

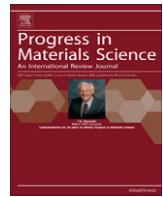


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Chemical functionalization of graphene and its applications

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ABSTRACT

Functionalization and dispersion of graphene sheets are of crucial importance for their end applications. Chemical functionalization of graphene enables this material to be processed by solvent-assisted techniques, such as layer-by-layer assembly, spin-coating, and filtration. It also prevents the agglomeration of single layer graphene during reduction and maintains the inherent properties of graphene. Therefore, a detailed review on the advances of chemical functionalization of graphene is presented. Synthesis and characterization of graphene have also been reviewed in the current article. The functionalization of graphene can be performed by covalent and noncovalent modification techniques. In both cases, surface modification of graphene oxide followed by reduction has been carried out to obtain functionalized graphene. It has been found that both the covalent and noncovalent modification techniques are very effective in the preparation of processable graphene. However, the electrical conductivity of the functionalized graphene has been observed to decrease significantly compared to pure graphene. Moreover, the surface area of the functionalized graphene prepared by covalent and non-covalent techniques decreases significantly due to the destructive chemical oxidation of flake graphite followed by sonication, functionalization and chemical reduction. In order to overcome these problems, several studies have been reported on the preparation of functionalized graphene directly from graphite (one-step process). In all these cases, surface modification of graphene can prevent agglomeration and facilitates the formation of stable dispersions. Surface modified

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graphene can be used for the fabrication of polymer nanocomposites, super-capacitor devices, drug delivery system, solar cells, memory devices, transistor device, biosensor, etc.

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Nomenclature

Acronyms

AFM	atomic force microscopy
ANS	6-amino-4-hydroxy-2-naphthalenesulfonic acid
APTS	3-aminopropyltriethoxysilane
CCG	chemically converted graphene
CCl ₄	carbon tetrachloride
CNT	carbon nanotube
CPT	camptothecin
CR	congo red
CS	chitosan
CTE	coefficient of thermal expansion
CVD	chemical vapor deposition
DA	dodecyl amine
DCM	dichloromethane
DMF	N,N-dimethyl-formamide
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
FT-IR	Fourier transform infrared
GNP ^{IL}	ionic liquid functionalized graphene

GO-CS	chitosan grafted graphene oxide
GO	graphene oxide
GOS	esterified graphene oxide
GS-CR	congo red modified graphene sheet
hKMG	hydrazine hydrate reduced, potassium hydroxide modified graphene oxide
HOPG	highly oriented pyrolytic graphite
HPC-Py	pyrene-containing hydroxypropyl cellulose
HR-TEM	high-resolution transmission electron microscopy
HRP	horseradish peroxide
IL-NH ₂	amine-terminated ionic liquids
IL	ionic liquids
KOH	potassium hydroxide
LTEG	low-temperature exfoliated graphene
MG	methylene green
NaBH ₄	sodium borohydride
NADH	nicotinamide adenine dinucleotide
NMP	N-methylpyrrolidone
O-DCB	ortho dichlorobenzene
ODA-G	octadecyl amine modified graphene
ODA	octadecyl amine
OVA	ovalbumin
PBA	pyrenebutyric acid
PC	polycarbonate
PCA	1-pyrenecarboxylic acid
PE-CVD	plasma-enhanced (PE) chemical vapor deposition
PEG-NH ₂	amine terminated poly(ethylene glycol)
PLL	poly-L-lysine
PNIPAAm	poly(N-isopropylacrylamide)
POA	poly(oxyalkylene) amines
PPESO ₃ ⁻	poly(2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene)
PSS	poly(sodium 4-styrenesulfonate)
PSSA-g-PPY	poly(styrenesulfonic acid-g-pyrrole)
PVA	poly(vinyl alcohol)
PYR-NHS	pyrene-containing hydroxypropyl cellulose
RGO	reduced graphene oxide
SAED	small area electron diffraction
SCMC	sodium carboxymethyl cellulose
SDBS	sodium dodecyl benzene sulfonate
SiC	silicon carbide
SLS	sodium lignosulfonate
SOCl ₂	thionyl chloride
SPANI	sulfonated polyaniline
TCNQ	7,7,8,8-tetracyanoquinodimethane
TEM	transmission electron microscopy
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TPAPAM	triphenylamine-based polyazomethine
TPP-NH ₂	amine-functionalized porphyrin
UV	ultraviolet
XPS	X-ray photoelectron spectra
XRD	X-ray diffraction
β-CD	β-cyclodextrin
ε	molar extinction coefficient

1. Introduction

Graphene is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms densely packed in a honeycomb crystal lattice. It is the mother element of some carbon allotropes, including graphite, carbon nanotubes, and fullerenes (Fig. 1) [1,2]. Naturally occurring graphite has been known as a mineral for nearly 500 years. A large number of experiments focus on the insertion of additional chemical species between the basal planes of graphite [3–5]. Graphene, the building block of graphite, was theoretically established in 1940 [6]. Boehm and co-workers separated thin lamellae of carbon by heating and chemical reduction of graphite oxide in 1962 [7]. However, until 2004, single-layer graphene was believed to be thermodynamically unstable under ambient conditions [8,9]. Geim and co-workers at Manchester University successfully identified single layers of graphene in a simple tabletop experiment in 2004 [10]. This revolutionary discovery has added a new dimension of research in the fields of physics, chemistry, biotechnology, and materials science. The “thinnest” known material graphene exhibits excellent electrical conductivity, mechanical flexibility, optical transparency, thermal conductivity, and low coefficient of thermal expansion (CTE) behavior [10–15]. The unique features of graphene have attracted tremendous interest both in academics and industry. Recently, graphene has been used as alternative carbon-based nanofiller in the preparation of polymer nanocomposites [16–23]. Graphene-based polymer nanocomposites exhibit improved mechanical, thermal, and electrical properties [16–23]. Graphene is expected to play an important role in the fabrication of nano-electronic and bio-electronic devices in near future [2]. Graphene is also capable of replacing metal conductors in electronic and electrical devices due to its excellent electrical conductivity and mechanical flexibility [24–26]. Ongoing research shows that graphene can replace brittle and chemically unstable indium tin oxide in flexible displays and touch screens. Therefore, graphene as an electronic circuit material is

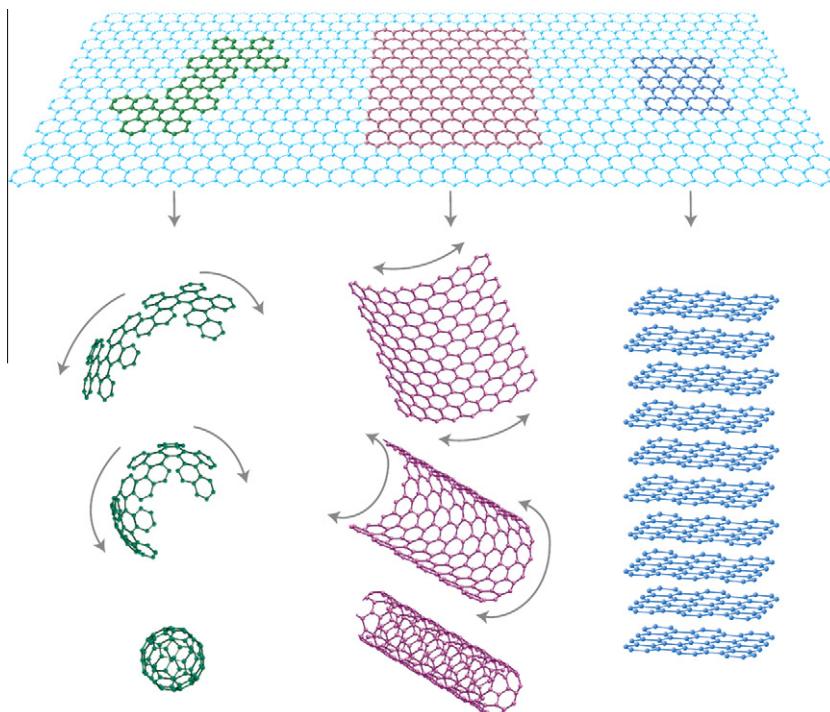


Fig. 1. Basis of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes, or stacked into 3D graphite. (Reproduced with permission from [2].)

considered to be potentially superior to other carbon-based nanofillers [27–29]. It is well established that the superior properties of graphene are associated with its single-layer. However, the fabrication of single-layer graphene is difficult at ambient temperature. Graphene sheets with a high specific surface area tend to form irreversible agglomerates or even restack to form graphite through π - π stacking and van der Waals interactions if the sheets are not well separated from each other [30,31]. Aggregation can be reduced by the attachment of other small molecules or polymers to the graphene sheets. The presence of hydrophilic or hydrophobic groups prevents aggregation of graphene sheets by strong polar-polar interactions or by their bulky size [31,32]. The attachment of functional groups to graphene also aids in dispersion in a hydrophilic or hydrophobic media, as well as in the organic polymer. The use of pristine graphene in nanoelectronic devices (especially for transistor purposes) is also not suitable for practical applications. Graphene based field effect transistors cannot be turned off effectively due to the absence of a band gap in pristine graphene [33]. Therefore, the problems associated with the band gap of pristine graphene should be solved before using the material as a transistor [34]. The controlled functionalization of graphene with electron-donating or electron-withdrawing groups (*n*-doping or *p*-doping) can be achieved very easily [34]. The molecular level doping of graphene via charge transfer between electron donor and electron acceptor molecules gives rise to significant changes in the electronic structure of graphene, as evidenced by changes in the Raman and photoelectron spectra [34–36]. Therefore, an efficient approach to the production of surface-functionalized graphene sheets in large quantities has been a major focus of many researchers, with the goal of exploiting the most frequently proposed applications of graphene in the areas of polymer nanocomposites, super-capacitor devices, drug delivery systems, solar cells, memory devices, transistor devices, biosensors etc.

A general review on the synthesis, characterization, properties, and applications of graphene is given by Singh et al. [1]. It describes a detailed overview of the synthesis of graphene by mechanical exfoliation of graphite, chemical vapor deposition (CVD), and chemical approaches. The application of functionalized graphene in various areas has also been suggested. In the present review, we present an updated overview that focuses on the procedures of surface modification, characterization, properties, and applications of functionalized graphene. Depending on the nature of chemical reactions occurring between the graphene oxide (GO) and organic modifier, a classification of the chemical functionalization of graphene has been presented in the present review. This article also provides a short review of graphene synthesis and different characterization techniques used to identify single-layer graphene. Extensive research has been carried out on the surface modification of graphene. However, limitations with respect to dispersibility, electrical conductivity, and the complications in the experimental procedures have been encountered. The present article discusses different surface treatment processes, such as covalent and non-covalent functionalization techniques, stabilization in ionic medium, and *in situ* surface treatments starting from graphite. This article also highlights present and future trends for application of surface-modified graphene.

2. Synthesis of graphene

In 2004, graphene was initially isolated by mechanical exfoliation of small mesas of pyrolytic graphite [10]. However, this method is not suitable for the large-scale production of graphene necessary to fulfill the requirements in different areas. In order to overcome this shortcoming, several synthetic methods for graphene have been reported in the literature [11,37–39]. These methods include exfoliation and cleavage of natural graphite, CVD, plasma enhanced CVD (PE-CVD), electric arc discharge, epitaxial growth on electrically insulating surfaces such as silicon carbide (SiC), un-zipping of carbon nanotubes (CNTs), and solution-based reduction of GO [30,37]. Among all these processes, large-area, single-layer graphene synthesized with the CVD method [24,25,40,41]. Recently, Li et al. have demonstrated the synthesis of graphene by CVD using centimeter-scale copper substrates [24]. Sun et al. have synthesized graphene by CVD from solid poly(methyl methacrylate) deposited onto a Cu substrate [41]. Kim et al. have prepared graphene films on a Ni substrate to use as transparent electrodes in flexible, stretchable, and foldable electronics (Fig. 2) [25]. Dato et al. have synthesized single-layer graphene using ethanol vapor and argon plasma inside a microwave-assisted plasma

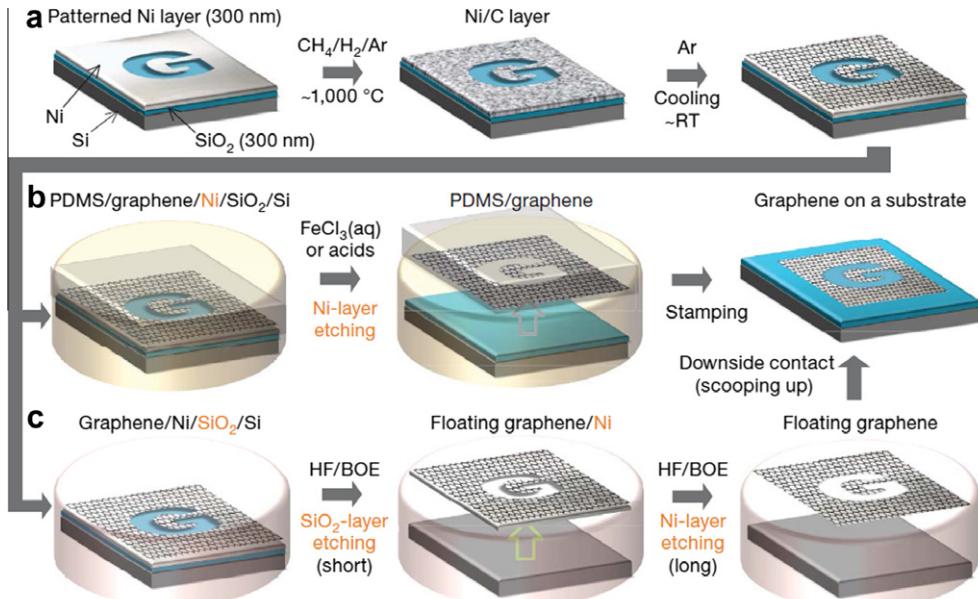


Fig. 2. Synthesis, etching, and transfer processes for large-scale and patterned graphene films: (a) Synthesis of patterned graphene films on thin nickel layers. (b) Etching using FeCl_3 (or acids) and transfer of graphene films using a PDMS stamp. (c) Etching using BOE or hydrogen fluoride (HF) solution and transfer of graphene films. (Reproduced with permission from [25].)

reactor [42]. Recently, Bae et al. have reported on roll-to-roll production and wet-chemical doping of predominantly monolayer 30-in. graphene films grown by CVD onto flexible copper substrates (Fig. 3) [26]. Compared to other CVD methods, the most important criterion for this method is described as the substrate-free synthesis of graphene. Dong et al. have prepared graphene from graphite flake by using 1,3,6,8-pyrenetetrasulfonic acid and heavy water [43]. It has also been found that graphene can be prepared on an H₂ etched surface of 6H-SiC when heated to a temperature of 1250–1450 °C for a short time (1–20 min) [44]. Vales et al. have prepared a homogeneous colloidal suspension of graphene sheets or ribbons by stirring the ternary potassium salt $K(\text{THF})_x\text{C}_{24}$ (graphite intercalation compound) in N-methylpyrrolidone (NMP) (Fig. 4). The thickness of the sheets or ribbons (length, ~40 mm) has been found to be 0.35–0.4 nm [45]. Hernandez et al. have prepared single-layer graphene by liquid-phase exfoliation of graphite in NMP. The exfoliation of graphite to a single layer has been verified by transmission electron microscopy (TEM) and Raman spectroscopy. However, the lower yield of each of these methods limits their application for mass production [46]. The chemical oxidation-reduction method has been found to be the best and most economic for the mass production adopted by most researchers.

3. Characterization of single-layer graphene

The unique properties of graphene are all associated with monolayer graphene. It has been reported that bi- or trilayer graphene does not demonstrate significant differences in electrical conductivity or mechanical flexibility, to that of the monolayers graphene, except lowering the but optical transparency [41,47]. Therefore, identification of single-layer graphene from a multilayer is a crucial step for its future application. There are different characterization techniques for the identification of graphene, but this section focuses only on the characterization of single-layer graphene. In this regard, TEM, ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM), Raman spectroscopy, and electrical conductivity will be discussed in detail.

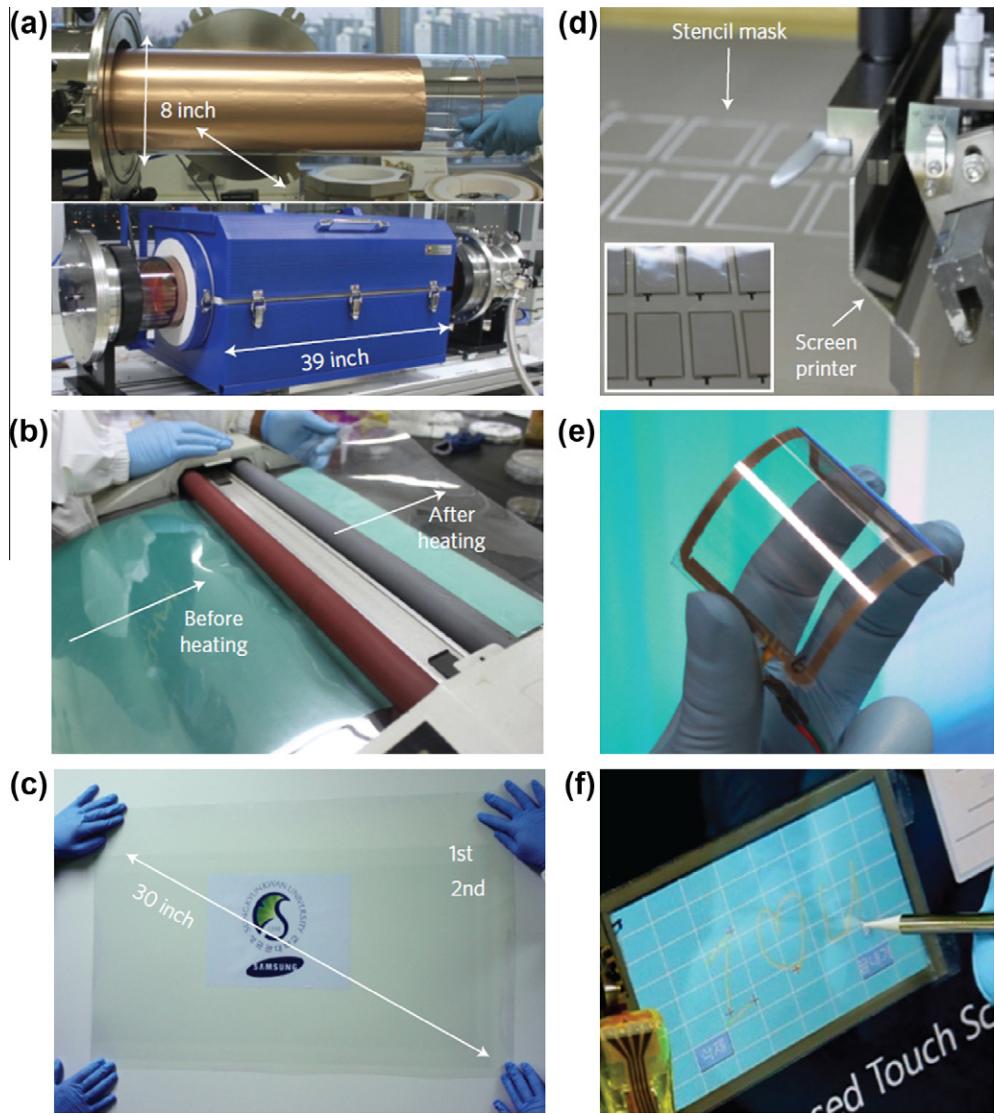


Fig. 3. Photographs of the roll-based production of graphene films: (a) copper foil wrapping around a 7.5-in. quartz tube to be inserted into an 8-in. quartz reactor. The lower image shows the stage at which the copper foil reacts with CH_4 and H_2 gases at high temperature. (b) Roll-to-roll transfer of graphene films from a thermal release tape to a PET film at 120 °C. (c) A transparent ultra-large-area graphene film transferred onto a 35-in. PET sheet. (d) Screen printing process of silver paste electrodes on a graphene/PET film. The inset shows 3.1-in. graphene/PET panels patterned with silver electrodes before assembly. (e) An assembled graphene/PET touch panel showing outstanding flexibility. (f) A graphene-based touch-screen panel connected to a computer with control software. For a movie of its operation, see Supplementary information. (Reproduced with permission from [26].)

3.1. UV-visible spectroscopy

The strictly two-dimensional graphene exhibits an absorption peak at around 262 nm, while a single-layer of GO shows absorption at 230 nm in the UV-visible spectrum. This is attributed to the $\pi-\pi^*$ transitions of aromatic C–C bonds. Fig. 5 shows that the transparency of GO is much higher than that

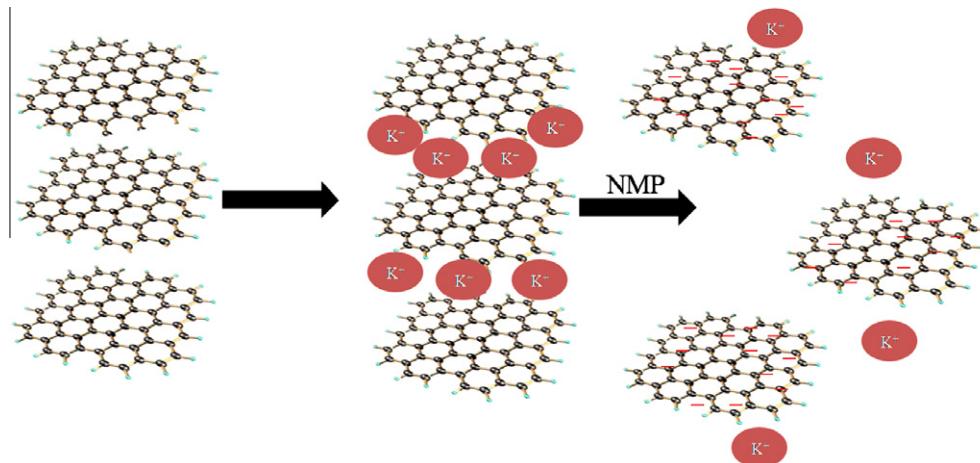


Fig. 4. Schematic diagrams of graphene preparation from a graphite intercalation compound.

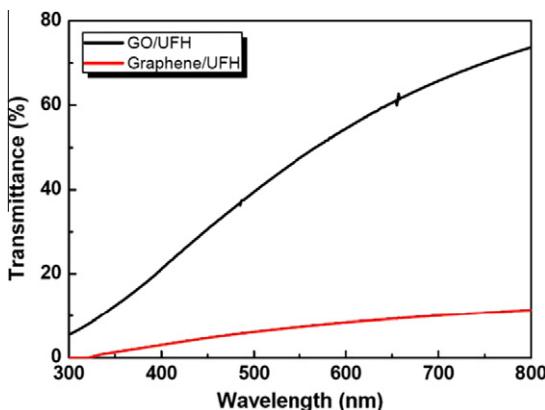


Fig. 5. UV-visible spectra of GO/unfractionated heparin (UFH) and graphene/UFH solution in water. (Reproduced with permission from [49].)

of graphene [48,49]. This decrease in transmittance originates from the recovery of sp^2 carbons from chemically reduced graphene after reduction [49]. This is an indication of the restoration of electronic conjugation in reduced graphene. In addition, the transparency of stacked graphene is much lower than that of the monolayer graphene. Sun et al. have reported that monolayer graphene shows transmittance of 97.1% at a wavelength of 550 nm. The transmittance ($\lambda = 550$ nm) of bilayer graphene is 94.3%, which shows linear enhancement in the ultraviolet absorption (Fig. 6). Graphene with six-layer thickness has a transmittance of 83% at a similar wavelength [41]. Therefore, analysis of UV-visible results provides both a tentative idea about graphene formation and the number of layers.

3.2. X-ray diffraction

Although XRD is not a perfect tool for identifying single-layer graphene, it is very informative. Pristine graphite exhibits a basal reflection (002) peak at $2\theta = 26.6^\circ$ (d spacing = 0.335 nm) in the XRD pattern. Upon oxidation of pristine graphite, the 002 reflection peak shifts to a lower angle at $2\theta = 11.2^\circ$ (d spacing = 0.79 nm). This increase in d spacing is due to the intercalation of water molecules and gen-

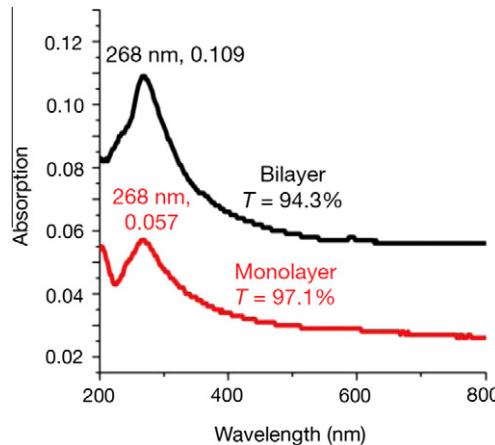


Fig. 6. The UV-visible absorption spectra of monolayer graphene and bilayer graphene; peaks are labeled with the wavelength of maximum absorption and the value of maximum absorption. The UV transmittance (T , %) is measured at 550 nm. (Reproduced with permission from [41].)

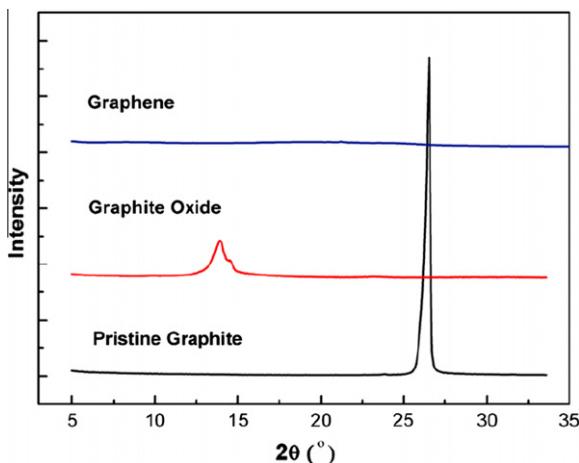


Fig. 7. X-ray diffraction patterns of pristine graphite, graphite oxide, and graphene. (Reproduced with permission from [50].)

eration of oxygen functionality in the interlayer spacing of graphite. When graphite oxide is completely exfoliated to a single layer of GO, a straight line with no apparent diffraction peak in the XRD pattern is obtained (Fig. 7). The XRD pattern of single-layer graphene is exactly the same to that of single-layer GO, indicating that the periodic structure of graphite has been eliminated and that it has been completely exfoliated into individual sheets [50].

3.3. Atomic force microscopy

AFM is currently one of the foremost methods used in definite identification of single-layer graphene. It has been reported in the literature that the thickness of single-layer graphene is in the range of 0.34–1.2 nm (Fig. 8a–c). The abnormally low thickness of graphene is due to the complete exfoliation of the graphitic structure into single-layer graphene [51–53].

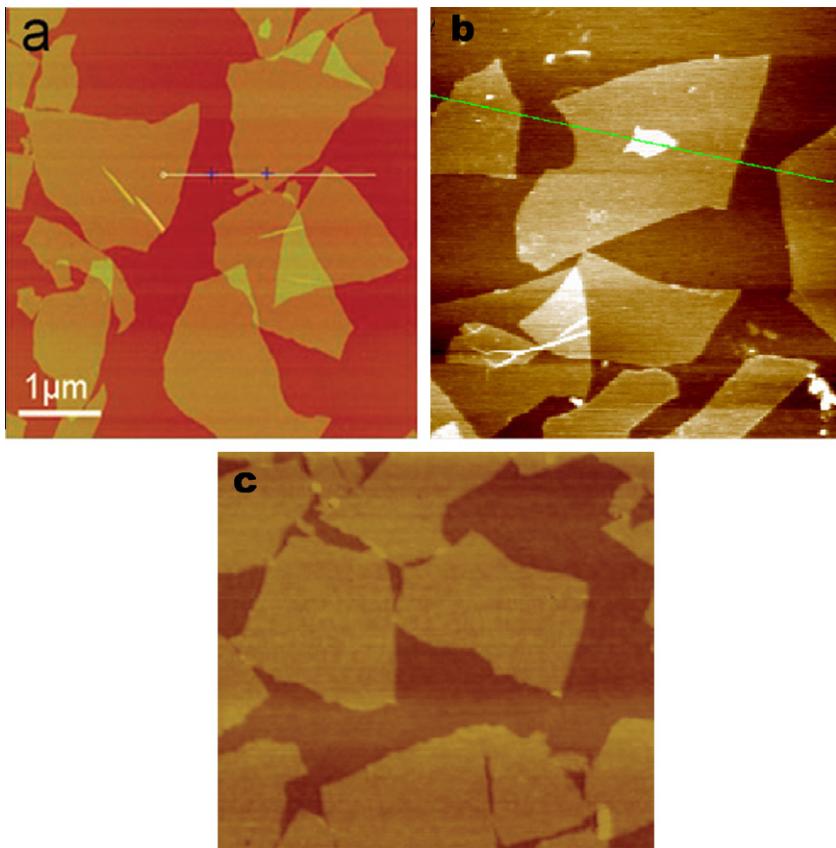


Fig. 8. Typical AFM images of (a) L-ascorbic acid and (b and c) hydrazine-reduced graphene sheets. (Reproduced with permission from [30,51,52].)

3.4. Transmission electron microscopy

Transmission electron microscopy analysis accurately confirms the thickness of a graphene sample. As reported by Hernandez et al. by analyzing a large number of TEM images and paying close attention to the uniformity of the sample, one can generate flake thickness statistics [46]. The appearance of stable and transparent graphene sheets in the TEM analysis indicates the presence of single-layer graphene. The edges of the suspended film always fold back, allowing for a cross-sectional view of the film (Fig. 9a–f). The observation of these edges by high resolution TEM provides an accurate way to measure the number of layers at multiple locations on the film [40]. A folded graphene sheet is locally parallel to the electron beam. For monolayer graphene, one fold appears as only one dark line [54]. For bilayer graphene, two dark lines should appear. A more definitive identification of graphene can be made by the analysis of small area electron diffraction (SAED) patterns. Hernandez et al. successfully described the SAED pattern of monolayer and bilayer graphene [46]. Fig. 9(a–e) shows the TEM images of monolayer and bilayer graphene and their corresponding SAED patterns. The SAED pattern of monolayer graphene (Fig. 9e) exhibits the typical sixfold graphene symmetry.

3.5. Raman spectroscopy

Raman spectroscopy provides a quick and simple structural and quality characterization of graphene. Graphene derived from the chemical oxidation–reduction method shows extensive defects, while

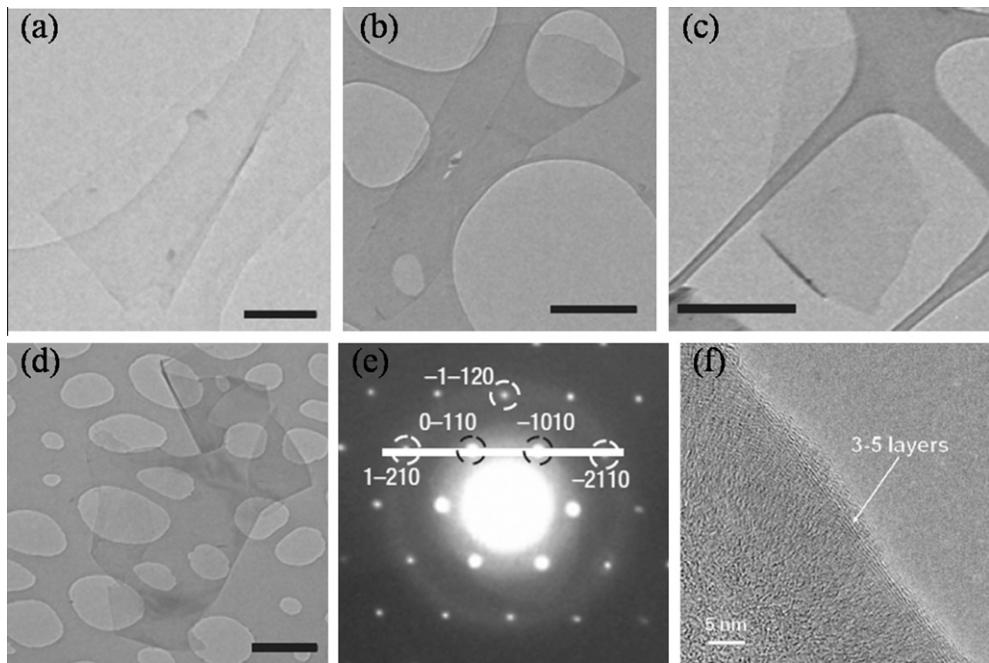


Fig. 9. (a–f) TEM and HR-TEM image of graphene (reproduced with permission from [46].)

graphene prepared by CVD, liquid phase production, and micromechanical cleavage of graphite exhibits no defects [10,40–42,46,55,56]. Chemically reduced graphene exhibits a peak at *ca.* 1576 cm⁻¹ (G band) corresponding to the doubly degenerate zone center E_{2g} mode. It is related to the vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice. However, the peak at *ca.* 1326 cm⁻¹ (D band) is characteristic of defects and disorders of chemically reduced graphene sheets. In contrast, Raman spectra of graphite and graphene prepared by other methods exhibit a band at *ca.* 1580 cm⁻¹ (G band) and a band at 2700 cm⁻¹ (2D band). The second order zone boundary phonon, 2D band, does not satisfy the Raman fundamental selection rule and is not seen in defect-rich graphene [57]. Such phonons give rise to a peak at *ca.* 1326 cm⁻¹. However, this type of D band is absent in the center of defect-free graphene. The 2D band of monolayer graphene shows a single sharp peak, while in graphite this band consists of two peaks. Moreover, the G band intensity of monolayer graphene is lower than that of bi-, tri-, or multi-layer graphene. G band intensity increases almost linearly with an increase in number of layers, as is evident in Fig. 10 [58]. Bilayer graphene has a much broader and up-shifted 2D band relative to monolayer graphene. Ferrari et al. have acquired Raman spectra at 514.5 nm and 633.0 nm excitations in order to identify graphene up to five layers. It has been deduced that Raman spectroscopy could clearly distinguish between a single layer, bilayer, and several layers (<5 layers) [59].

4. Chemical and physical properties of graphene

Two-dimensional graphene is an allotrope of carbon in which each carbon atom is bonded with another carbon by sp² bonds. The carbon atoms are densely packed in a honeycomb crystal lattice with a bond length of 0.141 nm. Different research groups have measured the thickness of graphene from 0.35 nm to 1.00 nm [60]. Novoselov et al. have determined platelet thicknesses of 1.00–1.60 nm [10]. Gupta et al. have measured the film thickness of single layer graphene by AFM as 0.33 nm [61]. The breaking strength of graphene is 200 times higher than steel, making it the strongest mate-

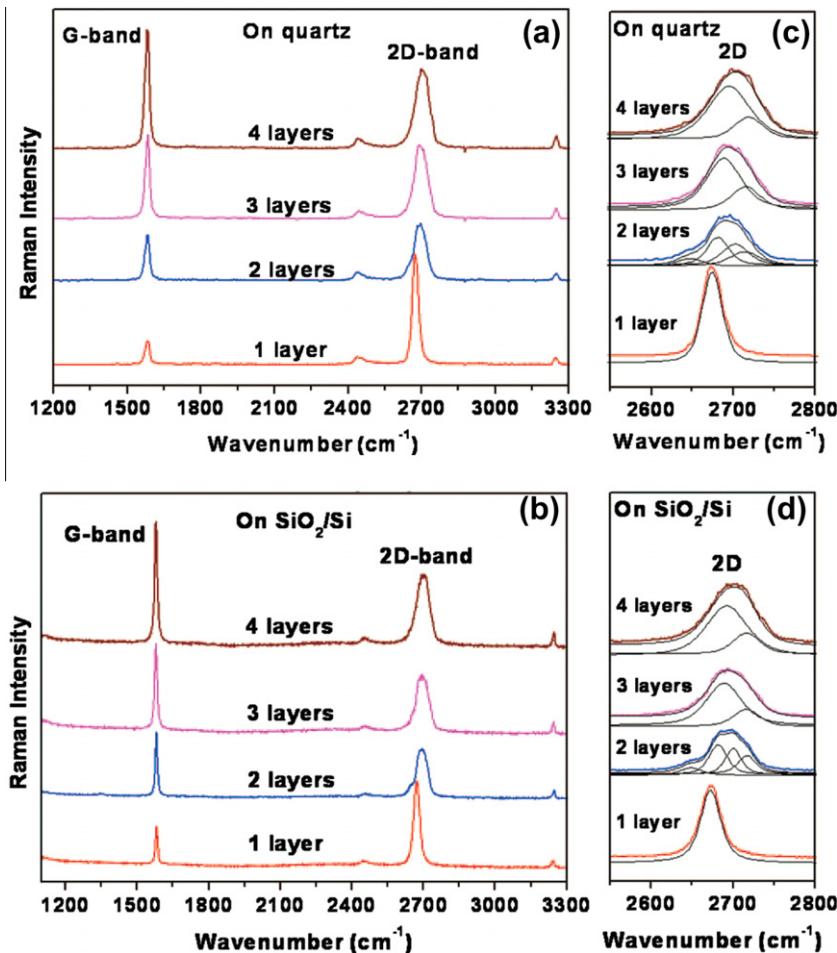


Fig. 10. The Raman spectra of monolayer, bilayer, tri-layer, and four-layer graphene on quartz (a) and SiO₂ (300 nm)/Si substrate (b). The enlarged 2D-band regions with the curve fit are shown in panels c and d. (Reproduced with permission from [58].)

rial ever tested. According to Kudin et al., the Young's modulus and Poisson's ratio for graphene are 1.02 TPa and 0.149, respectively [62]. Graphene is a zero band gap semiconductor, where the charge carriers have a linear dispersion relationship near the Dirac point, essentially giving them zero effective mass [10,63]. Room temperature electrical conductivity of graphene is 7200 S m⁻¹ with mobilities of $\sim 200,000$ cm² V s⁻¹. The room temperature thermal conductivity values have been determined to be $\sim (4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$ W mK⁻¹ for single-layer graphene [64]. The detailed chemical reactivity of graphene has been explained by Loh et al. in their feature article [34]. Graphene is aromatic in nature possessing highly dense electron cloud both above and below the plane. The frontier molecular orbitals of organic molecules can easily interact with the π -electrons of graphene. Therefore, electrophilic substitution of graphene is much easier than nucleophilic substitution. Graphene can take part in certain classes of reactions including cyclo-additions, click reactions, and carbene insertion reactions [34]. However, reactions on the surfaces of graphene hamper its planar structure. The destruction of the sp² structure leads to the formation of defects and loss of electrical conductivity. According to Loh et al., the chemical reactivity of geometrically strained regions of graphene lattices is much higher in comparison with other regions [34]. This is attributed to the easier displacement of

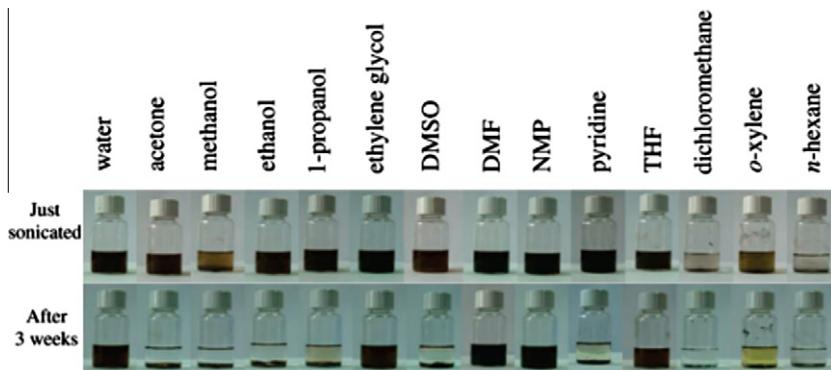


Fig. 11. Digital pictures of as-prepared graphite oxide dispersed in water and 13 organic solvents through bath ultrasonication (1 h). Top: Dispersions immediately after sonication. Bottom: Dispersions three weeks after sonication. The yellow color of the o-xylene sample is due to the solvent itself (reproduced with permission from [68].)

electron density from the upper plane of the ring. It has also been found that the zig-zag edges of graphene display higher chemical reactivity compared to arm-chair edges; this is because, the formation of aromatic sextets is perturbed in the zig-zag edges, leading to thermodynamic instability [34].

5. Chemical functionalization of graphene

Until the 1980s, the carbon family was limited to the well-known materials graphite and diamond. This has totally changed with the discovery of molecular carbon allotropes – fullerenes, CNT, and recently, 2-D graphene [65]. Among these carbonaceous materials, graphene has attracted tremendous research interest due to its unique structural features and outstanding performance. Moreover, the production cost of graphene is very low in comparison to other carbon-based nanomaterials. Therefore, there has been increasing interest in the scientific community in investigating different aspects, particularly the surface modification of graphene. Functionalization and dispersion of graphene sheets are of crucial importance in their applications. Chemically functionalized graphene can be processed further by solvent-assisted techniques, such as layer-by-layer assembly, spin-coating, and filtration. Proper chemical functionalization of graphene also prevents the agglomeration of single layer graphene during reduction in solvent phase and helps to maintain the inherent properties of graphene. GO has been used widely as a starting material for the synthesis of processable graphene. There are different methods for production of GO from natural graphite; the modified Hummers method is very fruitful in preparing GO [39,66]. The surfaces of GO sheets are highly oxygenated, bearing hydroxyl, epoxide, diol, ketone, and carboxyl functional groups that can alter the van der Waals interactions significantly and lead to a range of solubility in water and organic solvents as shown in Fig. 11 [11,18,39,67–70]. The presence of additional carbonyl and carboxyl groups located at the edge of the sheets makes GO sheets strongly hydrophilic, allowing them to readily swell and disperse in water [71,72]. Based on these oxygen functionalities, different model structures of GO (Fig. 12) have been proposed in the literature [69,70,73].

In order to prepare graphene, the reduction of GO is carried out chemically, thermally, or photo-chemically. However, the reduction of GO dispersion without stabilizer leads to precipitation of graphite particles due to the rapid, irreversible aggregation of graphene sheets. Therefore, prior to reduction, surface modification of GO sheets is usually carried out by covalent modifications or non-covalent functionalizations, followed by reduction [74]. In a typical procedure, reduction of alkylamine-modified GO produces stable dispersions of functionalized graphene sheets in organic solvents. Water-dispersible graphene sheets can be obtained by inducing carboxylic or sulfonate groups on the basal planes of graphene [22,32,75]. However, attempts have also been made to synthesize dispersible graphene directly from natural graphite [77–80]. Ionic liquid modified graphene has been prepared

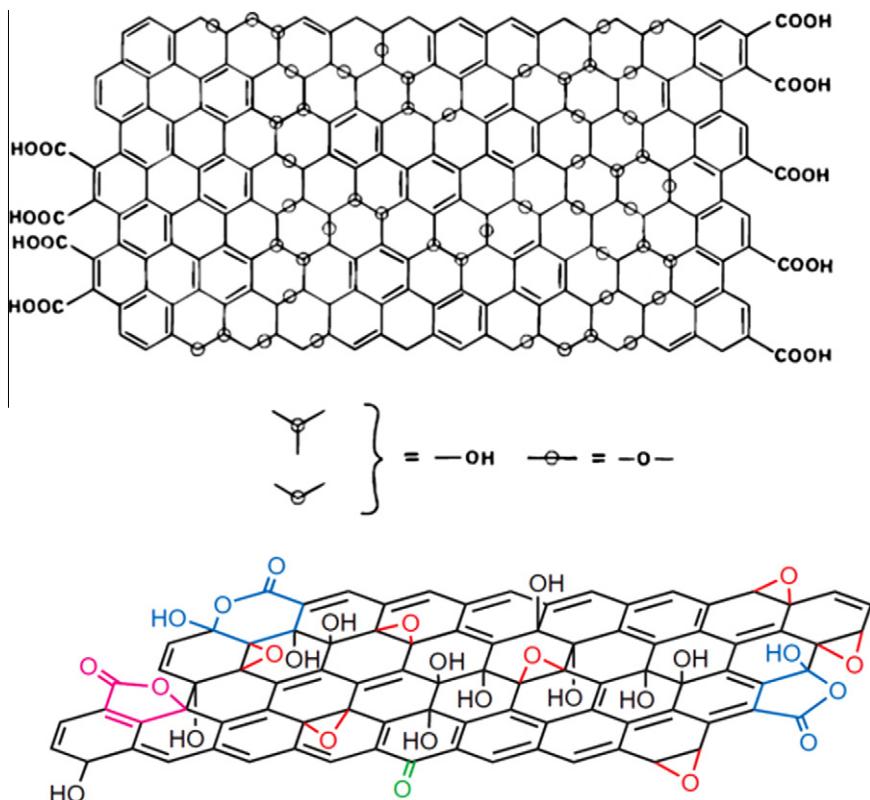


Fig. 12. Variations of the Lerf-Klinowski model indicating ambiguity regarding the presence (top, adapted from Ref. [69]) or absence (bottom, adapted from Ref. [70]) of carboxylic acids on the periphery of the basal plane of GO graphitic platelets. (Reproduced with permission from [70].)

electrochemically from natural graphite [77]. Several other methods have also been reported for the preparation of stable dispersion of non-functionalized graphene with high yields [79].

5.1. Covalent modification

This section exclusively deals with the covalent functionalization of a graphene framework. The structural alteration can take place at the end of the sheets and/or on the surface. Surface functionalization is associated with rehybridization of one or more sp^2 carbon atoms of the carbon network into the sp^3 configuration accompanied by simultaneous loss of electronic conjugation [65]. The covalent modification of graphene can be achieved in four different ways: nucleophilic substitution, electrophilic addition, condensation, and addition [80–126]. Table 1 shows different kinds of covalent modification of GO using different modifying agents, their dispersion stability in various solvents, dispersibility, and electrical conductivity.

5.1.1. Nucleophilic substitution reaction

The main reactive sites in the nucleophilic substitution reaction are the epoxy groups of GO. The amine ($-NH_2$) functionality of the organic modifiers bearing a lone pair of electrons attacks the epoxy groups of the GO. In comparison to other methods, nucleophilic substitution occurs very easily, also at room temperature and in an aqueous medium. Therefore, this method has been considered to be a promising method for large-scale production of functionalized graphene. All types of aliphatic and

Table 1

Different kinds of covalent modification of GO using different modifying agents, their dispersion stability in various solvents, dispersibility, and electrical conductivity.

Modification techniques	Modifying agent	Dispersing medium	Dispersibility (mg ml^{-1})	Electrical conductivity (S m^{-1})	Refs.
Nucleophilic substitution	Alkyl amine/amino acid	CHCl_3 , THF, toluene, DCM	–	–	[75]
	4-Aminobenzene sulfonic acid	Water	0.2	–	[89]
	4,4'-Diaminodiphenyl ether	Xylene, methanol	0.1	–	[89]
	POA	THF	0.2	–	[88]
	Allylamine	Water, DMF	1.55	–	[90]
	APTS	Water, ethanol, DMF, DMSO	0.5	–	[87]
	IL-NH ₂	Water, DMF, DMSO	0.5	–	[86]
	PLL	Water	0.5	–	[31]
	Dopamine	Water	0.05	–	[85]
	Polyglycerol	Water	3	–	[93]
Electrophilic substitution	Poly(norepinephrine)	Water, methanol, acetone, DMF, NMP, THF, toluene	0.1	–	[82]
	ANS	Water	3	145	[94]
	4-Bromo aniline	DMF	0.02	–	[97]
	Sulfanilic acid	Water	2	1250	[32]
Condensation reaction	NMP	Ethanol, DMF, NMP, PC, THF	0.2–1.4	21,600	[99]
	Organic isocyanate	DMF, NMP, DMSO, HMPA	1 (DMF)	–	[18,102]
	Organic diisocyanate	DMF	–	1.9×10^{-4}	[103]
	ODA	THF, CCl_4 , 1,2-dichloroethane	0.5 (THF)	–	[104]
	TMEDA	THF	0.2	–	[105]
	PEG-NH ₂	Water	1	–	[106]
	CS	Water	2	–	[107]
	TPAPAM	THF	–	–	[110]
	β -CD	Water, acetone, DMF	1 (DMF)	–	[111]
	α -CD, β -CD, γ -CD	Water, ethanol, DMF, DMSO	>2.5	–	[112]
	PVA	Water, DMSO	–	–	[113]
	TPP-NH ₂	DMF	–	–	[114]
	Adenine, cystine, nicotamide, OVA	Water	0.1	–	[117]
Addition reaction	POA	THF	0.2	–	[88]
	Polyacetylene	Ortho dichlorobenzene (O-DCB)	0.1	–	[124]
	Aryne	DMF, O-DCB	0.4	–	[125]
	Cyclopropanated malonate	Toluene, O-DCB, DMF, DCM	0.5	–	[126]

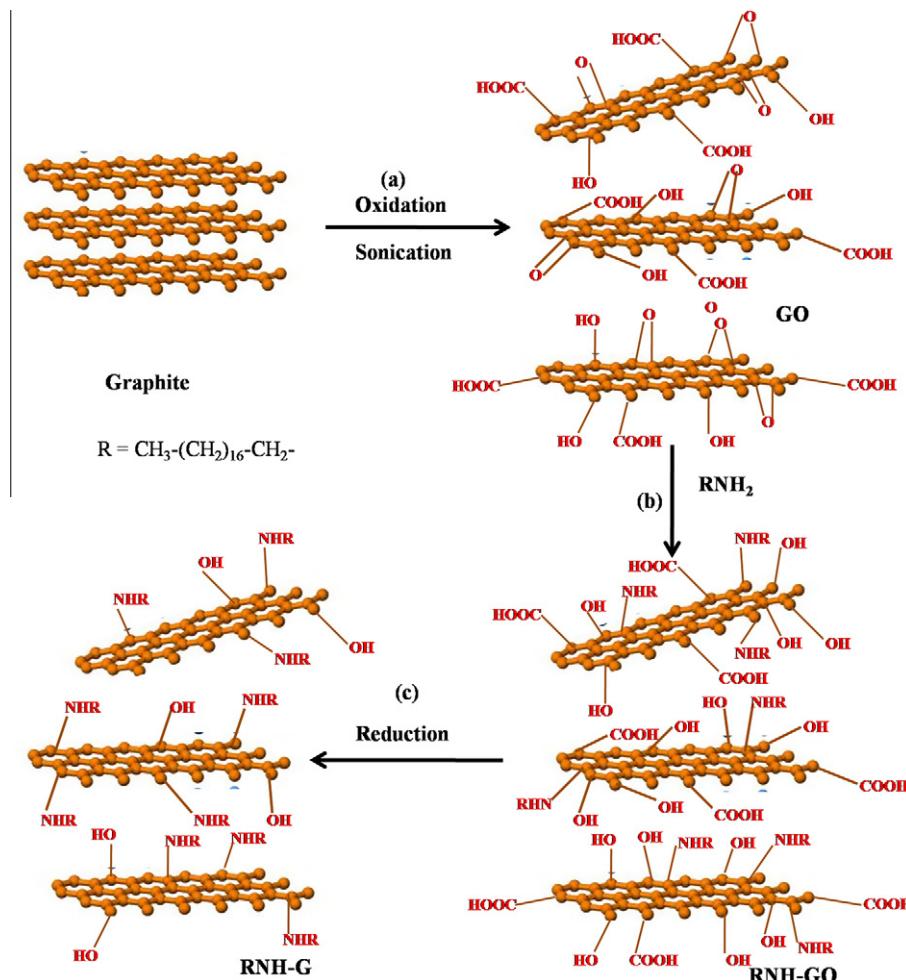


Fig. 13. A simple route for the preparation of functionalized graphene sheets from graphite: (a) Oxidation of natural flake graphite to graphite oxide, followed by ultrasonication; (b) an aqueous GO dispersion is treated with alkylamine to obtain amine-modified GO (RNH-GO); (c) RNH-GO is reduced using hydrazine to produce amine-modified graphene (RNH-G).

aromatic amines, amino acids, amine terminated biomolecules, ionic liquids, small molecular weight polymers, and silane compounds have been successfully used in the preparation of functionalized graphene [22,31,75,81–94].

Bourlinos et al. have used different primary amines, $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ ($n = 2, 4, 8, 12, 18$), and amino acids in the surface treatment of graphite oxide [75]. For small-chain primary amines, $\text{C}_n\text{H}_{2n+1}\text{NH}_2$ ($n = 2, 4, 8, 12$), grafting is completed at room temperature. Conversely, for long-chain aliphatic amines ($n = 18$), the reaction mixture is heated under reflux for 24 h. However, later GO derivatives can be more easily dispersed in organic solvents. XRD analysis showed that the interlayer distance of the amine-intercalated graphite oxide derivatives depends on the amine chain lengths and their orientation relative to the layers [75,76]. According to Bourlinos et al., the tilted orientation is more likely to be due to the hydrophilic nature of graphite oxide [75]. The reaction between the amino acids and graphite oxide occurs in the alkaline solution of amino acids. In this case, nucleophilic attack of the $-\text{NH}_2$ end group takes place on the epoxide groups of graphite oxide. XRD analysis suggests that the amino acid molecules adopt a flat orientation in the interlayer zone of graphite oxide. Kuila

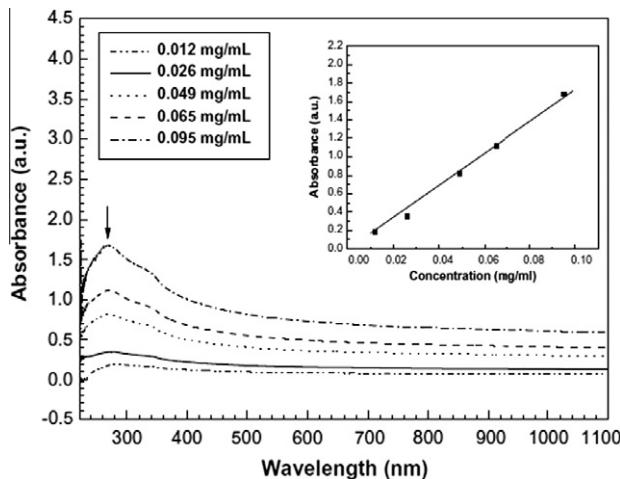


Fig. 14. UV-visible spectra of GNS-ODA sheets dissolved in THF solvent at different concentrations. The inset shows the linear relationship between the absorbance at 260 nm and the concentration of GNS-ODA. (Reproduced with permission from [13].)

Table 2

Mechanical properties of unmodified and PAA-modified GO paper samples^a (reproduced with permission from [84].)

Samples	E_1 (GPa)	E_S (GPa)	E_E (GPa)	σ (MPa)	ε (%)
GO	5.8 ± 1.4	16.6 ± 2.2	25.6 ± 1.1	81.9 ± 5.3	0.40 ± 0.03
PAA-modified GO	11.3 ± 3.2	25.5 ± 3.9	33.3 ± 2.7	91.9 ± 22.4	0.32 ± 0.08

^a E_1 = modulus in the initial region where loading is started; E_S = modulus at $\sigma = 10$ MPa in the straightening region; E_E = maximum modulus in the linear region.

et al. and Wang et al. have also used dodecyl amine (DA) and octadecyl amine (ODA) for the synthesis of organophilic graphene [13,22]. Both of these studies are in good agreement with the study of Bourlinos et al. [75]. Fig. 13 is a schematic depiction of the preparation of alkyl amine-modified graphene. According to Kuila et al., the thickness of DA-modified graphene was found to be *ca.* 1.5 nm; it was also found to be highly soluble in toluene [22]. Wang et al. showed that octadecyl amine modified graphene (ODA-G) is soluble in various organic solvents, such as tetrahydrofuran (THF), cyclohexane, toluene, N,N-dimethyl-formamide (DMF), and ethanol. Quantitative determination of solubility by UV-visible analysis showed that the molar absorption coefficient (ε) of ODA-G in THF is $18.37 \text{ mL mg}^{-1}\text{cm}^{-1}$ (Fig. 14) [13].

Shen et al. have prepared hydrophilic and organophilic GO through a two-step diimide-activated amidation [89]. Esterification of GO is performed by a standard process similar to the esterification of CNT [92]. Further modification of this esterified graphene oxide (GOS) is carried out using 4-amino-benzenesulfonic acid and 4,4'-diaminodiphenyl ether. Attachment of 4-aminobenzenesulfonic acid on the GOS surface leads to the formation of hydrophilic graphene. In contrast, 4,4'-diaminodiphenyl ether-modified graphene is highly dispersible in xylene and methanol. AFM analysis clearly revealed that the thickness of 4-aminobenzenesulfonic acid-modified graphene is higher than that of GOS. This is attributed to the adsorption of 4-aminobenzenesulfonic acid on the GOS surface. Hsiao et al. have prepared functionalized graphene by reacting poly(oxyalkylene) amines (POA) with the residual epoxy functionality of GO [88].

Wang et al. prepared hydrophilic GO sheets using a solvothermal method [90]. An aqueous GO dispersion reacts with allylamine in a Teflon-lined autoclave at 90 °C for 0.5–2 h. The hydrophilic affinity of GO sheets can be effectively enhanced by the reaction with allylamine. The maximum solubilities of GO and allylamine-functionalized GO in water were determined to be 0.69 and

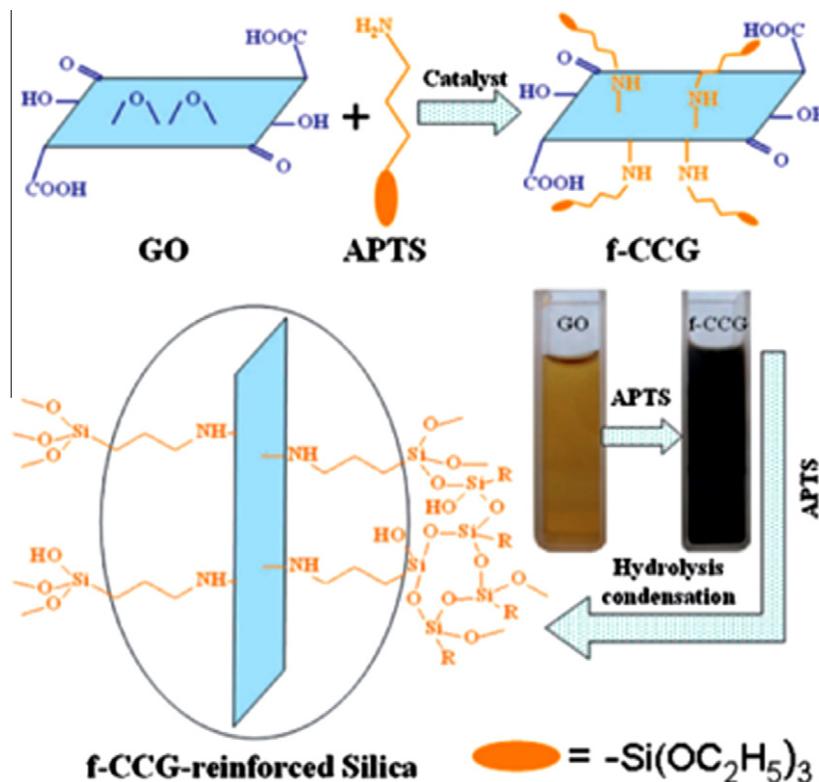


Fig. 15. Illustration of the reaction between GO and 3-aminopropyltriethoxysilane (APTS) and incorporation of f-CCG sheets into the silica matrix. R = —OH or —CH₂(CH₂)₂NH₂. (Reproduced with permission from [87].)

1.55 mg ml⁻¹, respectively. Park et al. prepared a homogeneous colloidal suspension of GO sheets chemically cross-linked with polyallylamine in an aqueous medium [84]. Chemical analysis using X-ray photoelectron spectra (XPS) and Fourier transform infrared (FT-IR) spectra suggests that the GO is cross-linked through the epoxy groups of the GO sheets. Thin films of the samples were made by simple filtration of cross-linked GO sheets. Table 2 shows that the stiffness and strength of cross-linked GO sheets are higher than those of the unmodified GO paper.

Chemically converted graphene (CCG) sheets were prepared via facile covalent functionalization with 3-aminopropyltriethoxysilane (APTS) [87]. CCG can be homogeneously dispersed into water, ethanol, DMF, dimethyl sulfoxide (DMSO), and APTS. A schematic illustration of the formation of APTS-functionalized graphene is shown in Fig. 15. The resulting functionalized-CCG sheets were characterized well and employed as reinforcing components in silica monoliths. Fig. 16 shows the stress-strain plot of neat APTS and f-CCG-reinforced APTS monoliths. It is noteworthy that CCG (0.1 wt.% loading)-reinforced APTS exhibits 19.9% and 92% improvements in failure strength and toughness compared to the neat APTS. This can be attributed to the favorable interfacial interactions between the CCG sheets and APTS due to the potential for covalent bonding with the matrix.

Yang and coworkers have used amine-terminated ionic liquids (IL-NH₂) for the functionalization of graphene sheets [86]. The functionalization proceeds through a nucleophilic ring-opening reaction between the epoxy groups of GO and the amine groups of IL-NH₂, as shown in Fig. 17. CCG disperses well in water, DMF, and DMSO due to the enhanced solubility and electrostatic inter-sheet repulsion provided by the ionic liquid units. Dispersions of CCG are stable for more than 3 months. Moreover, CCG is potentially an interesting starting material for the preparation of composites, precursor for metallic nanoparticles, which may have applications in various fields.

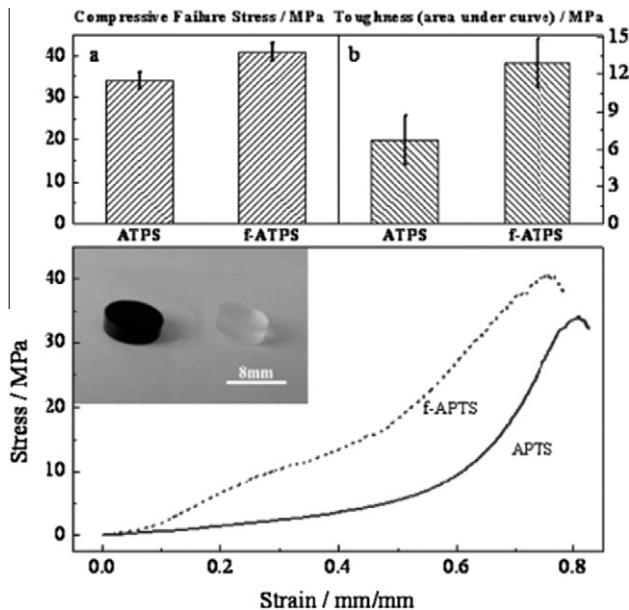


Fig. 16. Stress–strain plots of neat APTS monolith (solid) and f-CCGs-reinforced APTS monolith (dotted) and a summary of the mechanical properties of monoliths, including (a) compressive failure stress and (b) toughness. Inset: photographs of monolith disks for the compressive tests. Left to right: f-CCGs-reinforced APTS monolith and neat APTS monolith. (Reproduced with permission from [87].)

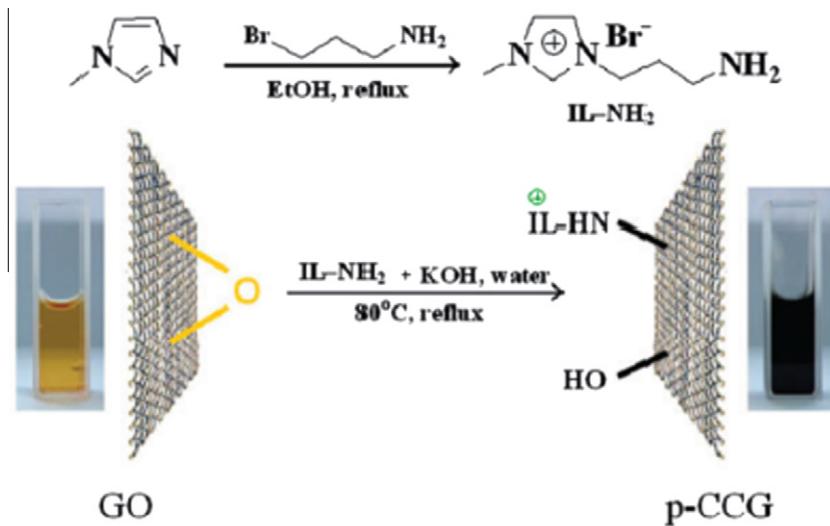


Fig. 17. Illustration of the preparation of p-CCG. (Reproduced with permission from [86].)

Poly-L-lysine (PLL) functionalized biocompatible graphene sheets were synthesized in an alkaline solution; the synthetic scheme is shown in Fig. 18 [31]. XPS clearly indicate the successful functionalization of graphene (Fig. 19). The thickness of graphene–PLL was determined to be *ca.* 3.6 nm, which originates from PLL coverage on both sides of the graphene. The biocompatible and relatively friendly

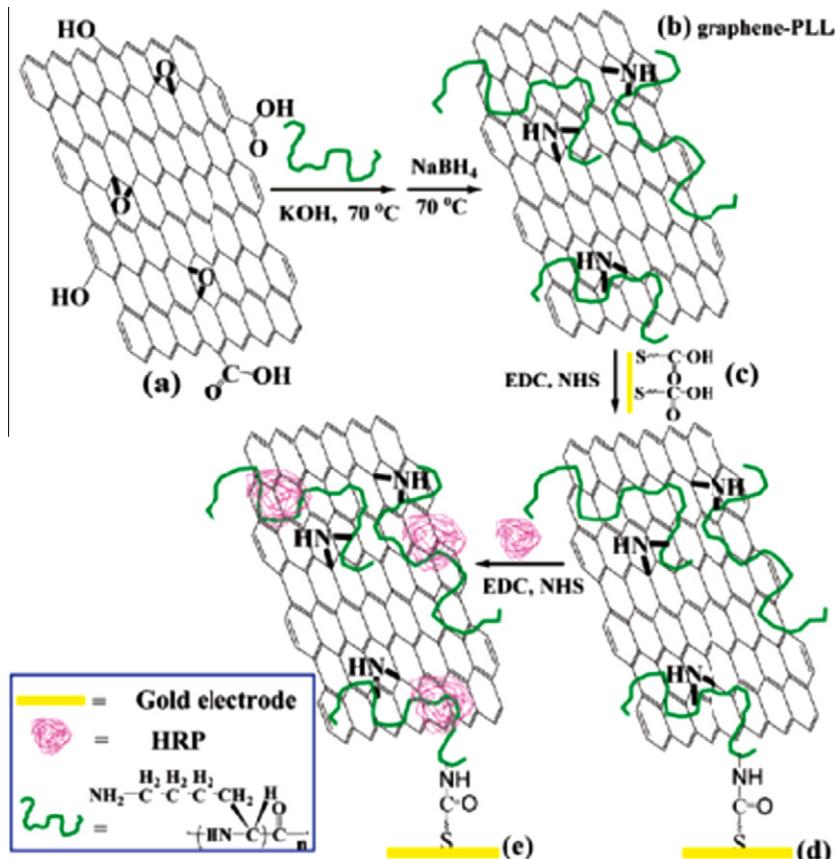


Fig. 18. Schematic diagram of graphene-PLL synthesis and assembly process of graphene-PLL and HRP at a gold electrode. (Reproduced with permission from [31].)

nature of PLL aids in further immobilization of biomolecules on the surface of graphene-PLL. In order to support this idea, horseradish peroxide (HRP) was successfully immobilized on these graphene-PLL nanocomposites. The ability of the resulting biosensor based on graphene-PLL/HRP composites to sense H_2O_2 is enhanced compared to other biosensors. Xu et al. have used dopamine as a reducing agent for the reduction of GO and as a capping agent to decorate the resulting reduced graphene oxide (RGO) surface for further functionalization [85]. Formation of polydopamine at weakly alkaline pH (8.5) results in a uniform coating on the graphene surface, and the resulting materials are highly soluble in water.

The general approach for the nondestructive chemical and biological functionalization of graphene for device platforms has been evaluated by Cui et al. [83]. An aqueous solution of peptides reacts with graphene and is incubated for 20 min in an enclosed chamber (relative humidity $\sim 100\%$), followed by extensive washing with deionized water and drying. Poly(norepinephrine), a catecholamine polymer has been selected for the chemical functionalization of GO [82]. The resulting graphene is highly dispersible in water and is suitable nanofiller for the preparation of graphene-based nanocomposites.

Recently, Pham et al. have proposed a new modification technique in which GO acts as a nucleophile in the presence of a base, such as potassium methoxide [93]. Fig. 20 shows a schematic depiction for the preparation of a water-dispersible polyglycerol-grafted GO nanostructure and its immobilization with boronic acid-functionalized Fe@Au nanoparticles. The as-synthesized novel hybrid materials formed a stable dispersion in water over 3 months and emerged as a promising material capable of

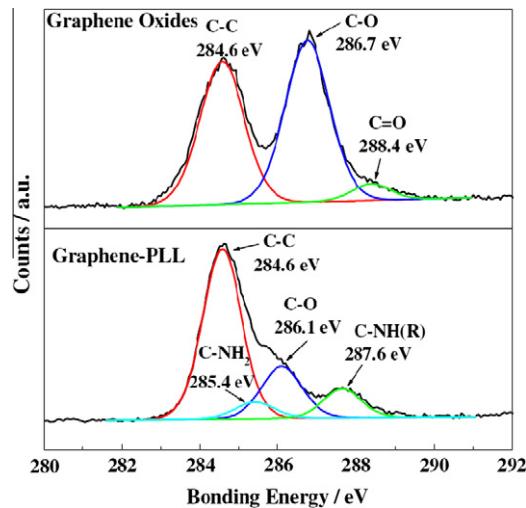


Fig. 19. C1s XPS spectra of GOs (upper) and graphene-PLL (lower). (Reproduced with permission from [30].)

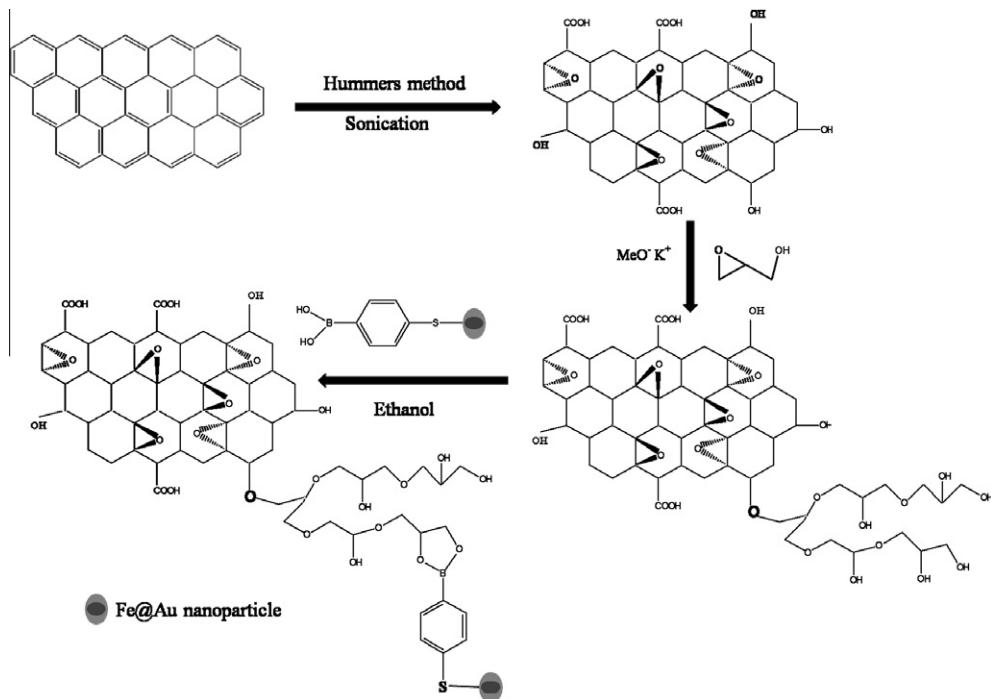


Fig. 20. Synthetic routes of water-dispersible PG-g-GO nanostructure and its immobilization with B-f-MNPs.

meeting various requirements for potential applications. Kuila et al. have prepared water-dispersible graphene by reacting graphite oxide and 6-amino-4-hydroxy-2-naphthalenesulfonic acid (ANS). The obtained product is highly dispersible in water (3 mg ml^{-1}). It has been found that $\sim 13 \text{ wt.\%}$ of ANS molecule has been doped on the surface of graphene. The electrical conductivity of the resulting functionalized graphene is $\sim 145 \text{ S m}^{-1}$ at room temperature [94].

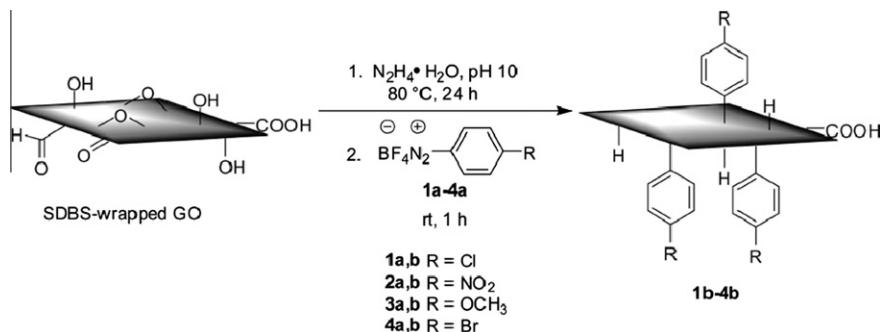


Fig. 21. Reduction and functionalization of intermediate SDBS-wrapped CCG with diazonium salts, starting with SDBS-wrapped GO. (Reproduced with permission from [55].)

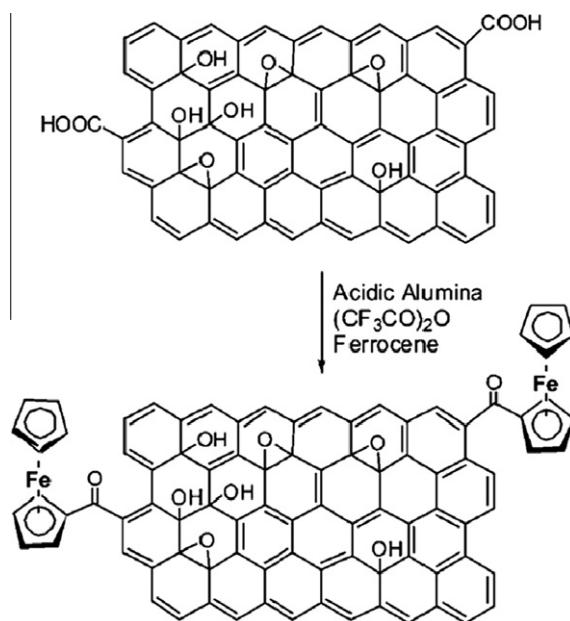


Fig. 22. Covalent modification of GO with ferrocene by Friedel–Crafts monoacetylation on an acidic alumina surface. (Reproduced with permission from [98].)

5.1.2. Electrophilic substitution reaction

Electrophilic substitution reactions with graphene involve the displacement of a hydrogen atom by an electrophile. Spontaneous grafting of aryl diazonium salt to the surface of graphene is an example of electrophilic substitution. The diazonium salt of para-nitro aniline can be grafted onto the graphene surface [95]. Lomeda et al. and Zhu et al. prepared organosoluble graphene by electrophilic substitution of aryl diazonium salt on the surface of surfactant-wrapped graphene [55,96]. Fig. 21 is a schematic depiction of the functionalization of graphene by diazonium salt. The surfactant sodium dodecyl benzene sulfonate (SDBS) is wrapped on the surface of GO at a pH ~10, followed by reduction at 80 °C for 24 h with hydrazine monohydrate. Then, the aryl diazonium salt is grafted on the surface of SDBS wrapped CCG at room temperature for 1 h. The functionalized graphene is highly dispersible in DMF solvent. Sun et al. have used the diazonium salt of 4-bromo-aniline for edge-selective

graphene functionalization [97]. These chemically functionalized graphene sheets are more dispersible than pristine graphene. The microscopic data indicates that more than 70% of the chemically exfoliated graphene flakes are less than 5 layers thick. A facile synthetic route for sulfonated graphene has been reported by Si and Samulski [32]. The electrical conductivity of the prepared graphene was found to be 1250 S m^{-1} . Therefore, it can be concluded that the electrical conductivities of sulfonated graphenes are much better compared to other functionalized graphenes.

Recently, Avinash et al. have demonstrated Friedel–Crafts acylation of GO with ferrocene [98]. Fig. 22 shows a schematic for the covalent modification of GO with ferrocene. The reaction takes place in solid phase alumina and trifluoroacetic anhydride at room temperature for the preparation of covalently-linked ferrocene-GO hybrid materials. Pham et al. have introduced a new concept for the functionalization of graphene through a solvothermal process by using GO and NMP as starting materials [99]. Free radicals are generated from NMP during solvothermal reduction and functionalization occurs in a similar way as in the functionalization of graphene by aryl diazonium salts [55,100]. It was found that the restoration of electronic conjugation of $\text{C}=\text{C}$ in graphene increases with increasing the reaction time. The functionalized graphene forms stable dispersion in DMF, NMP, polycarbonate (PC), THF, and ethanol. The electrical conductivity of the functionalized graphene was found to be $\sim 21,600 \text{ S m}^{-1}$ at room temperature. Fang et al. prepared covalently functionalized graphene using polystyrene [101]. The initiator molecules are covalently bonded to the graphene surface via a diazonium addition and the succeeding atom transfer radical polymerization links polystyrene chains (82 wt.% grafting efficiency) to the graphene sheets.

5.1.3. Condensation reaction

A condensation reaction is a chemical reaction in which two molecules (functional groups) combine to form one single molecule with a loss of entropy. In the case of graphene, condensation occurs with isocyanate, diisocyanate, and amine compounds through the formation of amides and carbamate ester linkages. Stankovich et al. used a series of isocyanate compounds in the surface modification of GO [18,102]. Fig. 23 is a schematic depiction for the formation of isocyanate-modified GO. The reaction occurs in DMF under nitrogen atmosphere. When solid isocyanates are used, both the isocyanate and GO are loaded into a flask prior to the addition of DMF. The resulting functionalized GO can be easily dispersed in DMF and is therefore very useful in the preparation of polymer nanocomposites [18].

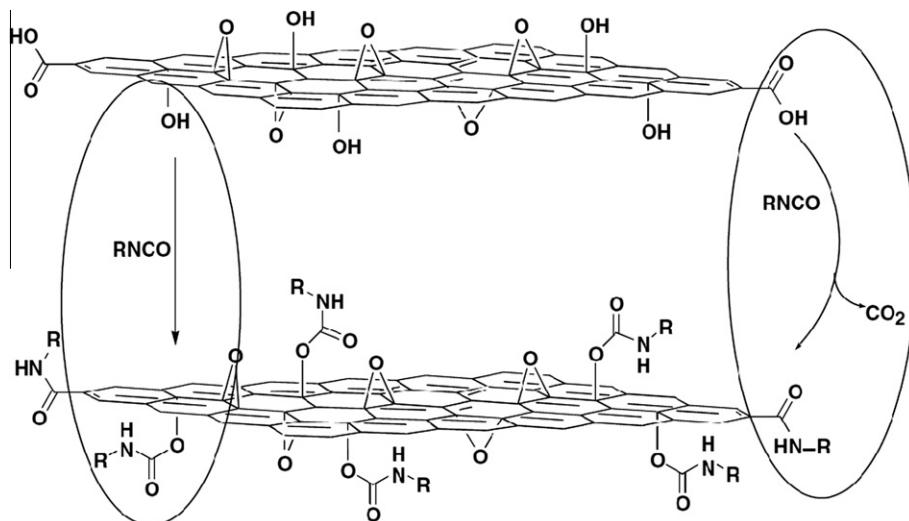


Fig. 23. Proposed reactions during the isocyanate treatment of GO, in which organic isocyanates react with the hydroxyl (left oval) and carboxyl groups (right oval) of GO sheets to form carbamate and amide functionalities, respectively. (Reproduced with permission from [102].)

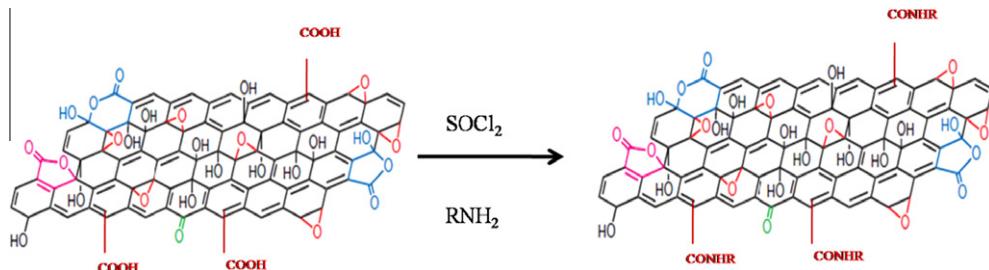


Fig. 24. Schematic of the preparation of ODA-modified GO. (Reproduced with permission from [70].)

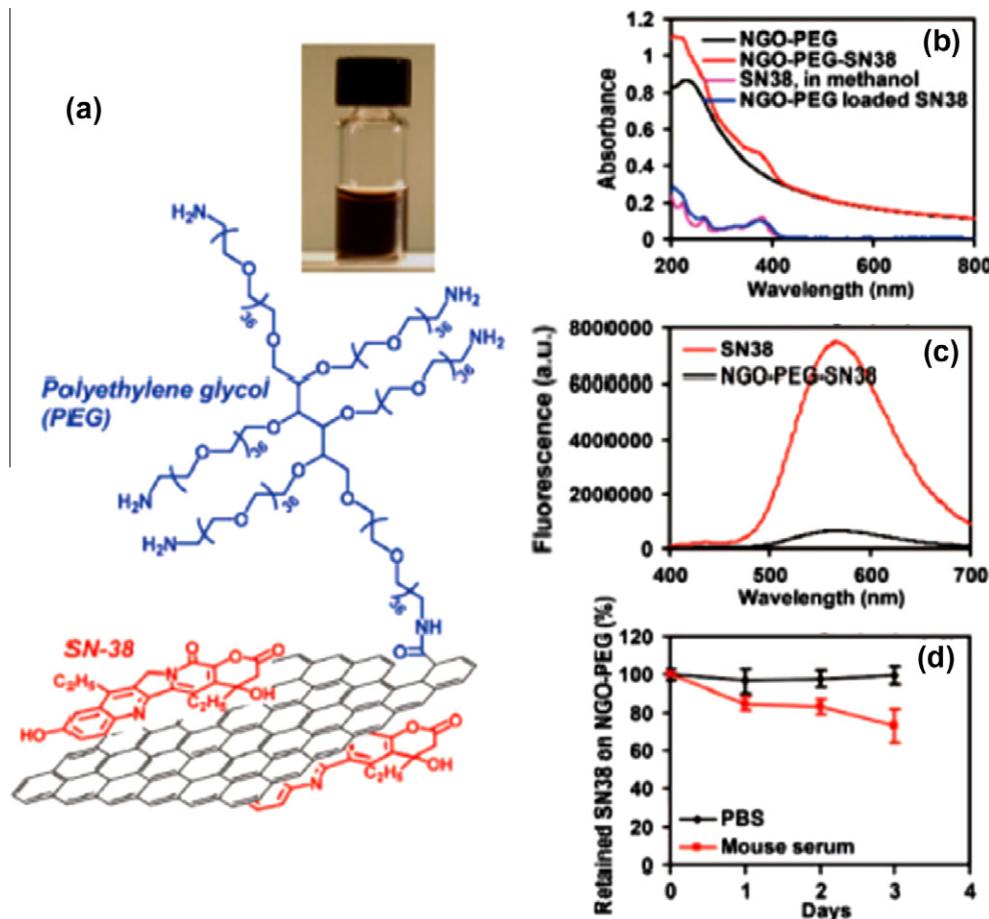


Fig. 25. SN38 loading on NGO-PEG: (a) Schematic of SN38-loaded NGO-PEG; (inset) a photo of NGO-PEG-SN38 water solution. (b) UV-visible absorption spectra of NGO-PEG, NGO-PEG-SN38, and SN38 in methanol and difference spectra of NGO-PEG and NGO-PEGSN38. The SN38 absorbance at 380 nm was used to determine loading. (c) Fluorescence spectra of SN38 and NGO-PEG-SN38 at $[\text{SN38}] = 1 \mu\text{M}$. Significant fluorescence quenching was observed for SN38 adsorbed on NGO. (d) SN38 retained on NGO-PEG over time incubated in PBS and serum, respectively. SN38 loaded onto NGO-PEG was stable in PBS and released slowly in serum. Error bars are based on triplet samples. (Reproduced with permission from [106].)

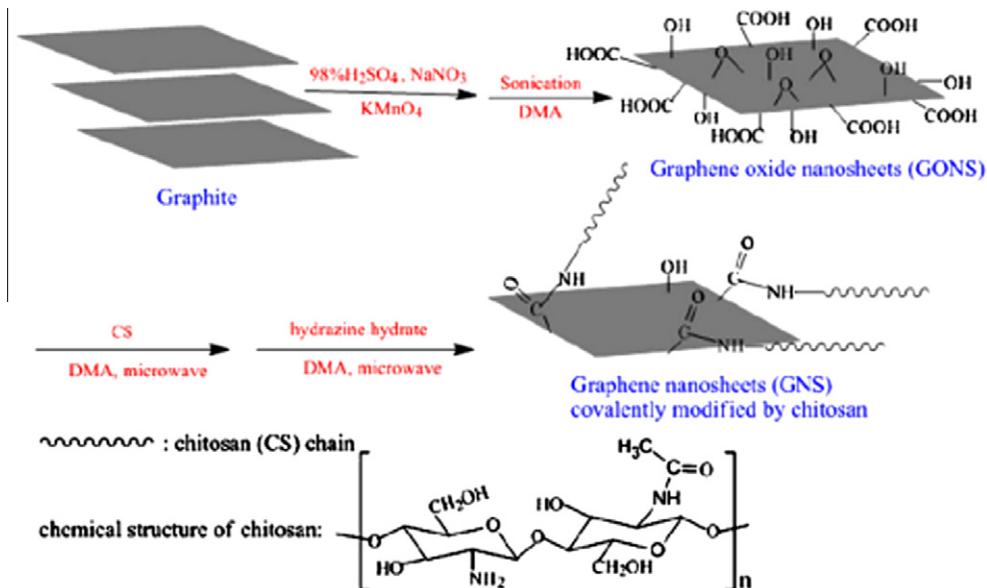


Fig. 26. Schematic of the formation procedure for CS chains grafted onto the surface of graphene sheets. (Reproduced with permission from [107].)

Similar to the organic isocyanate, organic diisocyanate is also very useful in GO functionalization and cross-linking [103]. Grafting of ODA onto the surface of GO can be accomplished by activating the carboxyl functionality of GO using thionyl chloride (SOCl_2). Functionalization occurs through the formation of a covalent (amide linkage) bond between the $-\text{COCl}$ functional groups of activated GO and the $-\text{NH}_2$ functional groups of ODA (Fig. 24). The product, $\text{G}-\text{CONH}(\text{CH}_2)_{17}\text{CH}_3$, has a dispersibility of 0.5 mg ml^{-1} in THF and is also soluble in carbon tetrachloride (CCl_4) and 1,2-dichloroethane [104]. Worsley et al. have proposed a reaction between tetramethylethylene diamine (TMEDA) and graphite fluoride in hexane solvent at 0°C to prepare functionalized graphene [105]. After stirring for three days, the reaction is quenched with isopropanol and ethanol. The resulting alkylated graphene disperses well in halogenated solvents such as dichlorobenzene, dichloromethane (DCM), and THF. The dispersibility of alkylated graphene in THF obeys Beer's law, which is helpful in the determination of molar extinction coefficient ($7 \text{ L g}^{-1} \text{ cm}^{-1}$) [105]. Liu et al. have reported the first example of GO functionalization using amine terminated poly(ethylene glycol) (PEG-NH₂) [106]. The functionalization of GO occurs via carbodiimide-catalyzed amide formation, as shown in Fig. 25. The product is highly dispersible in water and readily forms complexes with the water-insoluble aromatic molecule, SN38, a camptothecin (CPT) analog, via noncovalent van der Waals interactions. The high solubility (1 mg ml^{-1}) of drug-doped functionalized GO plays an important role in changing the hydrophilicity of the drug molecule. Recently, chitosan (CS) modified graphene has been successfully prepared with microwave radiation in a DMF medium [107]. The functionalization proceeds through the reaction between the carboxyl groups of GO and the amine groups of chitosan, followed by reduction using hydrazine monohydrate. A schematic of CS-modified graphene formation is shown in Fig. 26. The dispersibility of the GO in aqueous acidic media can be improved by the amidation of GO with CS [108,109]. The chitosan grafted graphene oxide (GO-CS) sheets consist of about 64 wt.% CS, which imparts them with a good aqueous solubility and biocompatibility. As a novel nanocarrier, GO-CS can be used to load a water insoluble anticancer drug, CPT, via $\pi-\pi$ stacking and hydrophobic interactions. It has been demonstrated that GO-CS possesses a superior loading capacity for CPT, and the GO-CS-CPT complexes show remarkably high cytotoxicity in HepG2 and HeLa cell lines compared to the pure drug. Zhuang et al. have synthesized conjugated polymer functionalized GO for the fabrication of

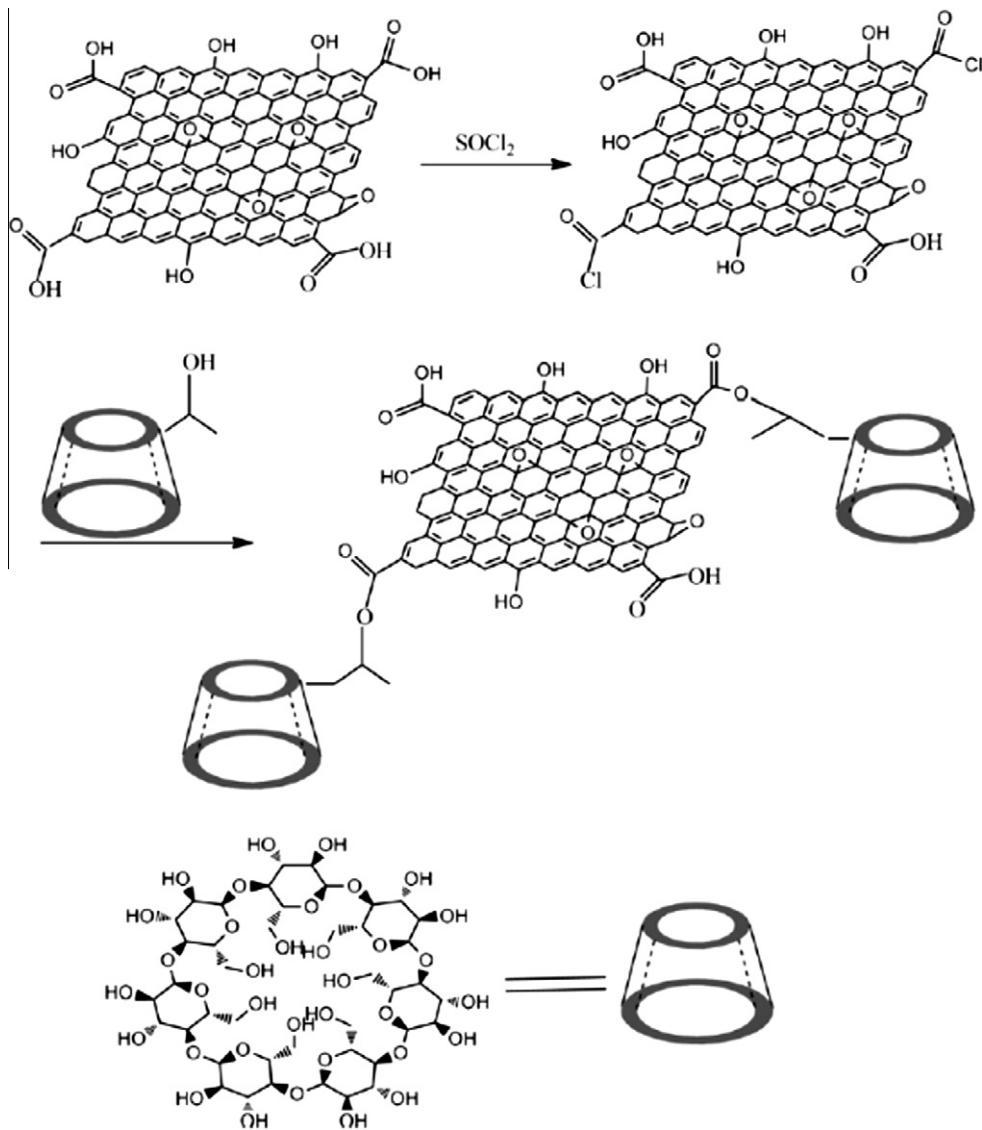


Fig. 27. Schematic of the synthesis of HPCD-GO composites. (Reproduced with permission from [111].)

nonvolatile rewritable memory device [110]. The amine groups of triphenylamine-based polyazomethine (TPAPAM) reacts with carboxyl functionalities of GO and forms an amide linkage.

Xu et al. have prepared functionalized graphene by the esterification of the GO carboxyl functional group with the hydroxyl groups of β -cyclodextrin (β -CD) in the presence of SOCl_2 [111]. Fig. 27 is a schematic diagram for the functionalization of GO with β -CD. Compared to pure GO, functionalized GO can be dispersed well in DMF, acetone, and water. The excellent electrocatalytic activity in the reduction and oxidation of hemoglobin can facilitate the utility of functionalized GO as a new biosensing material for the detection of hemoglobin. In comparison to this method, a relatively simple and fast method has been successfully developed to obtain CD (α , β , γ)-graphene organic-inorganic hybrid

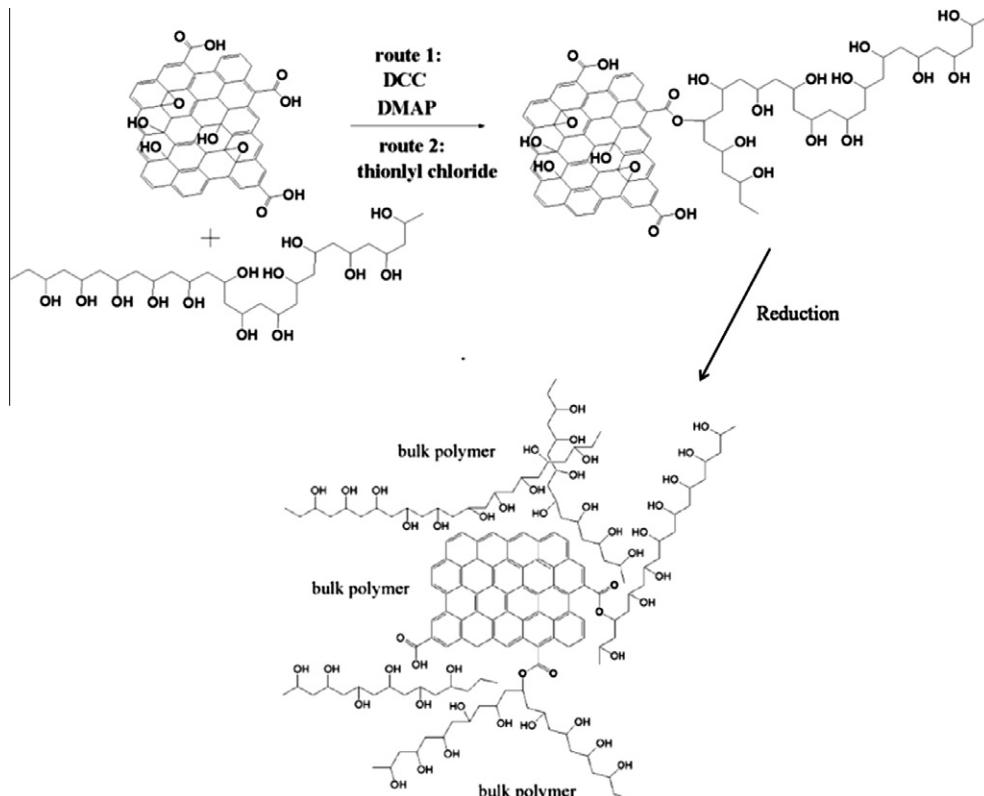


Fig. 28. Schematic of the preparation of PVA-modified graphene starting from GO. (Reproduced with permission from [113].)

nanosheets, which exhibit better dispersibility and stability in water, ethanol, DMF, and DMSO [112]. The functionalized graphene exhibits excellent electrochemical performances for the detection of biological drug molecules due to the presence of tunable cavity size of different kinds of cyclodextrins. Similar to β -CD, poly(vinyl alcohol) (PVA) can also be used in the surface modification of graphene by ester linkage formation (Fig. 28) [113]. Amine-functionalized porphyrin (TPP-NH₂) ring can also be used in the surface modification of GO via amide bond formation [114]. Attachment of TPP-NH₂ significantly improves the solubility and dispersion stability of graphene-based material in organic solvents. It has been suggested that the organic solution-processable functionalized graphene material can be used as a solar energy conversion material for optoelectronic devices. Matsuo et al. have prepared silylated GO with various alkylchlorosilanes in the presence of butylamine and toluene. The interlayer distance significantly increases with an increase in the number of chlorine atoms in the silylating reagents [115]. APTS-modified GO can be used as a precursor material in the preparation of pilared carbon by the pyrolysis of silane-functionalized GO [116]. Shen et al. have prepared a biocomposites of GO with adenine, cystine, nicotamide, ovalbumin (OVA), and propyl amine [117]. The two-step method was carried out at room temperature in buffer solutions and accomplished in a short time. Functionalization of graphene can also be done by using fullerene [118]. Fisher esterification occurs between the hydroxyl groups of graphite oxide and carboxyl group of fullerenoacetic acid. Chen et al. have prepared sulfanilic acid functionalized GO as ion-exchange material and studied its electrochemical behavior towards the detection of hydrogen peroxide [119]. The functionalization occurs through the formation of amide bond between the carboxylic group of GO and amine functionality of sulfanilic acid/cysteamine.

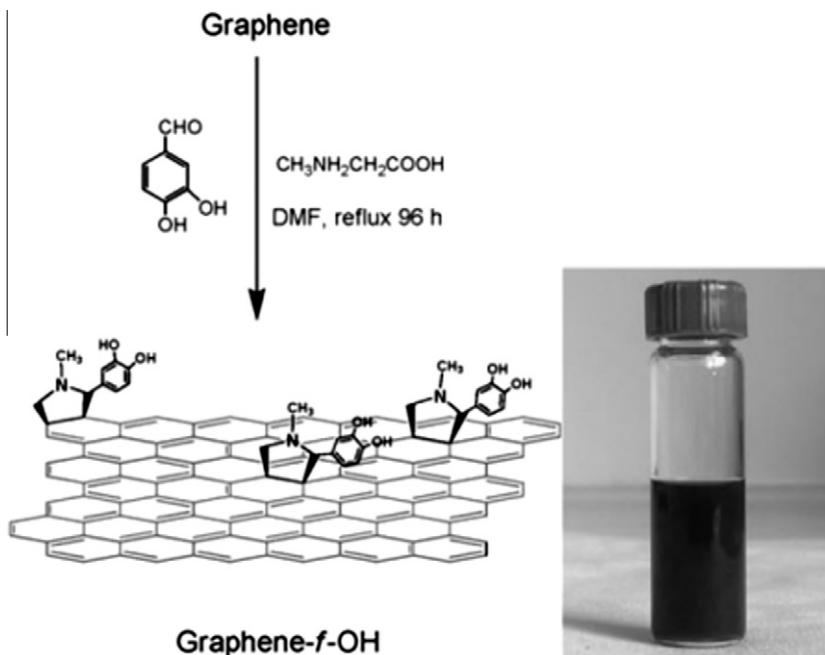


Fig. 29. Schematic representation of the 1,3-dipolar cycloaddition of azomethine ylide on graphene. (Reproduced with permission from [121].)

5.1.4. Addition reaction

Two or more molecules combine to form a larger molecule in organic addition reactions. A schematic representation of the 1,3-dipolar cycloaddition of azomethine ylide on the surface of graphene is shown in Fig. 29. A similar concept has been applied for the functionalization of epitaxial graphene by the cycloaddition of azidotrimethylsilane [120]. After removing N₂, nitrene reacts with graphene via an electrophilic [2 + 1] cycloaddition reaction or a biradical pathway to form functionalized graphene. The graphene sheets derived from graphite in pyridine and NMP have been functionalized using a similar procedure [121,122]. The organically modified graphene sheets are easily dispersible, thus easing their manipulation in various processes that involve mixing, blending, or dispersion. Hsiao et al. have prepared functionalized graphene using residual oxygen-containing functional groups RGO [88]. Poly(oxyalkylene) amines bearing one maleic anhydride have been used as a surface modifier for graphene. Maleic anhydride can be directly grafted on the surface of GO in presence of free radicals. The functionalized graphene is highly dispersible in THF and is stable for more than 2 months at a concentration of 0.25 mg ml⁻¹. Vadukumpully et al. have used various alkylazides for the functionalization of surfactant wrapped graphene sheets [123]. The azide functionalized graphene sheets with longer alkyl chains and polar functional groups show enhanced dispersibility in common organic solvents such as acetone and toluene. Polyacetylene can also be used as an organic modifier for graphene following the nitrene chemistry [124]. Zhong et al. have developed a simple and efficient approach for the synthesis of CCG sheets via aryne cycloaddition under mild reaction conditions [125]. A linear relationship exists between the concentration and the maximum adsorption value (279 nm) indicating that the functionalized graphene dispersions obey Beer's law and are homogeneously dispersed in ethanol. Economopoulos et al. have prepared chemically modified graphene sheets using microwave radiation [126]. The resulting hybrid materials possess cyclopropanated malonate units covalently grafted onto the graphene skeleton and form stable suspensions for several days in a variety of organic solvents. A unique approach for the functionalization of graphene sheets based on nitrene chemistry was reported [127]. This strategy allows many kinds of functional moieties and polymers to covalently

bond on graphene, resulting in the formation of functionalized graphene sheets. The resulting functionalized graphene can be easily dispersed in water, DMF, toluene, and chloroform. The electrical conductivity of the functionalized graphene has been found to be $0.1\text{--}1000\text{ S m}^{-1}$ at room temperature.

5.2. Noncovalent functionalization

Noncovalent interactions primarily involve hydrophobic, van der Waals, and electrostatic forces and require the physical adsorption of suitable molecules on the graphene surface. Noncovalent functionalization is achieved by polymer wrapping, adsorption of surfactants or small aromatic molecules, and interaction with porphyrins or biomolecules such as deoxyribonucleic acid (DNA) and peptides. Noncovalent functionalization is a well-known technique for the surface modification of carbon-based nano-materials. This technique has been previously employed extensively in the surface modification of the sp^2 networks of CNTs [128–130]. Ongoing research shows that the same techniques can be applied with graphene using different kinds of organic modifiers [130–152]. Table 3 shows different noncovalent modification of GO using different modifying agents, their dispersion stability in various solvents, dispersibility, and electrical conductivity.

Stankovich et al. have reported the first example of noncovalent functionalization of graphitic nanoplatelets using poly(sodium 4-styrenesulfonate) (PSS) [130]. Exfoliation and in situ reduction of GO in the presence of PSS can form noncovalently-functionalized graphitic nanoplatelets that are highly dispersible in water (1 mg ml^{-1}). Stable dispersion of graphene in water can be obtained by using sulfonated polyaniline (SPANI) as a surface modifier [131]. SPANI exhibits good electrical conductivity, electrochemical activity, and water solubility. Therefore, the composite film of SPANI-functionalized graphene exhibits good water dispersibility ($>1\text{ mg ml}^{-1}$), satisfactory electrical conductivity (30 S m^{-1}), and unique electrochemical properties. Xu et al. have prepared a large-area flexible film of modified graphene from GO and pyrenebutyric acid (PBA) in an aqueous medium. The functionalized graphene is highly soluble in water due to the presence of the 1-pyrenebutyrate, and the electrical conductivity of the functionalized graphene film (200 S m^{-1}) has been found to be seven orders of magnitude larger than that of the GO precursor [132].

Table 3

Noncovalent modification of GO using different modifying agents, their dispersion stability in various solvents, dispersibility, and electrical conductivity.

Modifying agent	Dispersing medium	Dispersibility (mg ml^{-1})	Electrical conductivity (S m^{-1})	Refs.
PSS	Water	1	–	[130]
SPANI	Water	>1	30	[131]
PBA	Water	0.1	200	[132]
Amine terminated polymer	1,3-Dimethyl-2-imidazolidinone, γ -butyrolactone, 1-propanol, ethanol, ethylene glycol, DMF	0.4	1500	[133]
PNIPAAm	Water	–	–	[134,135]
PSS-g-PPY	Water	3	–	[137]
Poly(propyleneimine) dendrimers	Water	–	–	[138]
Coronene derivative	Water	0.15	–	[139]
PPESO ₃ [–]	Water	0.25	30 k Ω (resistance)	[140]
SDBS	Water	1	80 Ω (resistance)	[142,143]
MG	Water	0.1	–	[146]
SLS, SCMC, HPC-Py	Water	0.6–2	–	[148]
PYR-NHS	Water	–	–	[150]
Porphyrin	Water	0.02	370 $\Omega \text{ cm}$	[151]
PIL	Water	1.5	3600	[153]

Stable dispersion of reduced graphene in various organic solvents has been achieved via noncovalent functionalization with amine-terminated polymers [133]. This is the first attempt to prepare functionalized graphene after the reduction of GO to graphene. According to this method, the reduction of GO is first carried out in aqueous medium using an ammonia–hydrazine mixture, followed by washing and removal of aggregated graphene sheets. For noncovalent functionalization of RGO, the amine-terminated polymer is dissolved in organic solvents. Then, the aqueous dispersion of RGO is added to the organic polymer solution. The vial including phase-separated organic and aqueous phases is subjected to 5-h sonication for the noncovalent functionalization and phase transfer of graphene. The functionalized graphene can easily be dispersed in a variety of solvents and exhibits satisfactory electrical conductivity. Liu et al. have reported a modification technique for graphene by considering the π – π interaction between the π orbitals of graphene and poly(N-isopropylacrylamide) (PNIPAAm) [134]. Fig. 30 is a schematic depiction for the preparation of functionalized graphene using this technique. In this method, pyrene-terminated PNIPAAm is dissolved in water, followed by the addition of an aqueous suspension of graphene. Water-dispersible graphene has been produced by sonicating the resultant mixture in an ice-water bath. Recently, Pan et al. have prepared CCG sheets by grafting a well-defined thermo-responsive PNIPAAm via click chemistry [135]. The PNIPAAm modified graphene consist of about 50% polymer, which endows the sheets with a good dispersibility and stability in physiological solutions. Qi et al. have demonstrated an effective method to prepare amphiphilic

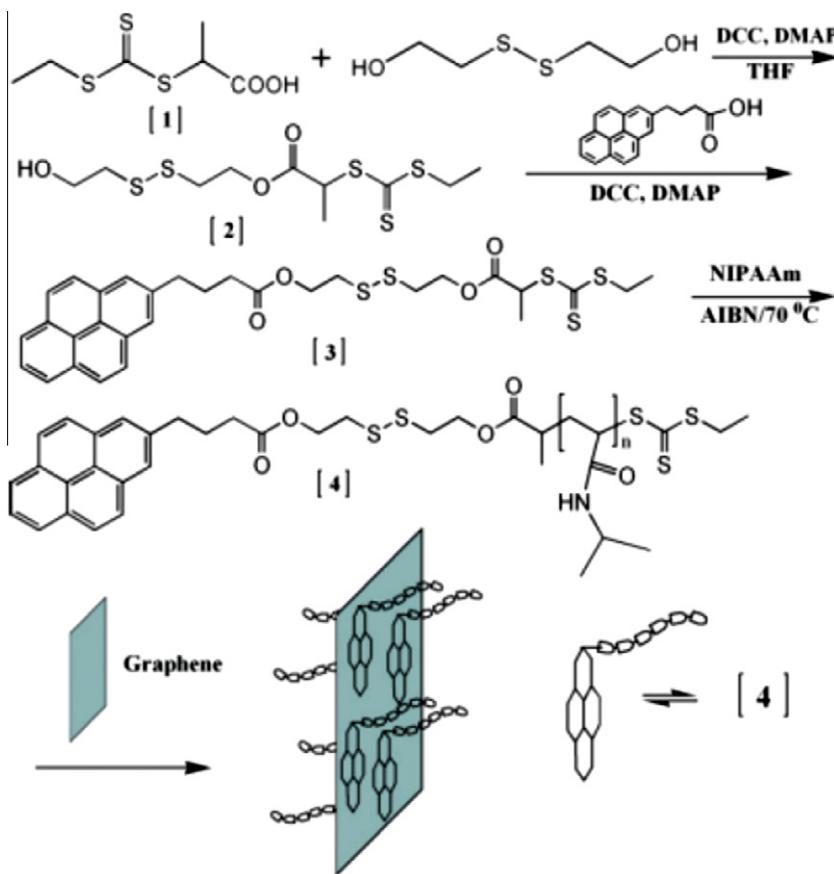


Fig. 30. A schematic depicting the synthesis of pyrene-terminated PNIPAAm using a pyrene-functional RAFT agent and the subsequent attachment of the polymer to graphene. (Reproduced with permission from [134].)

philic reduced GO sheets by using a coil-rod-coil conjugated triblock copolymer (PEG-OPE) as the π - π binding stabilizer [136]. The functionalized GO disperses well in a series of organic solvents and water. The poly(ethylene glycol) moieties of the functionalized GO may render good biocompatibility and high stability in different physiological environments. This may allow one to explore graphene in biological systems and discover its potential applications in the attachment and delivery of aromatic, water insoluble drugs into cells.

Zhang et al. have designed a biosensing platform by the functionalization of RGO with a conducting polypyrrole graft copolymer, poly(styrenesulfonic acid-g-pyrrole) (PSSA-g-PPY), via noncovalent interaction [137]. However, this method involves the functionalization of GO with PSSA-g-PPY followed by hydrazine reduction at 100 °C. The resulting functionalized graphene exhibits a uniform sheet nanostructure and can be well dispersed in water. It also possesses excellent electrocatalytic activity for the electrochemical detection of hydrogen peroxide and uric acid.

Poly(propyleneimine) dendrimers with terminal amine groups have also been used in the noncovalent surface modification of graphene [138]. The reduction of exfoliated GO is carried out in the presence of dendrimer molecules. Unlike GO, the functionalized graphene forms a stable aqueous dispersion when the dendrimer molecules are supplied in excess. The UV-visible spectra shows that the transmittance of the functionalized graphene is decreased compared to pure GO. Ghosh et al. have selected anionic coronene derivative (a blue fluorescent material) for the noncovalent functionalization of graphene [139]. The negative charge of the coronene derivative prevents both inter- and intra- π - π stacking of graphenes, leading to stabilization of the functionalized graphene sheets.

Supramolecularly functionalized graphene-based material with conjugated poly(2,5-bis(3-sulfonatopropoxy)-1,4-ethynylphenylene-alt-1,4-ethynylphenylene) (PPESO_3^-) has been successfully prepared by Yang et al. [140]. Fig. 31 is a schematic depiction of PPESO_3^- -modified graphene preparation. The resulting graphene exhibits high electrical conductivity and dispersion stability (even for 8 months without any aid of free polymer in solution). Moreover, the negative charges of the resulting graphene facilitate further functionalization of graphene sheets and can be used in a variety of optoelectronic device applications.

SDBS is a very well known surfactant that has been widely used in the surface modification of CNTs and graphene [141–143]. Recently, Chang et al. and Zeng et al. have prepared SDBS-modified graphene [142,143]. Reduction of SDBS-functionalized graphene produces surfactant-wrapped graphene sheets.

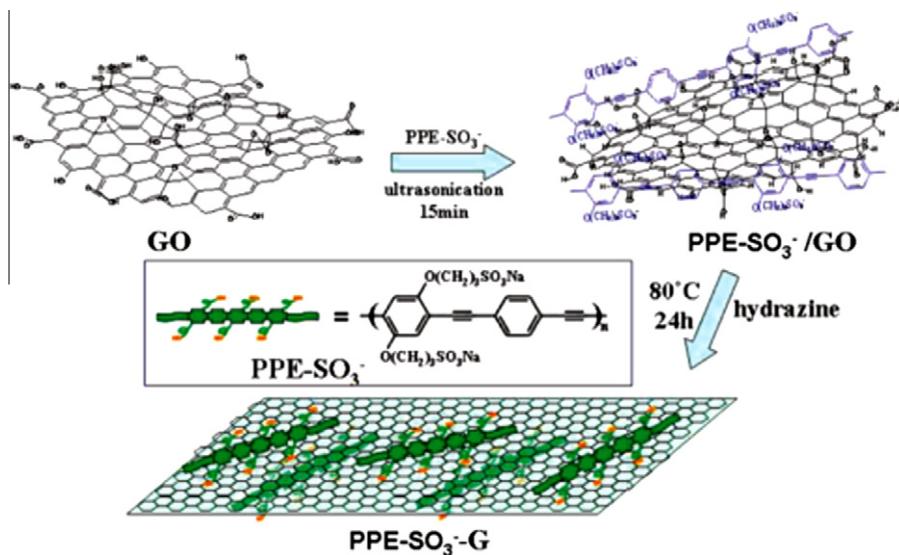


Fig. 31. Chemical structure of PPE-SO_3^- and schematic of the preparation of PPE-SO_3^- -modified graphene sheets. (Reproduced with permission from [140].)

The modified graphene is highly dispersible in water and exhibits good electrical conductivity and transparency. The electrochemical stability of the functionalized graphene remains almost unchanged after 1000 cycles. SDBS-wrapped graphene can also be used as a biosensing material for the detection of hydrogen peroxide.

Blood compatibility is an important and critical issue in both in vivo and in vitro applications [49,144]. Recently, Lee et al. prepared a blood-compatible graphene/heparin conjugate through non-covalent interaction between chemically-reduced graphene and heparin [49]. It was proposed that the design of a graphene/biomolecule conjugate via noncovalent chemistry is very simple and more versatile than covalent chemistry. A novel noncovalent functionalization approach was presented to exfoliate and stabilize chemically converted graphene and the low-temperature exfoliated graphene (LTEG) in aqueous solution by using thionine. The electrical conductivity of thionine coated GO is 10.1 S m^{-1} while that of the LTEG is 23.6 S m^{-1} [145]. Liu et al. demonstrated a facile method to process graphene nanosheet through noncovalent functionalization of chemically reduced graphene with water-soluble aromatic methylene green (MG) [146]. It has been found that the performance of MG modified graphene towards the detection of nicotinamide adenine dinucleotide (NADH) is much better than that of chemically reduced GO. Kamada et al. have used π -conjugated disk-like molecules for the functionalization of graphene sheets [147]. The resulting functionalized graphene disperses readily in organic solvents such as DMF and NMP. Noncovalent functionalization of graphene can be performed by using biomolecules such as sodium lignosulfonate (SLS), sodium carboxymethyl cellulose (SCMC), and pyrene-containing hydroxypropyl cellulose (HPC-Py) [148]. The bio-functionalized graphene forms an aqueous dispersion which is stable for more than 4 months. Ren et al. has shown that the graphene sheets can be stably dispersed in water by hydrophilic interaction [149]. The surface modified graphene are highly sensitive to a change in solution pH indicating its potential application in sensors, biology, medicine, nanoelectronics and other relevant areas. Kodali et al. have prepared chemically modified graphene by using bifunctional molecule pyrene-containing hydroxypropyl cellulose (PYR-NHS) for protein micropatterning [150]. The aromatic pyrenyl group in PYR-NHS interacts strongly with the basal plane of graphene via $\pi-\pi$ stacking, without perturbing the sp^2 bond structure of the carbon honeycomb lattice, or the π band responsible for the characteristic electronic properties of graphene. Geng et al. have developed a new method that makes the use of the $\pi-\pi$ interactions between porphyrin and graphene to stabilize the CCG in water [151]. The dispersibility of CCG in water is

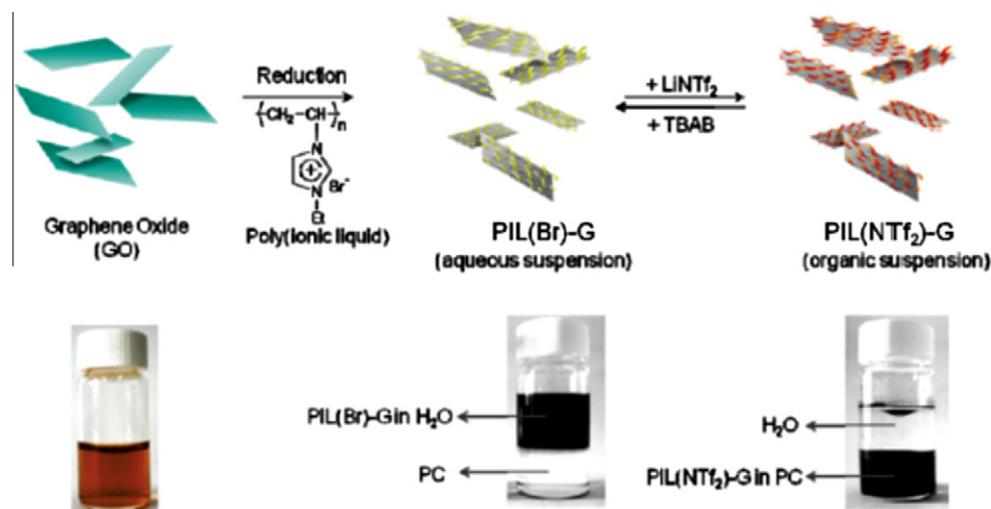


Fig. 32. Schematic illustration of the synthetic process for the PIL-modified graphene sheets (PIL-G). Chemical reduction of the graphene oxide (GO) dispersion with hydrazine in the presence of water-soluble PIL(Br) produced a stable aqueous suspension of the PIL(Br)-G. Anion exchange of PIL leads to the phase transfer of PIL-modified graphene sheets between aqueous and organic solvent media (propylene carbonate). (Reproduced with permission from [153].)

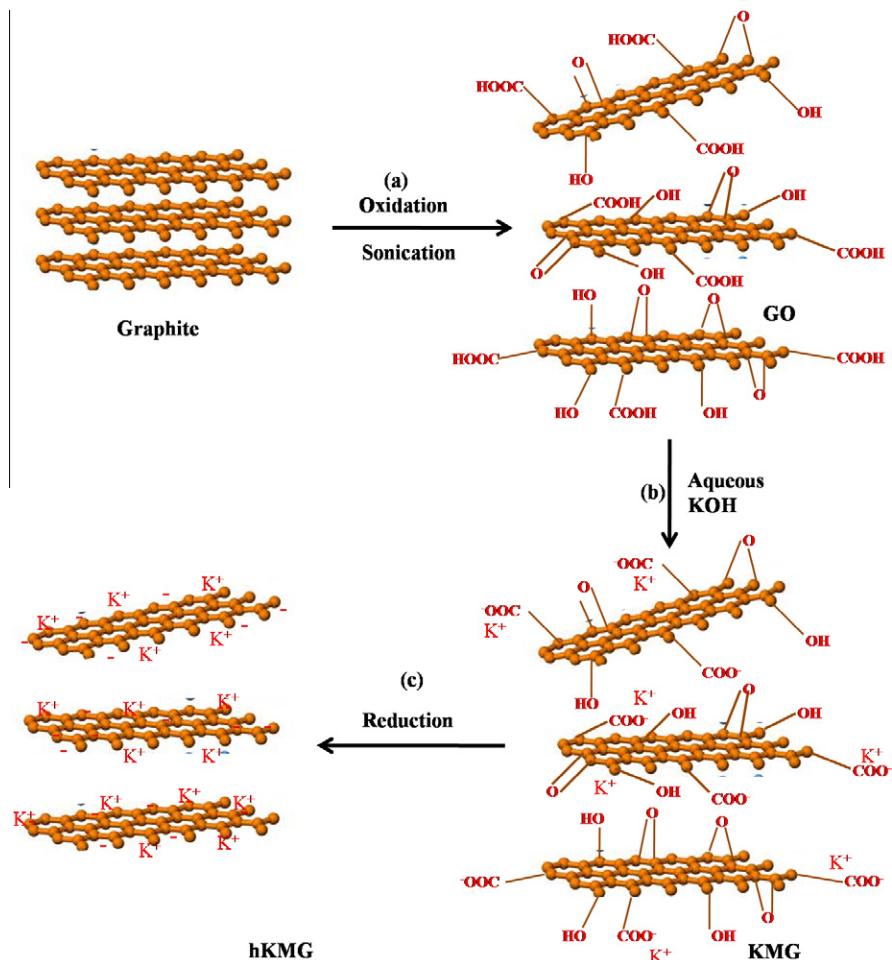


Fig. 33. A simple route for the preparation of a homogeneous aqueous suspension of graphene sheets from a graphite stack: (a) Oxidation of natural flake graphite to graphite oxide, followed by ultrasonication; (b) GO is dispersed in water and treated with aqueous KOH solution to obtain KOH-modified oxidized graphene (KMG); and finally, (c) KMG is reduced using hydrazine to produce hydrazine-reduced KOH-modified graphene (hKMG) in the form of a stable aqueous dispersion of individual graphene sheets.

attributed to the presence of $-SO_3Na$ and ammonium ion-pair in the porphyrin ring. The surface of graphene can be functionalized by using congo red (CR) as a surface modifier [152]. The aromatic ring of CR interacts strongly with the basal plane of graphene via $\pi-\pi$ stacking. The functionalized graphene, congo red modified graphene sheet (GS-CR) are highly dispersible (0.5 mg ml^{-1}) in different solvents such as water, methanol, ethanol, DMF, DMSO, NMP, m-cresol, and 1,4-dioxane. The electrical conductivity of GS-CR is $\sim 6850 \text{ S m}^{-1}$ which is close to the conductivity of unfunctionalized graphene. High molecular weight ($M_w \sim 17,000$) ionic liquid polymers are very effective for the noncovalent surface modification of graphene [153]. Fig. 32 shows the schematic depiction for the preparation of PIL functionalized graphene. The CCG sheets decorated with PIL have been found to be stable against the chemical reduction and well dispersed in aqueous phase without any agglomeration.

Malig et al. have used zinc phthalocyanines (ZnPc) complex for the surface modification of graphene through $\pi-\pi$ interaction [154]. Transient absorption measurement shows that ZnPc acts

as electron donor and graphene as electron acceptor. Therefore, the functionalized graphene can be applied to transparent electrode material for solar-cell applications.

5.3. Stabilization in an ionic medium

The use of foreign stabilizer molecules significantly reduces the electrical conductivity of the functionalized graphene. Therefore, in order to achieve processable graphene without impairing its electrical conductivity, reduction of GO in an ionic medium was introduced. Park et al. have reported a simple route for preparation of a homogeneous aqueous suspension of CCG with good electrical conductivity [155]. In this method, the precursor of GO is first dispersed in water, followed by the addition of an aqueous potassium hydroxide (KOH) solution (Fig. 33). According to Park et al., KOH (a strong base) can confer a large negative charge through reaction with the reactive hydroxyl, epoxy, and carboxylic acid groups on the GO sheets, resulting in extensive coating of the sheets with negative charges and K⁺ ions surrounded GO. The addition of hydrazine monohydrate to KOH-treated GO produces a homogeneous suspension of hydrazine hydrate reduced, KOH modified GO (hKMG), which can remain stable for at least 4 months. Recently, Li et al. have prepared stable aqueous colloids of graphene sheets through the electrostatic stabilization of graphene [30]. First, the aqueous dispersion of GO is reduced with a weighed amount of hydrazine monohydrate (hydrazine to GO weight ratio of ~7:10). Excess hydrazine is removed by dialysis against a ~0.5% ammonia solution after complete reduction. This discovery enabled the development of a straightforward approach to the large-scale production of aqueous graphene dispersions without the need for polymeric or surfactant stabilizers.

5.4. Directly from graphite

Chemical routes of graphene fabrication offer significant advantages over the microcleaving of highly oriented pyrolytic graphite (HOPG) or CVD synthesis of graphene [24,25]. However, with chemical methods, the surface area of graphene is tremendously decreased compared to CVD-grown graphene or mechanically-exfoliated graphene from HOPG. In contrast, a basic requirement in electronic applications is large-area graphene. Therefore, much effort has been directed towards the synthesis of large-area graphene directly from graphite. In the current section, we will discuss the synthesis of functionalized graphene directly from graphite using different organic modifiers [78,156–161]. The current method avoids the problem of a defect site in the graphene generated during the oxidation steps. Different kinds of organic modifier used for the preparation of functionalized graphene, their dispersion stability, and electrical conductivity are listed in Table 4.

The first attempt in the preparation of functionalized graphene directly from graphite has been conducted by Hao et al. [156]. An expanded graphite powder (1 mg) is mixed with 7,7,8,8-tetracyanoquinodimethane (TCNQ) (2 mg) using a mortar and pestle for about 10 min, followed by the addition of several drops of DMSO (~0.5 ml). The mixture is stored at room temperature for ~12 h, followed by

Table 4

Functionalized graphene directly from graphite using different modifying agents, their dispersion stability in various solvents, dispersibility, and electrical conductivity.

Modification techniques	Modifying agent	Dispersing medium	Dispersibility (mg ml ⁻¹)	Electrical conductivity (S m ⁻¹)	Refs.
Sono-chemical	TCNQ	DMF, DMSO	–	–	[156]
	SDBS	Water	0.05	35–1500	[78,157]
	Sodium cholate	Water	0.3	7000–17,500	[78,157]
	PCA	Water	–	–	[159]
	Benzoyl peroxide	Water	2.1	212 Ω (Resistance)	[160]
	Styrene	Toluene, DMF, THF, CHCl ₃	2	–	[161]
	Ionic liquids	DMF	1	–	[77]

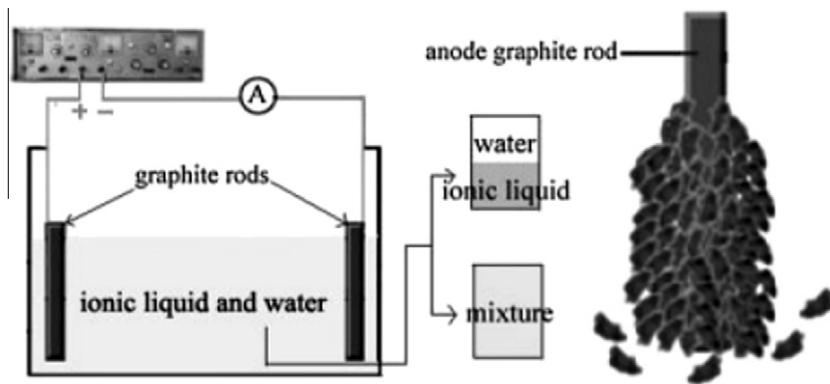


Fig. 34. Experimental setup (left) and exfoliation of the graphite anode (right). (Reproduced with permission from [77].)

drying at 80 °C for 6 h. The resulting solid powder is mixed with KOH and sonicated continuously for 90 min, after which a stable aqueous dispersion of graphene is obtained. The TCNQ-stabilized graphene is also dispersible in highly polar organic solvents such as DMF and DMSO. In the same year, Liu et al. prepared ionic liquid-functionalized graphene directly from graphite by an electrochemical method [77]. Fig. 34 is shows a schematic depiction of the experimental setup of electrochemical exfoliation of graphite to graphene. Commercial graphite electrodes have been used as the cathode, which is immersed in a mixture of water and ionic liquids. Ionic liquid functionalized graphene (GNP^{IL}) sheets have been fabricated from the graphite anode by the application of a constant potential of 10–20 V for 30 min. Ultrasonication of the dried GNPs^{IL} in DMF results in a homogeneous dispersion (1 mg ml⁻¹). A TEM study reveals that the average length and width of the GNPs^{IL} are 700 and 500 nm, respectively.

Lotya et al. have demonstrated a method to disperse and exfoliate graphite to yield a graphene suspension in water-surfactant solutions [78,157]. Two different surfactants, SDBS and sodium cholate, were selected separately for this purpose. In both the cases, natural flake graphite is sonicated with an aqueous solution of the surfactant in a low-power sonic bath. More than 40% of the SDBS-functionalized graphene has less than 5 layers, with ~3% of flakes consisting of monolayers. TEM analysis shows that the sodium cholate-stabilized graphene consisted of 1–10 stacked monolayers, with up to 20% of flakes containing just one layer. The average flake consists of approximately four stacked graphene layers and had a length and width of ~1 μm and ~400 nm, respectively. These dimensions are surprisingly stable under prolonged sonication. However, the mean flake length decreases from ~1 μm to ~500 nm as the centrifugation rate increases from 500 to 5000 rpm [157].

Smith et al. have systematically studied the effects of a range of ionic and non-ionic surfactants on dispersion stability of graphene in water [158]. They have selected 12 ionic surfactants such as SDBS, sodiumdodecylsulfate, lithium dodecyl sulfate, cetyltrimethyl ammoniumbromide, tetradecyltrimethylammonium bromide, sodium cholate, sodium deoxycholate and sodium taurodeoxycholate. Four non-ionic surfactants such as Polyoxyethylene (40), 4-(1,1,3,3)-Tetramethylbutyl phenyl-polyethylene glycol (TritonX-100), Polyoxyethylene Sorbitan Monolaurate (Tween 20) and Polyoxyethylene (20) sorbitan monooleate (Tween 80) have also been used to study the effect on the dispersion stability in water. In each case, the surfactant-stabilized graphene was prepared directly from graphite by the sonochemical method in an aqueous medium. A constant concentration of graphite (5 mg ml⁻¹) and surfactants (0.1 mg ml⁻¹) has also been maintained in all cases. It has been found that the degree of exfoliation was independent of the surfactant type but the dispersion stability of functionalized graphene was dependent on the solvent type. The prepared graphene sheets were typically 750 nm long and, on average, four layers thick. Smith et al. have suggested that the dispersion stability of ionic surfactant stabilized graphene is controlled by the zeta potential of the graphene dispersion [158]. The electrostatic repulsive forces on the surface of graphene sheets prevents their aggregation. Similarly,

for non-ionic surfactants, the dispersed graphene concentration scaled linearly with the magnitude of the steric potential barrier stabilizing the flakes.

An et al. described a facile technique for the noncovalent functionalization of graphene with 1-pyrenecarboxylic acid (PCA) that exfoliates single-, few-, and multilayered graphene flakes into stable aqueous dispersions [159]. The mechanism for exfoliation of graphite flakes to graphene using PCA has been described in terms of “molecular wedging”; the proposed scheme is shown in Fig. 35. Raman studies confirmed that the quality of the graphene produced is far superior to RGO and quite similar to that produced by “micromechanical exfoliation.” The resulting product is highly dispersible in water due to the presence of PCA that is noncovalently attached to the surface of graphene.

Recently, Mukherjee et al. reported a simple route to produce water-dispersible graphite nanoplatelets using graphite as the starting material [160]. A reaction of graphite powders with benzoyl peroxide was carried out at 80 °C using benzene as a solvent. The product is washed with chloroform and dispersed in oleum under argon at 80 °C for 4 h. The washing of the resulting product with NaOH produces water-dispersible graphene. The material has an average sheet resistance lower than the starting material graphite. It remains suspended in water indefinitely and exists as a single to a few layers of graphene, as determined by microscopic studies.

Xu et al. prepared polystyrene functionalized graphene starting from graphite flakes and a reactive monomer, i.e. styrene [161]. Ultrasonic irradiation of flake graphite in the presence of styrene monomer results in the mechanochemical exfoliation of graphite flakes to graphene sheets along with the

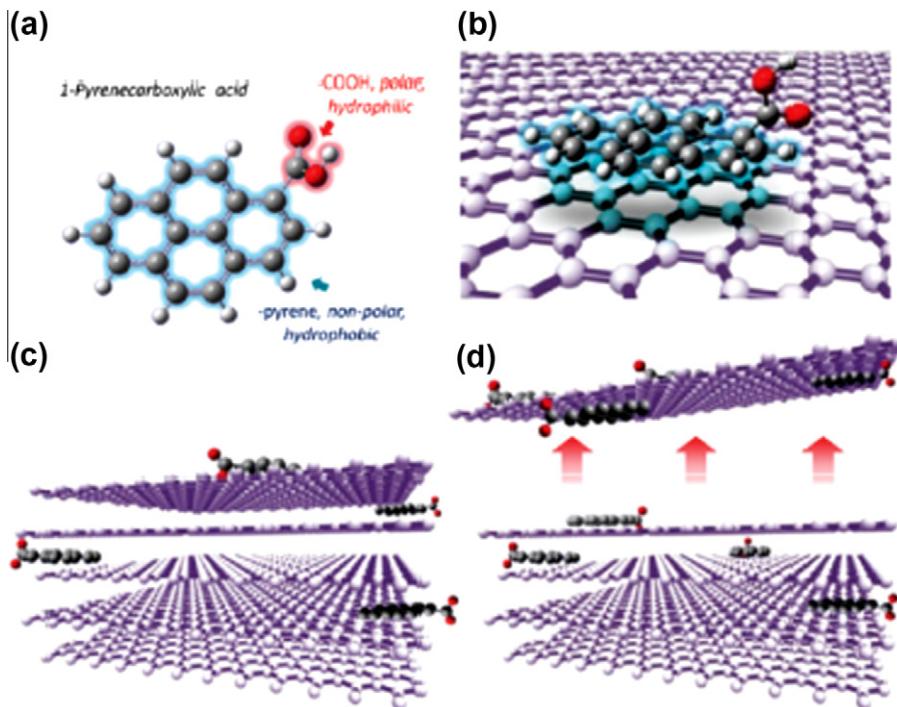


Fig. 35. (a) Molecular structure of 1-pyrenecarboxylic acid, with its polar (hydrophilic) and nonpolar (hydrophobic) parts indicated. (b) A PCA molecule can form a stable π -stacking bond with graphitic surfaces. (c) In a polar medium (H_2O) and with agitation, the nonpolar pyrene part prefers to attach itself on top of the graphitic surface via the π -stacking mechanism, or it penetrates within the layers of graphite to reduce hydrophobic interactions with water. With continuous agitation, more molecules enter between the layers and move in deeper, breaking the π -bond of the intergraphene layers of the graphite. (d) Continuing this process releases single or few layers of graphene. The $-COOH$ groups of the PCA molecules (attached to the released graphene flakes) prefer the polar medium and keep the graphene flakes stably suspended in water. (Reproduced with permission from [159].)

conversion of styrene monomer to polystyrene polymer. The polystyrene chains are formed from sonochemically initiated radical polymerization of styrene and noncovalently stabilized graphene sheets. The polymer functionalized graphene can easily be dispersed into different common organic solvents ($\sim 2 \text{ mg ml}^{-1}$ in DMF, and similarly soluble in THF, toluene, and CHCl_3), and does not precipitate even after 6 months.

6. Reduction of graphene oxide

Functionalization of graphene by different chemical, electrochemical, and sono-chemical methods has been discussed in the previous sections. However, most of the referenced studies deal with the functionalization of GO only. In order to obtain functionalized graphene from functionalized GO, reduction is an essential step. All reducing agents that are generally used for the reduction of organic ketones, carboxylic acids, and epoxy functional groups can be used in the reduction of pure GO or functionalized GO [162,163]. The most commonly used reducing agents are hydrazine monohydrate, sodium borohydride (NaBH_4), p-phenylene diamine, hydroquinone, and sodium hydrosulfite [162–165]. However, these chemicals are hazardous to human health and the environment. Hydrazine, hydrazine hydrate, and sodium borohydride are highly poisonous and explosive materials. Therefore, precautions must be taken when large quantities of strong reducing agents are used. In order to avoid these shortcomings, metal/hydrochloric acid reduction, such as aluminum/HCl and iron/HCl, has been conducted [166,167]. However, the use of metal/HCl as a reducing agent is also problematic due to the presence of residual metal particle impurities in the graphene sample. Therefore, some alternative methods have been recently proposed. Acetic acid and HCl can act as good reducing agents, and their reducing ability is comparable to that of hydrazine monohydrate [168,169]. Deoxygenation of GO using an aqueous alkaline solution is also described in the literature [170]. Recently, we have published a paper on the efficient reduction of GO using pyrrole monomer as a reducing and surface-modifying agent [171]. A method for reducing graphite oxide using a variety of commercially available alcohols has also been described. The reduced graphene exhibited a high C:O ratio (up to 30:1, as determined by elemental

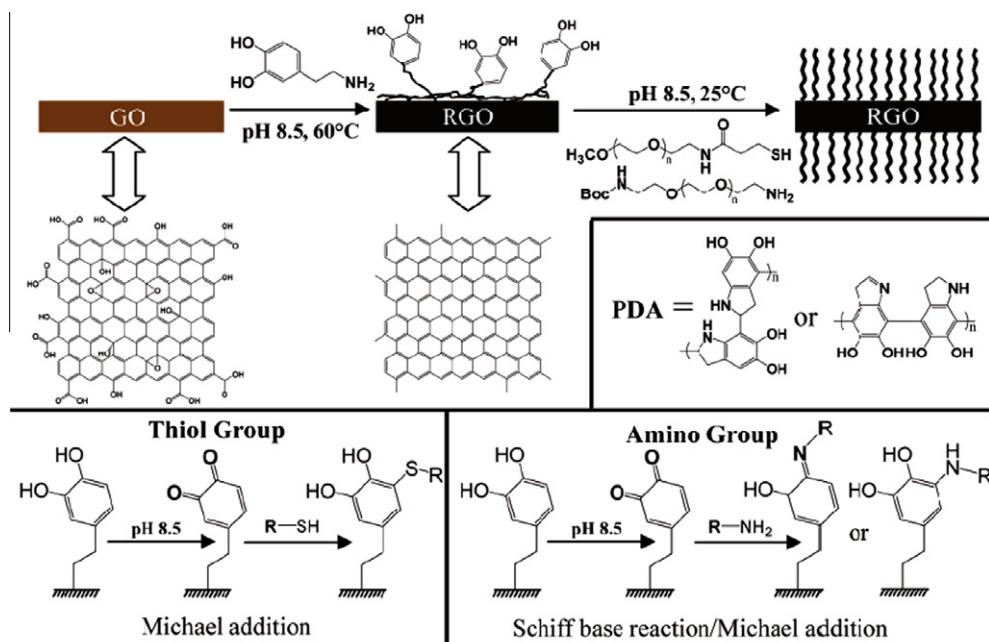


Fig. 36. Schematic illustration of the preparation of PDA-capped RGO and RGO-g-PEG. (Reproduced with permission from [85].)

analysis), high conductivity (up to 4600 S m^{-1}), and good specific capacitance (up to 35 F g^{-1}) [172]. In recent years, significant research efforts have been directed towards reagentless, eco-friendly, and green technology for the reduction of GO [52,173–180]. Microwave-induced reduction, flash reduction, solvent-assisted thermal reduction, and thermal reduction of GO have also attracted significant interest for the production of large-scale graphene [173–180]. Biological reduction of GO is also a current topic in graphene research. Zhang et al. have suggested that the reducing ability of L-ascorbic acid is very close to that of hydrazine monohydrate [52]. Xu et al. have reported the dopamine-induced reduction and functionalization of GO sheets. Dopamine has been found to be polymerized during the reduction process and adsorbed on the surface of graphene (Fig. 36) [85]. Dextran has also been used as an effective, multifunctional reducing agent [180]. Salas et al. have shown that GO can be reduced via bacterial respiration [178]. Very recently, Wang et al. have demonstrated a simple synthesis of soluble graphene via a green reduction of GO in a tea solution [179].

7. Applications of functionalized graphene

The two-dimensional carbon network of graphene has attracted tremendous research interest due to extensive applications in the field of nanoelectronics, biosensors, drug delivery, supercapacitors, fuel cells, H_2 storage, transistors, and polymer nanocomposites [1,16–23,25,31,181–187]. However, in some cases, the use of pure graphene is problematic due to its tendency toward aggregation and processing difficulty [34]. In order to overcome this problem, the use of functionalized graphene in the aforementioned areas has attracted extensive research interest. The current section will highlight the application of functionalized graphene in biosensors, supercapacitors, transistors, drug delivery, flexible electrodes, and polymer nanocomposites [18,79,101,120,187].

The development of nanodispersions of graphene in a polymer matrix has opened a new and interesting area of materials science in recent years. These nanohybrid materials show considerable improvement in physicochemical properties that cannot normally be achieved using conventional composites or virgin polymers. The extent of improvement is related directly to the degree of dispersion of functionalized graphene in the polymer matrix. The most important aspect of these nanocomposites is their very low graphene content [18,22,188–190]. Graphene-based composites are suitable for applications as high-performance composites, where good mechanical properties such as high strength and modulus are required with small amount of fillers. Graphene-based conducting polymer composites are suitable for application in the design of flexible electronics, as well as supercapacitors and energy storage devices [191–193]. It has been found that the electrochemical stability of graphene-based conducting polymer composites is much better than that of pure graphene.

One of the most promising applications of functionalized graphene is the fabrication of sensors to diagnose diseases [193–199]. These sensors are based upon the large surface area of graphene and the fact that molecules are sensitive to particular disease indicators and can attach to the carbon atoms in graphene. The electroactive prosthetic groups are deeply embedded in the biomolecules [188]. Graphene acts as an “electron wire” by decreasing the electron transfer distance between the active sites of the biomolecules and the electrode areas. However, the interaction between the functional groups of biomolecules and pristine graphene is unfavorable due to the absence of hydrophilic groups. On the contrary, functionalized graphene disperses well in the matrix and interacts very easily with the biomolecules compared to pure graphene. For example, researchers have found that functionalized graphene, single-stranded DNA, and fluorescent molecules can be combined to diagnose diseases [194–199]. A sensor can be formed by attaching fluorescent molecules to single-stranded DNA and then attaching the DNA to graphene. Immobilization of different enzymes on functionalized graphene leads to the formation of a cost-effective, highly sensitive, and very stable biosensor. It has been found that the functionalized graphene-based biosensors can successfully detect glucose, NADH, cholesterol, hydrogen peroxide, and other molecules. It is also noteworthy that the efficiency of functionalized graphene-based biosensors is much better than that of pure graphene in some cases.

A supercapacitor is an energy storage device applicable to electric vehicles, consumer electronics, and other devices. In comparison to conventional batteries, supercapacitors have advantages of high power density, long cycle life, and low maintenance cost [200,201]. The preferred electrode for

supercapacitor should exhibit high specific capacitance and good electrochemical stability. Graphene based materials fulfill all the criteria for this kind of electrodes. However, the electrical double layer capacitance performance of graphene is limited by the aggregation and poor interaction between graphene and electrolyte. In order to overcome this limitation, surface modified graphene has been introduced as a supercapacitor electrode material. A specific capacitance up to 276 F g^{-1} has been recorded for solvothermally reduced GO [200]. PCA functionalized graphene are shown to be very advantageous as conductometric sensors and ultracapacitors with extremely high specific capacitance ($\sim 120 \text{ F g}^{-1}$), power density ($\sim 105 \text{ kW kg}^{-1}$), and energy density ($\sim 9.2 \text{ W h kg}^{-1}$) [159]. Thermally exfoliated GO exhibits a specific capacitance value of 230 F g^{-1} , whereas carbonized GO shows only 100 F g^{-1} [202]. Due to its high energy density and favorable power density, functionalized graphene is a potential candidate for supercapacitor electrodes. The specific capacitance of PSS modified graphene is 34 F g^{-1} at scan rate of 100 mV s^{-1} [202].

A transistor device needs to have a good on-off ratio to be viable. The absence of a bandgap in graphene is one of the fundamental problems that must be resolved before the material can be employed as transistor [34]. The chemical functionalization of graphene offers an alternative approach in controlling its electronic properties. During functionalization, the sp^2 network is destroyed and converted to a sp^3 structure with the conversion of metallic graphene to an insulator. The metallic character of graphene can be converted to a semiconductor after appropriate surface modification [97]. The specially designed FETs of bilayer graphene and organic seed layer made from a derivative of poly-hydroxystyrene shows an on/off current ratio of around 100 at room temperature [33]. The transport measurement suggests a Schottky barrier height $> 65 \text{ meV}$ at D_{ave} of 2.2 V nm^{-1} , corresponding to an electrical (transport) band gap of $> 130 \text{ meV}$. At 20 K, the on/off current ratio of the device is about 2000 demonstrating $D_{ave} \sim 1.3 \text{ V nm}^{-1}$. Therefore, the band gap of bilayer graphene can be increased significantly which enables a number of novel nanoelectronic and nanophotonic applications.

The biocompatibility of graphene with microorganisms and living cells need to be explored. Several research efforts have been focused to analyze the biocompatibility of GO and graphene with microorganisms [203]. GO decreases cell adhesion while entering the cytoplasm and nucleus [204], and it can also cause lung inflammation and kidney failure. However, the blood circulation time in GO-deposited lungs is far better than for other carbon-based nanofillers [205]. The growth of Gram-positive and Gram-negative (e.g., *Escherichia coli*) bacteria is significantly affected by the sharp edges of the reduced graphene nanowalls [206,207]. Ongoing research shows that surface modification of GO significantly reduces the toxicity of GO and graphene [106,208]. Liu et al. have shown that chemically functionalized graphene not only converts water-insoluble drug molecules into water-soluble ones, but also can release the drug molecule in a controlled way [106]. Yang et al. have reported that pegylated graphene at a dose of 20 mg kg^{-1} is not toxic to Balb/c female mice based on blood biochemistry, hematology, and histology analysis [208]. However, the exact mechanism is still not clear. Therefore, making GO more biocompatible and decreasing or preventing toxicity for future *in vivo* biomedical applications continue to be challenging.

8. Conclusions and future scope

The functionalization of graphene by various techniques has been discussed in detail in the current review. The surface of graphene can be functionalized by covalent and noncovalent modification techniques. In covalent modification, nucleophilic substitution of an amine-terminated organic modifier is the easiest way to produce functionalized graphene. In this case, large-scale production of functionalized graphene from GO is also possible. However, the electrical conductivity of the functionalized graphene is greatly reduced with this type of modification. In order to obtain highly conductive graphene, electrophilic substitution of diazonium salt onto the surface of partially reduced graphene is highly recommended. Noncovalent modification of a small organic polymer on a pre-reduced graphene surface can also yield better electrical conductivity. Apart from covalent and noncovalent techniques, preparation of processable graphene directly from graphite has attracted significant research interest. However, in all these cases, the electrical conductivity of the functionalized graphene is significantly decreased. Moreover, the separation of excess organic modifier from the function-

alized graphene is a major concern. Therefore, further research on the functionalization of graphene is required in order to improve its electrical conductivity, dispersibility, and address the unquestionable need for a facile synthetic route. Finally, it should be noted that a method for the mass production of graphene has not yet been identified. Therefore, research efforts should focus on achieving large-scale production of graphene in order to drive modern science and technology in terms of mobility, environmental safety and security, health, and energy production.

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