



## **GRAPHENE-CA**

**Coordination Action for Graphene-Driven Revolutions in ICT and Beyond**

### **Coordination and support action**

#### **WP6 Project Management of the CA project**

#### **Deliverable 6.3 “Publishable flagship proposal report”**

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## Deliverable Summary

This deliverable summarizes the plans for the FET flagship Graphene-based Revolutions in ICT and Beyond. In contrast to the more detailed Deliverable D6.2, we discuss the research program from the point of view of a scientific and technological roadmap rather than from the work package structure that will be implemented in the CP-CSA instrument.

## 1 Introduction

The FET Flagship Pilot on graphene and related two-dimensional materials targets a revolution in information and communication technology, with impacts reaching into most areas of the society. Our mission is to take graphene and related layered materials from a state of raw potential to a point where they can revolutionize multiple industries – from flexible, wearable and transparent electronics to high performance computing and spintronics. This will bring a new dimension to future technology – a *faster, thinner, stronger, flexible, and broadband revolution*. Our program will put Europe firmly at the heart of the process, with a manifold return on the investment of one billion Euros, both in terms of technological innovation and economic exploitation.

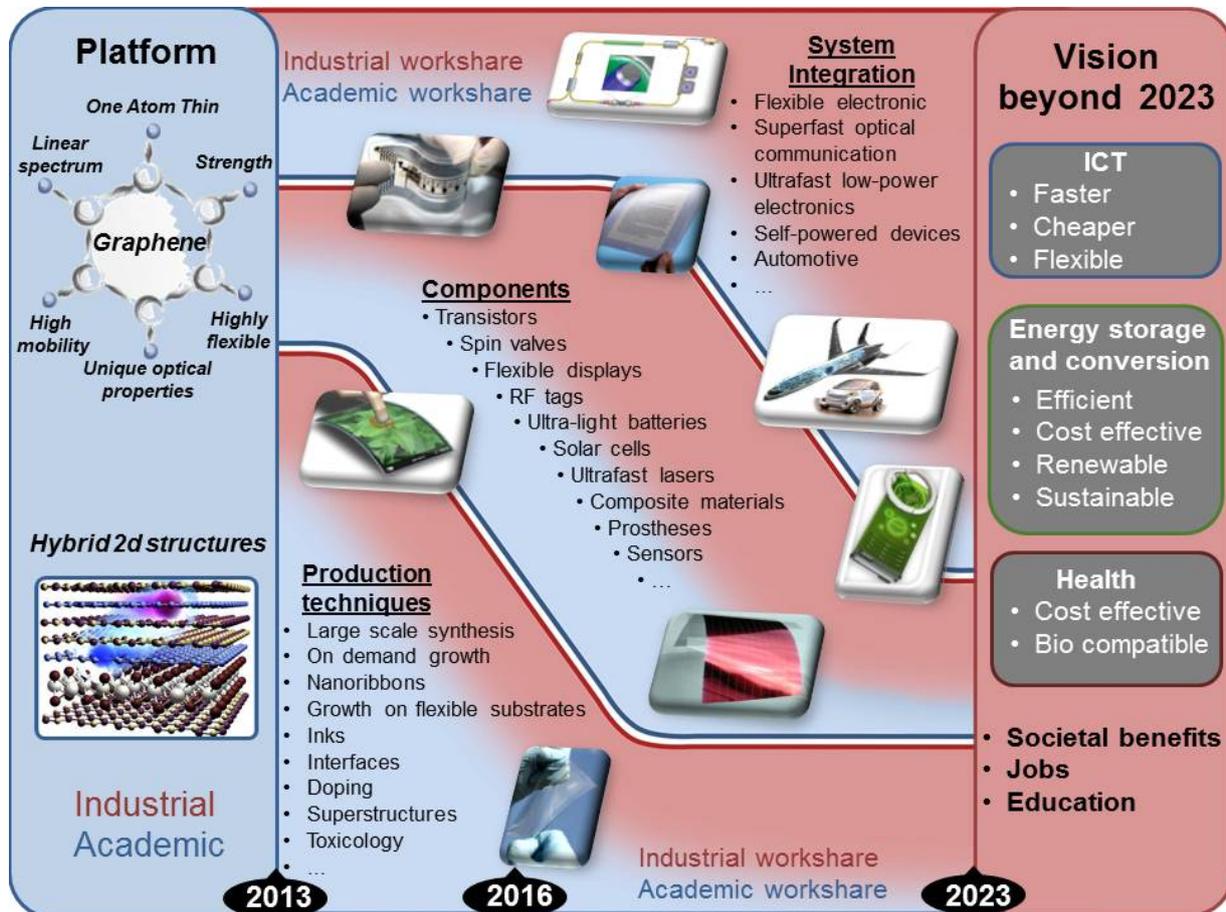
Graphene research is an example of an emerging *translational nanotechnology* where discoveries in academia are rapidly transferred to applications. The concept translational nanotechnology is typically associated with biomedicine where it is a well-established link between basic research and clinical studies, but the principle can be applied to ICT as well: the most striking example is giant magnetoresistance that moved from an academic discovery to a dominant information storage technology in a matter of a few years. Similarly, graphene has the potential to make a profound impact in ICT in the short and long term: Integrating graphene components with silicon-based electronics allows not only substantial performance improvements but, more importantly, enables completely new applications. By exploiting the unique electrical and optical properties of graphene, we will develop novel electronics systems with ultra-high speed of operation and electronic devices with transparent and flexible form factors. We will advance methods to produce cheap graphene materials which combine structural functions with embedded electronics, in an environmentally sustainable manner. The flagship initiative will extend beyond mainstream ICT to incorporate novel sensor applications, batteries, and composite materials that take advantage of the extraordinary chemical, biological and mechanical properties of graphene and related two-dimensional materials.

The flagship consortium has been built by a combination of bottom-up and top-down activities. Over 500 research groups in over 25 European countries expressed interest in joining the flagship through our online consultation, and many of them contributed to the scientific and technological roadmap and helped shape the research program of the flagship. The groups represent academic institutions, research centers and private companies from a variety of sectors. This level of industrial participation is unheard of in a field that has only existed for 8 years, and witnesses the strong conviction by European industry that graphene and related two-dimensional materials are the basis of a rapidly emerging disruptive technology that will have profound effects on many different fields.

While the flagship funding is substantial, it is nevertheless insufficient to incorporate all European research activities in graphene and related materials. In order to guarantee sufficient funding to key areas and to ascertain the societal and technological impacts of the flagship, we have been forced to prioritize and focus on a number of specific areas. During the ramp-up phase the flagship will focus on ICT and energy applications and the supporting materials technologies; work along these directions is carried out in 11 interlinked work packages that work together to create the new grapheme-based technology. Other key impact areas, among them applications in health and life sciences, will be introduced as the funding increases when the flagship moves into the Horizon 2020 period.

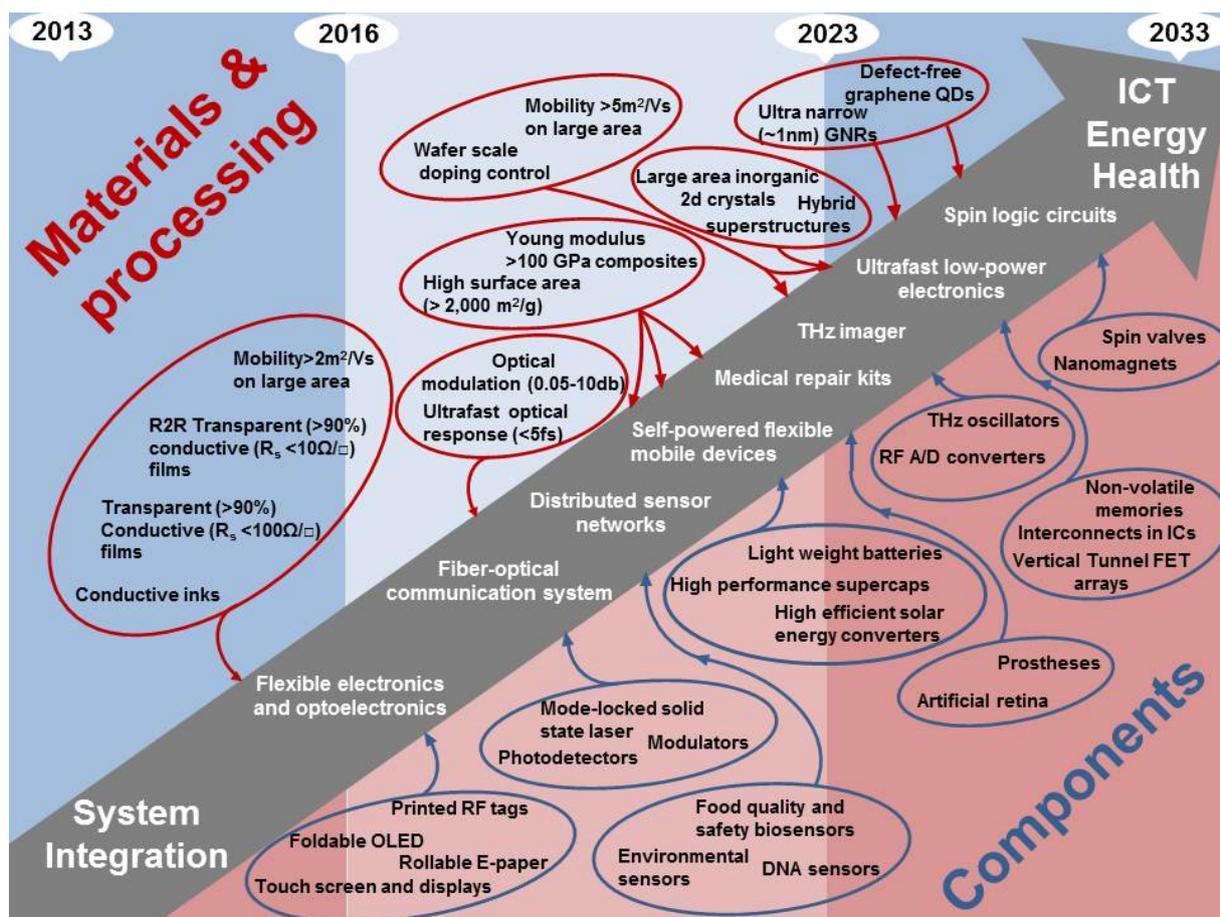
Based on inputs collected from the international academic and industrial research community, we have produced a defining roadmap for the science and technology based on graphene and

related two-dimensional materials, This 200 page document, which will be regularly updated during the voyage of the flagship, forms a solid ground for our research program. The authoritative roadmap shows how the unique properties of graphene can be brought together through development of production techniques, new components and systems to create societal and technological impacts in a wide range of fields and address the grand challenges that Europe faces in the coming decades.



*Figure 1: Schematic presentation of the scientific and technological roadmap*

The roadmap follows a hierarchical structure where the strategic level is connected to more detailed roadmaps and analyses in different areas of science and technology. These topical roadmaps are summarized in a condensed form in the figure below that gives the key technological targets that must be met in order for some key applications to become commercially competitive and the forecasts for when the targets are predicted to be met.



**Figure 2:** A technology-oriented graphene roadmap

We have designed an implementation and governance structure that allows an efficient coordination of the large flagship program and a seamless transition between the FP7 and Horizon 2020 phases. During FP7, the flagships are expected to be implemented using a combination of a large, EC-funded collaborative project and a network of nationally funded projects. Our governance structure unifies the leadership functions of the different instruments in order to guarantee alignment towards common goals. In Horizon 2020 we are aiming at a structure which accommodates the different funding streams and has built-in co-decision procedures that allow all funding bodies to exercise power on the direction of the flagship and the allocation of funds.

The Flagship program targets a revolutionary, disruptive technology shift rather than an evolutionary, gradual improvement of an existing technology. As such, it is an extremely bold initiative associated with substantial risks. To manage the risks in a fiscally responsible manner and to allow the Flagship the flexibility to adjust to new developments, we have defined an implementation structure that relies on a series of renewable projects. The projects are topically collected into scientific and technological divisions that target specific areas such as high-frequency electronics, nanocomposites or energy storage technologies.

Despite being a very young research area, graphene research has already attracted substantial funding both from national and European sources. Combined, the EC and the ERC have funded graphene research with about 50 million Euros and the member states with slightly more, both through national programs and transnational collaborations such as the ESF Eurocores program EuroGraphene. These projects aim at advancing expertise in graphene devices, material characterization, or simulation, and at the development of functionalities such as composite materials and spintronic or photonic applications. However, the existing

research effort is fragmented in sub-critical small projects that end up duplicating each other’s efforts, leading to reduced impacts and sub-optimal usage of national and EC resources. Member states are continually increasing their investment on graphene: for example, on October 3, 2011, the Chancellor of the Exchequer in the United Kingdom announced 50 MGBP new funding to transfer graphene from research laboratories to factories (recently, this has been increased to 68 MGBP), and was followed by similar domestic funding decisions in Sweden and Denmark on October 4 and 5. The strong national support for our initiative is documented by the letters attached to this report and our future CP-CSA application. The FET Flagship on graphene and related two-dimensional materials will extend these national commitments to the European level, and unite the national resources with those of the European Commission to maximize the impact of these investments.

## 2 Graphene-based technologies

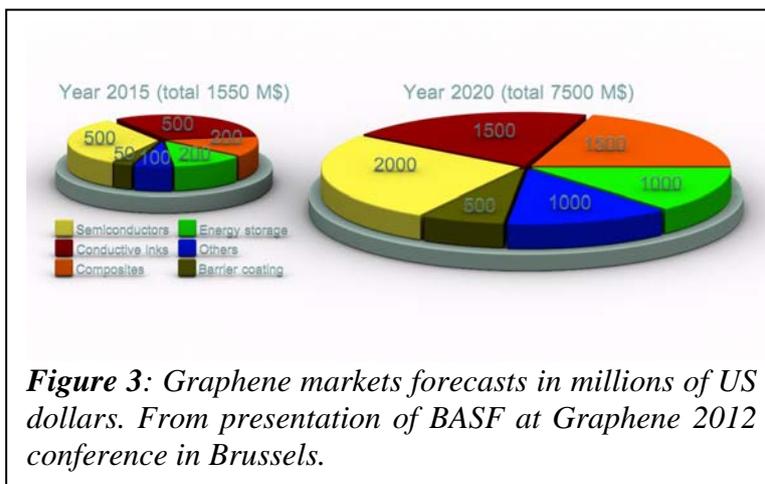
Technologies, and our economy in general, usually advance either by incremental steps (e.g. gradually increasing the number of transistors on a chip) or by quantum leaps such as, for example, the transition from vacuum tubes to semiconductor switches. Disruptive technologies, which are behind such revolutions, are usually characterised by universal, versatile applications, which change many aspects of our life simultaneously, penetrating in its every corner.

In order to become disruptive, a technology needs to offer not incremental, but dramatic, order of magnitude, improvements over the existing state of the art. The more universal the technology, the better chances it has for broad base success. Consider plastics, they are being used everywhere, from automotive industry and health to packaging and electronics.

Does graphene have a chance to become the next disruptive technology? In terms of its properties graphene certainly has the potential. Many of its characteristics are unique and superior to those of other materials. More importantly, graphene offers an extensive combination of the “super”-properties. So, it is really a

question of how many applications graphene can be used for and how pervasive it can become. Are the properties of graphene indeed so unique that they will overshadow inconveniences of the switching to a new technology, a process usually accompanied by large R&D and capital investments?

Note that there are many other 2D crystals such as boron-nitride, molybdenum disulphide, etc[1]. Being structurally related to graphene but having their own distinctive properties, they offer possibilities to fine tune material and device characteristics to suit better a particular technology or to be used in combination with graphene (see, e.g., 2D-based heterostructures[2, 3]). This new kind of material improves graphene’s chances of success but is not covered in this article. They probably deserve a separate roadmap.



**Figure 3:** Graphene markets forecasts in millions of US dollars. From presentation of BASF at Graphene 2012 conference in Brussels.

## 2.1 Graphene properties

One of the reasons for the incredibly fast progress of graphene research is the multitude of very special properties observed in this 2D crystal: it possesses a number of characteristics which are unique or superior to those of other materials. Graphene holds the leading position in many parameters, including mechanical stiffness, strength and elasticity, electrical and thermal conductivity, it is optically active, chemically inert, impermeable to gases, and so on... These properties allow graphene to earn its place in current technologies as a replacement for other materials in existing applications. For instance, in principle, graphene with its high electrical and thermal conductivities could be used for interconnects in integrated circuits in place of copper and its high mechanical stiffness would allow its use for ultrastrong composite materials.

However, what makes this 2D crystal really special and what gives it a chance to become disruptive is that all these properties are combined in one material. The combination of transparency-conductivity- elasticity will find uses in flexible electronics; high mobility-ultimate thinness in efficient transistors for RF applications, transparency-impermeability-conductivity for transparent protective coatings and barrier films. The list of such combinations is endless and grows day by day. The most important combinations are probably those which have not been explored yet, as they would lead to new, revolutionary applications, which were unthinkable prior to the isolation of graphene in 2004[4].

### 2.1.1 Where we are at this instance?

Currently several record high characteristics have been achieved with graphene, with some reaching theoretically predicted limits: room temperature electron mobility of  $2.5 \times 10^5$   $\text{cm}^2/\text{V}\cdot\text{s}$ [5] (theoretical limit [6]  $\sim 2 \times 10^5$   $\text{cm}^2/\text{V}\cdot\text{s}$ ); a Young modulus of 1TPa and intrinsic strength of 130GPa[7] (very close to that obtained in theory [8]); complete impermeability to any gases[9] and so on. It has also been documented to have a record high thermal conductivity [10] and can sustain extremely high densities of electric current (million times higher than copper)[11].

Graphene's many superior properties demonstrate that it may indeed be a miracle material. However, some of these characteristics have been achieved only for the highest quality samples, mechanically exfoliated graphene, and for graphene deposited on special substrates like hexagonal boron nitride[5, 12]. As yet, equivalent characteristics have not been observed on graphene prepared by other techniques, though these methods are improving day by day. The area will receive even greater attention from industry when it will be proven that mass-produced graphene can have the same outstanding performance as the best samples obtained in research laboratories.

## 2.2 Challenges in production

The market of graphene applications is essentially driven by progress in the production of graphene with property appropriate for the specific application, and this situation is likely to continue for the coming decade or at least until each of its many potential applications meets its own requirements. Currently, there are probably a dozen methods being used and developed to prepare graphene of various dimensions, shapes, and quality. It would be most logical to categorise these by the quality of the resulting graphene (and thus the possible applications): (i) planar graphene for high performance electronic devices, (ii) planar graphene for lower performance active and non-active devices, (iii) graphene or reduced graphene oxide flakes for composite materials, conductive paints, *etc.* There is also a large number of

graphene preparation methods which are difficult to adopt for mass production (mostly variations of the micromechanical cleavage technique) and thus they will not be discussed here.

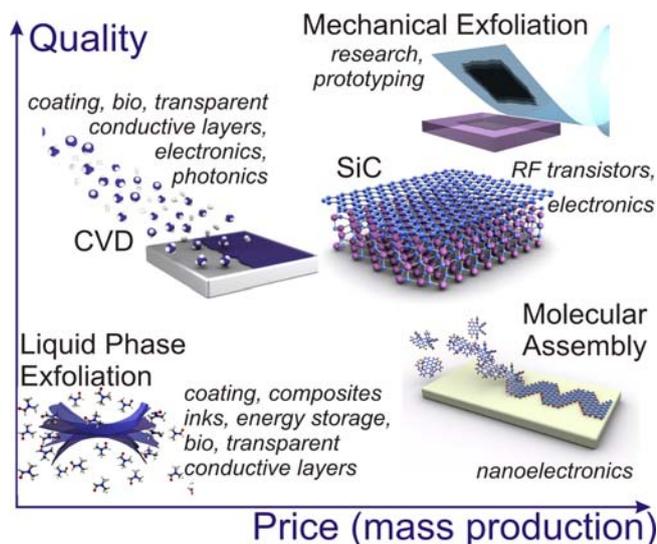
We note that the properties of graphene depend very much on the quality of the material, type of defect, substrate and overlayer materials, which in turn are affected to a large extent by the production method. For instance the carrier mobility is determined by scattering on the covalently bonded impurities, ripples (flexural phonons), wrinkles; and Coulomb scatterers – and the presence and concentration of such scattering centres depends strongly on the production method of the material and device integration details[13]. The quality of the material, in turn, determines the pool of applications which can utilise graphene prepared by a particular technique.

### 2.2.1 Liquid phase exfoliation

The method which is conceptually the closest to the mechanical exfoliation is liquid phase exfoliation. In this method graphite[14, 15] (or any other layered material [16]) is exposed to a solvent with a surface tension which favours the increase in the total area of graphite crystallites. The solvent is typically non-aqueous, but aqueous solutions with surfactant can also be used. With the aid of sonication, graphite splits into individual platelets, and prolonged treatment yields a significant fraction of monolayer flakes in the suspension. Separation in a centrifugal field leads to further narrowing of the thickness and size distribution, eventually achieving an 80% fraction of monolayers in suspension.

A related method is the graphite oxide route where graphite pellets are first oxidised[17] and then exfoliated in an aqueous solution[18, 19]. The suspension, after further processing by centrifugation, can then be deposited as a thin film on practically any surface and reduced (chemically or thermally) back to the parent graphene state. The advantage of this method is that the typical flake size is larger, the fraction of monolayers is higher and the resulting flakes laminate much better when deposited on a desired surface. In addition, the stability of the aqueous suspensions of graphene oxide has improved greatly, thus facilitating processing and handling. The disadvantage of the method is that the reduction does not yield pristine low defect graphene but a graphene with a large number of defects.

Such suspensions can be readily used for a number of non-demanding applications, where the inherent electrical, mechanical, optical and chemical properties can improve the performance of existing products. Thus, graphene-based paints and inks will be finding their way (or, in some cases, have already found) into printed electronics, electromagnetic shielding, barrier coatings (since it is impermeable to most gases), heat dissipation, supercapacitors, smart windows[20], etc. A number of flake-based products can be expected in the marketplace within a few years' time, and prototype applications for conductive inks have already been demonstrated on a commercial level. Moreover, some products have already found



**Figure 4:** Currently there are a number of methods for graphene mass production, which allow a significant choice in terms of sizes, quality and price for any particular application.

applications; for example, saturable absorbers based on liquid phase exfoliated graphene flakes are successfully utilised in ultrafast lasers[21].

### 2.2.2 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a natural technique for growth of high quality and low cost materials. It is a well-developed technology that is widely used in the semiconductor industry. Very large uniform polycrystalline graphene films are now being grown by CVD on copper foils and films, and show promise for many applications[22]. One of the shortcomings of this process, however, is that it requires transfer from the copper substrate material to a dielectric surface or other substrates of interest[23]. While this process can be cumbersome and difficult, production of square meters of graphene has already been achieved[24]. These films have also been transferred onto 200 mm Si wafers where state-of-art devices have been demonstrated. On a smaller scale these films show transport properties equivalent to those of exfoliated graphene on both SiO<sub>2</sub> substrates and hexagonal boron nitride substrates. However, further improvements are required before the films can be used on a large production scale.

The CVD method of graphene growth is already reasonably well developed and ready to be used for certain applications. Despite the presence of defects, grain boundaries, inclusions of the thicker layers, *etc.*, such films can be used for touch screen applications or electromagnetic shielding. Furthermore, CVD growth has one large advantage over other methods, that is, it offers the possibility of precise substitutional doping with boron or nitrogen by adding nitrogen or boron containing precursors.

At present, the process is somewhat expensive due to large energy consumption and because the underlying metal layer has to be removed. However, a number of processes are being developed to decrease the cost of the transfer process. Once the transfer process is optimized it is possible that this process will indeed be disruptive and cost effective. A number of issues need to be resolved before graphene CVD technology can become universal. The growth on thin (tens of nanometres) films of metals needs to be achieved, simultaneously gaining control of the domain (grain) size, ripples, doping level and the number of layers. The control of the number and relative crystallographic orientation of the graphene layers is critical since it will enable a number of applications which would require double, triple and even thicker layers of graphene including demonstration and, later, production of high performance electronic devices. Simultaneously, the transfer process should be improved and optimized with the objectives of minimizing the damage to graphene and of recovering the sacrificial metal. Judging from the rapid progress of the recent years, there are excellent prospects for these problems being resolved in the next few years.

The transfer process might be as complicated as the growth of graphene itself. However, there are a number of applications which rely on conformal growth of graphene on the surface of the metal, and do not require graphene transfer at all: high thermal and electrical conductivities allow graphene to strongly enhance these characteristics for the case of copper interconnects in integrated circuits. Also, since graphene is an inert material, it is an excellent barrier for most gases, and forming a conformal layer on surfaces with the most complex topographies: these graphene coatings can be used as material for protection against corrosion.

The longer term plan is to grow graphene on arbitrary surfaces, e.g. using plasma enhanced CVD or other methods. This would allow one to avoid the complex and expensive step of transfer and promote better integration of this 2D crystal with other materials (like Si or GaAs). Work in this direction has only just started but it is hoped that CVD growth on insulating substrates will become the technique of choice within the next several years.

### 2.2.3 Silicon carbide

Silicon carbide is a common materials used for high power electronics. It has been demonstrated that graphitic layers can be grown either on the silicon or carbon faces of a SiC wafer by sublimating Si atoms thus leaving a graphitised surface[25]. Initially, such growth was exercised on C-terminated face of SiC, with a turbostratic stack of a large number of polycrystalline layers grown[26]. In recent years this process has been developed to such an extent that a controlled number of graphene layers can be grown[27]. The quality of the grown graphene can be very high with crystallites approaching hundreds of microns in size[28-30].

The two major drawbacks of this method are the high cost of the SiC wafers and the high temperatures (above 1000°C) used, which are not directly compatible with silicon electronics technology. There are potentially a number of solutions to take advantage of the growth of graphene on SiC, including growth of SiC on Si. However, at present there is limited amount of data on this approach and will require a significant effort to make it a reality. As a result of the high temperature growth, high substrate cost, and small diameter wafers, the use of graphene on SiC will probably be limited to niche applications. High-frequency transistors based on SiC-grown graphene[31-33] may well find applications within a decade when the existing technology based on III-V materials reaches its limit at ~1THz. The short gate transistors typically used will make even current 20µm size domains suitable for such applications. Another very attractive, though niche, application of this type of graphene is in metrological resistance standards[34, 35], where samples of this type have already been demonstrated to deliver higher resistance accuracy at higher temperature than conventionally used GaAs heterostructures.

Apart from the high growth temperature, which presently seems to be an insurmountable problem, the other issues which need to be addressed in the next decade are the elimination of terraces, growth of the second/third layers at the edges of the terraces (which also strongly contribute to carrier scattering), increase in the size of the crystallites and control of the unintentional doping from the substrate and buffer layers.

### 2.2.4 Other growth methods

Although there are a number of other growth methods, at present it is difficult to imagine that they will become dominant or commercially viable in the next 10 years. Nevertheless, some of these methods have certain advantages and should be researched further.

Surface-assisted coupling of molecular monomer precursors into linear polyphenylenes with subsequent cyclodehydrogenation is an exciting way to create graphene nanoribbons and even more complex structures (like T and Y shaped connections)[36] by a chemistry driven bottom-up approach[37]. Currently, however, the structures grown are interlinked with the metal surface, which makes the investigation of the transport properties complicated. Also, this technique is not yet compatible with the modern top-down technologies, so realistic use of this approach is not to be expected in the short term.

Molecular beam epitaxy (MBE) has been used to grow graphene[38, 39], but it is unlikely to be used on a large scale because of its high cost in comparison to CVD methods. There may be cases where one could envisage using MBE in connection with integration of other materials in a cluster fashion; however, the high temperature and the potential for cross contamination may make it an undesirable growth technique.

Laser ablation is another potentially interesting growth technique which allows the deposition of graphene nanoplatelets on arbitrary surfaces[40]. This method could find niche applications as a corrosion protection layer, gas barrier, transparent conductive coatings and electro-

magnetic shielding, *etc.* However, this relatively expensive method is in direct competition with the spray-coating of chemically exfoliated graphene, and so it is unlikely to be widely used. We can envisage its use for multilayer structure, where graphene will be part of more complex stacked structure assembly, and where the required high purity is not achievable with chemically exfoliated graphene.

Method	Crystallites Size, $\mu\text{m}$	Sample Size, mm	Charge Carrier Mobility (@RT)	Applications
Mechanical Exfoliation	>1,000	>1	$>2 \times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ $>10^6 \text{ cm}^2/\text{V}\cdot\text{s}$ (@low $T$ )	research
Chemical Exfoliation	$\leq 0.1$	$\infty$ as layer of overlapping flakes	$100 \text{ cm}^2/\text{V}\cdot\text{s}$ (for a layer of overlapping flakes)	coating paint/ink composites transparent conductive layer energy storage bioapplications
Chemical Exfoliation via Graphene Oxide	$\sim 1$	$\infty$ as layer of overlapping flakes	$1 \text{ cm}^2/\text{V}\cdot\text{s}$ (for a layer of overlapping flakes)	coating paint/ink composites transparent conductive layer energy storage bioapplications
CVD	500	$\sim 1000$	$10^4 \text{ cm}^2/\text{V}\cdot\text{s}$	Photonics nanoelectronics transparent conductive layer sensors bioapplications
SiC	50	100 (6'')	$10^4 \text{ cm}^2/\text{V}\cdot\text{s}$	RF transistors other electronic devices

### 2.3 Graphene electronics

It is unlikely that graphene will make it into high performance integrated logic circuits as a planar channel material within the next 10 years because of the absence of a band gap. Several possible routes to address these problems have been proposed and are being investigated (for example bilayer, nanoribbons, chemical functionalization). In addition, a few other device concepts that take advantage of the remarkable properties of graphene have been proposed

(e.g. the bilayer pseudospin field effect transistor or vertical geometries utilizing tunneling between two graphene layers[41]). Although significant resources have been dedicated to these approaches, a device to meet the basic characteristics of a transistor has not yet been demonstrated. However, we can soon expect some products utilizing graphene even if the available material is less than ideal in terms of quality for less stringent applications. Fig. 5 and Table 1 show some possible applications and the time that we might anticipate for graphene-based devices.

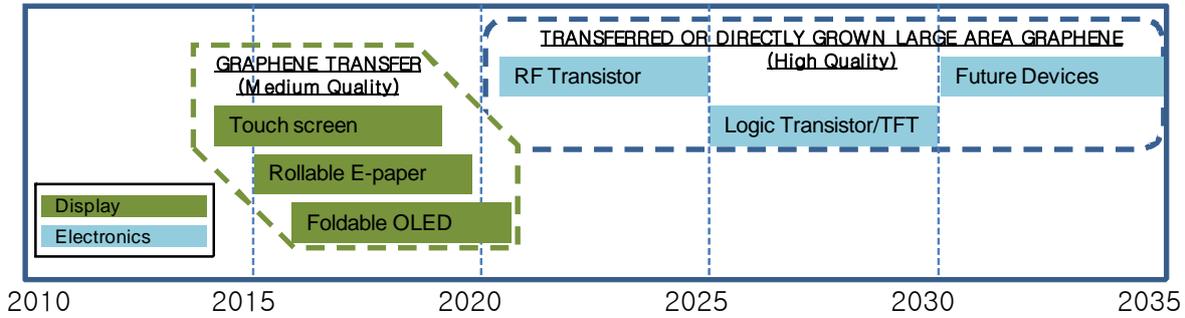


Figure 5 : Graphene electronics' application timeline

Year	Application	Drivers	Issue to be addressed
2014~	Touch screen	- Better endurance with graphene compared to benchmark materials	- Need to better control contact resistance - Need to reduce the sheet resistance (doping)
2015~	E-paper	- High transmittance of monolayer graphene could provide visibility	- Need to better control contact resistance
2016~	Foldable OLED	- Graphene with high electrical property has a bendability of below 5mm - Efficiency improved due to graphene's work function tunability - Atomically flat surface of graphene helps to avoid electrical shorts and leakage current.	- Need to improve the sheet resistance of graphene - Need to control contact resistance - Need a conformal coverage of 3D structures
2021~	RF Transistor	- No manufacturable solution for InP HEMT(low noise) after 2021 according to the 2011 ITRS	- Need to achieve current saturation - $f_T = 850\text{GHz}$ , $f_{max} = 1200\text{GHz}$ should be achieved
2025~	Logic Transistor	- High mobility	- New structures - Need to resolve the bandgap / mobility trade-off - Need an on/off ratio larger than $10^6$

Table 1 : The drivers and issues leading to the implementation of graphene for different electronics applications.

### 2.3.1 Flexible Electronics

Transparent conductive coatings are used as common electrodes, pixel electrodes, as well as wiring in electronic products such as touch screen displays, e-paper and OLEDs (organic light emitting diode). Basically, a transparent conductive electrode requires a low sheet resistance with high transmittance, of over 90 %, depending on the specific device application. Graphene meets the electrical and optical requirements as its sheet resistance can reach 30  $\Omega$ /sq (in doped samples) and an excellent transmittance of 97.7% per layer in its ideal 2D state[42]. It also has outstanding mechanical flexibility and chemical durability which are very important for flexible electronic devices[24].

The requirements of electrical properties (i.e. sheet resistance) for each electrode type differ from application to application. The first application for graphene will probably be as an electrode for touch screens requiring a relatively high sheet resistance, which could be implemented as early as 2014. These electrodes tolerate a sheet resistance in the range of 50 to 300  $\Omega$ /sq for a transmittance of 90% (with a substrate absorption of 5~10 %) and have to withstand repeated touches during the product's lifetime. The advantage of graphene electrodes in touch panels is that its endurance is much longer than any other available candidate at the moment. Moreover, fracture strain of graphene is ten times higher than that of ITO (indium tin oxide)[7] meaning that it could also successfully be applied to bendable and rollable devices.

Rollable e-paper is a future electronic product. It requires a bending radius of 10-5 mm which is well within the performance of a graphene electrode. In addition, graphene's neutral colour is beneficial for color e-papers. However, the contact resistance between the graphene electrode and the metal line of the driving circuitry present a problem at present. A working prototype could be expected by 2015, but it will probably need more time for a product to appear in the market as the manufacturing cost needs to decrease.

Another application to watch out for is flexible OLED devices (non-graphene) to be commercialized by 2013, which requires a sheet resistance of below 30  $\Omega$ /sq. In these devices, the work function and the electrode's surface roughness must be taken into account as they are very important factors governing the application. The work function tunability of graphene could improve the efficiency, and its atomically flat surface would help avoid electrical shorts and leakage currents. Graphene electrodes have already been demonstrated in an OLED test cells[43]. Nonetheless, contact resistance control and reliability are still insufficient if graphene is integrated into the device circuit. In an actual OLED device, the graphene pixel electrodes should extend down to the transistor's source or drain making a contact with the via hole, which demands that graphene be deposited on a flat surface as well as its sidewalls. Therefore, conformal deposition of graphene on 3D structures and contact resistance between graphene and the source/drain are critical. Advanced flexible and/or foldable OLED devices could be introduced after 2016 once device integration issues are resolved.

### 2.3.2 RF Transistors

Graphene has been considered and very intensively researched for RF transistor applications[32]. However, this material has to compete against more mature technologies such as compound semiconductors (III-V) and at this time graphene has not been adopted yet despite the progress in recent years. Thus, graphene will likely be used after 2021, when even III-V material will fail to satisfy device requirements. (Projection shows that III-V materials will struggle to obtain the required  $f_T = 850\text{GHz}$  (cut-off frequency – top frequency for current modulation),  $f_{max} = 1.2\text{THz}$  (maximum oscillation frequency – top frequency for power modulation) after 2021). A recent graphene progress report presented  $f_T$  as having reached as

high as 300 GHz[44], with the possibility to extend it up to 1THz at a channel length of about 100nm[45]. On the other hand,  $f_{max}$  has only reached 30 GHz in traditional graphene structures, which is far from the 330 GHz Si RF transistor performance (according to the 2011 International Technology Roadmap for Semiconductors- ITRS). Thus, the principal remaining research issue is the low value of  $f_{max}$  for graphene transistors which trails  $f_T$  by an order of magnitude for comparable conventional device. There are two ways to improve  $f_{max}$ : lowering  $R_G$  (gate resistance) and  $g_{SD}$  (source-drain conductance at pinch-off)[46, 47]. The former approach could be done using well-established semiconductor processes. The latter will require a current saturation in the graphene RF transistor, which will likely involve finding a new CMOS-compatible dielectric layer with similar properties as boron nitride[48]. An  $f_{max}$  of 58GHz has been reported[47] using graphene on top of an exfoliated hexagonal boron nitride film[5, 12]. Major progress in the current saturation for graphene transistors would have to be addressed by 2016 for it to be ready by 2021.

### 2.3.3 Logic Transistor

It is widely accepted that Si technology will be extended to near or even sub-10 nm levels. From the time-scale point of view, the graphene transistor might have an opportunity to replace the silicon technology after 2020. According to the 2011 ITRS Roadmap, research on graphene logic transistors may be completed by 2020, and its development will begin afterwards. At present, it is too soon to suggest a clear research path. Until 2019 several avenues of research should be explored with regard to graphene logic devices. The current approach using a channel with graphene-metal junctions as source and drain is limited by the on/off ratio. By using a semi-metallic graphene, an on/off ratio of even  $10^3$  cannot yet be achieved, since changes in conductivity are brought about by carrier density modulations. In contrast, most logic applications require an on/off ratio above  $10^6$  for any practical VLSI circuit.

Several research paths are being targeted at opening a bandgap in graphene to make it a semiconductor. There are currently several approaches: nanoribbon[36, 49-51] and single electron transistor[52, 53] formation, bilayer control [27, 54-56], perforated graphene[57-59] and chemically modified graphene[60, 61]. All of these approaches (apart of chemical modification) have so far been unable to open a bandgap wider than 360 meV[62] – significantly smaller than 0.5-0.6eV which is required for stable operation at room temperatures. Even worse - all of these approaches also lead to the degradation of the carrier mobility in graphene to below that of Si[63]. Unless a method of creating a bandgap in graphene without sacrificing all of the mobility advantage can be found, it is unlikely that graphene will be introduced into logic applications as a replacement of Si in similar transistor geometries.

As the current graphene device structure cannot meet the on/off ratio requirement for logic devices, new structures that take advantage of graphene's unique properties of work function modulation, will be required in order to achieve the  $10^6$  on/off ratio[63]. Some work has already been presented using a sandwiched transistor for vertical carrier transport[41]; however, further research on device structures is needed for graphene logic transistors to become a reality by 2025.

Graphene electrical and thermal conductivities might push this material towards use as interconnects in integrated circuits. It has been shown theoretically that graphene nanoribbons have the potential to outperform copper wires for sub-10-nm widths[64]. It remains to be seen if real graphene nanoribbons (with disordered edges) will live up to expectation, but,

considering that graphene can be easily grown on copper by CVD, we might see the two materials used together for interconnects and thermal dissipation applications.

### 2.4 Transparent conductive coating

As it is probably the most dynamic and realistic application, this area of graphene research goes along several parallel routes. Those routes are mostly determined by the grades of transparent conductive coating (TCC) that can be produced from graphene: starting from the most cheap and affordable to high-performance.

In the cheap sector everything is set-up for mass production. Liquid phase exfoliation allows one to produce such coating without the use of expensive vacuum technology. Although the resistance of these films is on the high side, they still perform well enough for smart window, solar cells and some touch screen applications. Graphene still underperforms in comparison with traditionally used Indium-Tin-oxide in terms of sheet resistance (for applications which require sheet resistance below 30Ω) but has one important advantage – flexibility and mechanical strength – which ensures that graphene-based devices will probably dominated flexible applications. Still a few performance-boosting developments are possible: combination with metal wires/nano-whiskers or carbon nanotubes; chemical doping of the flakes, etc.

The expensive sector will most probably be based on CVD grown graphene, subject to successful development of the transfer technique or a technique for growth of graphene on insulating materials. The development of the technique will probably require another 5 years. It might make sense to start moving towards flexible applications. Additional benefits might come from the ability to grow double-layer graphene, intercalated graphene and doped graphene. Targets for the next ten years are sandwiched heterostructures which would bring some extra functionality.

### 2.5 Photonics

In graphene, electrons behave as massless two-dimensional particles which leads to a significant wavelength-independent absorption ( $\alpha \approx 2.3\%$ ) for normal incident light below  $\sim 3$  eV, despite its one atomic layer thickness[42]. Additionally, mono- and bi-layer graphene become completely transparent when the optical energy is smaller than double the Fermi level, due to Pauli blocking[65, 66]. This property brings many suggestions of controllable photonic devices shown in Fig6.

Table 2 also lists the drivers and issues for each possible photonic application.

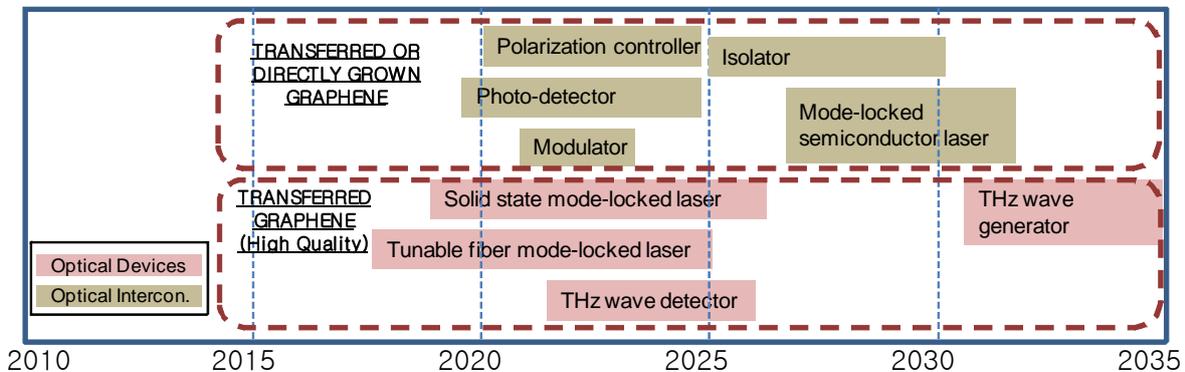


Figure 6 : Graphene photonics application timeline

### 2.5.1 Photo-detector

Graphene photo-detectors are presently one of the most actively studied photonic devices. Compared with semiconductor photo-detectors which have limited detecting spectral width; graphene, in principle, can be applicable to a wide spectral range from ultraviolet through visible to infrared. Furthermore, the constant absorptivity of graphene can be especially useful in designing a multi-wavelength detector, e.g. for image sensors, allowing the same responsivity regardless of spectral region.

Another advantage of the graphene photo-detector is its high operating bandwidth, which makes it suitable for high speed data communications. The maximum bandwidths of InGaAs (for optical communication) and Ge (for optical interconnection) photo-detector are limited to 150GHz[67] and 80GHz[68] respectively, due to the carrier transit times. The high carrier mobility of graphene enables ultra-fast extraction of photo-generated carriers, possibly allowing extremely high bandwidth operation. The transit time limited bandwidth of graphene photo-detectors is calculated to be 1.5 THz[69] at the reported saturation carrier velocity[70]. In practice, the maximum bandwidth of graphene photo-detector would be limited to 640 GHz[69] by the time constant resulting from the resistance capacitance ( $RC$ ) delay, rather than the transit time.

Due to the absence of a bandgap, the graphene photo-detector requires a different carrier extraction model from that of semiconductor photo-detectors. Currently, graphene photo-detectors utilize the local potential variation near the metal-graphene interfaces to extract the photo-generated carriers[71, 72]. Photo-response up to 40GHz [69] and 10GHz detector operation[73] have been demonstrated. However, the maximum responsivity is low (6.1 mA/W[73]) because of the limited absorption due to the small effective detection areas and the thinness of graphene. In order for graphene photo-detectors to be competitive with respect to other technologies, responsivity must be much higher ( $\sim 1A/W$ ).

There are several possible routes to improve the sensitivity of graphene photodetectors, for example by using plasmonic nanostructures for enhancement of local optical electric field[74] or by integrating it with a waveguide to increase the light-graphene interaction length[62]. The latter suggests that the graphene photo-detector may be more suitable for Si photonic based interconnection than a standalone detector. Considering the maximum bandwidth of the Ge photo-detector and optical interconnection roadmap, over 100GHz bandwidth graphene photo-detector will be competitive in 2020, provided that high quality graphene-CMOS compatible process is secured with a mobility of over  $20,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ .

### 2.5.2 Optical Modulator

Optical modulators are one of the key active building blocks for optical interconnects to encode transmission data by altering the properties of light[75] such as phase, amplitude, and polarization using electro-refraction or electro-absorption. Si optical modulators, such as Mach-Zehnder interferometers[76], ring resonators[77, 78] and electro-absorption modulators[79, 80] are based on interference, resonance and bandgap absorption, respectively. Their operating spectra are usually narrow, however, and their slow switching time limits operation bandwidths. For Si waveguide modulators, a large resistance in the p-n junction through the Si core regions is a problem, confining bandwidths to usually less than about 50GHz.

Year	Application	Drivers	Issue to be addressed
2019~	Photo-detector	<ul style="list-style-type: none"> <li>- Fast increase of bandwidth between chip to chip/intra-chip.</li> <li>- Higher bandwidth per wavelength is not possible with IV or III-V detector in 2020</li> <li>- Graphene photo-detector can increase bandwidth per wavelength to 640GHz.</li> </ul>	<ul style="list-style-type: none"> <li>- Need to increase responsivity, which might require a new structure and/or doping control.</li> <li>- Modulator bandwidth has to follow suit.</li> </ul>
2027~	Mode-locked semiconductor laser	<ul style="list-style-type: none"> <li>- Bandwidth increase between core to core and core to memory requires Dense WDM (D-WDM) optical interconnect with over 50 wavelengths which is not possible by a laser array.</li> <li>- Graphene saturable absorber enables passively mode-locked semiconductor lasers, a candidate for D-WDM.</li> </ul>	<ul style="list-style-type: none"> <li>- Market will be open in 2020's.</li> <li>- Competing technologies: actively mode-locked semiconductor lasers or external mode-lock lasers</li> <li>- Interconnect architecture should consume low power.</li> </ul>
2018~	Solid-state mode-locked laser	<ul style="list-style-type: none"> <li>- Graphene saturable absorber can be simpler and cheaper and easy to integrate into the laser system.</li> </ul>	<ul style="list-style-type: none"> <li>- Need a cost effective graphene transferring technology.</li> </ul>
2017~	Tunable fiber mode-locked laser	<ul style="list-style-type: none"> <li>- Wide spectral range of graphene is suitable for widely tunable fiber mode-locked laser.</li> </ul>	<ul style="list-style-type: none"> <li>- Need a cost effective graphene transferring technology.</li> </ul>
2022~	Optical modulator	<ul style="list-style-type: none"> <li>- Si operation bandwidth is currently limited to about 50GHz. Graphene is a good candidate without using complicated III-V epitaxial growth or bonding on Si for increased operating speed</li> </ul>	<ul style="list-style-type: none"> <li>- High quality graphene with low sheet resistance is a key for increasing bandwidth to over 100GHz.</li> </ul>
2020~	Polarization controller	<ul style="list-style-type: none"> <li>- Current polarization controlling devices are bulky and/or difficult to integrate.</li> <li>- Graphene can contribute to realizing compactness and integration of these devices with Si.</li> </ul>	<ul style="list-style-type: none"> <li>- Need to gain full control on parameters of high quality graphene</li> </ul>
2025~	Isolator	<ul style="list-style-type: none"> <li>- Graphene can provide both integrable and compact isolators on a Si substrate, which will have a dramatic impact on miniaturization of such devices</li> </ul>	<ul style="list-style-type: none"> <li>- Decreasing magnetic field strength and process architecture are important to products</li> </ul>

**Table 2** *The drivers and issues leading to the implementation of graphene for photonic applications.*

Excellent optical modulator performance could be expected by exploiting graphene’s ability to absorb a small amount of incident light over ultrawide ranges of wavelengths and its ultrafast response. To this end, the interband transitions of photo-generated electrons in a single

graphene layer[81] are modulated over broad spectral ranges by a drive voltage, leading to operating speeds of more than 1GHz bandwidth in the near infrared range[82]. With some structural changes, an even wider operation bandwidth of more than 50GHz has been suggested using inter-gated dual graphene layers[62] to reduce the resistance in the  $RC$  time delay. Breakthroughs in growth and processing techniques which would minimize the sheet and the contact resistances could increase this value to several hundreds of GHz. In order for these graphene modulators to find a major role in the photonics technology roadmap, the operation voltage should be lowered below 1V in order to reduce power consumption. Due to the aforementioned processing and device integration limitations, these devices will not be ready for the market before 2020.

For THz range wireless communications (THz modulators), similar issues could be anticipated, even though, compared with other natural noble metals, optical losses for graphene is still an order of magnitude smaller up to the 30 THz[83]. The key issues for implementing THz modulators are: (i) a structural design for reducing  $RC$  time delay, (ii) mobility comparison between materials, and (iii) the driving input power.

### 2.5.3 Mode locked laser/THz Generator

Ultrafast passively mode-locked lasers have been used for various applications in spectroscopy, material micromachining[84], bio-medicine[85, 86] and in security applications. Unlike actively mode-locked lasers which use intra-cavity modulators, passively mode-locked lasers utilize saturable absorbers to cause intensity modulation by selectively transmitting high intensity light only. Compared to the widely used semiconductor saturable absorber (SESAM)[87], graphene absorbs a significant amount of photons per unit thickness[42] and, therefore, reaches saturation at a lower intensity over a wide spectral range[21, 88]. Ultrafast carrier relaxation time, controllable modulation depth, high damage threshold and high thermal conductivity are other benefits of graphene saturable absorbers[10, 89, 90]. A wide spectral range tunability has also been realized in graphene mode-locked fiber lasers[91]. Since these applications need only a small area of graphene, commercialization could take place roughly before 2020.

While most studies are focused on fibre and solid-state lasers[92], a graphene saturable absorber can also find applications in semiconductor laser technology. Optical interconnection with wavelength division multiplexing (WDM) scheme needs a laser array with different wavelengths. Another way to provide many different wavelengths is to use a single laser with multiple longitudinal modes, such as a mode-locked laser[93]. Actively mode-locked Si hybrid laser has been studied for this purpose[94], but a graphene saturable absorber could enable a passively mode-locked semiconductor laser with a simple fabrication and operation. However, we expect this application will be useful only after developing a highly integrated optical interconnection around the late 2020's.

THz generators can be used in various applications such as (1) medical imaging, (2) chemical sensors, and (3) security devices. Early proposals based on THz electromagnetic wave generation use graphene as a gain medium to generate stimulated emission by optical pumping[95]. However, due to similar mobility values of electrons and holes, photo-Dember effect may not be effective. Hence it is difficult to obtain a continuous-wave operation overcoming stimulated emission thresholds without damaging the material. Recent studies on THz wave generation suggest using a pulsed excitation of single-layer graphene or using multilayer graphite[96] under a femtosecond laser pulse field to generate carriers that will be accelerated in order to generate the THz wave. However, the intensity is  $10^3\sim 10^4$  times weaker than that generated from III-As semiconductor based photoconductive antenna or resonant

tunnelling devices[97]. Practical THz wave generators using graphene are unlikely to emerge before 2030.

#### 2.5.4 Optical Polarization Controller

Polarization controllers such as polarizers and polarization rotators are crucial passive components to manipulate the orthogonal polarization properties of photons. Conventional polarizers are divided into three categories, sheet polarizers by anisotropic absorption, prism polarizers by refraction and Brewster-angle polarizers by reflection. These polarizers are not easily integrated with an optical interconnect because they are usually bulky with low extinction ratios or limited operation bandwidths. The differential attenuation in transverse magnetic mode due to the excitation of Dirac fermions can provide an excellent extinction ratio of 27dB covering very broad communication bands. Compact optical polarizers are demonstrated in data communication optical fibers integrated with graphene as an in-line conductive layer[98]. High quality mm-sized graphene needs to be integrated with an optical fiber or silicon as a hybrid devices. Therefore, if graphene processing technology becomes mature, these devices could come into play as early as 2020.

Faraday rotation is a popular way to manipulate with light polarization[99, 100]. Conventionally, expensive magneto-optically active materials have to be used in order to achieve any reasonable value of rotation. In contrast, Landau quantization of the two-dimensional electron gas in graphene[101] results in a giant rotation with a fast response and a broadband tunability. Such a strong rotation stems from the classical cyclotron resonances or the quantum mechanical inter-Landau level transitions. Proper polarization rotations can be achieved with multi-stacking graphene structures. Two polarizers combined with these Faraday rotators could be made into very compact hybrid isolators. However, a magnetic field smaller than Tesla levels in graphene isolators will be a serious challenge that would delay its debut till the late 2020's.

#### 2.5.5 Future Photonic Devices

Another possible type of strong light-matter interaction in graphene is surface plasmon polariton (SPP) formation. These strong couplings have benefits for in-plane THz wave modulation[102] and large enhancement of the photonic density of states [103], which can be used to enhance the photon emission rate or absorption rate of a nearby dipole (Purcell enhancement). By patterning graphene or by localized chemical doping, incident electromagnetic waves gain additional functionalities, such as photonic bandgap structures and metamaterials. Graphene-based photonic crystals are suggested as frequency filters and waveguides for the far IR, which are beyond the capability of current Si based technologies[104]. Also, studies on waveguides, planar lenses, superlenses and other devices using transformation optics have been suggested[102, 105]. However, graphene would have to compete against more mature technologies based on other small bandgap materials such as InSb and PbS. Plasmonic or metamaterial based devices are not currently available, so it is unlikely that graphene will be used as frequency filters or waveguides in the near future.

Lastly, we discuss the potential test material for fundamental research such as quantum optics and quantum plasmonics. Traditional quantum optics usually requires trapped and cooled gaseous atoms or semiconductor samples under extremely low temperature environments in order to obtain a long coherence time of light in the media. Since graphene provides high mobility and little scattering of photo-generated carriers, the photonic or the plasmonic mode can be sustained relatively longer than any other material even at room temperatures. A recent manifestation on plasmonic localization even at a single atom defect shows potentially

promising plasmonic sub-nano devices based on graphene[106]. This opens a new possibility of providing relevant material for a single photon source or a plasmonic quantum computer in the most distant future.

## **2.6 Composite materials, paints, coating and energy**

Graphene-based paints can be used for conductive ink, antistatic, EMI shielding, and gas barrier applications. In principle, the production technology is simple and reasonably developed with most of the graphite mining companies having programs on liquid phase exfoliated graphene. In the next few years major developments will be made in the area of chemical derivatives of graphene in order to control conductivity and optical opacity of the products.

Graphene, being an highly inert material can also act as a corrosion barrier against water and oxygen diffusion. Given that it can be grown directly on the surface of practically any metal under the right conditions, it could form a protective conformal layer, i.e. it could be used on rather complex surfaces. However, given that it may be difficult to precisely control the number of layers the chemical properties of mono- bi- tri-layers of graphene would need to be accessed. Also, high growth temperatures might become the show-stopper both in technological and economical terms.

### **2.6.1 Composite materials**

The mechanical, chemical, electronic and barrier properties of graphene make it attractive for applications in composite materials. The position held by carbon fibres, however, is so strong (in terms of price) and the quality of modern composites is so good that graphene will need substantial development before it will be economically reasonable to use it as the main reinforcement component. The target set by industry for carbon fibres is to achieve a 250 GPa Young modulus at the price of €25 per kilogram. In addition, pure graphene might not have the same adhesion properties to the matrix as carbon fibres (although the fibres are usually treated to add hydroxyl or epoxy functionality to their surface). More research is therefore required on the possible chemical modification of graphene without having a detrimental effect upon its mechanical properties (first results are reasonably encouraging with fluorographene being only a fraction weaker mechanically than the pristine material[61]). Hence, in order to replace carbon fibres, considerable work on lowering the cost of production of large (>10  $\mu\text{m}$ ), chemically-modified (in a controllable way) graphene flakes is required.

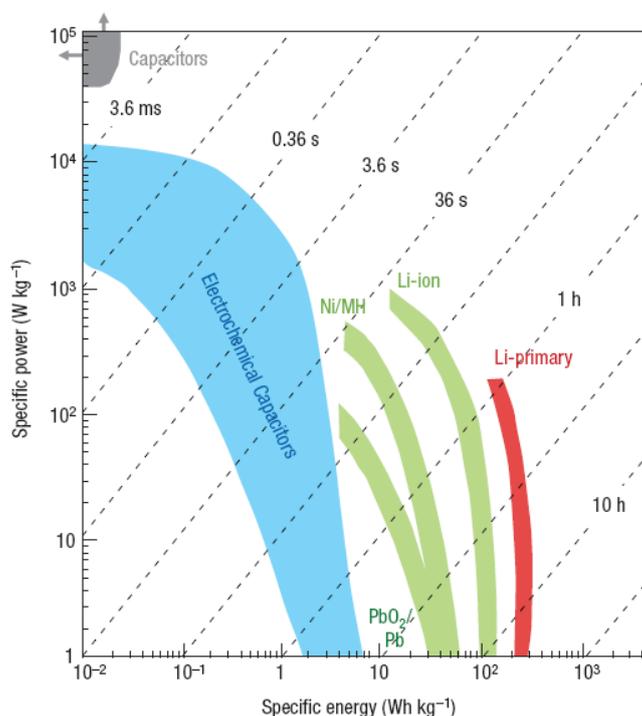
An equally-large market exists in bringing extra functionality to composites, where the scope of graphene might be large and it may be realised more rapidly. Graphene can combine gas and moisture barrier properties, electro-magnetic shielding, electrical and thermal conductivity, and a strain monitoring capability to the surrounding polymer matrix. As an additive to a composite matrix polymer it might increase the operating temperature level of composites, reduce moisture uptake, induce antistatic behaviour, give lightning strike protection and improve composite compressive strength. There are also a number of applications where it is difficult to use carbon fibres that would still benefit from excellent mechanical reinforcement. The use of chopped carbon fibres or carbon nanotubes in injection-moulded composites is difficult as their addition leads to a massive increase in polymer viscosity, making processing difficult. Graphene platelets increase viscosity much less and paints or coatings containing graphene flakes used could be used as gas or moisture barriers.

Considering that most of the mining companies that produce graphite have now established programs on graphene and/or graphene oxide production, it is possible to expect graphene composites to appear on the market within a few years. The real breakthrough, however, will

be expected when graphene flakes above 10  $\mu\text{m}$  in size are easily obtainable – the dimension required to utilise in full the advantage of the high Young’s modulus of graphene[7, 107]. Fortunately, it has been demonstrated that graphite flakes thicker than one monolayer can provide a significant level of reinforcement, thus making the implementation of graphene – based composite realistic within a shorter time.

### 2.7 Energy storage

Energy storage is an essential element of energy production and savings. Energy can be stored in a variety of ways depending upon the intended use with each method having its advantages and disadvantages. Batteries, supercapacitors, and fuel cells have been used and studied for over a century to store electrical energy. The need to develop sustainable and renewable energy sources is leading society to develop energy from sources that are not continuously available, such as the sun and wind. In addition there is a significant need to have portable energy not only for portable devices but also for transportation to decrease the reliance on fossil fuels. Batteries and electrochemical supercapacitor storage devices are the most common means of storing energy and fuel cells are also coming into their own[108-113]. However, there are a number of challenges that need to be addressed in order to improve their performance and to make them economically viable. Therefore, electrochemical devices which can deliver high energy density are increasingly important. The so-called Ragone plot shown in Figure 7, of power against energy density, is a useful way of comparing different technologies and judging usefulness for a particular application[109].



**Figure 7:** Specific power as a function of specific energy, also called Ragone plot for various electrical energy storage devices[109].

Supercapacitors are based on storage of energy within electrochemical double layer capacitors (EDLC)[109] and the devices consist of two electrodes, a separator and an electrolyte, similar to a traditional battery. The performance of state of the art EDLCs is largely determined by the combination of a high surface area activated carbon material and a nanoscopic charge separation at the electrode-electrolyte interface. . The carbon material should offer a high intrinsic electrical conductivity, a controlled pore structure, good resistance towards oxidative

processes, high temperature stability and must be easily processable in electrode slurries. After its first isolation, graphene became an obvious material choice for this application[23]. There are a number of reports on the fabrication of graphene-based electrodes for EDLC where the primary objective was to demonstrate the capability of graphene materials for this application as well as develop a low cost material: indeed some of the highest reported capacitance, and highest energy and power densities, have been recently reported with graphene-based EDLCs[114].

In a similar way graphene can be used to improve the storage capabilities of Li ion batteries. For example, as an additive it can improve the performance of the cathode and anode of the system. At present, traditional metal-oxide materials used in Li-ion battery cathodes frequently suffer from a poor electrical conductivity which is overcome by the addition of graphite and carbon black additives to the electrode formulation. Graphene with its sheet-like morphology would not only act as an advanced conductive filler in this respect but may give rise to novel core-shell or sandwich type nanocomposite structures greatly improving performance and stability. Furthermore, on the anode side, graphene nanosheets can be used to reversibly intercalate Li into the layered crystals. In fact Yoo et al. [113] used GNS in conjunction with carbon nanotubes and fullerenes,  $C_{60}$ , to increase the battery charge capacity.

Many of the detailed performance aspects of the graphite electrode used in the lithium ion battery are not so well understood, particularly the factors leading to limitations in cycle life and the formation of so-called solid-electrolyte interfaces. Use of graphene as a model system can lead to new insights in understanding the lithium intercalation process. On a more technological level, a key limitation with batteries is their low specific power (see Fig 5). The use of graphene based materials, with associated reduction in diffusion lengths of ions within the solids, should lead to large improvements in the rate capability of graphite-based batteries.

There are also reports on the use of GNS as a support material for Pt catalyst for fuel cells [112, 115]. Unlike, carbon black, which is the baseline support material for Pt catalysts, graphene decreases the Pt particle size to sub 1 nm because of the strong interaction between Pt atoms and graphene. The strong interaction of Pt and graphene and the small particle size is leading to increased catalytic activity for methanol reaction.

While there is continuing to be much excellent work on graphene for energy storage, there is still a need to understand not only the basic role of graphene for EDLCs, batteries, and fuel cells performance enhancement but also to address ways of introducing the graphene into these products in large scale manufacturing. Common benchmark materials (activated carbon, graphite, carbon black) will only be replaced if graphene is proven superior both in terms of performance and cost. Significant efforts made to develop new ways of forming inexpensive graphene for energy storage[108]. In comparison to the use of graphene for nano-electronic applications the growth and preparation of graphene for energy storage may be an easier target.

## **2.8 Graphene for sensors and metrology**

Graphene, being a two-dimensional fabric and a surface without bulk, has properties that are extremely sensitive to the environment: from changing the local dielectric constant and presence of covalently bonded impurities on its surface, to strain and illumination. Thus, it is natural to consider using graphene for sensor applications.

Strain gauges are probably the most competitive and promising application. Graphene is the only crystal which can be stretched by 20%, thus enhancing the working range of such sensors significantly. Furthermore, different strain configurations would result in different responses.

The readout can be either electrical or optical. Combining strain gauges with composite materials would make the latter yet more attractive: the strain can be directly monitored and mapped by means of Raman spectroscopy. Existing CVD-grown graphene or graphene obtained by liquid phase exfoliation are already suitable for strain gauges (if thermal drift problem could be resolved) and so one can expect such applications to appear in the next few years.

Currently graphene gas sensors, although being extremely sensitive, hold only a minor competitive edge over existing devices. Despite being able to detect single molecule of some gases, the selectivity of pristine graphene is still poor. Being sensitive to water, such sensors can be easily poisoned in ambient environment. However, since such detectors can be produced cheaply (using liquid phase exfoliation of graphite for example) they can be utilised in certain niche applications.

The selectivity of graphene can be increased by functionalization. However, being a rather expensive method, it is probably most suitable for bio-sensing. Both electronic or optical readout are possible, the latter include Raman, photoluminescence or quenching of the luminescence.

Graphene's extreme sensitivity to the environment suggests a number of sensor applications. Ultrasmall (<100nm) graphene Hall sensors could be used for measurements of magnetic field; DNA sequencing is a possibility with graphene membranes and the streaming potential on graphene can be used to measure the velocity of surrounding liquid.

The major advantage of graphene sensors is their multi-functionality. Thus, a single device can be used in multidimensional measurements, for example, strain and gas environment, pressure and magnetic field. In this sense graphene offers unique opportunities. With the development of increasingly interactive consumer electronic devices, such sensors will certainly find their way into many products.

The unique bandstructure of graphene, with its anomalously large energy splitting between the zero-energy and the first Landau level makes it an ideal material to develop the universal resistance standard based on the quantum Hall effect (QHE) [116-118], one of the most fundamental effects in solid-state physics. The QHE relates the Hall resistance quantized at strong magnetic fields to integer fractions of  $h/e^2$ , and hereby offers a possibility of redefining the SI-units for kilogram and ampere in terms the fundamental constants of Nature,  $h$ , the Planck constant and,  $e$ , the electron charge. For two decades, metrology has successfully used the QHE observed in the two-dimensional electron gases (2DEG) formed inside Si field-effect transistors or group III-V heterostructures to implement the resistance scale. It turns out that epitaxial graphene grown on the Si face of SiC is the best material for quantum resistance metrology[34, 119]. The journey from the original demonstration of the QHE in graphene to a quantum resistance standard which outperforms the established technology has been remarkably short. The recently achieved one part per 10 billion precision of Hall resistance quantisation[35] is determined by the unusual filling factor 2 pinning[120] in graphene, due to the dominance of quantum capacitance of graphene in SiC – graphene charge transfer[121].

Graphene has the potential to provide the most elusive of the electrical standards - the quantum standard for electrical current. The idea is to produce a quantized current source based upon quantized current,  $I = ef$  in a single-electron turnstile driven with the frequency  $f$ . Single electron transport in these devices is caused by a dominance of Coulomb charging effects on a small island - a 'quantum dot'. Here graphene is a promising material as it provides high working temperatures for the Coulomb blockade effect[52, 53], whereas, compared to molecular systems where similarly large energies have been observed, graphene offers the potential for large-scale integration and parallelisation.

## 2.9 Bioapplications

Graphene has a number of properties which make it potentially promising for bioapplications. Large surface area, chemical purity and possibility of easy functionalization provide opportunity for drug delivery; unique mechanical properties bring interest for tissue engineering applications and regenerative medicine[122]; combination of ultimate thinness, conductivity and strength make it an ideal support for imaging biomolecules in TEM[123, 124]; sensor properties could be used in diagnostics and mobile-medicine applications. However, much of the research is at a very early stage of development with many hurdles still to overcome.

Fast biosensors with good sensitivity and selectivity for biomarkers related to disease could significantly speed up diagnosis and effective treatment and reduce overall healthcare costs. Biosensors based on graphene have been made that use a variety of mechanisms to detect a range of biological molecules including glucose, cholesterol, haemoglobin and DNA[125]. The advantages of these systems over alternative approaches will need to be demonstrated in both in terms of performance and the availability of a cost effective and robust manufacturing process.

The first clinical trial of a wirelessly controlled implanted microchip-based drug delivery device was reported recently[126]. The material properties and electronic applications of graphene could be used to improve future generations of both wearable and implantable medical devices, including those used for the controlled delivery of drugs such as insulin. In the latter case, it would be particularly beneficial if feedback from a biosensor, either incorporated in the device itself or present elsewhere in the body, could be used to control the rate of drug release so that optimum drug dosing can be achieved for effective treatment.

As a result of their large surface area and delocalised  $\pi$  electrons, graphene derivatives can solubilise and bind drug molecules and thus have the potential to be drug delivery vehicles in their own right if sufficiently high drug loadings and suitable *in vivo* drug distribution and release profiles can be achieved. Graphene, being a lipophilic material might help in solving another challenge in drug delivery – membrane barrier penetration. This is especially important for brain and lung treatments, as only a few percent of drugs can penetrate the 200-400nm gap of blood-brain barrier. Most of the limited work that has been done to date has focussed on investigating the loading and *in vitro* behaviour for aromatic anticancer drugs such as doxorubicin[127-129]. It is essential that the *in vivo* behaviour and the fate of such systems is determined to assess their potential for drug delivery and targeting. Intravenous administration of PEGylated graphene oxide, labelled with an NIR fluorescence dye but without any drug, has shown passive tumour targeting in mouse xenograft models. The tumours were killed when irradiated with a low-power near-infrared laser showing the potential of using graphene derivatives for photothermal cancer treatment[130]. However, given the high safety, clinical and regulatory hurdles and long timescales associated with drug development, which are exacerbated when new materials are involved, it is unlikely that products that use graphene-based drug delivery technology will be at or near to the market before 2030. For comparison, although liposomes were discovered in the early 1960s and quickly identified as a potential drug delivery system because of their biocompatibility and ability to encapsulate drugs, products utilising liposomal drug targeting technology were not launched until the mid 1990s due to the long time taken for development and clinical trials. There has also been significant research into the use of carbon nanotubes as drug delivery carriers, including investigating *in vivo* behaviour in animals, but they do not appear to have been used in any clinical studies yet.

Tissue engineering is an emerging area of technology with potential for significant impact on patient treatment across a range of disease areas although, as yet, only a small number of potential products have entered clinical trials. Graphene can be incorporated into the scaffold materials used for tissue engineering to improve their mechanical properties such as strength and elasticity and potentially to modulate the biological performance such as cell adhesion, proliferation and differentiation[129].

The biggest hurdle that needs to be overcome before graphene can fulfil its promise in the biomedical area is to understand its biodistribution, biocompatibility and acute and chronic toxicity under conditions that are relevant to exposure during manufacture and subsequent use. Ultimately, this will probably need to be done for the particular form of graphene being used in a given application as the outcome is likely to vary with size, morphology and chemical structure. It will thus also be important to fully characterise the form of graphene used. In some cases it may also be possible to exploit the biological activity that gives rise to a particular toxicity profile. For example, a 'toxic' graphene derivative could potentially be therapeutic in its own right as an antibiotic or anticancer treatment.

### **2.10 Conclusions**

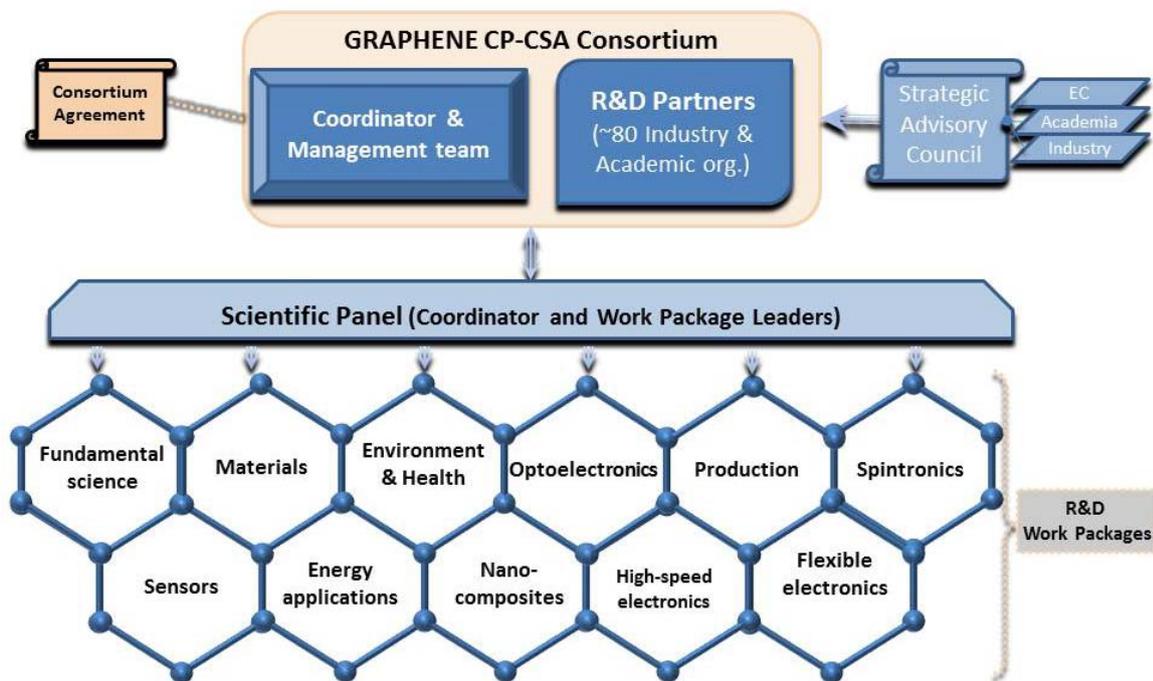
Physicists use to think of graphene as a perfect two-dimensional lattice of carbon atoms. However, the paradigm shifted, when the research area expanded from pure science into technology: even less than-perfect layers of graphene can be used in certain applications. In fact, different applications requires different types (or grades) of graphene, which makes this material so multifaceted that its chances of becoming a disruptive technology significantly improve.

As the current market for graphene applications is driven by the production of this material, there is a clear hierarchy in how soon the applications will reach the user or consumer. Those that use the lowest grade, cheapest and most available material will be the first to appear, probably as soon as in a few years, and those which require the highest, electronic-quality grades or biocompatibility may well take decades to develop. Also, because the developments in the last few years were truly explosive, graphene's prospects continue to rapidly improve. Still, we must bear in mind that established benchmark materials will only be replaced if the properties of graphene, however appealing, can be translated into applications which are sufficiently competitive to justify the cost and disruption of changing existing industrial processes. One thing is certain: scientists and engineers will continue looking into prospects offered by graphene and, along the way, many more ideas for new applications are likely to emerge.

## **3 Flagship Implementation**

In FP7 the flagship will be implemented as a combination of two instruments, a collaborative project (CP-CSA) and a network joining national research initiatives (ERA-NET+). The two will be aligned through joint management structures such as a Scientific Panel, which includes leaders of the focused scientific and technological work packages, and a Strategic Advisory Council (SAC). The SAC includes world leading competence such as four European Nobel Laureates who are all personally engaged in graphene research, and several high level industrial representatives. The CP-CSA part of the flagship will comprise about 100 academic and industrial research groups representing about 80 legal parties, coordinated by Chalmers University of Technology in Sweden. The participation in the ERA-NET+ instrument will be based on an open, competitive call, which ensure a high deal of flexibility in the Flagship consortium and allows close alignment between the Flagship and the national priorities.

The graphene-based technologies described in Section 2 cover such a wide range of topics that they cannot all be addressed by the Flagship in its initial form. We have chosen to focus on selected topic where Europe can make a difference, both in terms of the underlying science and the possibility to exploit the research results commercially. Therefore, the Flagship is organized in eleven interlinked scientific and technological work packages that implement the research program. The work packages can be divided into three tiers. Tier 1 includes Fundamental Science, Materials and Health & Environment, which form the basis for the entire Flagship. Tier 2 focuses on components and comprises work packages on Optoelectronics, Spintronics, High-speed Electronics and Sensors, while Tier 3 is geared towards system integration in work packages on Production, Flexible Electronics, Nanocomposites and Energy Applications. This structure allows the Flagship to integrate the entire vertical value chain from basic academic research to nearly commercial applications, which is a necessary requirement to realize the disruptive technology shift we are targeting.



*Figure 8: Organization of the CP-CSA instrument of the Flagship*

Graphene research is a clear priority of both the European Union and of the member states. This is clearly demonstrated the substantial resources that have been invested by the EC and the individual states on graphene and related two-dimensional materials. Based on a survey of national funding agencies in the fall of 2011, member state funding of this research area amounts to approximately 50 M€ per year, and the EC funding is presently about 18 M€ per year; both funding trends are increasing. However, most of the funded projects are short term and independent of each other, which results in duplication of efforts and waste of resources. A long-term coordinated action such as a Flagship is a much more cost-effective way of creating the desired impacts. The member states have clearly recognized this fact, as demonstrated by the numerous support letters we have received.

## 4 Impact

The flagship on graphene and related two-dimensional materials aims at the most ambitious goal of establishing a completely new technology platform, based on new science, which will

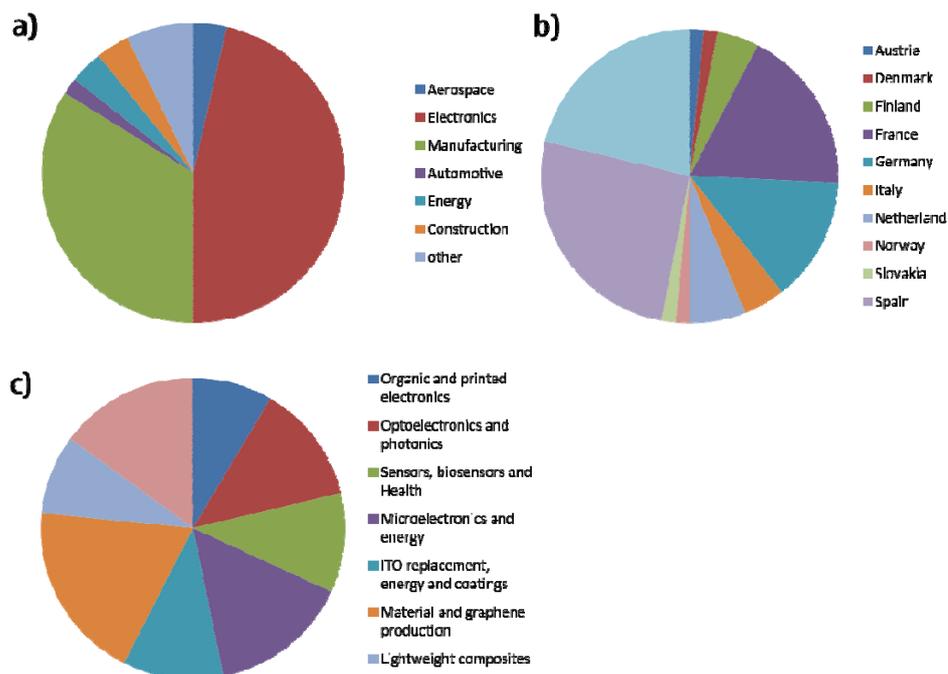
leverage the complementary advantages of carbon related materials with respect to silicon. The flagship originates within information and Communication Technology (ICT) but its impact extends far beyond ICT. Novel composites, more efficient batteries and supercapacitors and new types of sensors are examples of technologies that will benefit from the flagship and in turn enhance applications in a variety of fields of deployment: from energy to automotive, from chemical to material and aerospace.

In the ICT field, the flagship will focus on selected topics where Europe can make a difference, both in terms of the underlying science and the possibility to exploit the research results commercially. These areas include printable and flexible electronics, high-frequency electronics, novel devices taking advantage of the specificities of graphene (for instance ambipolarity), spintronics, photonic and plasmonic components, and integrated optoelectronic systems. Beyond ICT, the impact will be equally strong. Examples include graphene production, monolayer deposition methods, graphene composites, supercapacitors, batteries, and sensors. Given the scale of the opportunity for scientific and technological impact within and beyond the ICT sector, the flagship pilot project has prioritised the creation of a research strategy informed by deep understanding of emerging technologies, competitive trends and industry value chain. This is crucial to guarantee a *strong interlock between science and technology, exploration and exploitation*. The creation of such interlock from the onset of the flagship will maximise the return on research, in terms of scientific and technological impact, by guaranteeing that: *i*) sufficient research resources are allocated to areas that need intense exploration and/or offer great potential for breakthroughs and technology disruption and, *ii*) a sufficiently large technology portfolio is produced to continuously meet exploitation opportunities throughout the duration of the project. This ambition is perfectly aligned with the Innovation Union concept that is being introduced by the European Union as a means to maximize the societal and technological impact of EU research.

A clear technology roadmap has been produced by the GRAPHENE-CA flagship pilot after several rounds of consultations with academic and industrial experts. The technology roadmap (shown in section 1) represents in a single snapshot the vision of the entire flagship. It embeds the rationale followed in the development of our strategic research agenda for graphene and related two-dimensional materials. The roadmap highlights the role and evolution of the different technologies, thus creating a clear pull for scientific results. The roadmap for graphene-enabled ICT products covers a number of application fields including electronics, spintronics, photonics, plasmonics and mechanical devices, as well as enabling technologies such as materials production and chemistry. Rolling back from the identified markets opportunities and their enabling material and component technologies, the Graphene-CA has been able to organise activities and Work Packages in a coherent fashion, which is intrinsically optimised for scientific and technological impact.

#### **4.1 Impact on economy and society**

GRAPHENE-CA organized industrial workshop provided a concrete confirmation of the potential economic impact of graphene technologies from key European industry stakeholders. The workshop highlighted that the commercial potential of graphene has been spotted across many application sectors, see figure 9. However, expressing that raw potential to enable industrial applications and unlock socio-economic impact is not trivial due to a number of challenges. Some of these challenges are graphene specific, others are linked to the more general challenges of innovation in Europe.

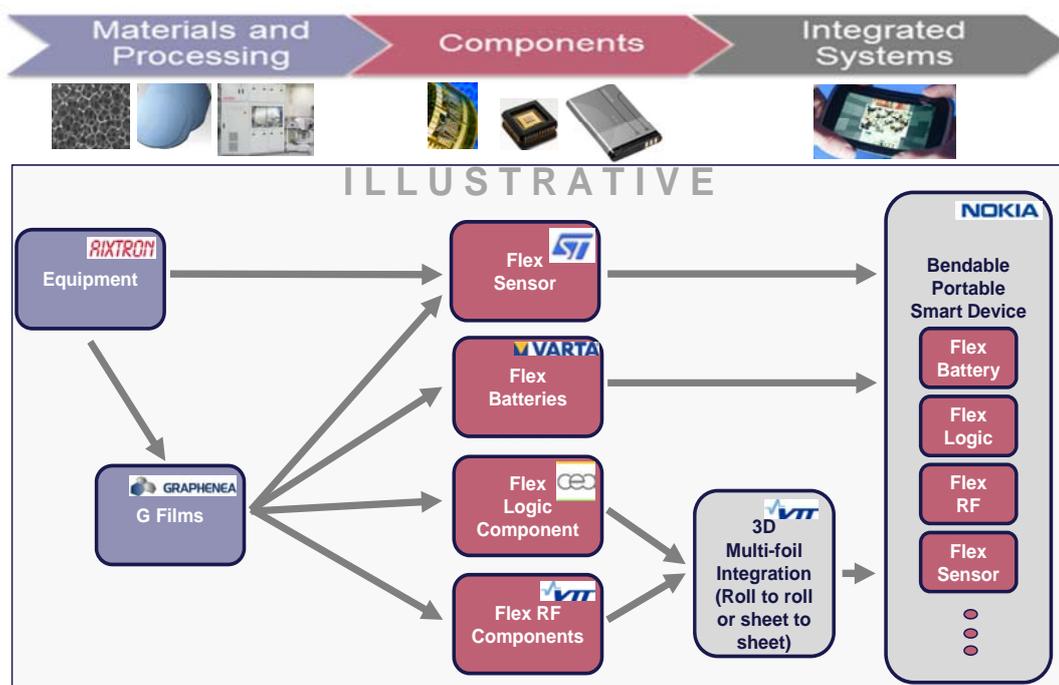


**Figure 9:** A summary of the participating 63 companies in the industrial workshop in Madrid in October 2011: a) Companies were presenting different industries and b) 11 different European countries. According the advance survey companies are seeing graphene to have a major impact in various different technology areas (Fig c.).

The first few graphene-enabled commercial products (*e.g.*, conductive inks) are expected to enter the market in 2013. The main ICT applications are still several years in the future, giving Europe enough time to secure a major role in the emerging graphene ICT field, with significant opportunities for industry development and economic growth. However, for this economic impact to materialise in Europe, European industry must be able to seize the graphene exploitation opportunities that will emerge from the scientific and technological advancements delivered by the flagship program. We believe that there is a concrete risk that the benefits of this European scientific effort could be harvested outside Europe. The pilot project has therefore considered the most critical risk factors (*challenges*) and identified a range of risk mitigation measures (*opportunities*) that could enhance the likelihood of a European industrial exploitation of graphene and related two-dimensional materials, which would lead to job creation and economic and societal impact.

**ICT Value Chain Challenge.** The ICT value chain can be split into three categories: materials suppliers, component manufacturers, and system integrators. Within Europe there are some world-leading system-integrator companies operating in the ICT space (*e.g.*, Philips or Nokia). However, if one compares their operation to that of competitors from South-East Asia, it is clear that the latter organisations are more vertically integrated and span a larger portion of the value chain compared to their European counterparts. The lack of vertical integration leads to a situation where component manufacturers cannot risk developing components when both the materials supply and the demand from system integrators are uncertain, and a system integrator cannot begin to plan a new product design and launch until the supply of all components is secure. This fragmentation of the ICT value chain can impair the ability of the European industry to rapidly take to market any emerging technology. The graphene flagship will alleviate this problem by integrating within one project the vertical value chain. To

achieve this *opportunity*, the flagship brings together academic researchers and companies from all parts of the value chain. The close cooperation of European academics and industry leaders throughout the pilot project has create a close interlock between product roadmap, technology development strategy and research agenda for the flagship. This will guarantee a higher chance of rapid industrial adoption and commercialization by European organisation of any achieved breakthrough. This will boost our common innovation capability and assure that Europe and Europeans will have a large share in the profitable fruits of European research breakthroughs: new products, new investment opportunities and new jobs, as outlined in detail in the EC plans for an *Innovation Union*.



**Figure 10:** An illustration of how a set of industrial partners within the flagship could create a fully European value chain, in this example a bendable portable smart device. This would enable them to take to market a range of graphene-enabled materials and components, following a co-development performed in close collaboration with a system integrator.

*Technology Transfer Challenge.* The lack of vertical integration in large corporations, the gap between the maturity of emerging technologies and the maturity required by corporate business units and IPR complexity, conjure to make the rapid roll-out of emerging technologies increasingly difficult. For SMEs, their innovation efforts can be insufficiently aggressive to qualify for venture capital funding. At the same time, SMEs rarely have the legal and financial capabilities to negotiate tech transfers and R&D collaboration with other organisations, for instance academia. The problem of securing venture capital stems from a general reduction in the available amount of funding and in early-stage, technology investments across Europe. This problem is particularly felt by non-software type of ventures such as those that one might foresee emerging from the graphene flagship. To achieve revenues, hardware focused start-up companies tend to require larger investments than software ventures. This leads to a perception of higher risk and longer time to exit and returns for investors. The Graphene-CA sees the GRAPHENE flagship as an *opportunity* to bypass these problems, and has already taken considerable steps to promote industry engagement and create a corporate route-to-market within Europe for graphene emerging technologies. Direct engagement of SMEs has also been made a priority of this Graphene-CA from the start. The consortium already includes some very promising European SMEs (e.g., Graphenea). To

promote entrepreneurship, the flagship will adopt a three-pronged strategy. Firstly, we will encourage business and entrepreneurial training among the scientists directly involved in the WPs, together with the promotion of a more risk-taking culture. Secondly, through a combination of efficient IPR management and technology promotion, we will attract talented entrepreneurs to the opportunities created by the flagship science and technology advancements. Thirdly and most challengingly, we will explore the possibility of promoting the creation of a dedicated seed investment fund that could provide capital and management expertise to start-up companies, which are willing to commercialise selected graphene technologies.

*IPR Management Challenge.* Proper management of and access to IPR is crucial for the commercial exploitation of research breakthroughs. Alongside basic FP7 rules and core requirements that might be provide forthcoming Horizon 2020 rules, our flagship is exploring the option to maintain but streamline the traditional licensing principles of EU research projects. There is also an opportunity to create a proactive and coordinated IP management system for selected IP results on top of the basic elements. Such enhanced elements can be tailored to increase the likelihood of venture capital investment and European start-up creation through management of submitted IP results. To enhance the IP management of the Graphene Flagship a number of options are being explored, including: *a)* a centralized entity for the protection, governance and monetization of Foreground IP. *b)* use of such an entity to promote Foreground IP and attract outside investors to provide start-up funding. *c)* assignment of Foreground IP to the centralized management on a voluntarily base, with the possibility for each partner to choose to manage their own IPR. *d)* authority to validate and manage Foreground IP for the central IP management entity *e)* administration and enforcement of selected results to be part of the mandate of the central entity. Regardless of the specific duties agreed for the central IP management entity, we expect at the very least to establish a central record of all the inventions produced by the partners. This will also provide a single information point for any enquire related to patents generated by the flagship, whilst creating an IP tracking tracking instruments for management and reporting purposes.

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