity of materials with large spin orbit interaction or ferromagnetism can enlarge and diversify the opportunities for all-graphene ASLD.

With the features of high electronic mobility, weak spin-orbit and hyperfine interactions and long spin diffusion length, while reducing dynamical crosstalk between wires, RC bottlenecks, and electromigration. graphene has also attracted considerable interest as channel material and spin-based interconnects. Metallic channels (e.g. copper) outperform graphene in terms of energy dissipation but seriously suffer from a low breakdown current limit - the breakdown current density of graphene is at least two orders magnitude larger than that of copper [448].

Spin-based interconnects cannot replace “long” chip interconnects but they can be used as local interconnects within specifics blocks. A trade-off needs to be found between function and speed requirement. The advantages of spin-based interconnects are low power transmission but also the ability to remain within the magnetic domain and at substrate level. The classical approach requires to use an extra metal layer adding cost and resistance. Spin-based local interconnects offer a higher density and potentially lower cost (no extra layers of metal, contact, via on substrate level), low power and more scalable solution (layers spacing, resistance, IR drop).

4.4.2.2.5 Promising advancements for graphene in spintronics

After one decade of intense research efforts to achieve long spin lifetimes in graphene [432, 451], the potential of graphene and two-dimensional (2D) materials for spintronic applications is now attracting the attention of large companies as well as small and medium enterprises, including EU-companies such as NanOsc AB and eVaderis, offering non-volatile solutions for the data-processing, wearable computing and Internet of Things (IoT) markets. Indeed, the first practical applications harnessing the unique properties of graphene, such as nano-oscillators based on spin transfer torque (STT) seem within reach.

Besides, graphene and h-BN materials have proven useful to unlock low-cost processes such as Atomic Layer Deposition (ALD) for the fabrication of spintronic devices and could play a role in novel memory concepts and realizations. Interestingly first proofs of principle of graphene-based spin logics has been reported (XOR logic functions), paving the way towards all spin-based information processing circuits.

4.4.2.3 Current weaknesses and challenges for graphene/2D materials use in computing/logic

4.4.2.3.1 Missing bandgap in graphene

The missing bandgap in graphene calls for additional tuning, making the preparation processes more complex. It is obvious nowadays that the GFET has no chance in logic applications/computing. Figure 44 summarizes values of mobility and bandgap of 2D materials. A major challenge for 2D transistors is thus to maximize the I_{on}/I_{off} ratio, whilst maintaining the speed.

4.4.2.3.2 Low maturity of 2D materials for logic make actual benefit assessment difficult

For conventional logic, other materials than graphene are more promising and needed (e.g. Germanene, TMD such as MoS_2, etc.). The maturity of these 2D materials is still very low, only on fundamental research level. Often concepts are not yet demonstrated, only simulated (especially for TMDs). However, recent results show very promising devices based on TMDs. [312, 313, 439] But there is still a gap in fundamental understanding and feasibility, e.g. in terms of fundamental understanding of 2D materials impact on a device, influence of defect density, grain boundaries, etc. Additionally, complete device architecture needs to be better understood.

For realistic broad "beyond Si" implementation in next 10 years, i.e. when the need will be largest, groundbreaking ideas/lab demos are needed already today and recent developments of MoS2 field effect transistors show promising results. There are rather low expectations on graphene, but after recent development, the opinion of 2D materials increased for logic and memory applications to be ready and competitive in 10 years from now.

4.4.2.3.3 Graphene is out, TMDs are in

Currently, the overall experimentally realized performance of graphene demonstrators fabricated with mass production compatible processes is not good enough to be competitive with other emerging solutions.

Also some new 2D/graphene-based logic devices have certain disadvantages. For instance, the graphene barristor suffers from a lot of parasitic capacitance. The 2D tunnelling FET also has a huge parasitic capacitance as the gate overlaps with source and drain. Such a high parasitic capacitance is a strong disadvantage for a beyond silicon technology. However, hot electron graphene base transistors could also be interesting for logic, as they make use of gapless graphene, although their true potential for the future is still not fully understood. [314] Spintronics can be a similarly interesting field where the bandgap is irrelevant. For most solutions, two-dimensional hBN is needed additionally, which is still at the exfoliation stage.

Another important issue is that there is some scepticism in industry towards comparisons/improvements in scientific publications: the comparisons are often not fair and helpful because they compare to a wrong competitor and not the SOTA ("50x improvement towards best graphene based FET”, instead of “towards CMOS Si based FET”).

However, the most recent developments with TMDs are very promising and might be a way forward towards further scaling. [312, 313, 439]

For RF, flexible RF an flexibled logic applications, TMDs and graphene are still both valid options and interesting candidates.

4.4.2.3.4 Implementation challenges: contact resistance and integration schemes

A critical issue for 2D materials is the contacting and related contact resistance which additionally limits device performance. This needs to be under control for further exploitation.

Besides that, the major challenge is the integration scheme and how 2D materials can be produced and integrated into electronic systems on large scale with necessary quality and adequate cost (see also 4.2 Electronics: Cross-cutting issues for wafer scale integration assessment and roadmap).

Also for spintronics, integration and CMOS compatible processes are essential.

4.4.2.4 Additional current weaknesses and challenges: spintronics

4.4.2.4.1 Spin relaxation

Spin relaxation is an important issue that needs to be solved for graphene. The origin of the spin relaxation mechanism is complex and and multiple theoretical advances have been accomplished by the EU Flagship consortium in recent years partly solving past controversies and false expectations and related to the variety of device fabrication techniques and lack of fundamentals on spin dynamics in supported graphene samples. [452]

4.4.2.4.2 Non-collinear spintronic phenomena such as spin transfer torque not yet explored

So far the use of graphene in spin transfer torque devices has not been investigated. An important next step is to explore the behaviour of non-collinear spintronic phenomena such as spin transfer torque, important for development of STT-MRAM and spin-torque nano-oscillators (STNO) [453, 454]. Magnetization dynamics properties play a key role for these devices and also need to be explored. Magnetic properties of ferromagnet|graphene and h-BN interfaces such as perpendicular magnetocrystalline anisotropy are also an important direction to pursue for downscaling of spintronic devices. In graphene based magnetic tunnel junctions, the contact resistance can be tailored to desired regimes by introducing heterostructures with h-BN tunnel barriers without compromising spin polarization, which would be useful for high-density MRAM [442]. It is also important to explore STT-related phenomena for lateral and more complex geometries. The use of such 2D materials heterostructures in magnetic tunnel junctions can also provide flexible spintronic devices.

4.4.2.4.3 Energy dissipation and long latency in spin-based interconnects (for ASLD)

Metallic channels (e.g. copper) outperform graphene in terms of energy but suffer from a low breakdown current limit. The energy performance of a graphene channel ASLD is partly restricted by its large contact resistance. Notwithstanding, it is possible to find new tunnel materials with lower contact resistance as well as high spin-injection efficiency.

Another intrinsic issue is to understand, and improve the energy efficiency, i.e. the mechanism of spin transfer torque from the graphene channel to the magnetic layer. A Japanese team has demonstrated the spin torque switching in a lateral spin valve network (similar to the ASLD geometry) via spin currents at room temperature using Cu as channel material [455]. However, this technology is still in its infancy and many issues - such as reliability, cascading and operation speed - have to be carefully addressed.

Another main disadvantage is the latency of a few nanoseconds.

4.4.2.4.4 Challenges and maturity of graphene ASLD

The concept of ASLD shows a potential advantage for future implementation. However, at this stage a number of technological challenges must be overcome before they can be adopted in applications, in particular the graphene-based all-spin logic gate with perpendicular magnetic anisotropy. The input write current must be further reduced to enable multi-gigabit memories, representing one of the most critical issues. Furthermore, increasing magnetoresistance to over 300% is necessary for large memories and fast reading. Other matters that need to be addressed include: new fabrication recipes need to be developed for deposition of magnetic materials; etching methods to give lower spread in resistance from bit to bit have to be improved; the stacking composition of the magnetic tunnel junction (or spin valve) needs to be simplified.

Graphene is an attractive material for non-volatile spin logic applications because of the long spin coherence at room temperature and gate-tunability. However, there are several challenges at this stage: (i) production of large area high quality graphene and h-BN heterostructures (ii) Reproducible fabrication of ferromagnetic tunnel junctions on graphene with reliable spin source-drain performance. (iii) Achieving the high speed switching of ferromagnets in graphene spin valve devices. (iv) Finding low energy schemes based on spin transfer torque for reading and writing. (v) Demonstration of a complete magnetologic gate operation at room temperature.

4.4.3 KPIs for computing/logic, beyond CMOS and spintronics

4.4.3.1 Logic/computing

Table 52: Desirable properties of ideal FET channel materials for logic. Hp: high performance, L: gate length. From [314]

Property	**Desireable**
Bandgap	≥0.4 eV
Carrier effective mass	For gate length L > 5 nm: light, $m_{eff} < 0.1\ m_e$ For gate length L ≤ 5 nm, heavy $m_{eff} \geq 0.5\ m_e$
Mobility	high, > 500 $cm^2\ V^{-1}\ s^{-1}$
Peak/saturation velocity	high, >10^7 $cm\ s^{-1}$
Heat transport	Thermal conductivity: High Thermal boundary resistance: Low
Contact resistance	Low ≤0.08 Ω mm
Scale length, channel thickness	Small

Typical quantities are on/off ratios of 10^4-10^6 for digital electronics and sub-threshold swing of 60mV/dec. The reduction of V_{DD} (<1V) would be favourable to reduce power consumption. For low power devices a subthreshold swing of <60mV/dec is desired.

For high performance transistors the saturation velocity of carriers and effective mass are relevant (for short channels, mobility is irrelevant), as well as the electron distribution and density of energy states [440].

Table 53: High performance and low power FET properties in the ITRS 2013 (PIDS Tables). [327]

High performance logic FET	**2014**	**2016**	**2019**	**2025**	**2028**
Physical Gate Length for HP Logic (nm)	18	15.2	11.6	6.7	5.1
V_{DD} Power supply voltage (V)	0.85	0.81	0.77	0.68	0.64
I_{off} (nA/µm)	100	100	100	100	100
I_{on} MG (multi gate, NMOS drive current, µA/µm)	1680	1660	1600	1100	900
I_{on}/I_{off} ($/10^3$)	16.8	16.6	16	11	9
Dynamic Power Indicator (fJ/µm)	0.77	0.69	0.58	0.33	0.24
τ (MOSFET Intrinsic Delay, ps)	0.541	0.512	0.474	0.446	0.423

Low power FET	**2014**	**2016**	**2019**	**2025**	**2028**
Physical Gate Length for LP Logic (nm)	21	18	13.3	7.7	5.9
V_{DD} Power supply voltage (V)	0.85	0.81	0.77	0.68	0.64
I_{off} (pA/µm)	10	10	10	30	50
I_{on} (multi gate, NMOS drive current, µA/µm)	610	589	550	396	295
I_{on}/I_{off} ($/10^5$)	610	589	550	132	59
Dynamic Power Indicator (fJ/µm)	0.86	0.78	0.65	0.38	0.28
τ (MOSFET Intrinsic Delay, ps)	1.661	1.64	1.525	1.422	1.492

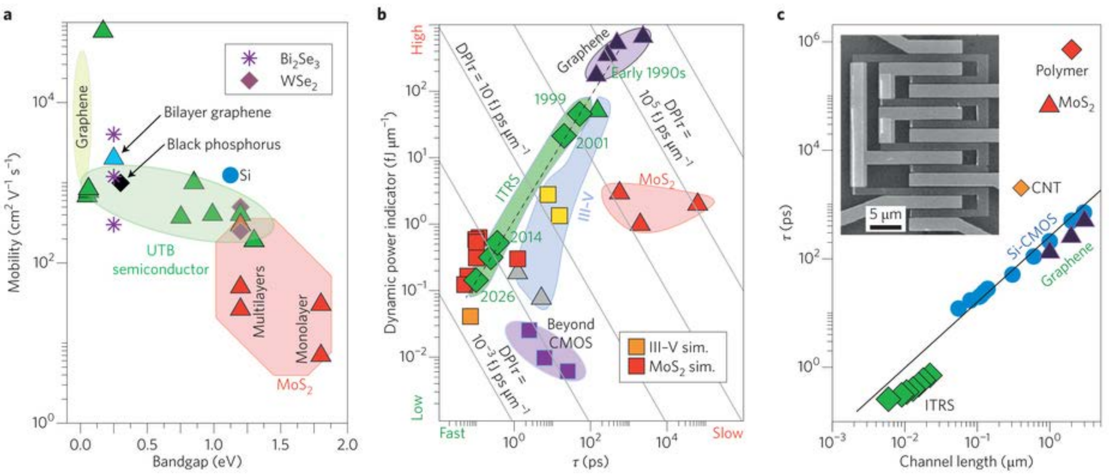


Figure 62: Comparison of 2D materials and bulk semiconductors figures of merit for high performance transistors. [438]

For TFTs, a digital transistor switch is needed without the extreme performance requirements of computational devices. The mobility of $\mu > 100\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ is sufficient for the longer channels. [440] Typicaly materials in used today are InGaZnO (IGZO), which replaced amorphous silicon due to the higher electron mobility.

4.4.3.2 Memory

Table 54: KPIs for STT MRAM from ITRS 2013, Table PIDS 7b. [327]

Year of Production	**2016**	**2019**	**2025**	**2028**
MRAM technology node F(nm)	65	45	22	16
MRAM cell size area factor a in multiples of F^2	20	14	8	8
MRAN typical cell size (μm^2)	0.08	0.028	0.004	0.002
MRAM materials technology: In-plane (IMA) or Perpendicular Magnetic Anisotropy (PMA)	IMA	PMA	PMA	PMA
MRAM switching current (µA)	175	100	35	25
MRAM write energy (pJ/bit)	2.5	1	0.18	0.15
MRAM active area per cell (μm^2)	0.008	0.005	0.0011	0.0006
MRAM resistance-area product (Ohm-μm^2)	11	10	9	6
MRAM magnetoresistance ratio (%)	120	150	180	200
MRAM nonvolatile data retention (years)	>10	>10	>10	>10
MRAM write endurance (read/write cycles)	>1E12	>1E12	>1E15	>1E15
MRAM endurance-tunnel junction reliability (years at bias)	>10	>10	>10	>10

Table 55: Field switching MTJ MRAM KPIs from ITRS 2013, Table PIDS 7b. [327]

Year of Production	**2014**	**2015-2017**
MRAM technology node F (nm)	90	65
MRAM cell size area factor a in multiples of F2	51	52
MRAM typical cell size (µm2)	0.41	0.22
MRAM switching field (Oe) [12]	67	82
MRAM write energy (pJ/bit) [13]	120	110
MRAM active area per cell (µm2) [14]	0.124	0.066
MRAM resistance-area product (Kohm-µm2) [15]	1.2	0.6
MRAM magnetoresistance ratio (%) [16]	65	90
MRAM nonvolatile data retention (years)	>10	>10
MRAM write endurance (read/write cycles)	>3E16	>3E16
MRAM endurance-tunnel junction reliability (years at bias) [17]	>10	>10

For STT-MRAM, the R&D focus has shifted from in-plane to perpendicular magnetization.

The following characteristics were demonstrated for perpendicular MTJ STT MRAMs [429]:

- Potentially near “infinite” endurance for switching voltage below 650mV
- Sub-5ns read and write operation in a 8Mb test chip between -25°C and 125°C
- Thermal stability after 400°C 90min annealing, ready for BEOL CMOS process
- Switching V/I reduced to <450mV/60µA at error rate below 10^{-7} for 37nm MTJs
- Scalability down to 15nm demonstrated

Carbon-based memories are more mature based on CNT (e.g. Nantero).

4.4.3.3 Spintronics

Spintronics has to compete with the KPIs of the addressed application, i.e. the KPIs for memory, logic, sensing or sources. Besides these KPIs, typical performance indicators for spintronics are:

- Spin diffusion length at RT (as long as possible)
- Spin relaxation time (as long as possible)
- Spin injection and spin polarisation
- Tunnel magnetoresistance (high difference between polarisations, low resistance in "on" state)

4.4.4 Roadmap for computing/logic, beyond CMOS and spintronics

4.4.4.1 Current maturity: 'Too early to assess actual potential'

In summary, for logic and beyond CMOS transistors, graphene has some benefits but many open questions and challenges. Therefore it is essentially out of the race for logic applications, besides spintronics. On the other hand, MoS_2 and TMDs have recently shown very promising results opening up great opportunities. It remains to be seen to which extent the processes can be implemented economically feasible, but the lab results are very promising. Still, the race is open and nothing is decided yet.

Spintronics is mostly in the proof of principle stage. Interesting theoretically described behaviours and benefits have to a certain extent been verified experimentally, but the readiness at the moment is still on a fundamental research stage.

4.4.4.2 Barriers/challenges (summarized)

Essentially, the same challenges apply as for wafer scale integration and other cross-cutting electronics issues (see chapter 4.2.4.2). Additionally, the following challenges are specifically relevant:

General

- Manufacturing and integration schemes of higher quality graphene, TMDs and other 2Ds, graphene nanoribbons and bilayer graphene
- Material quality
- Demonstration of theoretical predictions and benchmarking with competing technologies to allow a better and realistic assessment of the actual potential
- Current realized results are not promising enough for industry to justify investment to solve manufacturing
- Exploration of new device architectures
- Timing: for beyond CMOS, focusing will happen soon and in probably 5 years the decision will be made, so that demonstrators with strong advantages are needed very soon. The new developments for TMDs are suggesting that they will be in the race.
- Bandgap vs. mobility
- From European perspective: How shall the European economy benefit from advancements in logic transistors though 2D materials? Will the technology be implemented in Europe and how can it lead to a competitive advantage? How can equipment and material supplier benefit (who are already strong)?

High performance [438]

- Fabrication of ultrashort channel devices (channel length smaller than 10 nm), and large amounts of transistors per area
- Fabrication of devices based on new principles to reduce V_{DD} and subthreshold swing
- Good ohmic contacts with low source–drain parasitic resistance

Low power [438]

- Fabrication of doped tunnel junctions
- Low interface states to reduce subthreshold swing
- Design of new device architectures

Spintronics

- Wafer scale integration (especially with hBN and other heterostructures, also with magnetic materials
- Reproducible fabrication of ferromagnetic tunnel junctions on graphene with reliable spin source-drain performance
- Achieving the high speed switching of ferromagnets in graphene spin valve devices
- Missing fundamental understanding of spin relaxation and how to improve it
- Spin-transfer torque not yet investigated
- Finding low energy schemes based on spin transfer torque for reading and writing
- Missing investigation on magnetization dynamics
- Perpendicular magnetization unclear
- Need for new tunnel materials with lower contact resistance as well as high spin-injection efficiency to overcome energy problem
- understand, and improve the energy efficiency (mechanism of spin transfer torque from the graphene channel to the magnetic layer)
- Missing knowledge on reliability, cascading and operation speed
- graphene-based all-spin logic gate with perpendicular magnetic anisotropy not yet good enough (reduce write current, increase magnetoresistance, simplified stacking structure, lower spread resistance)
- No demonstration of a complete magnetologic gate operation at room temperature available
- Interface to CMOS logic not available
- Complex calculation schemes and minimal subset of functions needed to describe standard digital functions with a minimum number of electrical/magnetic interfaces
- Library of magnetic “standard cells” to be used in a spintronics+electronic design automation tool

4.4.4.3 Potential actions

If the area of graphene/2D in logic or spintronics is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

Also here, the major potential actions for wafer scale integration and cross-cutting issues apply (see chapter 4.2.4.3).

These additional conclusions are derived from the assessment:

Ecosystem

- Elaborate the cross-fertilisation with the other electronics areas

- Elaborate how the European economy can benefit from 2D material developments in logic (developed in Europe)

Materials and devices

- Investigate preparation methods to get rid of the material quality issues that currently dominate the device performance
- Focus on new device architectures that are capable of outperforming competing technologies
- Show actual potential with demonstrators that can be compared to existing devices in terms of functionality
- Compare results with competing technologies (e.g. III-V, Si CMOS) and not with the best “2D material based device” to allow serious potential assessment
- Further investigate integration schemes and processes to increase the maturity and reduce the manufacturing risk for companies (but at some point companies need to take over, which will only happen if demonstrators are promising enough)

Spintronics:

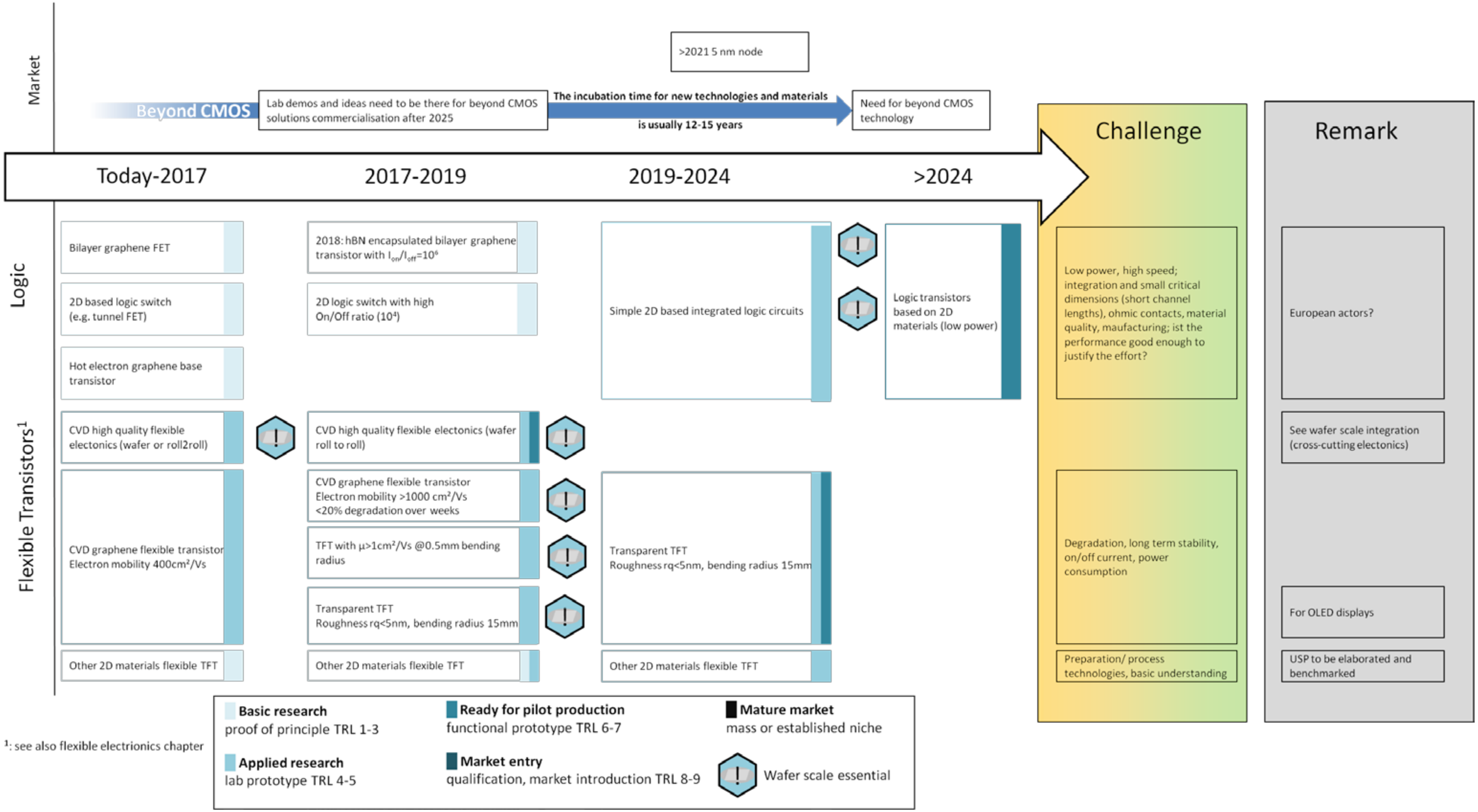
- Due to the low maturity of spintronics, more fundamental research would be needed to elaborate foundational building blocks and first competitive realizations of spin devices and architectures, either for new memory technologies or non-charge based information processing protocols
- An important next step would be to explore the behaviour of non-collinear spintronic phenomena such as spin transfer torque, important for development of spin transfer torque magnetic random access memories (STT-MRAM) and spin torque nano-oscillators (STNO), potentially interesting for for next generation high speed communications. Both are currently intensely explored within research labs, but are still waiting to be introduced to the market.
- Vertical 2D MTJ technology requires in-situ growth of ferromagnetic materials and large area CVD graphene/h-BN heterostructures with clean interfaces without air exposure.
- Explore graphene/2D heterojunctions for all-2D ASLD.
- Demonstrate the theoretical ideas in lab demonstrators that resemble the realistic device as much as possible and benchmark it to competing technologies/devices addressing the same function (no comparison with other graphene-based devices)
- Address challenges as described in the section above

In general, each new technologies in terms of devices or architectures should address the following questions: adapted from [456]

1. What are the key advantages of the device or architecture?
2. What are the main challenges of the device or architecture?
3. What are the most suitable applications for the device or architecture?
4. What are the figures of merit for assessment?
5. How does the architecture fit into the overall scheme of computing?
6. What range of problems can the architecture solve? (von Neumann? Learning?)
7. Do you have a programming model – or another way of controlling the system?
8. How does the architecture tie to SWAP, runtime, etc. in an implemented system?
9. Can this tie be quantified? (vs. CMOS? Is improvement path exponential?)
10. For a stored program model approach, please present a programming model.
11. Will you be better than the end of the roadmap CMOS?
12. Is exemplary application representative of a general class of applications?

13. What device characteristics are desired to implement the proposed architecture?
14. What are current device choices and future options?
15. How essential are emerging devices for your architecture?
16. How might emerging devices improve your overall system?

4.4.4.4 Roadmap



Market

>2021 5 nm node

Beyond CMOS

Lab demos and ideas need to be there for beyond CMOS solutions commercialisation after 2025

The incubation time for new technologies and materials is usually 12-15 years

Need for beyond CMOS technology

Today-2017

2017-2019

2019-2024

>2024

Challenge

Remark

Logic

Bilayer graphene FET

2D based logic switch (e.g. tunnel FET)

Hot electron graphene base transistor

2018: hBN encapsulated bilayer graphene transistor with $I_{on}/I_{off}=10^6$

2D logic switch with high On/Off ratio (10^4)

Simple 2D based integrated logic circuits

Logic transistors based on 2D materials (low power)

Low power, high speed; integration and small critical dimensions (short channel lengths), ohmic contacts, material quality, maufacturing; ist the performance good enough to justify the effort?

European actors?

Flexible Transistors[1]

CVD high quality flexible electonics (wafer or roll2roll)

CVD high quality flexible electonics (wafer roll to roll)

See wafer scale integration (cross-cutting electonics)

CVD graphene flexible transistor Electron mobility 400cm²/Vs

CVD graphene flexible transistor Electron mobility >1000 cm²/Vs <20% degradation over weeks

TFT with μ>1cm²/Vs @0.5mm bending radius

Transparent TFT Roughness rq<5nm, bending radius 15mm

Transparent TFT Roughness rq<5nm, bending radius 15mm

Degradation, long term stability, on/off current, power consumption

For OLED displays

Other 2D materials flexible TFT

Other 2D materials flexible TFT

Other 2D materials flexible TFT

Preparation/ process technologies, basic understanding

USP to be elaborated and benchmarked

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

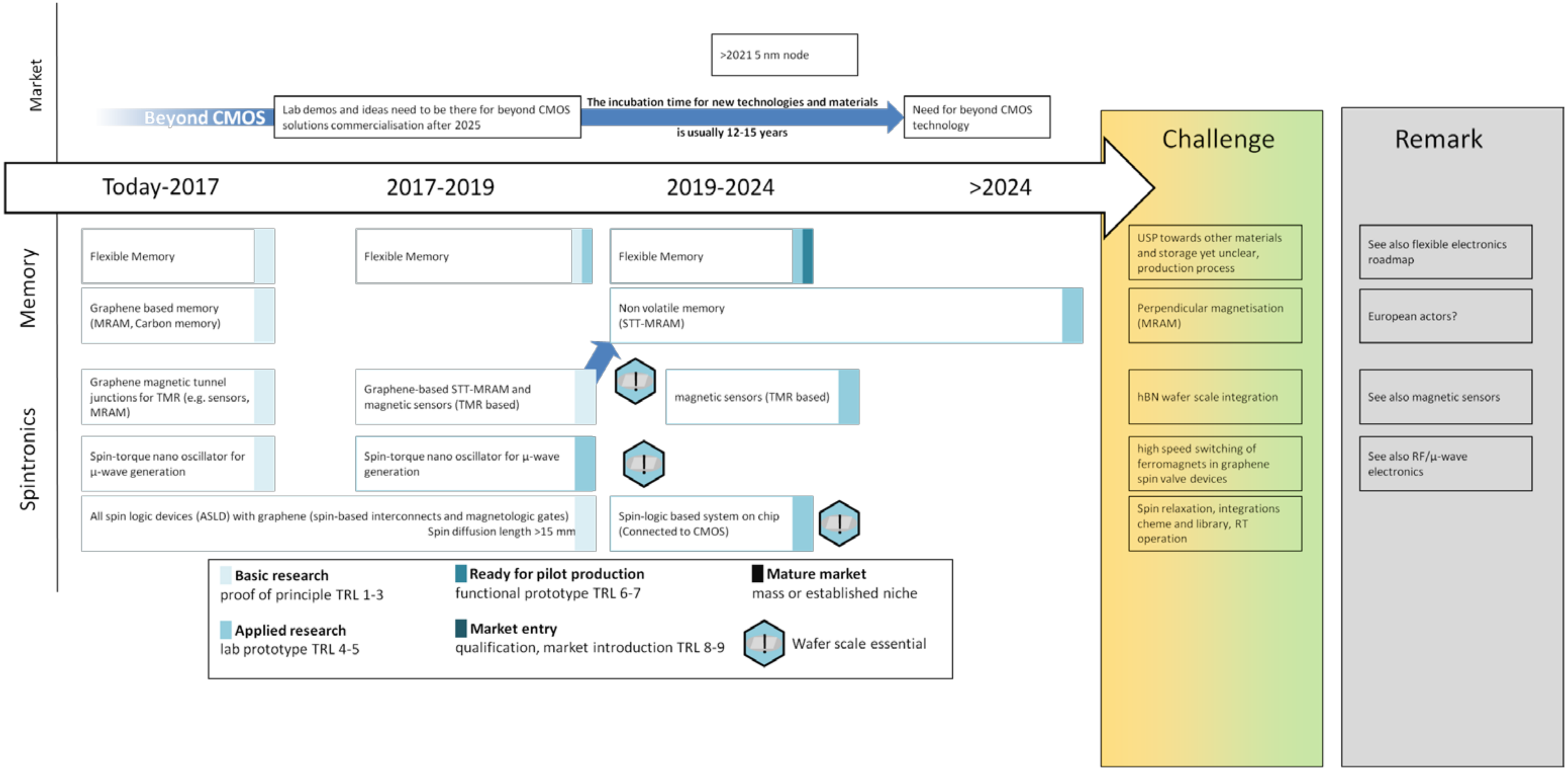
Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale essential

[1]: see also flexible electrionics chapter



Market

>2021 5 nm node

Beyond CMOS

Lab demos and ideas need to be there for beyond CMOS solutions commercialisation after 2025

The incubation time for new technologies and materials is usually 12-15 years

Need for beyond CMOS technology

Today-2017

2017-2019

2019-2024

>2024

Memory

Flexible Memory

Flexible Memory

Flexible Memory

Graphene based memory (MRAM, Carbon memory)

Non volatile memory (STT-MRAM)

Spintronics

Graphene magnetic tunnel junctions for TMR (e.g. sensors, MRAM)

Graphene-based STT-MRAM and magnetic sensors (TMR based)

magnetic sensors (TMR based)

Spin-torque nano oscillator for µ-wave generation

Spin-torque nano oscillator for µ-wave generation

All spin logic devices (ASLD) with graphene (spin-based interconnects and magnetologic gates) Spin diffusion length >15 mm

Spin-logic based system on chip (Connected to CMOS)

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale essential

Challenge

USP towards other materials and storage yet unclear, production process

Perpendicular magnetisation (MRAM)

hBN wafer scale integration

high speed switching of ferromagnets in graphene spin valve devices

Spin relaxation, integrations cheme and library, RT operation

Remark

See also flexible electronics roadmap

European actors?

See also magnetic sensors

See also RF/µ-wave electronics

4.4.5 Conclusion computing/logic, beyond CMOS and spintronics

In computing/logic, the further miniaturization and performance improvement of computer chips is addressed ("more Moore"). Europe has a particular strength in the material and equipment industry for that purpose, whereas the later parts of the value chain are mostly focusing on the more than Moore path.

There is indeed a need for novel approaches, as the Silicon era reaches miniaturization levels where the physical limits are reached in the next 10-15 years. This in turn means that the window of opportunity is on that time scale and for a large scale introduction important breakthroughs have to be reached in the next 5 years.

In search for new materials and concepts, graphene and 2D materials are also investigated. Graphene has a high electron mobility, but the intrinsic problem of a missing band gap. Graphene is essentially out of the race for FETs. Other 2D materials have a bandgap, but so far the mobilities were too low. Recent developments suggest that MoS2 is a hot candidate for further scaling of FETs. For completely new concepts, such as spintronics, graphene or 2D materials might have an opportunity.

The question remains, however, which European industrial basis integrates this technology in a fab for high performance logic (or whether this can be licensed or facilitated by new companies). An opportunity is rather seen for low power computing and "more than Moore" spintronics. USA and Asia are much stronger in the field of logic and memory.

Table 56: Assessment of market and technological potential of graphene/2D materials use in computing/logic on a scale - -, -, 0, +, ++

Computing/logic	**Current technological potential (USP)**	**Market potential (EU perspective)**
Equipment (wafer scale)	0	+
GFET	-	-
2D channel FET (MoS2)	+	-
New transistors (novel charge-based transistors, TFET, GBT)	0	0/+(low power)
Spintronics	+	-/0

4.5 Sensors

Sensors are transducer devices which detect events or changes in their environment and convert them into interpretable signals, their output often being electrical or optical signals.

This chapter covers all applications of integrated sensing, except photodetection, i.e. pure light sensing, which is covered under 0

Telecommunication, optoelectronics & photonics. Note that some of the integrated sensors can be based on optical principles, but with a focus on e.g. sensing of gases or other stimuli. Furthermore, the field of nanogenerators/micro-energy harvesters is also covered, where external energy sources are turned into electrical energy. The addressed areas are (see also Table 57):

- pressure sensors/microphones/NEMS, where graphene/2D materials are used as membrane to sense pressure changes, also possibly as mass sensor
- magnetic sensors, such as hall sensors
- mechanical force/stress/strain sensors
- nanogenerators/micro-energy harvesters to harvest mechanical/vibrational/thermal waste energy as micro-power supply
- gas/chemical sensors, e.g. for inline sensing, air pollution sensing.
- biosensors (according to UPAC 1996 a self-contained integrated device that is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element that is in direct spatial contact with a transduction element)

Biosensors are a special case where graphene/2D materials can be used as transducer and biomaterials as biological recognition element. Biologically important biospecies such as enzymes, proteins, nucleic acids and derivatives and antibodies can be used as biological elements of recognition (bioelements) for biosensors. Due to the substrate specificity of the bioelement, biosensors are especially suited for the analysis of biomolecules and/or in complex mixtures (e.g. body fluids). Detection of the binding event between analyte and bioelement can be done e.g. electrochemically, piezoelectrically, optically.

Sensors cover broad markets from highly specialized applications to broad mass markets. Some of the markets will be highlighted in the following section.

Table 57: Sensor applications of graphene/2D materials

Sensor	**Graphene/2D use**	**Recent review**
Magnetic	In hall sensors, magnetic tunnel junctions	[457–459]
Pressure/Microphone	as (piezoresistive) membrane in NEMS pressure sensors and microphones, also as nano-resonator for mass sensing	[460–462]
Mechanical force/stress/strain sensors	As flexible strain gauges in wearables, electronic skin, strain sensor in composites, included functionality in composites (technology covered in 4.6 Flexible and/or printed electronics)	[463–465]
Nanogenerator	As micro-energy harvester	[466]
Gas/chemical	As electrochemical, optical or GFET sensor for health monitoring, domestic and building applications (“domotics”), automotive, consumer, food packaging (e.g. ethylene); also possible as electrochemical biosensor if recognition element is a bio-molecule	[70, 338, 467–471]
Biosensor	As transducer for lab on chip applications, point of care diagnostics, label free analysis, e.g. blood analysis, sweat analysis; electrochemical gas and chemical sensing (with bio recognition element)	[70, 472–475]

4.5.1 Market perspective: graphene/2D in sensors

Sensors are becoming more and more important as the interface between the virtual and real world. Smart phones have witnessed a strong increase of sensors installed per phone. The same is true for automotive, where more and more sensors are integrated towards the autonomous car. This led to an unforeseen CAGR growth of sensor devices of over 200% between 2007 and 2012. [476]

In 2015, the global sensors market revenue was above $106 billion and is projected to grow at a CAGR of 11.6% to more than $162 billion in 2019. The market for pressure, temperature, flow and level sensors is expected to grow at a CAGR of 6.6% from $23.3 billion. The market for viscosity, tilt, vibration, torque, strain gauge, knock, speed, motion, acceleration, image, gas, humidity, dew-point, rain, moisture, LiDAR, and other application based sensors is expected to grow at a CAGR of 11.1% from $73.7 billion. Newly emerging sensors are expected to grow at a CAGR of 19.0% until 2019 from $9.9 billion in 2015. The market share of different sensor types relevant for graphene/2D materials is summarized in Table 58. Almost all end-user markets employ sensors, see Table 59. The increasing use of (combined) sensors in various applications along with the digitalisation, replacement and upgrading of mechanical technologies drives the sensor market growth. New sensor technologies are heavily researched to improve sensor products, sensing precision, energy consumption and communication protocols. Key trends are towards non-contact technologies, remote connectivity for IoT solutions and 3D vision sensing. Sensors are key enablers for IoT and increasing automation of industrial production processes (e.g. "Industry4.0"), autonomous driving robotics, etc. Further drivers and trends comprise sensor applications for the optimization of resource and energy consumption, smarter sensing systems and mobile/wearable applications, e.g. in consumer electronics. [353] Semiconductor based sensors accounted for global sales of $9 billion in 2015 (+3.7%). Sensors and MEMS are among the fastest growing semiconductor technologies. [289] The (MEMS) microphones market is expected to grow at a CAGR of 11% (2015-2019). The market is projected to reach with $1.3 billion revenue generated by 5.8 billion units. [477]

Table 58: Global market size by sensor type for relevant sensors. High growth markets are highlighted in the right column (CAGR 2015-2019) with a growth trend: ↑ = increasing growth; ↔ = stagnating growth; ↓ = low growth. *: see also 0

Telecommunication, optoelectronics & photonics. Source: [353]

Sensor Type	Market share 2015	Market size (billion US$)	High/low growth markets and trend
Biosensors	11.91%	12.7	CAGR 13.5% ↑
Image Sensors*	9.91%	10.6	
Emerging Sensors[12]	8.61%	9.20	CAGR 19.0% ↑
Pressure Sensors	6.81%	7.28	
Optical Sensors*	4.91%	5.25	
Temperature Sensors	4.53%	4.84	
Gas Sensors/ Detectors/ Analyzers	2.89%	3.09	
Touch/Haptic/Tactile Sensors	2.36%	2.52	CAGR 15.3% ↔

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[12] According to the source, emerging sensors include a large number of new and different sensors for diverse applications addressing a large number of vertical markets, among others tide gauge sensors, pyranometer, nitrogen oxide sensors, tilt sensors, contact image sensors, free fall sensors, boost gauge, zinc oxide nanorod sensors, leaf sensors, contact image sensors, colorimeter, flame detector, photodetector, photodiode, photoelectric sensors, photoionization detector, photoresistor, hydrometer, viscometer, bolometer, microbolometer, heat flux sensor, water sensors (water in fuel sensors) etc.

Sensor Type	Market share 2015	Market size (billion US$)	High/low growth markets and trend
Load Cells	1.94%	2.07	
Hall Effect Sensors (Magnetic Field)	1.69%	1.81	
Strain Gauge Sensors	1.53%	1.63	
LiDAR sensors*	0.84%	0.898	CAGR 15.2% ↑
Humidity Sensors	0.75%	0.801	
Moisture	0.42%	0.449	
Optoelectronic Color Sensors*	0.39%	0.417	CAGR 15.9% ↑
AMR Sensors (Magnetic Field)	0.32%	0.342	
Combined Sensors	0.26%	0.278	CAGR 15.3% ↑
Energy scavenging sensors	0.26%	0.278	CAGR 15.2% ↑
Distance Sensors	0.24%	0.256	CAGR 22.8% ↔
pH Sensors	0.22%	0.235	CAGR 12.8% ↑
(Micro-) Energy Harvesters	0.07%	0.0748	
GMR Sensors (Magnetic Field)	0.06%	0.0641	

Table 59: End-user markets for sensors 2015. Data taken from [353]

Application	Share of sensor market 2015	Market Size in billion US$
Automotive	11.52%	12.3
Chemicals & Petrochemicals	11.47%	12.3
Life Sciences	10.61%	11.3
Process Control	7.95%	8.50
Oil & Gas	6.13%	6.55
Aerospace & Defense	5.46%	5.83
Water & Wastewater	4.35%	4.65
Food & Beverages	4.30%	4.59

Application	**Share of sensor market 2015**	**Market Size in billion US$**
Military	3.75%	4.01
Power Generation	2.95%	3.15
Security	2.85%	3.05
Infrastructure	2.78%	2.97
Plastic Injection Molding	2.70%	2.89
Building Automation	2.30%	2.46
Agriculture	1.98%	2.12
Semiconductors	1.96%	2.09
Environment	1.90%	2.03
Test & Measurement	1.80%	1.92
Others	1.75%	1.87
Mining & Metals	1.45%	1.55
Paper & Pulp	1.45%	1.55
Research & Development	1.45%	1.55
Avionics	1.44%	1.54
Pharma	1.42%	1.52
Oceanography & Marine	1.20%	1.28
Consumer Electronics	1.17%	1.25
Metrology & Meteorology	0.99%	1.06
Shipping	0.47%	0.502
Smart Grid	0.45%	0.481

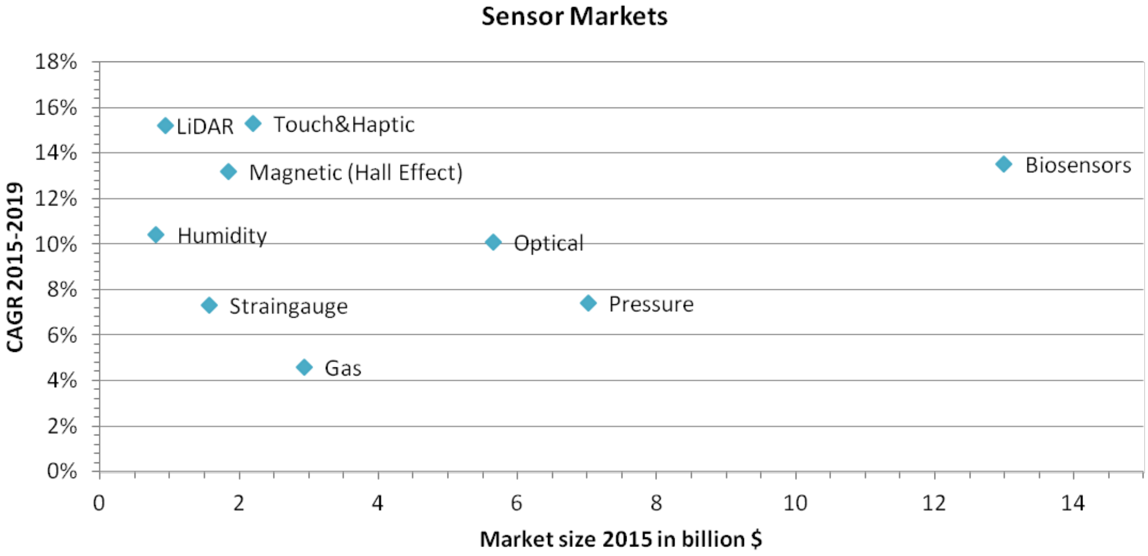


Figure 63: Different expectations of sensor markets in terms of market size 2015 and CAGR between 2015 and 2019. Data taken from [353]. Values also agree with other sources ~±10% deviation.

Actor landscape and patent activity

With respect to companies, the global sensor market is to a great extent highly fragmented: the top 10 key sensor companies have market shares of 20%, and there are numerable SMEs which develop and produce special sensors (about 385 companies worldwide and growing). More than 50% of sensor sales are done by distributors, followed by direct sales (30%) and sales by system integrators (10%). There is an increasing trend away from distributors to direct sales. [353]

The European semiconductor industry has a strong position worldwide and with Bosch Sensortec and STMicroelectronics, the two largest MEMS manufacturers are headquartered in the EU, see Figure 64. 4 Europe-based companies are within the top 30, generating revenues with MEMS of $2.5 billion in 2015 (28% of all top 30). Most revenues are generated by US-based companies (45%).

Looking at transnational patents on sensors in general (Figure 65), it becomes obvious that Europe has the strongest position in transnational patent activity pointing towards a strong and innovative industry. Also with respect to graphene related sensor patenting activities, Europe is strong and the efforts increased heavily in the last 4 years. Still, the USA is leading in terms of patent count. In terms of relative graphene/2D activity with respect to all sensor patents, South Korea is leading, showing that they specialise in graphene technologies.

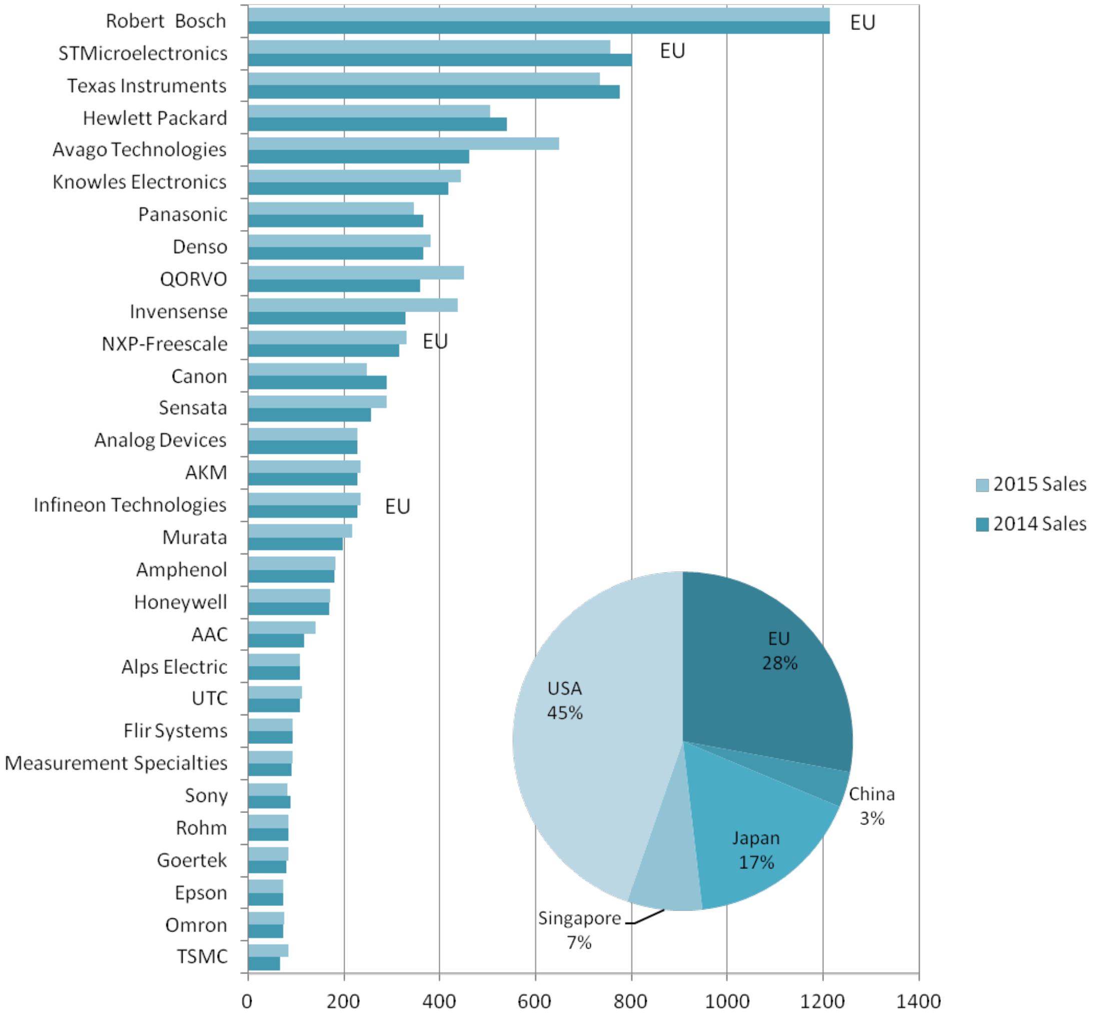


Figure 64: Major MEMS manufacturers (top 30) in 2015. The inset shows the regional distribution of revenue by headquarters. MEMS are mostly employed for sensor applications. [478]

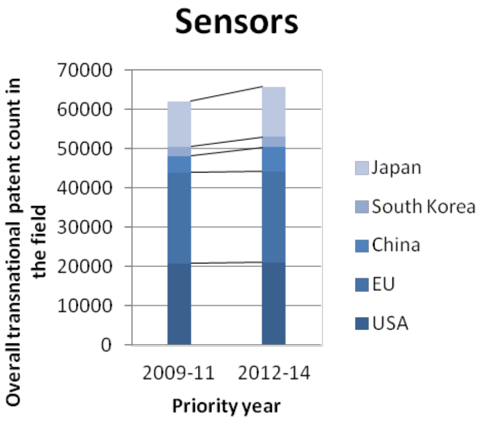
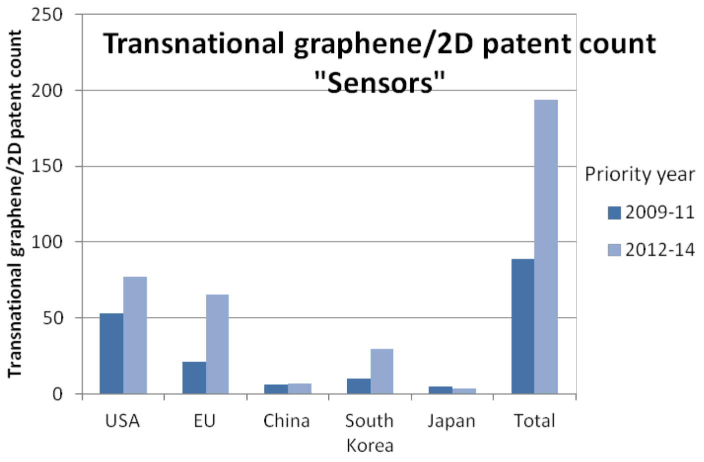


Figure 65: Overall transnational patent count in sensors. 2012-2014 values are projected. [21]



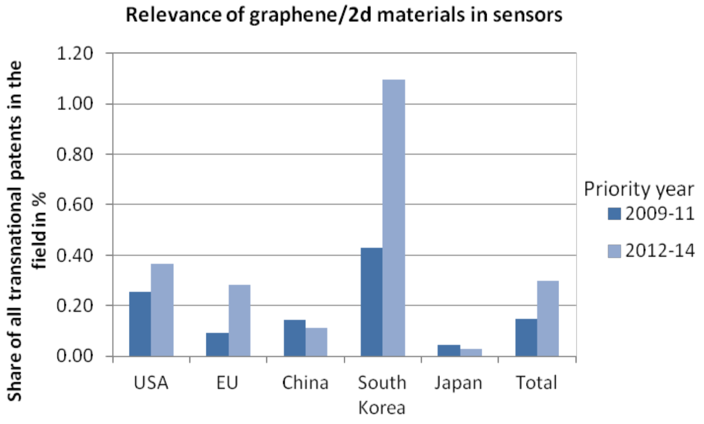


Figure 66: Patent analysis of graphene/2D materials in sensors (without optical sensors). Top graph: Number of graphene related transnational patents in 2009-2011 and 2012-2014. Bottom graph: Patent share of graphene/2D related materials with respect to all transnational patents in sensors (without optical sensors). 2012-2014 values are projected. [21]

Sensors in infrastructure and smart buildings

One key market of sensors is the infrastructure and smart buildings market, which was estimated at $4.2 billion in 2014 and expected to grow above average at a CAGR of 14.3% to reach $10.6 billion in 2021. The average price unit per sensor was $183.3 in 2014 with a clear downward trend. Infrastructure accounted for about 1/5 of the market, whereas 4/5 of the market was sensors for smart buildings. 66 companies were active in 2014 and 44.8% of the revenue was generated by the top 10 companies (60% by top 19). The 5 EU headquartered companies (Vaisala Inc, FI; Thermokon, DE; EnOcean, DE; HBM, DE; Sauter, CH) among the top 19 generated revenues of $480 million (11% market share). Of the 43 other market participants, 5 were headquartered in Europe. The market is dominated by US companies, which serve more than 43% of the market

(11 among the top 19 and 31 among the other 43 companies). [479] Thus, the market is dominated by the US, but there are considerable market participants in Europe.

Sensors in IoT

Another strongly growing key market for sensors is the internet of industrial things market. It had a size of about $3.8 billion in 2014 and is expected to grow at a CAGR of 16.8% to $11.23 billion in 2021. Major market shares of this market are held by industrial control applications (38.6%) followed by applications in smart cities (15.8%), eHealth (7.3%), safety & security (6.7%), smart meter (5.9%), and smart environment (5.6%). Industrial control is further expected to dominate the market in future (CAGR of 15.8%) with over 20 different sensor types used. The largest growth opportunities arise from the logistics market segment with an expected CAGR of 18.6%. The sensors with the highest revenue contribution in 2014 were temperature ($318.7 million), pressure ($264.6 million), flow ($245.2 million), image ($242.6 million), gas ($196.6 million) and accelerometers ($188.5 million). These sensors wills also dominate the market in 2021 with a revenue share of 30.7%. New and combined sensors are a particularly dynamic growing field. [480] More than 40 companies are active in sensors for IoIT. Of the top 16 companies, which create a revenue of >40% in the topic, 3 are headquartered in Europe, incl. Switzerland (Siemens AG, Germany; ARM Ltd., UK; ABB, CH) creating a revenue of $334 million (in 2014, 8.8% of the world market). Other major companies are from the USA (12 companies) and Canada (one company), top companies being Texas Instruments, Qualcomm, Intel and Honeywell (together holding a share of 15% of the market). 40 other companies with market shares below 1% are from the USA, 12 from Europe including Switzerland, another 4 from Korea and Japan, one from Israel and one from Canada, clearly demonstrating the leading role of the USA. [480]

(Micro-) energy harvesting

Micro energy harvesting and nanogenerators currently represent a nascent market with revenues of $1.2 billion in 2015. The projection for 2030 is $12.5 billion representing a CAGR of 16.4%. By 2026, revenue growth is expected to slow down. Figure 67 shows the market development by type of energy harvesting from 2015 to 2030. Figure 68 shows the most important markets for energy harvesting technologies. Europe is among the fastest growing regions. The average price per unit is 8.13$. [481] Other sources looking at off-grid power ranges of µW to MW foresee a market development from $1.4 billion in 2015 to above $6 billion in 2026 (CAGR ~15%). 5 out of 19 (micro-) energy harvesting manufacturers investigated in the F&S study are headquartered in the EU (inc. CH), being Perpetuum (UK), EnOcean (DE), Pavegen (UK), Ferrotec (DE) and GreenTEG (CH). 11 are from the US and Canada, three from China and Japan. For system integrators, 5 out of 13 are headquartered in the EU (incl. CH), ABB (CH), Schneider Electric (FR), Alphanetrix (GR), Lufft (DE) and Eaton Industries (DE/IR). [482]

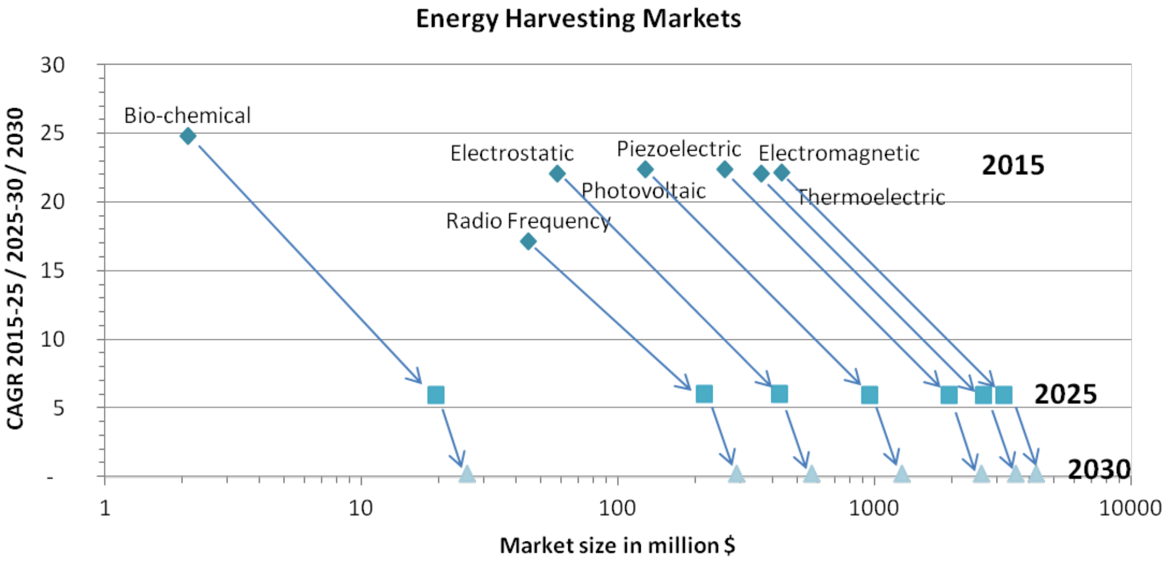


Figure 67: Energy harvesting markets. Data taken from [481]. Please not that the estimates vary for the different types. Especially piezo- and thermoelectric energy harvesters are estimated to have lower market shares in other sources. [482]

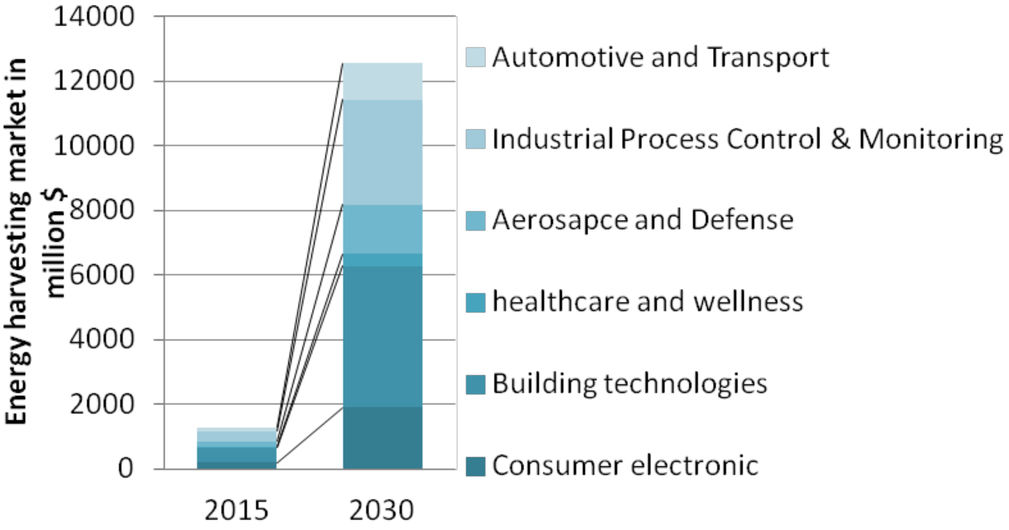


Figure 68: Energy harvesting market by application [481]

Gas sensors

Looking at gas sensors, detectors and analyzers, the global market was $2.8 billion in 2014. Estimates project it to reach $3.8 billion by 2021 (CAGR of 4.5%). The market share of the top 3 competitors (Honeywell, US; MSA, US; Dräger, DE) was 42.2% in 2014. Of other key companies, 9 were headquartered in Europe, 8 in the US and one in Japan. Gas detectors had the largest share in 2014 with a market value of $1.9 billion. Gas sensors contributed with $490 million to the market, whereas gas analyzers created a revenue of $391 million. [483] Figure 69 shows the market share of gas sensors, detectors and analyzers for different target gases.

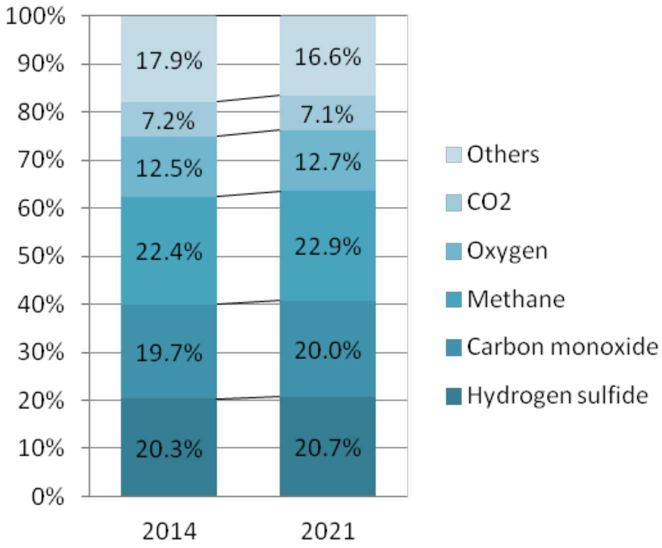


Figure 69: Market share of target gases for gas sensors. Others comprises of toxic and combustible gases, such as volatile organic compounds (VOCs), hydrocarbons, sulfur-dioxide, nitrous oxide, nitrogen-dioxide, ammonia, chlorine, and chlorine-dioxide. [483]

Looking at only the gas sensor market ($490 million in 2014), a steady market growth of 5% per year could be observed in the past. It is expected to grow to $713 million in 2021 at a CAGR (2014-2021) of 5.5%. Oil and gas companies are major customers of gas sensors. Declining oil prices will decrease the demand in this market and slow down the demand for gas sensors. The gas sensor market can be subdivided into toxic gas sensors and combustible gas sensors. The main technologies for toxic gas detection are electrochemical, photoionization and semiconductor sensors. Combustible gas sensors mostly use catalytic and infrared sensors. Gas sensors are integrated in gas detectors and analyzers. Those can be wireless or wired. All top 3 gas sensor companies addressed by the F&S study are headquartered in Europe and have a market share of roughly 1/3 of the gas sensor market (~$160 million). They are City Technology Ltd. (UK), Alphasense (UK), and SenseAir AB (SE). Of other key market participants, 8 are in the EU (incl. CH), 5 in the USA, 3 in Japan and one in New Zealand. [483] Europe therefore has a strong base in gas sensors.

Biosensors

The analysis of biological parameter, primarily in a medical context, attracts a considerable number of patent activities. Thus it is a large, competitive market where the US and the EU dominate (Figure 70). The share of graphene-based bioanalysis is still very modest, but growing. In particular the activities of the EU show a clear take-up (Figure 71).

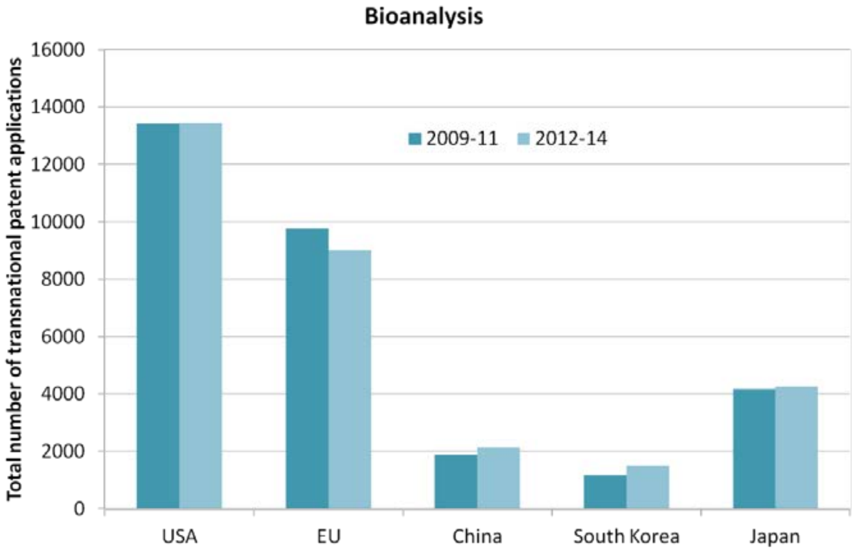


Figure 70: Transnational Patents in Bioanalysis. [21]

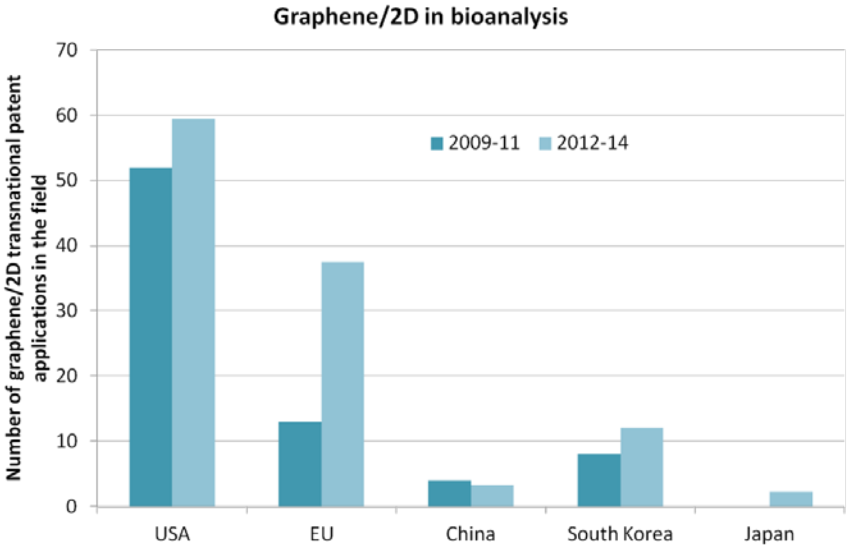


Figure 71: Transnational Patents in graphene-based Bioanalysis by Priority Years. [21]

With $11-14 billion in 2014, the volume of the biosensor market is highly relevant. It is expected to be worth more than $20 billion by 2020 (CAGR of 10-14%) [484, 485]. Diabetes/glucose sensors had the largest market share with almost 1/3 of the revenue in 2014. However biosensors are very versatile and used for more than 40 different pathogens and enzymes (Table 60). The market attractiveness for biosensors is high and they can be used in many different applications, see Figure 72 for the market shares of different end user markets. They are also getting into new markets, such as into mobile platforms (smartphones and other mobile devices) and into automotives. Established markets are research labs, fermentation and bioproduction industry (e.g. biopharmaceuticals, food, biobased chemicals), medical care, defense and safety. Biosensors are used in these areas for analysis, process and product control, quality control, environmental/pollutant/toxic substances monitoring, medical diagnosis or health monitoring (clinical, point of care, home care). A trend is observable towards portable and wearable biosensors and biosensors are more and more used in microfluidic devices (e.g. Lab-on-a-chip), point-of-care diagnostics, or medical implants. [485] However, this market comprises a broad variety of technologies and apparatus, so that the specific contribution of graphene-based approaches is difficult to assess.

Table 60: List of key pathogens and enzymes tests by biosensor devices. [485]

No.	Type of test	No.	Type of test	No.	Type of test
1	Glucose	15	E.coli/Coliform	29	Tetryl
2	A1C	16	Crypto	30	DNT
3	Cholesterol	17	Girdia	31	RDX
4	Infectious diseases	18	Micro cystins	32	Nitroglycerin
5	Coagulation PT	19	West Nile virus	33	PETN
6	Coagulation ACT	20	Anthrax	34	Drug discovery
7	Drugs of abuse	21	SARS	35	Virus detection
8	Lactic acid sensors	22	BSE	36	Cronobacter sakazakii
9	Peptide sensors	23	Cocaine	37	Campylobacter jejuni
10	E.coli 0157:H7	24	Methamphetamines	38	Listeria
11	E.coli O55	25	Ecstasy	39	Listeria monocytogenes II
12	Salmonella	26	Opiates	40	Pseudomonas aeruginosa
13	Salmonella enteritidis	27	THC (cannabis)	41	Staphylococcus aureus
14	Toxicity	28	TNT explosives	42	Clostridium perfringens

32 companies generate 2/3 of the total biosensors market. Within this top companies, there are 10 companies headquartered in Europe (including Switzerland) generating a revenue of 23.2% ($2.7 billion in 2014). Roche Diagnostics (CH, 10% market share) and Bayer (DE, 6.6% market share) are the largest Europe based companies in this statistics. Dominating country is the USA, with 35% market share of US based firms. Among the further companies beyond the top 30, European companies have a share of 13 out of 29, of which 10 are based in Germany. 11 companies out of 29 are based in the US. Looking at key biosensor manufacturers 17 out of 57 are headquartered in Europe and 37 are based in the US. [485] This shows that Europe plays a leading role in biosensors, but that the USA has more and stronger companies in that area.

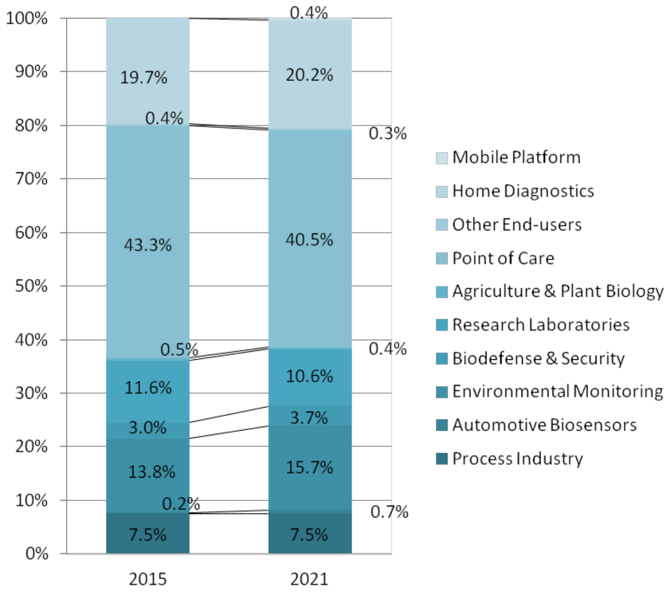


Figure 72: Biosensors markets by end users. Other end-users include: Mobile Platform (2015), Sericulture, Marine, Pharmaceuticals and Drug Research. [353, 485]

The major market of biosensor is the point of care testing (POCT) market, which accounted for \$5 billion in biosensor revenues in 2014. The overall POCT market was \$2.9 billion in 2015 in Western Europe with a projected CAGR of 5.8% until 2020 to reach \$3.9 billion. [486] Figure 73 summarizes the different segments of the POCT market in Western Europe. Highest growth potentials are seen in Cardiac, infectious disease and blood gas and electrolyte POCT. Opportunities due to low competition, high growth and high average prices can be seen in Infectious disease, Cardiac and Cholesterol POCT in Europe. [486]

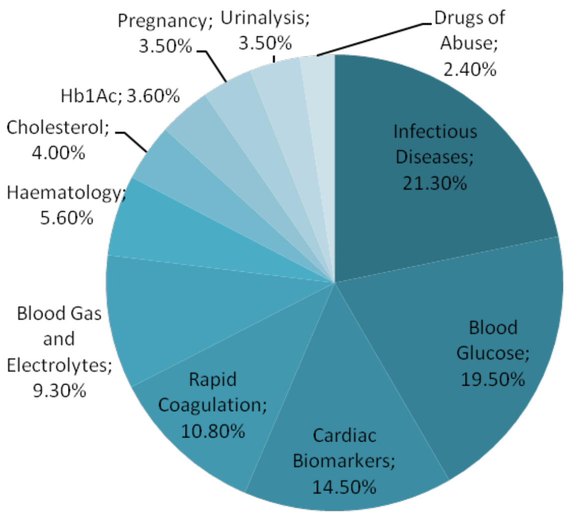


Figure 73: Western Europe POCT market by segment 2015. [486]

The European POCT market is dominated by non European companies (besides Roche, CH). Almost 60% of the revenue is generated by non-European companies (however, they also produce in Europe). Another 20% of revenue is generated by Roche. The majority of the remaining 20% are split between 6 EU based companies, 4 USA and 1 Japan based companies. [486]

4.5.1.1 Market Opportunities

4.5.1.1.1 Diverse growing markets with many niche applications and drivers

As presented in section 4.5.1 Market perspective: graphene/2D in sensors, the sensor market is a very fast and strongly growing market. It covers everything from low value high volume markets to high value markets with lower volume, where added sensitivity is paid for (as early adopters, e.g. in biosensing). Many niche markets available with potential early adopters.

Several areas are expecting extraordinary high growth rates, such as wireless sensors and sensor networks, cloud connectivity, remote monitoring – especially in the realm of IoT and industry 4.0. It is expected that the sensor demand from IoT will pick up pace in 5-10 years. Another strongly growing area is mobile sensors for smartphones and consumers, also in the realm of wearables and e-Health. In this respect also printed sensors for low cost applications will be required (see 4.6 Flexible and/or printed electronics for further assessments). The automotive market is also demanding sensors already and the demand will increase, the more the automobile is pushed towards (semi-) autonomous driving and intelligent vehicles. Further interesting areas are related to robotics and artificial intelligence. [353]

Regulatory frameworks can also increase the demand for sensor solutions, e.g. in terms of air quality regulation the demand for gas sensors/analysers in increased, or in terms of safety and security the compulsory use of smoke detectors in residential housing increased the demand for smoke detectors heavily.

4.5.1.1.2 Market requirements: accuracy, selectivity, response time, cost, lifetime, integrated sensing and multi-sensing

High level of accuracy, instant response time, and assured lifetime performance are main demands and selection criteria for sensor customers. Additional needs are cost reduction and miniaturization towards small footprints. The latter is demanded through chip-level integration as well as sensor integration on device, component and system level. The integration into complex systems and along with that increased smartness and intelligence are important aspects. [353] This is for example addressed by complex (wireless) sensor networks providing in-situ, real-time and continuous measurements.

These integrated sensing capabilities of previously inactive components can be seen as an opportunity e.g. for added functionality in composites (force sensors, strain gauge).

Higher sensitivity sensors can create or address new markets that previously were not possible to address due to high performance demands. Furthermore, there is a strong trend and wish towards for multi-sensor capabilities and combined sensors, i.e. one integrated sensor measuring different parameters.

Selectivity and reversibility of sensors is also important in particular for gas/chemical sensors.

4.5.1.1.3 Additional market needs: disposable, flexible, etc.

Some of the trends particularly demand flexible/conformable sensors, which can be easily confined to a certain host (e.g. wearables, IoT for small parts). Further interesting opportunities are existing for biodegradable/combustible sensors, e.g. for disposable/one-use applications. Depending on the addressed market and sensor type, flexibility, conformability or biodegradability can be important USPs.

In many sensors rare materials (rare earth materials, high value metals) are used. Graphene, an abundant and more sustainable material, can have an opportunity to address those sensors as an alternative material.

4.5.1.1.4 European strength and industrial basis in sensors

Europe is a strong player in sensors. This is obvious in transnational patent activities (see 4.5.1 Market perspective: graphene/2D in sensors and Figure 65). There is an innovative and strong basis in Europe that could take up graphene inventions and innovations. Also in the semiconductor field, Europe is strong in sensors and MEMS devices, with the two world leading MEMS companies being headquartered in Europe (see Figure 64).

4.5.1.2 Additional market opportunities: Magnetic sensors

4.5.1.2.1 Broad applications of magnetic field sensors

Magnetic sensors are used in a variety of applications from smartphones (e.g. compass function, position sensor) to cars (tire “pressure” sensors, ABS, ESP, seat belt alarm). Magnetic sensors can essentially be used for fast and accurate position and motion sensing among others in mechanical engineering, computer games, robotics and in minimally invasive surgery. With a CAGR of 8-13% until 2019, the magnetic field sensor market is expected to in-crease to $2.7-3 billion by 2019. [353, 487]

4.5.1.2.2 Performance of Si based sensors not very high

Silicon-based hall sensors have a rather low sensitivity but can be fabricated very cheaply. There is a demand for higher sensitivity, lower cost sensors. Higher performance sensors at similar or lower prices, footprint and energy consumption provide a good opportunity for new materials in magnetic sensing. Higher sensitivities can even justify slightly higher prices, especially in particular industries, e.g. automotive.

4.5.1.2.3 Interest from European key players

European key players are investigating graphene-based Hall effects. [459] The application focus lies especially possible in consumer and automotive areas, but both need manufacturability and rather low cost. There is a moderate competition on the market and some of the market leaders are European (Infineon, Germany; Melexis Microelectronic Systems, Belgium; AMS, Austria). The overall market of hall sensors, however, is dominated by Asahi Kasei Microdevices (Japan) and Allegro Microsystems (USA). [353] Honeywell (USA), MEMSIC Inc. (USA), Micronas (Switzerland) and NXP Semiconductors (Netherlands), NVE Corporation (USA) and Hitachi (Japan) play also a role in the magnetic sensor market in terms of AMR and GMR. [487] In the market for smartphones and semiconductor based hall sensors Yamaha (Japan), Bosch (Germany), STMicroelectronics (France), ALPS (Japan), Diodes (USA) also play important roles. [488]

4.5.1.3 Additional market opportunities: nanogenerators

4.5.1.3.1 Nanogenerators for micro energy harvesting for autonomous integrated systems

Upcoming autonomous systems and sensor solutions, such as in IoT or smart buildings, drive the demand for autonomous energy solutions. The obvious idea besides storage soluteons like batteries is to harvest energy from the environment of the device, e.g. movement, vibration, heat or radiation. Maintenance free solutions for building automation and industrial process control, self-powered sensors for smart energy and transport networks and more broadly IoT will drive the demand for such solutions. [481]

The window of opportunity is still there, as IoT will pick up pace in the next 5 years. The demand for such energy harvesting solutions is thus expected to increase strongly in the near future (CAGR >15%, see 4.5.1 Market perspective: graphene/2D in sensors).

4.5.1.3.2 Competing technologies not yet broadly marketed

Major solutions today are electromagnetic/-dynamic and photovoltaic energy harvesters, thermoelectric and piezoelectric energy harvesters are also present. However, these solutions are mostly not yet sufficiently powerful or cheap. The challenges for a broad market roll out (especially for mass markets like IoT or smart buildings) are still there. Thermoelectric energy harvesters have poor efficiency and most versions are toxic. Piezoelectric solutions are brittle, some are also toxic and they have poor power density. Emerging triboelectric harvesters have poor power density and unproven efficiency. [482]

Thus, the technologies and the market is still quite immature, due to either low power density or high cost/low maturity and graphene/2D material bases innovations can still contribute (e.g. in tribological nanogenerators). Especially the Si-based MEMS devices for energy harvesting are suffering from a too power density. The existing technologies are therefore not yet feasible for many applications and full market introduction has not yet happened. This can be either triggered by better energy harvesters (higher power, lower price) or by lower energy consumption of the devices driven by the harvesters, so that the low existing power density harvesters are sufficient. The market itself currently only has moderate competition, but is highly fragmented.

4.5.1.3.3 European companies in energy harvesting and system integration

There are several European companies active in the area of (micro-) energy harvesting, although the US dominates this emerging market. Especially for system integration, there is an equal number of key companies from the US and the EU, see 4.5.1 Market perspective: graphene/2D in sensors, energy harvesting).

4.5.1.4 Additional market opportunities: chemical/gas sensors

4.5.1.4.1 Promising and diverse market expectations

Several market drivers affect the need for chemical gas sensors/detectors, such as the increased need for air quality control in megacities or increased awareness of climate change, health and safety among end users. In the industrial space rising concerns about personnel and plant safety is a key market driver. Regulation also drives the market though rising enforcement of occupational health and safety regulations by government bodies. Furthermore, the increasing industrial standards for safety and monitoring drive the need for gas sensors. Some of the internationally accepted standards are IEC, NFPA, EN (ATEX), and ANSI/ISA [483]

There are several possible markets from high price to low price and niche to mass markets, e.g. from research/biomedical applications to food packaging or from very special devices to consumer markets. The market allows first market entry via higher valued niche products, but major markets with higher volumes will be rather moderate or low cost. Gas sensors provide a good opportunity for quick commercialisation of integrated systems.

One can distinguish 3 types of sensor/detectors:

1. extremely high quality measurement, but permanent installation
2. high quality measurement (20 ppb), portable;
3. ppm-range measurement, low cost, broad distribution (mass market)

All can be equipped with wireless functionality.

Gas sensors can in principle be seen as a platform technology, especially if selectivity can be changed through different functionalization.

4.5.1.4.2 High demand for innovation: competing technologies have deficiencies, e.g. are expensive and/or have a large footprint

Selectivity is the most important prerequisite for a gas sensor, as it is otherwise useless. There is a high demand for innovation in gas sensors to develop smaller products that are more robust, durable, and cost-competitive. A longer lifespan and maintenance-free products are requested from the end users. [483] Common systems are often too bulky and have high maintenance cost. An added value for customer can lie in longer periods of good performance of graphene-based sensors, as compared to conventional sensors, and thus lower costs per sensor life-time. Furthermore, the response time is also an important factor, that together with the other parameters mentioned above can create a unique selling proposition.

Competition in the market is mostly moderate but increasingly intense, especially in terms of new applications (e.g. for smart cities). Compact and cheap sensors addressing environmentally harmful compounds or compounds harmful to health, e.g. ions, heavy metals or volatile compounds, provide interesting opportunities for applications in safety monitoring.

4.5.1.4.3 Selective multi gas/chemical sensing

Developing selective multi gas sensors and several sensors integrated in one small footprint device is a major opportunity and one of the most important goals for gas sensors, as these devices are heavily sought for.

4.5.1.4.4 Opportunities for lower performing low cost sensors

Battery-powered wireless detectors and very-low power detectors open up more opportunities for gas detectors. [483] However, only very few sensors can satisfy the demanding specification for phones (usually < 5 mW, < 3.0 V, 2 year lifetime, <€2 price per sensor, small footprint of a few mm^3).

Although there is a need for higher sensitivity sensors on the one hand, on the other hand cheaper applications tolerate lower sensitivity. There is an opportunity in addressing these cheaper but less sensitive sensors. Often, the available gas sensors cannot meet these cost targets and have an overshooting sensitivity. Some potential products are not yet broadly available on the market (e.g. gas sensors in food packaging), mostly due to cost constraints.

Printed sensors, sensors based on organic electronics or on low cost Silicon platforms could address this, probably enabled by graphene/2D materials. Also sensors that are only used a few times (e.g. in packaging) could have their applications, as long as the cost is low enough.

A very important competing technology is metal-oxide gas sensors in CMOS packages. These are hitting the market and can achieve small form factors, high enough sensitivity, low enough energy consumption whilst being in an adequate cost range. [489]

4.5.1.4.5 European actors are strong

There are various European actors in the gas sensing area, especially when it comes to the gas sensors themselves. (see 4.5.1 Market perspective: graphene/2D in sensors, gas sensors).

4.5.1.5 Additional market opportunities: biosensors

4.5.1.5.1 Platform character of biosensor technologies

Biosensors are very diverse and can be seen as a universal platform with a large diversity of end products (= sensors, actuators, devices). Biosensors can be also used as gas/chemical sensors, so the market opportunities in 4.5.1.4 Additional market opportunities: chemical/gas sensors also apply.

Similar to gas sensors, it is also an opportunity to address functional hybrids, i.e. the combination of different target analytes in one sensor. Biosensors are usually used due to their high sensitivity, accuracy and specificity and because they are easy to use. [485]

4.5.1.5.2 Need for direct and fast testing (IVD, point of care testing)

The largest and classical markets for biosensors are in-vitro diagnostics and point of care testing, as well as direct-to-consumers testing markets (Home care and wellbeing).

In these markets, high specificity and fast diagnosis are important requirements. Opportunities lie in label free testing and high speed for POCT, because this eliminates the time needed to wait for incubation or labelling. These properties combined with high sensitivity – i.e. real-time detection of target analyte reaction and conversion into a usable electrical signal – are the most important performance indicators in these markets. POCT and lab on chip can complement complicated lab analysis (e.g. mass spectroscopy). However, so far POCT currently only is a smaller part of the in-vitro diagnostics (IVD) market, mostly in areas where time-to-testing-result is therapy-modifying, i.e. often in rescue vans, emergency rooms and hospitals. The POCT market in Europe is about 1/4 the size of the IVD market, i.e. $2.9 billion [486] POCT vs. ~$12 billion overall IVD market. [490].

A trend in POCT is the quantitative detection with electrical readout, allowing testing at home and sending/storing/analyzing health data online (e.g. in the cloud) or remote to a medical doctor. This area is for instance interesting for medicine dosing feedback, risk marker control.

A key opportunity for biosensors in point of care testing is to address multi-target detection of multiple biomarkers. Furthermore, not only purely medical diagnostics can be addressed, bit also wellbeing and home diagnostics are interesting and probably less demanding in terms of regulation. [485]

4.5.1.5.3 Trends driving biosensor demand

Demand for biosensors in increasing due to several trends in the market. For instance increasing interest in personal health and wellness, as well as monitoring of harmful pathogens can stimulates the use of biosensors. This is further supported by a shift towards rapid detection devices. From the regulatory point of view, implementation of strict food safety regulations further increases the demand.

In summary, the opportunities to expand into different and new applications is increasing, e.g. in the automotive sector, as more and more areas demand highly sensitive siosensor devices. [485]

4.5.1.5.4 Diverse markets from low cost to high value

Biosensors address many different markets with differing expectations in terms of sensitivity and cost. This means that market entry is possible via high value niches but also via cost advantages. In general, the medical diagnostics market, although under price pressure from health systems, is not as price sensitive as some other consumer markets. Good margins can usually be obtained for products delivering clear benefits towards existing technologies addressing the same functionality. Therefore, biosensors can possibly be early adopters for graphene/2D technologies. Biosensors are also used in less regulated markets (e.g. automotive, consumer/wellbeing, gas sensing, process monitoring and control), which opens up further opportunities. There is a chance that biosensors become more and more mainstream due to their versatility and ease of use.

Three kinds of market entry scenarios are conceivable:

1. Novel test analyzers/sensors not yet available with new functionality usually have a low cost sensitivity, so cost is not the major barrier (“first of a kind”), e.g. flexible biosensors in e.g. functional medical implants for instance for the eye or brain.
2. for lab analyzers/lab on chip/IVD: moderate to high valued systems using biosensors for measurement techniques that usually use even more expensive equipment (e.g. ICP mass spectrometers), medium cost sensitivity
3. for POCT or home testing/home care, automotive, consumer, domotics: very/rather price sensitive markets, e.g. glucose sensing, where lower cost and more adequate sensitivity are combined with disposability.

4.5.1.5.5 Competition is open

The competition between new technologies is open and there is always space for a new material or technology. If graphene/2D-based function/performance gain comes at a similar cost there will be a market opportunity. For some existing technologies, sensitivity sometimes is an issue as well as readout times; lack of long-term stability, size/miniaturization, cost and mass production compatibility and sufficient ruggedness. By addressing one or several of these issues, graphene/2D can find USPs towards existing solutions in this interesting market. The market itself has a moderate competition and is quite fragmented. The top 3 companies have a market share of less than 30% and the top 10 of ~50%.[485]

4.5.1.5.6 European industrial basis

Although the USA leads the biosensors market, European companies are in the business and there is an industrial basis for this large market. In terms of the POCT market, the European market is dominated by non-European companies.

4.5.1.6 Market Threats

4.5.1.6.1 Price is key for consumer markets and better performance only secondary

Consumer markets are large markets, but if they are to be addressed, low cost is a very decisive factor for success. These markets, e.g. as a sensor in mobile phones, typically demand cost of less than 1$ per detector and a volume of multi-million pieces. Only a small range of products are of interest for those markets. Usual prerequisites are to achieve better performance at the same price or even cheaper. Especially in this area the 10x better performance or 10x lower cost rules apply. In some areas, an increased performance/sensitivity is even not needed and price reduction is more important (e.g. in gas sensors or IR).

It appears that key players in these consumer markets are deeply cynical about timeframes of graphene/2D material development and the prospects for a medium term success are not very good according to their opinion and assessment.

4.5.1.6.2 Mobile phone market in very high competition

Especially the mobile phone sensors market is under very high competition. Diminishing returns are expected over the next 4-5 years and lower cost is ever more important. Hard competition fights are expected in this market. [488]

4.5.1.6.3 Expectations on reliability, durability and operating conditions are high

Reliability, durability (shelf life and in operation performance over lifetime), repeatability and flexible operating conditions are important assets of sensors and detectors. Lifetime and reliability expectations differ depending on the addressed markets, from, e.g. automotive (15 years) to consumer (2 years). First products entering the market need to have a good reliability to generate trust in the product and technology and to not spoil the technology in further uses.

4.5.1.6.4 Fragmented market, existing systems, interoperability and data analytics

The rather fragmented sensor market is on the one hand a big opportunity as new players can enter the market. On the other hand it also poses a threat and restraint. For example, different standards are pursued by different providers and interoperability is often difficult to achieve. This poses a problem for new technologies and broader use as a platform technology. [353]

For networked sensors, the IEEE 1451 family of standards is important. Connectivity and data analytics are becoming more and more important for networked and smart sensors and need to be regarded for a sensor system from the early design of prototypes. [353]

Another restraint in the sensor markets arises from the installed base of legacy systems with significant economic, technical and non-technical barriers to replace existing systems and to switch to novel, innovative sensor systems (even if they come with interesting improvements). [353]

4.5.1.6.5 Health applications have additional constraints

Health applications underlie further regulation (CE, FDA, reimbursement of health test), which are important for a success. For further information please see 5.2 Excursus: The specific structures of the health market.

4.5.1.6.6 Sensors in IoT and smart building markets are dominated by US companies

Although Europe is strong in sensors and sensor development, the emerging markets of sensors in IoT and smart buildings are dominated by US companies (see 4.5.1 Market perspective: graphene/2D in sensors, page 364). But there are also considerable efforts in Europe-based companies, so that there is an industrial basis for take-up of new technologies in Europe.

4.5.1.7 Additional market threats: Magnetic sensors

4.5.1.7.1 Mature market and competing technologies

Magnetic sensing addresses a very mature market with many established technologies. There are different technologies for different applications on the market, from magnetoresistive sensors (GMR sensors, AMR sensors, TMR) to hall sensors and MEMS-based Lorentz force sensors. [491] Hall Effect sensors dominate the market currently, with more than 70% of the market share [487]. Cheap and mass produced hall sensors are based on silicon (e.g. for mobile phones, automotive). Higher sensitivity hall sensors are based on InSb, which is currently not integratable and thus rather expensive. Higher sensitivity for smaller or similar prices has its demand, but there are also other technologies addressing this area (e.g. GMR sensors).

4.5.1.7.2 Low cost products

Mass produced magnetic sensors are produced in the billions (almost 6 billion units in 2014 [487]). For consumer/mass market products the prices are below 20-50ct per piece. For some automotive applications a higher quality and higher cost i possible, but also only in the few Euro range.

4.5.1.8 Additional market threats: pressure sensors/microphones/NEMS

4.5.1.8.1 Competing technologies are more mature and perform better in mass sensing

In terms of nano-resonators for mass sensing, better and more mature concepts are available than graphene based sensors. Graphene is pretty lossy, has a low Q-factor and silicon-based resonators are so cheap and good that it is tough/impossible to compete.

4.5.1.8.2 Competing MEMS microphones sensors are well established and cheap

Pressure sensors/microphones based on Si CMOS MEMS are already very cheap and quite good. It is an open question whether higher sensitivity or a broader spectral range is actually needed. To address consumer markets one has to have a cheap product and large volume or nothing. The market is not willing to pay more for more functionality, but rather expects more functionality for less or similar cost.

4.5.1.9 Additional market threats: nanogenerators

4.5.1.9.1 Nanogenerators only successful if stringent market requirements are met

It is yet not clear whether nanogenerators/energy harvesters in general can satisfy market needs, e.g. for IoT, i.e. small size, very low cost <1$, sufficient output power, maybe even disposable.

On the other hand, competing candidates/materials and principles of energy harvesting are more mature, established and closer to the market, although the above raised question still remains. Careful benchmarking with competing technologies is needed to address this barrier. Alternatives such as cabling or batteries and low power consumption are mature and well used.

4.5.1.10 Additional market threats: chemical/gas sensors

4.5.1.10.1 Unawareness of end users regarding improved gas sensing opportunities

Especially when it comes to innovative and wireless sensor solutions and networks, end users are not yet aware and convinced of the benefits and technical possibilities. The maturity of gas sensors and wireless detectors is currently rather underestimated. End users are often unaware of recent technological improvements. [483]

4.5.1.10.2 Price pressure increasing

The market becomes more and more price sensitive. A trend towards decreasing prices was observed in the last years and is expected to continue. Manufacturers increase the prices pressure by lowering product prices of marketed and established products to keep the market share and expand the market base. [483] This poses a threat for new and possibly more expensive technologies, but on the other hand, opens opportunities for cheaper/simpler technologies. For instance, new sensor technologies, such as low-power IR, CMOS MOx and wireless gas detectors, increase price pressure on traditional detectors. [483]

4.5.1.10.3 MOx sensors and other nanotechnologies as competitors

CMOS-integrated MOx sensors are a main competitor in terms of sensitivity and price towards graphene/2D based sensors, especially for compact and integrated sensors. [489]

Other nanotechnology based sensors are also heavily researched and propose interesting opportunities as competing materials to graphene/2D materials (e.g. CNT, nanowires) [468]

4.5.1.10.4 Patent thicket

The patent thicket in the sensor area is a major threat for new graphene-based sensors, especially for small companies and start ups.

4.5.1.10.5 Proof of benefit not necessarily straight forward

Often, the value for customer lies in longer periods of good performance of graphene-based sensors, as compared to conventional sensors, and thus lower costs per sensor life-time. This particular issue will be difficult to prove to customers, as the initial expenditures might be higher for a graphene based sensor. The critical factor in that case is not the overall sensitivity, but a good, continuous and reliable performance over long time periods (> 2yrs).

4.5.1.11 Additional market threats: biosensors

4.5.1.11.1 Diversity of biosensor applications and requirements pose a problem for focusing and creating a critical mass

The diversity of biosensors is both a blessing and a curse. It allows niches and early adopters on the one hand, but on the other hand, the market needs for so many sensors are so different making it hard to decide what to go for and to focus on in the first place. The variety and unsure potential and way of functionalization demand focussing on particular use cases, which then need to be tailored to the application area.

4.5.1.11.2 Usually long development time of biological recognition element and functionalization optimization

Additionally, the protracted time usually needed for technology transfer from laboratory to commercial applications (for biosensors in general) limits and hinders adoption. Furthermore, novel biosensors usually suffer from rather long development cycles, due to e.g. the development and optimization of the functionalization (biological recognition element). [485]

4.5.1.11.3 Medical/health applications: Regulation and cultural threats

For POCT and other medical applications conformity with EU/FDA medical device regulatory requirements is mandatory and it is important to meet the stringent and specific requirements of the medical device industry. Furthermore, medical applications depend on reimbursement by health insurances, which may be currently critical/difficult to obtain (see also 5.2 Excursus: The specific structures of the health market). Additionally, a lack of technology awareness among users and practitioners poses a barrier for further adoption. [485]

POCT (with or without graphene) competes with established laboratory testing but comes in most cases at a higher price (higher cost per test, no economy of scales as in laboratories). For POCT to become more custom, a paradigm shift towards prevention rather than post event testing is needed, requiring structural and organisational changes in the user institution (e.g. clinic, doctor).

Typical requirements for lab on chip systems are:

1. CE or FDA approval
2. Coefficients of Variation: 1-5%
3. Sensitivity, specificity, system control
4. 5-6 minutes TTR
5. < 1 USD per piece price at high volumes
6. Room temperature stability min 1 year

4.5.1.11.4 Large existing markets are well established and technologies are mature and cheap

Today’s major market for biosensor-based glucose (e.g. for diabetes) analysis works already fine and is reasonably cheap. There is no strong need for a completely new material like graphene and the market dominating technology will defend its share. The barrier to enter this market as a new technology is rather high and therefore it is not advisable to address this big existing market in the first place.

The market of bioanalysis is highly competitive, thus graphene-based approaches have a chance, only if the analyses can detect unique parameters or can achieve a much higher precision than other methods. Graphene/2D materials additionally compete with other emerging and partially more mature technologies, which have been studied for a longer time and where more demonstrators are available, such as nanostructure devices, e.g. CNTs and semiconductor nanowires.

Furthermore, the laboratory analyzer solutions in the market are also advancing (e.g. large laboratory equipment such as ICP spectrometers). The advancements in medical devices challenge biosensor manufacturers to keep pace [485]. But for instance with POC, other opportunities exist that cannot be addressed with laboratory equipment. But there are also many other technologies addressing POC.

4.5.1.11.5 Sterilization, reproducibility and durability in different environments

Reproducibility and only small variations between measurements are essential for biosensors. Furthermore, depending on the use case, the possibility to sterilize the sensor might be a prerequisite. In harsh environments, the limited resilience of biomolecules restricts the durability, rather than graphene. [485]

4.5.1.11.6 Not only graphene determines cost

The costs of a biosensor can heavily depend on the biomolecules used, its availability and production. Thus, this can possibly not be influence by graphene research but needs to be addressed when looking at different analytes and biological recognition elements.

4.5.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in sensors

4.5.2.1 Current strengths for graphene/2D materials use in sensors

4.5.2.1.1 Added value through added functionality and conformability

2D materials and especially graphene offers a large variety of sensor applications employed as an electrode (e.g. in electrochemical sensors), electrical conductor and electrically active material and transducer (e.g. in hall sensors, strain gauges, pressure sensor, nanogenerator, as GFET biosensor) and optoelectronic element (optical sensors). Adding new functions to sensors can enable sensors to address new markets.

In these applications graphene/2D materials can in principle deliver added values:

- It can act as a versatile platform, that can be also functionalized and used in different sensor application looking at different stimuli.
- The two-dimensionality and high specific surface area together with the interesting electrical and optical properties and the sensitivity of those properties to the direct environment make 2D materials highly sensitive transducers with several possible read-out options (electrochemical, transistor, optical)
- Mechanical flexibility: Flexibility and conformability can be important USP depending on the targeted market (see also 4.6 Flexible and/or printed electronics)
- Potential biodegradability/combustibility, which is interesting for end-of-life considerations and disposable sensors
- Transparency. Single layers or double layers of graphene are almost transparent and could be used in unobtrusive sensors.
- Multi-functionality: further interesting intrinsic properties such as the barrier properties and thermal conductivity can be beneficial for applications involving heat and protective layers. Graphene can therefore act as a barrier material an conductor
- Essentially, the substrate can be freely chosen (although this can influence the performance)

- High quality (encapsulated) graphene offers new realizations of quantum technology devices for multi-functional sensing
- Embedded or integrated sensor functionality in composites (e.g. strain gauge), for instance composites made conductive with graphene can change the conductivity depending on strain
- Graphene can be also used as a membrane to filter analytes (e.g. size selective filtering of nanoparticles) during detection (see also 2.5 Special application: Filtering, desalination/deionization and membrane applications)

4.5.2.1.2 Sensor applications also possible based on flakes

Sensors can be realised with high quality graphene as electrodes and in GFETs. Besides this high quality approach, it is also possible to realize sensors based on bulk graphene flakes. For some applications such as electrochemical sensors, some biosensors or strain gauges, the quality of graphene does not need to be as high as for transistors, so that also GO and LPE graphene can be used. These sensors are then usually also printable (see also 4.6 Flexible and/or printed electronics).

This also opens up applications that do not rely on the success of wafer scale integration and where higher readiness levels can be easier achieved and commercialisation is closer. For instance, there are screen printed electrochemical sensor electrodes based on graphene flakes already commercially available (e.g. from DropSens, Spain [492]).

4.5.2.1.3 Overall potential in sensing seen as promising

Sensor applications are seen as one of the most promising key applications for graphene/GO materials by many experts. Due to the variety of potential applications and benefits, as well as the market structure, sensor applications of graphene/2D materials seem feasible and in reach. Furthermore, the technological benefits are promising and USPs are quite evident in many sensor applications.

4.5.2.2 Additional strengths: Magnetic sensors

4.5.2.2.1 Orders of magnitude higher sensitivity proven on lab scale

Graphene/hBN based hall sensors have a 100x higher proven sensitivity on lab scale than Si-based hall sensors, which is similar to other ultra high sensitivity sensors (InSb). [458, 459] The graphene-based hall sensors have a high technological potential but the highest performances are currently based on manually exfoliated graphene and hBN and as such not scalable. Wafer scale integration of graphene and hBN is needed to achieve these performances in a mass manufacturing compatible way.

InSb has similar sensitivity but is very expensive. Graphene based sensors have a better potential in terms of manufacturability, although many questions are still open. The future cost reduction (if integration works) towards InSb can become eventually an advantage. On the other hand, hall sensors also have to compete with other magnetic sensors, such as magnetoresistance-based sensors (GMR, AMR, TMR) or Lorentz-force sensors.

Furthermore, high quality graphene-based (without hBN) flexible hall sensors were proven to have a comparable sensitivity compared to rigid Si-based hall sensors [457].

4.5.2.2.2 Spintronics based magnetic tunnel junctions

Graphene has interesting properties for spintronics and can be used in magnetic tunnel junctions for TMR sensors. This application still needs to be proven for magnetic sensing but could provide another opportunity for magnetic sensing. See also 0

Computing/Logic, beyond CMOS and spintronics for further considerations on spintronics.

4.5.2.3 Additional strengths: pressure sensors/microphones/NEMS

4.5.2.3.1 Ultimate membrane characteristics render it interesting for pressure sensing/microphones

2D materials are the ultimately thin membranes with unreachable mass, thinness and high strength and elasticity (1.1TPa Young’s modulus of graphene vs. ~130GPa for Si MEMS). Use of these membranes in NEMS as pressure sensors or microphones is possible in form of suspended piezoresistive membranes or membranes with electrostatic readout and it has been shown that they can be very sensitive and robust. [493] The former work because strain, e.g. induced through pressure, changes the density of states and induces a bandgap in graphene leading to changes in mobility and resistance.

The proof of concept has been shown and some parameters are better than standard MEMS microphones. [494] But the improvement does not justify a change to this type of microphone. Further implementations show a broad wavelengths range (ultra sonic). [495]

These results are promising to achieve smaller sensor (outstanding scalability), higher sensitivity and broad wavelength ranges, with potentially simpler readout. However, the improvements are not yet tested in terms of thermal stability and other important parameters for microphones. If the mechanical properties on macro scale are as theoretically expected and can be realized experimentally, the potential is quite high to outperform state of the art technologies, mostly because the elongation of membrane is large, which can compensate for the low k factor.

A completely different implementation are printed pressure and strain sensors, which are flexible but more coarse in terms of sensitivity. The implementation is quite easy but the technological advantage in terms of sensitivity is not extraordinary high. On the other hand, flexibility and the end-of-life characteristics (combustibility, disposability) and environmental properties also during manufacturing, can be very interesting (see also 4.6 Flexible and/or printed electronics).

4.5.2.4 Additional strengths: Nanogenerators

4.5.2.4.1 Rather simple realization if wafer scale integration is feasible

Graphene is especially tested as (flexible) triboelectric energy harvester [466]. It is also examined in piezoelectric nanogenerators, e.g. as substrate for piezoelectric materials [496], and in thermoelectric nanogenerators, e.g. as additive for thermoelectric composites [497]. Also other means of energy harvesting are investigated, such as acoustic wave harvesting [496] and for other new means of energy harvesting (e.g. from moisture [498]). Other 2D materials are also investigated, e.g. for piezoelectric energy harvesting. [466]

The application is in most cases rather simple (lower quality constraint on CVD, maybe even LPE possible) and a nanogenerator should be easily processable with wafer scale integration. Graphene-based tribological nanogenerators have been realized in the lab.

A major benefit is the flexibility and potential transparency. So far the lab results are interesting and expectations are good, but the proven performances and manufacturing is not yet sufficient for an actual uptake from industry.

4.5.2.5 Additional strengths: chemical/gas sensors

4.5.2.5.1 Sensitivity proof of concept promising

The high specific surface area and the sensitivity of electronic properties of 2D materials to the direct environment are important prerequisites for highly sensitive gas sensors. Graphene gas sensors have been demonstrated and the concepts have been proven with very promising sensitivity, response times and working at room temperature. The performance in terms of sensitivity realized in labs today is already as good as competing non-graphene sensors and there is still potential for further improvements of the performance. The sensors are potentially robust, as graphene is neither brittle nor prone to a high chemical reactivity. The sensitivity is expected to be similar or better to competing technologies, but due to the higher robustness with a significantly prolonged life-time and potentially shorter response time. Current major problem is the selectivity.

Several target gases and chemicals have already been addressed, ranging from humidity, nitrogen oxides and hydrides, carbon oxides, hydrogen to form- or nonanaldehyde.

4.5.2.5.2 Enabling new sensing capabilities

Graphene based sensors could enable completely new functionalities, e.g. multi-gas sensing through simply implemented and compact multiple sensor arrays for air quality or breath analysis. Sensitivity and robustness are already shown, but the selectivity and capability for multiple sensor arrays needs to be proven. 2D materials promise to have the potential to become cheaper, smaller and more sensitive and selective.

Graphene plays an important, but not unique role in gas sensing. Other nanostructured materials are competing with comparable results (e.g. metals, metal oxides, organic semiconductors) and higher maturity. However graphene/2D materials have the potential to provide a) the same level of performance, but over longer time periods or b) more sensitive (and probably selective) sensing.

As printed sensors, the uniqueness for low cost and flexible solutions might be higher.

4.5.2.5.3 Implementation with and without wafer scale

Gas sensors can be based both on high quality films and flakes. The implementation is in principle easier than for many other emerging competing technologies, such as CNT. Sensors based on rGO flakes are simpler to produce and no wafer scale integration is needed. But the reproducibility of LPE graphene and rGO is not good enough at the moment to prepare reliable sensors.

For electrochemical and GFET-based gas sensors, wafer scale integration is beneficial (for the latter a prerequisite). If wafer scale integration succeeds on a broad scale, cost reduction compared to existing technologies could become a major USP, as current technologies are usually quite costly (although there are now first low-cost CMOS based MOx sensors addressing the mobile market [489]).

4.5.2.6 Additional strengths: biosensors

4.5.2.6.1 Intrinsic properties are good for biosensors

Graphene can be used in several ways as biosensor. The two major kinds of implementation are as electrode for electrochemical sensing (measuring for instance impedance, amperometry or potentiometry for instance from a screen-printed electrode), and as GFET, where the analyte changes the transistor response by modifying the graphene channel. Further implementations are sensors based on surface plasmon resonance, fluorescence quenching (both optical measurements), as electrode to measure electrical/neural activity and as membrane with nanopores and sensing capabilities, e.g. for DNA analysis. For almost all sensors types GO, rGO, graphene and other 2D materials can be employed, depending on the need for sensitivity, loading, selectivity and response time. Graphene-based biosensors have been developed for various inorganic and organic analytes, e.g. glucose, proteins, DNA, NADH, biomarkers, antigens, pathogens, heavy metals, H_2O_2, NO.

Graphene materials offer good properties for biosensing, especially due to the following benefits:

- high **chemical stability** (for instance better than silicon nanowires)
- large **specific surface area**
- **capability of high bioelement loading for high sensitivity**: for instance, GO can be well used as a matrix for binding the bioelement due to many functional groups and a high surface area, thus allowing to create functional hybrids with an increased sensitivity due to high bioelement loading. There is also a potentially large range of surface chemistry available to modify/functionalize the surface.
- **Direct quantitative recording of analyte**: analyte can be directly and quantitatively recorded as electrical changes and output as data (the binding interactions themselves are electronically measuredand not via piezoelectrical or optical signals). The direct electron transfer between the bioelement and the electrode surface does not need a mediator. This can **reduce process complexity**, **response time** and **hardware costs** and **increase sensitivity**, **portability and ease of use**
- **rather simple device structure**
- high sensitivity, low noise, fast response time; potentially high specificity (depends on bioelement)
- **label free** detection possible, even of separate bases in DNA, which is unique.
- due to high sensitivity: **low sample volumes needed**
- mechanical flexibility for **flexible substrates** and sensors, allowing addressing new markets
- Biocompatibility
- Some realisations can be made **transparent**
- Hydrophilicity and hydrophobicity possible
- Potential for low power consumption

The combination of all the strengths makes graphene/2D materials rather unique for biosensors with a strong enabling character. There are of course also other options, e.g. CNT or other nanotechnologies, but there are only a few competing technologies which could be competitive from the technological point of view.

The available scientific analyses show that graphene-based biosensors can detect specific biomolecules with high precision. This may be a competitive advantage compared to other biosensing approaches. It will be decisive to establish graphene-based approaches in relevant segments of the biomedical market, e.g. in the context of cancer.

4.5.2.6.2 Multifunctionality: several functionalities in one material/layer

The combination of different sensing capabilities and functionalities seems possible with graphene materials. For instance in a process cell for IVD, graphene can be used for temperature control and as catalytic surface cell for enhancing reactions and sensing.

It is also possible to combine electrical and electrochemical measurements with optical measurements (high freq/optical plasmonic detection possible).

Graphene can also be applied in Lab-on-Chip devices, as multiuse sensing element that is possible to functionalize repeatedly. As a charge sensitive element, the only requirement for the analyte is a change in the charge distribution with bio-recognition. In this respect it competes with nanowires, but it is not yet clear which material is more stable.

For electrodes and neural sening, both sensing and actuation are possible (e.g. brain/heart electrode as sensor and to deliver electrical stimulus).

4.5.2.6.3 GO electrochemical biosensors for less demanding applications

With GO and rGO screen-printed electrodes, electrochemical electrodes and even GFETs can be prepared. GO has many functional groups and can thus be well functionalized and loaded. Functional hybrid materials can thus be obtained. However, the electrical properties are not as good as for high quality films, especially in GFETs. Thus, the sensitivity might be lower/different. On the other hand, even graphene/GO inks may be sufficient for less demanding applications, e.g. monitoring (food, environment).

4.5.2.6.4 GFET biosensors for more demanding applications

The functionalized bilayer-graphene based FET sensor benefitting from the above mentioned unique properties has the potential to challenge all biosensors (as a platform). The overall technological performance and advantages already realized in labs and proven by academia is often better than competing options such as carbon nanotubes or semiconductor nanowires. The sensor has the potential to overcome disadvantages of Si-based FETs, e.g. the high electric noise, integration with flexible substrates or stability under physiological conditions. The performance of the GFET based sensors are expected to be better than the state of the art in the future. Also, simpler to produce functionalized GFETs (e.g. based on rGO) are promising to provide quantitative electronic readout in biodetection with a simple device structure and low-cost fabrication as even on flexible substrates. The higher quality GFETs have a cost reduction potential towards common lab analyzers, but probably not towards other upcoming technologies (nanowires, CNT) at the moment. For the high performing GFETs based on high quality single or bilayer graphene to become cost competitive, a low-cost direct graphene layer generation and functionalization of graphene surface for specificity is required. With a larger scale and economically feasible wafer integration scheme this might be realisable.

There are already companies working on the use of graphene FET as biosensors and first implementations of commercial graphene-based FET biosensors are expected on the market in 2016/17.

4.5.2.6.5 Build on CNT experiences

CNT have been investigated for biosensing for a longer time and a lot of experience is in this field. This experience can in part be used for graphene-based biosensors, especially with respect to e.g. similar behaviour, surface chemistry or the use in electrochemical applications.

4.5.2.7 Current weaknesses and challenges for graphene/2D materials use in sensors

4.5.2.7.1 Current maturity too low for comprehensive feasibility assessment

Although many sensors show promising technological parameters, the available data and the means of manufacturing is still too immature to allow a comprehensive feasibility assessment for industry.

Especially issues that are besides the technological performance very important for a broader roll-out, such as reliability, power consumption, repeatability or cycle times need to be tested/proven. Furthermore, economically feasible and as simple as possible means of production are necessary, providing a high yield and good reproducibility. These factors are still too elusive for most sensor applications avoiding to go beyond the R&D stage or the “manually” manufactured low volume, high price niche sensors. Especially the sensors based on high quality films (such as GFET sensors, NEMS/pressure sensors, hall sensors) need wafer scale integration to become commercially viable (see SWOT analysis in 4.2 Electronics: Cross-cutting issues).

For sensors where the production is rather simple and possible, on the other hand, such as printed sensors, the technological USP is probably not high enough.

For almost all sensors, the design and fabrication are manually done at lab-scale and commercial scale-compatible design and fabrication is rarely done. Furthermore, also the technological assessments are mainly based on laboratory experiments and measurements in controlled laboratory environment. “Real world applications” in real samples and relevant environments are rarely done. For instance, very often improvements are only shown for one performance parameter (which is better than anything else), neglecting others, e.g. temperature stability, power consumption, etc.

4.5.2.7.2 Challenge to create adequately performing low-cost G-sensor

The requirements for particular sensors on the manufacturing, in terms of needed quality of 2D material, size of sheets, parameters such as mobility, etc. are often unclear and need to be systematically investigated to provide insights on the preferred production methods. This further calls for material standards to allow exchange between manufacturing and applications. The major idea needs to be that the quality should be high enough to provide the performance needed and low enough to allow simple and cost effective production methods.

4.5.2.7.3 Besides the material also data analysis and readout are important

For sensors, not only the sensor itself and the sensing element is important, but also data analysis and read-out is crucial to show the actual functionality. The full package of sensor, readout and even software is needed to show the actual potential of graphene in demonstrators and create awareness of the potential. This is particularly important for multiple sensor arrays, where the implementation, software and algorithms to reach the required performance are crucial to show the actual performance.

4.5.2.7.4 Autonomous sensing, IoT, mobile applications: Energy consumption

Especially for internet of things, autonomous and mobile applications, energy consumption is key and needs to be addressed. A sensor can be very sensitive, selective, small and cheap, but if the energy consumption is too high, which will lead to higher system cost as larger batteries or other power supply strategies are needed, it is out of the game. For these remote applications, power supply should be below few milliwatt, the smaller the better.

4.5.2.8 Additional current weaknesses and challenges: Magnetic sensors

4.5.2.8.1 Economically feasible manufacturability unclear

The best performing hall sensors reaching a one to two orders of magnitude better sensitivity than Si-based hall sensors require perfect graphene sheets encapsulated in two-dimensional hBN. Also magnetic tunnel junctions make use of hBN. Thus, manufacturability is the biggest issue for those sensors to become commercially viable. Beside the graphene production, especially the production and integration with hBN is a large challenge, as 2D hBN is still at the exfoliation stage and can yet not be produced industry-compatible in sufficient quality. But also the mass production-compatible quality of graphene is currently not good enough to reach the needed performance level. Further critical issues are graphene contacting, delamination of the stacks and reproducibility. Therefore, integration and manufacturability with CMOS compatible processes is a must to reach relevant markets (see 4.2 Electronics: Cross-cutting issues for further information on wafer scale integration).

Similar issues apply for flexible hall sensors, however, here the performance requirements are essentially lower and similar performance as Si-based sensors could be sufficient. On the other hand, the cost constraints are equally high and therefore a mass production method is needed.

4.5.2.8.2 Maturity: only lab scale experimental level at the moment

The realized impressive performance of graphene-based hall sensors has only been achieved on experimental laboratory level with manual preparation at the moment.

4.5.2.9 Additional current weaknesses and challenges: pressure sensors/microphones/NEMS

4.5.2.9.1 Manufacturability challenging and some intrinsic properties not convincing

The piezoresistive gauge factor k of graphene is only 2-4, which is not disruptive and rather low. But the elongation per force much is higher than for other materials, such as silicon, which can eventually lead to a better sensitivity per unit area.

Prototypes are currently made manually, but integration is needed for a commercialisation. As a free-standing graphene/multilayer graphene membrane on wafer, wafer scale integration is a must, in best case using standard MEMS equipment. Reliability and reproducibility investigations are additionally needed to clearly address the benchmark with existing solutions.

For some pressure sensors in form of touch sensors, especially printed ones, wafer scale integration is not a must but could be beneficial.

4.5.2.9.2 Mechanical/thermal stability unclear

The performance improvement has not been shown for all relevant parameters (e.g. thermal stability, reliability). So for a fair and complete benchmark, the actually realized mechanical/thermal stability of the membrane needs to be proven.

4.5.2.10 Additional current weaknesses and challenges: Nanogenerators

4.5.2.10.1 Maturity and unclear cost

The maturity of graphene-based nanogenerators is low compared to other materials under investigation. Cost/performance advantage towards other materials are not yet clear. In order to get a better assessment, the devices need to be further developed and tested and benchmarked with competing technologies.

4.5.2.11 Additional current weaknesses and challenges: chemical/gas sensors

4.5.2.11.1 Proof in relevant environments needed: Unclear long term performance/lifetime/stability

Laboratory prototypes are promising, but the functionality and working in different real systems needs to be proven. Besides sensitivity, the value for customer lies in longer periods of good performance of graphene-based sensors, as compared to conventional sensors, and thus lower costs per sensor life-time. This is especially the case if graphene-based sensors are more costly in the beginning. Thus it is very important to address KPIs such as stability and life cycle, by proving longer periods (this has not been done yet). For currently investigated graphene-based sensors, the critical factor therefore is not sensitivity, but good performance over long time periods (> 2yrs). Some even doubt, whether graphene can hold up to the promises of better stability and longer life cycle, as problems of aging/degradation have not been addressed or solved yet. The promises of longer lasting sensors will only be believed, if they are experimentally proven under realistic conditions, which is still unclear at the moment. An important aspect in this respect is that the sensors last longer without maintenance. This leads to a needed general prove of the quality and variability. If a proof succeeds, it can easily be turned into a strength for graphene-based gas sensors.

It is very important to address the full set of gas sensor KPIs, because performance is not only defined by sensitivity, but by the full set of KPIs. This also allows a fair and realistic benchmarking with other technologies, an important prerequisite for companies to consider a new technology.

4.5.2.11.2 Selectivity is a key challenge and needs to be solved: functionalization and surface chemistry

Selectivity to the target analyte is a key property of gas sensors. Depending on the analyte, there is a lack of recognition in graphene based sensor, which calls for functionalization. However functionalization also influences the graphene electrode or FET itself and can as such have an effect on the sensitivity. There is a trade off and optimal balance between loading of the recognition element and sensitivity (similar issues are true for biosensors). The functionalization can be key, although the potential selectivity through functionalization in some cases is not enough. It is therefore of crucial importance to further investigate different functionalization. This includes following challenges:

- Surface chemistry: the surface chemistry needs to be effective, simple and not too aggressive to affect the 2D material performance too much
- Functionalization needs to be stable to allow stability and long lifecycles, this is today still a huge challenge
- The functionalization needs to be compatible with resetting of sensors, the latter being an important issue. Also resistance to contamination should be possible to a certain extent, which depends on the application.

If specificity/functionality to one gas is solved regarding the above mentioned issues, the knowledge can be transferred to other gases and the material gets closer to being a gas sensing platform technology. Please also refer to the assessments of biosensors in this chapter, as bio recognition elements can also be used to functionalize for gas sensing. [499]

4.5.2.11.3 Manufacturability to a certain extent unclear (wafer scale, LPE/rGO reproducibility)

Wafer scale integration is necessary for higher performing sensors (see 4.2 Electronics: Cross-cutting issues for further assessments of wafer scale integration). If this integration scheme works economically feasible, cost competition could become possible. If not, rather high production costs can only be justified if the performance (sensitivity, selectivity, life cycle, stability, size) is significantly improved over competing sensors.

For the simpler preparation of lower performing sensors with LPE and rGO, reproducibility is a major obstacle for the sensors.

4.5.2.11.4 Unclear environment, health and safety barrier for some applications

As for all other nanotechnology-based sensors, the environmental, health and safety of the nano-sized layer is a matter of concern, in particular for applications in the food or medical sector. These concerns need to be actively addressed if such an application is pursued and it should be clear that this pushes the time frame or can be a killer argument against the use in these areas.

4.5.2.12 Additional current weaknesses and challenges: biosensors

4.5.2.12.1 Address the full set of KPIs

The full set of relevant performance parameters, such as sensitivity, selectivity, cost, stability, reliability, cycle time, waste management, etc., all are important aspects for a biosensor to be competitive in a certain application area. For a realistic comparison with competing technologies, the full set of relevant KPIs for an application needs to be addressed in relevant environments. Similar arguments as for gas sensors in 4.5.2.11.1 Proof in relevant environments needed: Unclear long term performance/lifetime/stability apply.

4.5.2.12.2 Challenge of device stability and contacting

Besides the optimisation of the sensitivity, e.g. through contact optimisation, device stability and cycle times are still key challenges for biosensors based on 2D materials. Furthermore, contamination in operation and how to dealt with it need to be addressed. The latter depends of course on the targeted application.

4.5.2.12.3 Challenge of reliable and economically feasible functionalization by surface chemistry

Label-free biosensing with graphene or other 2D materials heavily depends on the functionalization, in case of biosensors with a bio recognition element. Challenges are essentially comparable to the field of overall gas sensors, see 4.5.2.11.2 Selectivity is a key challenge and needs to be solved.

For biosensors, especially the optimisation of selectivity for different analytes is required, e.g. by selection/optimisation of the biocomponent as well as targeted and controlled coupling of the biocomponent to the graphene/GO surface by surface chemistry.

Most importantly, the trade off between covalent functionalization (right binding site, loading) and the properties of graphene (conductivity etc.) needs to be investigated and understood. The graphene/2D materials’ properties are influenced by the binding sites and biocomponent. For optimal selectivity and sensitivity, a balance/optimal point between the number of binding sites, i.e. the loading, and the properties of graphene (e.g. in a GFET) needs to be found.

Furthermore, there is a large variety of recognition elements possible [499], and it needs to be investigated which ones are feasible for use with graphene or whether there are even recognition elements that are of particular enabling character for graphene or vice versa.

Further challenges are related to the surface chemistry, which is often quite aggressive using for instance plasma, electrochemical oxidation, hydroxylation, silanization. Different types of binding need to be investigated, such as covalen/non-covalent, also looking at the orientation of the recognition element. For antibodies, this orientation is important. And a blocking chemistry is needed to avoid becoming unselective. Often, many steps are needed for functionalization and it should be a major goal to make it as efficient and simple as possible.

4.5.2.12.4 Adequate and tailored graphene quality

The needed graphene quality differs from application to application. It is most important to be able to provide the same quality in a reliable and continuous way. Defects or dangling bonds need to be controlled, as they can provide binding sites for recognition elements. Especially for GFET based high sensitivity (flexible) solutions, high quality SLG or FLG is needed and the quality is critical (need wafer scale integration, high quality transfer). For rGO or graphene flake based sensors it is also important to have an adequate, continuous and homogeneous quality from batch to batch.

Further specific production processes are required to apply the surface chemistry and functionalization with the bio recognitions elements.

4.5.2.12.5 Targeted developments according to best business case needed

The field of biosensors is very broad and many opportunities exist. However, to date it is unclear for which analytes/biosensors the specific features of graphene-based biosensors really provide an advantage over competing products. After broader screening of possibilities, a very careful choice of analytes and application scenarios is required to focus on the areas with highest relevance and added value.

4.5.3 KPIs for sensors

4.5.3.1 General KPIs relevant for all sensors

Mobile applications: <€2, < 5 mW, < 3.0 V, 2 year life, package in the lower mm range.

Table 61: Typical prices per unit for different sensor types. [479, 480]

Sensor Type	Price per unit	Trends
Pressure sensors	$49 to $195	▼
Temperature sensors	$59 to $350	▼
Humidity sensors	$25 to $250	▼
CO/VOC sensors	$240 to $310	●

Flow sensors	$15 to $300	▼
Strain gauge Sensors	$25 to $450	●
Vibration Sensors	$20 to $390	▼
Corrosion Sensors	$30 to $340	●
Image sensors	$17 to $230	●
Combined Sensors	$45 and Up	▲
Acoustic sensors	$3.6 to $4.5	
RFID reader and tags	$1 to $50	
Motion sensors	$4 to $35	
Obstacle sensors	$1.5 to $9	
Particle sensors	$28 to $35	
HVAC	$25 to $100	
Air quality sensors	$10 to $175	
Proximity sensors	$1.5 to $8	
Energy meters	$20 to $40	

4.5.3.2 Hall sensors for magnetic field sensing

Table 62: Comparison of KPIs of competing technologies and hall sensors based on graphene, adapted from [458] and supplemented with other sources and research

	S_I (V/AT)	S_V (V/VT)	B_{min} w $(pT/\sqrt{Hz}\cdot mm)$	Freq. (kHz)	Remarks
Si	100-200	0.1	1500	3	2W for Sensitivity 10mV/mT, 20-50ct per piece; temperature range: -40 ... 110°C (typical)
GaAs	1100	NA	8000	3	
InAsSb	2750	NA	50	1	(few $ per piece)
InSb	1250	3.8			~4$, values roughly estimated from data sheet; temperature range: -40 ... 110°C (typical) [500]
NiFe Thin film AMR		20			10mT saturation field [501]
GMR		200	<10 (not normalized to contact) @1Hz	~1-10	[502], operating temperature typical: -25 ... 85°C; price ~5-50$
Graphene	2093	0.35	5000	3	in air
Gr-hBN	4100	2.6	150	3	in vacuum (1 sample)
Gr-hBN	4000-6000	~3	NA	NA	in air (2 samples)

4.5.3.3 Pressure sensors/microphone and NEMS

Microphones: high Signal-to-noise ratio (SNR), high sensitivity

Table 63: ST Microelectronics MEMS microphone KPIs. [503]

Parameter	**MP45DT02**	**MP34DB01**	**MP34DT01**	**MP33AB01**	**MP33AB01H**
Sensitivity	-26 dBFS			-38 dBV	
Directivity	Omnidirectional				
SNR /dB	61	62.5	63	63	66
AOP /dB	120	120	120	125	125
EIN /dB	33	31.5	31	31	28
THD+N	<5% @115dB			<5% @120dB	
PSR	-70 dBFS			-75 dBV	
Maximum current consumption /µA	650	600	600	250	250
Package dimensions /mm	4.72x3.76x1.25	3x4x1	3x4x1	3.76x2.95x1	
Port location	Top	Bottom	Top	Bottom	Bottom
Operating temperature	-40°C<T<+85°C	-30°C<T<85°C	-30°C<T<70°C	-30°C<T<100°C	
Price range	~<1$				

Pressure sensors

ST MEMS: Current consumption: 0.5-1µA (for 260-1260hPa), 25µA for high precision (1Pa RMS), price ~2-3$.

Bosch BMP180 MEMS piezoresistive pressure sensor, incl. readout IC and package, size: 3.6 x 3.8 x 0.93 mm3, time/pt: 5 ms, RMS noise: 2 Pa.

Table 64: ITRS 2013 goals for 2017 MEMS microphones. [327]

Signal-to-noise ratio @1 kHz	70 dB(A)
Frequency response	0.02-20 kHz
Current consumption (1.5-3.6V)	100 µA
Package size (L*W*H)	2 x 3 x 1 mm³

4.5.3.4 Nanogenerators

Micro energy harvester (thermoelectrical, vibrational, etc.); very low cost needed for IoT and mobile applications ~1$ with reasonable output power and efficiency

The average price per unit currently is 8.13$ and falling [481]

4.5.3.5 Gas/chemical sensors

Table 65: KPIs for chemical/gas sensors [467, 504] supplemented with additional information.

Specification	**Description**
Sensitivity S	Change in the measurement signal per concentration unit of the analyte, i.e. the slope of a calibration graph, e.g. nA/ppb or µV/ppm.
Detection Limit (LOD)	The lowest concentration value which can be detected by the sensor in question, under definite conditions. Whether or not the analyte can be quantified at the detection limit is not determined. Procedures for evaluation of the detection limit depend on the kind of sensor considered. It can for instance be the concentration of target gas that gives a signal greater than three times the standard deviation of the noise level. Detection limits are depending on application usually in the ppb to ppm area. For instance for CO_2 100-1000ppm are often sufficicient, other analytes demand 100 ppb or less.
Dynamic range	The concentration range between the detection limit and the upper limiting concentration.
Selectivity	An expression of whether a sensor responds selectively to a group of analytes or even specifically to a single analyte. Quantitative expressions of selectivity exist for different types of sensors. It can for instance be the ratio of response to the target gas (Sc) and response to the disturbed gas (Si). D=Sc/Si
Linearity	The relative deviation of an experimentally determined calibration graph from an ideal straight line. Usually values for linearity are specified for a definite concentration range
Resolution	The lowest concentration difference which can be distinguished when the composition is varied continuously. This parameter is important chiefly for detectors in flowing streams.
Response time T_{res}	The time for a sensor to respond from zero concentration to a step change in concentration. Usually specified as the time to rise to a definite ratio of the final value. Thus, e.g. the value of T_{99}

Specification	Description
	represents the time necessary to reach 99 percent of the full-scale output. The time which has elapsed until 63 percent of the final value is reached is called the time constant.
Recovery time T_{rec}	If the sensor is resettable, which is usually desired, it is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.
Hysteresis	The maximum difference in output when the value is approached with (a) an increasing and (b) a decreasing analyte concentration range. It is given as a percentage of full-scale output.
Stability	The ability of the sensor to maintain its performance for a certain period of time. As a measure of stability, drift values are used, e.g. the signal variation for zero concentration. The stability can depend on temperature (which can be corrected). For a good and maintenance free sensor, the stability should be on the order of the life cycle.
Life cycle	The length of time over which the sensor will operate. The maximum storage time (shelf life) must be distinguished from the maximum operating life. The latter can be specified either for continuous operation or for repeated on-off cycles. The operating life cycle for consumer should be 2 years, for automotive 15 years and for domotics somewhere in between.
Peak power consumption	Maximum power consumption during measurement (especially when a heater or light source is involved)
Average power consumption	Average power consumption in a regular duty cycle (meaningful for the targeted applications
Operating conditions	Conditions for which the sensor is specified (e.g. temperature range, humidity) under operation
Package size	Size of the packaged sensor
End-of-life	For some sensors the end-of-life properties are interesting, e.g. is it disposable, combustible, degradable…

Competing technologies: CNT, MOX (metal oxides); MOX sensors are a good benchmark (in terms of cost/performance)

Table 66: Values of an ananlogue MOX CMOS sensor. Calculated from [505].

Specification	**Value**
CCS801 (Ethanol, CO, Toluene)	
Sensitivity / $10^{-3}(R_{air}/R_{analyte})$/ppm)	13 (ethanol); 4.4 (CO); 3.7 (toluene)
Detection limit	<20ppm
Response Time	~15 ms
Peak Power Consumption	33 mW
Average Power Consumption	0.9 mW (pulsed mode, duty cycle of 2.5% on-time)
Recommended operating conditions	-5 – 50°C; 15 – 85%RH (non-condensing)
Lifetime (operating)	>5 years
Package	2 x 3 x 1 mm^3
Price (end user)	~5-7$ (pre production series)

KPI of other competing emerging sensor technologies can be found here: [468]

4.5.3.6 Biosensors

Essentially, similar KPIs are applied as in gas/chemical sensors (see Table 65). Read-out time and long-term stability are key parameters usually not too good for biosensors.

Table 67: The price of biosensor devices varies from $10 in volume applications to $1,000 in some high-end applications. This table gives a few examples. [485]

Device	**Typical price**
handheld diabetes detector, glucose biosensor	<10$
food pathogen analysis system	10,000$ – >100,000$
E.coli testing biosensor	>150$
SARS detection biosensor	>250$
Devices for home diagnostic applications	<10$

IVD/lab on chip requirements:

- CE or FDA approval
- Coefficients of Variation 1-5%
- sensitivity, specificity, system control
- 5-6 minutes time to results (TTR)
- Sensitivity, specificity
- Immuno-chemistry
- < 1 USD piece price
- High volume manufacture
- Room temperature stability > 1 year

Table 68: POCT vs. laboratory typical turnaround times for some key tests. [486]

Test	Laboratory turnaround time	POCT turnaround time
Urinalysis	40 min	4 min
Pregnancy	78 min	5 min
Blood glucose	10 min	6 min
Cardiac	110 min	17 min

Table 69: Typical cost of key tests (laboratory vs. POCT). [486]

Test	Centralised Laboratory ($)	POCT ($)
Blood glucose	3.5	11.5
HbA1C	3.3	6.0
Blood gas and electrolytes	45.0	9.5
Chemistry tests	14-16	20

4.5.4 Roadmap for Sensors

4.5.4.1 Current maturity: Mostly at laboratory level

Most graphene or 2D material based sensors are still in the laboratory stage, either due to missing manufacturing technologies or due to immature prototypes.

In magnetic hall sensors graphene has already shown to be better in terms of sensitivity and power consumption by a factor of 100 compared to silicon. But this was realised with a hand-made BN-G-BN stack. So here, the manufacturing is limiting increased TRL levels. Experts think that it will take at least another 5-10 years until reasonable processes are available due to the currnet lack of large scale wafer based and transfer free synthesis, especially of BN, but also of high enough quality graphene.

Pressure sensor and force sensors are at the level of applied research. Graphene-based NEMS provide interesting opportunities but currently suffer from the missing integration scheme and reproducibility. Flexible strain and force sensors are easier to integrate and can be based on flakes/rGO and are demonstrated in functional prototypes (see also 4.6 Flexible and/or printed electronics).

Nanogenerators at the basic research level, mostly at quite early stages. First of all, the most promising type, the triboelectric nanogenerator (TENG) in general is still rather immature compared to other types. Second, the graphene-based TENG is still in its infancy. Other nanogenerators (e.g. generating energy from humidity and movement) are promising also at basic research stage.

Gas sensors are at the level of basic research. Demonstrations of potentially low cost disposable graphene-based gas sensors exist but they are still far away from consumer products (e.g. for smartphones). Lab scale gas sensors show good/better performance than state of the art, but not with respect to reliability and stability. Most applications are in the lab stage and performance needs to be shown and benchmarked, as well as stability, long term behaviour addressed. An important issue is the selectivity of the gas sensor to the targeted gases.

GFET based biosensors are available on lab scale. A major challenge is selectivity, whereas the sensitivity is already good. A benefit is that biosensing selectivity can rely on biorecognition, e.g. with aptamers or antibodies, which is extremely specific and broadly available. Furthermore, manufacturability is an issue and depends in wafer scale integration for most biosensor GFETs. Additionally, functionalization and surface chemistry is important. Other sensor concepts (e.g. electrochemical) are also on lab scale. There are already first companies currently commercializing the technology, e.g. Nanomedical Diagnostics in the US. [506] Some printed electrochemical sensors are already marketed, where graphene is used as a screen printed electrode for a sensor platform (DropSense). These electrodes are to date not functionalized and provide no selectivity, but a high surface area.

Electrical implants and body electrodes are in the laboratory to applied research stage.

4.5.4.2 Barriers/challenges (summarized)

Consumer markets:

- 10x better performance (sensitivity, power consumption) and/or 10x lower cost

Health market

- CE, FDA approval
- Reimbursement
- “cultural” barrier: paradigm shift towards prevention needed to drive POCT and biosensors

General:

- Lifetime and reliability expectations, long term stability, maintenance free
- Fragmented market and interoperability
- Focus on the right opportunities: too many different sensing types and functionalization possible so that a clear vision is hard to achieve which markets can be addressed
- Often unclear what is best for which application: single layer, double layer, few layer, doping, contact points, how they are applied
- Missing full set of KPIs (especially in terms of durability, life cycle, stability, power consumption) for most lab sensors prohibits realistic potential assessment: There is no actual market pull
- Missing demonstration in relevant environments to prove claimed benefits (also as full demonstrators with readout and data analysis)
- Unclear environmental, health and safety properties and end of life (can the promises be experimentally verified?)
- Manufacturability (wafer scale and/or printed) of devices; most sensors need wafer scale integration for mass market applications as it delivers read-out and electrical functionality; 200-300mm wafer needed with decent graphene quality (see 4.2 Electronics: Cross-cutting issues)
- SiC based graphene: most things are known, but expensive; 3” quite uniform (99.9% coverage), 6” also possible; price has gone down ½ in 2015, but is still too high to be competitive in most applications

Magnetic sensors

- Manufacturing of high enough quality graphene and hBN (wafer scale) unclear (especially for economic feasibility assessment)
- Low cost and high volume markets with many incumbent technologies
- Low maturity of 2D materials based magnetic tunnel junctions for sensing

Pressure sensors/microphones/NEMS

- Many mature technologies, unclear benefit (besides probably higher wavelength range)
- Unclear whether higher sensitivity is needed
- NEMS in general: wafer scale integration, especially for controlled multilayer membranes
- Low k-value needs to be compensated by large elongation per force
- Unclear mechanical and thermal stability

Nanogenerators

- Low cost necessary for low power energy harvesters (IoT, autonomous systems)

- Competing technologies are more mature
- Unclear cost and low maturity

Chemical/gas sensors

- Manufacturability: Reliable large scale production of GFET by wafer scale or reproducible LPE/rGO with adequate quality (depending on application and needed quality)
- contacting
- Missing proof of longer stability and life cycles (together with full set of KPIs)
- Missing proof in relevant environments of targeted applications
- Functionalization for selectivity/specificity and sensitivity is a key challenge: Finding a reliable binding site on graphene and the right one and the right amount without compromising the graphene properties
- Surface chemistry (reliable and economically feasible)
- Trade-off between functionalization/load and graphene properties: where is the optimal point for each recognition element?

Biosensors

- The same barriers/challenges as for chemical/gas sensors apply, besides the fact that selectivity is more straight forward due to the use of biorecognition elements
- High diversity of potential applications, hard to decide where to focus
- Biological recognition elements' large variety, long development times and cost
- Surface chemistry to functionalize graphene with bio elements and to achieve optimal loading (trade-off); different recognition elements demand different chemistries
- Specificity, coefficient of variation of measurements
- Cost
- GFET sensors (high performance): wafer scale integration, others are possible without wafer scale integration (pick&place on fluidics and polymers reaches fM sensitivity with non-top quality graphene)
- Flakes/GO based sensors: reproducibility, adequate and continuous quality
- Noise due to liquid environment and biological media
- Body electrodes: graphene properties not good for stimulation.

4.5.4.3 Potential actions

If the area of graphene/2D in sensors is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

General:

- Build on SiC for particular applications (where current prices are acceptable or SiC can be used anyway as a substrate)
- Be honest with deficiencies, so that those can be addressed
- Carefully assess potential of graphene/2D materials in sensors and European economy on a more detailed level to find most promising applications
- Investigate long term properties, life cycles and stability of graphene/2D materials in sensors
- Determine full set of relevant KPIs (and not only e.g. sensitivity) to allow realistic and objective benchmarking with other technologies addressing the same functionality
- Demonstrate the sensors' functionality in relevant environments to create awareness of actual functionality

- Assess environment, health and safety properties for relevant applications (e.g. if food sensing or health is targeted)
- Investigate end-of-life properties if necessary for an application
- When developing demonstrators, keep manufacturability in mind (especially when addressing sensors that have already been demonstrated)

Magnetic sensors:

- Focus on manufacturing of hBN-graphene-hBN stacks
- Further investigate flexible solutions

Pressure sensors/microphones/NEMS

- Investigate multi-layer membrane manufacturing
- Investigate mechanical and thermal stability
- Benchmark with existing technologies, also for ultrasound applications

Nanogenerators

- Further explore tribological nanogenerators and other new types of nanogenerators (increase readiness level, demonstrate), keeping manufacturability in mind
- Benchmark with other technologies harvesting the same type of energy on the same scale to elaborate USPs

Chemical/gas sensors

- Show and investigate functionalization/surface chemistry for GFET and electrochemical sensors (manufacturing compatible): reliable binding sites needed (whilst keeping the graphene properties), find optimal trade-off between loading and functionality
- elaborate “toolbox” for functionalization
- Address specificity
- Improve contacting
- Investigate stability and long term performance (longer lifetime could outweigh higher cost)
- Demonstrate in relevant environments with full set of relevant KPIs and benchmark with other (existing and emerging) technologies addressing the same application and analyte (e.g. MOX sensors, other nanostructured sensors)
- Benchmark results with MOX sensors and other existing technologies
- Investigate multi-gas sensing capabilities/multiple sensor arrays
- Printed could also be a solution for lower price/lower sensitivity (gas/chemical/bio)
- chemistries need to be combined, calibration and safety issues cleared

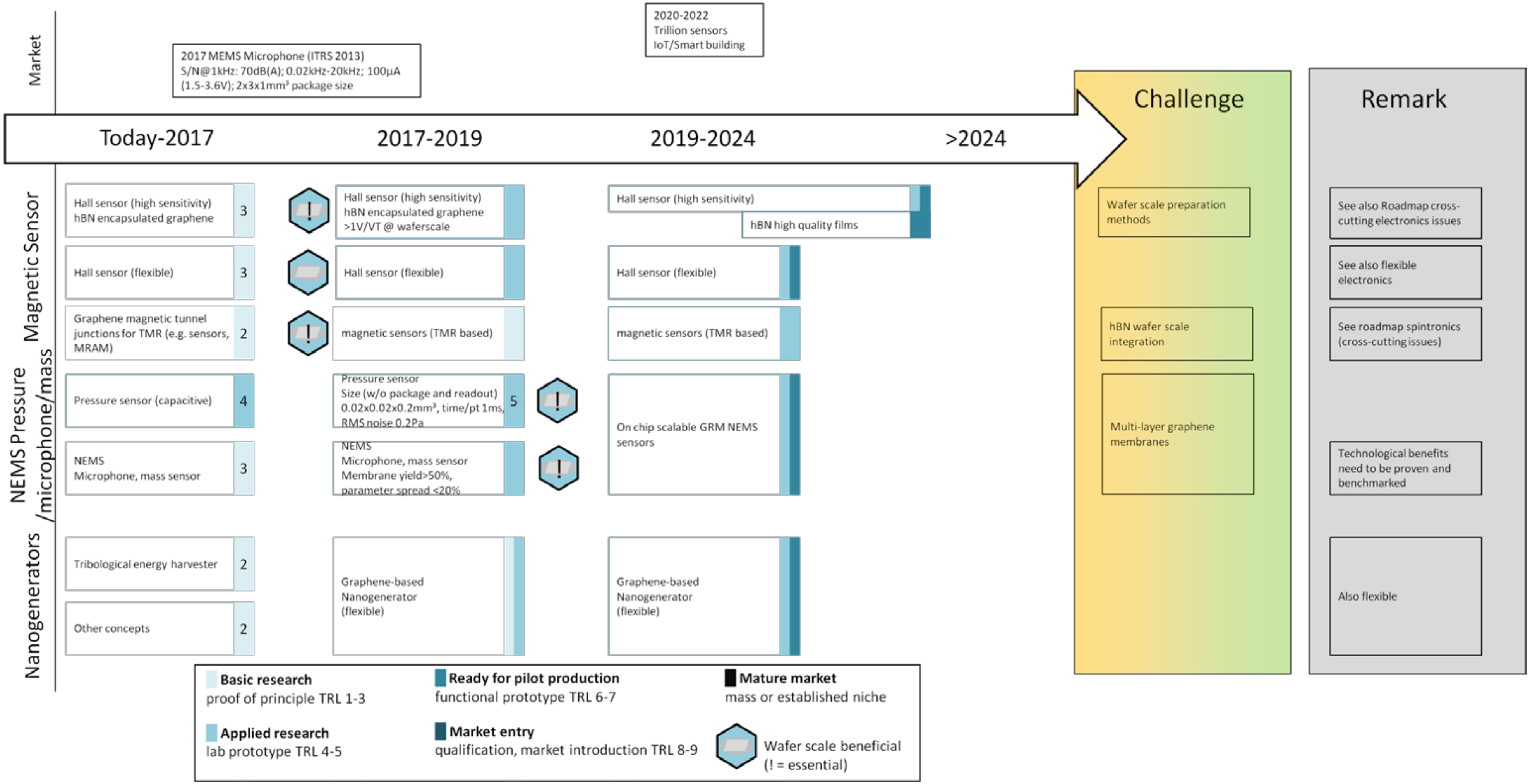
Biosensors

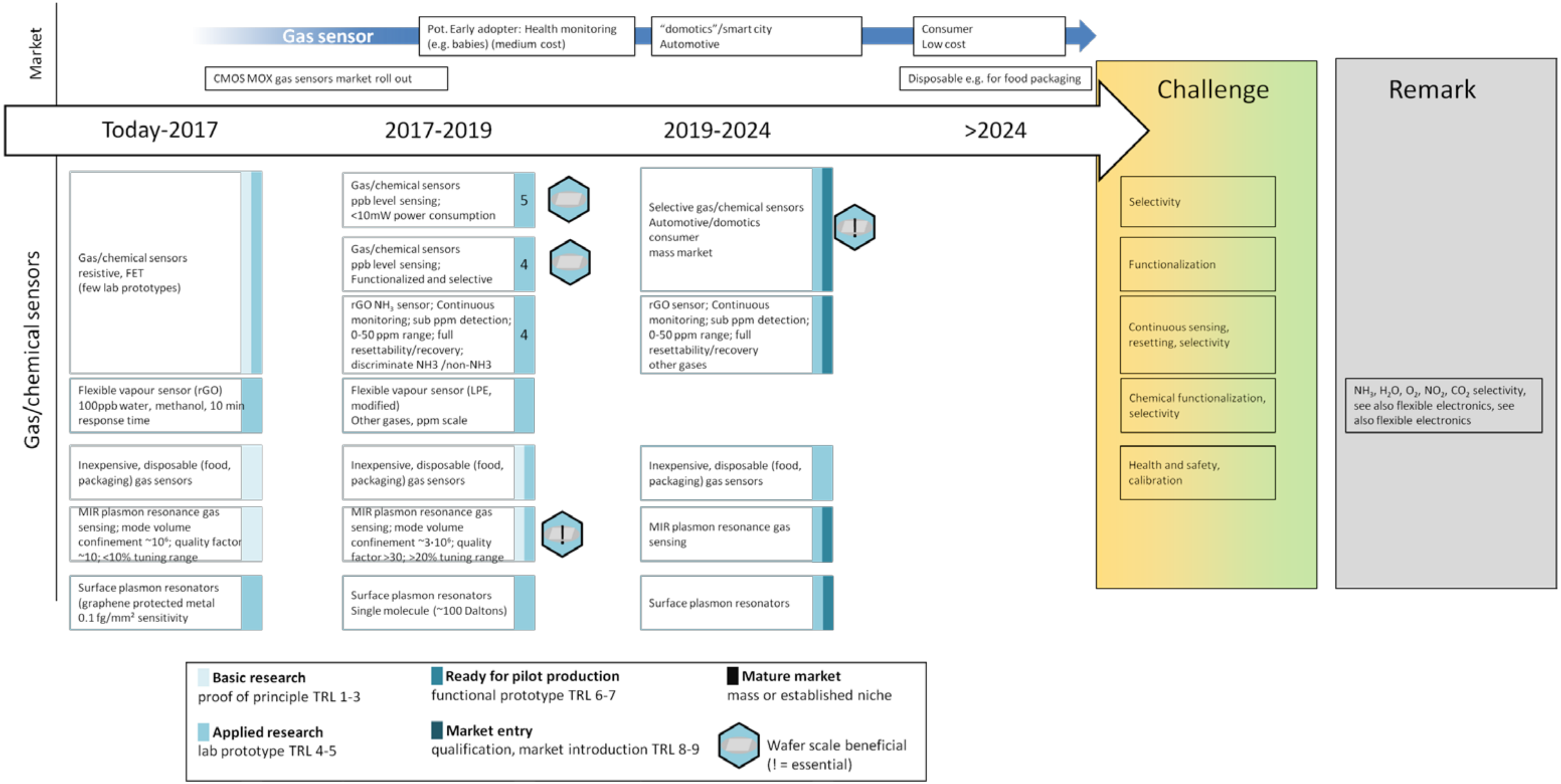
- Potential actions from gas/chemical sensors also apply for biosensors, with the differenc that biorecognition elements can be used
- Explore platform character of graphene for biosensors (toolbox of bio-elements)
- Demonstrate functionality on one promising analyte before screening too many
- Focus and benchmark with existing sensors (existing recognition elements) to proof the high performance and avoid additional costs; practically the same bioreceptors can be applied in all biosensor schemes, thus whatever is earlier developed, can be transferred to graphene when the platform is ready.
- Bioanalytics: At the present stage with a multiplicity of options for the use of graphene/GO in biosensing, it is important to focus on promising fields. Therefore it is recommended to use the already existing broad industrial basis in bioanalysis. Scientist

should engage in a dialog with enterprises to get information in which areas there is a high demand for effective bioanalysis

Determine full set of relevant KPIs for targeted application and benchmark with other technologies addressing the same functionality

4.5.4.4 Roadmap





Market

Gas sensor

CMOS MOX gas sensors market roll out

Pot. Early adopter: Health monitoring (e.g. babies) (medium cost)

"domotics"/smart city
Automotive

Consumer
Low cost

Disposable e.g. for food packaging

Today-2017

2017-2019

2019-2024

>2024

Challenge

Remark

Gas/chemical sensors

Today-2017:

- Gas/chemical sensors resistive, FET (few lab prototypes)
- Flexible vapour sensor (rGO) 100ppb water, methanol, 10 min response time
- Inexpensive, disposable (food, packaging) gas sensors
- MIR plasmon resonance gas sensing; mode volume confinement ~10^6; quality factor ~10; <10% tuning range
- Surface plasmon resonators (graphene protected metal 0.1 fg/mm² sensitivity

2017-2019:

- Gas/chemical sensors ppb level sensing; <10mW power consumption — 5
- Gas/chemical sensors ppb level sensing; Functionalized and selective — 4
- rGO NH_3 sensor; Continuous monitoring; sub ppm detection; 0-50 ppm range; full resettability/recovery; discriminate NH3 /non-NH3 — 4
- Flexible vapour sensor (LPE, modified) Other gases, ppm scale
- Inexpensive, disposable (food, packaging) gas sensors
- MIR plasmon resonance gas sensing; mode volume confinement ~$3{\cdot}10^6$; quality factor >30; >20% tuning range — !
- Surface plasmon resonators Single molecule (~100 Daltons)

2019-2024:

- Selective gas/chemical sensors Automotive/domotics consumer mass market — !
- rGO sensor; Continuous monitoring; sub ppm detection; 0-50 ppm range; full resettability/recovery other gases
- Inexpensive, disposable (food, packaging) gas sensors
- MIR plasmon resonance gas sensing
- Surface plasmon resonators

Challenge:

- Selectivity
- Functionalization
- Continuous sensing, resetting, selectivity
- Chemical functionalization, selectivity
- Health and safety, calibration

Remark:

- NH_3, H_2O, O_2, NO_2, CO_2 selectivity, see also flexible electronics, see also flexible electronics

Basic research
proof of principle TRL 1-3

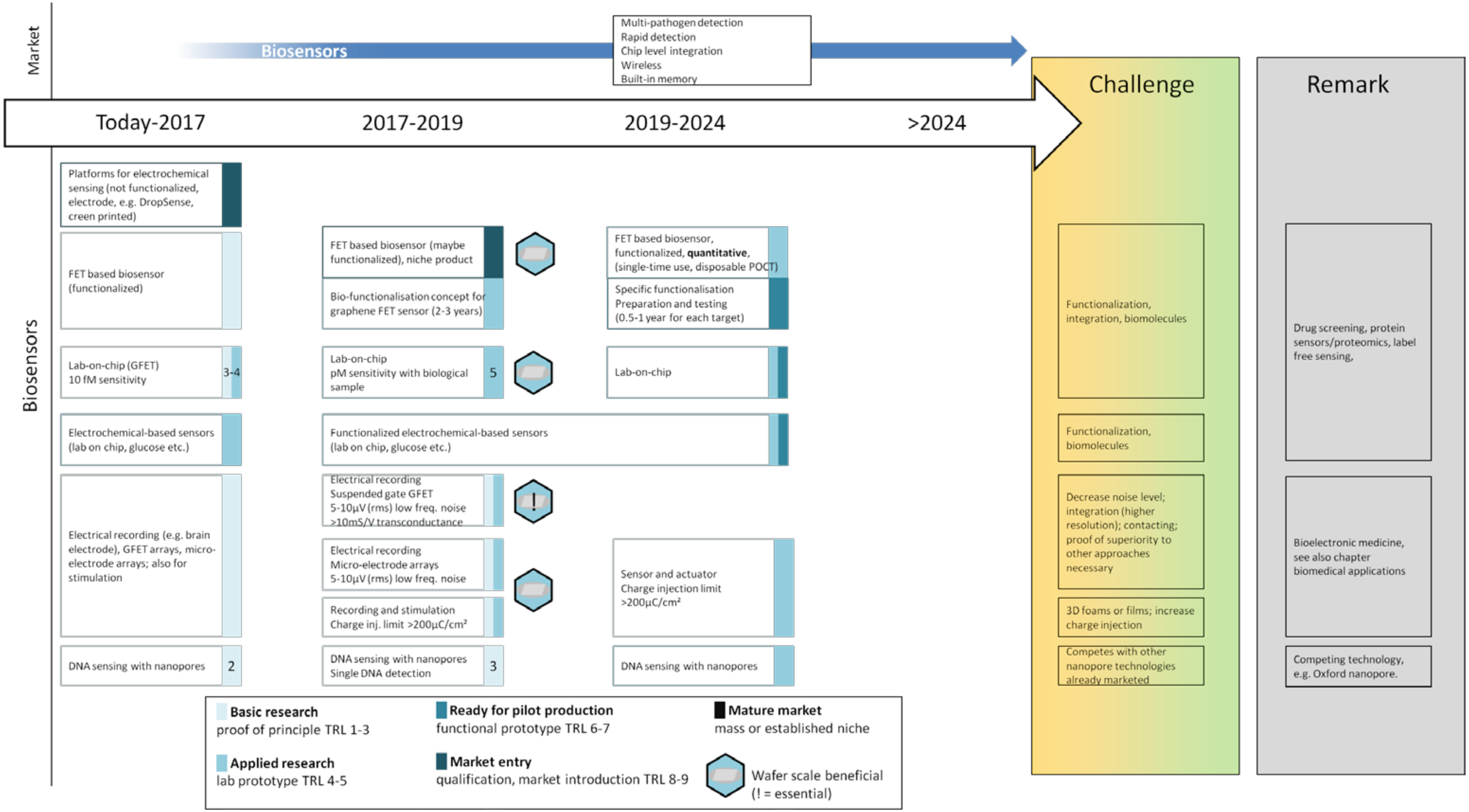
Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

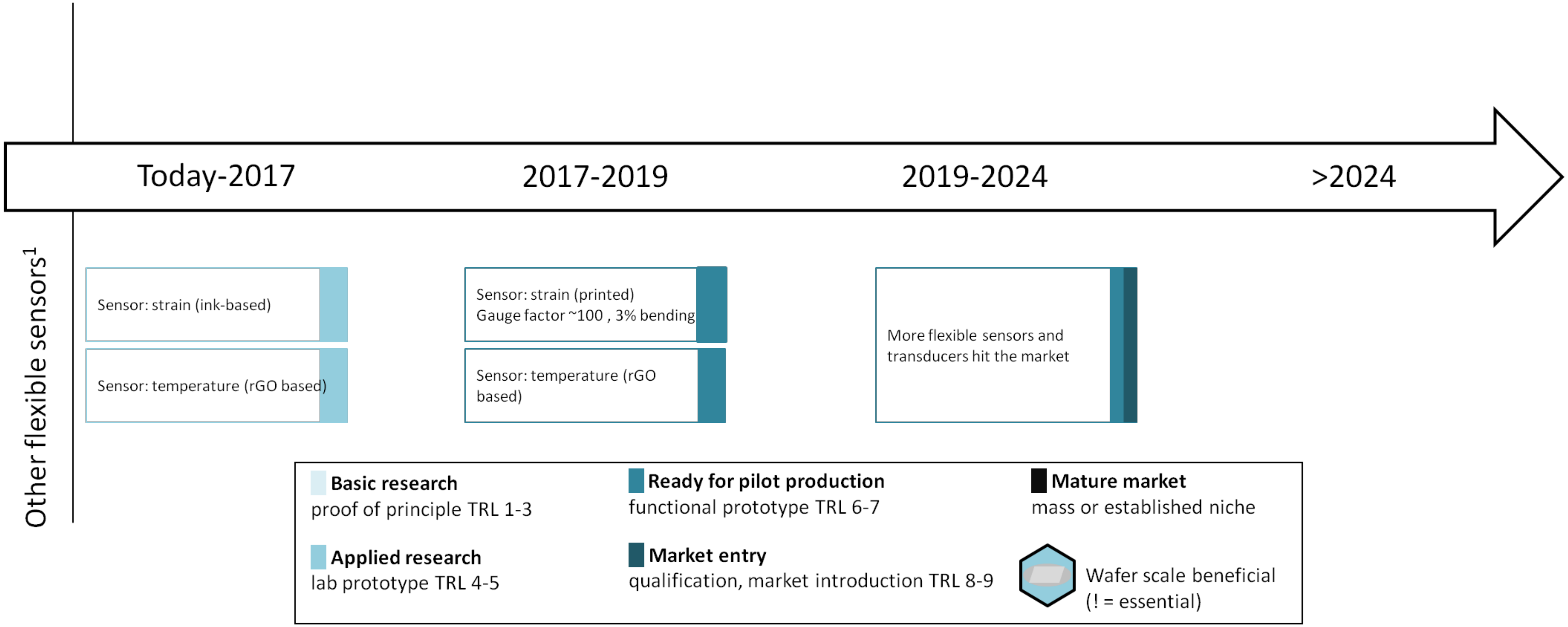
Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale beneficial
(! = essential)



See also biomedical applications and flexible electronics. Source for market: [353]



[1]: see also flexible electronics chapter

4.5.5 Conclusion sensors

The application area of sensors is a diverse field with many potential end user sectors. The integrated sensors market in general grows above average due to drivers like internet of things, industry 4.0, mobile electronics (wearables, health) or autonomous driving. All these trends demand new kinds of integrated emerging sensors or improvement and miniaturization of existing solutions. The market and potential technology integrators are very granulated, which on the one hand creates opportunities for niche applications and early market entry, but on the other hand creates difficulties in finding the applications where graphene and 2D materials actually can have a strong benefit. Besides, there are also important industrial players for sensors in Europe.

Graphene and other 2D materials can be used in different conformations in sensors, ranging from (r)GO or flakes to high quality films. The technological barrier is for sure lowest for flake-based technologies (e.g. strain sensors, some electrochemical sensors) compared to high quality films which usually require wafer scale integration and/or embedding in other materials (e.g. 2D boron nitride in the case of magnetic hall sensors). Due to the high fragmentation of the market, sensors is an interesting field for early commercialization. There are already first graphene-based sensors approaching the market in niche areas. However, other materials and technological approaches are also advancing, so that the overall competition of technologies is high and the USP towards these competitors or state of the art technologies needs to be clearly and objectively elaborated. In summary, the technological potential for 2D materials in sensors is there, although issues such as functionalization or production need to be resolved and the actual potential needs to be shown with commercially feasible production methods and in relevant environments.

Table 70: Assessment of market and technological potential of graphene/2D materials use in sensors on a scale - -, -, 0, +, ++.

Sensors	**Current technological potential (USP)**	**Market potential (EU perspective)**
Pressure sensors/microphones/ NEMS	0/+	++
Magnetic sensors	++	+
Mechanical force/stress/strain/ mass sensors	0/+	+
Gas/chemical sensors	+	+
Biosensors	+	++
Nanogenerators/micro-energy harvesters	0/+?	+

4.6 Flexible and/or printed electronics

This area deals with flexible and printed electronics (sometimes also called wearable electronics or large area electronics). It is a cross-lying area with elements from the other applications areas but with a particular focus on unconventional flexible/conformable substrates. Besides pure flexibility, stretchability is also increasingly important as a USP towards other technologies. In this chapter we refer to stretchability separately and consider flexibility only as the possibility to bend/flex a device. However, the overall term “flexible electronics” is defined to contain also stretchable devices.

This area covers:

- CVD/vacuum deposition flexible electronics
    - Transparent conductive films and touch sensors
- printed electronics and conductive inks

Typical applications of flexible electronics in general are

- Flexible conductors and antennas (e.g. NFC, RFID), printed circuit boards, also electrodes for bioelectronic medicines
- transistors for flexible ICs
- Flexible memory applications (in particular flexible resistive memory, RERAM)
- Flexible sensors and transducers, e.g. mechanical force/stress/strain sensors but also all other types of sensors
- Flexible displays

Flexible batteries/supercapacitors (see also chapters 0

- Batteries and 3.4 Supercapacitors for more general assessment)
- Flexible solar cells (fully covered in chapter 3.5 Photovoltaics)

For more general insights into the application areas, please refer to the respective chapters above on

Batteries (0), Supercapacitors (3.4), electronics cross-cutting electronics issues (4.2), telecommunication, optoelectronics and photonics (0), computing/logic (0) and sensors (4.5). This chapter treats only the flexible subset of the applications with a focus on the special opportunities, threats, strengths and weaknesses of graphene/2D materials when it comes to flexible electronics. This distinction is made because flexible electronics usually addresses different markets than rigid electronics and the requirements are also different. Of course it would be desirable to have flexible devices that compete with rigid devices in terms of performance. From a current technological perspective this is, however, wishful thinking and, if at all, a very rare case in the foreseeable future. Therefore flexible electronics will have an own market and will not compete with rigid CMOS electronics soon.

Uses of graphene and 2D materials in flexible electronics are summarized in Table 71.

In this chapter we will distinguish bulk graphene/2D-flake based (printed) electronics that can be used for antennas, conductors, as well as in sensors, and high quality graphene materials that can be used for sensors and logic and higher performing flexible electronics applications. This differentiation is especially important for the strengths and weaknesses.

Table 71: Uses of graphene/2D materials in flexible electronics

Application	Graphene/2D use	Recent review/ publication
Antennas (RFID, NFC), circuit boards, electrode	Flexible conductor, conductive ink, transparent conductive film	[507, 508]
Transistors	Channel material (e.g. GFET, TFT), electrode, for logic and RF transistors	[314, 509]
Memory	RERAM (resistive material as storage bit), carbon memory, tunnel memory	[510–512]
Sensors	Electrode for flexible electrochemical sensors, GFET, optical sensing elements, photodetectors, strain gauges, magnetic sensors, biosensors	[513]
Displays, OLEDs, photovoltaics	Transparent conductive film; PV is not addressed in this chapter but in chapter 3.5	[509, 514, 515]
Energy storage	Electrode material for flexible batteries/supercaps, nanogenerators	[516]

4.6.1 Market perspective: graphene/2D materials in flexible electronics

In 2014 products including flexible, organic and printed electronics with a value of $23-24 billion were sold with growth rates of more than 20%. The biggest product group are OLED displays, accounting for 2/3 of the revenues. The major pioneers in adopting flexible electronics technologies are automotive, consumer electronics/white goods, packaging/advertising and pharmaceutical and healthcare industries. More and more Flexible, lightweight and/or mobile products hit the market in these areas. [517] The market for printed and potentially printed electronics, including organics, inorganics and composites, will have grown to more than $26 billion in 2016 (see Figure 74) and is expected to extend to $69 billion in 2026. [90] The massive expectations from the early 2000s have not been met, but the technology is now approaching the plateau of enlightenment in the hype cycle and has become an actual growth industry, although it is still young. True mass markets only exist for OLED displays and healthcare applications right now. [90, 517] Besides displays, the largest markets are sensors and actuators, mostly healthcare electrodes, glucose strips, and conductive inks, mostly inorganic materials, all printed. [90]

However, flexible/conformal electronics still have a much smaller market of less than $10 billion (Figure 75) and printed electronics add up to $9.3 billion (Figure 76).

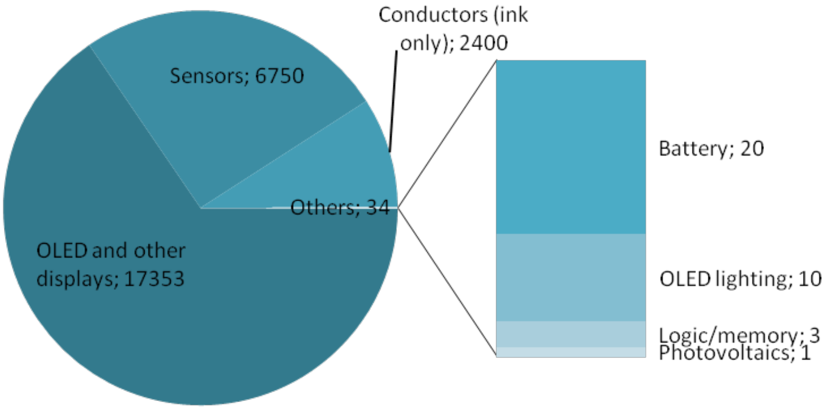


Figure 74: Flexible, printed and organic electronics markets by application, expected sales of products integrating the technology in million US$ in 2016. [90]

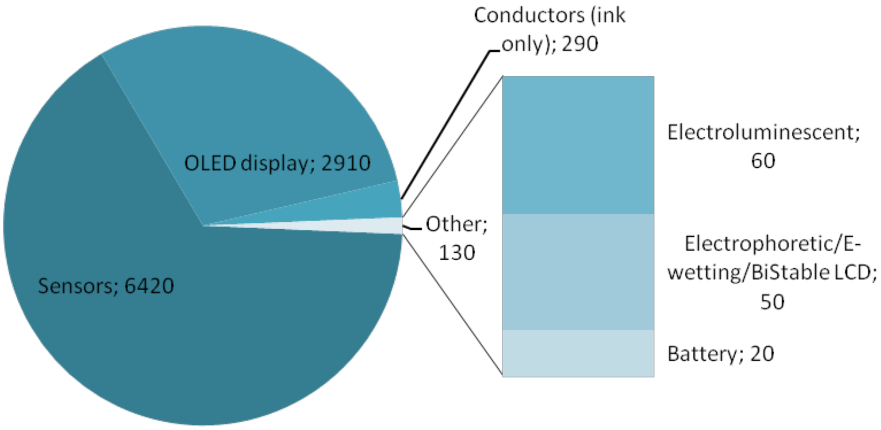


Figure 75: Flexible electronics markets by application, expected sales of products integrating the technology in million US$ in 2016. [90]

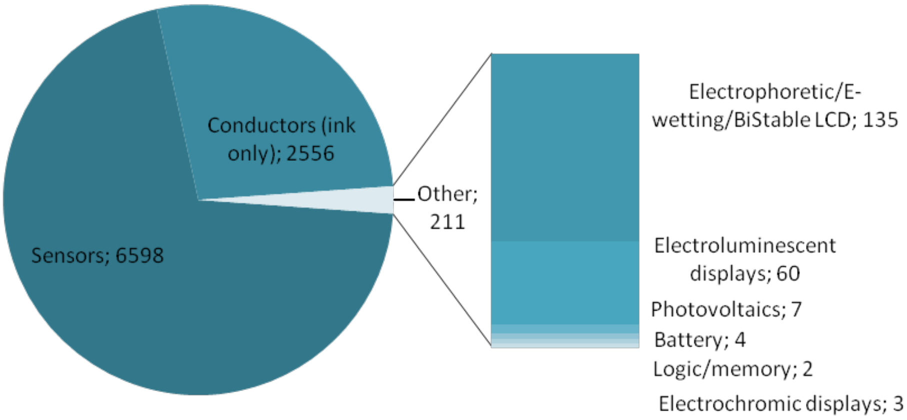


Figure 76: Printed electronics markets by application, expected sales of products integrating the technology in million US$ in 2016. [90]

Conductive inks

The conductive inks and pastes based products market is a multi-billion dollar market ($1.5-3.5 billion in 2016, depending on definition and source) expected to grow at a CAGR of 3-5% in the next decade. [90, 518–520].

The market is dominated by metal pastes, especially silver. Nanoparticulate pastes are approaching the market and become increasingly competitive, but will only get a small market share in the next 5-10 years. Largest applications are PV bars and automotive (e.g. window heater) and RFID. Antenna printing for mobile phones is increasingly interesting, i.e. 3D shape printing for better form factors. [519]

Transparent conductive films (flexible)

The market is expected to reach $1.2bn in 2025 at film level (for intermediate products, not including ITO on glass). It is dominated by ITO, but emerging solutions like silver nanowires (expectation $126m in 2025) and metal mesh (expectation $191m in 2025) increase their market share in the next years to cover ¼ of the market due to better processability and flexibility. [98]

Looking at all transparent conductive coatings, the market was ~$2 billion 2013 and is expected to reach $5.9 billion by 2020. Asia dominates this market with more than 50% market share, Europe only has 10%. [97]

RFID

The global RFID tags market is estimated at $4-5 billion in 2016. It has been growing rapidly in the last years (~29% CAGR). But growth is settling to 3-5% reaching a market of $7 billion in 2026. [519]

The RFID related markets (including tags, passive and active, readers and software/services for RFID cards, labels, fobs and all other form factors) are estimated to be ~ $10 billion in 2015 . It is projected to grow to >$13 billion in 2020 (CAGR >5%). The largest application markets for RFID are automobile/transportation (1/3). Healthcare & Medical is assessed to be the fastest growing end use sector until 2020 (CAGR of 21%) with a market share growing from ~1% to a few percent. [521, 522]

Sensors

The printed and/or flexible sensors market is estimated to be close to $7 billion in 2016 and expected to grow to $8-10 billion by 2020 (CAGR ~5%); dominated by glucose stripes (accounting for >95% of the market). Growth is driven by an increasing demand for printed/flexible electronic devices in sectors such as medical & healthcare, industrial and consumer electronics. [90, 523]

Looking at the markets beyond glucose sensors, a next generation of printed, flexible, and organic electronic sensors could enable new medical and athletic wearable devices. The market for those sensors is still open ranging from \$100 million to \$1000 million in 2024, the likeliest being ~\$400 million. The largest market at this time is expected to be a \$244 million market for wearables used by athletes and medical patients. This area is seen as highly interesting for new flexible sensors to successfully compete with CMOS sensors. Smart food packaging or monitoring store inventory accounts for another major part of \$117 million. The rest is made up of flexible sensors for transportation and building sectors. [524]

Logic and memory

There is hardly any logic/memory device printed and/or flexible at the market (excluding OLED transistor backplanes). The estimated revenue in 2016 is \$3 million, generated with mostly prototypes and demonstration samples and very few commercial products. It is expected to grow to \$240 million by 2026. It is not expected that it will compete with silicon at some point in the next 10-20 years. [90]

Flexible batteries and supercapacitors

The flexible battery market is estimated to be \$70 million in 2015 and expected to reach \$300 to >\$600 million by 2020 (CAGR ~53%). The packaging segment was leading the market with a ~30% share in 2014. Advancements in consumer electronics are expected to drive the market in the future. [201, 202] Flexible supercapacitors are also an interesting opportunity, as they are so far not commercially existing.

Wearable electronics

Wearable electronics are essentially all electronic devices that can be worn on the person. It is not a very precisely defined market or segment and therefore, the global wearable electronics market is estimated to be worth \$16-30 billion in 2016, depending on source and definition. Growth rates of 10-20% in the next years are expected and the market is projected to reach >\$100 billion in the next ten years. [525, 526]

Products are expected to shift towards high value wearable electronic products. Major applications are virtual reality, augmented reality/mixed reality devices, specialty medical devices and smart clothing / e-textiles. The value proposition for wearable devices in medical and healthcare is very strong and the sector is the largest at the moment. The growth rate is expected to be modest due to many new revenue opportunities. This segment is expected to reach over \$31.6 billion by 2026. Smartwatches and fitness trackers sales have increased rapidly since 2012/13, with the total market reaching over \$6 billion in 2015. The growth rate is expected to rapidly decrease so that there will be a market consolidation. [526] E-textiles were a ~\$100 million market in 2014 expected to grow to >\$ 600 million 2019. 1/3 of the market is addressed with electronic inks. E-textiles are mostly used for sports and fitness apparel. Japan and China are dominating the market. [519]

Smart packaging

The smart packaging market for electrical and electronic packaging excluding chemical smart packaging and RFID generated a revenue of ~$75 million in 2013. It is expected to grow to sales of $200 million in the next five years and then to >$1.4 billion in 2025. [90]

Actors

Europe is a major player for flexible electronics and many first movers come from Europe, also due to a strong political support. [90] The automotive industry as an important integrator of flexible electronics is also very strong in Europe. However, some other typical application industries and integrators (wearables, consumer products) are not in Europe.

4.6.1.1 Market Opportunities

4.6.1.1.1 Broad addressable markets for platform technology with many niches

Flexible electronics can be seen as a platform technology for new kinds of electronics products. Eventually, it could penetrate the whole electronics, lighting and power sector and thus address hundreds of billions of dollar markets. [90] Nowadays, there are several developments and emerging markets driving the need for flexible and lightweight electronics solutions, for instance Internet of Things or wearable electronics. The fact that a market is not yet developed can be an advantage for new technologies to enable it and push it forward. This is a huge opportunity for graphene/2D materials if they can provide lower cost, better reliability, functionality, processability and higher performance than other flexible electronics materials.

Flexible electronics address broad and versatile markets with many niches, e.g. logistics, smart packaging, brand protection, ticketing, advertisement, health, apparel, consumer electronics, energy, automotive. Applications can range from semiconductors/transistors, sensors to simple flexible conductors or flexible conducting layers for EMI/ESD (see 2.3 Industrial large scale coatings and paints). Flexible sensing elements, batteries or other functionalities have a large potential and functional flexible devices have higher value than just flexible conductors. New markets could also be created by enabling ubiquitous electronics in walls, fabrics or windows for the electronics industry towards the vision of “electronics everywhere”.

There are three possibilities how flexible electronics can be implemented: [90]

1. Replace a whole existing electronic / electrical product
2. Replace or do something simple in existing electronics/electrics
3. Replace nothing – create new products

Especially the latter demands new design rules.

There is no “killer application” for flexible electronics available, but the breadth of applications does not necessarily call for a killer application. It is a more likely scenario for this platform technology that market penetration increases incrementally in a variety of areas. [517]

The flexible electronics platform can provide integrated functionalities and the combination of different devices in one production on one substrate is very appealing and an important opportunity.[517]

The initial volumes of printed/flexible electronics products are low and address niche markets, e.g. special promotional items with volumes between several to max hundred thousand. [90] Mass markets do not exist yet, except for OLED displays for mobile phones. In recent years, however, it is observed that market penetration is increasing. The OEA expects strong growth in the coming years, depending on progress in the fields of material, equipment, processes and device design. Some of these areas still demand progress and even breakthroughs. [517]

4.6.1.1.2 Hybrid approaches are possible on short term

Especially in the short and medium term, hybrid solutions of flexible/printed parts with small and rigid silicon chips are a way forward and offer a great opportunity. For instance, a flexible sensor element, antenna, etc. can be combined with a small rigid silicon chip. This is essentially the principle of most flexible electronics products on the market at the moment, where the flexibility is used for the conductor and the actual electronics is rigid. This approach is expected to gain more interest as a primary path to further commercialization in the coming few years. [517] Especially flexible logic and battery applications are still way behind rigid solutions, so that those are nowadays and in the near future expected to be realized in a rigid format (coin cell battery and Si ICs) combined with flexible other elements (conductors, transducers). The biggest challenge there is related to the seamless integration of flexible and rigid electronics to have highest flexibility and in a commercially efficient and mass production compatible way avoiding manual steps (chip bonding, contacting, pick and place). [90]

4.6.1.1.3 Often lower performance requirements than for rigid electronics

The biggest opportunity for current fully flexible electronics technologies is where conventional electronics cannot be used, where e.g. lower requirements on performance (speed, quality of material, tolerances) are needed for ICs combined with high flexibility and ruggedness. Due to the flexibility, lower performance in some application cases is acceptable, because for instance other form factors and designs can be used. However, the business cases will be better, the better the performance. Lower requirements can be also achieved with organic semiconductors etc.

Silicon cannot provide low temperature processes, form factors, design options and CMOS performance on flexible substrates, which is why other materials such as 2D materials have a chance in replacing Si there. The question is how far silicon can take it in (partially) flexible electronics.

4.6.1.1.4 Flexibility and customizability as an added functionality

Flexibility is more and more acknowledged as an added functionality and a good selling proposition, especially nowadays with emerging IoT and wearables. The industry appears to be more and more open and realizes the value of flexibility. Other strength of flexible electronics are its thinness, potential for large area (interesting for e.g. sensors) and better integration into small sized products due to the flexibility in form factor. Printed/flexible electronics can actually deliver added values by realizing competitive advantages in terms of promotion and differentiation from other products and packaging. Besides that, completely new market opportunities are enabled by the technology. Flexibility offers more freedom of design and different form factors making new products possible (e.g. intelligent packaging). This even sometimes justifies premium pricing. [90, 517]

Further awareness creation of the real potential of flexible/printed electronics is needed and it is a matter of time to create a stronger market pull. There are already many end users who investigate printed/flexible electronics and invest money in research, prototyping and testing. But to actually convince internal selling and marketing, the arguments are mostly not good enough yet, e.g. because of too low volume or too high cost. [90]

For 2D materials and their combinations, the inherent functionality of flexibility combined with other functionalities (e.g. sensing, transparency, conductivity) is an opportunity to become part of the flexible electronics toolbox. For instance, the flexible transparency of graphene can be combined with flexible sensor elements from graphene or other 2D materials.

Customizability is also an important asset. Silicon electronics is usually only cheap when large volumes are produced (due to volume independent costs of lithography masks and equipment). Flexible electronics and printed electronics have the opportunity to be rather low cost also at smaller batch sizes.

4.6.1.1.5 Flexible electronics often good at lab scale but not on industrial scale

For flexible electronics there is often a gap between lab results and industrially relevant processed devices (e.g. p-type: 20cm²/Vs published for lab results, <5 cm²/Vs reached with industrially compatible process). This is on the one hand a threat, as lab results are not pointing towards real performances. On the other hand, it is an opportunity for graphene solutions, which might be able to perform similarly at lab scale and at larger scale.

Besides the performance it is very important that materials are improved in terms of processability, uniformity and stability, also including issues such as patterning. [517]

4.6.1.1.6 End-of-life and sustainability as a potential opportunity

Flexible electronics also offer opportunities in terms of sustainability. They address the trend towards green technologies and can offer sustainable production (e.g. low temperature, less material use) and eventually reduce the CO_2 footprint. [517] But the restricted use of chlorinated solvents or other hazardous materials is also important.

Besides flexibility and sustainability, organic, printed and flexible electronics can and in some areas (e.g. packaging) need to provide biodegradability, combustibility or simple recycling as USPs.

The sustainability is often not addressed, but companies demand sustainable products to improve the reputation and avoid being branded. Especially for batteries and Si chips, it is not desirable to send them to landfills. [90] Furthermore, some organic and inorganic electronics use rare materials (e.g. silver, or sometimes even rare earths). [90] Replacing these materials with more abundant (e.g. replace silver with copper) and proven environmentally friendly materials is a wish from industry.

Therefore it is a good opportunity for 2D materials to address the sustainability and end-of-life properties as additional USPs. Using non-chlorinated solvents and no rare or harmful materials during production can thus be an opportunity.

4.6.1.1.7 No dominating material for flexible electronics identified yet

Although there are many competing materials (see threats) for printed and flexible electronics, there is no clear winner at the moment. There is still an important need for new materials to improve overall performance, life time, encapsulation, efficiency and frequency [517].

4.6.1.2 Additional market opportunities: printed electronics and conductive inks

4.6.1.2.1 Conductive inks market exists and grows

The conductive inks market is a several billion dollar market (2-3b$ per annum). It is dominated by metal inks, especially based on silver (silver pastes had an overall market of ~$2.7 billion in 2013, this includes not only the flexible applications [90]). Conductive inks can be seen as a platform technology with broad range of applications, such as sensors, flexible conductors/interconnects, antennas (RFID, NFC), heaters, etc. 1/100Ω/□ sheet resistance are necessary/sufficient for a broad usability in most of these applications.

The greatest short term opportunity lies in the applications that currently are addressed by carbon inks or where silver inks over perform. Additional cost savings are possible when just one print is needed instead of e.g. 5 to reach the desired conductivity.

Conductive inks can be easily integrated into existing productions if the ink formulation is tailored to the need. Large volumes and simple processes are possible and in contrast to silver, graphene offers the potential to be disposable (combustible).

4.6.1.2.2 Developing printed electronics market

The printed electronics market is currently developing. Printed electronics address the need for low cost/lower performance flexible products in IoT, smart sensors, embedded energy harvesting etc. More and more products enter the market in various application areas and the industry approaches a phase of realistic growth and with significant revenues. [517] All printable electronics is already a well-designed niche.

4.6.1.2.3 Disadvantages of dominating metal inks or carbon inks

Typical metal-based inks, especially the widely used silver flake inks and pastes are rather expensive and suffer from corrosion problems. They usually also demand higher temperature annealing steps. Lower temperature processes are sought for, e.g. for automotive polycarbonate windows. Furthermore, the end-of-life properties are not very good and there is a need for metal-free conductive materials being recyclable, environmentally friendly, sustainable and corrosion resistant. But they are very well conducting, the basic functionality of a conducting ink. There is, however, an opportunity to address and replace silver-inks with graphene enhanced inks, in applications where silver ink is too expensive and “too good” or in corrosive environments.

Besides, carbon inks cover the other side of the spectrum, being corrosion resistant and cheap but offering a much lower conductivity.

The largest opportunity of graphene-based inks is in the space between silver inks and carbon inks, where it can be well suited in terms of cost and conductivity. Furthermore, graphene-enhanced carbon inks can lead to cheaper processing when you have to print once instead of 5 times to reach the desired conductivity.

Last but not least, a transparent graphene-based conductor without CVD could be a huge opportunity (e.g. based on printing).

4.6.1.2.4 Conventional printing as a large opportunity

Especially in packaging and advertisement, there is a need for cheap solutions compatible with standard print markets, so that the existing print industry and equipment can be used.

The good scalability of printing processes and the roll to roll processes offer large volume and simple integration of inks.

4.6.1.2.5 Additive manufacturing and 3D printing synergies, in-mold electronics

Another important trend that can be addressed by conductive inks is additive manufacturing/3D printing. Using different printing processes (e.g. stamp/aerosol) 3D objects can be coated with conductive layers and functionality can be added. Furthermore, printed and flexible electronics can be used for in-mold electronics, a more and more pursued way to integrate electronics on complex 3D objects.

4.6.1.3 Additional market opportunities: high quality 2D films for flexible electronics

4.6.1.3.1 High performance flexible CMOS currently not possible with available materials

Higher performance flexible CMOS is not possible with existing flexible n- or p-type materials, as no flexible semiconductors reach the performance of bulk semiconductors. This is an opportunity to fill this gap with 2D semiconductor materials. However, for instance graphene is not well suited for flexible logic but rather for flexible sensors and optoelectronics. But other organic semiconductors are also improving and CNTs are also suitable for flexible applications, so that the possibility is not unique and the race for the best materials is still open.

So far there is no reproducible processable semiconductor for flexible substrates achieving CMOS compatible performances. The search is especially ongoing to find a reproducible and processable n-type semiconductor which can be used together with p-type materials. [517]

4.6.1.3.2 Higher performing flexible sensors

There are hardly any high performance sensors on flexible substrates (hall, photodetectors, gas sensors), so that there is a potential opportunity to address these markets, where flexibility is of great importance.

4.6.1.4 Additional market opportunities: flexible (resistive) random access memory

4.6.1.4.1 Potential low end market, e.g. for smartcards

There is a potential market for non-volatile, cheap and low storage capacity markets, e.g. on smart cards or for packaging. This low-end market addresses new smart cards, maybe disposable products, health and point of care cards. These application only need ~80kB storage capacity.

4.6.1.5 Additional market opportunities: flexible batteries and supercapacitors

4.6.1.5.1 No satisfying solutions available yet, batteries a major problem for miniaturisation and flexible devices

Flexible batteries only exist in niche markets. They suffer from limited capacity and large footprints due to the limited energy density and existing material systems. Furthermore they have lower power density, higher degradation and costs compared to coin cells. [527] Therefore, flexible batteries are in need of new concepts and materials to become competitive and interesting for a broader market.

Supercapacitors are not available in conformable versions. If they can compete with batteries and reach high enough capacity and low self-discharge, supercapacitors or hybrid solutions with flexibility could have an interesting business case.

4.6.1.5.2 Interesting add-on in conjunction with other flexible devices: Interesting battery business case for Europe

Electronic devices are getting smaller, thinner and lighter and along with that the need for smaller and conformable power sources increases. Thin, flexible and printed batteries are a missing piece for smaller and flexible electronics. [90]

The trends in wearable technologies, medical/fitness devices and internet of things demand small/thin batteries with special form factors as energy sources (in conjunction with nanogenerators).[527]

For developers of flexible electronic devices (e.g. senors, antennas, etc.) it is interesting to also pursue the development of flexible batteries, although batteries are not necessarily the core business. This could eventually allow the production of a fully integrated device including a power source. Thus, although the battery/cell market is highly dominated by non-European actors, flexible batteries can still be an interesting field for Europe.

4.6.1.6 Market Threats

4.6.1.6.1 Strong players and industrial basis, especially for consumer products, mostly not in Europe

Major markets and industrial players for consumer products are currently in Asia (Samsung, LG) and US. The strongest European application industry is by far the automotive industry, but also more general sensor applications (e.g. in healthcare, machinery and special electronics) are relevant.

4.6.1.6.2 Conventional electronics seen as competitor

Conventional electronics also address wearable, portable and cheap applications. Although not flexible, very small rigid chips perform well in electronic and can be integrated into fabrics or other flexible devices just because of their size. These standard electronic chips usually set the standards and expectations in terms of cost and performance. The further miniaturization make them a moving target finding their way into more and more “flexible” applications and there is and will be a competition between truly flexible and conventional electronics, despite the lack of conventional electronics not to provide actual flexibility and performance at the same time. Conventional electronics build on a large and existing industry. For truly flexible electronics a new infrastructure, new designs, new products and new markets are needed, which increases the barrier to switch to this technology. It is also a matter of awareness and acceptance. [517] Currently it is hard to find an application which cannot be realized with standard semiconductors. In this case it is less flexible but still lives up to its purpose.

A way forward is the hybrid integration which combines the benefits of both approaches. Conventional silicon will be used combined with flexible electronics parts (e.g. sensor and antenna printed/flexible, readout and data processing in a standard silicon chip. [90] The goal is not to replace functionalities that are easier, better and cheaper made with silicon electronics (ICs), but rather add flexible functionality in form of a flexible conductor, sensor or antenna.

4.6.1.6.3 Competition of materials and technologies remains high – many different technologies under development

Flexible electronics is not seen as an established technology and is still often compared to silicon, although silicon is not really a competitor in terms of flexibility and performance at the same time. Still, silicon is often used in applications where true flexibility might be valuable but is neglected due to the availability of small silicon chips (see argument above). Or lower performing partially flexible amorphous or poly-silicon implementations are used.

Although flexible electronics is not yet an established technology, there is also competition with and between other (more mature) not Si-materials (organic semiconductors, CNT, nanowires, etc.). A clear winner is not yet seen and will probably not be, as different materials have different strengths. There is a wide range of other materials available that can increase performance and open chances in high performance applications.

Low performance and high flexibility can be also achieved with other materials, which have been under investigation for a longer time, are more mature and have not yet enabled the flexible electronics market to flourish. But the mobility and performance of organic semiconductors still increases and approaches levels to be competitive at least with poly-Si. [517]

4.6.1.6.4 Juvenile market of printed/flexible electronics and credibility gap

Although organic and printed electronics has become a growth industry with significant revenue, especially due to the OLED business, [517] and there are various flexible products on the market, the market has not picked up considerably. Conductive inks, sensors and displays are markets were some stakeholders can already work profitable. [90] It needs to be clear that the market is still juvenile, emerging and volatile, and that market and technology expectations are based on assumptions and uncertainties and only a short record. [517] In particular the market is not yet living up to its promises and expectations, which scares off investors and leads to a lack of strategic investors. This can be summarized in a credibility gap which needs to be narrowed. The technology and market were expected to improve faster, but still fail to live up to these expectations. [90]

4.6.1.6.5 Performance, lifetime and reliability perception

The credibility gap exists in market and technology expectations. The common perception of poor performance of flexible electronics changes slowly. Demonstrators are needed that show that it actually works and can live up to the expectations. And still then it is a long way until the credibility gap is fully closed.

Other concerns are related to lifetime and reliability. The lifetime problems are to a great extent solved and often not an issue, especially when the business case is tailored for the lifetime expectation of the device. Absolute reliability is very important for credibility. [90]

Until the credibility gap in terms of performance, lifetime and reliability can be closed technological breakthroughs are still needed in processes, encapsulation, materials and standards and regulations. Especially the poor availability of low cost, flexible encapsulation is a major threat to address lifetime and reliability issues for organic electronics. [517]

4.6.1.6.6 Solely low cost promise dangerous

Especially printed electronics is often promoted with being cheap. This might also eventually become true but initially this is a problem, as it is often a challenge for a new technology to only compete or enter via lower cost promises. The first market entry usually is only possible with higher cost and higher prices and costs come down with time and development until cost competition is achieved. In some cases higher costs for first generation low volume products are unavoidable [517], so that the technologies need to deliver an added value that customers are willing to pay for (adequate cost-performance, where performance also related to the added value proposition, e.g. flexibility). Lower costs are more likely to become a USP for a more mature technology that has already entered the market in niches where the higher prices are paid for a USP. When costs are decreased new markets can be opened up with the cost argument.

4.6.1.6.7 Sustainability and health and safety perception and concerns

Companies demand sustainable products as customers and regulation more and more demand them. They for instance wish to avoid sending coin cell batteries and Si chips to the landfill. [90] So sustainability of flexible electronics needs to be proven and can actually be turned into an added value.

Especially for nanotechnology products, the perception of integrity/durability and environment, health and safety are important issues. For graphene, the toxicity is often perceived similar as CNT, although this is potentially not true. To avoid the threat of being perceived as toxic, it is best to address it openly and pro-actively. Health & safety concerns especially regard the release of graphene, contact with graphene, handling in production and solvents used. Measurements of release and possible exposures are needed. In particular if the material is used for health and wearable products which are in direct contact with the environment or body, or even body fluids, a safety assessment is needed.

4.6.1.6.8 New value chains needed and not yet established

Although truly flexible and organic electronics address similar products as conventional electronics as well as completely new products, the value chain is different and is not really fully existent yet. This is especially the case for printed electronics. Current supply chains for flexible electronics are diffuse and exist in niches (besides the established ones for OLED). The existing value chains are strongly push related with not so much pull from users. [90] To fully exploit the potentials of flexible electronics in general, creative design companies need to get involved and the industry needs more exchange with end users. [90] Most importantly there is a lack of integrators. End users see the potential benefit of flexible electronics but do not want to become integrators themselves. Instead, they rather want to buy simply integratable components, prototypes and solutions. This shifts the development work to integrators. [90] Besides, different parts of the value chain are at different maturity levels and there is no overview of European actors in the flexible electronics area and their capabilities.

To support the innovation to market process, these challenges need to be addressed for the overall industry (independent of graphene). This, however, is not only a threat to 2D material's role in flexible electronics but also an opportunity, as the space is still open for new (venture) companies and SMEs to address and establish new markets [517]

Standards are also related to the establishment of a reliable supply chain needed to address large and regulated markets (such as automotive or healthcare). The different quality and variety of available materials (for all applications) calls for common standards. It is still an open challenge to develop standards suitable for organic electronics. [517]

It further appears that there is an imbalance between “front end” and “back end”. There are many effort to produce flexible components, but the assembly (e.g. pick and place, flip chip), contacting and packaging as well as quality control is not addressed likewise. This can especially be a cost driver and outweigh a potential cost advantage of for instance a printing process.

4.6.1.7 Additional market threats: printed electronics and conductive inks

4.6.1.7.1 Conductive inks market complex and competitive

The conductive ink market is an established, complex and competitive market dominated by metallic inks and pastes. Depending on the needs of an application (conductivity, cost, production method, substrate) many different materials are used in inks. Besides the high performance and high cost silver flakes there are conductive inks from carbon, CNT, copper, conductive polymers (e.g. PEDOT:PSS) and metal nanowires and –particles. Finally, the inks also compete with other technologies, such as sputtered metals. Copper inks are seen as an emerging competitor to silver inks having a similar maturity as graphene inks. For flexible applications it is most important to have a preparation which does not need high temperatures.

Customers usually do not care which ink is used, as long as the functionality and cost/performance is adequate, as it does not change the experience of the product. Benefits and arguments for a particular technology can be (besides the performance and properties in the product) in the production process, e.g. when a single coat is needed instead of multiple coats. Therefore customers will not buy an ink because it is made of graphene, but only because it is better suited and functional in the addressed application.

Another threat is that printed electronics might be too complicated, which increases the barrier for usage. In reference [90] an example is presented where a packaging company needed more than 40 additional production steps to deposit a fully printed light with a switch on corrugated cardboard.

4.6.1.7.2 Low cost applications addressed: difficult entry scenario for a new technology

Printed electronics usually addresses low cost applications, where also a poorer functionality is accepted. Systems can be very simple but they must be cheap. Thus, the product needs to be low cost high volume, to be more than a nice to have. Some applications require costs of a few cents (e.g. in packaging). So the cost constraints are substantial. However, printed electronics remains expensive despite cost being the main potential attraction. [90] But it is hard for a new technology to enter a market only via cost arguments, as it is usually not easily possible to come up with a large scale very cheap product in the first place. The profit margin of those applications is usually low and a very high volume is needed to become profitable. Therefore, the USPs of graphene-based inks need to be seen as a whole and potential future cost reductions is only one amongst them. If product cost will be decreased in the first place, it will most probably be via production cost or reduced cost of ownership (e.g. less material needed, less coating steps), etc.

Competing technologies addressing similar applications are also very cheap, e.g. a silicon RFID chip can be made for 1 cent. This is a threat and prohibits new technologies in these markets. [90] Also the RFID antennas made with aluminum are very cheap (less than one cent per inlay), but suffer from sustainability issues.

It is therefore more likely to be successful in areas where the added functionality (e.g. corrosion resistance) is paid for and the other applications can potentially follow afterwards. It appears to be more promising to focus on customizability in conjunction with lower cost, rather than mass production and lower cost (see opportunities). Another area where printed devices can find particular niches with USPs is the flexible sensors area.

4.6.1.7.3 Perception of 2D materials in printed electronics

Graphene-based inks are currently seen as a slightly better but more expensive carbon ink. Some actors perceive that graphene material inks will not be a game changer for printed electronics at the moment, as the added value of GRM is not yet clear. The printed electronics expectations for graphene are not so high, as the USPs are somewhere between silver and carbon.

It needs to be made clear, that graphene material inks at the moment should not be seen as drop-in for high performing silver inks in terms of conductivity. If this is not the case, it is a threat that graphene does not fulfil the expectations. They, however, can have a USP where for instance corrosion resistance is more important than conductivity.

4.6.1.8 Additional market threats: high quality 2D films for flexible electronics

4.6.1.8.1 Competition with rigid electronics

High quality films particularly compete with small footprint rigid electronics (see also 4.6.1.6.2 Conventional electronics seen as competitor).

4.6.1.8.2 TCF competition: strong incumbent, markets and players not in Europe

The TCF market is dominated by Indium-Tin-Oxide (ITO). Where lower cost, higher thermal and chemical stability is needed, fluorinated Tin-Oxide is the material of choice. China, Japan and the Republic of Korea are the world’s major ITO producers and user, mostly due to the display panel production. The TCF technologies for ITO and FTO are very established and used since many years. A new technology needs to fit into the current production process so that it can be taken up in the nearer future. The price of ITO depends on the indium price, which was fluctuating but not heavily increasing in the last 10 years. Increasing prices will lead to increasing drivers for new materials.

There are upcoming novel materials besides graphene, e.g. metal meshes, nano-wires or CNT. However, ITO is expected to remain the dominant materials used for at least the next decade, followed by metal mesh and silver nanowires.

For TCFs transparency and optical properties, conductivity (low sheet resistance), etchability (property to allow simple patterning), price and substrate/flexibility and for OLED/solar cells efficient charge extraction/injection across the electrode/organic interface are very important aspects.

A major drawback of ITO is the poor performance on flexible/conformable substrates and the optical properties. All new technologies therefore also address the search/need for ITO replacement with this added functionality of flexibility or optical properties (e.g. lower reflectance). Although a TCF application of graphene has been already demonstrated (Wuxi [528] and Chongqing Morsh Technology), it is still not clear whether the potentially graphene-based TCFs are commercially viable. Due to the advancement in other competing new technologies in terms of cost/performance and the current lower levels of conductivity in graphene, graphene materials might come too late for TCF (narrowing window of opportunity). All in all, graphene based TCFs are more likely to be successful in flexible or stretchable applications (see chapter 4.6 Flexible and/or printed electronics) or as additive for enhancing other TCF technologies, or in certain niche application such as UV-LEDs (see box on page 287)

However, there are rumours that graphene TCFs might be used in OLED displays due to an optical advantage. [529] The potential use in OLEDs is also matter of research of a EU project GLADIATOR. [530]

Besides, the major player for TCFs are not in Europe, so only for particular niches there might be a chance to gain ground in this market. Another opportunity is to license technologies to the major manufacturers.

4.6.1.9 Additional market threats: flexible (resistive) random access memory

4.6.1.9.1 Competition with other materials and low end markets require very low cost

The flexible resistive memory is also possible with other nano-carbon materials and the material will succeed which offers the best performance with a low-cost process.

4.6.1.10 Additional market threats: flexible batteries and supercapacitors

4.6.1.10.1 Flexible batteries are on the market

There are already thin film flexible batteries on the market, even with a nano graphite material. However, the market is not yet profitable and the batteries are only successful in small niche applications. Still, the maturity of existing thin film batteries is higher. But graphene could be used as an additive to improve the performances enabling to address new markets.

4.6.1.10.2 Coin cells are mature, small, cheap, have higher power density and are broadly used

Coin cells or button batteries are a success and hundreds of millions of these batteries are used in many applications from gift cards, active RFID tags, hearing aids, wristwatches to car keys and calculators. Laminar and flexible batteries are only used, where the need for thinness and flexibility is extreme. But in most cases coin cells are used, eventhough thinness would be desirable. An important reason for that is the much higher cost for thin film batteries compared to coin cells as well as the poorer performance, reliability, etc. [90]

4.6.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in flexible electronics

4.6.2.1 Current strengths for graphene/2D materials use in flexible electronics

4.6.2.1.1 Multifunctionality and intrinsic flexibility as a key proposition for flexible electronics

2D materials are ultrathin bendable materials with charge carrier mobility larger than in most other materials already available (>40 $cm^2 V^{-1} s^{-1}$). [438] They can be printed as inks, usually made from LPE/GO flakes leading to lower performance devices, but much simpler to produce and apply, even on large area; and transferred as high quality films, leading to higher performing devices but with the problem of a much more sophisticated transfer and preparation.

The intrinsic flexibility and stretchability of 2D materials is a major USP for flexible electronics. Although for printed and bulk-material based devices the boundary between flakes, the binders and ink formulation are determining the performance under binding to the larger extent.

Besides the electrical properties and intrinsic flexibility, 2D materials offer additional functionalities, such as amphiphobicity, (anisotropic) thermal/electrical conductivity, barrier, anti-reflectance, corrosion resistance. This multi-functionality makes the material class very interesting for flexible electronics. Especially the combination with the barrier properties is very interesting for combination with other flexible electronics. Bio compatibility (with environment, tissue and body) and end-of-life properties, in terms of combustibility and environmental compatibility, of graphene could be also beneficial. This, however, needs to be shown for the different material types and flake sizes.

Furthermore, functionalization offers an additional degree of freedom in particular interesting for printed/flexible sensor, batteries, etc.

Especially where the combination of the different functionalities are required, a unique added value and competitive advantage could be generated that might actually justify the initial cost. For instance, transparent conductive surfaces have been achieved with tunable wettability. [99]

4.6.2.1.2 First demonstrators are promising and first products are entering the market

Especially graphene flake and GO based applications are already quite mature. Conductive inks are on the market (Sigma, Vorbeck) and lie between carbon and silver inks in terms of conductivity.

The potential of graphene for flexible electronics is shown in the lab (proof of principle devices) for sensors, antennas, conductors, etc. Issues such as degradation on flexible substrates are already addressed. First tests look promising but a full investigation of degradation is pending. The graphene flagship is developing a toolbox of technologies and processes for a GRM flexible electronics platform.

There are even first devices based on conductive inks (antennas, RFID, glucose sensors) announced to come to the market soon. The devices that are already on the market are, however, no blockbusters yet.

4.6.2.1.3 Printing or CVD are possible: wide range of applications

Depending on the requirement of an application, graphene and most other 2D materials can be used either as flakes in inks, transferred high quality films or in best case low temp CVD grown. Also the compatibility and use of both types of graphene/2D materials (ink/flake and film) in a device should be possible and might be interesting for integrated devices.

The transfer of lab results to industry-scale and compatible processes is not fundamentally problematic, but improvements need to be achieved. Especially for high quality films, the wafer scale integration assessment is valid (4.2 Electronics: Cross-cutting issues).

Cost could also be eventually a USP, as lower temperatures are needed and a higher yields are possible with time and increasing efforts.

4.6.2.1.4 Electronic, thermal and barrier functionality at the same time: addresses needs for most flexible electronics materials

Flexible electronics usually need encapsulation and barrier materials. Graphene and 2D materials can be an active component and a barrier at the same time. This added functionality is an interesting property of graphene, although the preparation needs to be cheap enough, because especially for encapsulation the price pressure is usually quite high. Using graphene as barrier and e.g. electrode might relax the cost constraints a little bit, as additional steps can be avoided. Still, large scale high quality graphene transfer would be needed or the ink film quality needs to be good enough to avoid edge effect or impurities that reduce the properties. Also 2D materials such as hBN can be used for encapsulation without electrical conductivity, see 2.3 Industrial large scale coatings and paints for more information on barrier materials.

4.6.2.2 Additional strengths: printed electronics and conductive inks

4.6.2.2.1 First marketed inks available based on graphene

First graphene based inks are commercially available on the market (e.g. from Sigma Aldrich or Vorbeck). They perform better than common carbon inks in terms of conductivity and already now have a better price point than metallic nanowires and silver inks.

4.6.2.2.2 Filling the gap between carbon and metal inks in terms of price and performance

As mentioned above, graphene bases inks are cheaper than metal inks but also have lower conductivity. The inks are positioned between metal inks and graphite inks (in terms of performance and price). The business idea is fill the gap between carbon and silver/other metal inks and to replace metal inks as a cheaper alternative, where metal over-performs but graphite inks under-perform. They are also better than conductive polymers and directly competing with CNTs and metal nanowires. Thus, for this space between graphite and metal inks, graphene inks are one out of a few in terms of uniqueness.

Current graphene material based inks are ~30% better than carbon inks, but will never be as good as silver inks, which is also not the goal. The flexibility/stretchability is better compared to metal and carbon inks.

In terms of prices, silver inks are about one order of magnitude more expensive already today (~200-1000€/kg depending on density and quality). Carbon inks are priced at 40-45€/kg plus the cost of some 5% graphene. Usually at least 3l are needed for a large scale printing process (to also account for dead volume). Besides, less process steps might be needed when silver is replaced which can lead to additional benefits.

However, the question is still open to which extent this area in between metal and carbon inks is economically interesting. This needs to be further investigated before it is clear whether this actually is a strength.

4.6.2.2.3 Additional USPs: corrosion resistance and chemical resistance

The USP of corrosion resistance is very interesting for graphite and graphene based inks, as silver inks are usually prone to degradation and corrosion. So graphene does offer something that cannot be offered by another material, i.e. chemical and corrosion resistance similar to graphite but with a higher performance. Therefore graphene inks might be especially interesting where combination of these properties is needed and a better conductivity than graphite inks is desirable.

4.6.2.2.4 Potential to replace/enhance conventional carbon-based inks

Carbon black based inks are used as conductive inks in areas where conductivity does not need to be high and where low cost is priority. Graphene-enhanced carbon inks perform better than standard carbon-based inks and are expected to be almost cost competitive in the near future.

In the last few years, a massive improvement in conductivity has been achieved for pure graphene material conductive inks and processes (from kΩ/□. to <1 Ω/□, e.g. 1.4 Ω/□ at 25µm thickness [508]). There are no critical technical challenges/limitations anymore regarding the conductivity.

When the electronic design of flexible circuits, antennas and devices is adjusted to these achievable conductivities, the inks can even compete in application areas where metal inks are normally used. With adjusted processing, design and thickness, even flexible NFC antennas can be realized.

However, the pure conductivity of printed graphene is not a game changer at the moment. Only the full package of process, cost and performance might eventually become a USP. It remains an open question whether the sheet resistance be further reduced and to which extent especially the processing can be adjusted to achieve highest possible sheet resistances with for instance one print. It is therefore necessary to look at Ω/□/mil or /print. 1 Ω/□/print is already possible.

In summary and as mentioned above, graphene inks or graphene-enhanced inks can address the market and replace silver inks for applications where silver inks are too expensive and too good, e.g in touch sensors, or where carbon/graphite inks are performing not good enough.

4.6.2.2.5 Added functionalities beyond pure conductivity

Functionalization offers further technological opportunities for graphene and 2D material based printed electronics. Graphene/2D materials offer a broad range of functionalities beyond pure conductivity: 2D printed systems can be for instance used for temperature sensors, humidity sensors, RF circuits, pressure and strain sensors, gas and bio sensors. This opens up the potential to have a 2D materials toolbox for flexible/printed electronics to create flexible systems combining the functionalities. In that respect, the combination of flexibility with several functionalities can create an USP for these materials.

4.6.2.2.6 Substrate independence

It has been shown that graphene inks can be used on various substrates, even on porous ones. Similar to other printed electronics materials, any substrate is possible with proper engineering. Even tissues and textiles are possible to be used, still reaching a quality compatible with NFC antennas.

4.6.2.2.7 Printability and simplification of integration processes

Conductive inks based on graphene/2D materials can be printed with standard equipment and there is a good integratability in existing printing systems. This process is much simpler compared to transferred high quality CVD graphene. Thus, a shorter time to market is possible for printed electronics and inks.

Different printing/coating techniques are in use and possible, e.g. bar/rod coating, screen printing and flexographic printing. It is possible to produce/print multi-layer structures and heterostructures, which increases the freedom of design and the potential applications.

Using graphene inks in the conductivity space between carbon and metal inks can reduce the effort of printing, e.g. through the need of just one printing unit instead of two for printed touch sensors (replace silver ink). This also offers the chance to print a device in a single step or very few steps instead of multiple coats.

Furthermore, although higher performing graphene inks need post processing (e.g. compression, laser treatment), there is potentially no overall heat curing needed.

Graphene has also the potential to become eventually cheap enough to allow broad use and to bear the dead volume of ordinary printing machines (several litres).

4.6.2.2.8 Potential environmental properties as USP towards metal inks

Similar to carbon inks, the potential environmental properties of graphene-based inks, i.e. recycling, combustion, biodegradation, lower environmental impact, are better than for most metal inks. However, not only graphene materials influence the EHS properties, but also the binders and residual additives in the films.

4.6.2.2.9 Ultimate goal: printed and transparent electrode

So far, a purely printed transparent and sufficiently conductive film has not been achieved with graphene. The question remains open whether it is possible to print a transparent conductive layer e.g. from single layer graphene (oxide). The realisation of such a printed TCF would be a very interesting opportunity. Some stakeholders do not expect it to be possible due to the difficulty to achieve percolation in thin (one layer) films.

4.6.2.2.10 Other 2D material inks could enable flexible (printed) electronics

Other 2D material inks (e.g. MoS_2, WS_2, MoO_3) and their combination have the potential to become key enabler of flexible electronics, if they can be manufactured and applied in a controlled way. There is a potential for all-inkjet printed heterostructures by sequential printing of graphene and other 2D materials. But the maturity is still rather low and many challenges need to be addressed, e.g. the role of grain boundaries in printed structures. [531]

4.6.2.3 Additional strengths: high quality 2D films for flexible electronics

4.6.2.3.1 High quality semiconducting 2D materials as good candidate for flexible electronics: Essentially all devices can be made flexible

High quality 2D materials are better suited for higher performing flexible electronics. Possible applications are hall sensors, photodetectors, RF electronics/transistors, and logic. For logic other 2D materials, such as MoS_2 or SnS_2 are more promising due to the intrinsic bandgap.

If large-area deterministic materials growth is successful, 2D materials technology could enable a new generation of flexible electronics for wearable and bendable systems. MoS_2 or other 2D materials could be n-type or p-type semiconductor with sufficiently high mobility.

Essentially all devices that are mentioned in this electronics chapter (also in the sensors, logic, RF/telecomm and optoelectronics chapters) can in principle be made on flexible substrates (if the preparation uses limited temperatures <200°C). This is a great strength and opportunity for graphene electronics to leave the competition well behind . Flexibility is one of the very clear USPs of graphene based electronics. Please refer also to the other electronics chapters depending on the application of interest.

4.6.2.3.2 CVD graphene/2D materials with high quality can reach better performances than flakes

CVD graphene is more likely to be used for higher performing for end products, but only if low temperature direct growth or transferability is controllable (see wafer scale assessment in 4.2 Electronics: Cross-cutting issues). For flexible applications also direct roll to roll or sheet to sheet transfer (deposition of flexible substrate on graphene, before Cu delamination/etching) is already established and could become economically viable, reducing the dependence on the wafer scale integration success. CVD processes and high quality films are better suited for higher performance/electronics (transistors, sensors) and transparent applications. In particular the transparency is a potential selling proposition. Interesting for future fully integrated devices is also the potential compatibility of high quality films and ink-based components.

4.6.2.3.3 Substrate independence

Once lamination/transfer of high quality films works, one is essentially independent on substrate (only dielectric needed). But the specific interaction of graphene with the substrate needs to be considered. If graphene is encapsulated, e.g. in BN, substrate independence is essentially given.

4.6.2.3.4 TCF: good flexibility and optical properties

The optical properties and the flexibility of graphene based TCFs is better than for the incumbent ITO and can compete with other emerging technologies. The downturn is the complex preparation and not so good conductivity compared to other solutions.

4.6.2.4 Additional strengths: flexible (resistive) random access memory

4.6.2.4.1 Multi-storage per bit potentially possible

Simple configurations (printed) of graphene oxide sandwiched between two contacts can be used as RERAM. The CareRAMM project investigated graphene-oxide RERAM and realized switching speeds of 10ns and sizes of 100x100 nm² per bit. [532]

With RERAM, multi-storage is in principle possible, i.e. more than two stages are available per “bit”.

4.6.2.4.2 Rather simple preparation method based on flakes

A simple version of the memory can be prepared with spray gun (that is also used for supercaps) or by piezo printing, both roll to roll processes. Water can be used as solvent and plasma for patterning, which only needs 100°C.

4.6.2.5 Additional strengths: flexible batteries and supercapacitors

4.6.2.5.1 Simple use of graphene materials

Graphene materials can be easily used as an additive for graphite electrodes (e.g. in form of GO). Besides that, the strength of graphene in batteries as provided in chapter 0

Batteries can be applied. Vorbeck materials already introduced the first graphene-enhanced flexible battery. Please also refer to chapter 3.3.2.1.3 “An additional approach for printing of flexible batteries” for further strength of graphene in printed batteries.

4.6.2.5.2 Graphene is the only material enabling flexible supercapacitors

So far, graphene is the only materials that potentially enables conformable supercapacitors. This might be a unique opportunity.

4.6.2.6 Current weaknesses and challenges for graphene/2D materials use in flexible electronics

4.6.2.6.1 Compatibility with different processes and technologies

One of the main challenges for flexible low cost GRM ICs is the compatibility between different processes and technologies (printed, transferred, CMOS, substrates, other materials, etc). This also refers to the compatibility of high quality graphene films and printed graphene films based on inks.

4.6.2.6.2 Exploiting the full potential of graphene/2D materials with economically feasible processes compatible with flexible substrates

The extraordinary microscopic properties (e.g. high mobility) of graphene have gathered a lot of attention for flexible electronics. First companies are offering conductive inks and it is still explored for many applications as semiconductor and conductor in flexible electronics (as high quality film and printed ink). One of the key challenges is to maintain the microscopic and highly interesting properties of pure graphene sheets after converting the material into a processing form, i.e. an ink or a scalable grown film and transfer. [533]

Besides, the production processes are partially not easily scalable and thus drive the cost. For instance, currently often non-scalable sonication and centrifugation processes are used and high temperature annealing. However, new scalable production methods (e.g. microfluidization) are developed. [534]

4.6.2.6.3 Maturity of flexible applications beyond conductive inks is still rather low

Graphene-based or enhanced conductive inks are used in consumer products such as flexible RFID or security labels [535]. First products are about to hit the market.

Besides the rather simple use as slightly better carbon ink for conducting layers, the maturity of flexible applications with graphene/2D is still low. Graphene based "real flexible electronics" solutions are still far away from commercialization.

There is no established GRM based IC platform for large area flexible electronics available at the moment. There is still some lack of fundamental knowledge about the GRM properties in flexible applications and a better understanding of the material and preparation is needed. Key challenges are to improve the material mobility, the development of roll-to-roll fabrication processes and the development of device/circuit fabrication technologies [438]. Finding an efficient way to make a system out of the materials/modules is a limiting factor.

Another challenge is reproducible, reliable and homogeneous doping and functionalization: For some applications doping is needed and it remains yet unclear how to do that uniformly on large scale. The quality demand of course demands on the application. Disposable devices for instance have lower requirements than multi-use sensors/devices.

In particular for sensor applications more knowledge on functionalization is needed (surface chemistries, processes and influence/optimization of functionalization on performance).

The amount of potential application of GRM materials in flexible electronics is very large. This is of course an opportunity, but also makes it hard to figure out and decide on which applications are worthwhile exploring more deeply. So far there is no “quick win” foreseeable and it is not a fast-selling item in terms of technological and non-technological properties combined with the still open questions on processing and applications.

4.6.2.6.4 Reliability, long term stability need to be proven

For non-disposable products, the long term performance and durability is often still unclear and needs to be proven (also in air and different ambient conditions). More efforts on reliability are needed. For disposable products, the shelf-life needs to be investigated.

4.6.2.6.5 Other 2D materials need more attention

Graphene has already gained quite some attention in terms of production and demonstrators. Other 2D materials are gaining more and more attention, especially for electronics. On MoS_2 already a lot of work has been done, but it is still very far away from being assessed on its potential properly.

There are opinions stating that for flexible electronics the efforts on MoS2 are currently too low and other 2D materials do not get the same attention as graphene. On the other hand, if graphene proves to be viable in a flexible electronics product it might pave the way for other 2D materials.

Competing materials (e.g. organic electronics) are more mature, but also have constraints. The frequency of operation is lower than for printed inorganic materials. The yield and matching to other components for or graphene and pinted electronics in general is still open. Multiple manufacturing techniques have to be investigated for best performance, number of transistors and lifetime. The competition with ultra-small silicon chips needs to be taken into account. [90]

4.6.2.7 Additional current weaknesses and challenges: printed electronics and conductive inks

4.6.2.7.1 Is positioning between metal inks and carbon black inks a sweet spot for graphene?

Graphene conductive inks are positioned between graphite inks and metal inks in terms of performance (conductivity) and cost. The conductivity in comparison to silver is a factor of 100 lower (and processing dependent) and the improvement towards graphite inks is some 30%.

The conductivity achieved today is good enough for RFID and even NFC antennas with reasonable range. It is, however, not good enough for a one to one replacement of printed circuit boards. One intrinsic problem of graphene is the low charge carrier density, which in part counteracts to a certain extent the high mobility for conductivity applications.

The technological USP is still somewhat vague, although the rather non-technological USPs as corrosion resistance and potential environmental properties appear promising combined with the expectations of falling prices. Still, the cost/benefit advantage is not yet clear enough. To compete in this area on a broader basis the inks need to be rather low cost and high volume and there is probably nothing in between, because else metals or carbon inks could do the job better or cheaper. If this is not met, it will remain in a niche product for special applications, such as in corrosive environments.

Several companies are in the business (e.g. Vorbeck in the US since several years) but so far none seems to have reached the breakeven point.

4.6.2.7.2 Graphene alone is not the key enabler of printed electronics

Graphene is potentially one component among others in printed electronics and it is neither a driver, nor an enabler for printed electronics. Depending on the application, graphene material based inks do not technologically enable things that cannot be done with carbon and silver inks, only the price and non-technological benefits (corrosion, end of life) can be an argument at the moment and the positioning between metal and carbon inks (see above).

The black colour/lack of transparency of graphene inks could be a disadvantage in applications where the colour or appearance is important.

In combination with other 2D material inks, graphene might become more important for heterostructures.

4.6.2.7.3 Engineering knowledge needed, especially expertise in ink formulation needs to be involved

The conductivity of graphene and 2D materials based films made from conductive inks not only depends from the material itself, but to a great extent from the ink formulation, binders, surfactants, additives (all tailored for the targeted printing process), the printing process itself and post processing. The type of flakes and their influence on printability need to be considered as well. Furthermore, the targeted application requirements (also non-technological), e.g. in terms of shelf lives, need to be regarded alongside with the type of substrate. 0.1-1 or 2µm flakes are stable and shelf lives of several months have been achieved.

The further improvements demand considerable engineering efforts and engineering knowledge on ink formulation and a lot can be learned from the ink community. The following challenges remain:

- unknown adhesion between different substrates and inks (wear resistance…), find the most suitable substrate
- better understanding of particle interfaces, bridge/reduce contact between different flakes needed to allow influencing structure of film and interfaces
- Need to find a formulation that increases the conductivity of carbon inks whilst not changing the printability (rheology, viscosity)
- Ink formulation and tuning of properties, stability: maturity not yet far enough, but in principle manageable with enough effort
- Stable dispersion without losing target properties of graphene
- Use industrial standard tests for the targeted application (e.g. for RFID, sensors, etc.)
- Stability/lifetime of the devices
- Contacting of devices

4.6.2.7.4 Challenge: building the value chain and providing consistent supply

Many companies are already active in the bulk graphene business. Most of them also offer a conductive ink. However, there is a poor current availability of reliable, consistent and stable inks, especially for larger volumes. Although the ink provided by one supplier might be stable and reproducible, it is hardly possible to change form one supplier to another. This introduces a barrier, as many industries demand second sources.

It is a challenge to find the right supplier who has the ink with the required properties. Especially in Europe, the supply is still unsatisfactory.

Also in terms of consistency and volume of bulk graphene material supply (at 100kg scale) there are many differences between suppliers. In this case the consistency of one supplier is usually high enough (at least from one or the other), but again the change to another supplier is hardly possible. The quality of bulk graphene depends on the synthesis route and can even depend on the raw material graphite quality for certain routes.

Missing material standards and a lack of standard characterization tools for quality control of large volume of material (powders, inks) accompany this problem. For inks, standards are there and have to be addressed when developing inks that should be sold to the market. It appears that in the current situation, companies have a better chance of success when they cover the value chain up to where standards exist (e.g. ink supplier).

4.6.2.7.5 Some printing techniques might suffer with larger sheet size

For some printing techniques (e.g. inkjet) the wear of printing heads and nozzles from large size sheets is unknown. For larger sheets, some printing techniques (especially inkjet) might not be suitable as clogging could appear. This is not relevant for screen/flexo printing.

4.6.2.7.6 Yield, performance and market differentiation

Not only on ink level, but also on applications level, the USPs are often not yet clear enough – compared to competing technologies addressing the same functionality – for a company to invest in the material. For instance for flexible/printed sensors, the yield, performance and market differentiation are unclear. For flexible conductors, the cost and conductivity are challenges. [90]

4.6.2.8 Additional current weaknesses and challenges: high quality 2D films for flexible electronics

4.6.2.8.1 Challenge for integration processes: wafer scale or transfer free

The largest challenge for high quality films is economically viable preparation and transfer to the flexible substrate with sufficient quality. The overall assessment for this process is comparable to wafer scale integration and can be found in chapter 4.2 Electronics: Cross-cutting issues. Direct sheet to sheet or roll to roll transfer is also an established option for flexible electronics. A flexible substrate can be deposited (laminated or printed) on graphene where the requirements and the barrier is somewhat lower compared to wafer scale like transfer processes. The process is already quite mature, but economical feasibility is not yet sure.

The best case would be a low temperature (<100°C) CVD transfer-free process for uniform and large sheets with reasonable properties, which at the moment appears to be rather illusionary. Therefore a feasible transfer process from CVD grown graphene seems to be more likely at the moment. But the feasibility of this process also needs to be shown (especially in terms of quality and economical viability).

The scalability of these processes for large samples is not yet clear and an industrial compatibility/manufacturability is not available yet. This is an important bottleneck for lab demonstrators to be scaled up. GRM need to perform very well compared to other materials in the lab, and the applications need to be compared with other devices addressing the same functionality to justify the effort for scale up and integration.

Due to the multiple risks of unclear performance, competitiveness, production yield and cost, there are no larger investments on company level at the moment to address high quality flexible electronics with graphene/2D materials.

4.6.2.8.2 TCF: conductivity and overall value proposition not good enough

Currently graphene is not seen as an important competitor for the incumbent ITO. Ag nanowires and metal meshes are assessed to be more promising. Graphene offers good optical properties and flexibility. However, the preparation technique makes it too expensive at the moment and also the electrical properties are not good enough. It requires doping mechanisms, which need to be applied homogeneously, which is an additional step besides transfer that makes it too process intensive at the moment. Based on the current knowledge it is therefore assessed to remain a niche product in the next years.

4.6.2.9 Additional current weaknesses and challenges: flexible (resistive) random access memory

4.6.2.9.1 Maturity still low and reliability uncertain

The maturity of GO RERAM is still quite low and it is at the basic research level. Issues such as the contacting and approaching of the storage pixels need to be solved avoiding cross-talk. So far only 300 read/change/write cycles have been demonstrated (need: >10000).

4.6.2.9.2 Other carbon materials similarly promising

Other carbon base memories are similarly promising. For instance, amorphous carbon performs well in resistive memory [536]. There are also many other non-carbon technologies addressing this area.

4.6.2.10 Additional current weaknesses and challenges: flexible batteries and supercapacitors

4.6.2.10.1 Good enough?

Environmentally friendly versions of flexible batteries are low power for a given area and cost. E.g. they are a magnitude more expensive than coin cell batteries which have higher power [90]. The question remains whether the use of graphene can push the properties of flexible batteries far enough to become more attractive and feasible for more applications and interesting as competitor to coin cells.

The same is true for flexible supercapacitors, which so far are only researched at laboratory level, if at all. It is not clear to which extent they can compete with small batteries or coin cells.

4.6.3 KPIs for flexible electronics

In general KPIs for flexible devices can often be poorer than for rigid applications (but this depends on actual application and cost). Expectations for flexible devices are usually not that high. Besides, the types of KPIs used in flexible applications are essentially the same as in rigid applications. The following application KPIs are of particular relevance and importance for flexible electronics (adapted from [517]):

- Flexibility/bending radius: key selling point of flexible electronics is the flexibility, i.e. the ability to bend, roll or fold the device without damage/degradation. The requirements can range from rigid but robust to rollable/foldable.
- Complexity and density of circuits: reliability, applicability and production yield are influenced by the complexity of circuits (e.g. number of transistors) and the number of different integrated devices – i.e. sensors, switches, power supply, logic – on the same substrate.
- Lifetime / stability / homogeneity / reliability: operational lifetime, shelf life, stability against the environment, other materials and solvents, and homogeneity of the materials are important for successful applications.
- Power efficiency: is important for many applications, especially mobile and light weight ones. the conversion efficiency of light to electricity or electricity to light is key for photovoltaics or LEDs, respectively.
- Environmental and toxicological safety: “environmentally friendly electronics” can be an important USP. This includes no or limited use of toxic materials in the production processes and products, the latter especially for disposable products. Also lower energy consumption and resource need in production and product are relevant. Products in contact with the environment (e.g. soil/drinking water/food) sensors) and in contact with the body, e.g. clothing, healthcare, wellbeing, fitness need to avoid any materials with toxicological issues or environmental, health and safety (EHS) conformity needs to be assessed and proven.
- Cost: costs have to be low enough, but premium can be charged for added functionalities. E.g. for rollable displays, a cost premium over conventional rigid displays may be accepted. In some applications low cost will be a major driver or barrier, e.g. in packag-

ing. Typically it is rather tough to bring a new technology to the market only by cost arguments.

KPIs in terms of technology, processes and material are (adapted from [517]):

- Electrical performance: Operating frequency/switching speed, energy (conversion) efficiency, brightness and/or energy storage capacity are products performance indicators that depend on charge carrier mobility and bandgap of the semiconductor, conductivity of the conductor and/or the dielectric properties of the dielectric materials. Thus, mobility, efficiency, conductivity, operating voltage, current density, on/off currents are major electrical performance parameters. See the application focused chapters for more information.
- Barrier properties / environmental stability: depending on the sensitivity of the material to oxygen and moisture, barrier properties and protective layers can be relevant. The necessary barrier properties vary for the different applications and use cases over several orders of magnitude, depending on expected life time, shelf life, stability, reliability, purpose and context of use etc. Some barrier properties of common materials are provided in Table 16.
- Resolution / printing registration / uniformity: reduced feature sizes and accurate overlay layers are important for printed and transferred devices and can be relevant for certain applications (e.g. when miniaturization and small footprints are needed). For high performing applications also high uniformity and defect free layers over large areas are critical.
- Processing and process parameters: The process conditions are important aspects for the later cost of a product as well as for the barrier to integrate or use a technology. Speed, needed temperatures, used solvents, necessary ambient conditions, vacuum, inert gas atmosphere, etc. are relevant process parameters that need to fit to the targeted applications. Adjustment and compatibility of the process parameters for different materials is important for working flexible systems and devices. Improving process characteristics can be decisive for the success of a material/technology. Reaching better/fitting processability is so important that industry even seeks it at a certain expense of improving mobility or sacrificing device performance.
- Yield: Yield is strongly correlated to processing and a high yield production is prerequisite to achieve high volume and low cost. Safe and reliably processes with either a known and certain range of process parameters (safe parameter space) and/or a good process control , in-line quality control, tailored materials and circuit designs are cornerstones of high yield processes.

4.6.3.1 Flexible electronics (transistors/active components)

Felxible transistors are usually thin film transistors (TFT)

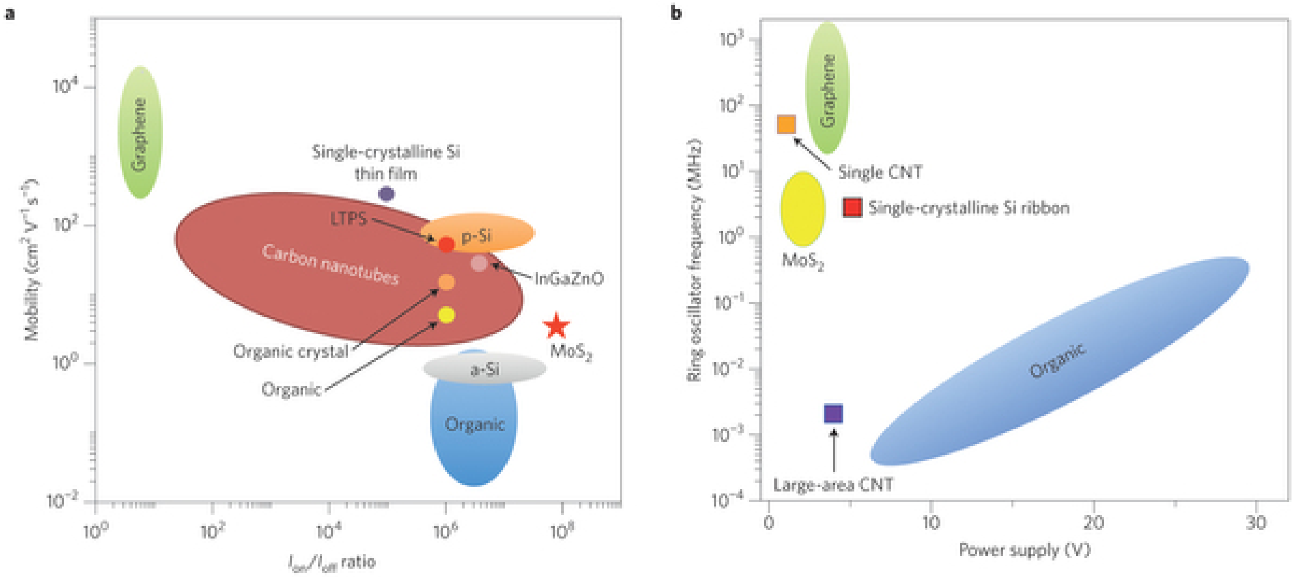


Figure 77: Figures of merit for flexible electronics transistors and comparison of different competing materials. From [438].

RFIC, flexible radio, flexible HF electronics/transistors, photodetectors: see 4.3.3 KPIs for telecommunication, optoelectronics & photonics.

Flexible sensors (gas, bio, magnetic): see 4.5.3 KPIs for sensors.

4.6.3.2 Flexible transparent conductive films (TCF)

For TCF: conductivity (Ω/□), transmission spectrum, patterning/etchability, flexibility, optical properties, roughness.

Prices of the incumbent (ITO) are 18-23 $/sqm in 2015 (reduced prices since 2013, before that it was 25-35 $/sqm. [98]

Table 72: KPIs of several competing TCF technologies.

Material	**Transmittance**	**Sheet resistance /(Ω/□)**	**Remark**
ITO	80-85%	60-200	on PET
Metal Mesh	>85%	5-30	PolyIC
Ag nanowire	>90%	10	Cambrios ClearOhm, wet process
CNT/CNB	95-98%	100-300	Canatu CNB Flex
PEDOT	85-95%	100-350	Agfa, better performances under development
Graphene	90-97%	~30-125	[515]

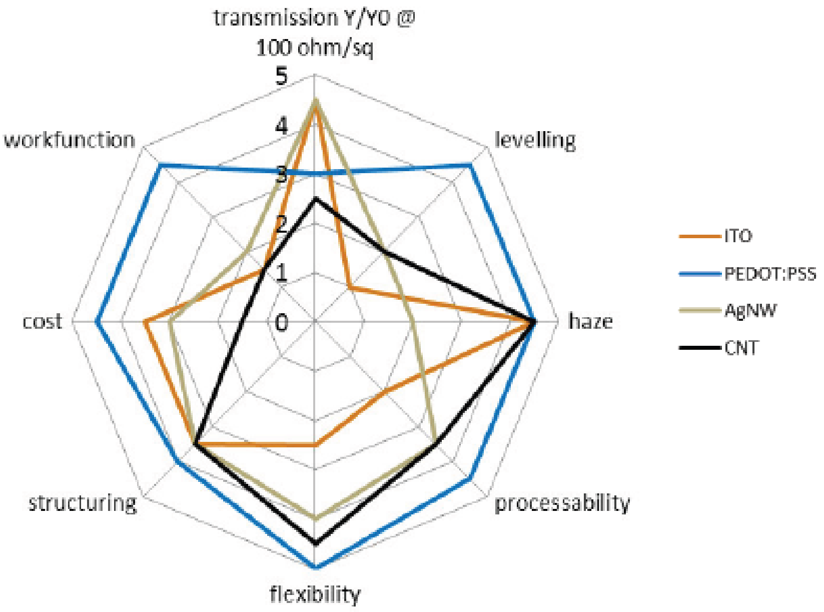


Figure 78: Key properties of competing technologies for TCF. [517]

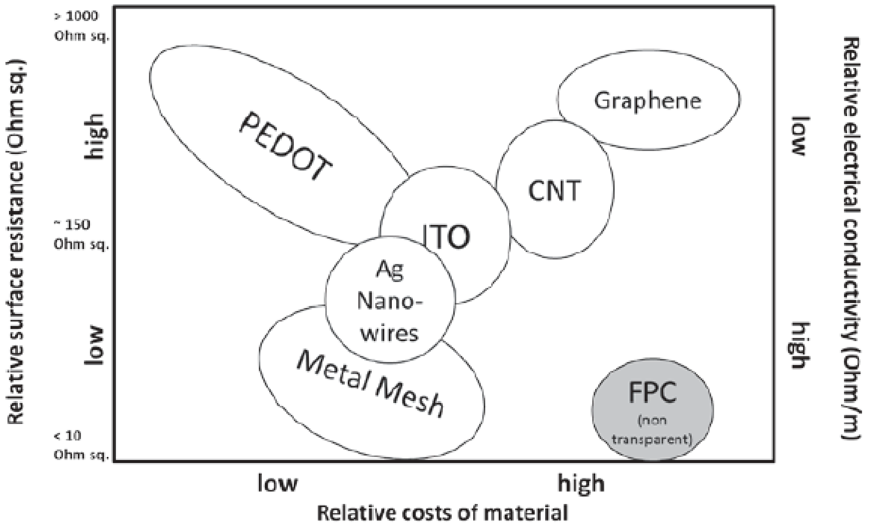


Figure 79: Performance vs. Cost of several materials. [517]

4.6.3.3 Printed electronics & cond. inks (conductors)

Cond. Inks and printed conductors:

- Printing on 3D objects (e.g. aerosol), in mold
- Ω/□/mil or Ω/□/print; 1 Ω/□/print has been achieved by Vorbeck 3 years ago
- Silver inks: >10^6S/m, <0.1Ω/□ (25µm film thickness)
- Carbon inks: ~50Ω/□ (25µm film thickness)
- First graphene inks (on market), best performance: ~10-50 Ω/□ (25µm film thickness)

- solar cell interconnect: 1/100Ω/□ necessary
- Flexibility: 100k cycles with bending radius to thickness ratio of 100

Typical prices:

- pure Silver metal: ~400€/kg
- pure polymer: 16€/kg
- pure graphite: 0,5-2€/kg
- pure solvent: 1€/kg
- 1l high grade silver ink retail: 1000€/kg

Table 73: Typical material cost of conductive inks. Typical content: 40-60%. Adapted from [537]

	Conductivity	Raw material cost /kg
45% Ag content	30-45 mΩ/□ @10µm	~190€
65% Ag content	30 mΩ/□ @10µm	~120€
45% carbon content	15 Ω/□ @1mm	~2.5€

4.6.3.4 Flexible memory

80kB storage for smartcards, 10000 read/change/write cycles

KPIs are: manufacturing cost, production capacity, disposability, retention time, envrionmental stability and bit error rate. [517]

Important material characteristics are: memory film uniformity, memory cell drive voltage, endurance, , compatibility with (flexible/printed) transistor, preparation/printing method, electrode conductivity, production conditions (inert atmosphere, …) [517]

4.6.3.5 Flexible batteries and supercapacitors

For a full set of KPIs please refer to the batteries and supercapacitors chapter (0 and 3.4, respectively).

Application KPIs are: Energy density, power density, voltage, (peak) current, lifetime, cycles, temperature range, bending radius [517]

Important material parameters are: layer thickness, ionic conductivity, thermal stability, encapsulation/gas permeation, flexibility [517]

4.6.3.6 E-textiles, functional textiles

Use for functional textiles: Performance requirements in terms of stretchability, adhesion and washability (>50 washing cycles) are very important and stringent.

4.6.4 Roadmap for flexible electronics

4.6.4.1 Current maturity: 'lab demonstration for real flexible electronics, marketed conductive inks and flexible conductors'

Conductive inks are on the market (e.g. Heraeus graphene-based conductive inks, Vorbeck, Sigma Aldrich and others), but still have potential to be improved.

Flexible sensors are marketed, but only where inks are used as a conductor. There are no marketed flexible products where graphene/2D materials actually provide active electronic functionality.

TCFs are to a certain extent marketed in China (Wuxi), but it is questionable if these are commercially viable and the broad use in a device is pending. There are rumours that graphene might be used in OLED displays in the next few years. However, issues of doping and long term stability and the production process are still not resolved yet.

CVD based films are not commercially mature or feasible at the moment.

The majority of flexible electronics based on graphene is at the lab demonstrator stage. Memory and more comprehensive applications (transistors, high quality film) have a lower maturity than printed conductors.

Other 2D materials and their heterostructures have promising properties and first lab scale demonstrators of flexible high quality or printed devices exist. However, the maturity is much lower than for graphene, although the overall prospect for these materials to become an enabler for flexible electronics is not so bad.

4.6.4.2 Barriers/challenges (summarized)

Value chains:

- Completely new value chain needed with typically different stakeholders than in conventional electronics
- Seamless value chain for flexible electronics in general and for graphene/2D materials does not exist yet
- Different parts of the value chain are at different readiness levels
- Missing material standards and characterization tools

Markets:

- Markets are broad, but finding the most promising application is tricky and demands on the one hand broad screening, on the other hand focussing of resources

- Conventional electronics/batteries as strong incumbent hinder new technologies (although the new technology might fit better to certain applications)
- Credibility gap: flexible electronics has not lived up to its promises yet. Besides it has not yet delivered the “cheap and high volume” products that are often promised.

Devices/Production:

- Transformation of lab scale results to relevant production environments without losing too much performance. The gap between performance and processing limits and slows down application development, industry interest and commercialization [517]
- Maintaining the microscopic properties of graphene on flexible substrates
- Low maturity of flexible electronics besides flexible conductive paths
- Process optimization is crucial and as important as demonstration of devices
- Unclear conductivity depending on frequency (especially in the GHz range) for ink based and CVD based (important for antennas and other RF applications, CVD graphene is currently not conductive enough for antennas, inks can create the conductivity via the thickness)
- Other 2D materials (inks and films) are potentially promising (e.g. for flexible logic, sensors) but the maturity is still quite low and it is yet unclear how actual performances compare to other materials
- Missing (stable) logic/comparison electronics is one of the major bottle necks in the emergency of flexible large area electronic devices
- Functionalization with processes compatible with the production of the original material (seamless integration) needed
- Hybrid electronics: seamless integration and packaging (pick and place, bonding)
- Reliability, lifetime, shelf life, long term stability not proven
- Compatibility between different processes and technologies (integration of printed, transferred, CMOS etc.)
- Contacting of films/devices
- In line control and characterisation tool missing

End of life and sustainability

- Usage of hazardous materials
- Unclear end of life properties (biodegradability, recycling, etc.)
- Unclear health and safety properties, perception of nanomaterials as dangerous

Conductive inks

- Flexible conductor: no principle/fundamental technical challenge/limitation at the moment but still further engineering and market assessment needed
- Need for large area (roll to roll) processes to achieve good processability and good conductivity
- Complex market and unclear value of “niche” between metal inks and standard carbon inks
- No replacement of metal inks (but expectations are often that it can replace metal inks)
- Ink formulation knowledge, property tuning and engineering knowledge for optimization (i.e. regarding substrate adhesion, better performance and processability, stability and shelf life)
- Understanding of particle interfaces/contact between flakes
- Value chain and consistent supply in sufficient amounts

High quality films:

- Addresses areas with strong incumbents (e.g. TCF)
- Reliable and larger scale preparation and transfer of high quality films on flexible substrates (wafer scale integration related challenges for flexible substrates)
- Other 2D materials: lower efforts and less knowledge
- Clear elaboration of USP and benchmark

Flexible batteries

- Increased capacity (per footprint) and decrease cost
- Competition with incumbent (rigid) coin cells
- See batteries chapter

Flexible memory

- Contest with other emerging technologies (e.g. amorphous carbon)
- Low maturity
- Increased storage density and read/write cyclability
- How to address the single pixels without cross-talk

4.6.4.3 Potential actions

If the area of graphene/2D in flexible electronics is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

General

- benchmark with common and emerging technologies (flexible and **not flexible**) by means of processability and functionality; depending on the targeted application, non-flexible solutions (e.g. small logic chips for a few cents) might be the competitor rather than other flexible approaches
- Explore different applications and focus early on most promising applications
- Investigate the potential of other 2D materials and heterostructures, focus on the ones that are easy to produce/integrate and have a higher potential for industrial manufacturing (also in terms of stability in air, etc.)
- Explore stretchability
- Engage with printed and flexible electronics community and build on existing efforts, many challenges are similar and actions can be combined (e.g. packaging, hybrid integration, pick and place etc.)
- Link with design companies and creative product designers, demonstrate capabilities
- Engage with researchers that address the markets (e.g. fibre/textile researchers, automotive researchers, design)
- Analyse existing and potential value chains and how graphene/2D materials can fit into them
- Address USPs besides potential cost reduction, e.g. added value through lower cost for lower customized volumes
- Address existing standards and identify gaps where additional standards are needed
- Investigate in-line quality control, measurement and characterisation
- Address processability, which is as important as demonstrators and prototypes
- Investigate interfaces and grain boundaries, electrical and mechanical properties under different conditions (frequency, environment)

- Demonstrate compatibility with different processes (also in terms of compatibility of high quality films and inks and the related processes)
- Explore/prove reliability, lifetime, shelf life and long term stability of devices and materials
- Investigate process compatible functionalization methods
- Explore end of life properties (recyclability, combustibility, health & safety), explore especially process that avoid hazardous substances

Conductive inks

- Address ink standards/application standards
- Further develop cost efficient roll to roll processes
- Investigate printing on 3D objects (aerosol printing), in mold electronics
- Engage with researchers with printing/ink expertise, gain formulation expertise
- Further explore large area printing (with adequate resolution)
- Address USPs towards metal and carbon inks
- Address shelf life and stability in solution as well as in the device
- Investigate film forming and compatible post processing

High quality films:

- Further explore possibilities beyond conductive films (e.g. transistors, RF, etc.) and elaborate clear USPs and benchmarks
- Further investigate other 2D materials for flexibl electronics (preparation and process technologies as well as demonstrators based on those)

Flexible batteries_

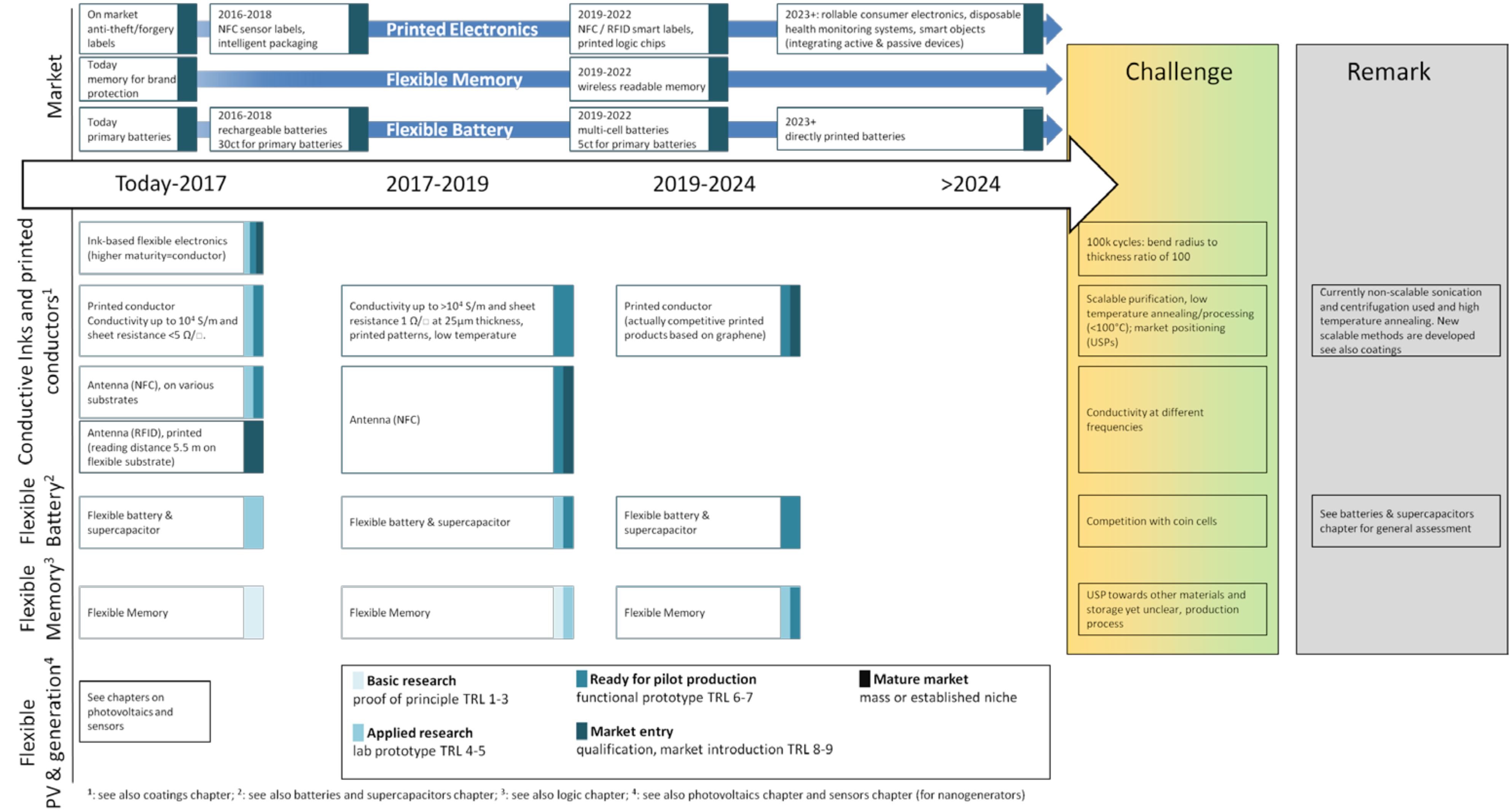
- Benchmark with coin cells

Flexible memory

- Investigate whether graphene/GO is a better material than competing ones
- Increase maturity, investigate possibilities to increase storage density and read/write cycles
- Figure out best way of preparation
- Investigate contacting and cross-talk

4.6.4.4 Roadmap

The proof of concept of fully flexible integrated systems (TRL4/5) is expected by 2019.



Market

Printed Electronics
On market anti-theft/forgery labels
2016-2018 NFC sensor labels, intelligent packaging
2019-2022 NFC / RFID smart labels, printed logic chips
2023+: rollable consumer electronics, disposable health monitoring systems, smart objects (integrating active & passive devices)

Flexible Memory
Today memory for brand protection
2019-2022 wireless readable memory

Flexible Battery
Today primary batteries
2016-2018 rechargeable batteries 30ct for primary batteries
2019-2022 multi-cell batteries 5ct for primary batteries
2023+ directly printed batteries

Today-2017 | 2017-2019 | 2019-2024 | >2024

Challenge

Remark

Conductive Inks and printed conductors[1]
Ink-based flexible electronics (higher maturity=conductor)
Printed conductor Conductivity up to 10^4 S/m and sheet resistance <5 Ω/□.
Conductivity up to >10^4 S/m and sheet resistance 1 Ω/□ at 25µm thickness, printed patterns, low temperature
Printed conductor (actually competitive printed products based on graphene)
Antenna (NFC), on various substrates
Antenna (RFID), printed (reading distance 5.5 m on flexible substrate)
Antenna (NFC)
Challenge: 100k cycles: bend radius to thickness ratio of 100
Challenge: Scalable purification, low temperature annealing/processing (<100°C); market positioning (USPs)
Remark: Currently non-scalable sonication and centrifugation used and high temperature annealing. New scalable methods are developed see also coatings
Challenge: Conductivity at different frequencies

Flexible Battery[2]
Flexible battery & supercapacitor
Flexible battery & supercapacitor
Flexible battery & supercapacitor
Challenge: Competition with coin cells
Remark: See batteries & supercapacitors chapter for general assessment

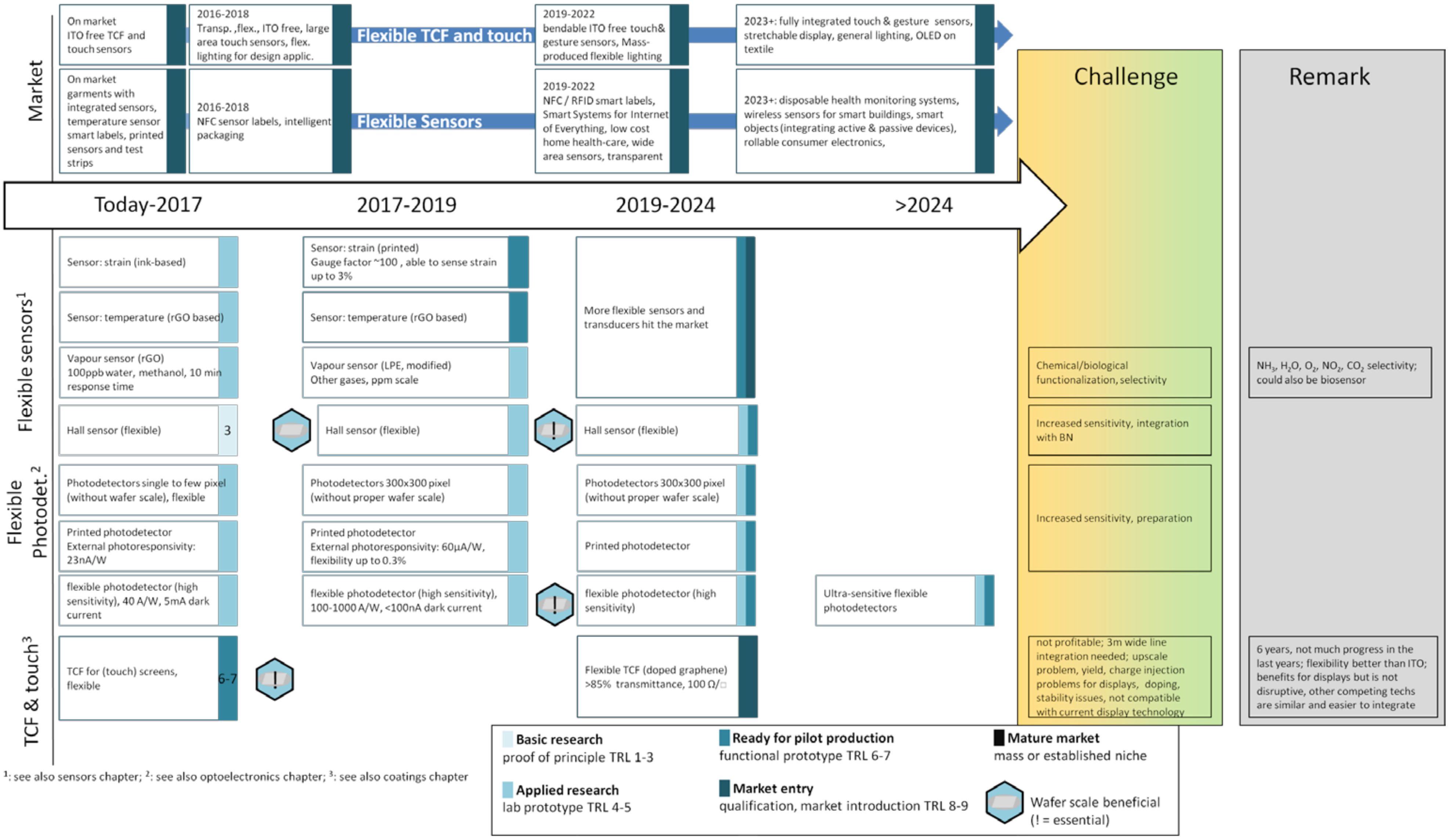
Flexible Memory[3]
Flexible Memory
Flexible Memory
Flexible Memory
Challenge: USP towards other materials and storage yet unclear, production process

Flexible PV & generation[4]
See chapters on photovoltaics and sensors

Basic research proof of principle TRL 1-3
Applied research lab prototype TRL 4-5
Ready for pilot production functional prototype TRL 6-7
Market entry qualification, market introduction TRL 8-9
Mature market mass or established niche

[1]: see also coatings chapter; [2]: see also batteries and supercapacitors chapter; [3]: see also logic chapter; [4]: see also photovoltaics chapter and sensors chapter (for nanogenerators)

Market sources: [90, 517]



Market

On market ITO free TCF and touch sensors

2016-2018 Transp. ,flex., ITO free, large area touch sensors, flex. lighting for design applic.

Flexible TCF and touch

2019-2022 bendable ITO free touch& gesture sensors, Mass-produced flexible lighting

2023+: fully integrated touch & gesture sensors, stretchable display, general lighting, OLED on textile

On market garments with integrated sensors, temperature sensor smart labels, printed sensors and test strips

2016-2018 NFC sensor labels, intelligent packaging

Flexible Sensors

2019-2022 NFC / RFID smart labels, Smart Systems for Internet of Everything, low cost home health-care, wide area sensors, transparent

2023+: disposable health monitoring systems, wireless sensors for smart buildings, smart objects (integrating active & passive devices), rollable consumer electronics,

Today-2017 | 2017-2019 | 2019-2024 | >2024

Flexible sensors[1]

Sensor: strain (ink-based)

Sensor: strain (printed) Gauge factor ~100 , able to sense strain up to 3%

More flexible sensors and transducers hit the market

Sensor: temperature (rGO based)

Sensor: temperature (rGO based)

Vapour sensor (rGO) 100ppb water, methanol, 10 min response time

Vapour sensor (LPE, modified) Other gases, ppm scale

Hall sensor (flexible) 3

Hall sensor (flexible)

!

Hall sensor (flexible)

Flexible Photodet.[2]

Photodetectors single to few pixel (without wafer scale), flexible

Photodetectors 300x300 pixel (without proper wafer scale)

Photodetectors 300x300 pixel (without proper wafer scale)

Printed photodetector External photoresponsivity: 23nA/W

Printed photodetector External photoresponsivity: 60µA/W, flexibility up to 0.3%

Printed photodetector

flexible photodetector (high sensitivity), 40 A/W, 5mA dark current

flexible photodetector (high sensitivity), 100-1000 A/W, <100nA dark current

!

flexible photodetector (high sensitivity)

Ultra-sensitive flexible photodetectors

TCF & touch[3]

TCF for (touch) screens, flexible 6-7

!

Flexible TCF (doped graphene) >85% transmittance, 100 Ω/□

Challenge

Chemical/biological functionalization, selectivity

Increased sensitivity, integration with BN

Increased sensitivity, preparation

not profitable; 3m wide line integration needed; upscale problem, yield, charge injection problems for displays, doping, stability issues, not compatible with current display technology

Remark

NH$_3$, H$_2$O, O$_2$, NO$_2$, CO$_2$ selectivity; could also be biosensor

6 years, not much progress in the last years; flexibility better than ITO; benefits for displays but is not disruptive, other competing techs are similar and easier to integrate

Basic research proof of principle TRL 1-3

Applied research lab prototype TRL 4-5

Ready for pilot production functional prototype TRL 6-7

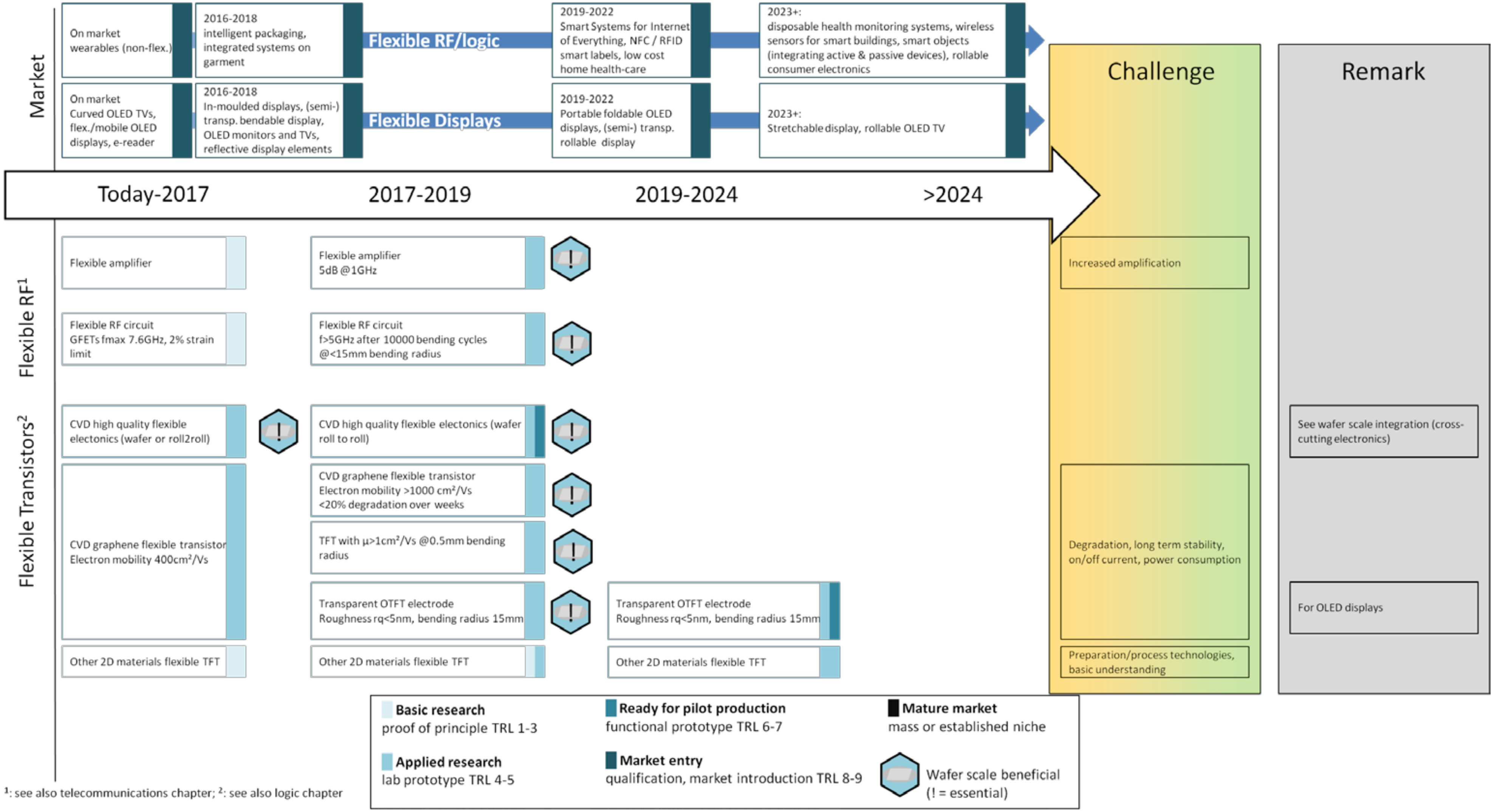
Market entry qualification, market introduction TRL 8-9

Mature market mass or established niche

Wafer scale beneficial (! = essential)

[1]: see also sensors chapter; [2]: see also optoelectronics chapter; [3]: see also coatings chapter

Market sources: [90, 517]



Market

On market
wearables (non-flex.)

2016-2018
intelligent packaging, integrated systems on garment

Flexible RF/logic

2019-2022
Smart Systems for Internet of Everything, NFC / RFID smart labels, low cost home health-care

2023+:
disposable health monitoring systems, wireless sensors for smart buildings, smart objects (integrating active & passive devices), rollable consumer electronics

On market
Curved OLED TVs, flex./mobile OLED displays, e-reader

2016-2018
In-moulded displays, (semi-) transp. bendable display, OLED monitors and TVs, reflective display elements

Flexible Displays

2019-2022
Portable foldable OLED displays, (semi-) transp. rollable display

2023+:
Stretchable display, rollable OLED TV

Today-2017 | 2017-2019 | 2019-2024 | >2024

Challenge

Remark

Flexible RF[1]

Flexible amplifier

Flexible amplifier
5dB @1GHz

Increased amplification

Flexible RF circuit
GFETs fmax 7.6GHz, 2% strain limit

Flexible RF circuit
f>5GHz after 10000 bending cycles @<15mm bending radius

Flexible Transistors[2]

CVD high quality flexible electonics (wafer or roll2roll)

CVD high quality flexible electonics (wafer roll to roll)

See wafer scale integration (cross-cutting electronics)

CVD graphene flexible transistor
Electron mobility 400cm²/Vs

CVD graphene flexible transistor
Electron mobility >1000 cm²/Vs
<20% degradation over weeks

TFT with µ>1cm²/Vs @0.5mm bending radius

Transparent OTFT electrode
Roughness rq<5nm, bending radius 15mm

Transparent OTFT electrode
Roughness rq<5nm, bending radius 15mm

Degradation, long term stability, on/off current, power consumption

For OLED displays

Other 2D materials flexible TFT

Other 2D materials flexible TFT

Other 2D materials flexible TFT

Preparation/process technologies, basic understanding

Basic research
proof of principle TRL 1-3

Applied research
lab prototype TRL 4-5

Ready for pilot production
functional prototype TRL 6-7

Market entry
qualification, market introduction TRL 8-9

Mature market
mass or established niche

Wafer scale beneficial
(! = essential)

[1]: see also telecommunications chapter; [2]: see also logic chapter

Market sources: [517]

4.6.5 Conclusion flexible electronics

Flexible electronics is cross-lying to all electronics applications. The potentially added functionality of flexibility is one of the key propositions of 2D materials. Therefore, 2D materials have a better technological potential for any application that requires flexibility.

As the actual flexible/printed electronics market (besides printed circuit boards and OLED displays) is still juvenile, there are chances of early entry. But many of the targeted applications are consumer electronics related where the actual integrators are quite often not in Europe. On the other hand, another strong integrator sector is automotive, where Europe is strong. Besides, many first movers of flexible electronics are in Europe and the political support is strong.

In terms of printed electronics, conductive inks are already on the market, also made of graphene. They are positioned between carbon black inks and metal inks in terms of pricing and conductivity. The market chances in this void between carbon black inks and metal inks are still not absolutely clear, but there are some indications that it might be an interesting market position. The actual applications in that area need to be identified. Many applications are already solved with metal inks (although the conductivity is higher than needed), e.g. RFID antennas made of etched aluminium or copper reach low prices. Other technologies are also emerging (e.g. metal nanoparticles, CNT). 2D material based inks can only compete, when they have an additional added value (e.g. added (electronic) functionality, substrate independence, simpler preparation, corrosion resistance, recyclability, lower cost).

For more advanced applications beyond conductive paths (i.e. transistors, sensors) lab demonstrators are available and need to be further developed to assess the industrial compatibility and commercial viability (printed and high quality films). Printed 2D heterostructures, e.g. for logic, might become an enabler, because there is currently no reliable material solution for flexible and printed logic. However, these 2D material inks are still at an early stage of development and it is yet unclear whether they can live up to the expectations. Flexible solutions often do not need to meet highest performances and the technological requirements are often lower than for non-flexible solutions. This lowers the barrier of entry. On the other hand, there are many other, more mature materials (conductive polymers or small molecules) that are already entering the market. Also silicon based rigid chips are available with very small form factors and for very low prices, so that introduction onto flexible structures is possible.

The upcoming and growing wearables and internet of things markets are the major drivers for flexible and lightweight electronics solutions, sometimes with rather simple functionalities. Broad markets are addressed, such as logistics, smart packaging, advertisement, health, apparel, consumer electronics). These trends create a strong market pull for conformable solutions, however, some of these markets are also very price sensitive. On the other hand, these markets also offer many niches for early market introduction.

In conclusion, the high quality film based applications often promise larger technological added values but have a higher barrier for integration, whereas flake-based mass applications (e.g. printed electronics or composites) have a lower barrier for integration but usually lead to less disruptive and smaller technological improvements.

Table 74: Assessment of market and technological potential of graphene/2D materials use in flexible electronics on a scale - -, -, 0, +, ++

Flexible electronics	**Current technological potential (USP)**	**Market potential (EU perspective)**
Flexible TFT	+	0/+
Flexible HF electronics	++	+
Flexible sensors	++	++
Printed electronics/conductive inks	0/+	+
Flexible antennas	0/+	+
Flexible transparent conductive films	0	-
Flexible memory	0	+
Flexible batteries	0/+	+
Flexible logic (e.g. TMDs)	+	-/0

4.7 Summary electronics & photonics

Due to the interesting electronic and optical properties of graphene and 2D materials, it is obvious that many different applications are possible in this field. It is additionally a field that often deals with thin films and layered materials, although the change from bulk to 2D materials actually reflects a paradigm change. The market perspective is generally very interesting, as large and typically growing markets are addressed. Especially trends like wireless networks/5G and beyond, ubiquitous computing, wearables or internet of things create demands for new technologies in electronics, optoelectronics, power supply and sensors. However, the market is also highly competitive and there are stronger industries in USA and Asia (especially Korea and Japan). Europe is particularly strong in More than Moore technologies and special logic applications, e.g. for vertically integrated markets, such as automotive, energy, security, smartcards, industrial electronics and data processing electronics. European companies possess leading positions in sensors and MEMS markets. Besides that, Europe has strengths in virtual components and low power processors, and in the supply of equipment, materials and IP (Intellectual Property) into the value chain. First movers in the flexible electronics area are in Europe and the political support is strong, so that this emerging field appears to be also interesting from a European perspective.

A major obstacle for many applications is economically feasible wafer scale integration and scalable high quality preparation of graphene and other 2D material films with sufficient quality and yield. Open questions regard contacting, delamination, transfer processes, quality and yield. If these processes are not viable, many applications will only remain in niche and low volume applications, if at all. Only a few applications in sensors, flexible memory, flexible batteries and flexible conductors/electronics are currently possible with printed solutions and thus do not need wafer scale integration. On the other hand, if wafer scale integration works, many applications suddenly become interesting and viable.

A first proof is needed for a simple demonstrator prepared by viable processes, so that the risk for industry to take up the development is lowered. This risk is currently too high and there is no reliable ecosystem available, although interest exists from end users and OEM companies to investigate graphene further. However, they will not integrate the material and as long as no pilot production is demonstrated feasibly, no company or foundry will invest heavily. Usually a 10x performance improvement and/or 10x cost improvement (or a mixture of both) along with a realistic integration scheme is needed so that an investment into a new technology is realized (in contrast to most bulk applications, where usually both cost and performance need to be improved at the same time). This is not a fundamental problem, as many questions are still open and under investigation due to the novelty of the 2D material technology. But at the same time it is not yet foreseeable for graphene/2D materials, whether the threshold of performance/demonstration and viable production can be met. The incumbents are very strong and everything that can be realized with silicon and existing technologies will be realized. Usually new materials/technologies need more than 10 years until broader diffusion in the electronics industry.

In terms of applications from a functional point of view, hybrid approaches with silicon appear promising, where graphene is added in the back-end-of-line or back end to deliver additional functionalities (e.g. optoelectronics, THz, sensors). Besides that, flexible applications appear to be very interesting for 2D materials, especially as there is no leading incumbent (silicon does not perform well) and there is still a need for new materials. Flexible solutions often have lower requirements than non-flexible solutions, which reduces the barrier for commercialization.

Niche markets for early adoption and potential later scale up are possible in sensors, THz, radar applications and photonics applications (lasers). Logic and HF transistors typically address larger volumes and need scalable processes. From a technological point of view, especially flexible HF electronics appear interesting. In optoelectronics especially optical switches/modulators, ultrafast photodetectors and hyperspectral imaging detectors are promising from a technological point of view. Furthermore, 2D materials in general have a particular advantage in all kinds of sensors due to the high sensitivity of electrical properties on the surrounding.

For beyond CMOS applications in logic and memory, the silicon era will reach limits in the next 10-15 years. To address this window of opportunity, breakthroughs in novel technologies have to be available on lab and probably pilot scale in the next 5 years. TMDs recently had such a breakthrough making them a reasonable candidate. For completely new concepts, such as spintronics, graphene or 2D materials might have an opportunity.

Major common challenges throughout all electronics applications are functionalization/homogeneous doping and contacting. Reliability, lifetime and end of life properties, as well as health and safety assessments are recurring topics to be addressed. USPs towards competing, emerging and state of the art technologies need to be clearly and objectively elaborated based on the targeted functionality.

Table 75: Summarized assessment table of all electronics and photonics application areas primarily sorted by European market potential and secondary sorted by USP.

Cross-cutting electronics	Current technological potential (USP)	Market potential (EU perspective)
Flexible sensors	++	++
Photonic networks	++	++
Biosensors	+	++
Wireless communication	+	++
Pressure sensors/microphones/NEMS	0/+	++
Photodetectors/Imaging systems/Spectrometers	++	+
Magnetic sensors	++	+
Flexible HF electronics	++	+

Cross-cutting electronics	**Current technological potential (USP)**	**Market potential (EU perspective)**
Optical switches and modulators	++	+
Electronics in general	+	+
Wafer scale CMOS integration	+	+
Laser/photonics	+	+
Gas/chemical sensors	+	+
Mechanical force/stress/strain/mass sensors	0/+	+
Printed electronics/conductive inks	0/+	+
Flexible batteries	0/+	+
Flexible antennas	0/+	+
HF transistors	0/+	+
Nanogenerators/micro-energy harvesters	0/+?	+
Equipment (wafer scale)	0	+
Flexible memory	0	+
Resonators	+	0/+
Antennas (large area, unobtrusive)	-	0/+
Flexible TFT	+	0/+
New transistors (novel charge-based transistors, TFET, GBT)	0	0/+(low power)
Interconnects	+	0
Thermal material	+	0

Cross-cutting electronics	**Current technological potential (USP)**	**Market potential (EU perspective)**
Barrier material	+	0
THz/sub-mm wave components	+	0
Flexible logic (e.g. TMDs)	+	-/0
Spintronics	+	-/0
2D channel FET (MoS2)	+	-
GFET	-	-
Flexible transparent conductive films	0	-

5 Biomedical applications

5.1 Potential areas of applications of GRM in biomedicine

This chapter covers special applications of graphene in biomedicine in a more sector oriented approach. The spectrum of applications in biomedicine proofs to be quite broad and diverse, so that it is not possible to apply a single principle on all biomedical applications. Generally the following application areas of graphene in biomedicine prove to be relevant:

- Drug/gene delivery
    - Cancer therapy
- Bioimaging & Biosensing
- Antibacterial materials
- Biocompatible devices
    - Prostheses
    - Bioelectronic medicine (e.g. brain electrodes)
    - Small implants
    - Tissue engineering

Thus the applications refer to all three broad commercial areas of medicine, i.e. drugs & pharmaceuticals, Medical Devices & Equipment, Research& Testing [538]. Wearables for consumer lifestyle health monitoring are covered in chapter 4 Electronics & Photonics. Furthermore, the more technology related area of in vitro diagnostics, POCT and biosensors is covered in 4.5 Sensors on a broader basis. Antibacterial materials and coatings that are also of interest to prostheses or for biocompatible devices are covered more broadly in 2 Composites, bulk applications and coatings This chapter focuses on the peculiarities of the health sector and highlights particular biomedical applications.

The relevance of the above mentioned fields is reflected in patent and publication databases in different ways. Beginning with the file World Patents Index, Transnational Patents, the topics in Table 76 appear most frequently in the context of the use of graphene in biomedicine.

Table 76: Most frequent main-groups of Transnational Patents in the area of the use of Graphene in Biomedicine sorted by Frequency. [21]

Main Group	Frequency
Investigating or analysing materials by specific methods	139
Measuring or testing processes involving enzymes or micro-organisms	76
Investigating or analysing materials by the use of optical means, i.e. using infra-red, visible or ultra-violet light	45

Main Group	Frequency
Medicinal preparations characterised by the non-active ingredients used, e.g. carriers, inert additives	31
Measuring for diagnostic purposes	25
Medicinal preparations containing organic active ingredients	23
Medicinal preparations characterised by special physical form	27
Preparations for testing in vivo	17
Electrotherapy; Circuits therefore	13
Materials for prostheses or for coating prostheses	13
Materials for other surgical articles	11
Filters implantable into blood vessels	9
Chemical aspects of, or use of materials for bandages, dressings or absorbent pads	7

In patents, i.e. in present commercial applications, various methods of analysis and measuring biological materials dominate. In particular the first category “investigating or analyzing materials by specific methods” is linked to medical analysis. Drug delivery appears in “preparations characterised by non-active ingredients”.

In the database Web of Science, reflecting scientific publications, the clear focus is on medical engineering, whereas the treatment of special diseases is rarely addressed, in the database Compendex, reflecting scientific publications in applied fields, the focus is on biomaterials.

In the following chapters, the various applications will be discussed in more detail. Before that, there is an excursus on the peculiarities of the health market.

5.2 Excursus: The specific structures of the health market

The health market has a large volume and is quite independent of economic crises. Nevertheless, it has very specific structures which make the access difficult.

Products or processes for application in the prevention, analysis, diagnosis, therapy or monitoring of human diseases or physiological processes can be either drugs or therapeutic agents such as organs, tissues, blood or cells, medical devices, or laboratory procedures. They can further be differentiated according to their use in (in vivo) or outside (ex vivo) the human body.

In order to ensure the high quality of these products and processes, especially with respect to patients' and medical staff safety and public health, a large body of legislation has been developed since the 1960s in the EU and worldwide. It is based on the principle that the placing on the market is made subject to the granting of a marketing authorization by the relevant authorities on EU or member state level [539]. Similar, but not identical regulatory regimes apply in other regions of the world, e.g. Northern America, Asia. The process of harmonization and amendment of requirements for the granting of marketing authorizations, both within the EU as well as between the different regions of the world, is ongoing. While uniform marketing authorization procedures have been implemented throughout the EU, obtaining reimbursement for the products, procedures and services from statutory and private health insurances is subject to individual EU member states' policies and regulations, and may differ significantly both in requirements to be fulfilled, procedures, and extent and timing of reimbursement.

As a consequence, the EU and worldwide health care sectors are highly regulated, and this aspect has to be taken into consideration very early in the innovation process, so that the R&D activities can to be designed in a way that the regulatory requirements for obtaining marketing authorization and reimbursement by health insurances can be fulfilled: Figure 80 gives a schematic overview of the R&D and authorization process of a new drug. Mandatory for obtaining marketing authorization is preclinical and clinical research (phase I to III) in order to collect all the data that are required for obtaining marketing approval. Depending on the novelty of the drug, this process may take 7-12 years. However, different procedures apply for medical devices.

In the following paragraphs, a short overview of the relevant regulatory regimes and the procedures for obtaining marketing authorization with a focus on the European Union is given.

In the EU, two fundamentally different regulatory approaches govern the marketing authorization:

1. the medicinal products regulation, and
2. the medical device regulation.

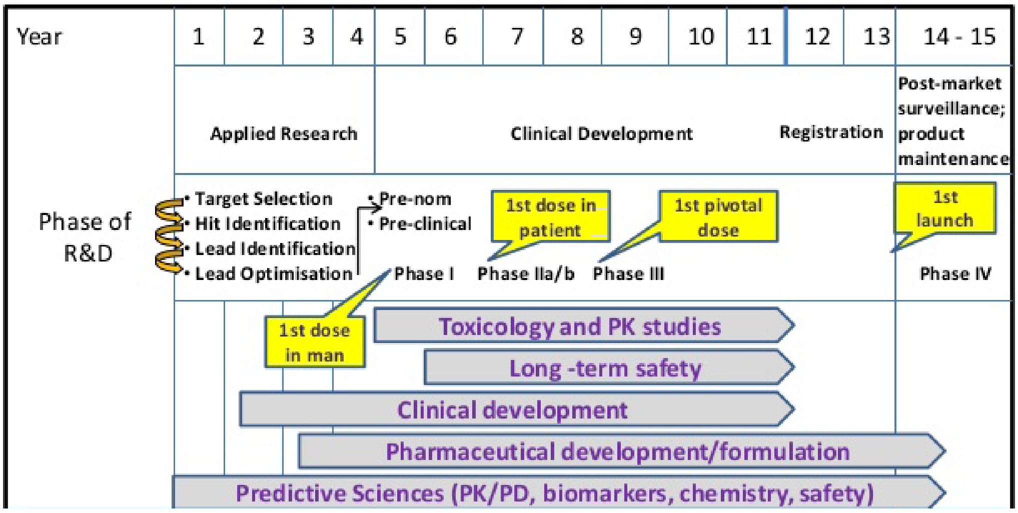


Figure 80: Schematic Overview of the R&D and Authorization Process of a Medicinal Product. [540]

5.2.1 Medicinal products regulation

Medicinal products are – in general – drugs, i.e. small chemical molecules or biopharmaceuticals, such as antibodies, therapeutic proteins, but also advanced therapies such as tissue engineered products, cell therapies etc.

Graphene and related 2D materials (GRM) are not so much considered as drugs themselves, but mainly as drug delivery vehicles, as matrices for tissue engineered medicinal products etc. Nevertheless, as the GRMs will be combined with medicinal products, (parts of) the medicinal products regulation must also be taken into account when developing GRM based drug delivery system, matrices etc.

Overall responsibility for the legislation regarding medicinal products lies with the DG Health and Food Safety. Depending on the class of medicinal products, authorisation procedures are either carried out by an individual EU member state regulatory authority, followed by a mutual recognition procedure for the whole EU; or a centralised authorisation procedure is carried out by the European Medicines Agency (EMA). This is the Community regulatory agency in charge of providing the EU institutions with scientific advice on medicinal products.

The legal basis for the regulation of medicinal products for human use in the EU is *REGULATION (EC) No 726/2004 OJ L 136* and *DIRECTIVE 2001/83/EC OJ L 311* [541, 542]. They lay down the requirements and procedures for the marketing authorisation for medicinal products, the rules for the constant supervision of products after they have been authorised, as well as provisions for manufacturing, wholesaling or advertising. The body of European Union legislation in the pharmaceutical sector is compiled in Volume 1 of the publication "The rules governing medicinal products in the European Union" [543]. In order to facilitate the interpretation of the legislation and its uniform application across the EU, numerous guidelines of regulatory and scientific nature have additionally been adopted. They are compiled in the volumes 2-4 and 6-10 of the above mentioned publication: A detailed explanation of the marketing authorisation procedures and other regulatory guidance intended for applicants is contained in volume 2 (Notice to Applicants), whereas scientific guidance on the quality, safety and efficacy of medicinal products is provided in volume 3. Specific guidance on the legal requirements concerning good manufacturing practices, pharmacovigilance and clinical trials is laid down in volumes 4, 9 and 10, respectively[13].

In addition, various rules have been adopted to address the particularities of certain types of medicinal products and promote research in specific areas: orphan medicinal products [544], medicinal products for children [545] and advanced therapy medicinal products [546].

The key points of the medicinal products regulations with relevance for GRM at the present state of development are:

- All medicines offered for sale in the EU must have prior authorisation from either a national authority or the European Medicines Agency.
- To receive the authorisation, manufacturers must provide a range of detailed therapeutic information about the product, including any possible side-effects.
- Authorisation may be refused, if a medicine’s risk-benefit ratio is not considered favourable or its therapeutic effect is insufficiently substantiated.
- National authorities should make every effort to complete the authorisation procedure within 210 days from the submission of a valid application. Authorisation is valid for 5 years and is renewable.
- A mutual recognition procedure exists to enable medicines already authorised in 1 EU country to be sold in another.
- The legislation does not apply to whole blood, plasma or certain medicinal products, such as those prepared in a pharmacy or used for research and development.
- The European Commission has also issued guidelines for good practices in the manufacture and distribution of medicinal products.

5.2.2 Medical devices regulation

Medical devices comprise a very diverse set of products, ranging from simple wound dressings, surgical instruments to high-tech diagnostic devices, such as magnetic resonance imaging devices, or medical implants, e.g. pacemakers, or software.

Most of the potential applications of graphene and related 2D materials in the health sector are medical devices for in vivo or in vitro use, e.g.

- medical implants, prostheses, e.g. equipped with GRM coatings or sensors for in vivo use

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[13] The different EudraLex Volumes can be accessed via http://ec.europa.eu/health/documents/eudralex/index_en.htm; accessed 2016-06-16

- diagnostic devices such as labs on chip, e.g. for point-of-care diagnostics, wearable electronics with GRM-based sensors for monitoring purposes
- Improved methods for biomedical laboratory analytical or diagnostic procedures (e.g. DNA sequencing).

Overall responsibility for the regulation of medicinal products lies with the DG Growth. Regulations relating to the safety and performance of medical devices in the EU follow the so-called “New approach”: in contrast to the medicinal products regulation which lays out product specifications in detail, the new approach only gives quite general basic requirements. The task of defining detailed technical specifications is delegated to European Standards Organisations, e.g. to Comité Européen de Normalisation (CEN) or to Comité Européen de Normalisation Electrotechnique (CENELEC). If products conform with these standards, it is assumed that they are safe and are thus marketable in all EU member states.

In the current medical device legislation, the core legal framework consists of three directives, which have been amended several times, and consolidated versions are available:

- Council Directive 90/385/EEC on Active Implantable Medical Devices [547]
- Council Directive 93/42/EEC on Medical Devices [548]
- Council Directive 98/79/EC on In Vitro Diagnostic Medical Devices [549]

They aim of these Directives is to ensure a high level of protection for human health and safety and a good functioning of the Single Market.

In order to adapt the existing regulations to the technological and scientific state of the art, the European Commission adopted, on 26 September 2012, two regulation proposals to revise existing legislation on general medical devices and *in vitro* diagnostic medical devices [550, 551]. Revisions include the extending of the scope for legislation; better supervision of independent assessment bodies; clear rights for manufacturers/distributors; and stronger requirements for medical evidence. The ordinary legislative procedure for these proposals, involving the European Parliament and the Council, is ongoing. Once adopted, the revised regulations will replace the existing three medical devices directives.

All in all, the procedure for obtaining marketing authorisation for medical devices differs from the respective procedures for medicinal products. The key steps are the following:

1. Status of the product. It must be decided whether the product is a medical device and falls under the scope of the medical device regulation, and whether specific provisions apply (e.g. for in vitro diagnostics). Although the regulation provides definitions and guidance for clarifying the status (principal intended action by chemical or physical means; intended use specifically for diagnostic and/or therapeutic purposes), it may be necessary to consult the responsible regulatory authority or experts, especially if the product is a combination of medical devices and medicinal products.
2. Classification. The medical device has to be classified according to type (e.g. in vitro diagnostics; active implantable medical device; general medical device) and risk poten-

tial. This classification is crucial, because it determines the scope and extent to which the conformity assessment procedure must be carried out. In general, three risk classes are distinguished (Table 77).

Table 77: Risk Classification of Medical Devices

Risk class	**Description**
Risk class I (incl. cass $I_{sterile}$ and class $I_{measurement\ function}$)	- Risk potential low - e.g. walking frames
Risk class II a	- Risk potential medium - e.g. hearing aids
Risk class II b	- Risk potential elevated - e.g. lung ventilators
Risk class III	- Risk potential high - E.g. active implants

3. Certification. In the certification procedure, the conformity assessment is carried out. If completed successfully, the medical device receives the CE mark and thus market authorisation. For higher risk class devices, the conformity assessment is carried out by a Notified Body, of which there are appr. 80 in the EU. The manufacturer has to submit a technical documentation to the notified body which forms the basis for the conformity assessment. While clinical trials are mandatory for the marketing authorisation of medicinal products, this is the case for only few medical devices. However, the revision of the medical device regulation will implement stricter requirements.

5.2.3 Reimbursement and users' acceptance

The reimbursement systems in Europe of novel medicinal technologies and products represent a major hurdle. Novel technologies are often more expensive and therefore the companies struggle to prove their cost-benefit over already existing and established technologies (medico-economic studies to prove effectiveness). The reimbursement schemes for health technologies are heterogeneous, also among European countries. In Eastern Europe innovative technological solutions are less frequently covered by health insurance compared to Western Europe - the expenditure per head of population is highest in Luxembourg and countries outside the EU belonging to EFTA – in excess of 4,000 Euros per person per year, it is way below 1,000 Euros in most countries that joined the EU in 2004 or later [552].

Also the users' acceptance is often a challenge for the medicinal technologies, since the majority of medical specialists have not received special training. This is especially true for point-of-care diagnostics but also other product categories, where medical specialist prefer traditional treatment schemes to innovative and disruptive technologies that require change in already existing treatment routines and habits. Some medicinal technologies reach the level of maturity to be "fully developed", but do not manage to reach out further into the medical world, e.g. because they do not manage to create demand for their product. There are weak links between R&D, engineering and clinicians which hold back the introduction of “intelligent” Smart Systems.

A further problem is that research-intensive medical products and devices are in general only profitable, if they reach the global market. However, the conditions of official approval, reimbursement by insurances and acceptance by users differ by country and region. In particular, it is important to get access to the US market, but the Asian market gets increasingly attractive.

To sum up, the access to the health market is highly regulated. For each product or device a detailed dossier has to be submitted and the approval process carried out by the regulatory authority in charge may require several months to even years. Furthermore, the reimbursement by the health insurances must be achieved and the acceptance by users.

5.3 Drug/gene delivery and photothermal/photo-enhanced cancer treatment

By attaching drug/gene to suitable carriers, the bioavailability of the drug/gene can be maximized due to efficient loading, target delivery, and controlled release. Following the successful use of carbon nano tubes in lab experiments (CNTs) for **drug/gene delivery**, graphene sharing a similar chemical structure with CNTs, can also be used as drug/gene delivery carrier. Graphene/GO is primarily used for drug/gene delivery in cancer therapy. In the literature, drug delivery is discussed as primary option in this context. Further potentials for the use of graphene/GO in cancer therapy are phototherapy and enhancement of drug efficiency through photo-enhancement.

In **phototherapy**, heat generated by light absorption in graphene induces thermal destruction of cancer cells containing significant concentrations of graphene [553, 554]. The scientific results in this context are very promising, but they are still in the stage of mouse models.

The photothermal effect of graphene can be also used for enhancing the efficiency of chemotherapeutical drugs such as DOX (Doxorubicin) [553]. When photothermal therapy is combined with a photosensitizer an alternative therapeutic modality called **photodynamic therapy** can be developed/achieved[555]. The results of scientific research in this context are promising, but it is still too early for relevant market estimates.

In this chapter, we will discuss drug delivery, on phototherapy and photothermal enhancement of drug efficiency.

5.3.1 Market perspective: graphene/2D materials in drug delivery and other cancer therapy

In general, the market of drug delivery is quite large and attractive reflected in a high number of patent applications in the last years (Figure 81). The US is leading in patents, but the EU has almost the same level. Whereas the total patents in drug delivery are decreasing, those with graphene exhibit a substantial increase although still at a moderate absolute level (Figure 82). In this segment, the US is in the lead, but the absolute level is moderate, so that a catch-up of the EU in this highly attractive market appears to be realistic.

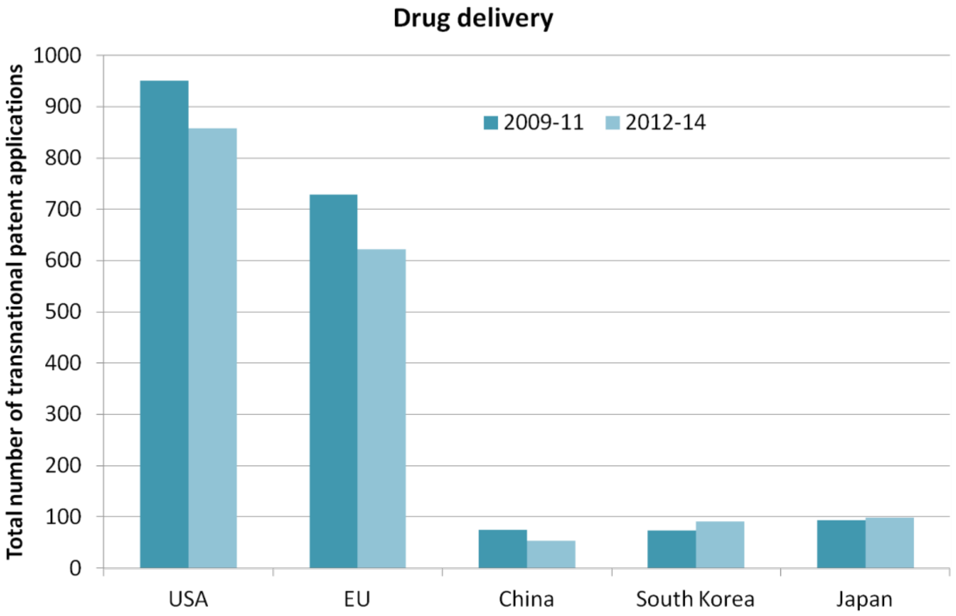


Figure 81: Transnational Patents in Drug Delivery by Priority Years. [21]

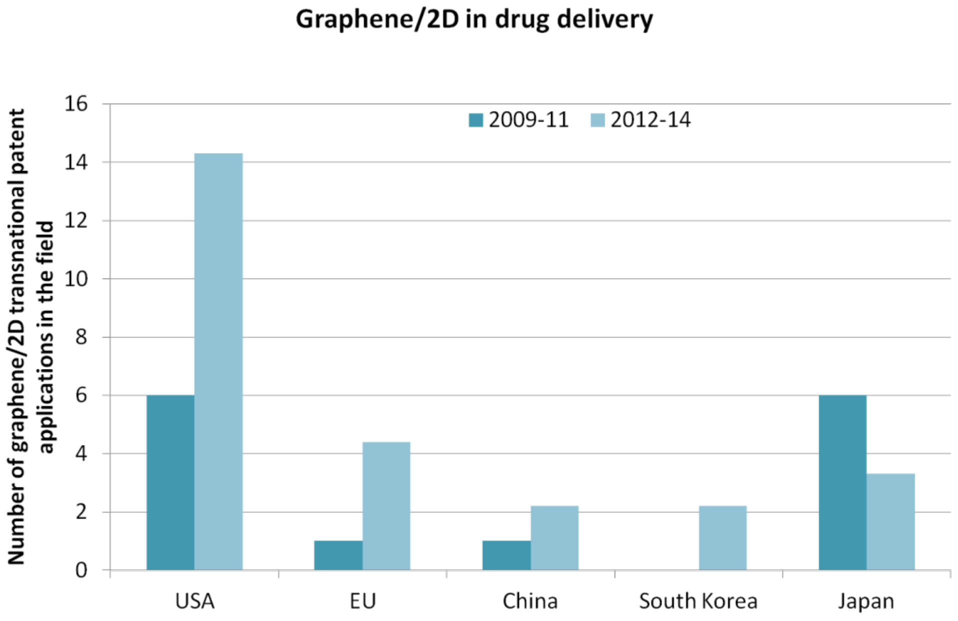


Figure 82: Transnational Patents in graphene-based Drug Delivery by Priority Years. [21]

The drug delivery based on graphene has to be considered as part of the general market of drug delivery. The worth of the global oncology drug delivery market is estimated at a level of $96 billion in 2014 with an annual growth rate of 5 % [556].The volume for 2020 will reach about $141 billion. The share of the European market in 2014 was $23 billion and will reach $30 billion in 2020.

The number of Transnational Patents for the radiation therapy of cancer is quite high with more than 800 in the period of 2012 to 2014, thus it is a relevant market segment.

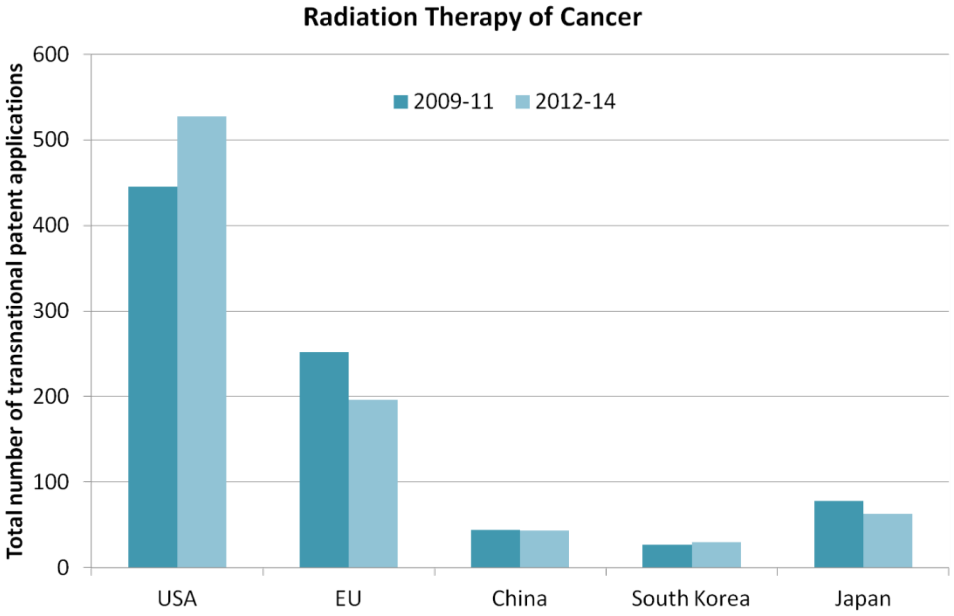


Figure 83: Transnational Patents in Radiation Therapy of Cancer. [21]

The number of patent applications for graphene based phototherapy is still very low with a level of about 10 in total, but it can be assumed that the share will grow rapidly, as soon as the usefulness in human therapy can be verified.

5.3.1.1 Market opportunities

5.3.1.1.1 Oral delivery as preferred market

The market is subdivided in oral and intravenous delivery where the oral part is about 25 %. It is assumed that nano-particles (micro-needles, patches, and orals) will lead the market in the future wherein graphene could have a major relevance. There is a preference for oral delivery, but the intravenous (IV) delivery is still more effective. With nano-particles, also oral forms of drug delivery will become more effective. In 2014, the oral drug delivery market had a size of $24 billion and get at $40 billion in 2020, thus the growth rate is already quite high with 8% and even increase to 14%.

At present the focus is still on basic scientific research, but there is a strong perspective to achieve reliable results in applied research until 2020.

5.3.1.1.2 Cancer therapy as a large, promising and rapidly adopting market

The potential of getting access to a large market is very high, as any promising method of improving the results of cancer therapy will be adopted rapidly.

5.3.1.1.3 Cancer therapy as first entry point

Cancer therapy is discussed as one of the potential areas of graphene, especially for delivery of combined drugs. The latter is very interesting for cancer therapy and personalized medicine both fields with increasing relevance and importance.

5.3.1.2 Market threats

5.3.1.2.1 Competing nano carrier technologies

In nano-drug delivery systems, various materials are discussed such as silica, iron gold, silver, glass, polymers etc. Thus graphene represents only a limited part of nano drug delivery. All these approaches are in early stages, so that insufficient experiences as to advantages and disadvantages exist. So it is possible that some materials exhibit positive features that cannot be reached by graphene.

5.3.1.2.2 High competition: Many stakeholders and other technologies

The market referring to cancer therapy is very large and commercially attractive. Therefore this market has attracted many enterprises, traditional pharmaceutical enterprises, enterprises in bioengineering, and enterprises in all types of medical devices. The competition is very fierce. For instance the number of patent applicants in cancer drugs comprises more than 1000 enterprises. This means that the scientific basis must be quite large and the evidence for validity of the claims must be strong.

A competitive approach is the use nano gold particles for similar purposes [557]. The market for radiation therapy of cancer is estimated at $3.5 billion where phototherapy is a limited part besides x-radiation.

5.3.1.2.3 User acceptance

A further potential problem is the users’ acceptance. The use of graphene in drug delivery will imply a change of chemical treatment of cancer from hospital-based infusion to home-based treatment with micro-needles, patches, or oral delivery. It is a question whether the physicians will be ready to reduce their monitoring in cancer treatment. At least a longer period of transition of the habits has to be taken into account.

5.3.1.2.4 Competition and strong players defending traditional systems

Furthermore, the attractive market of drug delivery is characterised by high competition and the providers of traditional delivery systems will try to defend their market shares with a vengeance.

A major problem for graphene/GO-based delivery systems will be convincing solution to the toxicity apprehension. The stigma of toxicity can stop all endeavours to bring graphene-based delivery into the market.

5.3.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in drug delivery

In this very early stage it is not possible to say anything sound as to strengths and weaknesses performance, or barriers/challenges with respect to phototherapy and photothermal enhancement of drug efficiency. This chapter therefore focuses on drug delivery.

5.3.2.1 Current strengths of graphene/2D materials in drug/gene delivery

5.3.2.1.1 GO as attractive delivery system

Due to the specific features of graphene such as the high surface area available, the numerous chemical strategies and the abundant chemical functions, especially graphene oxide (GO) attracts great interest as novel drug/gene delivery system with high efficiency, multi-targeted drug delivery and controlled release [553].

Major arguments for graphene are the possibility of a targeted delivery and the delivery of a set of combined drugs. Therefore it can be assumed that graphene will get a major weight in nano drug delivery market due to these specific advantages. Compared to CNTs graphene/GO has the main advantage of a much lower risk of toxicity [558].

5.3.2.1.2 Combined drugs

In the literature, drug delivery is discussed as primary option for the use of graphene in cancer therapy. Major arguments for graphene are the possibility of a targeted delivery and the delivery of a set of combined drugs, these features can be seen as unique selling point of graphene. Therefore it can be assumed that graphene could get a major weight in nano drug delivery market due to these specific advantages.

5.3.2.1.3 First in vitro studies are promising

Numerous reports on the in vitro efficacy of the drug delivery systems based on graphene/GO have been published. Various successful ways of drug/gene delivery are documented in vitro in [553, 559, 560].

5.3.2.2 Current weaknesses and challenges of graphene/2D materials in drug delivery

5.3.2.2.1 Low maturity and missing in vivo studies

Only few examples of drug delivery with graphene/GO in vivo are reported yet. Most studies are base on in vitro models. For further investigations, in vivo studies are necessary

5.3.2.2.2 Potential toxicity

A potential barrier to the application of graphene in drug/gene delivery is the toxicity of graphene and GO. Here, [561] suggest amine-modified graphene as alterative. Zhou and Liang [553] report of a variety of studies on toxicity of graphene/GO with no clear result, [560] see a low level of toxicity of GO. Sasidharan et al. (2016) [562] see a relevant DNA-damaging potential of few-layer graphene. Bussy et al. [563] warn of generalizations on the toxicity of graphene/GO. Sunil et al. (2012) [561] suggest an amine-modified version of graphene for reducing toxicity. Tissue distribution and elimination studies of functionalized GO suggest rapid elimination. [564] Further studies on biodegradation through enzymes suggest that hydrophilicity, negative surface charge, and colloidal stability of the aqueous GO play key roles in the biodegradability. [565]

To summarize, there is a certain risk of toxicity of graphene/GO, but it is no absolute barrier for the use in gene/drug delivery. There obviously exist various ways to cope with this problem. Recent studies are rather in favour of a safely use of GO for drug delivery, but further studies are needed.

5.3.3 KPIs for of drug delivery

In the context of the use in biomedicine, it is difficult to establish simple key performance indicators (KPI), as the efficiency of a health product or a device closely linked to a health product can only be investigated in clinical tests. Clinical test take about ten years, and can be shortened only, if a very high impact appears to be probable. Clinical trials imply statistical tests which shares of the treated persons show a very positive, positive, low, no, negative, very negative impact. If the overall assessment based on a variety of parameters is better than drugs/devices of the same category, the drug/device is given a new class where higher prices can be achieved.

In any case, it can be expected that drug delivery systems are considered either as drugs (new combinations of drugs) or high risk devices requiring long and complex admission procedures.

5.3.4 Roadmap for drug/gene delivery

5.3.4.1 Current maturity: Lab scale and early investigation

There are some promising results in terms of drug delivery, mostly in vitro. But further investigations are needed, especially on how to deal with the toxicity and how efficient graphene is in comparison to other investigated drug carrier systems. Therefore benchmarking is also needed.

Photothermal therapy and photo-enhancement are at a very early stage and currently basic research.

5.3.4.2 Barriers/Challenges (summarized)

The major barriers/challenges of the use of graphene/GO for drug delivery are

- Sufficient proof of usefulness compared to other delivery systems, in particular in the context of cancer therapy
- Convincing solutions for the problem of toxicity
- Conception of easy-to-handle products home use.

Major barrier for photothermal treatment and photo-enhancement at the moment is the low maturity. Before further assessments can be made, the actual functionality and feasibility needs to be proven and benchmarked.

5.3.4.3 Potential actions

If the area of graphene/2D in drug/gene delivery is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

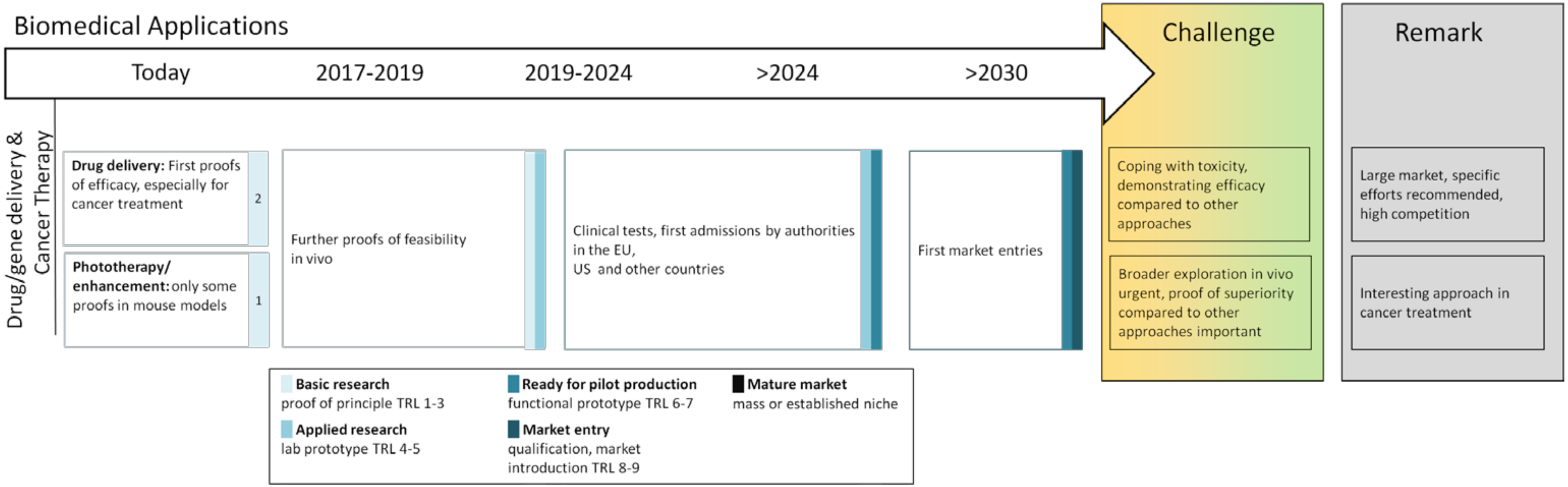
Broader expansion of in vivo investigations and clinical tests are needed for market entry of graphene/GO in drug delivery.

Benchmarking of graphene/GO with other drug delivery systems

The scientific research in photothermal effects of graphene/GO in the context of cancer should be intensified, as this is a promising market. Especially the use in human therapy has to be substantiated in a profound way. Only against such a background, it will be possible to raise the interest of enterprises for this perspective.

5.3.4.4 Roadmap

At present the focus is still on basic scientific research, but there is a strong perspective to achieve reliable results in applied research until 2020.



Drug delivery: First proofs of efficacy, especially for cancer treatment

Phototherapy/ enhancement: only some proofs in mouse models

Further proofs of feasibility in vivo

Clinical tests, first admissions by authorities in the EU, US and other countries

First market entries

Coping with toxicity, demonstrating efficacy compared to other approaches

Broader exploration in vivo urgent, proof of superiority compared to other approaches important

Large market, specific efforts recommended, high competition

Interesting approach in cancer treatment

Basic research proof of principle TRL 1-3

Applied research lab prototype TRL 4-5

Ready for pilot production functional prototype TRL 6-7

Market entry qualification, market introduction TRL 8-9

Mature market mass or established niche

5.4 Biosensing & Bioimaging

Various applications of graphene in biosensing and bioimaging are reported [553, 559, 560, 566]. Thus some novel fluorescence resonance energy transfer (FRET) based biosensors were developed based on the super efficient fluorescence quenching ability of graphene. Its unique electronic property allowed for making FET type biosensors whereby important biomolecules can be detected such as nucleic acids, proteins, or growth factors. Controllable self-assembling of graphene-biomolecules enabled to build ultrasensitive biosensors for the detection of DNA and other molecules. As a matrix for the detection of molecules, a graphene-based nanoplatform for matrix-assisted laser ionization mass spectrometry was conceived etc. GO-based instruments for cellular imaging were built. Manipulation of the size, shape and relative fraction of domains of GO by reduction chemistry provides opportunities for tailoring its optoelectronic properties. To summarize, graphene and GO allow for highly specific ways of biosensing and bioimaging. Please refer to chapter 4.5 Sensors for further, more generic assessments on biosensors and the roadmap.

5.5 Antibacterial material

In many research projects, the potential toxicity of graphene towards bacteria could be shown, but some other studies did not show significant cytotoxicity [553, 559]. Thus there is a controversy about the toxicity of graphene towards bacteria. Nevertheless, a filter pare with a strong antibacterial effect was developed useful for clinical applications. The general field of coatings is covered in chapter 2.3 Industrial large scale coatings and paints, here we will only focus on the biomedical application part.

5.5.1 Market perspective: graphene/2D materials as antibacterial material

5.5.1.1 Market opportunities

5.5.1.1.1 Potentially high volume and strong industrial base in EU

Despite the scientific controversy, various patent applications concern sterile absorbable surgical homeostatics with graphene. As the experiences are still at the early beginning and the advantages and disadvantages compared to other material are not clear yet, it is not possible to provide reliable market estimates. In any case, these applications refer to daily use in biomedicine and will have a high volume. In any case, the overall number of patent applications in this market is considerable, and enterprises from the EU are in the lead (Figure 84).

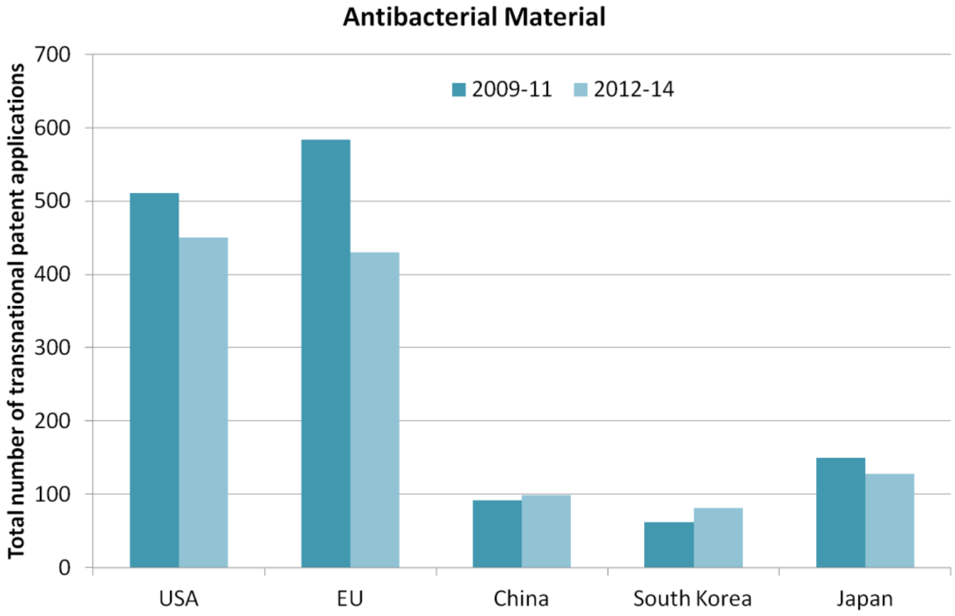


Figure 84: Transnational Patents for Antibacterial Material in Biomedicine by Priority Periods. [21]

5.5.1.1.2 Toxicity against bacteria but not human cells as an opportunity

This special market for medical devices is quite attractive. In particular, if graphene-based solutions can bring in unique selling points, e.g. toxic effects against bacteria and not against human cells. Also in this segment the studies on graphene-based approaches are still in an early stage, so that more detailed statements on the potential market volume are not possible.

5.5.1.2 Market threats

5.5.1.2.1 Highly competitive market

The market of antibacterial material for biomedicine is highly competitive. In particular, many conventional, cheap methods are available, and only if graphene-based approaches can provide specific advantages, they will succeed to establish themselves in the marketplace.

5.5.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use in antibacterial materials

Please refer to chapter 2.3 Industrial large scale coatings and paints for a broader analysis of the topic.

5.5.2.1 Current strengths of graphene/2D materials in antibacterial materials

5.5.2.1.1 First prototypes show functionality

There are first proof of principles (e.g. a filter paper) with antibacterial properties. However, the actual effect of graphene needs to be proven.

5.5.2.2 Current weaknesses and challenges of graphene/2D materials in antibacterial materials

5.5.2.2.1 Controversy about actual cytotoxicity

As mentioned above, there is a scientific controversy on the potential toxicity of graphene towards bacteria. There are reports, where antibacterial properties could be shown, but some other studies did not show significant cytotoxicity. Benchmarking with other materials is needed.

5.5.3 Roadmap for antibacterial materials

5.5.3.1 Current maturity: open question of actual effect

The question is still open to which extent graphene can contribute to antibacterial materials

5.5.3.2 Barriers/challenges (summarized)

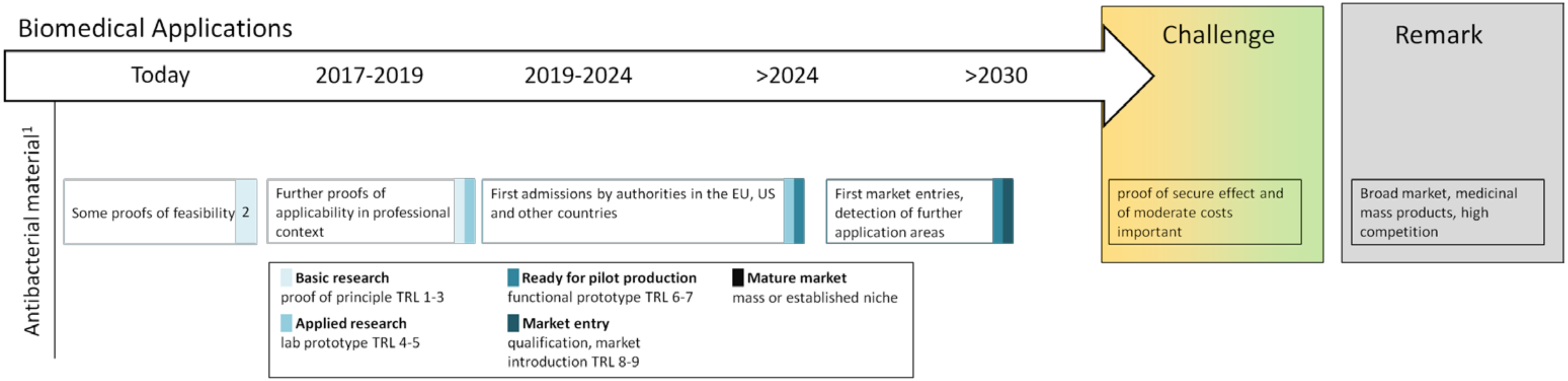
The major barrier is to show the actual potential of graphene in antibacterial applications.

5.5.3.3 Potential actions

If the area of graphene/2D in antibacterial materials is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

In view of the diversity of enterprises in this segment, also many European ones, it will be favorable that scientific institutions get in dialogue with enterprises for identifying attractive needs that can be met by graphene-based approaches.

5.5.3.4 Roadmap



Biomedical Applications

Today | 2017-2019 | 2019-2024 | >2024 | >2030

Antibacterial material[1]

- Today: Some proofs of feasibility 2
- 2017-2019: Further proofs of applicability in professional context
- 2019-2024: First admissions by authorities in the EU, US and other countries
- >2024: First market entries, detection of further application areas

Challenge

proof of secure effect and of moderate costs important

Remark

Broad market, medicinal mass products, high competition

- **Basic research** proof of principle TRL 1-3
- **Applied research** lab prototype TRL 4-5
- **Ready for pilot production** functional prototype TRL 6-7
- **Market entry** qualification, market introduction TRL 8-9
- **Mature market** mass or established niche

[1]: see also coatings chapter

5.6 Biocompatible devices

Due to the high biocompatibility of graphene and GO, and their unique parameters, notably their considerable electron mobility, thermal conductivity, high surface area and electrical conductivity, are bringing heightened attention into biomedical applications. In addition to the already mentioned areas of applications, many potential applications in the area of biocompatible devices are suggested and studied in the literature, in particular the use of graphene/GO for

- Prostheses
- Brain/nerve electrodes, bioelectronic medicine
- Small implants
- Tissue engineering

These potential applications are described in more detail in the following paragraphs. This broad variety of applications illustrates that many other application fields will be detected in the next years.

5.6.1 Prostheses

Graphene and GO attract increasing interest for use as coating material of prostheses, it is easy to attach it to the surface of bones, the friction and wear are low, thus there are good prospects that graphene will become a standard in this context, although the present number of patent applications is still limited.[14]

The number of patents on bone prostheses is considerable, but decreasing, obviously new ideas with traditional approaches lack (Figure 85). The share of EU enterprises in patents is almost equivalent to the US ones. The number of graphene-based patents is still too low for any reliable statements.

The markets for orthotics had a level of $4.7 billion by 2015 according to Global Industry Analysts (GIA) [567], thus the market has a relevant level, as the loss or failure of bone tissue is one of the most frequent and costly problem of human health care.

The major challenge for graphene/GO in this market segment is to achieve high, competitive durability, low friction and low wear, and in the case of abrasion low toxicity for humans. The strain of bone prostheses, in particular hip joints, are extreme, and high performance in comparison to competing materials such as special steel or ceramics will be important for the break-through of graphene-based solutions. In any case, the market is very promising.

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[14] In this context, many considerations on coatings in chapter 2.3 of this report apply.

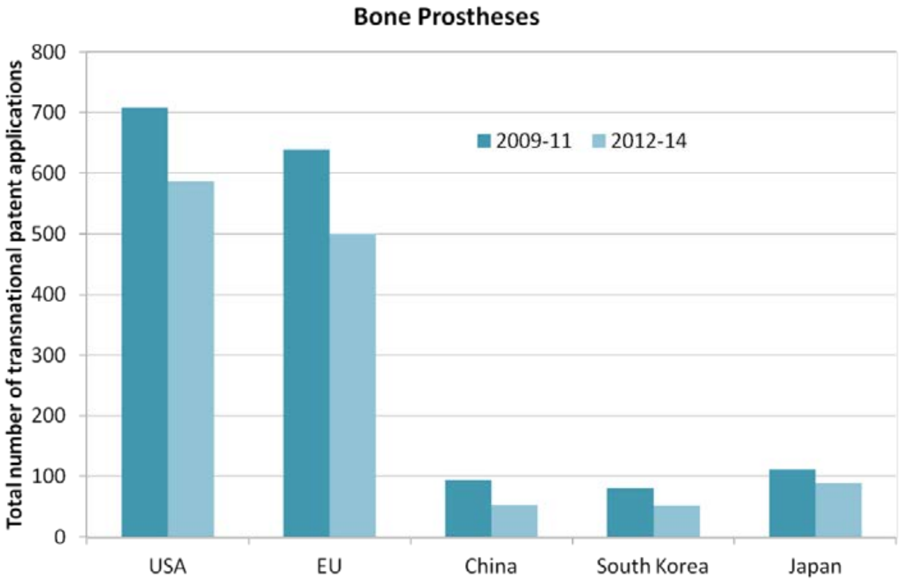

Figure 85: Transnational Patents on Bone Prostheses by Priority Periods. [21]

5.6.2 Neural electrodes and electrically functional implants (bioelectronic medicine)

Various studies show that graphene is a promising material for use in electrodes that interface with neurons, based on its excellent conductivity, flexibility for molding into complex shapes, biocompatibility, and stability within the body.

Major areas of application of graphene in the area of neural sensing and stimulation are in clinical research:

- Electrode arrays for mapping brain in preoperative settings (awake surgery – epilepsy, GBM)
- Epicortical and intracortical electrodes for brain-machine interfaces (control of artificial limbs, stimulation of limbs with brain signal after spinal cord injury) (clinical research)
- PNS stimulating electrodes for brain-machine interfaces

Neurostimulation technology can improve the life quality of those who are severely paralyzed or suffering from profound losses to various sense organs, as well as for permanent reduction of severe, chronic pain which would otherwise require constant (around-the-clock), high-dose opioid therapy (such as neuropathic pain and spinal-cord injury). It serves as the key part of neural prosthetics for hearing aids, artificial vision, artificial limbs, and brain-machine interfaces. In the case of neural stimulation, mostly an electrical stimulation is utilized and charge-balanced biphasic constant current waveforms or capacitively coupled charge injection approaches are adopted. The vision of bioelectronic medicine is to also address widespread diseases such as rheumatoid arthritis, sleep apnea or hypertension.

Medical devices using electrical, mechanical, or light stimulation to affect electrical signal-ing in relevant tissue types are sometimes called electroceutical devices. In this area many papers show promising approaches for the application of graphene.

5.6.2.1 Market perspective: bioelectronic medicine

The global electroceuticals/bioelectric medicine market is expected to reach $ 25 billion by 2021 from $ 17 billion in 2016 with an annual growth rate of about 8 %. [568] Although not all areas of the electroceutical/bioelectric market are relevant for graphene applications, the market size and its growth are considerable. The largest market share is currently held by implantable cardioverter defibrillators.

Also the number of Transnational Patents for electroceuticals/bioelectrics is quite high with 279 in the period of 2012 to 2014 (see Figure 86). The USA dominates the market and, at present, the number of graphene-related patents is quite moderate. Thus, there is a good chance to seize this specific segment. European companies such as Medtronic, LivaNova, Biotronik, Cefaly Technology or Oticon Medical are active in various areas of electroceuticals.

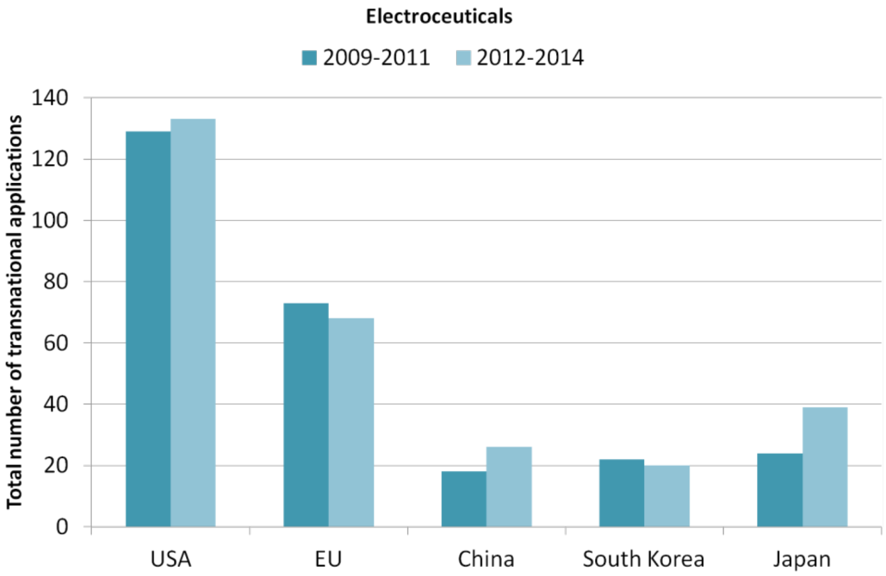

Figure 86: Total number of transnational patent applications in the field of electroceuticals. [21]

A major area of bioelectric medicine is nerve stimulation with two primary targets of application:

- The control of artificial limbs by brain for handicapped persons
- The modulation of the immune system by neural stimulation as alternative to pharmaceutical drugs.

As to the stimulation of nerves, the transnational patent applications per country is depicted in Figure 87. Compared to that, the number referring to the modification of the immune system is much smaller (see Figure 88). Thus, this subfield is still in a very early stage. The present relation between the USA and the EU can change rapidly due to the low number of applications. Looking at the scientific publications on neuro stimulation of the immune system first prominent contributions already appeared in 2000 [569] and later in 2004 and 2009 (e.g. Steinmann [570] and Tracey [571]). Thus, a longer experience with this topic already exists.

In addition, the activities of the EU are on the same level as those of the USA (see Figure 89). In consequence there are good prospects that the EU gets a major player in this new field where large dynamic markets can be expected.

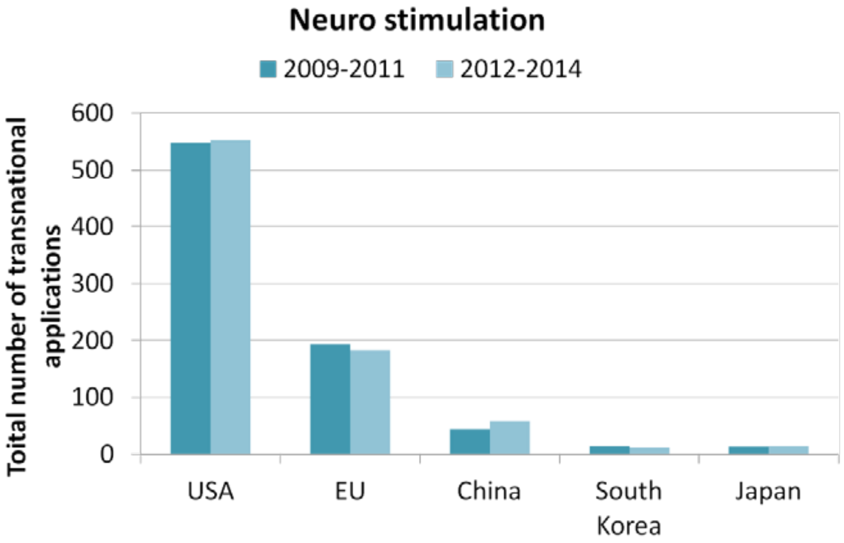

Figure 87: Total number of transnational patent applications in the field of neuro stimulation. [21]

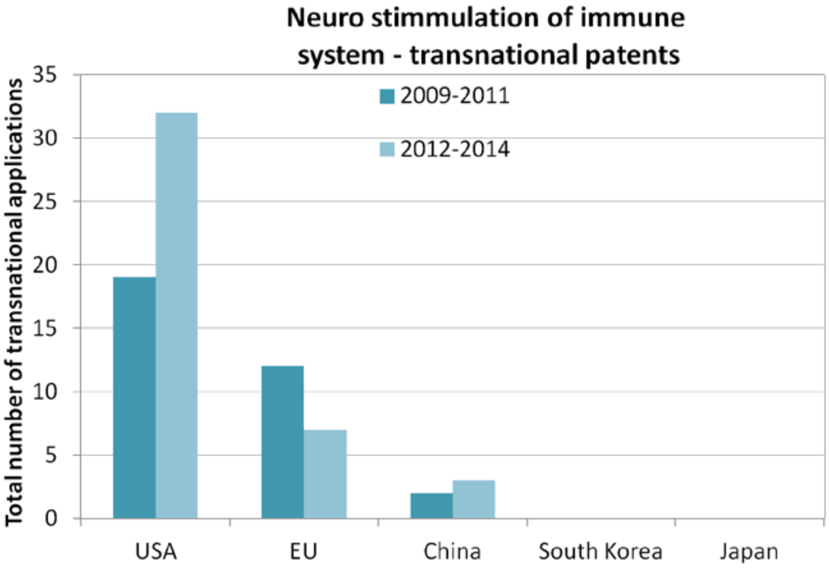

Figure 88: Total number of transnational patent applications in the field of neuro stimulation for the immune system. [21]

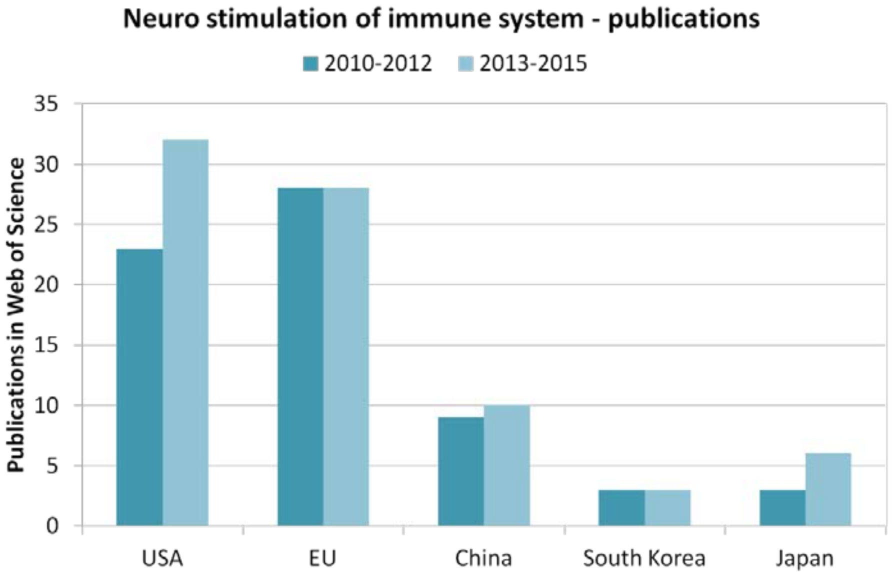

Figure 89: Total number of publications in the field of neuro stimulation for the immune system. [164]

5.6.2.1.1 Market opportunities: Special opportunities of graphene in nerve stimulation

The market of electroceutical devices has many segments such as implantable cardioverter defibrillators, cardiac pacemakers, spinal cord stimulators, cochlear implants, deep brain stimulators, transcutaneous electrical nerve stimulators, vagus nerve stimulators, sacral nerve stimulators, or retinal implants. The graphene applications seem to be most appropriate for nerve and brain stimulation [572], but also the other areas appear to be promising. The referring research is still in an early stage – as reflected in the low number of patent applications - , but these applications are medical devices and not medicinal products, thus the admission barriers are lower and the delay for market entry is limited.

A special area is the modulation of the immune system by nerve stimulation. This is a very promising alternative to pharmaceutical treatments and will affect a considerable market volume. At present it is still in an early stage of research, but the scientific results of the last years are very promising.

Electrodes are used as neural biosensors and for prosthetic applications — such as deep-brain intracranial electrodes used to control motor disorders (mainly epilepsy or Parkinson’s) and for brain-computer interfaces (BCIs), used to recover sensory functions or control robotic arms for paralyzed patients. These applications require an interface with long-term, minimal interference [573]. This bioelectronic medicine approach can be also employed for other diseases, where electrical or neuronal stimulation help to relieve or suppress symptoms, such as in sleep apnea, rheumatic arthritis or hypertension. Please also refer to chapter 4.5 Sensors, where the possibility of a combined bio sensor and actuator is seen as an opportunity in biosensors.

Neurons and nerves are electrically excitable cells that transmit and process information in the nervous system. General challenges and opportunities for new technologies for bioelectronic medicine are:

- Signal to noise: Recording neural activity from peripheral nerves is difficult due to low extracellular voltages. Higher electrode resolutions (orders of magnitude) and low signal to noise are needed to address these peripheral nerves. Removal of artefact noise from pulsation and movement (from muscles etc.) is required
- Conformational interfaces: Close approximation of electrodes to tissue is needed requiring novel soft array designs needed, especially for small, irregular nerves of the viscera and in disparate and difficult anatomy
- Non-damaging stimulating interface designs
- Miniaturisation: Miniaturised circuits to ensure minimally invasive techniques for implantation, allow outpatient procedures and broader patient uptake
- Biocompatibility: small mechanical mismatch between tissue and electrode, activation of fibrotic scar and death of neurones.

Areas of research for bioelectronic medicine address these challenges by architectural optimization (softening, conformation, small curvature) and electro-chemical research to improve biocompatibility, charge injection and reduce electrode corrosion.

5.6.2.1.2 Market threats

High competition, but no resistance from established enterprises

Like in all growing segments of the health market, the competition in the bioelectronic market is very fierce. Thus, various other materials for nerve electrodes such as gold, platinium or silicon are suggested as well, but as the referring markets are very new, no competitors defending traditional markets will appear and there is no incumbent technology.

Fierce competition with pharmaceutical companies can be expected

This market segment will directly affect the pharmaceutical one, thus fierce resistance can be expected from this side. In the end, the effectiveness compared to chemical druds and the cost will de decisive.

Viability of nerve stimulation as bioelectronic medicine not yet demonstrated commercially

Although first studies on bioelectronic medicine appear promising, there is no product or treatment on the market that addresses nerve stimulation, yet. Graphene is only a small element within the complex research on neural stimulation, thus, the major delay until broader market penetration will be due to the early stage of clinical research on neural stimulation which does not only refer to the movement of artificial limbs, but also affects the immune system. The potential market is large, but it will take some time until the achievement of a relevant size. Thus, the main uncertainty is not the appropriateness of grapheme for this application, but the effects of nerve stimulation on the immune system in general. Further research on the impact of neural electrodes will be needed.

User acceptance

A potential problem is the user acceptance of bioelectronic medicine. On the one hand, the avoidance of chemical drugs with substantial side effects will increase the user acceptance of bioelectronic medicine, on the other hand the longterm implantation of electrodes in the brain and at other sensitive places may hamper the user acceptance.

5.6.2.2 Graphene/2D materials perspective: current strengths, weaknesses and challenges for the use as neural electrodes and electrically functional implants (bioelectronic medicine)

5.6.2.2.1 Current strength: potentially enabling character

Graphene exhibits specific strengths in the area of bioelectronic devices such as for use in electrodes that interface with neurons, based on its potentially excellent conductivity, flexibility/stretchability for molding into complex shapes, potential biocompatibility, and stability within the body. With the use of graphene for electrodes or electrode coatings, a major bottleneck of the research in nerve stimulation could be removed.

Other applications suggest the use in ophthalmology for retinal prostheses. The graphene-based substrates they studied promise to overcome problems with “glial scar” tissue formation (caused by electrode-based brain trauma and long-term inflammation). [574] To avoid that, current electrodes based on tungsten or silicon use a protective coating on electrodes, which reduces charge transfer. Current electrodes are also rigid (resulting in tissue detachment and preventing neurons from moving) and generate electrical noise, with partial or complete loss of signal over time.

5.6.2.2.2 Current weaknesses and challenges: low maturity and unclear reliability

The clinic research on the electric stimulation and its effect on the immune system already has a tradition of several years, but the transfer into application is still in an early stage. Thus, the main challenge does not refer directly to graphene, but indirectly to the impact of electrical stimulation of nerves the movement of artificial limbs and the immune system and to achieve an appropriate level of costs for practical applications. The main uncertainty is a clear prove that the level of toxicity is minimal or can be handled appropriately.

In the literature, various suggestions to realise graphene-based electrodes for biomedical applications are forwarded. The graphene-related developments are still in an early scientific stage, so the potential market prospects cannot be determined in a reliable way yet. However, it can be expected that an agreement on satisfying and promising solutions will be reached soon. Major barriers for graphene at the moment are long term stability and performance in vivo from the technological side. In terms of production, a reproducible GMP process is the main hurdle. A specific challenge for graphene applications is the possible toxicity of long-term implants.

5.6.2.3 Potential actions for neural electrodes and electrically functional implants (bioelectronic medicine)

It will be important that in the new markets of movement of artificial limbs and stimulation of the immune system first visible results leave the laboratory and enter the markets. Their success will open up the market for follow-up products. In particular in the health market referring to the immune system, a powerful demonstration is necessary that a valuable alternative to chemical drugs exists. Valid clinical research is performed in the EU and close cooperation of enterprises in the market of medicinal products and medical devices with scientific research groups will yield appropriate products with high probability.

5.6.3 Animal trials of neural electrodes and electrically functional implants

Linked to the considerable potential of neural electrodes in biomedicine, there are also various applications in animal research as precursor of clinical research, in particular

- Flexible epicortical devices for recording brain activity (arrays with different recording sites)
- Rigid/flexible intracortical devices for recording brain activity (linear array with different recording sites)
- Stimulating electrodes for peripheral nervous system
- Cuff electrodes for nerves
- Spinal cord electrodes for neuromodulation, injury, etc
- In vitro arrays to study electrical activity in cell cultures

These applications in animal tests will become a self contained market, as the knowledge on the application potential of neural electrodes is still in an early stage and a broad number of possible uses has to be tested in preclinical research.

5.6.3.1 Market opportunities

It is difficult to assess the volume of this market of animal trials, as the general area of this very new activity is difficult to define. It is – to a certain extent – testing of medical devices and also a part of animal testing. However, the conventional animal testing of drugs, cosmetics or agrochemicals refers to the toxicity of chemicals and not the effects of new medical devices.

To get an idea of the market volume of this type of research, the NIH budget for projects including animal experimentation was $10 billion in 2015.[15] In any case, this special market will be much smaller than the bioelectronic market in general, but the barriers to market entry are lower than those for biomedical products, so that the market introduction can be achieved much earlier, and the market volume is still considerable. A substantial growth is in all probability.

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[15] http://www.navs.org/the-issues/the-animal-testing-and-experimentation-industry/#.WHzMn3opVaR

5.6.4 Small implants

Graphene proves to be suitable for extremely small implants in blood vessels as filters or stents. The whole field of small implants attracts a considerable number of Transnational Patents (Figure 90), even more than for bone prostheses (Figure 85), and relevant market volume can be assumed. The few patents refer to heart stents, but the small number does not allow for any further statement on the development of the next years.

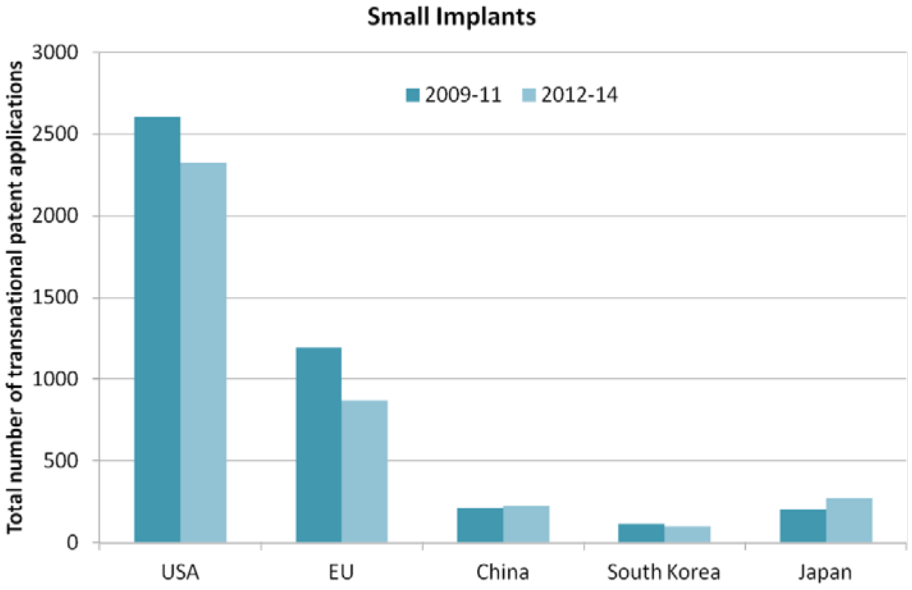


Figure 90: Transnational Patents on Small Implants by Priority Periods. [21]

5.6.5 Tissue engineering

Various authors have described the use of GO or RGO (reduced graphene oxide) as scaffolds in tissue engineering [553]. The whole field of tissue engineering is a dynamic area of modern medicine and graphene will bring in new prospects. For instance, substrates from stem cell differentiation or components for implant devices can be generated. In particular, tissue regeneration in the nervous area appears to be very promising. In the recent period of 2012 to 2015 190 publications on tissue engineering were published, but only 9 Transnational Patents. Thus the field is promising, but still in an early exploratory stage. For the whole field of tissue engineering a relevant number of Transnational Patents were registered in recent years, but less than for prostheses or small implants. Thus the market is relevant, but quite specialised.

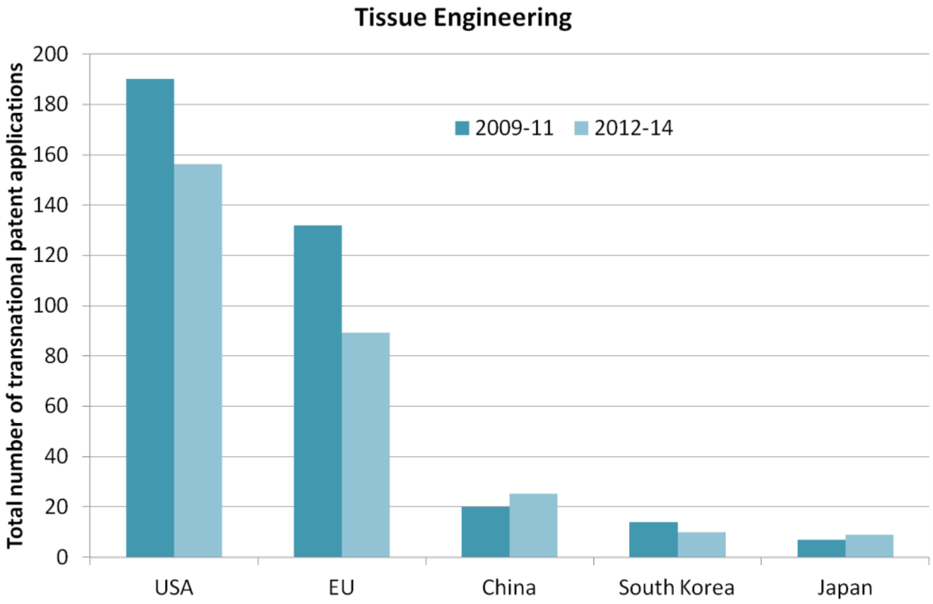


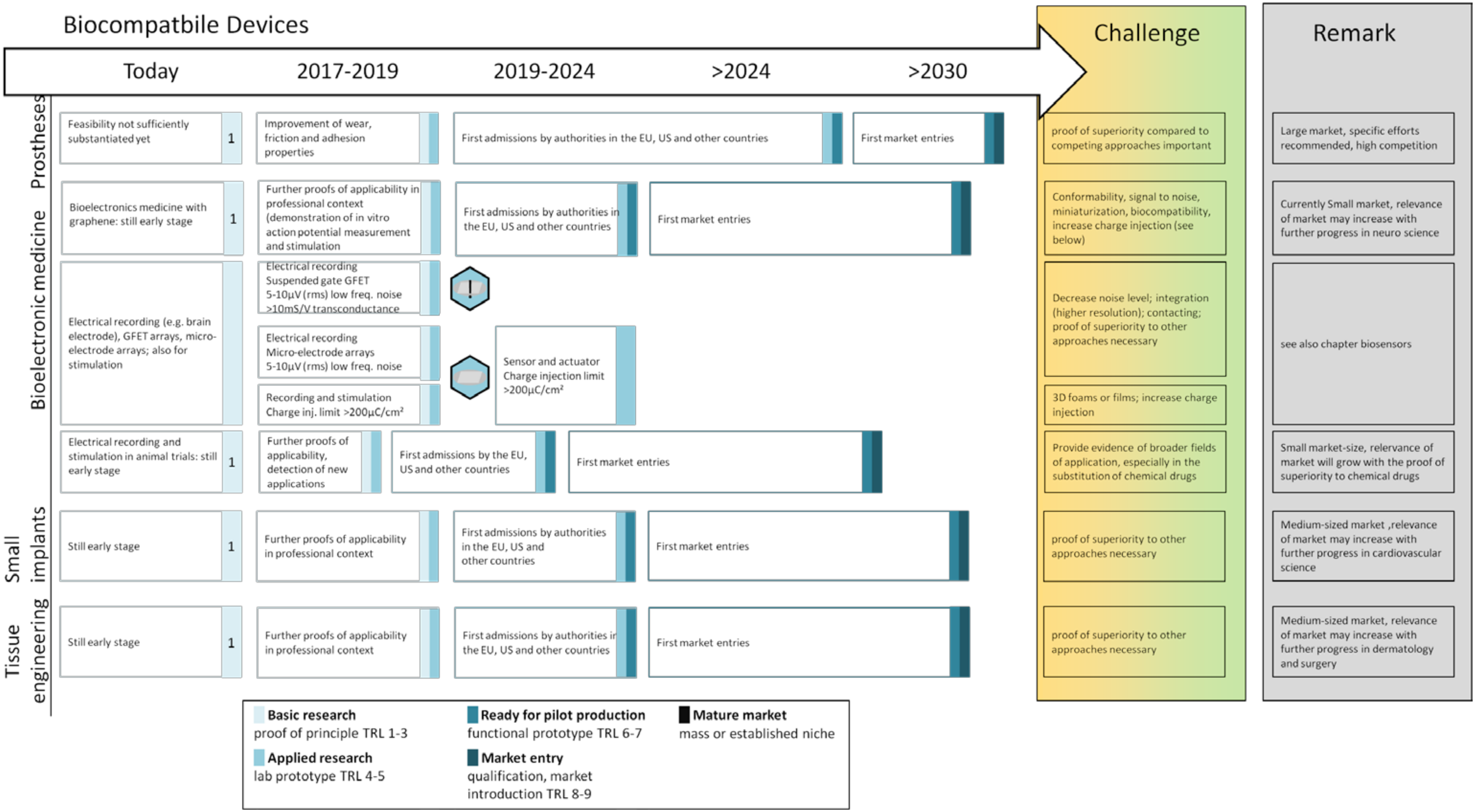
Figure 91: Transnational Patents in Tissue Engineering. [21]

5.6.6 Potential actions for biocompatible devices in general

If the area of graphene/2D in biocompatible devices is seen as promising for Europe and the topic is further pushed, the following potential actions, derived from the challenges, are suggested:

For biocompatible devices, especially the markets for bioelectronic medicine, bone prostheses, small implants and tissue engineering are relevant. A considerable number of EU enterprises already work in these fields. However, the activities referring to graphene/GO are still in an exploratory stage. It is recommendable to get in contact with the enterprises in the market for getting information how to focus the research on graphene/GO and to demonstrate them the advantages of graphene/GO.

5.6.7 Roadmap for graphene in biocompatible devices



Biocompatbile Devices

	Today	2017-2019	2019-2024	>2024	>2030	Challenge	Remark
Prostheses	Feasibility not sufficiently substantiated yet 1	Improvement of wear, friction and adhesion properties	First admissions by authorities in the EU, US and other countries		First market entries	proof of superiority compared to competing approaches important	Large market, specific efforts recommended, high competition
Bioelectronic medicine	Bioelectronics medicine with graphene: still early stage 1	Further proofs of applicability in professional context (demonstration of in vitro action potential measurement and stimulation	First admissions by authorities in the EU, US and other countries	First market entries		Conformability, signal to noise, miniaturization, biocompatibility, increase charge injection (see below)	Currently Small market, relevance of market may increase with further progress in neuro science
	Electrical recording (e.g. brain electrode), GFET arrays, micro-electrode arrays; also for stimulation	Electrical recording Suspended gate GFET 5-10 μV (rms) low freq. noise >10mS/V transconductance	!			Decrease noise level; integration (higher resolution); contacting; proof of superiority to other approaches necessary	see also chapter biosensors
		Electrical recording Micro-electrode arrays 5-10 μV (rms) low freq. noise Recording and stimulation Charge inj. limit >200 μC/cm^2	Sensor and actuator Charge injection limit >200 μC/cm^2			3D foams or films; increase charge injection	
	Electrical recording and stimulation in animal trials: still early stage 1	Further proofs of applicability, detection of new applications	First admissions by the EU, US and other countries	First market entries		Provide evidence of broader fields of application, especially in the substitution of chemical drugs	Small market-size, relervance of market will grow with the proof of superiority to chemical drugs
Small implants	Still early stage 1	Further proofs of applicability in professional context	First admissions by authorities in the EU, US and other countries	First market entries		proof of superiority to other approaches necessary	Medium-sized market ,relevance of market may increase with further progress in cardiovascular science
Tissue engineering	Still early stage 1	Further proofs of applicability in professional context	First admissions by authorities in the EU, US and other countries	First market entries		proof of superiority to other approaches necessary	Medium-sized market, relevance of market may increase with further progress in dermatology and surgery

Basic research proof of principle TRL 1-3

Applied research lab prototype TRL 4-5

Ready for pilot production functional prototype TRL 6-7

Market entry qualification, market introduction TRL 8-9

Mature market mass or established niche

5.7 Conclusions for graphene in biomedicine

The market for graphene/GO in biomedicine is quite segmented. In all potential areas the research is still in an early exploratory stage. In particular applications in drug delivery, biosensing, antibacterial material, bone prostheses and small implants are quite interesting. However, the research in all fields of application is still at an early stage, and often the final proof of feasibility is still missing. However, it can be expected that further cases for application will be detected in the next years, for instance in biosensing.

Table 78: Summarized assessment table of biomedicine application areas primarily sorted by European market potential and secoondary sorted by USP.

Application sub topics	**Current technological potential (USP)**	**Market potential (EU perspective)**
Drug/gene delivery	+	++
Prostheses	+	++
Brain electrodes/bioelectronic medicine	+	+/++
Biosensing & bioimaging	+	+
Small implants	+	+
Tissue engineering	+	+
Antibacterial material	+?	+
Phototherapy	?	+
Enhancement of drug efficiency	?	+

It is recommendable to get in close contact to enterprises which are already present in the marketplace to get information on specific requirements of the different market segments and thus focus the research in graphene/GO. Furthermore the enterprises could be sensitized to the specific advantages of graphene/GO-based approaches. A specific feature of the market in biomedicine is the requirement that all products and devices must be admitted by the public authorities of the respective countries. This brings in a delay or at least three years.

In any case, there is a broad industrial basis in the EU which could adopt graphene/Go in biomedicine. Therefore the market potential in an EU perspective is generally positive.

A.1 Appendix: Readiness Levels

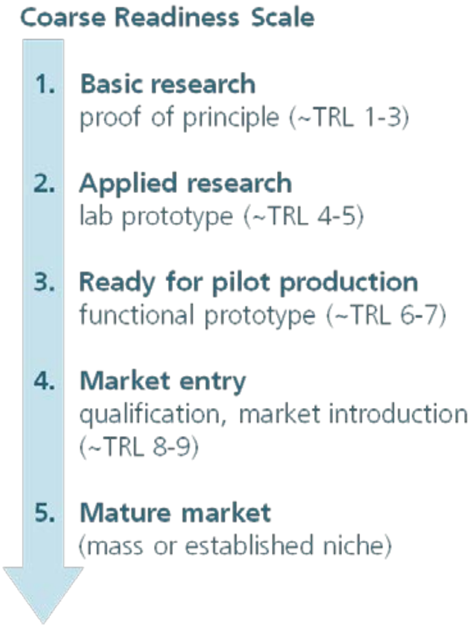
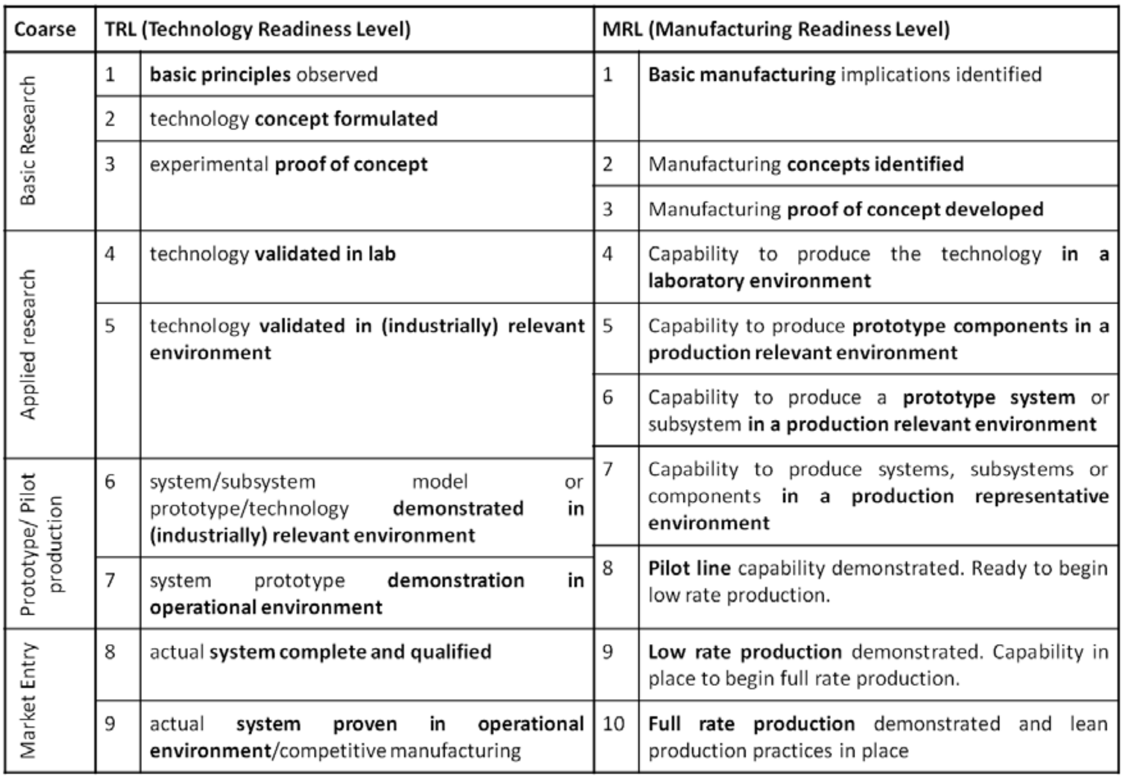


Figure 92: Coarse readiness scales used in the roadmaps



Coarse	TRL (Technology Readiness Level)		MRL (Manufacturing Readiness Level)	
Basic Research	1	**basic principles** observed	1	**Basic manufacturing** implications identified
	2	technology **concept formulated**		
	3	experimental **proof of concept**	2	Manufacturing **concepts identified**
			3	Manufacturing **proof of concept developed**
Applied research	4	technology **validated in lab**	4	Capability to produce the technology **in a laboratory environment**
	5	technology **validated in (industrially) relevant environment**	5	Capability to produce **prototype components in a production relevant environment**
			6	Capability to produce a **prototype system** or subsystem **in a production relevant environment**
Prototype/ Pilot production	6	system/subsystem model or prototype/technology **demonstrated in (industrially) relevant environment**	7	Capability to produce systems, subsystems or components **in a production representative environment**
	7	system prototype **demonstration in operational environment**	8	**Pilot line** capability demonstrated. Ready to begin low rate production.
Market Entry	8	actual **system complete and qualified**	9	**Low rate production** demonstrated. Capability in place to begin full rate production.
	9	actual **system proven in operational environment**/competitive manufacturing	10	**Full rate production** demonstrated and lean production practices in place

Table 79: TRL and MRL scales.

A.2 Appendix: Definition of graphene materials

The document follows the definition of graphene materials from Carbon, 2013, Vol 65, 1–6 [1].

Graphene – a single-atom-thick sheet of hexagonally arranged, sp^2-bonded carbon atoms that is not an integral part of a carbon material, but is freely suspended or adhered on a foreign substrate. The lateral dimensions of graphene can vary from several nanometers to the macroscale. Note with this definition, other members of graphene family of 2D materials cannot be simply called “graphene” but must be named using a unique multi-word term that distinguishes them from the isolated monolayer (see below).

Graphene layer – a single-atom-thick sheet of hexagonally arranged, sp^2-bonded carbon atoms occurring within a carbon material structure, regardless of whether that material structure has 3D order (graphitic) or not (turbostratic or rotationally faulted). The “graphene layer” is a conceptual structural unit that has been used for many years to describe the structure and texture of 3D carbon materials with primary sp^2-hybridized bonding.

Multi-layer graphene (MLG) – a 2D (sheet-like) material, either as a free-standing flake or substrate-bound coating, consisting of a small number (between 2 and about 10) of well-defined, countable, stacked graphene layers of extended lateral dimension. If the stacking registry is known it can be specified separately, such as “ABA-stacked multi-layer graphene”, “Bernal-stacked multi-layer graphene” or “rotationally faulted multi-layer graphene”. Carbon films containing discontinuous or fragmented graphene layers of very small lateral dimension should be called ‘‘carbon thin films’’ rather than ‘‘multi-layer graphene’’, since they do not consist of a defined number of countable graphene layers of extended lateral dimension.

Few-layer graphene (FLG) – a subset of multi-layer graphene (defined as above) with layer numbers from 2 to about 5.

Graphite nanoplates; graphite nanosheets; graphite nanoflakes; 2D graphite materials with ABA or ABCA stacking, and having a thickness and/or lateral dimension less than 100 nm. The use of nanoscale terminology here can be used to help distinguish these new ultrathin forms from conventional finely milled graphite powders, whose thickness is typically >100 nm. An acceptable alternative term is ‘ultrathin graphite”, though “ultra” is less specific than “nano” in describing the maximum thickness.

Graphene nanosheet – a single-atom-thick sheet of hexagonally arranged, sp^2-bonded carbon atoms that is not an integral part of a carbon material, but is freely suspended or adhered on a foreign substrate and has a lateral dimension less than

100 nm. “Graphene nanosheet” is now commonly used in the literature to refer to all graphene materials, but “nano” is not needed here as all “graphene” samples are very thin. That use of “graphene nanosheet” is not recommended as it interferes with its more logical use to describe the important subset of graphene materials with lateral dimension in the nanoscale (<100 nm).

Graphene microsheet – a single-atom-thick sheet of hexagonally arranged, sp2-bonded carbon atoms that is not an integral part of a carbon material, but is freely suspended or adhered on a foreign substrate and has a lateral dimension between 100 nm and 100 µm. This term is recommended over the more general “graphene”, when one wants to emphasize the micrometer scale of the lateral dimension in cases where it is key to properties or behaviors.

Graphene nanoribbon – a single-atom-thick strip of hexagonally arranged, sp^2-bonded carbon atoms that is not an integral part of a carbon material, but is freely suspended or adhered on a foreign substrate. The longer lateral dimension should exceed the shorter lateral dimension by at least an order of magnitude to be considered a ribbon, and the shorter lateral dimension (width) should be less than 100 nm to carry the prefix “nano”.

Graphene oxide (GO) – chemically modified graphene prepared by oxidation and exfoliation that is accompanied by extensive oxidative modification of the basal plane. Graphene oxide is a monolayer material with a high oxygen content, typically characterized by C/O atomic ratios less than 3.0 and typically closer to 2.0.

Reduced graphene oxide (rGO) – graphene oxide (as above) that has been reductively processed by chemical, thermal, microwave, photo-chemical, photo-thermal or microbial/bacterial methods to reduce its oxygen content.

Graphene materials (also graphene-based materials, graphene nanomaterials, graphene-family nanomaterials) – overarching terms for the collection of 2D materials defined above that contain the word “graphene”, including multilayered materials (*N* less than about 10), chemically modified forms (GO, rGO), and materials made using graphene, graphene oxide, or another graphene material as a precursor.

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