

# The chemistry of graphene

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A review on the latest developments on graphene, written from the perspective of a chemist, is presented. The role of chemistry in bringing graphene research to the next level is discussed.

## 1. Introduction

The discovery of graphene by Andre Geim and co-workers at the University of Manchester using the deceptively simple Scotch tape method<sup>1,2</sup> has created a revolution in condensed matter physics. Thereafter, graphene is heralded as the next-generation material for nanoelectronic devices. Electrons in graphene obey a linear dispersion relation and behave like massless relativistic particles,<sup>3</sup> resulting in the observation of a number of very peculiar electronic properties such as the quantum hall effect,<sup>4–7</sup> ambipolar electric field effect,<sup>1,8</sup> good optical transparency,<sup>9–11</sup> and transport *via* relativistic Dirac fermions.<sup>4–7</sup> Due to its unprecedented high carrier mobilities (200 000 cm<sup>2</sup>/V s),<sup>12</sup> high thermal and electrical conductivity,<sup>13–15</sup> graphene-based electronic platforms can potentially revolutionize post-complementary metal oxide semiconductor (CMOS) electronics. Strong non-linear optical conductance of graphene has also paved the way for the fabrication of terahertz detectors and emitters for applications in defence technology and telecommunications.<sup>16–18</sup> The “Scotch tape” graphene provides the first platform for the

investigation of physics. However the monolayer yield from the “Scotch tape” method is so low that no chemists will consider it viable for doing chemical reactions. In order to scale up the production of graphene for technological applications, new production methods and surface treatment schemes for graphene have to be developed.<sup>19</sup> The emerging applications of graphene in optics, polymer composites, thin coatings *etc.* will most likely be driven by breakthroughs in chemistry that combine the economy of scale with function.

Graphene, which consists of a single atomic sheet of conjugated sp<sup>2</sup> carbon atoms, has a wide open double-sided surface that can undergo a broad class of organic reactions analogous to unsaturated systems in organic molecules. For chemists, graphene is an analog of a giant aromatic “poly-molecule” possessing high electrical conductivity, mechanical strength and optical absorption properties. It can be incorporated into polymers and inorganic systems to enhance mechanical strength, thermal and electrical conductivity. In order to incorporate graphene into batch type processing required for forming blends and composites, solution-processable chemistry has to be developed. In the most ideal picture, a well dispersed solution of homogeneously sized graphene sheets is the perfect raw material for chemists to use as scaffolds for the bottom-up synthesis of giant polycyclic aromatics, with these important differences:

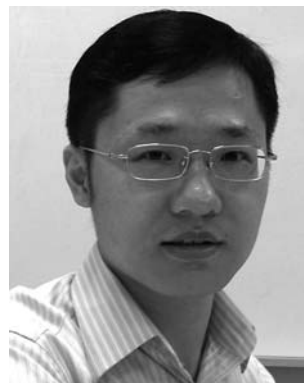
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Qiaoliang Bao

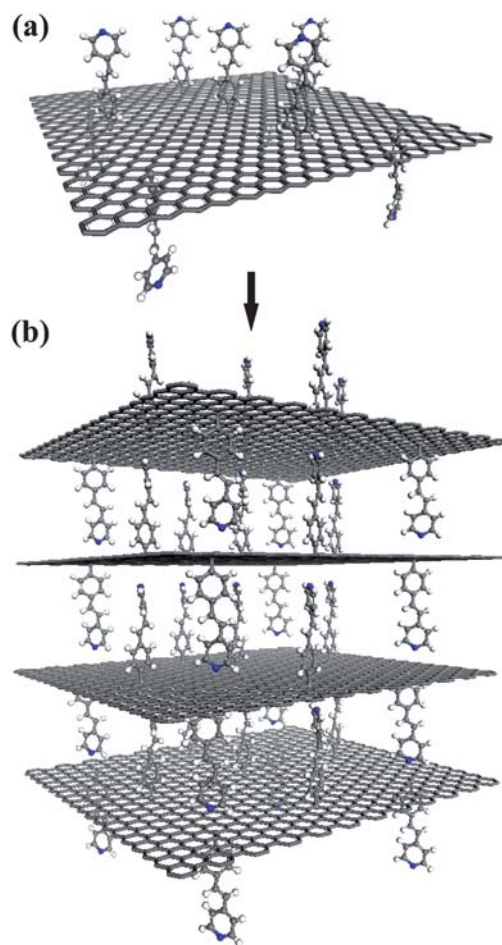
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erties of graphene and related materials. He has published the first few works on the mode-locking properties of graphene for ultrafast lasers.

(i) graphene sheets are extended conjugated systems that are 100 to 1000 times larger than the size of typical organic molecules, thus the functionalization of these extended frameworks allows an entirely new library of organic–graphene hybrids to be created; (ii) graphene is not a polyaromatic hydrocarbon, but is a pure aromatic carbon system.<sup>20</sup> Its optical absorption can extend to beyond the far infrared, and its electrical conductivity and charge carrier mobilities surpass the most conductive polymers by several orders; (iii) as illustrated in Fig. 1a, graphene sheets allow double sided functionalization. This creates a unique structural motif with double-sided decoration of functional groups on an extended sheet. In principle these functional groups allow layer-by-layer coordination assembly in a “supramolecular” fashion, schematically shown in Fig. 1b. Graphene oxide (GO) has been incorporated into a metal–organic framework (MOF-5) where the metal ion chelator connects with carboxylic groups on GO and the inorganic matrix.<sup>21,22</sup> If homogeneously sized graphene sheets can be produced, supramolecular arrangement of these sheets, analogous to the supramolecular assembly of fullerenes, may be attainable. Essentially, graphene, as well as its derivatives, provide a rich playground for synthetic chemistry. This review will discuss the chemical concepts in the functionalization of graphene, as well as the latest developments in the preparation of functional graphene composites.

## 2. Reactivity of graphene

The detailed reactivity of graphene sheets, in terms of size, shape and possibility for stoichiometric control are currently not well understood.<sup>23</sup> However it can be expected that regioselectivity based on zig-zag or arm-chair conjugated tracks on the graphene plane will manifest for certain classes of reactions, *e.g.* cycloadditions, click reactions and carbene insertion reactions.<sup>24–26</sup> Reactions, which involve the frontier molecular orbitals of organic molecules with the  $\pi$  electrons of graphene, may not be constrained by classical Woodward–Hoffmann symmetry rules for concerted reactions since the band-like electronic states in graphene relax the requirements for symmetry matching.



**Fig. 1** (a) Schematic structure of a double-sided decoration of functional groups (4-(2-(pyridin-4-yl)vinyl) phenyl) on graphene. (b) Supramolecular by layer-by-layer assembly of functionalized graphene.

However, the formation of a covalent bond on the basal plane of the graphene sheet necessitates the breaking of  $sp^2$  bonds and formation of  $sp^3$  bonds.<sup>27</sup> An unpaired electron which is created



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at the site adjacent to the point of covalent bonding enhances the reactivity there, leading to a chain reaction from the point of initial attack and a regioselective “unzipping” of the conjugated tracks. Based on the principle of “minimization” of dangling bonds in reaction,<sup>28</sup> chemisorption of functional groups on different sublattices is much more energetically favorable than on the same sublattice. In addition, the principle of minimization of geometric strain may dictate the reactivity. For example, Fig. 2a–c illustrates that the covalent bonding between one hydrogen and carbon atom will cause atomic displacement of the bonded carbon above the plane of the sheet, and this strain can be minimized by having the second atomic hydrogen attached to the opposite side of the sheet as a form of “countersink” in stress relief.

Geometrically strained regions in the graphene lattice are areas of preferential reactivity because of the displacement of electron density above the plane of the ring. Engineering strain in a periodic manner on the surface lattice to control reactivity is a potential way of achieving stoichiometric functionalization of graphene. Like a strained plastic wrapper, ripples can develop on the graphene surface when it is suspended or subjected to thermal stress. Using simple thermal manipulation,<sup>29</sup> the orientation, wavelength and amplitude of these ripples can be controlled (Fig. 2d). In a macroscopic sense, the amplitude of the fluctuations is much smaller than the sample size. This means that the long-range order of graphene is preserved, although the curvature induced stress in these ripples will generate sites of enhanced reactivity. By controlling the orientation and amplitude of these ripples, it can be envisaged that well-controlled stoichiometric functionalization of graphene can be potentially attained, as schematically illustrated in Fig. 2e.

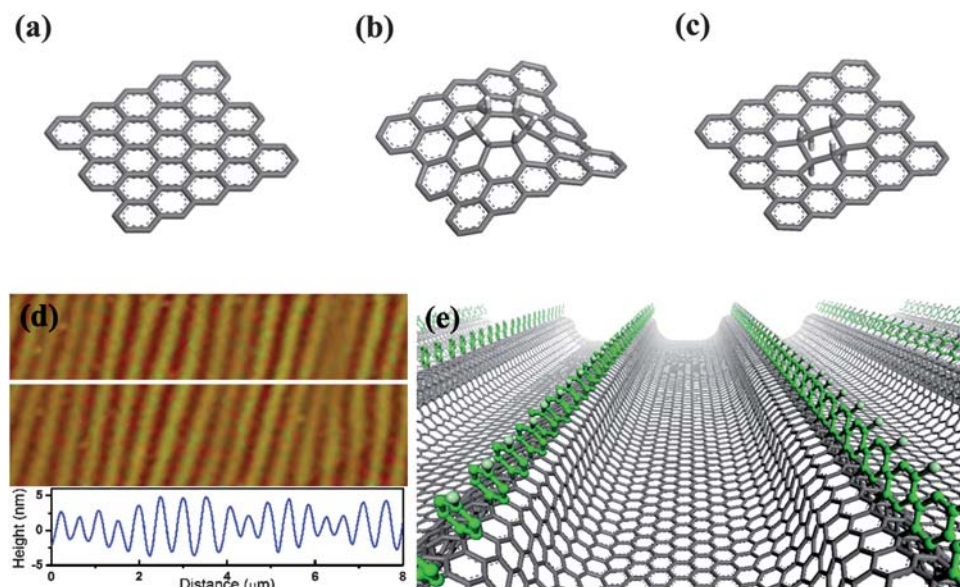
Due to the two-dimensional nature of graphene sheets, the edge regions play an important role in the electronic structure of

the molecules.<sup>30–33</sup> The edges can manifest as either zig-zag tracks or arm-chair tracks. In the zig-zag edges, the attainment of aromatic sextets is frustrated in the majority of the rings, hence such a structure is thermodynamically unstable compared to the arm-chair edges. It can be expected that the zig-zag edges will display higher reactivity as compared to the arm-chair edges.<sup>34</sup> Parallel insights into the graphene reactivity can be obtained from graphene-like polyaromatic hydrocarbons where stable zig-zag edged molecules are more challenging to synthesize than the arm-chaired ones.

### 3. The purpose of functionalization

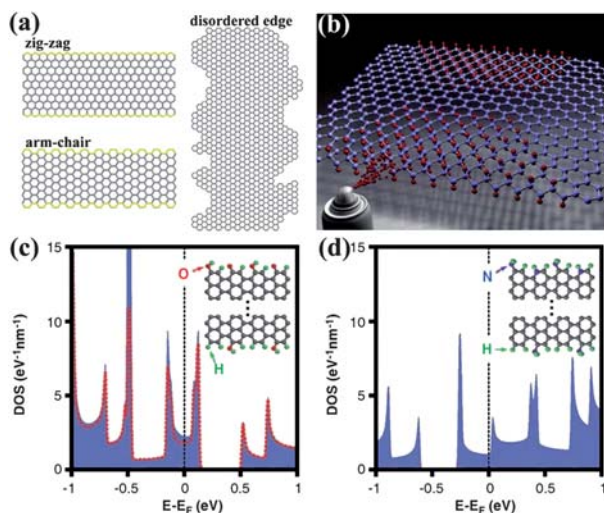
#### 3.1 Bandgap opening

A transistor device needs to have a good on-off ratio to be viable. The absence of a bandgap in graphene constitutes one of the fundamental problems that needs to be resolved before the material can be deployed as a transistor. For graphene which is grown epitaxially on silicon carbide, a bandgap can be engineered due to electronic coupling between graphene and the underlying substrate. However, bandgap tailoring by external electrostatic gate<sup>35,36</sup> or substrate<sup>37–40</sup> are external controls with limited tuneability for the on-off ratio. Fig. 3a shows another approach to circumvent this problem by fabricating graphene nanoribbons<sup>41,42</sup> with edges adopting the arm-chair conformation. It has been demonstrated that such a structure can be semiconducting, as opposed to a nanoribbon with edges that adopt zig-zag conformation.<sup>43–48</sup> However, in reality, it is technically challenging to control the edge structure of the graphene nanoribbons and in most cases, the resultant graphene nanoribbons adopt a disordered edge conformation and a transport gap is created by Coulomb blockage effects.<sup>49</sup>



**Fig. 2** Reactivity of graphene. (a) Pristine graphene flake. (b) Chemisorption of hydrogen on the same sublattice. Strong strain causes obvious deformation after geometry optimization (simulated by DMol3 code). (c) Chemisorption of hydrogen on the different sublattices. Graphene plane maintains flatness by having hydrogen absorbed on both sides of the plane (simulated by DMol3 code). (d) AFM image and cross-section profile of graphene membrane with nearly periodic ripples. Reprinted with permission from Z. H. Ni, Nanyang Technological University. (e) Stoichiometric functionalization of graphene on the ripples which can have enhanced reactivity.





**Fig. 3** (a) Graphene nanoribbons with zig-zag (up left), armchair (bottom left) and disordered edges (right). (b) Selectively functionalizing graphene to make a graphene nanoribbon conductive channel.<sup>51</sup> Reprinted with permission from Kostya Novoselov, University of Manchester. (c) Calculated density of states (DOS) showing p-type doping effect of a semiconducting 21-armchair graphene nanoribbon (width:  $\sim 2.5$  nm) terminated by oxygen-containing groups. (d) DOS showing n-type doping effect of a 21-armchair graphene nanoribbon functionalized with nitrogen-containing groups on the edge sites. Reprinted with permission from ref. 53, copyright 2009, the American Association for the Advancement of Science.

The chemical functionalization of graphene offers an alternative approach to the control of its electronic properties. The hydrogenation of graphene, which involves the change of electronic structure from  $sp^2$  to  $sp^3$ , results in a conversion from a metallic graphene to an insulator (Fig. 3b).<sup>50,51</sup> Sofo *et al.*<sup>52</sup> first predicted the existence of graphane, which is a two dimensional hydrocarbon. The fully fluorinated analog such as poly-(carbon monofluoride) with the formula CF, has also been synthesized. However, attempts made to produce graphane by exchanging F with H failed as only graphite and HF were produced. Direct hydrogenation and intercalation of graphite by  $H_2$  is also challenging due to the higher binding energy of  $H_2$  ( $\sim 2.4$  eV/atom) compared to  $F_2$  ( $\sim 1.5$  eV/atom). The key ingredient for successful hydrogenation involves atomic hydrogen, this experiment was first demonstrated by Geim and co-workers.<sup>50</sup> They exposed graphene to atomic hydrogen generated by a remote discharged low-pressure (0.1 mbar) hydrogen–argon (10%  $H_2$ ) plasma. It was found that it typically required 2 h of plasma treatment to attain the saturation in measured transport characteristics. The metallic state can be restored by annealing at  $450^\circ\text{C}$  in Ar atmosphere for 24 h. However, it is well known in the literature of diamond growth that atomic hydrogen in excess of surface saturation coverage can induce etching of carbon phase to produce volatile hydrocarbon species, this is a kinetically favourable reaction.<sup>54</sup> It can be expected that exposure to excess atomic hydrogen or energetic hydrogen ions will create defects in graphene. Therefore, careful control is needed to allow surface termination by hydrogen without the collateral damage of etching. At present, the chemical structure of graphane is still a mystery.

Besides atomic hydrogen, organic molecules can be covalently coupled to the graphene sheet *via* carbon–carbon bonding. Haddon and co-workers<sup>55</sup> demonstrated the chemical modification of epitaxial graphene (EG) by covalent attachment of aryl groups to the basal carbon atoms. This reaction is facilitated by the spontaneous electron transfer from the graphene layer to the diazonium salt. The resultant few-layer EG functionalized by covalent carbon–carbon bond formation with nitrophenyl groups transforms the electronic structure and transport properties of EG from near-metallic to semiconducting.

### 3.2 Doping

The motivation of doping is to control the type and concentration of charged carriers. Increasing the carrier concentration to fill the electronic bands, by two orders of magnitude from the intrinsic level ( $10^{12}\text{ cm}^{-2}$ ), would allow the filled energy levels to reach the van Hove singularity ( $\sim 10^{14}\text{ cm}^{-2}$ ).<sup>56,57</sup> At very large carrier concentrations, a very fascinating energy landscape for the electrons, more exciting than that observed in the limited energy window around the Dirac point can manifest. This can be predicted from the band structure of graphene, thus, achieving high doping can bring the physics to another realm which can have implications for room temperature superconductivity and ferromagnetism.<sup>58–60</sup>

If graphene is covalently bonded to electron-withdrawing oxygen functionalities, *p*-doping can be induced. Similarly, if it is functionalized by electron-donating nitrogen functionalities, *n*-doping can be achieved. Fig. 3c and d show the possibility of *p*-type or *n*-type chemical doping with different oxygen or nitrogen groups. With precise control of the interface between *p*-doped and *n*-doped graphene regions, it is possible to selectively engineer a graphene *p*–*n* junction by chemical doping.

Alternatively, graphene can also be *p*-doped by absorbing metals with higher electron affinity such as gold.<sup>61</sup> In comparison, alkaline metals are good electron donors owing to their strong ionic bonding. This facilitates the release of their valence electrons into the conduction band of graphene. Therefore, the formation of ionic bonds makes alkaline metals an attractive candidate for *n*-type dopants.<sup>62,63</sup> In addition, the doping of graphene with transition metals such as Ca,<sup>64</sup> K and Pd<sup>65</sup> can theoretically result in ferromagnetism due to the hybridization between the transition metal and the carbon orbital.

Molecular 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<sup>66–68</sup> and photoelectron spectra.<sup>69</sup> Dong *et al.*<sup>67,68</sup> investigated graphene monolayers sandwiched by the aromatic molecule tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (TPA) and found that larger aromatic rings such as anthracene and pyrene exhibit stronger interactions with graphene, evidenced by pronounced Raman G-band splitting due to the symmetry breaking of the graphene A–B sublattice.

## 4. Functional composites and their associated chemistry

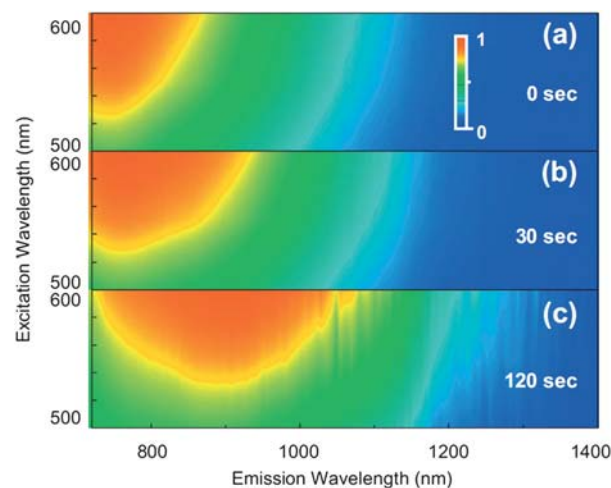
The chemistry of graphene concerns itself foremost with the solubilization of graphene. Pure graphene is hydrophobic and

has no appreciable solubility in most solvents.<sup>70</sup> To impart solution processability on graphene, chemists turned to the well established wet chemistry developed for carbon nanotubes and graphite. The conjugated graphene sheet can be readily functionalized *via* non-covalent  $\pi$ - $\pi$  stacking or covalent C-C coupling reactions. By derivatizing graphene with different organic moieties, the solubility of graphene can be tuned to suit different solvents needed for the processing of composite films.<sup>71–73</sup> Functional groups can broaden the properties of the graphene through the formation of donor-acceptor complex with graphene, which affords tuneability in electrical conductivity, optical and photovoltaic properties.<sup>74,75</sup> It can be expected that based on the superlative properties of graphene and its derivatives, significant improvements in viscosity, electrical, mechanical and thermal properties of the graphene-polymer composite can be achieved.

#### 4.1 Covalent functionalization

The most convenient method in terms of solution processing, but certainly not the best method where electronic application is concerned, involves the acid oxidation of graphite to impart oxygenated species like carboxyl, epoxy and hydroxyl on the material, generating graphite oxide.<sup>77,78</sup> These negatively charged oxygenated species help to disperse the graphite oxide as a single sheet (called graphene oxide (GO)) by providing electrostatic repulsion and solvation. The drawback is that the presence of oxygenated groups on the basal plane of graphene disrupts the  $\pi$ -conjugation, as a result, GO is insulating. In addition, GO is a non-stoichiometric material because the density of oxygen groups cannot be precisely controlled, which means that functionalization chemistry based on coupling chemistry to the oxygenated groups will inevitably lead to non-stoichiometric functionalization.

Compared to zero-gap graphene, GO exhibits insulating properties and can be fluorescent because of a defect-related optical gap as oxidation produced a disruption of the  $\pi$  network gap. Fig. 4 shows that a controllable reduction of GO by hydrazine at 50 °C with increased exposure times causes a significant redshift in the photoluminescence emission.<sup>76</sup> In an opposite report,<sup>79</sup> the fluorescence emission of ultrasmall nano-GO (NGO) peaked at  $\sim 570$  nm was blue-shifted to  $\sim 520$  nm after covalently grafting polyethylene glycol (PEG) star polymers. These suggest the possibilities of tuning the optical properties of GO by controlled reduction or by coupling it to other functionalities. A variety of chemical and thermal techniques have been developed for this purpose.<sup>10,15,80–86</sup> Recently, we developed an environmentally friendly hydrothermal route for the dehydration of oxygenated groups in GO.<sup>87</sup> The hydrothermal method is based on the use of superheated H<sub>2</sub>O which can promote acid-catalyzed reactions of organic compounds because of a sufficiently high H<sup>+</sup> concentration compared to the normal liquid phase. Compared to chemical reduction processes using hydrazine, the “water-only” hydrothermal route has the combined advantages of removing oxygen functional groups and repairing the aromatic structures. By controlling the hydrothermal temperatures, the physical properties of GO can be changed to obtain tunable optical limiting performance. In previous reports,<sup>76</sup> through chemical reduction of GO, band gap

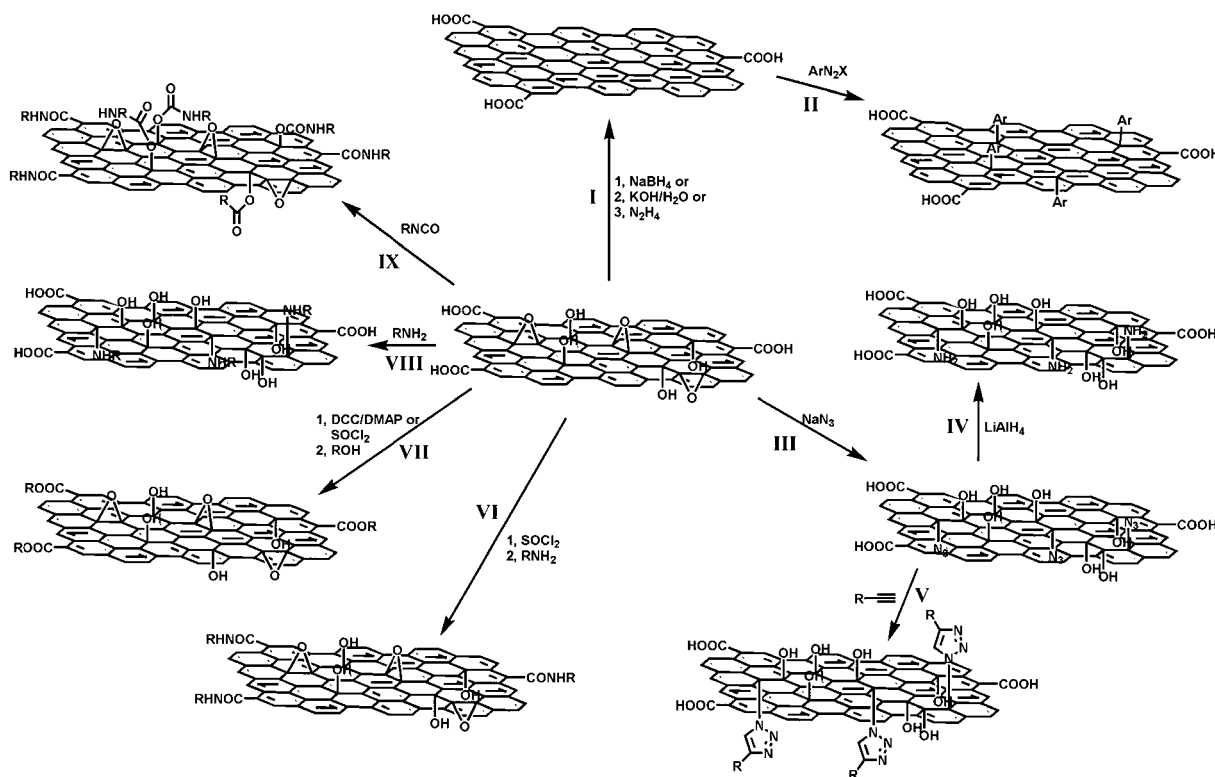


**Fig. 4** Normalized photoluminescence excitation-emission maps for GO solution taken in transmission mode during hydrazine vapor exposure. A significant red-shift in the photoluminescence emission can be seen with increasing of exposure time. Reprinted with permission from ref. 76, copyright 2009, American Institute of Physics.

modulation was observed and evidenced by broadband visible photoluminescence, which suggests a dispersion of hard gaps that may arise from bond alternation within the GO plane, giving rise to inter-valley scattering. Analogous to a single-walled carbon nanotube, the fluorescence of GO in the NIR and IR range are potentially useful for biological applications since cells and tissues exhibit little auto-fluorescence in this region.<sup>79,97</sup>

Fig. 5 displays a schematic representation of possible chemical routes to functionalized graphene. In terms of chemical reactions, acylation reactions are among the most common approaches used for linking molecular moieties onto oxygenated groups at the edges of GO. The acylation reaction between the carboxyl acid groups of GO and octadecylamine (after SOCl<sub>2</sub> activation of the COOH groups) can be used to modify GO by long alkyl chains (reaction VI in Fig. 5).<sup>91</sup> The functionalized GO has a solubility of 0.5 mg mL<sup>-1</sup> in THF and it is also soluble in CCl<sub>4</sub> and 1,2-dichloromethane. By the acylation methods, the carboxylic groups can be tethered to amine-functionalized molecules. Extending on this functionalization chemistry, NGO can be functionalized with PEG to obtain a biocompatible GO-PEG conjugate which can be used as a platform for high density loading of hydrophobic drugs like camptothecin, which can bind to the graphene *via*  $\pi$ - $\pi$  stacking.<sup>79</sup> It is known that many potent, often aromatic drugs are water insoluble, which has hampered their use for disease treatment. The resulting NGO-PEG-SN38 complex exhibited excellent water solubility while maintaining its high cancer cell killing potency similar to that of the free drug in organic solvents. The efficacy of NGO-PEG-SN38 was far higher than that of irinotecan (CPT-11), a FDA-approved water soluble SN38 prodrug used for the treatment of colon cancer.<sup>98</sup>

GO contains some epoxy groups. Therefore, nucleophilic ring-opening reaction can occur between the epoxy groups of GO and the amine groups of an amine-terminated organic molecular (reaction VIII in Fig. 5).<sup>94,95</sup> The surface of GO can be modified *in situ* with octadecylamine (ODA) in dichlorobenzene using the



**Fig. 5** Schematic showing various covalent functionalization chemistry of graphene or GO. I: Reduction of GO into graphene by various approaches (1,  $\text{NaBH}_4$ ; 2,  $\text{KOH}/\text{H}_2\text{O}$ ; 3,  $\text{N}_2\text{H}_4$ ). II: Covalent surface functionalization of reduced graphene *via* diazonium reaction ( $\text{ArN}_2\text{X}$ ).<sup>88,89</sup> III: Functionalization of GO by the reaction between GO and sodium azide. IV: Reduction of azide functionalized GO (azide-GO) with  $\text{LiAlH}_4$  resulting in the amino-functionalized GO. V: Functionalization of azide-GO through click chemistry ( $\text{R}-\text{C}\equiv\text{CH}/\text{CuSO}_4$ ).<sup>90</sup> VI: Modification of GO with long alkyl chains (1,  $\text{SOCl}_2$ ; 2,  $\text{RNH}_2$ ) by the acylation reaction between the carboxyl acid groups of GO and alkylamine (after  $\text{SOCl}_2$  activation of the  $\text{COOH}$  groups).<sup>74,91</sup> VII: Esterification of GO by DCC chemistry or the acylation reaction between the carboxyl acid groups of GO and  $\text{ROH}$  alkylamine (after  $\text{SOCl}_2$  activation of the  $\text{COOH}$  groups) (1,  $\text{DCC}/\text{DMAP}$  or  $\text{SOCl}_2$ ; 2,  $\text{ROH}$ ).<sup>92,93</sup> VIII: Nucleophilic ring-opening reaction between the epoxy groups of GO and the amine groups of an amine-terminated organic molecular ( $\text{RNH}_2$ ).<sup>94,95</sup> IX: The treatment of GO with organic isocyanates leading to the derivatization of both the edge carboxyl and surface hydroxyl functional groups *via* formation of amides or carbamate esters ( $\text{RNCO}$ ).<sup>96</sup>

same reaction to give a black ODA-GO nanosheet well dispersed in organic solvents.<sup>95</sup> Another extension of this concept involves the stabilization of GO nanosheets by amine-terminated ionic liquids (ILs). The resultant IL-functionalized graphene composite nanosheets could be dispersed well in water, *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) due to an enhanced solubility and electrostatic inter-sheet repulsion provided by the ionic liquid units.<sup>94</sup>

Besides small organic molecules, graphene nanosheets can be functionalized with polymers like poly(vinyl alcohol) (PVA) through the carbodiimide-activated esterification reaction between the carboxylic acid moieties on the nanosheets and hydroxyl groups on PVA using *N,N*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridine (DMAP), and *N*-hydroxybenzotriazole (HOBT) in DMSO (reaction VII in Fig. 5).<sup>92</sup>

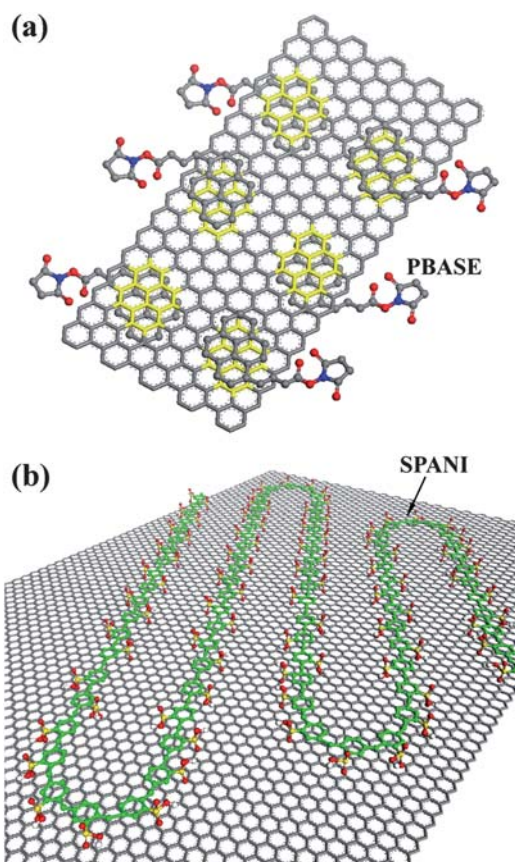
Recently, Salvio and co-workers<sup>90</sup> developed an elegant method to transfer GO sheets onto silicon oxide surface. GO was reacted with sodium azide, and then reduced to form amino groups on both sides of the sheets (reaction III and IV in Fig. 5). Using microcontact printing, these functional groups react with the isothiocyanate monolayer on the pre-functionalized silicon oxide substrate to form covalent bonds. The graphene sheets that are not covalently bound to the surface can be exfoliated by

ultrasonication, leaving single-layer sheets attached to the substrate. Following reduction, the immobilized sheet exhibits resistivity which is approximately seven times larger than that of unprocessed graphite. This is potentially an important step towards a chemical approach for immobilizing graphene monolayer on silicon oxide.

## 4.2 Non-covalent interactions

The non-covalent interactions are based on van der Waals forces or  $\pi$ - $\pi$  stacking of aromatic molecules on the graphene plane.<sup>99–101</sup> The advantage is that this does not disrupt the extended  $\pi$  conjugation on the graphene surface, unlike covalent functionalization which creates defects on the graphene sheet. Both graphene and GO can undergo  $\pi$ - $\pi$  stacking and different schemes have been developed to form hybrid organic-graphene systems based on these interactions. Pyrene derivatives have strong affinity with the basal plane of graphene *via*  $\pi$ - $\pi$  interaction<sup>102</sup> and this helps to stabilize graphene in aqueous solutions. Fig. 6a shows how pyrene butanoic acid succidymidyl ester (PBASE) can absorb on graphene *via*  $\pi$ - $\pi$  interaction. In principle, donor type and acceptor type aromatic molecules can be  $\pi$ - $\pi$  stacked on the graphene surface, respectively, to tune the





**Fig. 6** Noncovalent interactions between (a) small molecules (PBASE), (b) polymer (SPANI) and graphene through  $\pi$ - $\pi$  stacking.

electron density on graphene. For example, a donor-acceptor complex can be created on graphene using pyrene-1-sulfonic acid sodium salt (PyS) as the electronic donor, and the disodium salt of 3,4,9,10-perylenetetracarboxylic diimide bisbenzenesulfonic acid (PDI) as the electronic acceptor.<sup>103</sup> Both PyS and PDI have large planar aromatic structures that strongly anchor them onto the hydrophobic surface of graphene sheets *via*  $\pi$ - $\pi$  interaction. In addition, the negative charges in both molecules act as stabilizing species to maintain a strong static repulsion force between the negatively charged graphene sheets in solution, giving rise to high monolayer yield. Remarkably, the composite of PDI with graphene sheets resulted in a significant increase in conductivity for graphene-PDI ( $13.9 \text{ S cm}^{-1}$ ) compared to pristine reduced graphene ( $3.0 \text{ S cm}^{-1}$ ), whereas a 30% decrease in conductivity was observed for graphene-PyS ( $1.9 \text{ S cm}^{-1}$ ). Finally, an improvement of the overall power conversion efficiency (PCE) from 0.78 to 1.12% was achieved using graphene-PyS as anodes in bulk heterojunction solar cells instead of pristine graphene.<sup>103</sup>

Recently, by applying the chemical vapor deposition (CVD) method, we developed large-area, continuous, transparent, and highly conducting few-layered graphene films as anode for application in photovoltaic devices.<sup>104</sup> As-grown CVD graphene film is hydrophobic and not compatible with the spin coating of poly(3,4-ethylenedioxythiophene) (PEDOT) needed in photovoltaic device fabrication. It is noteworthy that the noncovalent modification of the graphene films with PBASE improves the hydrophilic characteristics, work function and power conversion

efficiency. The PCE of organic solar cells increased from 0.21% of the unmodified films to 1.71% of anodes using the PBASE-modified graphene. This performance corresponds to  $\sim 55.2\%$  of the PCE of an identical device made with an indium tin oxide (ITO) anode, *e.g.*, ITO/PEDOT-PSS/P3HT/PCBM/Al (PCE = 3.1%). This finding paves the way for the substitution of ITO in photovoltaic and electroluminescent devices with low cost graphene films.

Lu *et al.*<sup>105</sup> exploited the  $\pi$ - $\pi$  interactions and fluorescence quenching effects of GO with nucleobases and aromatic dye compounds for sensing applications. Their ingenious design is based on a fluorescence-enhanced detection that is sensitive and selective to the target molecule. GO binds dye-labeled ssDNA and completely quenches the fluorescence of the dye. In the presence of a complementary target, the binding between the dye-labeled DNA and target molecule alters the conformation of dye-labeled DNA, and disturbs the interaction between the dye-labeled DNA and GO. Such interactions release the dye-labeled DNA from the GO, resulting in the restoration of dye fluorescence.

### 4.3 Graphene-polymer composites

Perhaps the largest application of functionalized graphene lies in the area of polymer nanocomposites. Polymer nanocomposites combine two concepts in material design, *i.e.*, composites and nanomaterials. Tailor-made nanocomposites which exploit the superlative properties of both components can show enhanced performance in a myriad of applications ranging from flexible packaging, printable electronics, and interlayer dielectrics to thermoplastics. Mechanical reinforcement can be achieved when the graphene nanofiller is dispersed homogeneously in the matrix and the external load is efficiently transferred *via* strong interaction at the interface between the filler and the matrix.<sup>106-111</sup> Recently, Bai *et al.*<sup>112</sup> reported that graphene functionalized by conjugated polymer sulfonated polyaniline (SPANI) is soluble in water and has good air stability and electrochemical activity. The interactions are due mainly to the strong  $\pi$ - $\pi$  interaction between the backbones of SPANI and the graphene basal planes, as shown in Fig. 6b, and the electrostatic repulsion between the resulted negatively charged SPANI/graphene sheets. Triblock copolymers (poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide), PEO-b-PPO-b-PEO) had also been used as a solubilizing agent for graphene to form a supramolecular hydrogel.<sup>113</sup> The formation of the stable aqueous copolymer-coated graphene solution is due to the noncovalent interaction between the hydrophobic PPO segments of the triblock copolymer and the hydrophobic graphene surface, whereas the hydrophilic PEO chains extend into water. Utilizing the dual roles of pluronic copolymer in dispersing graphene in aqueous solution and forming supramolecular hydrogel with  $\alpha$ -cyclodextrin, a facile and effective method to hybridize the well-dispersed graphene into a supramolecular hydrogel can be developed. The viscosity of the supramolecular hybrid hydrogels decreased significantly as compared to those of the native hydrogel resulting from the lamellar structure of the hybrid hydrogel because of the presence of the graphene sheets.

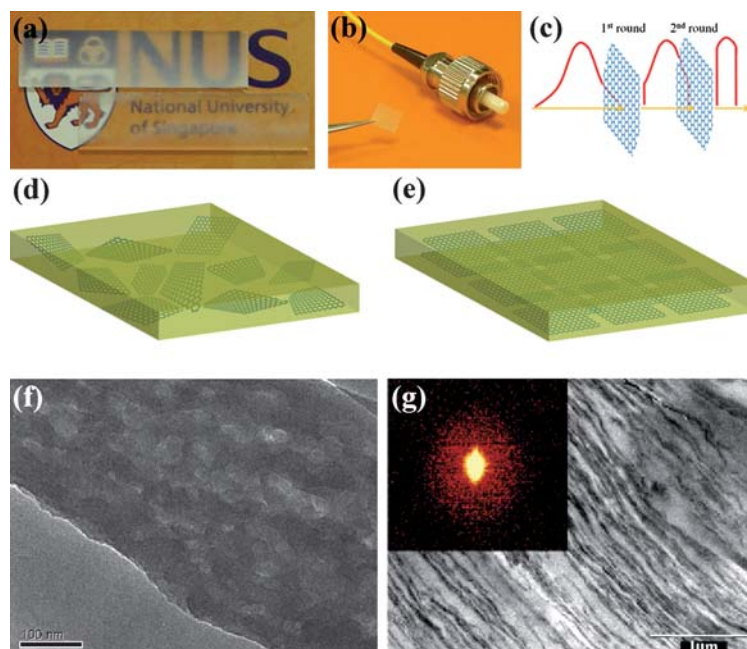
Although the initial focus of the graphene community is on the wonderful electronic properties of graphene, the optical applications of graphene composites may emerge in the market before

the high-end electronic application due to the relatively less stringent processing conditions of films for optical applications. A single atomic sheet of graphene can absorb  $\pi\alpha = 2.3\%$  of incident white light, where  $\alpha$  is the fine structure constant. The universal wide band absorption of graphene renders the material attractive as a saturable absorber, *i.e.* an optical element used in mode-locking of lasers, based on its properties to exhibit optical loss at high optical intensity. Recently, we investigated the saturable absorption of few-layers graphene.<sup>114,115</sup> Laser pulses can be reshaped into sub-picosecond width in telecommunication wavelength band, of which the concept is illustrated in Fig. 7a–c. Fig. 7d and e schematically illustrate the incorporation of graphene sheets into a polymer matrix in a random<sup>116</sup> or aligned fashion.<sup>117</sup> Such graphene composites afford a new class of optical material by marrying the special optical properties of graphene with the structural properties of the polymer. The use of graphene is inspired by the fact that single-walled carbon nanotubes (SWNTs) have been used as effective saturable absorbers for the mode locking of lasers to generate ultrashort pulses in the telecommunication bandwidth.<sup>118,119</sup> SWNTs dispersed in a polymer matrix have proven to be highly effective saturable absorbers due to their ultrafast recovery time and modulation depth.<sup>120–123</sup> Fig. 7f and g show the transmission electron microscopy (TEM) images of graphene encapsulated in polymer hosts, the advantage of polymer encapsulation passivates graphene from ambient oxygen and prevents photo-oxidation and optical bleaching by high powered lasers. This is very important for developing organic photonics components that do not photo-degrade with time.

The focus of future developments in graphene–polymer hybrid film used as optical elements is to obtain strong resonant saturable absorption and to achieve wideband tuneability. It can be envisaged that the successful deployment of graphene–polymer composites in high performance composites or optical films require multidisciplinary inputs from chemists, material scientists, physicists and engineers.

## 5. Production of graphene *via* chemical routes

Although GO sheets exfoliated from graphite can be dispersed as single sheets in aqueous solution, graphene generated from these GO precursors are invariably defective and its electrical conductivity is several orders below that of graphite even after thermal and chemical reduction. A method which can bypass the oxidation of graphene while allowing individual graphene sheets to be dispersed well in solution is ideal, since this will allow the extended conjugation to be preserved and avoid the tedious post-reduction treatments. Another fundamental reason is the issue of stoichiometric functionalization of graphene *versus* non-stoichiometric functionalization, as discussed earlier. Chemical derivatization of GO which relies on the linking of molecules to epoxide, carboxylic or hydroxide functionalities is inherently non-stoichiometric due to the random distributions of these groups. In principle, functionalization chemistry of pure graphene which involves binding to its  $\pi$ -conjugated network can be regioselective, thus stoichiometric functionalization on the basal or edge planes may be achievable.



**Fig. 7** Graphene polymer composites. (a) Graphene–PVAc (poly(vinyl acetate)) membrane on quartz fabricated by electrospinning. (b) Transferring free-standing graphene–polymer membrane onto optical fiber as photonics component. Reprinted with permission from ref. 124, copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaH. (c) Schematic showing pulse shaping mechanism of graphene as saturable absorber. The low intensity wings of the input optical pulse are absorbed by graphene while high intensity components pass through. (d) Schematic of graphene flakes randomly distributed in polymer matrix. (e) Schematic of graphene flakes aligned in polymer matrix. (f) TEM image of graphene–PVDF (poly(vinylidene fluoride)) nanocomposite. Reprinted with permission from ref. 116, copyright 2009, American Institute of Physics. (g) TEM image and small-angle X-ray scattering profile (inset) of the edge plane of GO–Nafion nanocomposite. Reprinted with permission from ref. 117, copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaH.

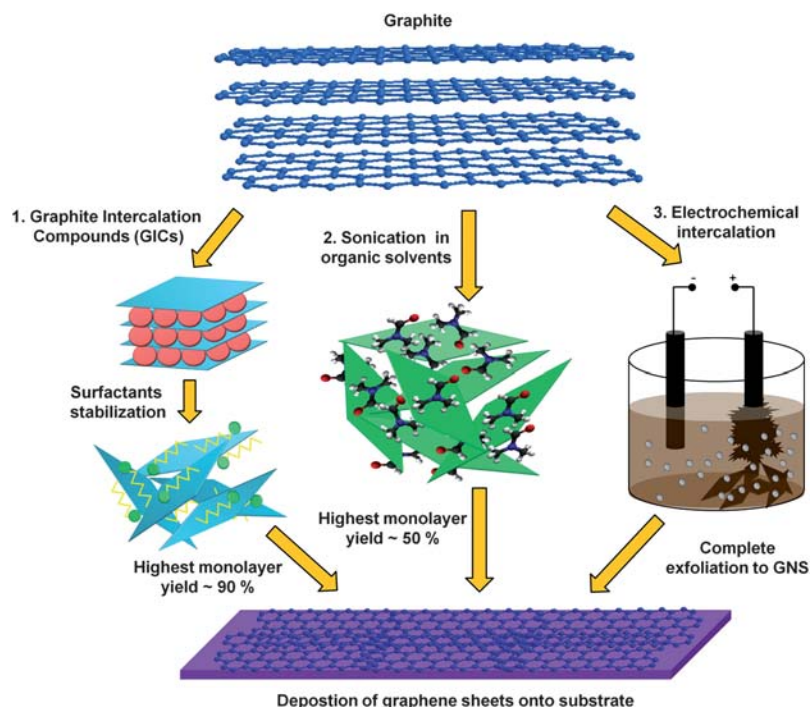


To develop alternative approaches to the oxidation–exfoliation method, chemists have re-visited old chemistry developed for “expanded graphite” used in batteries and fuel cells, with the aim of uncovering recipes that allow graphene sheets to be directly obtained from expanded graphite using intercalation and exfoliation methods. Fig. 8 illustrates three main approaches used to obtain solution-processable, high quality graphene sheets from graphite intercalation compounds, electrochemical as well as liquid phase exfoliation of graphite.

### 5.1 Graphene from graphite intercalation compounds (GIC) and expandible graphite

The rich intercalation chemistry of graphite presents an attractive avenue to obtain single-layer graphene sheets based on the favourable expanded interlayer spacing and which facilitates long-range exfoliation. However, previous research in the past two decades had shown that although graphite intercalation compounds are excellent precursors for exfoliated graphite,<sup>128</sup> intercalation–exfoliation of graphite *via* thermal shock, acid treatment and intercalation yielded only thin graphite nanoplatelets, and not single sheets.<sup>129</sup> Following the generation of expanded graphite by acid treatments and thermal shocks, intercalants must be added to further expand the interlayer distance. Sonication of the resultant GIC in stabilizers (or surfactants) results in stable colloidal suspension of graphene monolayer sheets in organic or aqueous solutions, as demonstrated by Dai and co-workers.<sup>41,125</sup> In one report, Dai and

co-workers sonicated expanded graphite in a long-chain aromatic polymer called poly(*m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV) dissolved in dichloroethane to produce a stable dispersion of chemically modified graphene (CMG) sheets and semiconducting graphene nanoribbons.<sup>41</sup> To improve the monolayer yield, oleum and tetrabutylammonium cations were used as intercalants.<sup>125,130</sup> This method afforded a high monolayer yield of ~90% after ultrasonication and film formation by Langmuir–Blodgett method. Yoo and co-workers<sup>131</sup> demonstrated a simpler one-step intercalation and exfoliation of GIC, which enables dispersion in water or organic solvents with the help of surfactants, by using fluorinated GIC (FGIC  $C_2F \bullet nClF_3$ ) as a starting material. Unlike graphite oxide, exfoliated graphene sheets from fluorine functionalized graphite are not electrically insulating as exposing the dry FGIC to thermal shock leads to the exfoliation of graphene sheets accompanied by the evolution of gaseous fluorocarbons. Another demonstration of efficient exfoliation from GIC is based on the ternary potassium salt  $K(THF)_x C_{24}$ , first demonstrated by Pénicaud's and co-workers.<sup>132</sup> By eradicating the sonication step and simply stirring the potassium GIC in *N*-methyl-pyrrolidone (NMP), spontaneous exfoliation occurs to give a high monolayer yield of large sized negatively charged graphene sheets and long ribbons. The spontaneous exfoliation of GIC was explained in terms of the entropy-driven intercalation of potassium ions between the graphene sheets. The graphene sheets and ribbons were measured by atomic force microscopy to be 0.4 nm thick, very close to that of pristine graphene (0.35 nm). In addition,



**Fig. 8** Schematic shows the various exfoliation routes to graphene. Route 1 shows graphene sheets obtained from graphite intercalation compounds (GIC) in which the graphite interlayer distance is increased by intercalants. A high monolayer yield (~90%) of graphene sheets stabilized by surfactants was achieved by Dai and co-workers.<sup>125</sup> Route 2 illustrates graphene sheets produced *via* direct sonication of graphite in organic solvents which yield a monolayer yield of 50% by Novoselov and co-workers.<sup>126</sup> Route 3 displays a recent method which involves ionic-liquid assisted electrochemical exfoliation of graphite anode to obtain graphene sheets with almost complete exfoliation to graphene nanosheets (GNS), demonstrated by Luo and co-workers.<sup>127</sup>

based on a simple rinsing procedure, all traces of NMP and potassium were effectively removed as confirmed by X-ray photoelectron spectroscopy. Deposition onto a variety of substrates yielded air-stable graphene films with desirable low resistance of 235  $\Omega$  untainted by organic or inorganic residues.

## 5.2 Liquid phase exfoliation of graphite

Liquid phase exfoliation of graphite and graphite derivatives are viable routes to obtain stable colloidal suspension of graphene sheets. The quality of these graphene sheets are undoubtedly higher than those derived from graphite oxide due to the absence of oxygen functionalities which disrupt electrical conductivity and carrier mobility. Without the aid of intercalants, this method is only possible if the right solvent or solvent mixtures produce an adequate graphene–solvent interaction which can overcome the graphene–graphene interlayer van der Waals interaction.<sup>133</sup> The enthalpy of mixing of graphene in solvents should be close to zero. This can occur when the solvent surface energy (or surface tension) is close to that of graphene surface energy. In most cases, the net energetic penalty for long-range exfoliation is small and can be overcome by mechanical agitation such as sonication. However, prolonged sonication leads to undesirable fragmentation of exfoliated graphene sheets which results in small sized graphene sheets of lateral dimension  $\sim 1$   $\mu\text{m}$ . Colloidal suspension of graphene sheets in organic solvents such as DMF,<sup>126</sup> NMP<sup>134,135</sup> and chloroform<sup>136</sup> have been reported. Novoselov and co-workers<sup>126</sup> reported that sonicating graphite in DMF returned a high yield of monolayer flakes up to 50%. DMF sufficiently prevents exfoliated graphene sheets from agglomerating due to its good wetting of individual graphene sheets. Direct dispersion of the graphene sheets in aqueous alkaline solution has also been achieved by Hou and co-workers<sup>137</sup> *via* the use of 7,7,8,8-tetracyanoquinodimethane (TCNQ) for the non-covalent functionalization of graphene. TCNQ exhibits a strong  $\pi$ – $\pi$  stacking interaction with aromatic systems and upon reduction in KOH aqueous solution, the absorbed TCNQ anions on graphene surface can sufficiently repel individual graphene sheets to form a homogenous suspension. TCNQ-anion-stabilized graphene sheets can be readily dispersed in water as well as highly polar organic solvents such as DMF and DMSO.

## 5.3 Graphene from electrochemical exfoliation of graphite

The electrochemistry of graphite has a rich history and vast interests are displayed in the electrochemical intercalation, de-intercalation and functionalization of graphite to obtain functionalized exfoliated graphite and GICs, which have potential applications in electrochemical energy systems.<sup>138,139</sup> Luo and co-workers<sup>127</sup> devised an electrochemical approach to obtain imidazolium-based ionic-liquid-functionalized graphene sheets. Exfoliation of ILs functionalized graphene sheets readily formed a stable colloidal suspension in DMF, DMSO and NMP. Loh and co-workers<sup>140</sup> demonstrated a facile one-pot ionic-liquid assisted electrochemical exfoliation approach to obtain fluorescent carbon nanoribbons, nanoparticles and graphene from graphite. The mechanism of the exfoliation is due to a complex interplay of anodic oxidation of water and anionic intercalation from the ionic liquid. Using ILs with high water content

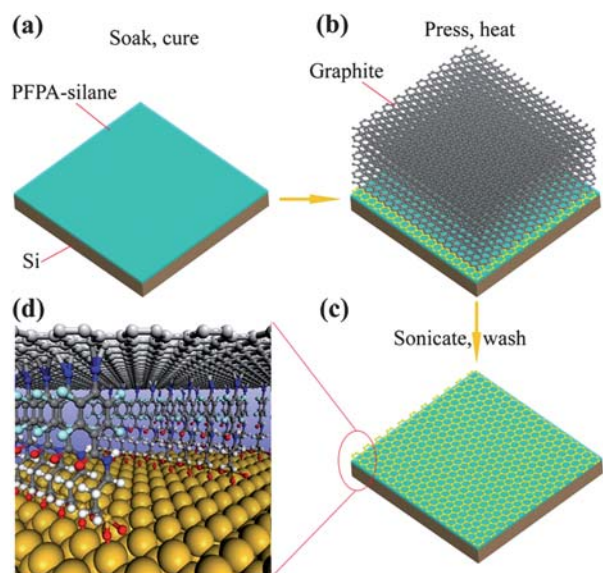
(>10% water) as the electrolyte, water-soluble, oxidized carbon nanomaterials were generated. In the case of electrolyte using concentrated ILs (<10% water), IL-functionalized carbon nanomaterials were generated instead. The chemical composition and surface passivation of the exfoliated carbon nanoparticles can be controlled by changing the water/IL ratio in the electrolyte, thus allowing the fluorescence from the exfoliated nanoparticles to be tuned from the ultraviolet to visible regions. The marriage between ILs and graphene can form a gel-like composite called “bucky gel” and these designer materials show great versatility for applications as electrodes, capacitors, sensors and actuators.

## 6. Challenges and prospects

In the course of the next ten years at least, it can be expected that there will be endless streams of reports on new chemical or physical ways to produce or functionalize graphene. In terms of high throughput, large area deposition, chemical vapor deposition of graphene may offer the most viable option.<sup>104,141–146</sup> In terms of bulk chemical processing of graphene in solution, the most ideal chemical method is one which integrates the easy exfoliation of graphite into pure graphene sheets with its stable dispersion and functionalization, all in one pot. Such a method, if successfully derived, will allow convenient solution processing of graphene-based composites and new technological niches may emerge.

At the present moment, regardless of the chemical methods applied, the size and shape of chemically derived graphene are heterogeneous, so size or mass-selection separation methods have to be developed to narrow the size distribution of the graphene sheets. The chemical cutting of graphite into strips of the same size or shape will be inherently difficult *via* the acid oxidation route, since the oxidation and defect generation, which influences the subsequent chemical cutting, is random.<sup>41</sup> Cutting open uniformly sized and shaped carbon nanotubes may be one way to produce uniformly sized nanoribbons,<sup>147</sup> but it is difficult to see how a high throughput process can be developed. A rational synthesis approach that has succeeded in the case of fullerene can be considered for graphene if the synthesis of specifically shaped, or sized, graphene is needed.<sup>148</sup> One method may be the two dimensional assembly of polyaromatics on catalytic metal surfaces followed by its dehydrogenation and molecular restructuring to produce graphene. Alternatively, large size graphene samples placed on substrate can be cut into well-defined strips in a high throughput fashion using lasers. For example, our recent work demonstrates that laser micro-structuring of GO into well-defined strips are possible.<sup>149</sup>

The successful implementation of graphene electronics on a silicon platform will create a new paradigm shift for post-CMOS electronics. Efficient methods which allow the stamp transfer of large area, continuous graphene onto silicon must be developed. Strategies to anchor graphene sheets at the device channel region, while uncoupling it from the deleterious ionic impurity scattering of the negatively charged siloxyl groups on the substrate will be ideal. Surface chemists, who have long worked on the lithographical patterning of polymer resists and organic films on silicon, realized that the chemistry developed for the stamp transfer of organic materials onto silicon can be



**Fig. 9** Chemical approach to immobilize graphene on silicon wafer via the PFPA (perfluorophenylazides)-silane coupling agent.<sup>150</sup> (a) The wafer was soaked in a PFPA-silane toluene solution (12.6 mM) for 4 h, washed with toluene, and cured at room temperature overnight. (b) HOPG (highly ordered pyrolytic graphite) was pressed on PFPA-functionalized wafer at 140 °C for 40 min. (c) One or few layers graphene was obtained after removing HOPG followed with sonicating, washing and drying. (d) Schematic showing the covalent bonding between graphene and PFPA-silane, the latter functions as a coupling agent to immobilize graphene on the silicon substrate.

applied to immobilize graphene.<sup>150</sup> Essentially, as illustrated in Fig. 9, graphite can be stamp-transferred onto pre-anchored functional groups on silicon. The chemical bonding between the functional groups and the graphite allows a thin sheet of graphene to be exfoliated and anchored onto the substrate when the graphite is peeled off. This is perhaps the most elegant demonstration of exfoliation of graphite into a graphene sheet which can be incorporated directly onto the silicon for further processing, without going through the “oxidation” route of a GO precursor.

Graphene research is an exciting field that interfaces disciplines like chemistry, physics, materials science and engineering.<sup>151–153</sup> In the coming years, researchers from the organic electronics, carbon nanotube and CVD diamond research communities may find in graphene a new testing ground for the ideas and methods they have been researching on these related materials. This will perhaps lead to novel hybrid platform consisting of diamond–graphene, graphene–carbon nanotube, or graphene–organics, paving the way for the roadmap towards all-carbon electronics. Being the next generation material, it is certain that surprises from graphene will continue to be delivered from the collective efforts of chemists, physicists, engineers and materials scientists.

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