

Graphene for energy solutions and its industrialization

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Graphene attracts intensive interest globally across academia and industry since the award of the Nobel Prize in Physics 2010. Within the last half decade, there has been an explosion in the number of scientific publications, patents and industry projects involved in this topic. On the other hand, energy is one of the biggest challenges of this century and related to the global sustainable economy. There are many reviews on graphene and its applications in various devices, however, few of the review articles connect the intrinsic properties of graphene with its energy. The IUPAC definition of graphene refers to a single carbon layer of graphite structure and its related superlative properties. A lot of scientific results on graphene published to date are actually dealing with multi-layer graphenes or reduced graphenes from insulating graphene oxides (GO) which contain defects and contaminants from the reactions and do not possess some of the intrinsic physical properties of pristine graphene. In this review, the focus is on the most recent advances in the study of pure graphene properties and novel energy solutions based on these properties. It also includes graphene metrology and analysis of both intellectual property and the value chain for the existing and forthcoming graphene industry that may cause a new 'industry revolution' with the strong and determined support of governments and industries across the European Union, U. S., Asia and many other countries in the world.

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1. Introduction

Graphene is one of the most popular topics that attracts scientists and industry researchers from different scientific backgrounds. With the introduction of graphene to the public by the BBC, it has wider implications. What is graphene? What differentiates graphene from other materials? What special features can graphene bring when it is used in energy devices? These questions are interesting not only to the scientific community across chemistry, physics, materials science and engineering but also to the general public.

There are reviews on the electrochemical¹ and mechanical² properties of graphene and analysis on the relationship between its properties and functionalization.^{3–5} Different tailored physicochemical properties can be produced when graphene is made from reduction of graphene oxide (GO).^{6–10} Both small molecules and polymers can be covalently attached to the reactive oxygen functionalities of GO, or non-covalently attached to the graphitic surfaces. The functional entities themselves will also cause the ballistic transport of charge carriers effectively scattered or spatially confined to be used as nanoelectronic memory devices.¹¹ Graphene has been making a profound impact in the development of solar cells, photo-electrochemical and photocatalytic applications.^{12,13} Many published reviews have emphasized use of graphene in energy conversion devices (mainly solar cells).^{14,15} Dimensionally-

tailored (0D, 1D, 2D, 3D) functional graphene structures for energy harvesting and storage (graphene-quantum dot solar cells, actuators, fuel cells, supercapacitors) have also been reviewed.^{16,17} It was found that free standing 3D graphene foam gives rise to beneficial electrochemical signatures in ionic liquids in contrast to its poor voltammetric responses in aqueous solutions, due to the quasi-super-hydrophobicity created by the material and the structure.¹⁸ Since a considerable number of publications on graphene were not dealing with pristine graphene, but with reduced graphene from GO, reviews^{14,15,19} based on these publications actually did not discuss the unique properties that intrinsic graphene can offer to existing energy devices. With the significant progress of graphene research in recent years, it is necessary to review this important topic with a focus on the intrinsic properties of pristine graphene for energy solutions and its scaling up protocols. This review will discuss *what real differentiations graphene can bring to energy devices* and its *value chain for the existing and forthcoming graphene industry*.

2. Conjugation from Nobel Prize to Nobel Prize

Graphene is the fundamental building unit for fullerene, carbon nanotubes and graphite. The sp² hybrid carbon atoms are arranged in a hexagonal configuration within a planar sheet. Like the conjugation in conjugated polymers,²⁰ such sp² electron hybridization leaves a free electron per carbon atom in the p-orbital located perpendicular to the hexagonal plane, which

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means that graphene has huge potential in various applications.^{21–23} There are indeed intrinsic correlations between conjugated polymers (2000 Nobel Prize in Chemistry) and graphene (2010 Nobel Prize in Physics), since both Nobel prizes involve the same structure chemistry of the sp^2 hybridization bonding of carbon in either 1 or 2 dimensions. The single and double bond alternation (π bond) makes the polymer conducting because the perpendicular p-electrons can move freely in the 1D linear structure. In the case of graphene, it has a structure analogous to benzene and can be considered as a polycyclic aromatic hydrocarbon of quasi-infinite size²⁴ with the p-electrons moving freely on a 2D plane. Both 'organic' conjugated polymers and 'inorganic' graphene materials have unique electric, thermal and electrochromic properties.

Fig. 1a is an example of simple π bonding in polyacetylene. This conjugation exists in many materials, from small organic molecules such as 1,3-butadiene, larger polymers like polyacetylene, to graphene and its derivatives. Fig. 1b shows details of the conjugation (π bonds) across the 2D graphene. Using the π - π interaction of graphene, ultra-light and super-elastic graphene-based cellular monoliths (with high elasticity in 3D graphene networks) can be made through a cost-effective freeze casting process.²⁵ The interaction of graphene with small molecules can be as strong as the inter-sheet interaction in graphite.^{26,27} It is not only small molecules that can interact with graphene, but also larger ones, sometimes with dramatic results. As an example, insulin, which is a key regulator for the synthesis of fatty acids, can be denatured upon π - π adsorption on graphene, in contrast to GO, which instead binds with insulin electrostatically.²⁸ The chemical bonding and electronic structure of graphene-metal contacts have been studied as well.²⁹ Strong covalent metal-d-graphene-p hybridization and hole doping of graphene is observed upon deposition of Ni and Co metal contacts onto graphene/SiO₂. Of single-crystalline substrates, the most commensurate (111) facets exhibit the strongest interactions with the graphene lattice. At the same time, the anion- π interactions on graphene flakes were also found to be unexpectedly strong compared to those on simple aromatic compounds.³⁰ The unexpectedly large adsorption energies of the halide anions on the graphene flake are ascribed to the effective donor-acceptor interactions between the halide

anions and the graphene flake. These favourable interactions of anions with electron-deficient graphene flakes may be applicable to the design of a new family of neutral anion receptors and detectors. They can also be applied in a novel energy generation device.³¹

In the semiconductor and organic electronics industry, not only is the band gap important, but the type of charge carriers present in the substrate are essential to the device. Pristine graphene displays ambipolar behaviour in its FET devices with a neutrality point at zero.³² For silicon, the dopants (usually phosphorus or boron atoms) provide an excess of electrons or holes as the charge carriers, producing both n-type and p-type semiconductors. Similarly, substitution of the carbon atoms in the structure of graphene with heteroatoms could produce a material with either electrons or holes, exhibiting both n-type and p-type behaviours. In general, p-type graphene is easily obtained by the adsorption of water molecules from air and n-type graphene is a bit more difficult but can be made using several nitrogen-doped methods.^{33–35} In addition to physical doping, there are some similarities in electrochemical doping and photon dopings between graphene derivatives and conjugated polymers. For example, both polyaniline (type of conjugated polymer)^{36–39} and graphene oxide^{40,41} are pH sensitive (*i.e.* both color and conductivity change with pH), sensitive to humidity^{42,43} and flash light.^{44,45}

2.1 Graphene properties

A lot of materials will become unstable on the nanoscale. Graphene, being only a few atoms thick, is however, very stable under ambient conditions. The typical size of graphene is monoatomic (*ca.* 0.33 nm) in one dimension, and up to tens of mm in the other two. Thus, while being one-atom thick, a sheet of graphene has a lateral size which is 10²–10⁵ times larger than the size of typical small molecules. This provides graphene with lots of unique properties.⁴⁶

Graphene has extremely high Young's modulus (1 TPa) and highest intrinsic strength (\sim 130 GPa).^{47,48} It can act effectively as nano-fillers in polymers to reinforce the elastic modulus of the polymer composite.⁴⁹ Loading of graphene in a matrix can be as high as >75% by weight and its low inter-platelet friction promotes reduced matrix viscosity. Graphene can reduce fiber entanglements, thus allowing higher than normal carbon nanotube and carbon nanofiber loadings, and it improves processability of nanocomposites. Graphene also has a high breaking strength of 42 N m⁻¹,^{50–53} which is ideal to be used in the blades of wind turbines to generate electricity.

The high electric conductivity and electron mobility in monolayer graphene results from a very small effective mass. Since the electronic structure of a monolayer graphene overlaps between two conical points in the Brillouin zone, the charge carriers can be understood as mass-less electrons or Dirac fermions.^{46,54} Thus electrons in a single layer graphene behave like massless relativistic particles, travelling at a speed of around 10⁶ m s⁻¹. This electronic behavior of graphene was theoretically studied by local density of states.⁵⁵ Graphene has exceptional in-plane electrical conductivity (up to \sim 20 000 S

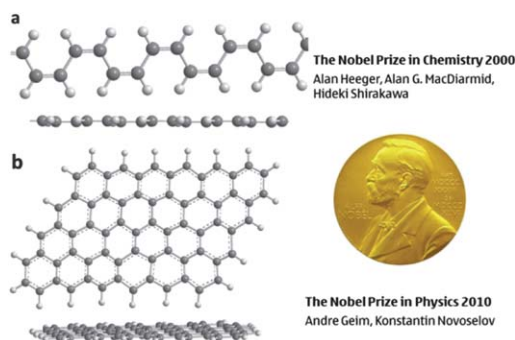


Fig. 1 (a) Conjugation along 1D conjugated polymer, (b) conjugation along 2D graphene.

cm^{-1}) and charge mobility of $\approx 200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$,⁵⁶ which is more than 100 times higher than that of silicon and over 20 times higher than gallium arsenide (~ 1500 and $8500\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively). Atomically thin carbon films exhibit such a strong ambipolar electric field effect that electrons and holes in concentrations up to 10^{13} cm^{-2} can be induced by applying a gate voltage and the films have an anomalous quantum hall effect^{46,50} with ballistic transport (negligible electrical resistivity).^{46,57} In addition, graphene can be readily surface-functionalizable and dispersible in many polymers and solvents with high loading in nanocomposites. This is not only useful to enhance the mechanical properties of the composites but also to use its high conductivity and charge carrier mobility as electrode materials in batteries, supercapacitors and bipolar plates in fuel cells.

Graphene also has outstanding resistance to gas permeation and a large surface area ($2630\text{ m}^2\text{ g}^{-1}$).⁵⁸ Such a high surface area is an essential criteria for porous electrodes in batteries and supercapacitors, catalyst supports for fuel cells and for hydrogen storage. Graphene also has a highest thermal conductivity of $\sim 5300\text{ W m}^{-1}\text{ K}^{-1}$ (ref. 59) and is an ideal material to facilitate heat dissipation for highly efficient power management systems.

Regarding the optical properties of graphene, it nearly has total transparency. Graphene can absorb a 2.3% fraction of light with a very wide spectral width (optical transparency of 97.7%).^{47,60} Moreover, the absorption range can be modified in double-layer graphene by tuning the electrical gating.^{60,61} Therefore, by means of an external gate field, the Fermi energy levels of graphene can be changed resulting in modified absorption properties. Photodetectors and plasmonic devices are application examples that are based on these electrical and optical properties.^{62,63}

The correlation between the properties of graphene and its use in different energy devices are summarized in Fig. 2. Energy solutions can not only be enhanced by the existing

physicochemical properties (optical, electrical and mechanical *etc.*) of graphene, but also from its special nano-properties. For example, energy can be harvested from water flow through a graphene layer and voltage can be generated by mechanical strain. These details will be discussed in the latter part of this review.

2.2 Electrochemical properties of pure graphene (monolayer graphene)

In spite of many reports on graphene applications in numerous devices,²⁻⁴ very few results were shown on the electrochemical property of monolayer graphene,^{64,65} which is essentially important in understanding the function of graphene in different devices. Quantitative interface-specific thermodynamic information on how aqueous phase species interact with monolayer graphene was studied within the electrical double layer over the single-atom thick layer of graphene.⁶⁶ The kinetics of interfacial electron transfer at single layer graphene electrodes in solutions show that mechanical imperfections and chemical modifications/impurities of graphene give rise to enhanced electrochemical activity or cause large kinetic effects at the monolayer graphene.⁶⁷⁻⁷⁰ This may explain why some suggested that if there are no defects introduced in the graphene sheet, the basal plane of graphene is almost electrochemical inert,⁷¹ and on the other hand, some observed monolayer graphene to have anomalously large reactivity compared to bi- or multilayer graphenes.⁷² Electrochemical studies of monolayer graphene sheets from both mechanically exfoliated graphene and chemical vapour deposition (CVD) graphene were carried out and it was found that the electron transfer rates of graphene electrodes are more than 10 fold faster than the basal plane of bulk graphite, likely due to the presence of corrugations in the graphene sheets.^{73,74} All these studies involve the transfer of the grown CVD graphene to other substrates such as silicone, and these may introduce contaminants and corrugations that can dramatically affect electrochemical processes.⁷⁵ Elegant work by Compton and co-workers has allowed the electrochemical characteristics of highly ordered pyrolytic graphite (HOPG) to be fully understood and confirms that edge-plane sides/defects are the predominant origin of electrochemical activity.⁷⁶ Defects in graphene are supposed to enhance electrochemical⁷⁷ and hydrogen storage⁷⁸ ability of graphene sheets.

3. Graphene synthesis and its relationship to properties

The different methods used to produce graphenes influence them with different properties. Firstly, graphene can be prepared by a scotch tape method, *i.e.* micromechanical exfoliation of HOPG.^{32,79,80} These processes can obtain pristine graphene flakes for basic scientific research. However, they are not suitable for volume production and the flake size is limited to the micrometer range. Many efforts have been made to produce graphene in bulk including epitaxial growth on silicon carbide.⁸¹⁻⁸⁴ Although high quality graphene film can be grown

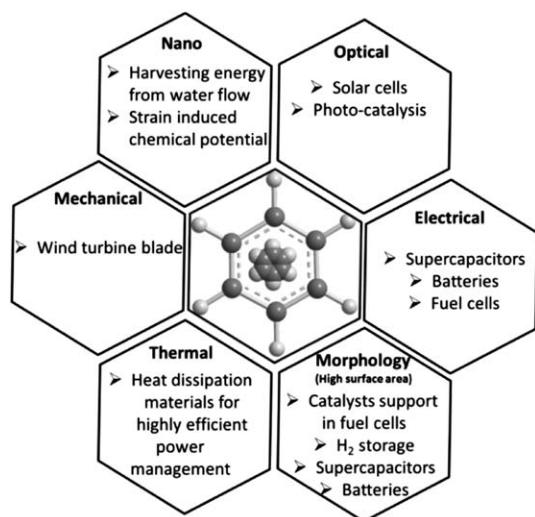


Fig. 2 Relationship between graphene properties and their applications in energy solutions.

on silicon carbide, it requires costly substrate materials and ultrahigh vacuum conditions, which significantly limit its usage. Other synthesis methods include solvothermal synthesis (a pyrolysis of an alcohol, usually nano-dispersed ethanol, and an alkali metal (Na) that gives fused monoatomic sheets of graphene);^{69,85} the unzipping of carbon nanotubes; electron beam irradiation of poly(methyl methacrylate) (PMMA) nanofibres, arc discharge of graphite, thermal annealing of GO and organic synthesis *etc.*⁸⁶ Fig. 3 summarizes some of these synthesis schemes, among which the solution based methods (chemical reduction of GO, electrochemical exfoliation and liquid phase exfoliation) and CVD methods are currently the only ones that can be used for scaled-up graphene production.

In a mass production and cost-effective manner, graphene can be prepared *via* chemical reduction from GO,^{10,88–91} electrochemical exfoliation⁹² or liquid phase exfoliation starting from graphite.^{93–97} Chemical modifications of graphene would help tackle the problems regarding its production, storage, handling and processing as the modified graphene composites can have synergistic properties resulting from both the graphene and the modifiers.⁹⁸ Stability, solubility, electrical, thermal, mechanical and magnetic properties of graphene-related materials could be tuned by chemical functionalization.⁵ A detailed discussion on the relationship of graphene synthesis to its properties was reviewed by Edwards and Coleman.⁹⁹ However, the defects created during reactions in solution-based methods increase the sheet resistance and it is also relatively challenging to make a monolayer graphene device from these methods. Defects in graphene planes and residual oxygen groups from GO result in tens of thousands ohms per square of sheet resistance with a transparency of 60–80% at 550 nm, which fails to meet the requirements for high-quality transparent conductors.¹⁰⁰

CVD is perhaps one of the most popular techniques to grow high quality graphene on metal substrates.^{101,102} It has been shown to produce monolayer graphene sheets of the order of

30 inches.^{103,104} Because the electrical properties of graphene are closely related to its thickness, controlling the thickness is as important as controlling the width. For example, bilayer graphene has a tuneable band gap, while monolayer graphene does not.¹⁰⁵ It is possible to use CVD synthesized monolayer graphene as building block to produce the required thickness through layer-by-layer transfer and stacking. Properties of graphene from CVD methods and solution-based methods (chemical reduction of GO, liquid phase exfoliation and electrochemical exfoliation) are compared in Table 1.

Table 1 depicts the state of the art performance values of graphene inks from the three different solution-based synthesis methods. Clearly, graphene inks have to improve their performance significantly in order to aspire to replace indium tin oxide (ITO) at the highest end of the spectrum ($10\text{--}30\ \Omega\ \text{sq}^{-1}$ at over 85%). CVD graphene has by far the best performance in terms of transparency with the lowest sheet resistance, and is as good as, if not even better than, the widely used ITO in industries. CVD methods can produce high quality graphene with decent sheet sizes, and it can also make controlled, perfect monolayer graphene to replace ITO as a conductive transparent material. Currently industries will likely be more interested in growing huge areas of graphene using CVD-type processes¹¹³ even though its cost is high and it often involves complicated processes to transfer the substrate. Due to higher sheet resistance, current solution-cast graphene films may be suitable for some cost-effective applications such as electrostatic dissipation, electromagnetic interference shielding *etc.* which do not require excellent values of transmittance and sheet resistance. However, the chemical reduction of GO and liquid phase exfoliation offer the optimum mix of throughput, cost, electronic quality and versatility in terms of chemical functionalization for potential applications in printable electronics.¹¹⁴

4. Graphene for energy devices

4.1 Graphene for solar cells

Widespread concern about energy sources has created a surge in efforts to explore solar cells. Graphene has an optical transmission rate of over 98% in the visible bandwidth region, an improvement on its closest competitor, ITO,^{104,115,116} that make it a highly viable option in optoelectronic devices.^{62,117,118}

Optical transparent conductors (OTCs) in the industry currently are mainly ITO and fluorine-doped tin oxide (FTO). For ITO and FTO, the transmittance decreases in the IR ($>1200\ \text{nm}$) regions (Fig. 4A). Fig. 4B compares the constant resistivities of different OTCs, and graphene has the smallest constant resistivity among all OTC materials. It exhibits the astounding properties of a two-dimensional electron gas at room temperature *i.e.* very high electron mobility combined with high transmittance. Bae *et al.* demonstrated a sheet resistance of $\approx 30\ \Omega\ \square^{-1}$ for graphene layers grown by CVD and layer-transferred to a polymer foil, which provided a transmittance of $T \approx 90\%$.¹⁰⁴ This gives graphene the potential for use in photovoltaic cells.⁶²

One of the simplest photovoltaic cells is from Schottky junctions. The Schottky junction, formed by contacting a metal

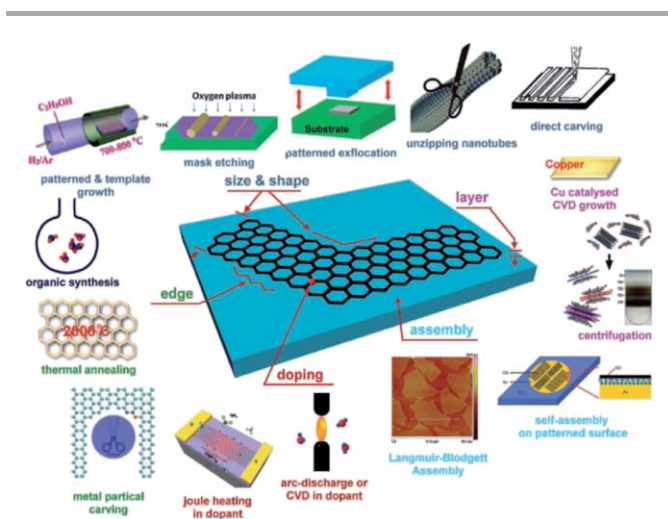


Fig. 3 Synthesis methods for graphene with controlled sizes, shapes, edges, layers, doping and assembly. (Reproduced from ref. 87 with copyright permission.)

Table 1 Comparison of the performance of CVD graphene with graphene inks from solution-based methods

Synthesis method	Sheet resistance (ohm sq ⁻¹)	Transparency (%)	References
Chemical reduction of GO	1000–70 000, 31 000–19 M	80–95%	106 and 107
Liquid-phase exfoliation	520–3110, 5000–8000	63–90%	106 and 108
Electrochemical exfoliation of graphite	210–43 000 (210 after thermal annealing at 450 C)	96%	106 and 109
CVD graphene and micromechanical cleavage graphene	8.8–600	84–97.7%	110–112

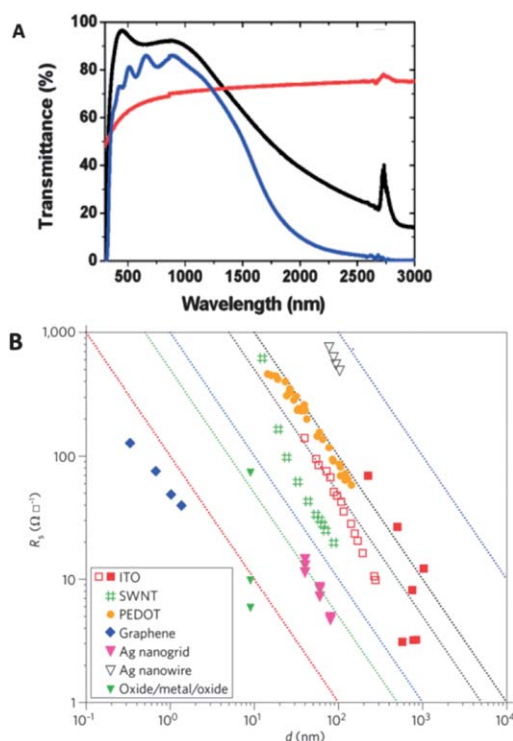


Fig. 4 (A) Transmittance of a ca. 10 nm thick graphene film (red), in comparison with that of ITO (black) and FTO (blue). (B) Sheet resistance R_s as a function of film thickness d for different transparent conducting films: Ag, Al and Cu metal grids; PEDOT-PSS; ITO films; SWNTs; Ag nanogrid; oxide-Ag-oxide films; and graphene. The dotted lines correspond to constant resistivities ρ of 1×10^{-5} , 5×10^{-5} , 1×10^{-4} , 5×10^{-4} , 1×10^{-3} and $1 \times 10^{-2} \Omega \text{ cm}$ (from left to right). (Reproduced from ref. 119 and 120 with copyright permission.)

with a moderate doped semiconductor, is a promising structure for solar-to-electric energy conversion. Compared to the p-n junction, the Schottky junction has the merits of material universality, low cost, and easy fabrication. However, in a conventional Schottky junction solar cell, the metal layer, which should be thick enough to form a continuous film, will absorb most of the solar radiation and hence limit the energy conversion efficiency. In order to overcome this drawback, researchers have used ITO films to replace the metal film in the Schottky junction solar cell. However, the limited resources of indium will lead to high production costs. Besides, the diffusion of indium ions will cause a degradation of the device performance and the brittle nature of ITO will limit its application for flexible devices. Graphene sheds new light on the *Schottky junction solar cell*, owing to its fascinating

physical properties, such as a near-zero band-gap, high electrical conductivity, ultrahigh mobility, high elasticity and transparency.¹²¹

Dye-sensitized solar cells (DSSCs) could potentially replace traditional silicon solar cells in the future since they have high photon-to-electron efficiencies and low costs.¹²² Generally, a DSSC has a film of dye-sensitized TiO₂, a conductive transparent electrode, a counter electrode and an electrolyte. The dyes are photoexcited and produce an injection of an electron to the semiconductor film.¹² The conversion rate achieved so far with TiO₂ electrodes with ruthenium-based dyes is approximately 12%. This low rate is caused by the trapping of electrons and random pathways. The high specific area and electron mobility of graphene allows for longer lifetimes and better conversion rates. Kim *et al.*¹²² embedded graphene on the top layers of an inverse opal TiO₂ structure. C-Ti bonds enhance electron transport, and therefore, electron injection and collection efficiencies. Besides, graphene improved the visible light absorption and, as a consequence, reduced the energy absorption by the dyes. The incorporation of graphene sheets improved the electron lifetime by increasing the chemical capacitance and decreasing the resistance. At the moment, a 55% enhancement in conversion rate for a DSSC with graphene was obtained over a DSSC with pure TiO₂.¹²² In addition, the work function of graphene is 4.42–4.5 eV,¹² much lower than the TiO₂, making the electron transport easier. Tang *et al.* has reported on the use of graphene/TiO₂ on top of ITO as a photoanode for a DSSC. The increase in electron transport manifested itself in an increase of the short-circuit current density. They achieved a power conversion five times higher than pure TiO₂ and a conductivity with two orders of magnitude improvement.¹²³ Surface wettability, work function alignment and carrier transport are the greatest challenges in using pure graphene in both organic photovoltaics and DSSCs. Thus the majority of the work on such applications is focused on using more solvent-processable GO^{58,124–126} instead of pure graphene. The pre-reduction of GO has been required to fabricate TiO₂-graphene based DSSCs.¹²⁷ A simple approach without pre-reduction of GO was demonstrated to be effective as well.¹²⁶ Incorporation of graphene into a TiO₂-based DSSC increases the short current density and power conversion efficiency by 52.4% and 55.3% respectively. However, there is an optimal concentration of GO, beyond which the efficiency will decrease due to the light absorbance of GO.¹²⁶ Monolayer graphene has been modified by an Al-TiO₂ composite as an efficient transparent cathode for *organic photovoltaics*. This gives rise to enhanced power conversion efficiency of 2.58%, which is a 2-fold improvement on the best

efficiency reported for graphene cathode organic photovoltaics, reaching ~75% of the performance of the control devices using indium tin oxide.¹²⁸ The excellent conductivity of graphene, mobility of electrons, transparency, wide band tunability and flexibility provided by graphene may improve the state-of-the-art devices.¹² Continuous, transparent and highly flexible CVD graphene was made and used in organic photovoltaics.¹²⁹ CVD graphene offers a comparable performance to the ITO substrate but an outstanding capability to operate under bending conditions up to 138°, whereas ITO cracks under bending of 60°. Both Wang *et al.* and Park *et al.* also showed the feasibility of using graphene/doped graphene as substitutes for ITO in organic photovoltaics.^{130,131} Organic photovoltaics based on solution-processable GO and P3HT were also made.¹²⁵ The GO was functionalized by organic isocyanate to change its hydrophilic nature to a hydrophobic one to tailor the organic solvents used. Similar to DSSCs, the device efficiency increases first and then decreases with further increases in the GO content.

Quantum dots solar cells (QDSCs) have the same structure as DSSCs but with inorganic quantum dots (QDs), for example, CdS, CdSe, PbS, and ZnS, instead of organic dyes. The advantages of QDs in comparison to organic dyes are the high extinction coefficients, tunable band gaps, large intrinsic dipole moments and good stability.¹² Therefore, the enhancements made with graphene/TiO₂ have the same characteristics as in DSSCs and the main point would be to improve the electron transport between those QDs and graphene/TiO₂. Graphene-QDs material for energy-related applications were heavily studied¹³² due to its large surface area, high carrier transport mobility, superior mechanical flexibility and excellent thermal/chemical stability. 0D QDs are interesting materials and the development of new types of QDs will allow the control of the fundamental properties of materials through size/shape effects, which will further allow new devices to be developed with distinctive properties and functions for numerous optoelectronic applications. Graphene-CdSe hybrids composed of CdSe quantum dot arrays directly grown on CVD graphene have ultrafast carrier dynamics.¹³³ The original fabrication and performance of a photocurrent device was reported using directly grown CdSe QDs on a graphene basal plane. The junction between the QDs and graphene and the high quality of the graphene grown by CVD enables highly efficient electron transfer from the QDs to the graphene. Therefore, the hybrids show large photocurrent effects with a fast response time. A lot of QDSCs were also made from reduced GO functionalized with CdSe *etc.*¹²⁴ Cu₂S-GO composites exhibit significant improvement in the fill factors of quantum dot solar cells and benchmark efficiencies in range of 4.4–5.4% were achieved.^{134,135}

4.2 Graphene for supercapacitors

There are two types of supercapacitors: electrochemical double layer capacitors (EDLCs) and pseudo-capacitors based on the charge storage mechanism. In EDLCs, a purely electrostatic attraction occurs between the ions accumulated at the electrode-electrolyte interface, and the resulting double layer is the

origin of the capacitance. This is the mechanism relevant for carbon-based electrodes. The second type of supercapacitor is a pseudo-capacitor that uses fast and reversible surface, or near-surface reactions for charge storage. Reported specific capacities for graphene in EDLCs range from 62.6 F g⁻¹ to 215 F g⁻¹.^{136–139} Galvanostatic charge-discharge analysis was performed on both graphene and graphite-modified electrodes (under identical conditions) where the specific capacities of 62.6 F g⁻¹ and 5.4 F g⁻¹ were obtained respectively at a discharge current of 67 nA.¹³⁶ It appears that although graphite has a larger portion of edge plane sites than that of graphene, it is a 'bulk' material where tightly stacked layering leads to the reduced accessibility of available surface area.¹³⁶ The larger capacitance of graphene can be attributed to a combination of capacitance due to available edge plane sites and surface area, where enhanced layer spacing results in the superior accessibility of these available components in flexible graphene sheets as opposed to bulk graphite, consequently leading to the higher capacitance values observed.¹³⁶ It is known that surfactants and additives to graphene will add Faradaic reactions that bring a pseudo-capacitor response. Graphene-based hybrid materials involving various metals, oxides and polymers were used to further improve the energy and power density of the supercapacitors.^{140–145} Among them, a graphene-polyaniline composite synthesized by *in situ* polymerization obtained the highest specific capacitance of 1046 F g⁻¹.¹⁴⁰ Supercapacitors were also made from the reduced GO. Porous carbon with a surface area of up to 3100 m² g⁻¹ was made by the chemical activation of exfoliated GO.¹⁴⁶ Such carbon electrodes yield high values of gravimetric capacitance and energy density with organic and ionic liquid electrolytes. GO can also be reduced using lasers and a scalable fabrication of graphene micro-supercapacitors over large areas by direct laser writing on GO was achieved.^{147,148} These micro-supercapacitors demonstrate a power density of ~200 W cm⁻³, which is among the highest values for any supercapacitor.

The advantage of using graphene in EDLCs is not only to increase the specific capacity. EDLCs are essentially DC devices, *i.e.* they take several seconds to fully charge and then several seconds to fully discharge again. They operate efficiently at frequencies below about 0.05 Hz and are therefore good for applications like hybrid vehicles, which can take up to a few seconds to charge (when braking) and a few seconds to discharge (when accelerating). However, at higher frequencies, they become much less efficient and start to behave like resistors rather than capacitors due to the porous carbon used in EDLC electrodes. An EDLC that contains vertically oriented high-surface-area graphene electrodes that aren't porous at all can overcome this problem. EDLCs made from graphene push the operating frequency of an EDLC to well beyond 5000 Hz, which is a factor of 105 better than commercial EDLCs. What's more, graphene supercapacitors can be six times smaller than low-voltage aluminium electrolytic capacitors and can be charged and discharged at high efficiency in times much shorter than 1 ms.

Fig. 5 shows the high-frequency AC "supercapacitors" containing graphene electrodes. The thickness of the supercapacitor is as thin as a human hair. EDLCs from graphenes can

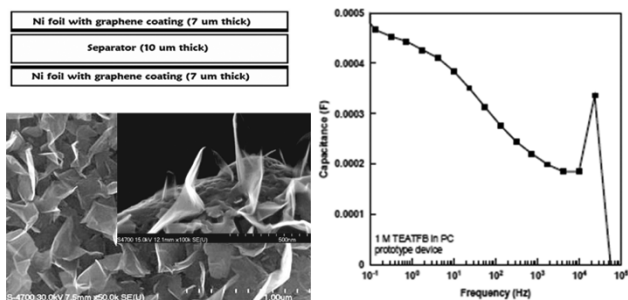


Fig. 5 SEM micrograph of a coated Ni electrode (left), and capacitance versus frequency for the graphene electrode prototype evaluated using an organic electrolyte comprised of 1 M TEATFB salt in PC solvent (right). (Reproduced from ref. 149 with copyright permission.)

minimize electronic and ionic resistance and produce capacitors with an RC time constant of less than 200 ms, in contrast with ~ 1 s for typical EDLCs.¹⁴⁹

4.3 Graphene for batteries

There is a dilemma between energy density and power density in current energy storage devices as the Ragone plot shows in Fig. 6. Supercapacitors that usually have high power density can release the energy in a very short time but their capacity for energy storage (energy density) is low. On the other hand, batteries can store more energy but they can not release energy quickly due to their relatively lower power density. One of the most challenges for current batteries is the low power density. With the advances of electrical vehicles and modern smart devices, electrochemical energy storage devices that have both high power density and high energy density are needed. Graphene is one of the few materials that can enable these combined battery–supercapacitor properties.²³

Ref. 23 reported an approach based on the exchange of lithium ions between the surfaces (not the bulk) of two nanostructured electrodes, completely obviating the need for lithium intercalation or deintercalation as Fig. 7 shows. In both electrodes, massive graphene surfaces in direct contact with the liquid electrolyte are capable of rapidly and reversibly capturing lithium ions through surface adsorption and/or surface redox reactions. An energy density of 160 W h per kg cell was obtained that is 30 times higher than that (5 W h per kg cell) of

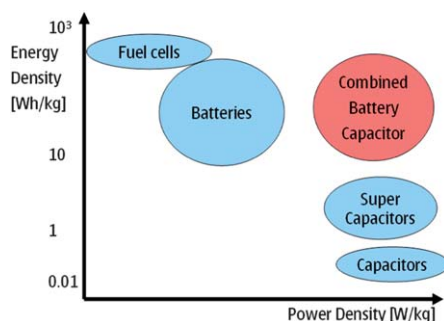


Fig. 6 Ragone plot for energy storage devices.

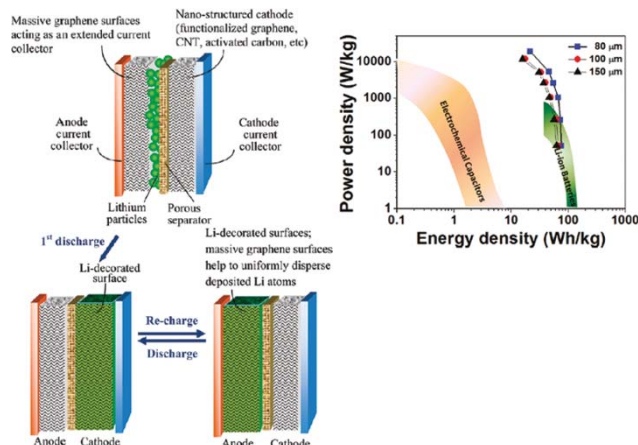


Fig. 7 The structure of a fully surface enabled, Li ion-exchanging cell when it is made, containing an anode current collector and a nanostructured material at the anode, a Li ion source (e.g., pieces of Li foil or surface-stabilized Li powder), a porous separator, liquid electrolyte, and a nanostructured functional material at the cathode. The lower left portion shows the structure of this cell after its first discharge (Li is ionized with the Li ions diffusing through the liquid electrolyte to reach surface-borne functional groups in the nanostructured cathode and rapidly reacting with these groups). Lower right portion shows the structure of this cell after being recharged (Li ions are rapidly released from the massive cathode surface, diffusing through liquid electrolyte to reach the anode side, where the huge surface areas can serve as a supporting substrate onto which massive amounts of Li ions can electrodeposit concurrently. The Ragone plot of graphene surface-enabled Li ion-exchanging cells with different electrode thicknesses is shown left. (Reproduced from ref. 23 with copyright permission.)

conventional symmetric supercapacitors and comparable to that of Li-ion batteries. They are also capable of delivering a power density of 100 kW per kg cell, which is 10 times higher than that (10 kW per kg cell) of supercapacitors and 100 times higher than that (1 kW per kg cell) of Li-ion batteries.

An ultrathin battery made from pristine monolayer graphene was reported.¹⁵⁰ It was shown that a battery made of only one atom layer of carbon can even light up an LED. Currently the anode material employed for lithium-based batteries is usually graphite because of its high coulombic efficiency which means it can be reversibly charged and discharged under intercalation potentials with a reasonable specific capacity.¹⁵¹ To improve battery performances, the relatively low theoretical capacity associated with graphite batteries (372 mA h g^{-1}) and the long diffusion distances of the Li-ions, need to be overcome.^{151,152} Enhanced interlayer spacing, increased availability of the surface area and fewer layers of graphene samples that are disordered/porous in nature exhibit superior characteristics for applications in battery electrodes.^{153,154} Lian *et al.*¹⁵⁵ report the first reversible specific capacity of a graphene electrode to be as high as 1264 mA h g^{-1} at a current density of 100 mA g^{-1} . After 40 cycles, the reversible capacity was retained at 848 mA h g^{-1} at a current density of 100 mA g^{-1} ; note that this is higher than general values reported at both CNT and graphite electrodes.¹⁵⁵ This favorable performance is most likely due to the increased flexibility and degree of accessible surface area at the graphene structure.¹⁵⁵ Additionally the graphene nanostructures utilized in the above study were thought to have significant disorder and

defects, which, as verified by comparable reports, is beneficial for Li-ion storage where highly disordered graphene nanosheets exhibit high reversible capacities (794–1054 mA h g⁻¹) and good cycling stability.¹⁵⁶ Doped graphene sheets as anode materials also demonstrated super-high rates and large capacities for lithium ion batteries.¹⁵⁷ The doped graphene shows a high reversible capacity of >1040 mA h g⁻¹ at a low rate of 50 mA g⁻¹. A very high capacity of *ca.* 199 and 235 mA h g⁻¹ was obtained for the N-doped graphene and B-doped graphene at 25 A g⁻¹ (about 30 s to full charge).¹⁵¹ The unique 2D structure, disordered surface morphology, hetero-atomic defects, better electrode/electrolyte wettability, increased sheet distance, improved electrical conductivity and thermal stability of the doped graphene are beneficial to rapid surface lithium ion absorption and ultrafast lithium ion diffusion and electron transport. In terms of modifying the graphene as to improve its performance, work by Bhardwaj *et al.*¹⁵⁸ confirmed that oxidized graphene nano-ribbons (ox-GNRs) outperformed CNTs and pristine graphene, presenting a first charge capacity of about 1400 mA h g⁻¹ and a reversible capacity of about 800 mA h g⁻¹. In this case it is likely that both the large edge plane surface area possessed by the ox-GNRs, favourable interlayer spacing (porosity, disorder) and the oxygenated species contributed beneficially towards the enhanced performance of the device in terms of favourable Li-ion intercalation. It is no surprise therefore that the majority of research is focused on achieving greater disorder of the graphene utilised or on enhancing other contributing factors, which can be achieved *via* a variety of methods including electron-beam irradiation¹⁵⁶ and, of course, the fabrication of hybrid graphene composite materials.

A lot of efforts have also been focused on using graphene-nanoparticle composites^{159–165} or graphene-polymer composites^{166,167} to enhance the energy density of the batteries. Ordered metal oxide-graphene composites can be made by self-assembly methods using graphene as building block. A graphene-Fe₃O₄ composite was shown to exhibit a reversible specific capacity of 1026 mA h g⁻¹ after 30 cycles at 35 mA g⁻¹ and 580 mA h g⁻¹ after 100 cycles at 700 mA g⁻¹.¹⁵⁹ NiO nanosheets can also be bonded strongly to graphene through oxygen bridges that mainly originate from the pinning of hydroxyl/epoxy groups from graphene onto the Ni atoms. At a current density of 50 mA g⁻¹, the graphene-NiO composite exhibits a discharge capacity of 1478 mA h g⁻¹.¹⁶² When the discharge and charge current density increase to as high as 2.5 A g⁻¹, the specific capacity of the graphene-NiO composite remains at 550 mA h g⁻¹. SnO₂ is a good high-capacity electrode for lithium ion batteries, but usually shows rapid capacity fading during discharge-charge cycles because of a phase transformation and a large volume expansion upon lithiation.¹⁶⁸ Graphene sheets prevent the aggregation of nanoparticles during the Li ion charge-discharge process and SnO₂-graphene nano-composites form a stable 3D architecture.¹⁶⁹ A steady specific capacity of 625 mA h g⁻¹ from graphene-SnO₂ was obtained at current density of 10 mA g⁻¹.¹⁶⁴ Other graphene-nanoparticle composites such as a TiO₂-graphene composite were synthesized scalably and exhibited high rate performances for lithium ion batteries.¹⁶⁰ A graphene-TiO₂ composite is able to deliver a

capacity of 230 mA h g⁻¹ at 17 mA g⁻¹.¹⁶⁰ The specific capacity of the graphene-TiO₂ composite at a high discharge rate can remain at 97 mA h g⁻¹, 6 times higher than that of the reference TiO₂.¹⁶³ Studies have shown that inorganic-graphene intercalated nanosheets are an effective solution to optimize the transport property of graphene using ultrathin lithium vanadate-graphene hybrid nanosheets.¹⁷⁰ Thus graphene-inorganic composites may have synergistic effects between graphene and inorganic nano-materials to improve the energy capacity of batteries. A percolated graphene network can increase electrode conductivity and the dimensional confinement of active material particles by the surrounding graphene sheets limiting the volume expansion upon lithium insertion. Graphene foam, a three dimensional, flexible and conductive interconnected network can be used as current collectors loaded with Li₄Ti₅O₁₂ as the anode and LiFePO₄ as the cathode.¹⁷¹ No metal current collectors, conducting adhesives or binders are need in such a structure. Such batteries with ultrafast charge and discharge rates exhibits about 100 mA h g⁻¹ at 200 C, equivalent to a full discharge in 18 s, and it also retains over 95% energy capacity when repeatedly bent to a radius of 5 mm without structural failure.¹⁷¹ Conducting polymers can contribute by enhancing both the mechanical flexibility and electric conductivity of the graphene batteries. Hierarchically nanostructured graphene-MnO₂-poly(3,4-ethylenedioxythiophene (PEDOT) was used in batteries. The battery exhibits a large discharge capacity of 1835 mA h g⁻¹ at the first cycle with rate of 50 mA g⁻¹. The discharge capacity drops to 1105 mA h g⁻¹ on the second cycle but remains at 948 mA h g⁻¹ after 15 cycles.¹⁶⁵ As for the pure graphene-conducting polymer composites, the graphene-polypyrrole composite delivers a discharge capacity of 1013 mA h g⁻¹ in the first cycle and a reversible capacity of 493 mA h g⁻¹ in the second cycle at rate of 100 mA h g⁻¹.¹⁶⁷ A good review on graphene-conducting polymer composites can be found in ref. 166. Flexible graphene paper electrodes made from reduced GO show enhanced rate capabilities for energy storage¹⁷² and batteries made from such graphene inks can be printable.^{173,174} A highest energy capacity for such batteries of 819 mA h g⁻¹ was obtained at rate of 25 mA g⁻¹, and it remained 178 mA h g⁻¹ at 1 A g⁻¹.¹⁷² In summary, batteries based on graphene and its derivatives can provide both high energy density and high power density. *i.e.* when using graphene, a hybrid battery and supercapacitor device with robust mechanical flexibility becomes feasible.

4.4 Fuel cells

The performance of a fuel cell is strongly dependent on its catalytic efficiency. For example, proton exchange membrane (PEM) fuel cells will convert chemical energy to electrical energy and an appropriate catalyst is required to initiate and promote the electrochemical reaction. Platinum (Pt) is the most efficient catalyst used for fuel cells. However, the high price and the poor utilization efficiency of Pt catalyst loading per unit area limits its practical applications. Graphene can be used in fuel cells as in the following applications.

Firstly, graphene can act as a catalytic support (bipolar plate) for enhanced electro-catalytic activity. The requirements of catalyst support materials are (1) high specific area for dispersion of the catalyst, (2) high electrochemical stability under the operating conditions, (3) chemical stability at the relevant temperature and (4) high electrical conductivity.¹⁴ Graphene is an ideal candidate for this application due to its high electrical and thermo-conductivity and high surface area. The bipolar plate is one of the most costly components in a PEM fuel cell (typically amounting to 33% of the stack cost) and typically accounts for more than 80% of the weight and 95% of the volume of the stack, determining the gravimetric and volumetric power density of a fuel cell stack. A high surface area and light weight make graphene an ideal catalyst support and its use results in a significant improvement in electro-catalytic activity, long term durability, and CO tolerance.¹⁷⁵ Graphene as a supporting material for metal catalysts provides anchoring sites to obtain a uniform distribution of nano-sized metal particles, which results in high catalytic activity. Nitrogen-doped graphene,¹⁷⁶ microwave-heating of graphene in a NH_3 atmosphere,¹⁷⁷ the chemical reduction of graphene¹⁷⁸ and functionalized graphene sheets^{179–181} all can be used as such catalyst supports.

Secondly, graphene can be used effectively to reduce the Pt loading and so reduce the cost. In other words, graphene acts as catalyst for an enhanced oxygen reduction reaction. Replacing precious and nondurable Pt catalysts with cheap and commercially available materials to facilitate cathodic oxygen reduction reactions is a key issue in the development of fuel cell technology. 2D graphene materials from both N-doped CVD graphene¹⁸² and S-doped graphene from the annealing of GO¹⁸³ can be used in this application as metal-free catalysts. There is a good review article on nanostructured metal free electrochemical catalysts based on graphene.¹⁸⁴ Last but not least, graphene can be used as a filler in polymer electrolyte membranes for enhanced charge transport properties due to its high mechanical strength and electrical conductivity.

4.5 Graphene for novel energy generating devices

The nano-properties of high-surface area and conjugation in 2D can make graphene useful in many novel energy generating devices.

It was reported that energy can be harvested from water flow over few-layered graphene.³¹ The surface ions can efficiently glide or drift on the surface of flat sheets of graphene leading to the induced voltage and current. This has aroused much interest in the study of electrochemistry at graphene interfaces. Fig. 8 shows that water flowing over multi-walled carbon nanotubes (MWNTs) can produce only a small electric current in the direction of the flow. Adding HCl to water and streaming it over flat sheets of graphene can generate 85 nW of power using a few hundred micrometers of graphene film. It is suggested that the voltage is generated by chloride ions that hop along the surface of the graphene interacting with and dragging the material's electrons along. The graphene sheets boosted power generation because of their high electron mobility and

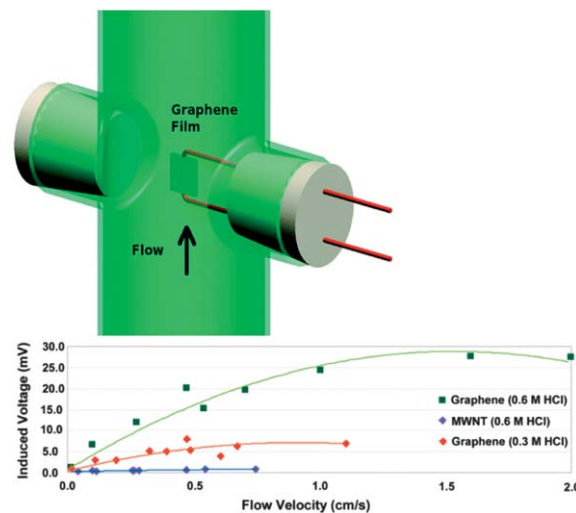


Fig. 8 Harvesting energy from water flowing over graphene³¹ which induced voltage as a function of fluid flow velocity over the graphene film (exposed to ~ 0.6 and ~ 0.3 M HCl solutions) and a multi-walled carbon nanotube (MWNT) film exposed to a ~ 0.6 M HCl solution. (Reproduced from ref. 31 with copyright permission.)

continuous surface for efficient ion gliding.³¹ It has also been noticed that chemically induced charge carriers were generated in single-layer graphene exposed to different concentrations of gas molecules such as NO_2 , NH_3 and CO *etc.* The adsorbed molecules change the local carrier concentration in graphene one by one electron, which leads to step-like changes in resistance.¹⁸⁵

The electrochemical properties of the graphene-PDMS (polydimethylsiloxane) substrate and pure PDMS under uniaxial strain are very different. A strain-induced chemical potential difference between monolayer graphene sheets was reported.¹⁸⁶ Monolayer graphene sheets were deposited on a transparent and flexible polydimethylsiloxane (PDMS) substrate, and a tensile strain was loaded by stretching the substrate in one direction. It was found that an electric

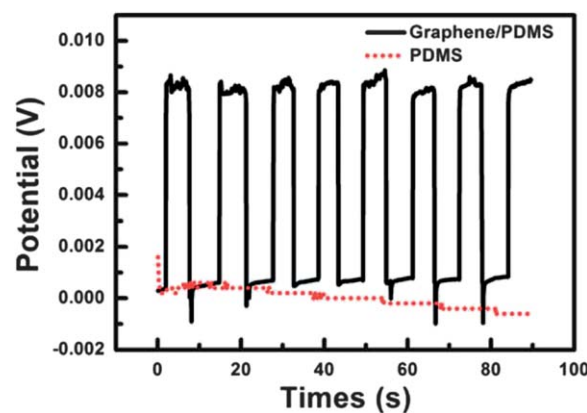


Fig. 9 The electrochemical properties of the graphene-PDMS substrate and pure PDMS under uniaxial strain. (Reproduced from ref. 186 with copyright permission.)

potential difference between stretched and static monolayer graphene sheets reached 8 mV when the strain was 5% as Fig. 9 shows. Theoretical calculations for the band structure and total energy revealed an alternative way to experimentally tune the band gap of monolayer graphene, and induce such a generation of electricity.

Graphene, as a transparent conducting material, can also be embedded in fully rollable transparent nano-generators based on transparent piezoelectric ZnO materials.¹⁸⁷ An energy scavenging nano-generator using a piezoelectric ZnO nanowire was developed in 2006.^{188,189} CVD-grown large scale graphene sheets could be used as transparent electrodes to realize fully rollable transparent piezoelectric energy harvesting nano-devices (nano-generators), which consist of a heterogeneous 3D nanostructure composed of 1D ZnO nanorods on a 2D graphene electrode. By applying a pushing force of 1 kgf to the top of the nano-generator in the vertical direction, a current density of $2 \mu\text{A cm}^{-2}$ was generated by such a graphene based nano-generator.¹⁸⁷

5. Technology transfer and industrialization

Nature has provided us with large amounts of high-quality graphene sheets, stacked inside the graphite mineral. Differently from carbon nanotubes, graphene can be produced on a ton scale without any high temperature processes, and without the need for metal catalysts; at the same time, differently from organic materials, it can be produced at high temperatures, in a clean vacuum, with no exposure to the solvents needed for organic synthesis. Graphene research is where science meets business.

5.1 Industry metrology

Since graphene made from different methods will have different properties, quality control is vital in all scalable material productions. Wafer scale transferable silicon and silicon carbide nanowire arrays with improved electrical contact have been successfully grown directly on graphene and transferred onto arbitrary substrates for their applications as robust supercapacitor electrodes.¹⁹⁰ With recent advances in synthesizing large area graphene sheets, engineers have begun investigating variable methodologies for conducting graphene metrology and quality control at industrial scales, to understand a variety of reliability issues including defects, patternability, electrical and physical properties.¹⁹¹ Standardization and metrology will be fundamental to benchmark different results published on this topic, allowing a clear and objective distinction between various graphene materials from different synthesis methods and the quality of materials produced in different labs. This is particularly essential in evaluating graphenes made from CVD methods.

The following tables (Tables 2 and 3)¹⁹¹ summarize the different characterization techniques for graphene and their industrial metrology capabilities.

Ref. 191 covered currently available graphene metrology techniques. It should be noticed that Raman spectroscopy

generally has very low environment sensitivity but in the case of graphene Raman measurements can be sensitive to temperature or the substrate. To increase the use of graphene in industry, high-throughput metrology techniques still need to be developed. Metrology techniques based on fluorescence quenching allow the quick and easy identification of graphene layers on arbitrary substrates and are well-suited for many industrial applications.¹⁹¹ Unfortunately, it was found that they can not meet all of the criteria for industrial applications. Some industrial applications may require information about the graphene sheets other than the layer thickness and uniformity. Therefore, the incorporation of graphene in industry could be improved by the development of additional high-throughput metrology techniques. The development of new industrial metrology techniques may involve a combination of creating new optical methods for probing the characteristics of graphene and employing advanced digital image processing techniques. It is well known that even monolayer graphene can be observed with a conventional optical microscope when deposited on a silicon substrate, due to a weak interference-like contrast.³² This method, which currently is the most practical way of identifying graphene sheets adsorbed on surfaces, works only on substrates having a suitable interference layer, like 300 nm thick SiO_2 and 67 nm thick Si_3N_4 , and thus cannot be utilized to visualize floating graphene sheets in solution. In 2009, Palermo *et al.*²⁴¹ described a new technique with which they were able to visualize single graphene sheets on substrates such as glass and quartz, exploiting the quenching of the light emitted by a fluorescent layer of molecules, achieving an optical contrast of up to 0.8. Such a technique²⁴¹⁻²⁴³ did not depend on light interference, and could also be used to visualize single sheets of solvated graphene, allowing people to follow its dynamics in solution in a fast and versatile way using a simple fluorescent microscope. The evaluation of large-scale quantification of CVD graphene surface coverage has also been enabled by electrochemical methods. Chemical vapor deposition (CVD) of graphene on Cu and Ni substrates is one of the most promising procedures to synthesize large-area and good quality graphene films. Parallel to the fabrication process, a large-scale quality monitoring technique is equally crucial. A rapid and simple methodology was developed to probe the effectiveness of the growth process over a large substrate area for both Ni and Cu substrates.²⁴⁴ This method is based on inherent electrochemical signals generated by the underlying metal catalysts when fractures or discontinuities of the graphene film are present. It can be applied immediately after the CVD growth process without the need for any graphene transfer step and represents a powerful quality-monitoring technique for the assessment of the large-scale fabrication of graphene by the CVD process. The good sensitivity of the electrochemical method may facilitate a rapid and large-scale quantification of graphene surface coverage after the CVD growth process on Ni and Cu catalysts. It was also demonstrated that the signal generated by the underlying Ni or Cu metal in an alkaline solution can be directly correlated to fractures, holes or discontinuities in the graphene films.²⁴⁴ This provides an opportunity to rapidly evaluate the efficiency of the CVD growth process right

Table 2 Industrial metrics measured by graphene characterization techniques (reproduced from ref. 191 with copyright permission)

	Layers	Edge structure	Defects	Fermi level	Thermal conductivity
TEM (transmission electron microscopy)	Cross-section of cut of fold ^{192–194}	Atomic edge structure imaged directly ¹⁹⁵	Variations in lattice structure imaged directly ^{196,197}		
SEM (scanning electron microscopy)		Identified in extended edges of high quality exfoliated flakes ⁵⁰			
LEEM (low energy electron microscopy)	Oscillations in the electron reflection spectrum ^{198–200}		Reciprocal lattice structure determined from diffraction pattern ^{198,201,202}		
AES (Auger electron spectroscopy)	Ratio of element peak intensities ^{203–205}		Relative peak height/positions ²⁰³		
AFM (atomic force microscopy)	Sharp height variations at edges ^{32,206–208}				
STM (scanning tunnelling microscopy)		Scanning bias voltage ²⁰⁹	Density of state measurements ^{193,210–213}	Scanning bias voltage ^{211,214}	
Raman spectroscopy	Relative peak height (G and 2D) and location (2D) ^{215–219}	D peak height using horizontal polarization ^{220,221}	D peak height ^{101,222–225}	G peak position ^{210,226–229}	Relationship between G peak position and dissipated power ^{59,230}
XPS (X-ray photoemission spectroscopy)			Relative peak height/positions ^{204,206,215,216,219,231}	Determined from dopant type and concentration ¹⁷	
Optical transmission Ellipsometry	2.3% attenuation per layer ^{94,104,115,232} Amplitude of polarization angle shift ^{233–235}				
Reflection microscopy	Colour contrast, depends on substrate ^{206,216,236–238}				
FQM (fluorescence quenching microscopy)	Intensity contrast, customized by dye layer thickness ^{239,240}				

after the cooling step without the need for any mechanical transfer of graphene. Quality control during graphene growth and after transfer is also extremely important and ideally non-destructive techniques will be favored. *In situ* optical methods can enable both in-line (graphene flakes in solvent) and off-line (graphene flakes on a substrate) quality control. Electrochemical methods can also enable efficient off-line monitoring. It will be ideal for analytical methods in the metrology technique to be coupled to industrial fabrication processes, for example, to roll-to-roll graphene electrode fabrication. This will become more important for automating these techniques into a production-line of graphene.

5.2 Patent analysis for graphene

Tannock²⁴⁵ observed a surge in patent filings on graphenes around the world in recent years and the contribution of multinational corporations to the graphene patent landscape is and remains significant. Among these patents, graphene has been used in various devices. Graphene transistors are evolving at a rapid pace and are being considered as an option for post-Si electronics.²⁴⁶ It is also considered as an outstanding candidate

for electrode materials in supercapacitors and batteries due to its properties of high surface area, excellent conductivity and high intrinsic capacitance.²⁴⁷ The most near-term demand is for composites and electrodes for application in the automotive, plastics, metals, aerospace and energy markets.²⁴⁸ For instance, graphene can be used to make lighter and more efficient aircraft and automobile parts, stronger wind turbines, and better medical implants. It could also serve as a transparent conductive coating for solar cells. Spreading one sheet of graphene throughout polymers makes both strong and lightweight materials, and the electrical conductivity and thermal stability in the composite material is even better than in the polymers alone. Graphene is also reported to be an excellent material for solid-state gas detection for toxic or harmful gases.¹⁸⁵ In addition, graphene has huge potential in the printable electronics industry. Research has shown flexible graphene-based chemical sensors printed on paper substrates are possible²⁴⁹ and high performance energy devices like supercapacitors have also been made from flexible graphene–polyaniline composite papers.²⁵⁰ It was discovered that after the publication of the Novoselov paper,³² new themes that become visible in the patent applications are Li-ion batteries, transistors and biosensors.²⁵¹ There

Table 3 Industrial metrology capabilities provided by graphene metrology techniques (reproduced from ref. 191 with copyright permission)

	Throughput	Characterization area	Substrate/environment requirements	Qualified results
TEM (transmission electron microscopy)	Very low, a great deal of sample preparation is required and image formation is slow	Very small	Support substrate with large holes/vacuum environment	
SEM (scanning electron microscopy)	Mediocre, sample preparation required but image formation is fast	500 × 500 μm ² regions demonstrated. ¹⁰¹ Limited by desired resolution	Conductive substrate/vacuum environment	
LEEM (low energy electron microscopy)	Somewhat high, parallel image formation but high resolution means small regions are imaged	50 × 50 μm ² regions demonstrated. ²⁰² Limited by desired resolution and image objective	Reflection spectrum altered by substrate/vacuum environment	
AES (Auger electron spectroscopy)	Low, spatial mapping is rare. Requires extensive calibration steps	100 × 100 μm ² regions demonstrated (5 μm ² resolution) ²⁰³	Vacuum environment	
AFM (atomic force microscopy)	Low, data acquisition speed limited by probe scanning control	Small, limited by throughput, scan size and feedback drift	Atomically flat substrate	
STM (scanning tunnelling microscopy)	Very low, data acquisition speed limited by probe scanning control	Small	Atomically flat, conductive substrate/vacuum, low temperature environment	
Raman spectroscopy	Very low, 0.5–1 minute per collection point	Small, limited by throughput	Very low substrate and environment sensitivity	
XPS (X-ray photoemission spectroscopy)	Extremely low, usually only one or two points are measured		Vacuum environment	
Optical transmission	Mediocre, fast data collection but limited resolution	Large. Resolution is limited by contrast	Substrate must exhibit high, uniform transmittance	
Ellipsometry	Mediocre, data points are collected sequentially. Industrial implementations typically average over large areas using wide illumination spots or generalize from a small number of points	1 cm ² regions demonstrated (250 μm ² resolution) ²³⁴	Polarization change affected by substrate	
Reflection microscopy	Very high, thousands of data points collected simultaneously	120 × 120 μm ² regions demonstrated. ²³⁷ Limited by contrast	Substrate stacking and refractive index determine contrast	Image segmentation according to layers (exfoliated graphene, calibration required)
FQM (fluorescence quenching microscopy)	Very high, thousands of data points collected simultaneously	1 cm ² regions demonstrated. ²³⁹ Unlimited due to high contrast	Very low substrate and environment sensitivity	Highly repeatable image segmentation according to layers (CVD graphene, no calibration required)

has been a rapid rise in the number of graphene patents since 2004 when the material was discovered to 2010 at a CAGR (Compound Annual Growth Rate) of 35%.²⁵¹ The rapid growth in the rise of patent applications suggests that graphene is on the upward curve of the hype cycle. The total graphene market was \$196 000 in 2008 and was expected to rise to \$59 M in 2015.²⁵² A most recent analysis from Lux Research reveals that the aggregate graphene market will grow from a base of \$9 million in 2012 to a modest \$126 million in 2020 (ref. 253) in contrast to a more ambitious forecast made in 2011.²⁵⁴

Composites and energy storage will duke it out for graphene supremacy, while conductive opaque inks and anti-corrosion coatings also provide meaningful volumes.²⁵³

Fig. 10 shows the value chains of the current graphene industry. The scaling up of graphene production can be realized either by solution-based methods (liquid exfoliation) or the CVD method. The raw material for liquid exfoliation is from graphite ore and the CVD method relies on the production of a CVD machine. Various academic research institutes, industry labs and start-up companies are heavily involved in commercializing

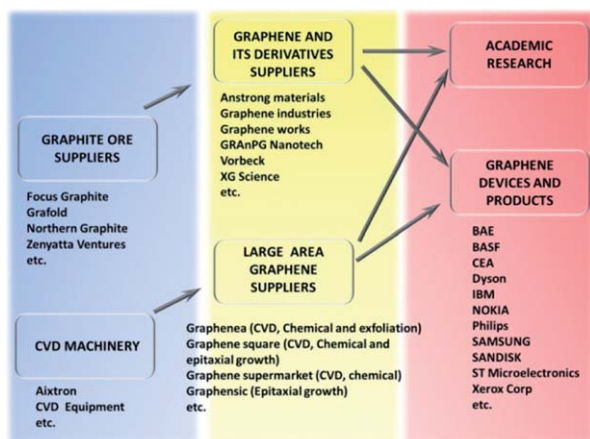


Fig. 10 Value chains in graphene industry. A map of different stages in the production of graphene and the companies involved in each.

different graphene products. With the exception of Samsung, the top corporations have a narrower technology focus than the top academic research institutes. For example, despite Sandisk's large company size they have a narrow interest in graphene's applications in memory devices. Likewise IBM, Xerox, McAlister Technologies and Bayer *etc.* are likely to have focused interests, whereas the academic institutions are likely to be interested in a wider range of potential applications by exploring different potential research directions. The exception to this is Rice University's concentrated interest in graphene for antenna-related uses, presumably reflecting the areas of interest of their research programmes.²⁵⁵

Science-based innovations generally originate in academia and graphene is no exception. Since most graphene inventions will cite directly or indirectly the original graphene work made by Novoselov and Geims' that lead them to the Nobel Prize, it has been discovered that there is a correlation between filed patent families and scientific publications, and citations to the Novoselov paper.²⁵¹

The vertical (red) bar in the Fig. 11 marks the publication of the Novoselov paper. It had an immediate and large impact on

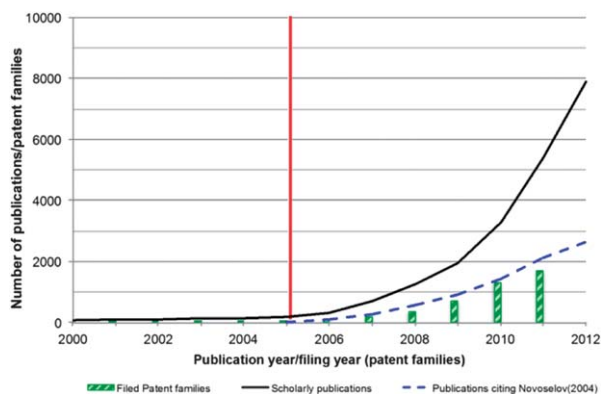


Fig. 11 Scholarly publications, patent filings and citations to the Novoselov-paper.²⁵¹

the R&D community: a sharp rise in the number of scholarly publications and at the same time as an increase in the number of filings for patent applications. This suggests that the number of patent applications is strongly related to the number of scholarly publications. An updated number of patent publications in 2012 is 3500 (ref. 255) and it follows the exponential growth trend predicted in Fig. 11. Taken into account the time needed for publication and the time needed for developing an invention there seems to be an almost instantaneous effect on R&D, an explosion of activity.²⁵¹ The correlation indicates that graphene R&D is currently still science-based.

Based on the worldwide patent application record, the discovery of pristine graphene, not graphene oxide, was dated back to at least 2002.²⁵⁶ The number of published graphene patent applications worldwide between 2010 and 2012 has more than tripled and there has been an order of magnitude difference in the yearly publication figures over the last five years. With a huge array of potential applications, there is no doubt that firms, state enterprises and research institutes are filing patents to protect potential product and market shares. Firms in China, the U. S. and South Korea lead the way in the number of patents filed over the past five years in potential applications of graphene. By the beginning of 2013, Chinese firms and institutes filed 2204 patents (30% of the filed patents), followed by U. S. entities with 1754 (23% of the filed patents), then South Korea with 1160 (15% of the filed patents) and finally the UK owning 54 filed patents, which is less than 1%.²⁵⁷ This means that 68% of all global patents filed on graphene related materials and applications have been taken out by firms and institutes in just three countries, even though graphene was discovered in the UK. Fig. 12 demonstrates this using the patent data focusing on four countries.

UK applicants currently hold the 6th largest number of patent families after Chinese, American, Korean, Japanese and German applicants. The Relative Specialisation Index (RSI)

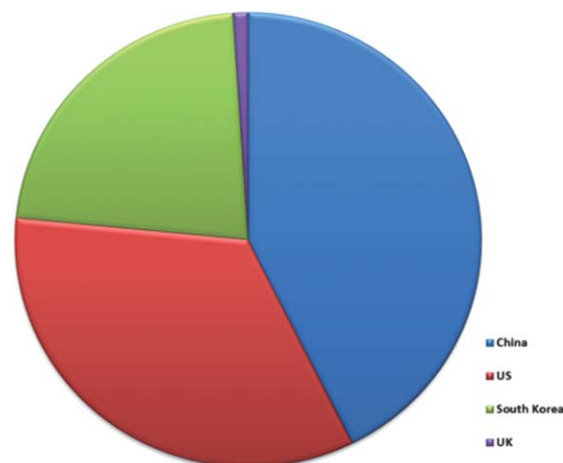


Fig. 12 Number of graphene patent publications up to 2013 vs. nationality. Data source from BBC news.²⁵⁷

suggests that despite relatively low levels of patenting, the UK is still outperforming its major European competitors (France and Germany) when it comes to graphene patenting.²⁵⁵ It is also interesting to note that when the number of academic publications from all European Union countries are combined, the EU comes out on top with more academic publications related to graphene than China or the USA; when considering the EU as a whole, this could be considered a more accurate measure for comparison against China and the USA in terms of size and population.

In addition to the £50 million grant announced by the UK's Chancellor of the Exchequer to support UK-based graphene research in 2011,²⁴⁵ another £21.5 million was invested in 2012²⁵⁸ to fund a national research programme that will take this Nobel Prize-winning discovery from the British laboratory to the British factory. Currently both Manchester and Cambridge universities have tried and tested successful technology transfer capabilities. The European Commission is also boosting graphene research this year by launching one billion Euros funding in the Graphene Flagship. These will help Europe face the global competition and create early roadmaps that will ultimately become new products in high-tech markets.

6. Conclusions

As the thinnest material ever known in the universe, graphene has been attracting tremendous amounts of attention in multi-disciplinary subjects since its successful isolation a few years ago. This one-atom-thick pseudo-infinite nano-crystal consists of sp^2 -hybridized aromatic carbon atoms covalently packed into a continuous hexagonal lattice. Graphene exhibits a range of unique properties, like a high 3D aspect ratio and large specific surface area, superior mechanical stiffness and flexibility, remarkable optical transmittance, extraordinary thermal response and excellent electronic transport properties, which means it has great promise for applications in the next generation electronics. With respect to other nanocarbon materials like CNTs and fullerenes, graphene and its derivatives are quickly gaining ground for large scale applications and have already established a position in academia and in the industry, thanks to the disruptive innovation their peculiarities might bring. In the field of energy harvesting and storage, the implementation of graphene into solar cells, supercapacitors, batteries and fuel cells is still at the developmental stage, but some performance enhancements have already been observed in a few specific areas.

As well as being used as an additive to many functional materials, graphene can enable special applications for various energy devices. The high frequency response from supercapacitors made of graphene as thin as human hair can release the energy in milliseconds, and improvement of thousands of times over conventional supercapacitors that respond in seconds. Graphene is the one of the only materials that can potentially enable a hybrid battery and supercapacitor device (both high energy density and power density). Graphene can act as a special load in fuel cells to facilitate the catalysis as well as to improve efficiencies of solar cells due to its optical

transparency and highly conductive properties. Scientists have proven the material's technical superiority in the replacement of rare and expensive materials like platinum and ITO as well as the synergistic effect brought about by the synthesis of graphene composites obtained with metals, semiconductors or polymers. With the highest Young's modulus, graphene can be used in wind turbines and its high thermo-conductivity can make it useful in heat dissipating materials for efficient power management systems. Different manufacturing methods will give different properties to graphene. CVD and solution-based methods (liquid-phase exfoliation) are currently the two options to scale up graphene production. The former can grow the best transparent conducting graphene directly on metal substrates and transfer it to other substrates and the latter can be enabled by printing technology. The CVD method can produce a perfect layer of graphene with less defects (preserving all the superlative physical properties), lower sheet resistance and tailored layers, but the cost is high and it usually needs the transfer of a substrate for specific applications. Solution-based methods are very cost-effective and functional groups can be added directly onto graphenes during physiochemical reactions and formed as inks in the formula directly. However, such methods will create a lot of defects resulting in higher sheet resistance. On the other hand, graphene can be easily mixed into composites for functional materials and tailored to different applications from liquid-based methods. The global printed electronics market is expected to grow rapidly in the future. Graphene-based conductive inks have the potential to play a key role in specific parts of the overall market. These inks offer reasonably good functionality at very competitive costs along with the element of flexibility. They are also compatible with all existing printing technologies. The inks are likely to enter the market in stages – gradually moving from low cost low functionality to high cost high functionality applications. This will enable energy solutions to be scaled up in an effective printable way. In summary, the distinctive electronic, thermal and mechanical properties of graphene make it a potentially disruptive technology across a range of industries.

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