

Chemical methods for the production of graphenes

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Interest in graphene centres on its excellent mechanical, electrical, thermal and optical properties, its very high specific surface area, and our ability to influence these properties through chemical functionalization. There are a number of methods for generating graphene and chemically modified graphene from graphite and derivatives of graphite, each with different advantages and disadvantages. Here we review the use of colloidal suspensions to produce new materials composed of graphene and chemically modified graphene. This approach is both versatile and scalable, and is adaptable to a wide variety of applications.

The development of various methods for producing graphene — a single layer of carbon atoms bonded together in a hexagonal lattice — has stimulated a vast amount of research in recent years¹. The remarkable properties of graphene reported so far include high values of its Young's modulus ($\sim 1,100$ GPa)², fracture strength (125 GPa)², thermal conductivity ($\sim 5,000$ W m⁻¹K⁻¹)³, mobility of charge carriers (200,000 cm² V⁻¹ s⁻¹)⁴ and specific surface area (calculated value, 2,630 m² g⁻¹)⁵, plus fascinating transport phenomena such as the quantum Hall effect⁶. Graphene and chemically modified graphene (CMG) are promising candidates as components in applications such as energy-storage materials⁵, 'paper-like' materials^{7,8}, polymer composites^{9,10}, liquid crystal devices¹¹ and mechanical resonators¹².

Graphene has been made by four different methods. The first was chemical vapour deposition (CVD) and epitaxial growth, such as the decomposition of ethylene on nickel surfaces¹³. These early efforts (which started in 1970) were followed by a large body of work by the surface-science community on 'monolayer graphite'¹⁴. The second was the micromechanical exfoliation of graphite¹⁵. This approach, which is also known as the 'Scotch tape' or peel-off method, followed on from earlier work on micromechanical exfoliation from patterned graphite¹⁶. The third method was epitaxial growth on electrically insulating surfaces such as SiC (ref. 17) and the fourth was the creation of colloidal suspensions.

Micromechanical exfoliation has yielded small samples of graphene that are useful for fundamental study. Although large-area graphene films (up to ~ 1 cm²) of single- to few-layer graphene have been generated by CVD growth on metal substrates^{18–20}, and graphene-type carbon materials have been produced by substrate-free CVD²¹, radio-frequency plasma-enhanced CVD²², aerosol pyrolysis²³ and solvothermal synthesis²⁴, the uniform growth of single-layer graphene is still a challenge. In this review, we discuss the production of graphene and CMG from colloidal suspensions made from graphite, derivatives of graphite (such as graphite oxide) and graphite intercalation compounds. This approach is both scalable, affording the possibility of high-volume production, and versatile in terms of being well-suited to chemical functionalization. These advantages mean that the colloidal suspension method for producing graphene and CMG could be used for a wide range of applications.

Graphenes from graphite oxide

Since it was first prepared in the nineteenth century^{25,26}, graphite oxide has been mainly produced by the Brodie²⁵, Staudenmaier²⁷ and Hummers²⁸ methods. All three methods involve oxidation of

graphite in the presence of strong acids and oxidants. The level of the oxidation can be varied on the basis of the method, the reaction conditions and the precursor graphite used. Although extensive research has been done to reveal the chemical structure of graphite oxide, several models are still being debated in the literature.

Solid-state ¹³C NMR spectroscopy of graphite oxide and recently of ¹³C-labelled graphite oxide favours the model shown in Fig. 1a; the *sp*²-bonded carbon network of graphite is strongly disrupted and a significant fraction of this carbon network is bonded to hydroxyl groups or participates in epoxide groups^{29–32}. Minor components of carboxylic or carbonyl groups are thought to populate the edges of the layers in graphite oxide. This indicates that further work with solid-state NMR on ¹³C-labelled graphite oxide is necessary, along with (for example) titration with fluorescent tags of carboxylic and other groups to identify their spatial distribution on individual graphene oxide platelets derived from graphite oxide as discussed further below.

Graphite oxide thus consists of a layered structure of 'graphene oxide' sheets that are strongly hydrophilic such that intercalation of water molecules between the layers readily occurs³³. The inter-layer distance between the graphene oxide sheets increases reversibly from 6 to 12 Å with increasing relative humidity³³. Notably, graphite oxide can be completely exfoliated to produce aqueous colloidal suspensions of graphene oxide sheets by simple sonication (Fig. 1b)³⁴ and by stirring the water/graphite oxide mixture for a long enough time³⁵. The measurement of the surface charge (zeta potential) of graphene oxide sheets³⁶ shows that they have negative charges when dispersed in water. This suggests that electrostatic repulsion between negatively charged graphene oxide sheets could generate a stable aqueous suspension of them. A considerable body of work^{37,38} on such aqueous colloidal suspensions was carried out in the 1950s and 1960s. Such graphene oxide sheets probably have a similar chemical structure to the layers in graphite oxide and are a promising starting material in the generation of colloidal suspensions of other CMGs through chemical tuning. Filtration of CMG suspensions has produced free standing paper-like materials^{7,36,39–41} that have a layered structure (Fig. 1c, d). Significant advances have also been made in using homogeneous suspensions of CMG sheets to produce thin films, which can be relevant to transparent and electrically conductive thin-film applications, among others^{36,39–44}.

Unreduced graphene oxide sheets

Several authors have stated that homogeneous colloidal suspensions of graphene oxide in aqueous and various organic solvents can be achieved by simple sonication of graphite oxide^{8,34,45–47}. The hydrophilic graphene oxide can be easily dispersed in water

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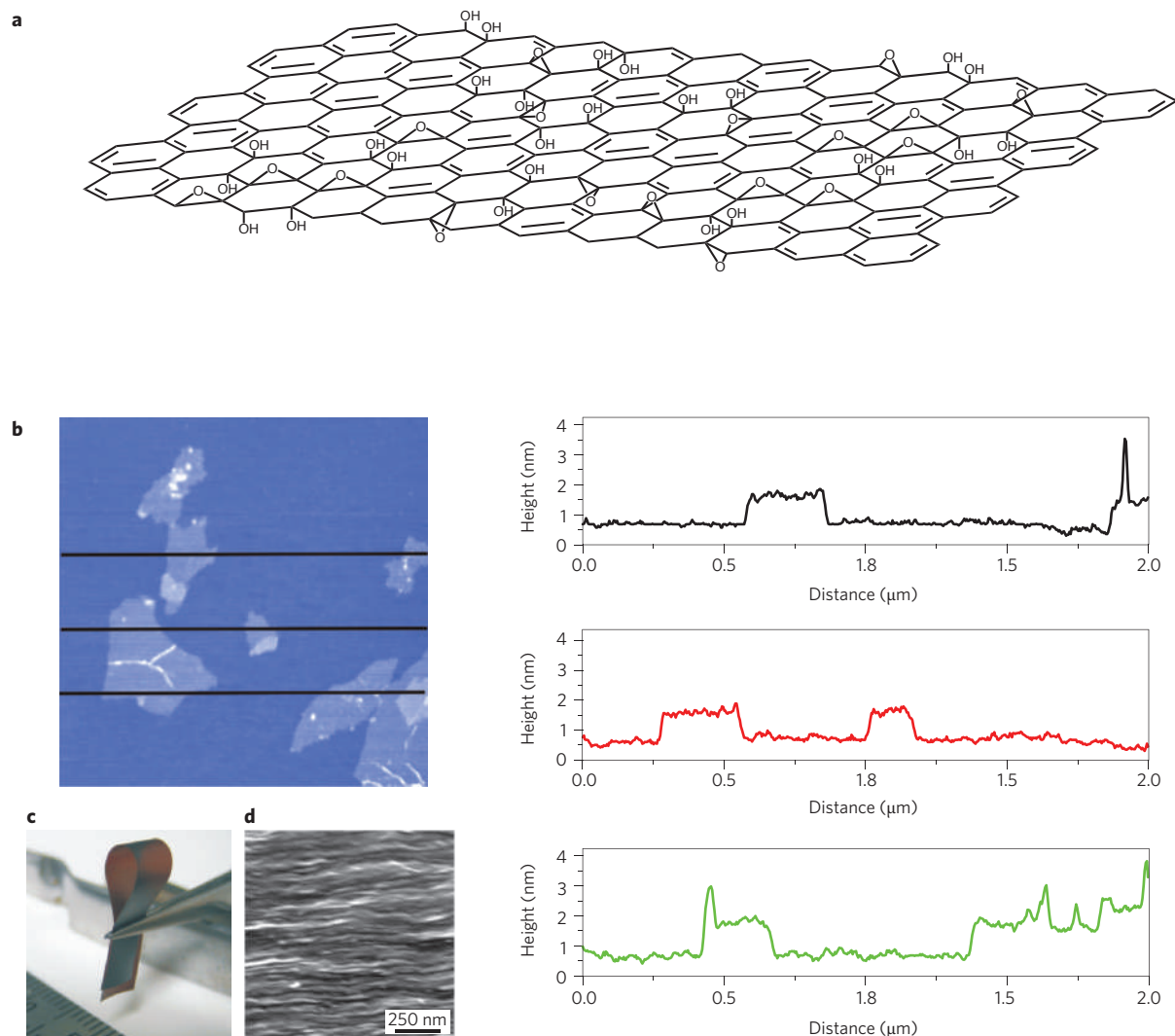


Figure 1 | Graphite oxide and graphene oxide. **a**, Chemical structure of graphite oxide³⁰. For clarity, minor functional groups, carboxylic groups and carbonyl groups have been omitted at the edges. Reproduced with permission from ref. 30. © 1998 Elsevier. **b**, An AFM image of exfoliated graphene oxide sheets⁴⁷; the sheets are ~1 nm thick. The horizontal lines indicate the sections corresponding (in order from top to bottom) to the traces shown on the right. Reproduced with permission from ref. 47. © 2007 Elsevier. **c**, Photograph of folded graphene oxide paper⁷ (© 2007 NPG). **d**, A scanning electron microscope image of the cross-section of the graphene oxide paper, showing layered structure⁷ (© 2007 NPG).

(at concentrations up to 3 mg ml⁻¹)^{8,34,45,47}, affording brown/dark-brown suspensions. (See Table 1 for a list of solvents used, the concentrations of colloidal suspensions, the lateral dimensions and heights of graphene oxide sheets, and the type of precursor material used, be it graphite oxide or graphite or expandable graphite.) The exfoliation to achieve graphene oxide sheets has been most typically confirmed by thickness measurements of the single graphene sheet (~1-nm height on substrates such as mica) using atomic force microscopy (AFM).

Graphite oxide can be dispersed directly in several polar solvents such as ethylene glycol, DME, NMP and THF at about 0.5 mg ml⁻¹ (ref. 46). It has also been shown that the chemical modification of graphene oxide sheets by organic molecules yields homogeneous suspensions in organic solvents⁴⁵; reaction of graphite oxide with isocyanate groups produced isocyanate-modified graphene oxide sheets that are well dispersed in polar aprotic solvents. It was proposed that carbamate and amide functional groups are generated by the reaction of isocyanate with hydroxyl and carboxyl groups (Fig. 2a)⁴⁵.

The amide-coupling reaction⁴⁸ between the carboxylic acid groups of graphene oxides and octadecylamine (after

SOCl₂ activation of the COOH groups) was used in ref. 49 to modify graphene oxides by long alkyl chains with 20 wt% yield. Interestingly, chemical modification of an alternative starting material, graphite fluoride, with alkyl lithium reagents produced alkyl-chain-modified graphene sheets that could be dispersed in organic solvents after sonication⁵⁰.

Reduced graphene oxides

Although the chemical modification of graphene/graphite oxide or graphite fluoride can generate homogeneous colloidal suspensions, the resulting CMGs are electrically insulating owing to disruption of the 'graphitic' networks. On the other hand, the reduction of the graphene oxide by chemical methods (using reductants such as hydrazine^{47,51,52}, dimethylhydrazine⁹, hydroquinone⁵³ and NaBH₄ (refs 42 and 54), thermal methods^{55,56} and ultraviolet-assisted methods⁵⁷ has produced electrically conducting CMGs. (See Table 2 for a list of electrical properties of graphene-based materials generated using their suspensions.)

The reduction of aqueous graphene oxide suspension by hydrazine at the pH of the suspension when used as made results in

Table 1 | Comparison of a set of chemical approaches to produce colloidal suspensions of CMG sheets

Ref.	Starting materials	Dispersible solvents	Concentration (mg ml ⁻¹)	Lateral size	Thickness (nm)
34	GO/MH	Water	1	—	—
36	GO/MH	Water	0.5	Several hundred nm	-1
39	GO/MH	Water	0.1	—	-1.7
40	GO/MH	Water	7	Several hundred nm	-1
42	GO/H	Water/methanol, acetone, acetonitrile mixed solvents	3-4	Several hundred nm	-1.2
45	GO/MH	DMF, NMP, DMSO, HMPA	1	~560 nm	-1
46	GO/H	Water, acetone, ethanol, 1-propanol, ethylene glycol, DMSO, DMF, NMP, pyridine, THF	0.5	100-1,000 nm	1.0-1.4
49	GO/O	DMF, THF, CCl ₄ , DCE	0.5	—	0.5-2.5
50	Graphite fluoride	DCB, MC, THF	0.002-0.54	1,600 nm	-0.95
51	GO/S	DMF, DMAc, NMP	1	Several hundred nm	1.8-2.2
52	GO/MH	Hydrazine	1.5	Up to 20 μm × 40 μm	-0.6
54	GO/S	THF	<0.48	—	1-2
55, 56, 10	GO/S	NMP, DMF, DCB, THF, nitromethane	0.1	100-2,500 nm	1.1-3.5 (ave. 1.75)
57	GO/H	Ethanol	1	Several hundred nm	-2
59	Graphite powder	NMP, DMAc, GBL, DMEU	0.01	Several μm	1-5
60	GIC	NMP	0.15	Several hundred nm	-0.35
61	EG	DCE	0.0005	Nanoribbon (width <10 nm)	1-1.8
62	EG	DMF	—	~250 nm	-1
63	EG	Water, DMF, DMSO	0.015-0.020	Several hundred nm to a few μm	2-3 (2-3 layers of graphene)
64	Graphite rod	DMF, DMSO, NMP	1	500-700 nm	-1.1

GO, graphite oxide; MH, modified Hummers method; H, Hummers method; O, their own method; S, Staudenmaier method; EG, expandable graphite; GIC, graphite intercalation compound; DMF, dimethylformamide; DMAc, *N,N'*-dimethylacetamide; DMSO, dimethylsulphoxide; NMP, *N*-methylpyrrolidone; THF, tetrahydrofuran; MC, dichloromethane; DCE, 1,2-dichloroethane; DCB, 1,2-dichlorobenzene; HMPA, hexamethylphosphoramide; GBL, γ -butyrolactone; DMEU, 1,3-dimethyl-2-imidazolidinone.

agglomerated graphene-based nanosheets, and, when dried, a black powder (Fig. 2b)⁴⁷ that is electrically conductive (powder conductivity, $\sim 2 \times 10^2 \text{ S m}^{-1}$). Elemental analysis (atomic C/O ratio, ~ 10) of the reduced graphene oxides measured by combustion revealed the existence of a significant amount of oxygen, indicating that reduced graphene oxide is not the same as pristine graphene. Theoretical calculations of the reduction of graphene oxide (the model used for graphene oxide had the graphene decorated with hydroxyl and epoxide groups) suggest that reduction below 6.25% of the area of the graphene oxide (C/O = 16 in atomic ratio) may be difficult in terms of removing the remaining hydroxyl groups⁵⁸.

Homogeneous colloidal suspensions of electrically conducting CMGs have been produced by chemical reduction with dimethylhydrazine or hydrazine in the presence of either polymer or surfactant^{9,34}. The reduction of an aqueous suspension containing a mixture of graphene oxide sheets and poly(sodium 4-styrenesulphonate) afforded an aqueous black suspension of reduced graphene oxide sheets coated in the polymer³⁴. The reduction of isocyanate-modified graphene oxide in the presence of polystyrene generated a suspension of reduced graphene oxide sheets in DMF that could then be 'crashed out' with methanol to yield a composite with well-dispersed and electrically conductive CMG sheets⁹. Reduction of sodium dodecylbenzenesulfonate (SDBS)-wrapped graphene oxide with hydrazine and then its chemical modification (Fig. 2c) with aryl diazonium salt produced SDBS-wrapped

CMG that was dispersible in DMF, *N,N'*-dimethylacetamide, and NMP at concentrations up to 1 mg ml⁻¹ (ref. 51).

Colloidal suspensions of modified graphenes decorated with small organic molecules or nanoparticles have also been reported. In ref. 39, the reduced graphene oxide sheets were functionalized using pyrenebutyric acid (a well-known organic molecule⁴⁸ with a strong adsorption affinity for the graphitic plane via π stacking). The aqueous graphene oxide suspension was reduced using hydrazine in the presence of pyrenebutyric acid, yielding a black aqueous colloidal suspension (0.1 mg ml⁻¹) of CMG adsorbed by pyrenebutyric acid. Its paper-like material, prepared by filtration, showed moderate electrical conductivity ($2 \times 10^2 \text{ S m}^{-1}$).

The suspension (<0.48 mg ml⁻¹) of gold-nanoparticle-modified graphene sheets in THF was generated by the reaction of NaBH₄ and octadecylamine-modified graphene oxide⁴⁹ and then the addition of AuCl₄⁻ to the suspension⁵⁴. The gold nanoparticles (diameter, ~ 5 –11 nm) were anchored to the modified graphene sheets. Graphene modified with titanium dioxide nanoparticles has also been studied⁵⁷; ultraviolet irradiation of this TiO₂/graphene oxide hybrid in ethanol was used to reduce the graphene oxide sheets (Fig. 2d), producing a black suspension of TiO₂-attached CMG sheets in ethanol. The TiO₂ was suggested to act as a photocatalyst, transferring photoelectrons from the TiO₂ to the graphene oxide sheets⁵⁷.

A few methods for creating colloidal suspensions of graphene sheets without the help of stabilizers or surfactants have

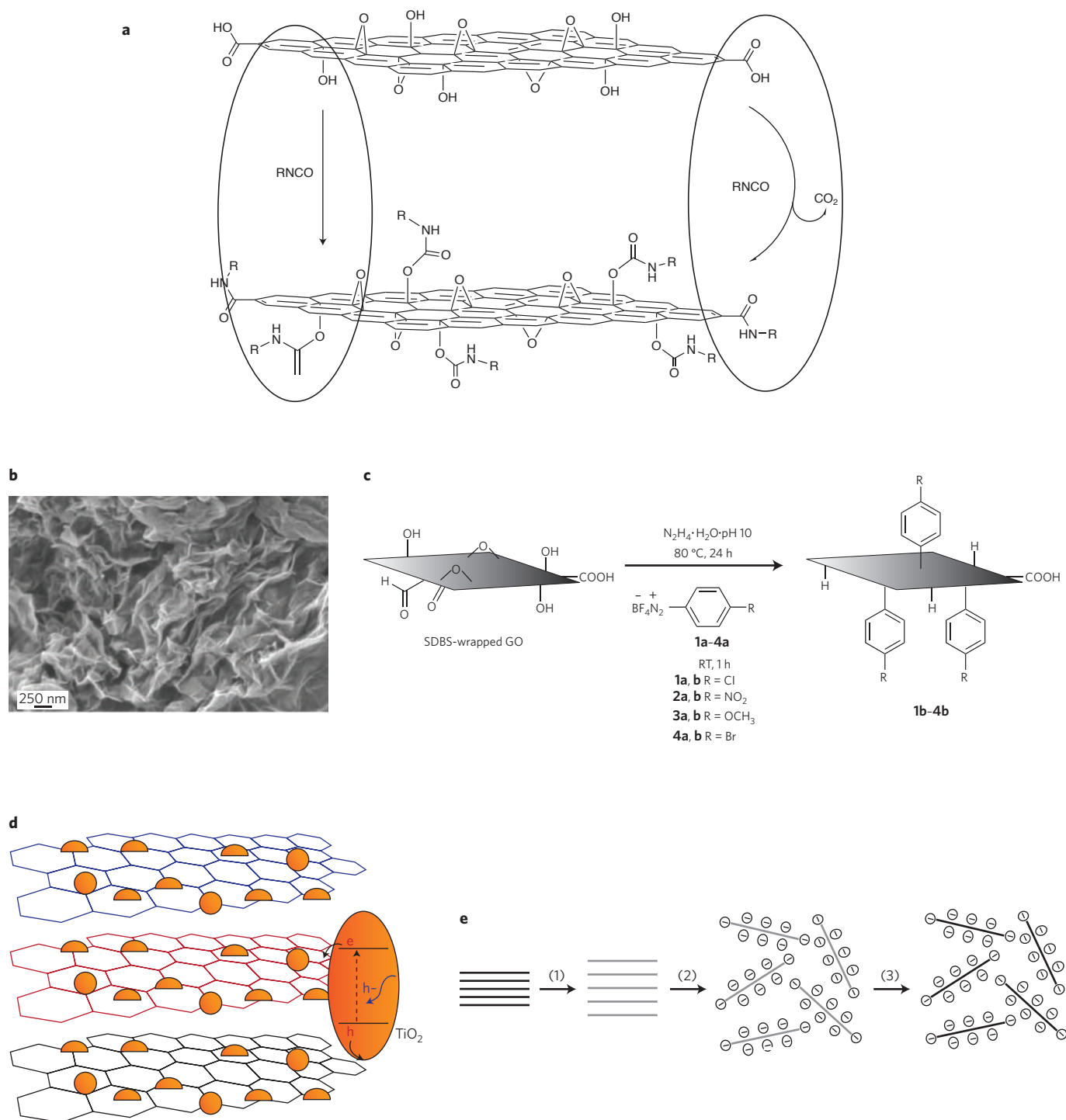


Figure 2 | CMG oxide sheets. **a**, Proposed reaction of graphene oxide sheets with isocyanates forming carbamate (left oval) and amide (right oval) functionalities⁴⁵. **b**, A scanning electron microscope image of aggregated graphene oxide sheets chemically reduced with hydrazine monohydrate⁴⁷. Parts **a** and **b** reproduced with permission from ref. 47. © 2007 Elsevier. **c**, Starting with SDBS-wrapped graphene oxide, reduction and functionalization of intermediate SDBS-wrapped CMG with diazonium salts⁵¹. RT, room temperature. Reproduced with permission from ref. 51. © 2008 ACS. **d**, TiO₂-graphene hybrid and its proposed response under UV excitation⁵⁷. Reproduced with permission from ref. 57. © 2008 ACS. **e**, Chemical route to produce aqueous suspension of reduced graphene oxide³⁶. (1) Oxidation of graphite to synthesize graphite oxide. (2) Exfoliation of graphene oxide in water by sonication of graphite oxide. (3) Controlled reduction of graphene oxide sheets by hydrazine yielding a colloidal suspension of conductive CMG sheets, which are stabilized by electrostatic repulsion (© 2008 NPG).

been reported. An aqueous suspension (0.5 mg ml⁻¹) of reduced graphene oxide sheets under basic conditions (pH 10) was described in ref. 36. The graphene oxide was reduced by hydrazine, and excess hydrazine was removed by dialysis. It was suggested

that shifting to pH 10 converts neutral carboxylic groups to negatively charged carboxylate groups, so that when the interior of the graphene oxide sheets are reduced by hydrazine, the negatively charged particles do not agglomerate³⁶; see Fig. 2e. Paper-like

Table 2 | Electrical properties of conductive CMG-based materials

Ref.	Forms	Electrical properties
36, 41	Free-standing paper	Conductivity (10^2 S m^{-1}): 72 (air dried), 120 (dried at 220 °C), 350 (dried at 500 °C)
39	Free-standing paper	Conductivity: $2 \times 10^2 \text{ S m}^{-1}$
40	Free-standing paper	Conductivity: $6.9 \times 10^2 \text{ S m}^{-1}$
42	Thin evaporated film (~3 μm thick) on a glass slide	Conductivity: $12.5 \times 10^2 \text{ S m}^{-1}$
47	Powder	Conductivity: $2 \times 10^2 \text{ S m}^{-1}$
55, 56	Powder	Conductivity: $(10\text{--}23) \times 10^2 \text{ S m}^{-1}$
57	Drop-cast film on a substrate	Resistance: 30.5 k Ω
59	Thin film (~30 nm thick) on the alumina membrane by filtration	Conductivity: $65 \times 10^2 \text{ S m}^{-1}$
61	Single graphene nanoribbon sheet	Semiconducting behaviour
62	Multilayer Langmuir–Blodgett film	Resistance: 8–150 k Ω

materials made by filtration and then dried in air showed good electrical conductivity ($\sim 7,200 \text{ S m}^{-1}$)³⁶.

In other work, an aqueous suspension (7 mg ml^{-1}) of partially reduced graphene oxides was produced, under basic conditions, by hydrazine reduction of KOH-modified graphene oxides⁴⁰. It was suggested that the K^+ ions and the carboxylate anions at the edges of the CMG sheets formed ion pairs. The electrical conductivity of air-dried 'paper' made from this material was $\sim 690 \text{ S m}^{-1}$.

In a third approach⁴², a graphene-based suspension was produced in three reaction steps: (1) 'pre-reduction' of graphene oxide by NaBH_4 ; (2) sulphonation by aryl diazonium salt of sulphanilic acid; and (3) 'post-reduction' of aqueous sulphonated graphene (2 mg ml^{-1} , pH 3–10) with hydrazine. The sulphonated graphene sheets of step 2 could be dispersed in water (2 mg ml^{-1} , pH 3–10), and after the post-reduction step the CMG sheets could be dispersed in mixed solvents of water with certain organic solvents. It was suggested that covalent functionalization in the CMG sheets by sulphonyl groups was occurring. The electrical conductivity of the thin evaporated film on a glass slide after drying at 120 °C was reported to be $1,250 \text{ S m}^{-1}$ (ref. 42).

A suspension of reduced graphene oxide sheets (some with lateral dimensions of up to $\sim 20 \text{ mm} \times 40 \text{ mm}$) in anhydrous hydrazine was produced by stirring graphene oxide paper in anhydrous hydrazine (10 ml for 15 mg of graphite oxide) for one week in a nitrogen-filled dry box⁵². The resulting CMG on SiO_2 was reported to be $\sim 0.6 \text{ nm}$ in height, measured by AFM. The anhydrous hydrazine thus acts both as a reduction agent of graphene oxide sheets and as a dispersing solvent in this approach. The individual CMG sheets were tested as a field-effect transistor and showed p-type behaviour⁵².

Thermal treatment of graphite oxide is another route that has been used to obtain reduced platelets. Rapid heating ($>2,000 \text{ }^\circ\text{C min}^{-1}$) up to 1,050 °C exfoliates as well as reduces graphite oxide, yielding a black powder^{55,56}. The platelets have a similar oxygen content (atomic C/O ratio, 10.3; elemental analysis by combustion) to that of hydrazine-reduced graphene oxide, and a powder conductivity in the range of $(1\text{--}2.3) \times 10^3 \text{ S m}^{-1}$ has been reported^{55,56}. The thermally reduced graphene sheets could be dispersed in several organic solvents (0.1 mg ml^{-1}) and their colloidal suspension was used to fabricate a set of composites of reduced graphenes and polymers¹⁰.

Graphenes from other graphite derivatives

Graphite, graphite intercalation compounds or expandable graphites (which are a particular type of graphite intercalation compound) have been used as starting materials in obtaining colloidal dispersions of single-layer graphene sheets. Ideally, the use of graphite, graphite intercalation compounds or expand-

able graphites allows production of dispersions of high-quality graphene sheets (almost pristine graphene; see below). Colloidal suspensions of graphene sheets in organic solvents such as NMP were obtained by sonication of graphite powder in ref. 59. Although the concentration (0.01 mg ml^{-1}) of the suspension and yields (1–12 wt%) of single-layer graphene were not high, high-quality graphene was reported. 'Good' solvents for a homogeneous colloidal suspension were classified using a model that included the surface energy of graphene and the cohesive energy of the solvent. Measurements on very thin films made from these sheets yielded, for example, an electrical conductivity of $\sim 6,500 \text{ S m}^{-1}$ at $\sim 42\%$ of optical transparency. After the films had been dried at 400 °C, residual NMP had not been completely removed and was estimated to be 7% by weight⁵⁹.

In ref. 60, a homogeneous colloidal suspension of graphene sheets or ribbons was produced by stirring the ternary potassium salt $\text{K}(\text{THF})_x\text{C}_{24}$ (which is a graphite intercalation compound) in NMP. The sheets or ribbons (length, $\sim 40 \text{ mm}$) were measured to be 0.35–0.4 nm thick (ambient scanning tunnelling microscopy on highly oriented pyrolytic graphite substrate(s) and by ambient AFM on mica substrate(s)) close to the interlayer separation in graphite 0.335 nm thick. The suspension was air sensitive, but after drying by being dropped onto a surface, the resulting deposits were stable when exposed to air.

Polymer-coated graphene sheets in organic solvents obtained using expandable graphite have been reported in refs 61 and 62. Commercial expandable graphite was thermally treated at high temperature (1,000 °C) for a short time (1 min)⁶¹. Further sonication of the expanded material in dichloroethane solution of poly(*m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV) produced a suspension (0.1 mg ml^{-1}) of semiconducting single-layer or few-layer CMG nanoribbons (of width less than $\sim 10 \text{ nm}$) with adsorbed polymer⁶¹. Another approach taken was exfoliation by heating at 1,000 °C for 1 min, re-intercalation with oleum and expansion with tetrabutylammonium hydroxide (Fig. 3a)⁶². The final suspension of graphene sheets, coated in 1,2-distearoyl-*sn*-glycerol-3-phosphoethanolamine-*N*-[methoxy(polyethyleneglycol)-5000] (DSPE-mPEG), was produced by sonication in DMF, with $\sim 90\%$ of the sheets reported as individual CMG sheets on the basis of AFM measurements⁶².

An aqueous suspension of organic-molecule-coated graphene sheets using expandable graphite was reported in ref. 63. The expandable graphite was rapidly heated to 1,000 °C for 1 min and the resulting expanded graphite was mixed with 7,7,8,8-tetracyanoquinodimethane (TCNQ) in the presence of several drops of dimethyl sulphoxide (DMSO). Then a black suspension ($15\text{--}20 \text{ mg ml}^{-1}$) of single- or few-layer TCNQ-coated graphene sheets in water was produced by sonication of the dried mixture. It was

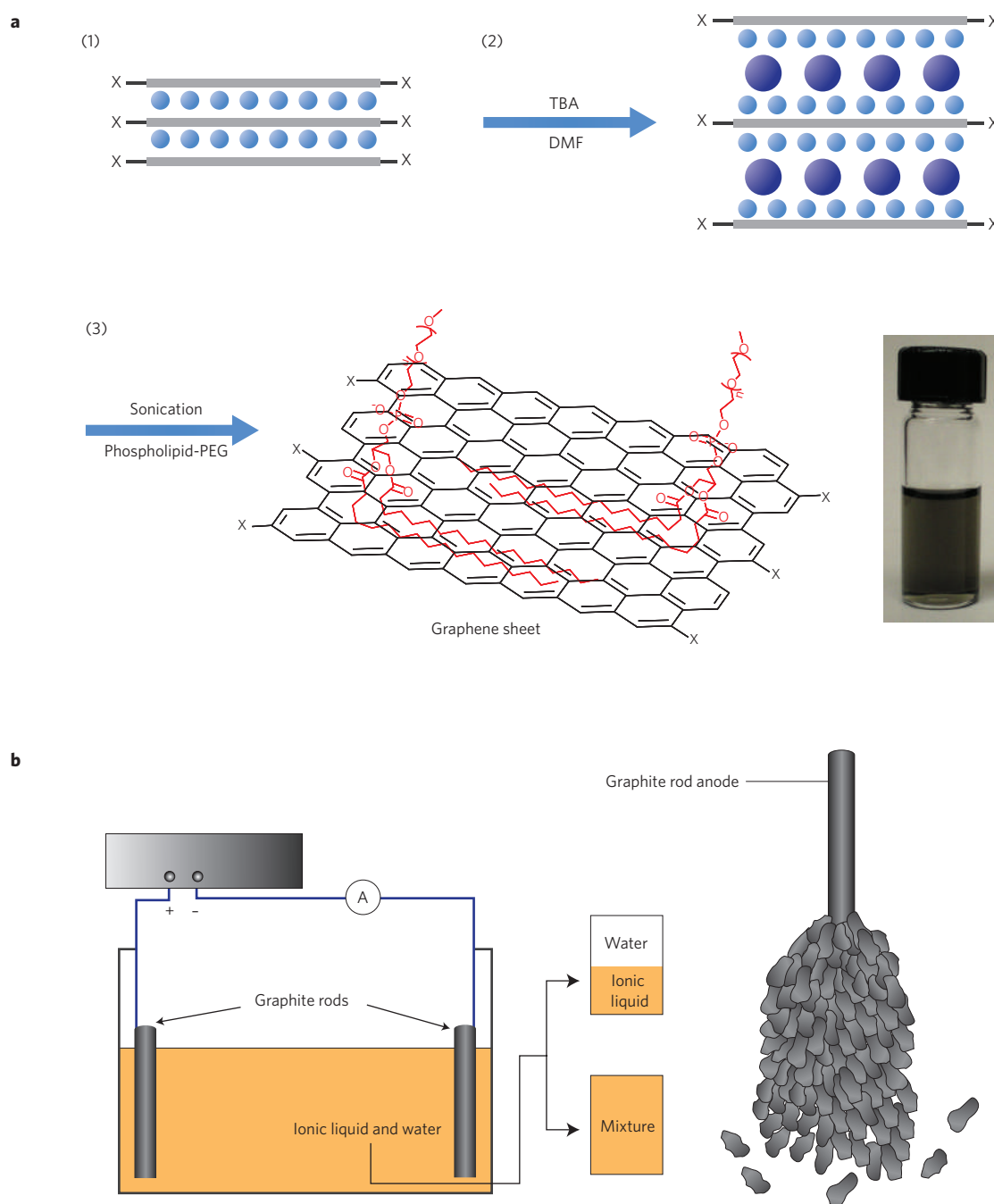


Figure 3 | Graphene sheets from graphite derivatives. a, Production of colloidal suspension of polymer-coated CMG sheets from graphite intercalation compounds⁶². (1) Exfoliated graphite reintercalated with sulphuric acid between the layers. (2) Insertion of tetrabutylammonium hydroxide (TBA) into the intercalated graphite. PEG, polyethyleneglycol. (3) CMG sheets coated with polymer molecules and a photo of the suspension in dimethylformamide. (© 2008 NPG). **b**, Graphene sheets ionic-liquid-modified by electrochemistry using graphite electrodes⁶⁴. Left, experimental set-up diagram; right, exfoliation of the CMG sheets from the graphite anode. Reproduced with permission from ref. 64. © 2008 Wiley.

suggested that TCNQ anions adsorb on graphene sheets and stabilize them in water⁶³. The TCNQ-stabilized graphene sheets were also dispersed in highly polar solvents (DMF and DMSO).

Electrochemical treatment of graphite was used in ref. 64 to generate a colloidal suspension of CMG sheets. The commercial graphite rods used as anode and cathode electrodes were immersed in a phase-separated mixture of water and imidazolium-based ionic liquids (Fig. 3b). After potentials of 10–20 V had been applied, it was claimed that ionic-liquid-functionalized graphene sheets originating from the graphite anode precipitated. Dried CMG could be re-dispersed in polar aprotic solvents (1 mg ml⁻¹)

after sonication. The average thickness of the CMG sheets from such a DMF suspension was measured by AFM and was ~1.1 nm. It was proposed that the imidazolium radicals, electrochemically driven, covalently attached to graphene sheets through the breaking of π bonds⁶⁴.

Challenges and perspectives

Colloidal suspensions are of great importance in the preparation of many types of materials, and the suspensions of CMGs hold great promise in this regard. Looming issues in terms of wide-scale applicability include scalability (yield, quantity, cost, etc.),

the safety of the solvents used and the removal from the product material (if necessary) of residual solvents or stabilizers used in the colloid. It is also worth emphasizing that although colloidal suspensions are normally only regarded as stable if they persist for very long periods of time, dispersions of CMGs might remain stable long enough to be processed into something else.

Another critical issue is related to our understanding of the chemical structure(s) of CMG sheets and their reaction mechanisms. The better our knowledge of the chemistry of these materials, the better the graphene-based composites, thin films, paper-like materials and so on that we can make. For example, the prospects for sensors based on CMG⁶⁵ will hinge on our ability to chemically tune the CMG for each sensing modality.

So far the graphenes derived by the reduction of graphene oxide have contained a significant amount of oxygen and, possibly, significant numbers of defects. Thermal annealing of reduced graphene oxide sheets has produced enhanced results^{62,66}, and finding routes for complete restoration of the *sp*² carbon network of pristine graphene is of interest. (The graphenes produced from graphite intercalation compounds or expandable graphite may have fewer defects, although they are also produced in lower yields and are less amenable to functionalization than graphenes derived from graphene oxide.)

Finally, we mention the development of new reaction routes and starting materials as an alternative. The worldwide supply of natural graphite has been estimated at 800,000,000 tonnes⁶⁷. If graphene or very thin platelets of multilayer graphene could be produced on a large scale by CVD from various precursors, new routes for creating colloidal suspensions might also be found, and the supply of graphene/few-layer graphene might be enormously increased.

References

- Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nature Mater.* **6**, 183–191 (2007).
- Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **321**, 385–388 (2008).
- Balandin, A. A. *et al.* Superior thermal conductivity of single-layer graphene. *Nano Lett.* **8**, 902–907 (2008).
- Bolotin, K. I. *et al.* Ultrahigh electron mobility in suspended graphene. *Solid State Commun.* **146**, 351–355 (2008).
- Stoller, M. D., Park, S., Zhu, Y., An, J. & Ruoff, R. S. Graphene-based ultracapacitors. *Nano Lett.* **8**, 3498–3502 (2008).
- Zhang, Y., Tan, Y.-W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **438**, 201–204 (2005).
- Dikin, D. A. *et al.* Preparation and characterization of graphene oxide paper. *Nature* **448**, 457–460 (2007).
- Park, S. *et al.* Graphene oxide papers modified by divalent ions—Enhancing mechanical properties via chemical cross-linking. *ACS Nano* **2**, 572–578 (2008).
- Stankovich, S. *et al.* Graphene-based composite materials. *Nature* **442**, 282–286 (2006).
- Ramanathan, T. *et al.* Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotech.* **3**, 327–331 (2008).
- Blake, P. *et al.* Graphene-based liquid crystal device. *Nano Lett.* **8**, 1704–1708 (2008).
- Bunch, J. S. *et al.* Electromechanical resonators from graphene sheets. *Science* **315**, 490–493 (2007).
- Eizenberg, M. & Blakely, J. M. Carbon monolayer phase condensation on Ni(111). *Surf. Sci.* **82**, 228–236 (1970).
- Aizawa, T., Souda, R., Otani, S., Ishizawa, Y. & Oshima, C. Anomalous bond of monolayer graphite on transition-metal carbide surfaces. *Phys. Rev. Lett.* **64**, 768–771 (1990).
- Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- Lu, X., Yu, M., Huang, H. & Ruoff, R. S. Tailoring graphite with the goal of achieving single sheets. *Nanotechnology* **10**, 269–272 (1999).
- Berger, C. *et al.* Electronic confinement and coherence in patterned epitaxial graphene. *Science* **312**, 1191–1196 (2006).
- Kim, K. S. *et al.* Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* **457**, 706–710 (2009).
- Sutter, P. W., Flege, J.-I. & Sutter, E. A. Epitaxial graphene on ruthenium. *Nature Mater.* **7**, 406–411 (2008).
- Reina, A. *et al.* Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett.* **9**, 30–35 (2009).
- Dato, A., Radmilovic, V., Lee, Z., Phillips, J. & Frenklach, M. Substrate-free gas-phase synthesis of graphene sheets. *Nano Lett.* **8**, 2012–2016 (2008).
- Wang, J. J. *et al.* Free-standing subnanometer graphitic sheets. *Appl. Phys. Lett.* **85**, 1265–1267 (2004).
- Campos-Delgado, J. *et al.* Bulk production of a new form of sp carbon: crystalline graphene nanoribbons. *Nano Lett.* **8**, 2773–2778 (2008).
- Choucair, M., Thordarson, P. & Stride, J. A. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nature Nanotech.* **4**, 30–33 (2009).
- Brodie, B. C. Sur le poids atomique du graphite. *Ann. Chim. Phys.* **59**, 466 (1860).
- Schaffhaeuti, C. On the combination of carbon with silicon and iron, and other metals, forming the different species of cast iron, steel, and malleable iron. *Phil. Mag.* **16**, 570–590 (1840).
- Staudenmaier, L. Verfahren zur Darstellung der Graphitsäure. *Ber. Deut. Chem. Ges.* **31**, 1481 (1898).
- Hummers, W. S. & Offeman, R. E. Preparation of graphitic oxide. *J. Am. Chem. Soc.* **80**, 1339 (1958).
- He, H., Riedl, T., Lerf, A. & Klinowski, J. Solid-state NMR studies of the structure of graphite oxide. *J. Phys. Chem.* **100**, 19954–19958 (1996).
- He, H., Klinowski, J., Forster, M. & Lerf, A. A new structural model for graphite oxide. *Chem. Phys. Lett.* **287**, 53–56 (1998).
- Lerf, A., He, H., Forster, M. & Klinowski, J. Structure of graphite oxide revisited. *J. Phys. Chem. B* **102**, 4477–4482 (1998).
- Cai, W. *et al.* Synthesis and solid-state NMR structural characterization of ¹³C-labeled graphite oxide. *Science* **321**, 1815–1817 (2008).
- Buchsteiner, A., Lerf, A. & Pieper, J. Water dynamics in graphite oxide investigated with neutron scattering. *J. Phys. Chem. B* **110**, 22328–22338 (2006).
- Stankovich, S. *et al.* Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate). *J. Mater. Chem.* **16**, 155–158 (2006).
- Jung, I. *et al.* Simple approach for high-contrast optical imaging and characterization of graphene-based sheets. *Nano Lett.* **7**, 3569–3575 (2007).
- Li, D., Muller, M. B., Gilje, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. *Nature Nanotech.* **3**, 101–105 (2008).
- Boehm, H. P., Clauss, A., Fischer, G. O. & Hofmann, U. Das Adsorptionsverhalten sehr dünner Kohlenstoff-Folien. *Anorg. Allg. Chem.* **316**, 119–127 (1962).
- Boehm, H. P., Eckel, M. & Scholz, W. Über den Bildungsmechanismus des Graphitoxids. *Anorg. Allg. Chem.* **353**, 236–242 (1967).
- Xu, Y., Bai, H., Lu, G., Li, C. & Shi, G. Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets. *J. Am. Chem. Soc.* **130**, 5856–5857 (2008).
- Park, S. *et al.* Aqueous suspension and characterization of chemically modified graphene sheets. *Chem. Mater.* **20**, 6592–6594 (2008).
- Chen, H., Muller, M. B., Gilmore, K. J., Wallace, G. G. & Li, D. Mechanically strong, electrically conductive, and biocompatible graphene paper. *Adv. Mater.* **20**, 3557–3561 (2008).
- Si, Y. & Samulski, E. T. Synthesis of water soluble graphene. *Nano Lett.* **8**, 1679–1682 (2008).
- Eda, G., Fanchini, G. & Chhowalla, M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotechmol.* **3**, 270–274 (2008).
- Wang, X., Zhi, L. & Müllen, K. Transparent, conductive graphene electrodes for dye-sensitized solar cells. *Nano Lett.* **8**, 323–327 (2008).
- Stankovich, S., Piner, R., Nguyen, S. T. & Ruoff, R. S. Synthesis and exfoliation of isocyanate-treated graphene oxide nanosheets. *Carbon* **44**, 3342–3347 (2006).
- Paredes, J. I., Villar-Rodil, S., Martínez-Alonso, A. & Tascón, J. M. D. Graphene oxide dispersions in organic solvents. *Langmuir* **24**, 10560–10564 (2008).
- Stankovich, S. *et al.* Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* **45**, 1558–1565 (2007).
- Tasis, D., Tagmatarchis, N., Bianco, A. & Prato, M. Chemistry of carbon nanotubes. *Chem. Rev.* **106**, 1105–1136 (2006).
- Niyogi, S. *et al.* Solution properties of graphite and graphene. *J. Am. Chem. Soc.* **128**, 7720–7721 (2006).
- Worsley, K. A. *et al.* Soluble graphene derived from graphite fluoride. *Chem. Phys. Lett.* **445**, 51–56 (2007).
- Lomeda, J. R., Doyle, C. D., Kosynkin, D. V., Hwang, W.-F. & Tour, J. M. Diazonium functionalization of surfactant-wrapped chemically converted graphene sheets. *J. Am. Chem. Soc.* **130**, 16201–16206 (2008).
- Tung, V. C., Allen, M. J., Yang, Y. & Kaner, R. B. High-throughput solution processing of large-scale graphene. *Nature Nanotech.* **4**, 25–29 (2008).
- Wang, G. *et al.* Facile synthesis and characterization of graphene nanosheets. *J. Phys. Chem. C* **112**, 8192–8195 (2008).

54. Muszynski, R., Seger, B. & Kamat, P. V. Decorating graphene sheets with gold nanoparticles. *J. Phys. Chem. C* **112**, 5263–5266 (2008).
55. Schniepp, H. C. *et al.* Functionalized single graphene sheets derived from splitting graphite oxide. *J. Phys. Chem. B* **110**, 8535–8539 (2006).
56. McAllister, M. J. *et al.* Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem. Mater.* **19**, 4396–4404 (2007).
57. Williams, G., Serger, B. & Kamat, P. V. TiO₂-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano* **2**, 1487–1491 (2008).
58. Boukhvalov, D. W. & Katsnelson, M. I. Modeling of graphite oxide. *J. Am. Chem. Soc.* **130**, 10697–10701 (2008).
59. Hernandez, Y. *et al.* High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature Nanotech.* **3**, 563–568 (2008).
60. Valles, C. *et al.* Solutions of negatively charged graphene sheets and ribbons. *J. Am. Chem. Soc.* **130**, 15802–15804 (2008).
61. Li, X., Wang, X., Zhang, L., Lee, S. & Dai, H. Chemically derived, ultrasmooth graphene nanoribbon semiconductors. *Science* **319**, 1229–1232 (2008).
62. Li, X. *et al.* Highly conducting graphene sheets and Langmuir–Blodgett films. *Nature Nanotech.* **3**, 538–542 (2008).
63. Hao, R., Qian, W., Zhang, L. & Hou, Y. Aqueous dispersions of TCNQ-anion-stabilized graphene sheets. *Chem. Commun.* 6576–6578 (2008).
64. Liu, N. *et al.* One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite. *Adv. Funct. Mater.* **18**, 1518–1525 (2008).
65. Liu, Z., Robinson, J. T., Sun, X. & Dai, H. PEGylated nanographene oxide for delivery of water-insoluble cancer drugs. *J. Am. Chem. Soc.* **130**, 10876–10877 (2008).
66. Jung, I. *et al.* Effect of water vapor on electrical properties of individual reduced graphene oxide sheets. *J. Phys. Chem. C* **112**, 20264–20268 (2008).
67. Olson, D. W. *Graphite (natural)*. USGS Mineral Commodity Summary 2008, 74–75 (US Geological Survey, 2008); available at <<http://minerals.usgs.gov/minerals/pubs/commodity/graphite/mcs-2008-graph.pdf>>.

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