REVIEW

A roadmap for graphene

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Recent years have witnessed many breakthroughs in research on graphene (the first two-dimensional atomic crystal) as well as a significant advance in the mass production of this material. This one-atom-thick fabric of carbon uniquely combines extreme mechanical strength, exceptionally high electronic and thermal conductivities, impermeability to gases, as well as many other supreme properties, all of which make it highly attractive for numerous applications. Here we review recent progress in graphene research and in the development of production methods, and critically analyse the feasibility of various graphene applications.

Could graphene become the next disruptive technology, replacing some of the currently used materials and leading to new markets? Is it versatile enough to revolutionize many aspects of our life simultaneously? In terms of its properties, graphene certainly has the potential. Graphene is the first two-dimensional (2D) atomic crystal available to us. A large number of its material parameters—such as mechanical stiffness, strength and elasticity, very high electrical and thermal conductivity, and many others[1,2]—are supreme. These properties suggest that graphene could replace other materials in existing applications. However, that all these extreme properties are combined in one material means that graphene could also enable several disruptive technologies. The combination of transparency, conductivity and elasticity will find use in flexible electronics, whereas transparency, impermeability and conductivity will find application in transparent protective coatings and barrier films; and the list of such combinations is continuously growing. However, is graphene special and versatile enough to justify the inconveniences of switching to a new technology, usually a lengthy and expensive process?

Graphene properties

One reason that graphene research has progressed so fast is that the laboratory procedures enabling us to obtain high-quality graphene are relatively simple and cheap. Many graphene characteristics measured in experiments have exceeded those obtained in any other material, with some reaching theoretically predicted limits: room-temperature electron mobility of 2.5×10^5 cm^2 V^{-1} s^{-1} (ref. 3) (theoretical limit[4] $\sim 2 \times 10^5$ cm^2 V^{-1} s^{-1}); a Young's modulus of 1 TPa and intrinsic strength of 130 GPa (ref. 5, very close to that predicted by theory[6]); very high thermal conductivity (above 3,000 W mK^{-1}; ref. 7); optical absorption of exactly $\pi\alpha \approx 2.3\%$ (in the infrared limit, where α is the fine structure constant)[8]; complete impermeability to any gases[9], ability to sustain extremely high densities of electric current (a million times higher than copper)[10]. Another property of graphene, already demonstrated[11–13], is that it can be readily chemically functionalized.

Graphene's many superior properties justify its nickname of a 'miracle material'. However, some of these characteristics have been achieved only for the highest-quality samples (mechanically exfoliated graphene[14]) and for graphene deposited on special substrates like hexagonal boron nitride[3,15]. As yet, equivalent characteristics have not been observed on graphene prepared using other techniques, although these methods are rapidly improving. Graphene will be of even greater interest for industrial applications when mass-produced graphene has the same outstanding performance as the best samples obtained in research laboratories.

Nature provides us with many other 2D crystals, such as boron nitride and molybdenum disulphide[16]. Being structurally related to graphene but having their own distinctive properties, they offer the possibility of fine-tuning material and device characteristics to suit a particular technology better or to be used in combination with graphene (for example, 2D-based heterostructures[17,18]). Being part of such a large and diverse family of 2D crystals and heterostructures will improve graphene's chances of commercial success, although we do not cover these other 2D crystals in this Review (see Box 1).

Challenges in production

The market of graphene applications is essentially driven by progress in the production of graphene with properties appropriate for the specific application, and this situation is likely to continue for the next decade or at least until each of graphene's 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. Here we concentrate only on those that are scalable.

It is logical to categorize these by the quality of the resulting graphene (and thus the possible applications): (1) graphene or reduced graphene oxide flakes for composite materials, conductive paints, and so on; (2) planar graphene for lower-performance active and non-active devices; and (3) planar graphene for high-performance electronic devices. The properties of a particular grade of graphene (and hence the pool of applications that can utilize it) depend very much on the quality of the material, type of defects, substrate, and so forth, which are strongly affected by the production method; see Fig. 1 and Table 1.

Liquid phase and thermal exfoliation

Liquid-phase exfoliation of graphite[19,20] (or any other layered material[21]) is based on exposing the materials to a solvent with a surface tension that favours an 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, which can be further enriched by centrifugation.

A related method is the graphite oxide route in which graphite pellets are first oxidized and then ultrasonically exfoliated in an aqueous solution[22]. After exfoliation of graphite oxide the suspension may be further processed by centrifugation, and can then be deposited as a thin film on almost any surface and reduced (albeit partially) *in situ* back to the parent graphene state.
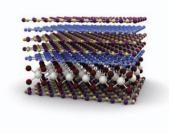
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Off-road with other 2D atomic crystals and their heterostructures

The study of graphene has triggered experiments on many other 2D atomic crystals, such as BN, NbSe$_2$, TaS$_2$, MoS$_2$ and many others. Similar strategies to those applied to graphene can be used to obtain new 2D materials by mechanical[16] or liquid-phase exfoliation of layered materials[21] or CVD growth. Another way to create new 2D crystals is to start with an existing one (like graphene) and use it as an atomic scaffolding, modifying it by chemical means (graphane[11] and fluorographene[13] are good examples). The pool of possible 2D crystals is huge, covering a massive range of properties: from the most insulating to the most conductive, from the strongest to the softest.

If 2D materials provide a large range of different properties, sandwich structures (made up of two, three, four or more different layers of such materials) can offer even greater scope. These 2D-based heterostructures[17,18] can be tailored with atomic precision and individual layers of very different character can be combined, so the properties of these structures can be tuned to fit an enormous range of possible applications. Furthermore, the functionality of heterostructure stacks is 'embedded' in their design. The first examples have already started to appear, with vertical tunnelling transistors based on this type of heterostructures having been demonstrated recently, showing very promising characteristics[51].

Box 1 Figure | Example of optically active 2D-based heterostructure. Two graphene layers are separated by several layers of boron nitride, which serve as a tunnelling barrier. A built-in electric field (created by the proximity of one of the graphene layers to a monolayer of MoS$_2$) separates the electron–hole pair, which is created by an incoming photon, resulting in a photocurrent.

An industrially important variation of the fully aqueous-based graphite-oxide route makes use of a thermal-shock procedure to achieve exfoliation and reduction simultaneously[23]. Even though the resulting material may contain graphene components with several layers, it still preserves many of the appealing properties of single-layer graphene. Similarly to oxidation, the parent graphite stacking can be disturbed via intercalation of small molecules. Such graphite intercalation compounds may then be used in a similar way as precursors and can subsequently be subjected to thermal or plasma processes to achieve their delamination into single sheets.

Also, there are several methods of producing suspensions of graphene nanoribbons—via unzipping of single-wall carbon nanotubes[24,25]. Although they are more expensive than chemical exfoliation of graphite or graphite oxide, these methods allow one to achieve suspensions with well-defined distributions (potentially very narrow) of graphene platelets. Similarly, nanotube unzipping allows better control over the chemical functionalization and quality of the edges.

Such bulk grades of graphene are already available on the tonne scale and are currently being evaluated in numerous fields of application[26]. Thus, graphene-based paints and inks will find their way into printed electronics, electromagnetic shielding, barrier coatings, heat dissipation, supercapacitors, smart windows[27], and so on. A number of flake-based products can be expected in the marketplace within a few years, and prototype applications for conductive inks have already been demonstrated on the commercial level.

Chemical vapour deposition

Large-area uniform polycrystalline graphene films are now being grown by chemical vapour deposition (CVD) on copper foils and films, and show promise for many applications[28]. Despite the fact that the complete process typically requires transfer from the copper support to a dielectric surface or other substrate of interest[1], the production of square metres of graphene has already been achieved[29]. These films have also been transferred onto 200-mm Si wafers on which state-of-the-art devices have been demonstrated. On a smaller scale, these films show transport properties equivalent to those of exfoliated graphene on both SiO$_2$ and hexagonal boron nitride substrates. Despite the presence of defects, grain boundaries, inclusions of thicker layers, and so on, such films are ready for use in transparent conductive coating applications (such as touch screens).

At present, the process is expensive owing to large energy consumption and because the underlying metal layer has to be removed. However, once the transfer process is optimized this method may indeed be disruptive and cost-effective. A number of issues need to be resolved before graphene CVD technology can become widely used. Graphene 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. Control of the number and relative crystallographic orientation of the graphene layers is critical because it will enable a number of applications which would require double, triple and even thicker layers of graphene. Simultaneously, the transfer process should be improved and optimized with the objectives of minimizing the damage to graphene and of recovering the sacrificial metal.

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 as well as excellent barrier properties allow graphene greatly to enhance the performance of copper interconnects in integrated circuits. Also, because graphene is inert, it is an excellent barrier for any gas, and it forms a conformal layer on metal surfaces with the most complex topographies: such coatings can protect against corrosion.

The game-changing breakthroughs would be the development of graphene growth on arbitrary surfaces and/or at low temperatures (for example, using plasma-enhanced CVD or other methods) with a minimal number of defects. The former would allow one to avoid the complex and expensive transfer step and promote better integration of this 2D crystal with other materials (like Si or GaAs). The latter would improve compatibility with modern microelectronic technologies and allow significant energy saving.

Synthesis on SiC

Silicon carbide is a common material 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 graphitized surface[30]. Initially, the C-terminated face of SiC was used to grow a turbostratic stack of many randomly oriented polycrystalline layers[31], but now the number of graphene layers grown[32] can be controlled. The quality of such graphene can be very high, with crystallites approaching hundreds of micrometres in size[33].

The two major drawbacks of this method are the high cost of the SiC wafers and the high temperatures (above 1,000 °C) used, which are not directly compatible with silicon electronics technology. There are potentially several ways to take advantage of the growth of graphene on SiC, including the growth of thin SiC on Si, although this approach requires further development. As a result of the high-temperature growth, high substrate cost, and small-diameter wafers, the use of graphene on SiC
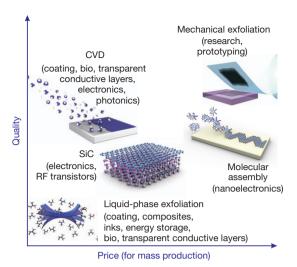
Figure 1 | There are several methods of mass-production of graphene, which allow a wide choice in terms of size, quality and price for any particular application.

will probably be limited to niche applications. High-frequency transistors based on SiC-grown graphene[34] may well find applications within a decade when the existing technology, based on III–V materials (such as InGaAs, GaN, and so on) reaches its limit at about 1 THz. The short gate transistors that are currently widely used make even the 20-μm size domains (currently achieved in graphene grown on SiC) suitable for such applications. Another very attractive, though niche, application of this type of graphene is in metrological resistance standards[35], where samples of graphene grown on SiC have already been demonstrated to deliver higher resistance accuracy at higher temperatures than do conventionally used GaAs heterostructures.

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

Other growth methods

Although there are a number of other growth methods, it is unlikely that they will become commercially viable in the next decade. 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 high-quality graphene nanoribbons and even more complex structures (like T- and Y-shaped connections)[36] using a chemistry-driven bottom-up approach. Molecular beam epitaxy has been used to grow chemically pure graphene[37], but it is unlikely to be used on a large scale because of its much higher cost than CVD methods.

Laser ablation is a potentially interesting growth technique allowing the deposition of graphene nanoplatelets on arbitrary surfaces[38]. This relatively expensive method is in direct competition with the spray-coating of chemically exfoliated graphene, so it is unlikely to be widely used.

Graphene electronics

It is unlikely that graphene will make it into high-performance integrated logic circuits as a planar channel material within the next decade because of the absence of a bandgap. However, many other, less stringent, graphene electronic applications are being developed, using the available (probably not ideal in terms of quality) material. Figure 2 and Table 2 list some of the possible applications and the time that it may take for graphene-based prototypes to be demonstrated.

Flexible electronics

Transparent conductive coatings are widely used in electronic products such as touch screen displays, e-paper (electronic paper) and organic light-emitting diodes (OLEDs) and require a low sheet resistance with high transmittance (of over 90%) depending on the specific application. Graphene meets the electrical and optical requirements (sheet resistance reaching 30 Ω per square of 2D area in highly doped samples) and an excellent transmittance of 97.7% per layer[8], although the traditionally used indium tin oxide (ITO) still demonstrates slightly better characteristics. However, considering that the quality of graphene improves every year (already making the difference in performance marginal), while ITO will become more expensive and ITO deposition is already expensive, graphene has a chance of securing a good fraction of the market. Graphene also has outstanding mechanical flexibility and chemical durability—very important characteristics for flexible electronic devices[29], in which ITO usually fails.

The requirements of electrical properties (for example, sheet resistance) for each electrode type differ from application to application. Depending on the production methods, various grades of transparent conductive coating could be produced from graphene. Thus, electrodes for touch screens (although requiring an expensive CVD method of production) tolerate a relatively high sheet resistance (50–300 Ω per square) for a transmittance of 90%. The advantage of graphene electrodes in touch panels is that graphene's endurance far exceeds that of any other available candidate at the moment. Moreover, the fracture strain of graphene is ten times higher[5] than that of ITO, meaning that it could also successfully be applied to bendable and rollable devices.

Rollable e-paper is a very appealing electronic product. It requires a bending radius of 5–10 mm, which is easily achievable by a graphene electrode. In addition, graphene's uniform absorption across the visible spectrum[8] is beneficial for colour e-papers. However, the contact resistance between the graphene electrode and the metal line of the driving circuitry is still a problem. A working prototype is expected by 2015, but the manufacturing cost needs to decrease before it will appear on the market.

OLED devices have become an attractive technology and the first (non-graphene) products are expected on the market by 2013. Besides

Table 1 | Properties of graphene obtained by different methods

Method	Crystallite size (μm)	Sample size (mm)	Charge carrier mobility (at ambient temperature) ($cm^2 V^{-1} s^{-1}$)	Applications
Mechanical exfoliation	>1,000	>1	$>2 \times 10^5$ and $> 10^6$ (at low temperature)	Research
Chemical exfoliation	≤0.1	Infinite as a layer of overlapping flakes	100 (for a layer of overlapping flakes)	Coatings, paint/ink, composites, transparent conductive layers, energy storage, bioapplications
Chemical exfoliation via graphene oxide	~100	Infinite as a layer of overlapping flakes	1 (for a layer of overlapping flakes)	Coatings, paint/ink, composites, transparent conductive layers, energy storage, bioapplications
CVD	1,000	~1,000	10,000	Photonics, nanoelectronics, transparent conductive layers, sensors, bioapplications
SiC	50	100	10,000	High-frequency transistors and other electronic devices

Figure 2 | Graphene-based display and electronic devices. Display applications are shown in green; electronic applications are shown in blue. Possible application timeline, based on projections of products requiring advanced materials such as graphene. The figure gives an indication of when a functional device prototype could be expected based on device roadmaps and the development schedules of industry leaders.

strict requirements for the sheet resistance (below 30 Ω per square), other crucial parameters for such devices are the work function and the electrode's surface roughness, which effectively governs the performance. The tunability of graphene's work function could improve the efficiency, and its atomically flat surface would help avoid electrical shorts and leakage currents. Graphene electrodes have already been demonstrated in OLED test cells[39]. Advanced flexible or foldable OLED devices could be introduced after 2016 once device integration issues (such as conformal deposition of graphene on three-dimensional structures and contact resistance between graphene and the source/drain) are resolved.

In the low-cost sector everything is set up for mass production. Liquid-phase exfoliation produces such graphene coatings 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 windows, solar cells and some touch screen applications. Graphene has the important advantage of flexibility and mechanical strength, which ensures that graphene-based devices will probably dominate flexible applications.

High–frequency transistors

Graphene has been considered and intensively researched for high-frequency transistor applications[34]. However, it has to compete against more mature technologies such as compound semiconductors (III–V materials). Thus, graphene will probably be used only after 2021, when even III–V materials will fail to satisfy device requirements. Projections show that III–V materials will no longer be able to obtain the required cut-off frequency $f_T = 850$ GHz (the top frequency for current modulation) and maximum oscillation frequency $f_{max} = 1.2$ THz (the top frequency for power modulation) after 2021 because device requirements will become more stringent. A recent graphene progress report[40] presented a value of f_T as high as 300 GHz, with the possibility of extending it up to 1 THz at a channel length of about 100 nm (ref. 41). On the other hand, f_{max} has only reached 30 GHz in traditional graphene structures, which is far from the 330 GHz Si high-frequency 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 in a comparable conventional device. There are two ways to improve f_{max}: by lowering the gate resistance or the source–drain conductance at pinch-off (ref. 42). The former approach could be done using well-established semiconductor processes. The latter will require current saturation in the graphene high-frequency transistor, which will probably involve finding a new dielectric layer with properties similar to those of boron nitride[43] and compatible with modern semiconductor technology. An f_{max} of 58 GHz has been reported[44] using graphene on top of an exfoliated hexagonal boron nitride film[3,15].

Logic transistor

It is widely accepted that Si technology will be extended to nearly or even below the 10-nm level. Graphene transistors might have an opportunity to replace the silicon technology only after 2020 (according to the 2011 ITRS).
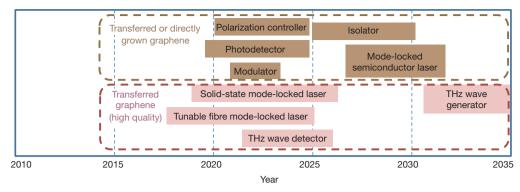
Several research paths are being targeted at opening a bandgap in graphene: nanoribbon[36,45] and single electron transistor[46,47] formation, bilayer control[32,48] and chemically modified graphene[11,13]. However, all of these approaches (apart from chemical modification) have so far been unable to open a bandgap wider than 360 meV (ref. 49), which limits the on/off ratio to about 10^3, much less than the required 10^6. Even worse, they also lead to the degradation of the carrier mobility in graphene[50].

The issue of the low on/off ratio is resolved in the new transistor designs, which exploits the modulation of the work function of graphene, gaining control over vertical (rather than planar) transport through various barriers[51]. Although such devices allow for spectacular on/off ratios of $>10^6$, more work on integration is required to enable the use of graphene for logic applications after 2025.

Graphene's electrical and thermal conductivities as well as its excellent barrier properties might push this material towards being used as interconnects as well as for thermal dissipation in integrated circuits. Graphene can easily be grown on copper by CVD, so we might see this combination used for such applications.

Table 2 | Electronics applications of graphene

Application	Drivers	Issues to be addressed
Touch screen	Graphene has better endurance than benchmark materials	Requires better control of contact resistance, and the sheet resistance needs to be reduced (possibly by doping)
E-paper	High transmittance of monolayer graphene could provide visibility	Requires better control of contact resistance
Foldable OLED	Graphene of high electronic quality has a bendability of below 5 mm, improved efficiency due to graphene's work function tunability, and the atomically flat surface of graphene helps to avoid electrical shorts and leakage current	Requires better control of contact resistance, the sheet resistance needs to be reduced, and conformal coverage of three-dimensional structures is needed
High-frequency transistor	No manufacturable solution for InP high-electron-mobility transistor (low noise) after 2021, according to the 2011 ITRS	Need to achieve current saturation, and $f_T = 850$ GHz, $f_{max} = 1,200$ GHz should be achieved
Logic transistor	High mobility	New structures need to resolve the bandgap–mobility trade-off and an on/off ratio larger than 10^6 needs to be achieved

Figure 3 | Graphene-based photonics applications. Optical applications are shown in pink; optical interconnect applications are shown in brown. Possible application timeline, enabled by continued advances in graphene technologies, based on projections of products requiring advanced materials such as graphene. The figure gives an indication of when a functional device prototype could be expected based on device roadmaps and the development schedules of industry leaders.

Photonics

Electrons in graphene behave as massless two-dimensional particles, which leads to a significant wavelength-independent absorption ($\pi\alpha = 2.3\%$) for normal incident light[8] below about 3 eV. Additionally, mono- and bi-layer graphene become completely transparent when the optical energy is smaller than double the Fermi level, owing to Pauli blocking[52]. These properties would suit many controllable photonic devices (Fig. 3 and Table 3).

Photodetectors

Graphene photodetectors are presently one of the most actively studied photonic devices. Unlike semiconductor photodetectors, which have limited detecting spectral width, graphene can in principle be used for a wide spectral range from ultraviolet to infrared. Another advantage of graphene 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) photodetectors are limited to 150 GHz (ref. 53) and 80 GHz (ref. 54) respectively, owing to the carrier transit times. The high carrier mobility of graphene enables ultrafast extraction of photo-generated carriers, possibly allowing extremely high bandwidth operation. The transit-time-limited bandwidth of graphene photodetectors is calculated[55] to be 1.5 THz at the reported saturation carrier velocity[56]. In practice, the maximum bandwidth of a graphene photodetector would be limited[55] to 640 GHz by the time constant resulting from the capacitive (RC) delay, rather than the transit time.

Owing to the absence of a bandgap, the graphene photodetector requires a different carrier extraction model from that of semiconductor photodetectors. Currently, graphene photodetectors use the local potential variation near the metal–graphene interfaces to extract the photo-generated carriers[57]. Photo-responses of up to 40 GHz (ref. 55) and 10 GHz (ref. 58) detector operation have been demonstrated. However, the maximum responsivity is low (a few mA W^{-1}; ref. 58) in comparison to the required $\sim$1 A W^{-1}) because of the limited absorption caused by the small effective detection areas and the thinness of graphene.

There are several possible ways to improve the sensitivity of graphene photodetectors, such as by using plasmonic nanostructures for the enhancement of the local optical electric field[59] or by integrating it with a waveguide to increase the light–graphene interaction length[49]. Given the maximum bandwidth of the Ge photodetector and optical interconnection roadmap, a graphene photodetector with a bandwidth over 100 GHz will be competitive after 2020, providing that a method compatible with modern semiconductor technology of growing high-quality graphene (with mobility $>$20,000 cm^2 V^{-1} s^{-1}) is secured.

Optical modulator

Optical modulators are one of the key active building blocks for optical interconnects used to encode transmission data by altering the properties of light[60] such as phase, amplitude, and polarization using electro-refraction or electro-absorption. Si optical modulators, such as Mach–Zehnder interferometers[61], ring resonators[62] and electro-absorption modulators[63] are based on interference, resonance and bandgap absorption, respectively. Their operating spectra are usually narrow, however, and their slow switching times limit operation bandwidths. For Si waveguide modulators, a large resistance in the p–n junction through the Si

Table 3 | Photonic applications of graphene

Application	Drivers	Issues to be addressed
Tunable fibre mode-locked laser	Graphene's wide spectral range	Requires a cost-effective graphene-transferring technology
Solid-state mode-locked laser	Graphene-saturable absorber would be cheaper and easy to integrate into the laser system	Requires a cost-effective graphene-transferring technology
Photodetector	Graphene can supply bandwidth per wavelength of 640 GHz for chip-to-chip or intrachip communications (not possible with IV or III–V detectors)	Need to increase responsivity, which might require a new structure and/or doping control, and the modulator bandwidth must follow suit
Polarization controller	Current polarization controlling devices are bulky or difficult to integrate but graphene is compact and easy to integrate with Si	Need to gain full control of parameters of high-quality graphene
Optical modulator	Graphene could increase operating speed (Si operation bandwidth is currently limited to about 50 GHz), thus avoiding the use of complicated III–V epitaxial growth or bonding on Si	High-quality graphene with low sheet resistance is needed to increase bandwidth to over 100 GHz
Isolator	Graphene can provide both integrated and compact isolators on a Si substrate, dramatically aiding miniaturization	Decreasing magnetic field strength and optimization of process architecture are important for the products
Passively mode-locked semiconductor laser	Core-to-core and core-to-memory bandwidth increase requires a dense wavelength-division-multiplexing optical interconnect (which a graphene-saturable absorber can provide) with over 50 wavelengths, not achievable with a laser array	Competing technologies are actively mode-locked semiconductor lasers or external mode-lock lasers but the graphene market will open in the 2020s; however, interconnect architecture needs to consume low power

core regions is a problem, confining bandwidths to usually less than about 50 GHz.

Excellent optical modulator performance can be achieved by exploiting graphene's ability to absorb a small amount of incident light over ultrawide ranges of wavelengths and its ultrafast response. To do this, the interband transitions of photo-generated electrons in a single graphene layer[64] are modulated over broad spectral ranges by a drive voltage, leading to operating speeds with bandwidth exceeding 1 GHz in the near infrared range[65]. With some structural changes, an even wider operation bandwidth of more than 50 GHz has been suggested, using inter-gated dual graphene layers[49] to reduce the resistance in the *RC* delay time, offering a pathway to a regime of hundreds of gigahertz, although such developments are not expected before 2020. Graphene is also promising for THz-range wireless communications[66] where optical losses are an order of magnitude smaller than those in noble metals.

Mode–locked laser / THz generator

Ultrafast passively mode-locked lasers have been used for various applications in spectroscopy, material micromachining[67], bio-medicine[68] and in security applications; they usually use saturable absorbers to cause intensity modulation by selectively transmitting high-intensity light only. Compared with the widely used semiconductor saturable absorbers[69], graphene absorbs a significant amount of photons per unit thickness[8] and therefore reaches saturation at a lower intensity over a wide spectral range[70,71]. Ultrafast carrier relaxation time, controllable modulation depth, high damage threshold, high thermal conductivity[8] and wide spectral range tunability[72] are other benefits of graphene-saturable absorbers[73]. These applications need only a small area of graphene, so commercialization could take place even before 2020.

Most studies are focused on fibre and solid-state lasers[74], but graphene-saturable absorbers can also find applications in semiconductor laser technology. Optical interconnection with a wavelength-division-multiplexing scheme requires a laser array with different wavelengths. One way to provide many different wavelengths is to use a single laser with multiple longitudinal modes, such as a mode-locked laser[75]. An actively mode-locked Si hybrid laser has been studied for this purpose[76], but a graphene-saturable absorber could enable a passively mode-locked semiconductor laser with simple fabrication and operation. However, we expect this application will be useful only after developing a highly integrated optical interconnection around the late 2020s.

THz generators can be used in various applications such as medical imaging, chemical sensors, and security devices. Early proposals based on THz electromagnetic wave generation use graphene as a gain medium to generate stimulated emission by optical pumping[77]. However, electrons and holes have similar mobility values, so the photo-Dember effect (formation of a dipole and resulting THz emission due to the difference in diffusion times of electrons and holes) 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[78] under a femtosecond laser pulse field to generate carriers that will be accelerated to generate the THz wave. However, the intensity is 10^3–10^4 times weaker than that generated from a III–V-semiconductor-based photoconductive antenna or resonant tunnelling devices[79]. Practical THz-wave generators using graphene are unlikely to emerge before 2030.

Optical polarization controller

Polarization controllers such as polarizers and polarization rotators are crucial passive components with which to manipulate the polarization properties of photons. The differential attenuation of the transverse magnetic mode due to the excitation of Dirac fermions can provide an excellent extinction ratio of 27 dB, covering very broad communication bands. Compact optical polarizers have been demonstrated in data-communication optical fibres integrated with graphene as an in-line conductive layer[80]. High-quality millimetre-sized graphene needs to be integrated with an optical fibre or silicon in a hybrid device. Therefore, if the graphene-processing technology matures, these devices could come into play as early as 2020.

Faraday rotation is a popular way to manipulate light polarization[81]. Landau quantization in the two-dimensional electron gas in graphene[82] results in a giant rotation with a fast response and a broadband tunability. Even larger 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 desirable magnetic field smaller than 1 T will be a serious challenge for graphene isolators, delaying its debut until the late 2020s.

Composite materials, paints and coating

Graphene-based paints can be used for conductive ink, antistatic, electromagnetic-interference shielding, and gas barrier applications. In principle, the production technology is simple and reasonably developed, with most of the major graphite mining companies as well as new start-up companies having programmes on liquid-phase or thermally exfoliated graphene. In addition, over the next few years chemical derivatives of graphene will be heavily developed to control the conductivity and optical opacity of the products.

Graphene is highly inert, and so can also act as a corrosion barrier against water and oxygen diffusion. Given that it can be grown directly on the surface of almost any metal under the right conditions, it could form a protective conformal layer, that is, it could be used on complex surfaces.

The mechanical, chemical, electronic and barrier properties of graphene along with its high aspect ratio make graphene attractive for applications in composite materials. The commercial position held by carbon fibres, however, is so strong that graphene will need substantial development before it will be economically feasible to use it as the main reinforcement component. The target is to achieve a 250 GPa Young's 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, which would require more chemical modification of graphene.

An equally large market exists in bringing extra functionality to composites, where the scope of graphene might be large and possibly realized more rapidly. Graphene can contribute gas and moisture barrier properties, electromagnetic 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 for which it is difficult to use carbon fibres that would still benefit from excellent mechanical reinforcement (injection-moulded composites).

Considering that many companies involved in the carbon business have already established programs on graphene and graphene-oxide production, it is possible to expect graphene-based composites to appear on the market within a few years. The real breakthrough, however, will be expected when graphene flakes over 10 μm in size are easily obtainable—the dimension required to use in full the advantage of the high Young's modulus of graphene[5,83]. Fortunately, it has been demonstrated that graphite flakes thicker than one monolayer can provide a significant level of reinforcement[83], thus making the implementation of graphene-based composites realistic within a shorter time.

Energy generation and storage

There is a constant search for highly efficient renewable energy technologies, and it would be surprising if graphene were not involved in this race. At present, most efforts are concentrated on solar cells, which could be divided into those where graphene acts as the active medium and those that use graphene as a transparent or distributed electrode material. The former use the same principle of operation as already discussed for photodetectors, and, in principle, would benefit from

uniform absorption over a broad spectrum[8]. However, owing to the low intrinsic optical absorption of graphene[8], such devices would require complex interferometry or plasmonic enhancement structures[59] to achieve the desired responsivity, and thus are unlikely to be widely used soon. Instead, the use of graphene as a transparent electrode in either quantum dots or dye-sensitized solar cells has proved highly beneficial. Doping can vary the position of the Fermi level in graphene significantly, so such electrodes have been used both as electron[84] and hole[85] conducting media. With the cost of graphene produced by liquid-phase or thermal exfoliation going down[26] we can expect wide use of graphene in dye solar cells, especially in applications where mechanical flexibility is paramount.

The use of graphene in next-generation lithium-ion batteries is currently being widely studied. Traditionally used in commercial lithium-ion batteries, cathodes frequently suffer from poor electrical conductivity, which is overcome by the addition of graphite and carbon black to the electrode formulation. Graphene, with its sheet-like morphology, would not only act as an advanced conductive filler but may also give rise to novel core–shell or sandwich-type nanocomposite structures[86]. The resulting increase in electrical conductivity of these new morphologies would help in overcoming one of the key limitations of lithium-ion batteries—their low specific power density. Lastly, the high thermal conductivity of graphene may be advantageous when it comes to high current loads that generate significant amounts of heat within the battery system. As anodes, graphene nanosheets can be used to intercalate lithium reversibly into the layered crystals. Graphene nanosheets used in conjunction with carbon nanotubes and fullerenes, C_{60}, increased the battery charge capacity[87].

Supercapacitors (Fig. 4) are based on storage of energy within electrochemical double-layer capacitors[88]. The superior rate performance of state-of-the-art devices (compared to lithium-ion batteries) is based on predominantly electrostatic storage of electrical energy and is determined by the combination of a high-surface-area activated carbon material and a nanoscopic charge separation at the electrode–electrolyte interface. Graphene is an obvious material choice for this application[1], offering high intrinsic electrical conductivity, an accessible and defined pore structure, good resistance to oxidative processes and high temperature stability. Currently the prototype graphene-based electrochemical double-layer capacitors[89] lead the field in capacitance as well as energy and power densities. Although the characteristics of graphene supercapacitors are very encouraging, there are still issues which must be addressed before the commercial use of such systems. In particular, the irreversible capacitance of graphene-based supercapacitors is still
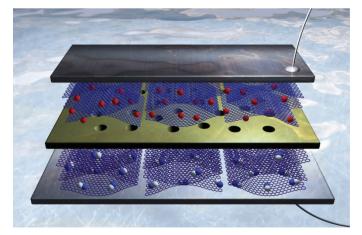

Figure 4 | In a supercapacitor device two high-surface-area graphene-based electrodes (blue and purple hexagonal planes) are separated by a membrane (yellow). Upon charging, anions (white and blue merged spheres) and cations (red spheres) of the electrolyte accumulate at the vicinity of the graphene surface. The ions are electrically isolated from the carbon material by the electrochemical double layer that is serving as a molecular dielectric.

too high, which could probably be improved by reducing the number of defects or choosing a better electrolyte.

There are also reports on the use of graphene nanosheets as a support material for platinum catalysts for fuel cells[90]. Unlike carbon black, which is the baseline support material for platinum catalysts, graphene decreases the platinum particle size to under a nanometre because of the strong interaction between the platinum atoms and graphene. The strong interaction of platinum and graphene and the small particle size is leading to increased catalytic activity in direct methanol fuel cells.

Common benchmark materials in energy-related applications (graphite, carbon black and activated carbon) will only be replaced if graphene is proved to be superior in terms of both performance and cost. That graphene of suitable grades for such applications is already available in scalable amounts[26] might speed its progression into real devices.

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. Thus, it is natural to consider using graphene for sensor applications, from measurements of magnetic field to DNA sequencing and from the monitoring of the velocity of surrounding liquid to strain gauges. The latter (with either electrical or optical readouts) are probably the most competitive application. Graphene is the only crystal which can be stretched by 20%, thus enhancing the working range of such sensors significantly[5].

Currently, graphene gas detectors, although extremely sensitive, have only a minor competitive edge over existing devices. Low selectivity and poisoning by water limit their area of applicability, although such detectors can be produced so cheaply that they could be used in certain niche applications. Functionalization might improve the selectivity of graphene sensors, but because it is rather an expensive method, it is probably most suitable for bio-sensing.

The major advantage of graphene sensors is their multi-functionality. A single device can be used in multidimensional measurements (for example, strain, 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 levels, makes it an ideal material to develop the universal resistance standard based on the quantum Hall effect[1]. The precision of quantum Hall effect quantization of 0.1 parts per billion for epitaxial graphene grown on the Si face of SiC by far outperforms that in the traditionally used GaAs heterostructures[35,91], and such devices are already being used by several metrological facilities.

Bioapplications

Graphene has a number of properties which make it potentially promising for bioapplications. Its large surface area, chemical purity and the possibility of easy functionalization provide opportunities for drug delivery. Its unique mechanical properties suggest tissue-engineering applications and regenerative medicine[92]. Its combination of ultimate thinness, conductivity and strength make it an ideal support for imaging biomolecules in transmission electron microscopy[93]. Also, chemically functionalized graphene might lead to fast and ultrasensitive measurement devices, capable of detecting a range of biological molecules including glucose, cholesterol, haemoglobin and DNA[94].

As a result of their large surface area and delocalized π electrons, graphene derivatives can solubilize 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 is also lipophilic, which might help in solving another challenge in drug delivery—membrane barrier penetration (Fig. 5). Most of the limited work that has been done so far has focused on investigating the loading and *in vitro* behaviour for aromatic anticancer drugs such as doxorubicin[95]. Intravenous
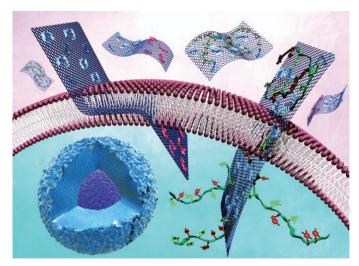
Figure 5 | Manipulating the hydrophilic–lipophilic properties of graphene (blue hexagonal planes) through chemical modification would allow interactions with biological membranes (purple-white double layer), such as drug delivery into the interior of a cell (blue region).

administration of polyethylene glycol-modified graphene oxide, labelled with a near-infrared fluorescence dye but not carrying 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 photo-thermal cancer treatment[96]. 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 using graphene-based drug delivery technology will be near the market before 2030.

Tissue engineering is an emerging area of technology with potential for a 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 could be incorporated into the scaffold materials used for tissue engineering to improve their mechanical (strength and elasticity) and selective barrier[97] properties and potentially to modulate their biological performance in areas such as cell adhesion, proliferation and differentiation[95].

Before graphene can fulfil its promise in the biomedical area we must 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 because the outcome is likely to vary with size, morphology and chemical structure. 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.

Conclusions

Physicists are used to thinking of graphene as a perfect two-dimensional lattice of carbon atoms. However, the paradigm is now shifting as pure science opens new technology routes: even less-than-perfect layers of graphene can be used in certain applications. In fact, different applications require different grades of graphene, bringing closer widespread practical implementation of this material.

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 in a few years, and those which require the highest, electronic-quality grades or biocompatibility may well take decades to develop. Also, because developments in the last few years were extremely rapid,

graphene's prospects continue to improve. Nevertheless, established benchmark materials will only be replaced if the properties of graphene, however appealing, can be translated into applications that are sufficiently competitive to justify the cost and disruption of changing existing industrial processes.

Graphene is a unique crystal in the sense that it combines many superior properties, from mechanical to electronic. This suggests that its full power will only be realized in novel applications, which are designed specifically with this material in mind, rather than when it is used to replace other materials in existing applications. Interestingly, such an opportunity is likely to be provided very soon with development of such new technologies as printable and flexible electronics, flexible solar cells and supercapacitors.

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