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Sunil P. Lonkar¹, Yogesh S. Deshmukh² and Ahmed A. Abdala¹(✉)

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Recent Advances in Chemical Modifications of Graphene

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ABSTRACT

Graphene has attracted the interest of chemists, physicists, and materials scientists due to its extraordinary structural, mechanical, and electronic properties. While pristine graphene is desirable for applications that require a high electrical conductivity, many other applications require modified or functionalized forms of graphene, such as graphene oxide, reduced graphene, or other functionalized forms. Structurally modifying graphene through chemical functionalization reveals the numerous possibilities for tuning its structure; several chemical and physical functionalization methods have been explored to improve the stabilization and modification of graphene. In this review, we report the recent progress toward the chemical modification of graphene, including both covalent and noncovalent methods, for use in various applications.

Introduction

Graphene is a two-dimensional sp²-hybridized carbon nanomaterial that has attracted significant interest in recent years to become the most intensely studied material [1]. In 2004 at Manchester University, Geim and Novoselov successfully isolated single layers of graphene by mechanically cleaving a graphite crystal [2]. This groundbreaking discovery and their subsequent work on graphene physics led to these authors being awarded the 2010 Nobel Prize in Physics, stimulating the research growth on graphene further to span various scientific disciplines. The boundless growth in graphene research has been demonstrated by the number of publications that appeared during the last decade and by the rising field of graphene functionalization research, as shown in Fig. 1.

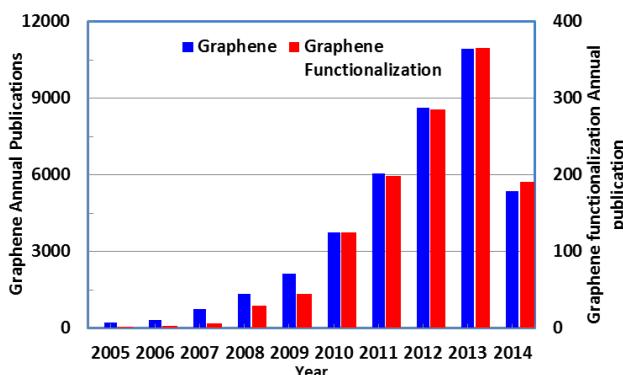


Figure 1. The number of annual publications on graphene and on graphene functionalization. Data sourced from Scopus database.

Graphene is the “thinnest” known material, and it exhibits extraordinary electronic, chemical, mechanical, thermal and optical properties that have made it a critical material in the 21st Century. Graphene holds a great promise for use in energy-storage materials [3, 4], drug delivery systems [5, 6], biosensors [7, 8], polymer composites [9, 10], liquid crystal devices [11], super-capacitors [12-14], nanoelectronics [15-17] and others.

Obviously, the excellent properties of graphene are associated with its ability to become and remain single sheets in various matrices. Therefore, the

aforementioned applications require the preservation of the intrinsic electronic properties of graphene during its incorporation and homogeneous dispersion into various matrices. The attractive van der Waals forces between the graphene sheets hinder the dispersion of graphene in common solvents. Moreover, graphene monolayers tend to re-aggregate due to those same attractive forces after the initial exfoliation and dispersion. Therefore, imparting sufficient solubility in different solvents is a prerequisite for applying graphene-based materials further. Specifically, the structural modifications that involve atomic doping, molecular impregnation and biomolecular immobilization require graphene derivatives with defined structures. These modifications may reveal new applications for graphene, ranging from solar cells to hydrogen storage to bioimaging. Currently, arduous work has been conducted to modify/functionalize the surface of graphene sheets, overcoming the poor dispersion of graphene sheets in aqueous solutions and most organic solvents [18-21]. The two most common methods adapted toward this purpose involved covalent [22-24] and noncovalent chemical modifications [20, 25, 26].

Covalent functionalization involves covalently linking external species, such as small molecules, polymers, biomacromolecules, and inorganic nanoparticles, without any cross-linking reagents or additional surface modifications. The surface functional groups of graphene oxide (GO) and reduced graphene oxide can provide the reaction sites required for such functionalizations. The uniquely large and atomically flat surface of graphene and GO provides a platform upon which to anchor various chemical species. However, noncovalent functionalization is a different approach used to modify graphene chemically. In this context, the graphene surface can be modified through secondary interactions, such as van der Waals forces, π-π interactions, or through adsorbing or wrapping with polynuclear aromatic compounds, surfactants, polymers, or biomolecules etc. The primary advantage of noncovalent functionalization over its covalent counterpart is that the former can introduce chemical functionalities to graphene without affecting the

structural integrity, which must be maintained to preserve the electronic conductivity of this material.

The functionalization of graphene has already been extensively reviewed [20, 25-31]. The histogram in Fig. 1 depicts the amount of research based on the number of publications that featured the functionalization of graphene over the past decade. In the present review, we have attempted to cover the latest developments in the field and to summarize the most important and intriguing results regarding the chemical modification of graphene, as well as the most recent developments toward applying graphene. This review is divided into two main sections: the first section is dedicated to the covalent modification of graphene, while the second section is focused on the recent advances in noncovalent modification of graphene. The various applications of the chemically modified graphene-based materials are also discussed.

1. Graphene: synthesis and structure

Graphene is the base structure of all graphitic forms, including graphite, charcoal, carbon nanotubes, and fullerenes (Fig. 2) [32]. Structurally, graphene is a

one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice with carbon-carbon bond lengths of 1.42 Å. Numerous graphene sheets stack with an interplanar spacing of 3.35 Å to form graphite; a 1-mm thick graphite crystal contains approximately 3 million layers of stacked graphene sheets.

Graphene can also be considered as an indefinitely large aromatic molecule, making it an extreme example of the family including flat, polycyclic aromatic hydrocarbons. The highly versatile properties and numerous projected applications have triggered the development of graphene synthesis, spurring the use of various methodologies and substrates. Several techniques for mass producing graphene encompass both bottom-up and top-down methods, which range from the mechanical exfoliation of high-quality graphite to direct growth on carbides or suitable metal substrates to chemical routes using graphene oxide, as summarized below. All of the developed methods allow for numerous choices in terms of the size, quality and cost during application (Fig. 3) [32, 33].

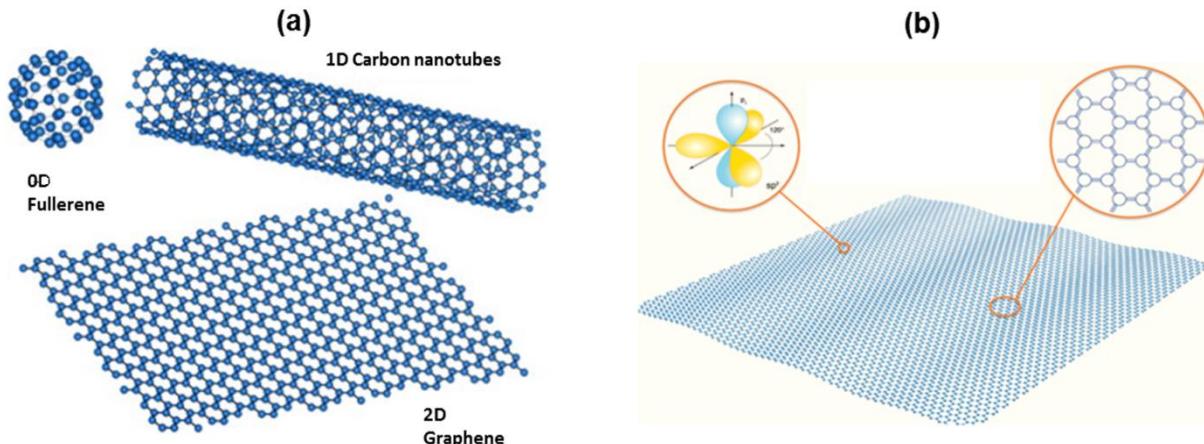


Figure 2. a) Low-dimensional carbon allotropes: fullerene (0D), carbon nanotube (1D) and graphene (2D) and b) atomic and electronic structure of graphene wherein carbon atoms are arranged in honeycomb lattice having sp^2 hybridization. Reprinted with permission from ref. [32]. Copyright 2010, Elsevier Ltd.

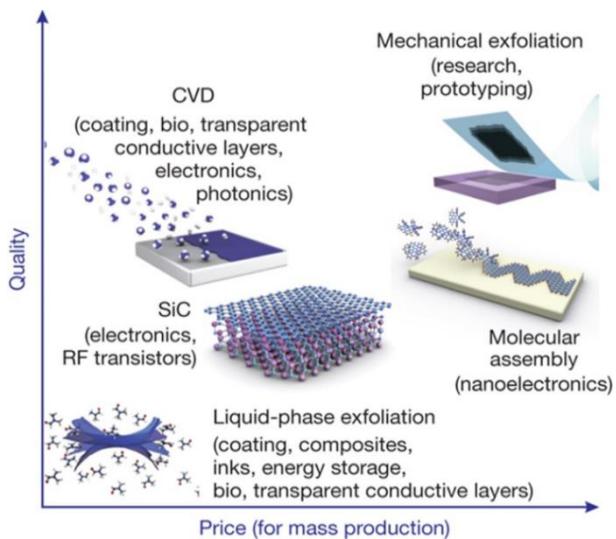


Figure 3 Methods for mass-producing graphene in terms of size, quality and price for particular applications. Reprinted with permission from ref. [33]. Copyright 2012, Nature Publishing Group.

The mechanical exfoliation method produces graphene sheets in various thicknesses through a simple peeling process: an ordered pyrolytic graphite (HOPG), single-crystal graphite, or natural graphite specimen is dry etched in oxygen plasma to form many 5 μm deep mesas. The mesas were then wedged onto a photoresist and peeled off layers using scotch tape. The collected thin flakes are later washed off in a suitable solvent and transferred to a substrate, such as a silicon wafer. These thin flakes were composed of a monolayer or a few layers of graphene [2]. Other physical exfoliation approaches include gradient ultrasonication and heating in a high-boiling-point solvent, such as N-methyl pyrrolidone [34, 35]. In general, these methods produce defect-free monolayer graphene. However, using a high-boiling solvent makes it difficult to deposit the resulting graphene sheets. Using surfactants, such as sodium dodecylbenzene sulfonate also reportedly enhanced the exfoliation of graphite in water; the graphene monolayers were stabilized against aggregation by the relatively large potential barrier generated through the Coulombic repulsion between the surfactant-coated sheets [36].

Chemical vapor deposition (CVD) is another promising method used to produce mono- or few-layer graphene on a large scale by using suitable metal surfaces at high temperatures [37, 38]. During a typical CVD process, the carbon is dissolved in a metal substrate before it is precipitated on the substrate through cooling. For example, a Ni substrate was placed in a CVD chamber, which was held under vacuum (10^{-3} Torr) and below 1000 $^{\circ}\text{C}$, with a diluted hydrocarbon gas [39]. The deposition process begins with the incorporation of a few carbon atoms into the Ni substrate at a relatively low temperature, similar to the carburization process. This method can control the thickness and crystalline ordering of the resultant graphene layers through the cooling rate and the concentration of the carbon dissolved in the nickel metal. In addition to nickel and copper, various metal substrates with different carbon solubilities and catalytic effects, such as Ru [40], Ir [41], and Co [42], are also documented.

In addition to thermal CVD, plasma-induced CVD offers an alternative route for graphene synthesis at relatively lower temperatures. The first reported production of mono- and few layers graphene by plasma CVD method involved using a radio frequency to synthesize graphene on various substrates with a methane hydrogen mixture containing 5 – 100% CH_4 at 900 W power and 680 $^{\circ}\text{C}$ [43]. The advantages of this method include its very short deposition time (< 5 min) and the lower growth temperature of 650 $^{\circ}\text{C}$ compared to 1000 $^{\circ}\text{C}$ for the thermal CVD approach. Graphene monolayers were also produced by thermally decomposing carbides, such as SiC. Subjecting a SiC surface to an ultrahigh vacuum annealing produces graphene-coated SiC substrates, which are attractive to the semiconductor industry because no transfers are required before the devices are processed [44].

The chemical exfoliation of graphite is another well-established procedure used to produce large quantities of graphene [45]. This method involves increasing the graphite interlayer spacing to weaken

the interlayer van der Waals forces. This change is achieved by intercalation or creating various active functional moieties between the graphene layers to prepare graphene-intercalated compounds [46]. Subsequently, these intercalated compounds are exfoliated to single to few-layered graphene through rapid heating, sonication or reduction processes. A classic example of chemical exfoliation is the generation of single layer graphene oxide (GO) from graphite oxide through ultrasonication [47, 48].

Graphite oxide can be synthesized by oxidizing graphite using strong chemical oxidizing agents in highly concentrated inorganic acids. Graphite oxide is generally produced through a top-down route, which uses concentrated H₂SO₄ along with the following: 1) concentrated nitric acid and a KMnO₄ oxidant (Hummers) [49]; 2) fuming nitric acid and a KClO₃ oxidant (Staudenmaier) [50]; or 3) concentrated phosphoric acid with KMnO₄ (Tour) [51]. The properties of the graphite oxides produced by using the above different methods are usually treated as though they were roughly similar; consequently, these methods have been used interchangeably. The chemical oxidation of graphite involves the creation of oxygen-containing groups, such as C-OH, C-O-C, on the graphene surface and COOH on the edges. The presence of these oxygen containing groups break the van der Waals forces and render the graphite oxide highly hydrophilic. Moreover, intercalating water molecules bound to the hydrophilic graphene surface into the gallery of the graphite oxide and the non-flat configuration of the Sp³ bonds increase the interlayer spacing to 7 – 10 Å. Large quantities of graphene are produced from graphite oxides through reduction process, which remove the oxygenated functionalities from graphite oxide and restore the sp² network. The reduction of graphite oxide is usually achieved through chemical, thermal and electrochemical methods. Chemical reductions of graphene oxide have been performed using several reducing agents, including hydrazine [52], sodium borohydride [53], hydroquinone [54], gaseous hydrogen (after thermal expansion) [55], strongly alkaline solutions [56], phenyl hydrazine [57], hydroxylamine [58], glucose

[59], and ascorbic acid [60]. However, hydrazine hydrate was the best reagent due to its low reactivity toward water and production very thin and fine graphite-like sheets. During the reduction process, the brown dispersion of GO in water turned black, and the reduced sheets aggregated and precipitated.

Thermal exfoliation and reduction of graphite oxide also produce good-quality graphene, which is generally called thermally reduced graphene (TRG). A rapid heat treatment is used to remove the oxide functional groups from the graphite oxide, and the exfoliation occurs on the surfaces after heating (> 2000° C/min) to 1050° C through the evolution of CO₂ [19, 61]. Electrochemical reductions can also reduce graphene oxide to graphene in large scale [62, 63]. The reduction process can be initiated at -0.8 V; this process is complete at -1.5 V, which is when a black precipitate forms on the bare graphite electrode. When coupling an electrochemical reduction with a spray coating technique, patterned RGO films with large areas and thicknesses ranging from a single monolayer to several micrometers can be produced on various conductive and insulating substrates [64]. The photo-thermal and photochemical reductions of graphite oxide have also become effective, rapid, and versatile methods for forming RGO because photoreduction does not rely on either high temperature or toxic chemicals. High-quality RGO has been prepared by irradiating graphite oxide with sunlight, ultraviolet light, and excimer lasers [65]. Recently, Zhang *et al.* [66] reviewed the various methods, properties and applications of photoreduction of graphene oxide. Photoreduction strategies including photothermal reduction, catalytic/catalyst-free photochemical reduction, and solid state/in-solution laser reduction are summarized. Such methods can give exquisite control over film conductivities, residual oxygen contents, porosity, and surface wettability, which lead to various functionalities towards a wide range of applications, such as field-effect-transistors (FETs), flexible electrodes, sensors, supercapacitors, Li-ion batteries, photovoltaic devices, and photocatalysis.

Henceforth, graphene terminology applies to both thermally reduced graphene and reduced graphene oxide according to the discussed literature.

2. Properties of Graphene

The increasing interest in graphene is due to its exceptional physical properties and chemical tunability, which increase its potential for various applications. We will briefly discuss the most important properties of graphene. Graphene is a semimetallic or a zero-gap semiconductor (with both holes and electrons as charge carriers) [67]. Micromechanically cleaved graphene showed extremely high electron mobilities ($15000 \text{ cm}^2 (\text{V s})^{-1}$) at room temperature; the electron and hole concentrations can reach 10^{13} cm^{-2} with ballistic transport up to submicrometer distances [68]. Fig. 4A shows the band structure of graphene near the Fermi level. In the hexagonal first Brillouin zone, the Fermi level lies at the crossing point between the cone-like dispersions (Fig. 4A (a) and (b)). Two- and three-layered graphene samples generated through a hydrogen arc evaporation of graphite (HG) have exhibited mobilities of $10428 \text{ cm}^2 (\text{V s})^{-1}$, while the other few-layered samples exhibited much lower mobilities. However, the quality of the graphene, which is indicated by the average number of layers, surface functionality, and concentration of defects, and the substrate limit different characteristics in different samples. Interestingly, few-layer graphene with defects still exhibits remarkable transistor characteristics [69, 70]. Moreover, the linear dispersion relation of graphene predicts that the resistivity of graphene due to isotropic scatterers is independent of the carrier density. Hwang and Das Sarma [69] calculated the phonon-scattering-limited extrinsic electron mobility in graphene as a function of temperature and carrier density; the intrinsic mobility at exceeded $105 \text{ cm}^2 (\text{V}\cdot\text{s})^{-1}$.

Chen *et al.* [71] demonstrated that electroacoustic phonon scattering in graphene is independent of the carrier density and contributes only 30Ω to the

resistivity at room temperature; the intrinsic mobility of graphene was $200\,000 \text{ cm}^2 (\text{V}\cdot\text{s})^{-1}$. The resistance of graphene also decreases significantly after heating to high temperatures. The resistivity decreases significantly after increasing the number of layers, as demonstrated with EG, HG, and RGO (ρ of RGO < HG < EG) samples containing three to four layers, two to three layers, and a single layer, respectively.

Mechanically, graphene is a highly robust material, and its mechanical properties, including its Young's modulus and fracture strength, have been validated by several numerical simulations [72, 73]. Atomic force microscopy (AFM) is used to measure the Young's modulus of few-layer graphene experimentally [74, 75]. Defect-free graphene exhibits a Young's modulus of 1.0 TPa and a fracture strength of 130 GPa . Lee and coworkers [76] measured the elastic properties and intrinsic strength of free-standing monolayer graphene using nanoindentation, Fig. 4b. The reported stiffness was $300\text{--}400 \text{ N/m}$ with a breaking strength of ca. 42 n/m , which represents the intrinsic strength of defect free sheet. Interestingly, regardless of their structural defects, graphene oxide sheets retained their mechanical performances to generate fair values for their Youngs modulus (0.25 TPa) [77]. Therefore, based on the high sustainable tension and modulus in a single sheet, graphene has tremendous potential in applications ranging from mechanical reinforcement for polymers [18] to nanoelectromechanical systems [78].

Unlike graphite, which is completely opaque, monolayer graphene is transparent; it absorbs only 2.3% of light [79]. Combined with its excellent conductivity and optical characteristics, graphene-based materials are cost effective alternatives to indium tin oxides (ITO). The visible range transparency of thin graphene films is high: for 2-nm thick films, the transmittance exceeds 95%, remaining above 70% for 10-nm thick films [80]. Additionally, graphene has a relatively flat optical spectrum between 500 and 3000 nm; its dominant absorption is below 400 nm [81]. Therefore, due to its combination of high film conductivity, optical transparency, and chemical and mechanical stability, graphene based materials are used in various applications, such as

transparent electrodes for solar cells or liquid crystals and processable transparent flexible electrode materials [36, 82-84]. In addition, the optical reflectivity and transmission properties of graphene were studied from 0.2 - 1.2 eV; these properties are based on the non-interacting, massless Dirac fermions [85, 86].

In addition to its exciting electronic properties, graphene also possess impressive thermal properties [87]. Graphene is one of the most thermally conductive materials; its room temperature conductivity ranges from 3000-5000 W/m-K as measured by laser flash as shown in Fig. 4c [88], exceeding the upper limit for CNTs [89]. Graphite, which is the 3D bulk limit for multilayer graphene, which is when the number of layers $n \approx \infty$, is still an outstanding heat conductor; its intrinsic room temperature thermal conductivity ≈ 2000 W/mK. A non-contact Raman optothermal technique was the first experimental method used to measure the thermal conductivity of graphene [90]. The measurements were performed with large-area, suspended graphene layers exfoliated from high-quality bulk graphite. The thermal conductivity exceeded 3000 W/mK at room temperature for sufficiently large graphene flakes. The measured thermal conductivity of graphene exceeds the upper limit for bulk graphite. The phonon mean-free path (MFP) for graphene was estimated to be ~ 775 nm [91]. The extremely high thermal conductivity enables

numerous applications, such as thermal management and the development of thermally enhanced plastics.

4. Covalent modification of graphene

As discussed earlier, graphene surfaces can be chemically modified using either covalent or non-covalent method. Covalently attaching different functionalities onto graphene surfaces usually occurs through oxygen linkages, which are called "oxygenated functional groups" or structural π - π networks. Moreover, the presence of carboxylic acid groups at the edges and epoxy/hydroxyl groups on the basal plane of graphene and graphene oxide are used to tailor the surface functionality of graphene surfaces.

In the following sections, we review the major routes developed for covalently modifying graphene.

4.1 Covalent Attachment with Organic Functionalities to the Pristine Graphene

The dispersion of graphene sheets in organic solvents is an essential step during the formation of graphene based nanocomposite materials. Hence, covalent modification of graphene with various organic functionalities is the key to achieve better dispersion. Graphene has been modified using two general routes: (1) combining free pristine graphene

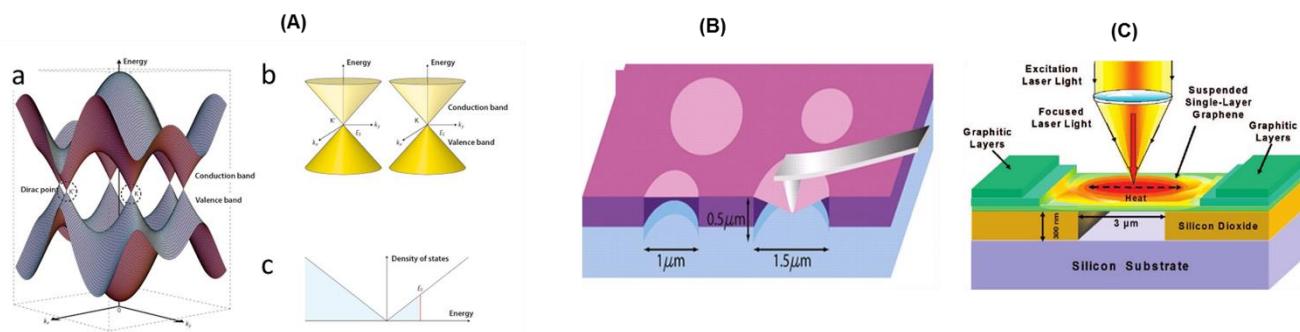


Figure 4 A. (a) Energy bands near the Fermi level in graphene. The conduction and valence bands cross at points K and K'. (b) Conic energy bands near the K and K' points. (c) Density of the states near the Fermi level with Fermi energy EF. Reprinted with permission from ref. [68]. Copyright 2009, Nature Publishing Group, B. Illustration of the nanoindentation process with an AFM tip on a graphene layer stretched over a circular void. Reprinted with permission from ref. [76]. Copyright 2008, AAAS, C. Schematic of thermal conductivity experiment during which a single layer of graphene is suspended over a channel and subjected to energy from a focused laser. Reprinted with permission from ref. [88]. Copyright 2008, American Chemical Society.

C-C bonds with radicals or dienophiles and (2) reacting the oxygen groups of GO with organic functional groups. Based on previous work on fullerene and carbon nanotubes, the most attractive organic species for reaction with sp^2 carbons in graphene are organic free radicals and dienophiles. Usually, both of these species are intermediate reactive components produced under certain conditions in the presence of the graphene.

4.1.1. Free Radical Addition to the sp^2 Carbon Atoms of Graphene

Free radical reactions are some of the most common reactions used with graphene nanomaterials to promote widen the band gap and modulate solubility. Toward this goal, radicals can be generated from diazonium salts and benzoyl peroxide. An electron transfer from graphene to aryl diazonium ions or photoactivated benzoyl peroxide yields aryl radicals that add to graphene to form covalent adducts (Fig. 5). At elevated temperatures, diazonium salts produce highly reactive free radicals that can form a covalent bond by reacting with the sp^2 carbon atoms of the graphene. Tour and co-workers used this method to modify graphene using nitrophenyl groups [91].

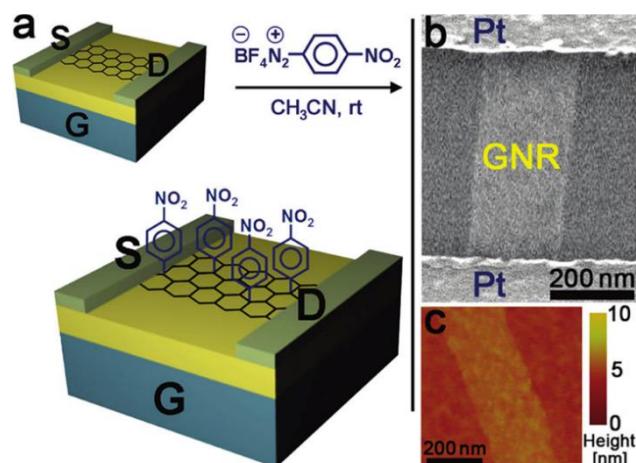


Figure 5 Chemical doping of graphene with 4-nitrophenyl groups: (a) schematic representation; (b) SEM image of a graphene nanoplatelet between Pt electrodes; (c) AFM image of a fragment of a graphene monolayer. Reprinted with permission from ref. [91]. Copyright 2010, American Chemical Society.

The conductivity of the graphene sheets can be controlled by varying the reaction time; longer times produce graphene with lower conductivity. Moreover, the reaction time and degree of modification can be used to control the band gap, potentially creating a semiconductive material based on nano-materials.

X-ray photoelectron spectroscopy (XPS) was used verify the covalent attachment of the 4-nitrophenyl groups to the graphene surface as shown in Fig. 6 (bottom).

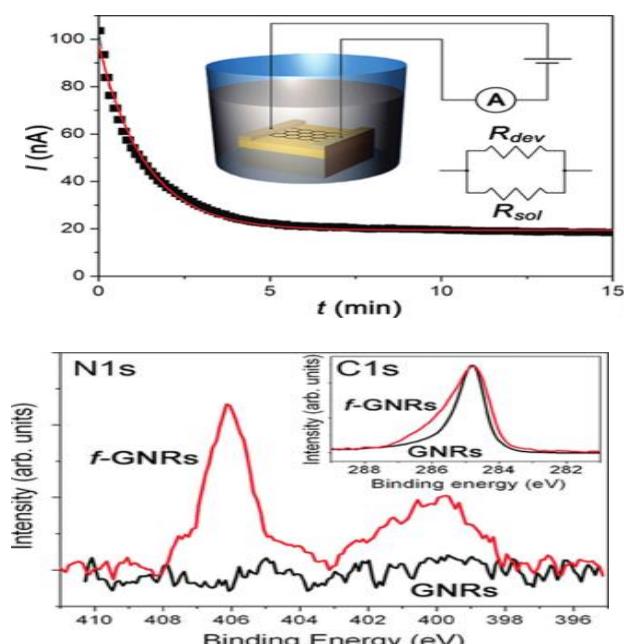


Figure 6 Time vs current I performance of a graphene diazonium salt: (top) Schematic representation of a device consisting of two parallel resistors derived from the graphene and the solution, and (bottom) XPS spectra of the GNRs: N1s and C1s before and after the chemical modification (f-GNRs). Reprinted with permission from ref. [91]. Copyright 2010, American Chemical Society.

The N1s XPS spectrum of the functionalized graphene contained two peaks with binding energies at 406 and 400 eV, corresponding to the nitrogen of the NO_2 and the partially reduced nitrogen of the product, respectively. Furthermore, diazonium salts have been used to functionalize chemically or thermally converted graphene. Single graphene sheets were obtained through micromechanical cleavage from bulk graphite, and epitaxial graphenes [92-96].

Recently, hydroxylated aryl groups were covalently attached to graphene through a diazonium addition reaction [97]. Afterwards, the hydroxylated aryl sites were connected to polymer chains (polystyrene) using an atomic transfer radical polymerization (ATRP). During the ATRP of styrene, diazonium radicals acts as initiators, catalyzing the covalent attachment of the polymer to the graphene surface. Feng *et al.* [98] also prepared reduced graphene oxide-azobenzene (RGO-AZO) hybrids via covalent functionalization using free radical diazotization for long-term solar thermal storage (Fig. 7). Liu *et al.* [99] modified a graphene surface with phenyl groups through a free-radical addition (Fig. 8). In this case, graphene isolated from Kish graphite was deposited on the silicon substrate and immersed in an initiator solution (benzoyl peroxide/toluene solution). An Ar-ion laser beam was used to initiate the reaction with graphene sheets in the solution.

The addition of the phenyl group was verified through the presence of a strong *D* band at 1343 cm^{-1} . The *D*-bands represent the formation of sp^3 -hybridized carbon atoms in the basal plane of graphene created when the phenyl groups were added. The resultant materials could be used to construct a field effect transistor (FET) device. In this device, a decrease in conductivity was observed due to the additional sp^3 carbon atoms created when

attaching the phenyl groups.

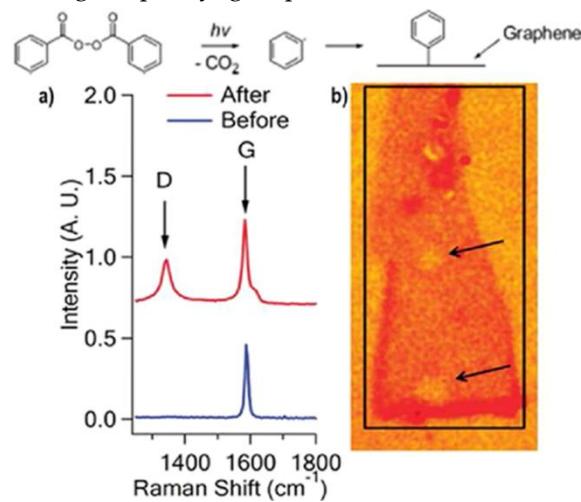


Figure 8 Reaction scheme for the radical addition reaction: (a) After the photochemical reaction, the *D* band in the Raman spectrum from a single layer graphene and (b) an optical image of a functionalized single-layer graphene. The arrows represent the holes resulting from prolonged laser exposure. Reprinted with permission from ref.[99]. Copyright 2009, American Chemical Society

Recently, Strano *et al.* [100] studied the physical and electronic structures and properties of bilayer graphene subjected to chemical functionalization using aryl diazonium salts (Fig. 9). The characteristic changes have been observed in the Raman spectra and conductive AFM when bilayer graphene is used

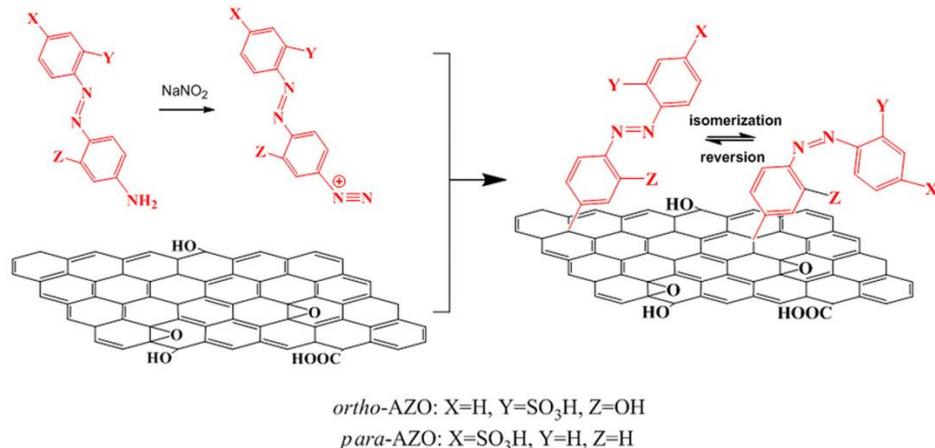


Figure 7 The synthetic route for and chemical structures of RGO-para-AZO and RGO-ortho-AZO hybrids produced through diazotization. Reprinted with permission from ref. [98]. Copyright 2013, Nature publishing Group.

4.1.1.2 Covalent modification of graphene using dienophiles

In addition to free radicals reactions using sp^3 hybridized carbon atoms, the sp^2 carbons in graphene can react with dienophiles. One of the most successful dienophiles used for these modifications is the azomethine ylide, which reacts through 1,3 dipolar cycloaddition. This dienophile has been used to functionalize carbon nanostructures, such as fullerenes, nanotubes, onions, nanohorns and their derivatives can be applied in several areas, such as composites, biotechnology nanoelectronics, drug delivery and solar cells [26, 101-103]. Georgakilas *et al.* [26, 101] demonstrated that graphene sheets obtained from graphite dispersed in organic solvents can be decorated with pyrrolidine rings via a 1, 3 dipolar cycloaddition with azomethine ylides. Through the pyrrolidine rings, these graphene sheets were functionalized with dihydroxyl phenyl groups. These groups can be attached orthogonal to the graphene surface by adding the azomethine ylide precursors depicted in Fig. 10. The azomethine ylide was formed by condensing 3, 4-dihydroxybenzaldehyde with sarcosine. This reaction adds a hydroxyl group to the graphene sheet, enhancing its dispersibility in polar solvents, such as ethanol and N, N-

dimethylformamide (DMF). This enhancement significantly increases the Raman intensity of D band/intensity of G band (I_D/I_G) ratio and peak broadening. These changes arise from functionalizing the graphene surface by increasing the number density of the sp^3 planar carbon atoms. Similarly, Salvagione *et al.* [104] used Cu-catalyzed Huisgen 1,3-dipolar cycloaddition reactions to couple graphene flakes with a conjugated polymer (poly[(9,9-dihexylfluorene)-co-alt-(9,9-bis-(6-azidohexyl)fluorene)] (PFA)).

Zhang and co-workers [105] have used tetraphenylporphyrin aldehyde (and a Pd analogue) and sarcosine to modify graphene surfaces. Quintana *et al.* [106] utilized a 1,3-dipolar cycloaddition with graphene sheets by employing paraformaldehyde and a specifically designed NH₂-terminated α -amino acid. These amino groups bind with gold nanorods selectively. Phenyl and alkyl azides react with the C-C bonds in graphene by forming a reactive nitrene intermediate. Reactions between organic azides and graphene have been used successfully by several research groups to form various graphene derivatives.

Reactions between organic azides and graphene have been used successfully by several research groups to form various graphene derivatives.

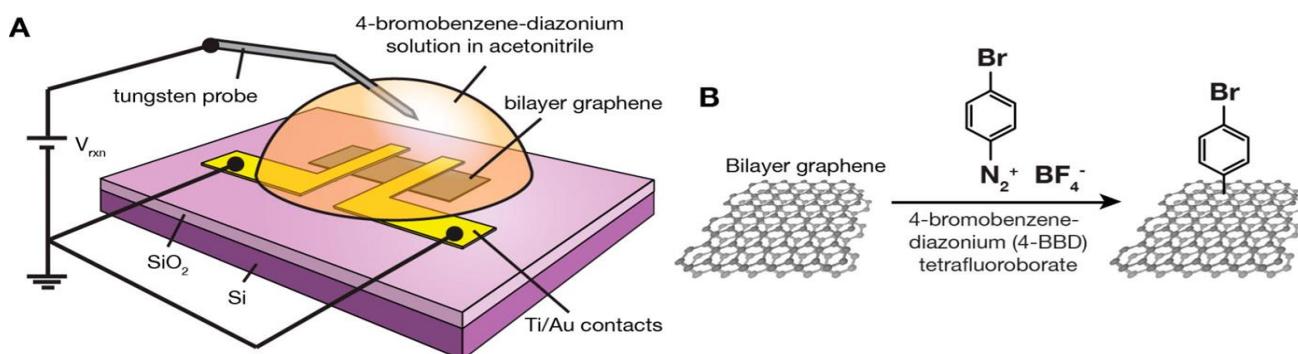


Figure 9 Covalent electrochemical functionalization of bilayer graphene. (A) Schematic for the experimental setup. Bilayer graphene generated through mechanical exfoliation is deposited on a SiO_2/Si wafer and is grounded using Ti/Au metal contacts. A droplet of 4-bromobenzene-diazonium (4-BBD) tetrafluoroborate solution in acetonitrile covers the bilayer flake. A tungsten probe is inserted into the solution droplet to apply a bias voltage during the reaction (V_{rxn}). (B) Reaction scheme for the covalent functionalization of 4-BBD on bilayer graphene. Reprinted with permission from ref. [100]. Copyright 2013, American Chemical Society.

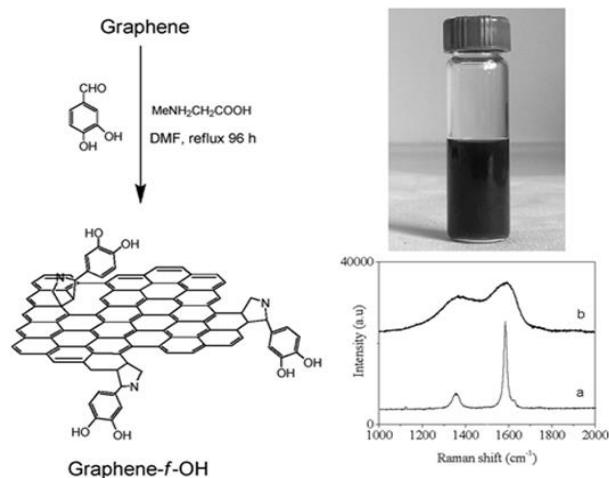


Figure 10 (left) Illustration of graphene modified through a 1, 3 dipolar cycloaddition with an azomethine ylide. (top, right) A sample vial containing functionalized graphene nanoplatelets dispersed in ethanol. (bottom, right) Raman spectra of (a) pristine graphene and (b) pyrrolidine-functionalized graphene. Reprinted from ref. [26]. Copyright 2010, Royal Society of Chemistry.

After thermally and photochemically activating various para-substituted perfluorophenylazides (PFPA), [107] different functionalities were appended to the graphene sheet through an aziridine ring, as depicted in Fig 11. These modifications alter the solubility-dispersibility and surface energy of the graphene derivatives. Nitrene additions have also been used to functionalize graphene.

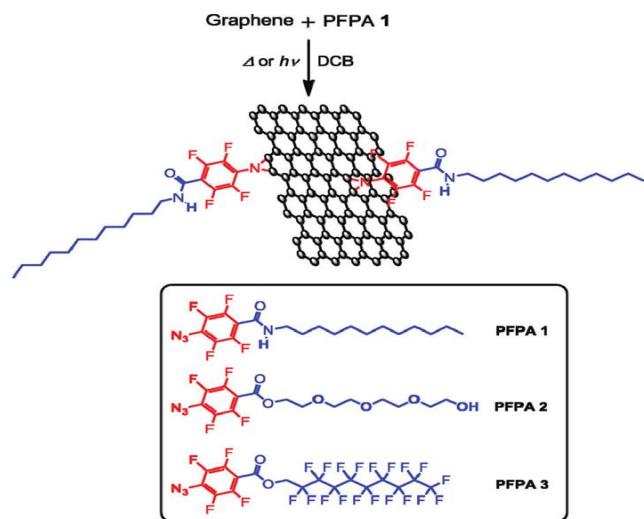


Figure 7 Pristine graphene functionalized with PFPA. Reprinted with permission from ref. [108]. Copyright 2010, American Chemical Society

Barron *et al.* [108] combined graphene and Boc-protected azidophenylalanine in *o*-DCB to produce graphene containing one phenylalanine substituent per 13 carbon atoms. To facilitate the attachment of biopolymers for use in a thermoresponsive nanodevice, Fu *et al.* [109] introduced cyclodextrin on the graphene surfaces using alkylazides (RGO-g-CD). The RGO-g-CD nanosheets were functionalized further with poly(*N*-isopropylacrylamide-*co*-vinylferrocene(II)) (PNIPAM-Fc) and ferrocene-modified hyperbranched polyglycerol (HPG-Fc) through a host-guest inclusion complexation between the CD and ferrocene (Fc) moieties to form RGO-g-CD/Fc-PNIPAM and RGO-g-CD/Fc-HPG nanohybrids, respectively (Fig.12).

Both RGO-g-CD/ Fc-PNIPAM and RGO-g-CD/Fc-HPG nanohybrids were dispersible and stable in a wider range of solvents than the RGO-g-CD precursor nanosheets. The RGO-g-CD/Fc-HPG nanohybrids exhibited low cytotoxicity toward 3T3 fibroblasts during a 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) cell viability assay.

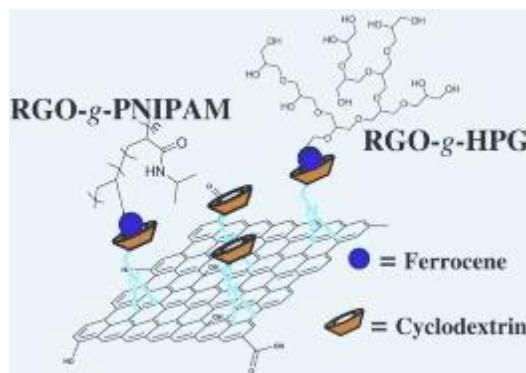


Figure 12 Schematic representation of RGO-g-CD/Fc-PNIPAM and RGO-g-CD/Fc-HPG nanohybrids. Reprinted with permission from ref. [109]. Copyright 2013, Elsevier Ltd.

He *et al.* [110] reported a versatile method for covalently functionalizing a graphene surface with various functional groups and polymeric chains via nitrene cycloaddition. This pathway allows for various types of functional moieties and polymers to be covalently bound to graphene, resulting



in functional graphene sheets and 2-D macromolecular brushes, respectively. The functionalized graphene sheets show enhanced chemical and thermal stability compared to GO and can be further modified through different chemical reactions, including amidation, surface-initiated polymerization, and the reduction of metal ions. The resulting functionalized graphene sheets are electrically conductive and highly dispersible and processable in solvents. Choi and coworkers have demonstrated that covalent bonds can be formed between thermally generated nitrenes and epitaxial graphene [111]. The band gap of the functionalized epitaxial graphene can be tuned through the amount of nitrene used in the reaction. An aryne cycloaddition to a graphene surface using 2-(trimethylsilyl)aryl triate as a precursor for the reactive benzyne intermediate has been recently reported by Zhong *et al.* [112] and depicted in Fig. 13 (top).

High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) were used to investigate the morphology of the pristine and aryne modified graphene. The HRTEM image in Fig. 13A (bottom) shows graphene sheets of 100–200 nm size. The AFM studies of methylated aryne modified graphene (Me-AG) shows average heights of 1.3 to 1.6 nm, which indicates that the Me-AG contain fewer than five layers of graphene Fig. 13B (bottom). The reaction formed a four-membered ring connecting the aromatic aryne rings to the graphene surface. The aryl-modified graphene species are dispersible in DMF, *o*-DCB, ethanol, chloroform, and water.

The use of graphene as a diene and as a dienophile has been demonstrated by Sarkar and coworkers [113]. The Diels-Alder reaction between each form of graphene and a dienophile (tetracyanoethylene (TCNE)) proceeds at room temperature (Fig. 14). The progress of this reaction was monitored using Raman spectroscopy: the spectra of pristine HOPG, few-layer graphene (FLG), and

single-layer graphene (SLG, XGflake) showed the characteristic G and 2D bands (Fig. 14c), while the D, D₀ and D_pD₀ peaks appeared in the spectra of the materials after the reaction with TCNE (Fig. 14d). The D band at 1345 cm⁻¹ became the most prominent feature of the Raman spectrum in SLG (Fig. 14b), and the 2D band was significantly weakened.

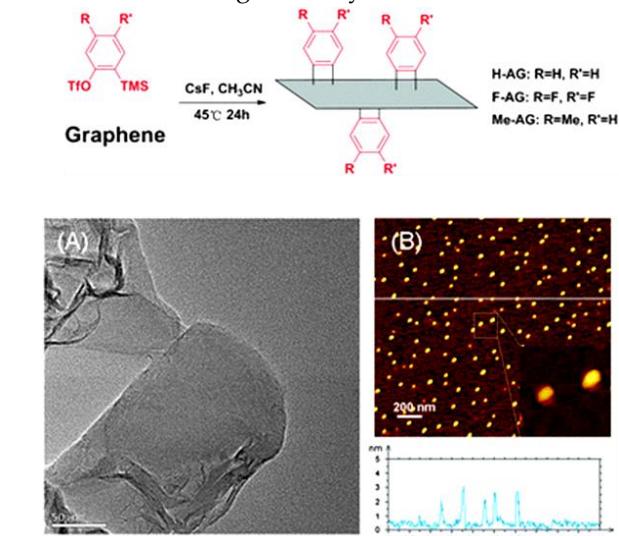


Figure 13 Graphene sheets modified using an aryne cycloaddition (Top). (A) HRTEM image of the graphene sheets (the scale bar is 50 nm); (B) tapping-mode AFM image and the corresponding height profile of methyl substituted aryne-modified graphene sheets (Bottom). Reprinted from ref. [113]. Copyright 2010, Royal Society of Chemistry.

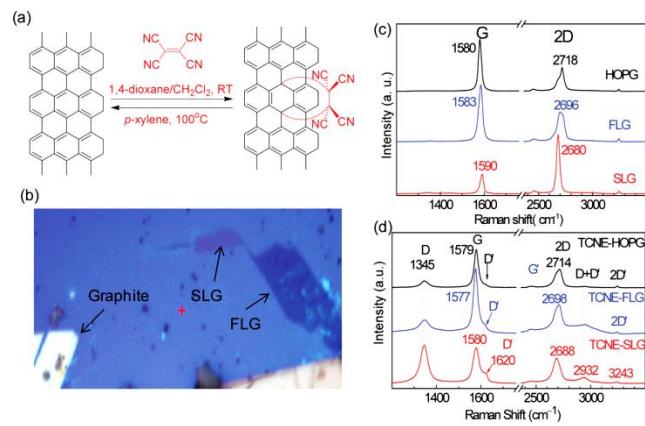


Figure 14 Room-temperature Diels-Alder (DA) reaction between graphene (diene) and tetracyanoethylene (TCNE, dienophile). (a) Schematic representation of the reaction. (b) Micrograph showing a large piece of HOPG, single-layer graphene (SLG), and few-layer graphene (FLG) on a Si substrate. (c, d) Raman spectra of HOPG, FLG and SLG (c) before and (d) after a DA reaction with TCNE. Reprinted from ref. [113]. Copyright 2011, American Chemical Society.

4.1.2 Covalent modification of Graphene Oxide (GO)

GO can be characterized as a single graphitic monolayer with randomly distributed aromatic regions (sp^2 carbon atoms) and oxygenated aliphatic regions (sp^3 carbon atoms) containing hydroxyl, epoxy, carbonyl, and carboxylic functional groups. The epoxy and hydroxyl groups are present above and below each graphene layer, while the carboxylic groups are usually found at the edges of the layers. Therefore, numerous functional groups with varying complexities can be anchored to GO through typical organic reactions, such as amidation, silanization, esterification, substitution, and cycloaddition reactions.

4.1.2.1 Amidation

This reaction links GO through reactions between the native edge -COOH groups and the -NH₂ group of the functional molecule, or vice versa. Because numerous methods can be used to create amino groups, amidation is a highly effective route toward chemically functionalized graphene, explaining its popularity relative to other methods. In the literature, various -NH₂-terminated functional groups, such as polymers, chromophores, biomolecules, ligands and many more have been anchored onto graphene to obtain desirable properties for various applications.

Macromolecules bearing amino groups have been successfully attached to graphene oxides through amidation. This modification generates materials with the properties of both reagents, such as dispersibility in certain solvents, mechanical strengthening, and several morphological characteristics of the polymer and graphene; these materials feature improved electrical conductivity, chemical reactivity, and mechanical properties.

Mallakpour *et al.* [114] reported a covalent functionalization of graphene sheets with biocompatible, natural amino acids (Fig 15). The resulting nanocomposites exhibit improved nonlinear optical properties. Modifying the surface-exposed epoxy and carboxylic acid groups on GO with naturally occurring amino acids, occurred easily

through nucleophilic substitution and condensation reactions. Amino acid-functionalized graphene can be stably dispersed in water and common organic solvents.

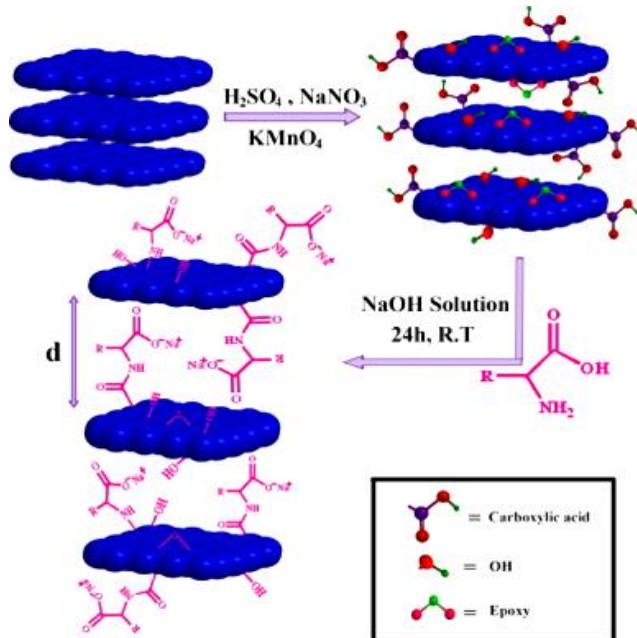


Figure 15 Synthesis of GO and functionalized graphene with different types of amino acids. Reprinted with permission from ref.[114]. Copyright 2014, Elsevier Ltd

Due to presence of hydroxyl groups in polyethylene glycol (PEG) and its biocompatible during applications such as example drug delivery, GO nano-platelets can be grafted to the amine-terminated PEG through amide bond formations [115]. This material exhibited the super-hydrophilicity of PEG, facilitating the dispersion of GO-grafted PEG in water and several aqueous biological solutions, such as serum or cell media. Therefore, GO-grafted PEGs are very interesting materials for delivering hydrophobic drugs in biological systems. For example, a camptothecin analogue (SN38), which is highly hydrophobic, can be placed on the surface of GO-grafted PEGs through van der Waals interactions to form a nanostructure that remains highly stable in biological solutions. Comptothecin is an organic aromatic molecule known for its anticancer activity. One of the major drawbacks of this molecule is its

insolubility in aqueous media. Covalently attaching camptothecin to GO nanoplatelets on PEG has been reported recently [116].

Recently, Yang et al. [117] obtained casein phosphopeptides (CPPs) biofunctionalized graphene composites through an amidation reaction between CPPs and carboxylated graphene (CGO), as shown in Fig 16. When immersed in stimulated body fluid (1.5 × SBF) at 37 °C for varying intervals, the CPPs layer on the composite facilitated efficient interactions between the CGO surface and mineral ions, which promoted HA nanoparticle formation and shortened the mineralization time versus pristine CGO. The synthesis of the composite mimicked the natural biomineralization of bone, demonstrating that CPPs can improve the bioactivity of graphene and be useful during HA formation. This biocomposite has great potential in various biomedical applications.

Other polymers, such as chitosan [118], polyethyleneimine [119], acid pectinase [120], poly(L-lysine) [121] and polyurethane [122], have also been attached to graphene surfaces through amide linkages. Apart from polymers with a conjugated molecular architecture, covalently attaching organic chromophores, such as porphyrins, phthalocyanines, and azobenzene on graphene nano-platelets has fascinated many researchers [123, 124]. Wang et al. [125]

synthesized soluble GO that was covalently functionalized with zinc phthalocyanine (PcZn) (GO-PcZn), through an amidation reaction (Fig 17). The formation of an amide bond between the PcZn and GO has been confirmed using X-ray photoelectron (XPS) and Fourier transform infrared spectroscopy (FTIR). At the same level of linear extinction coefficient, GO-PcZn exhibited much larger nonlinear optical extinction coefficients and broadband optical limiting performance than GO at both 532 and 1064 nm, indicating a remarkable accumulation effect due to the covalent link between GO and PcZn.

Recently, Long et al. [132] grafted haften onto GO through carbodiimide-assisted amidation using 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-Hydroxysuccinimide (NHS) catalyst system. The structure of hapten-grafted graphene avoids any activity loss by the biomolecules immobilized onto the graphene surface, preserving its binding affinity to small molecules and specific antibodies. The resulting hybrid was assessed during bisphenol A detection. Vasudevan et al. [133] synthesized reduced-graphene oxide (*r*GO) sheets covalently linked to β-cyclodextrin (β-CD) cavities through an amide linkage. The functionalized β-CD:*r*GO sheets, in contrast with *r*GO, are dispersible over a wide range of pH values (2–13).

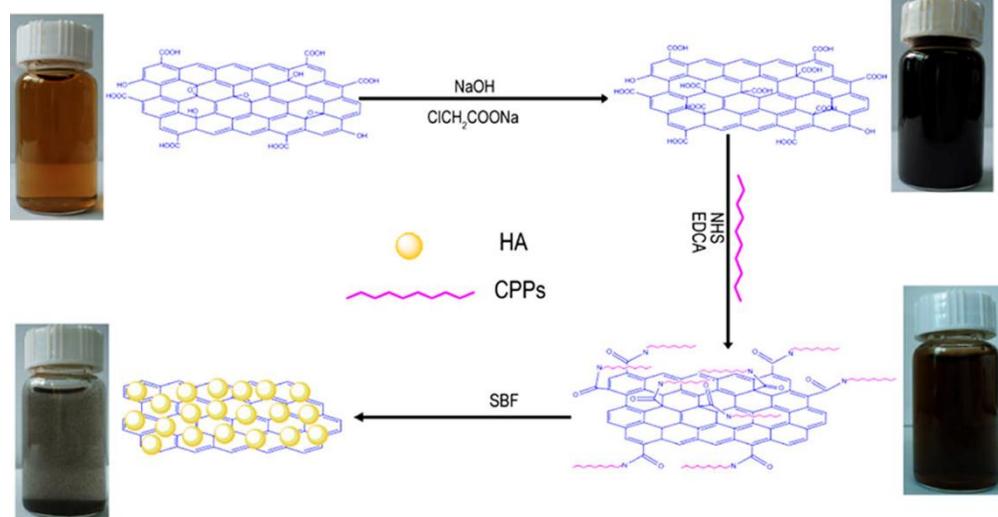


Figure 16 Illustration of the sample preparation and biomimetic mineral processes. Reprinted with permission from ref. [117]. Copyright 2013, American Chemical Society.

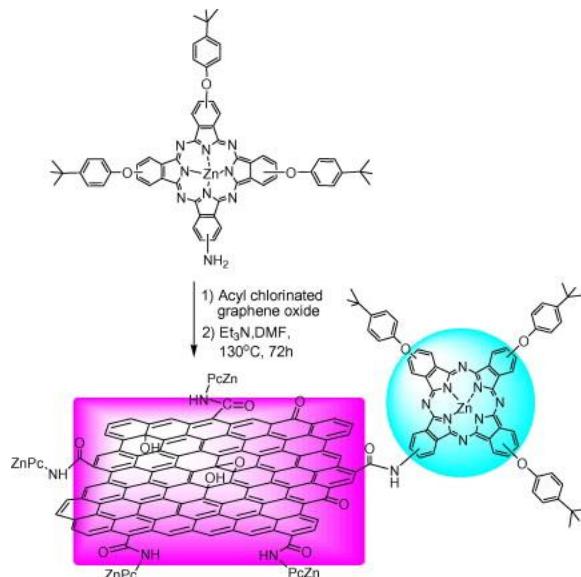


Figure 17 Schematic of the GO-phthalocyanines hybrids. Reprinted with permission from ref. [126]. Copyright 2011, Elsevier Ltd.

The zeta potentials indicate that more than one factor is responsible for the improved dispersibility. However, Dai *et al.* [127] grafted polyhedral oligomeric silsesquioxane (POSS) with well-defined organic/inorganic hybrids onto graphene via amide formation between the amine-functionalized POSS and oxygen-containing groups (e.g., epoxy and carboxyl groups) in GO (Fig. 18 a-d). The resulting hybrids are highly soluble in various organic solvents. Additionally, thin films formed by solution casting the POSS-graphene exhibit super-hydrophobic properties with water/air contact angle of $\sim 157^\circ$; the super-hydrophobic POSS-graphene constructs liquid marbles. In addition, the POSS-graphene hybrids also possess potential as novel nanofillers that increase the glass transition temperature and decomposition temperature of polymers.

4.1.2.2 Esterification

Similar to amidation, esterification is also an important approach used to modify GO with numerous functionalities. Esterification involves a reaction between the -COOH groups native to GO and CH₂OH-terminated functional groups.

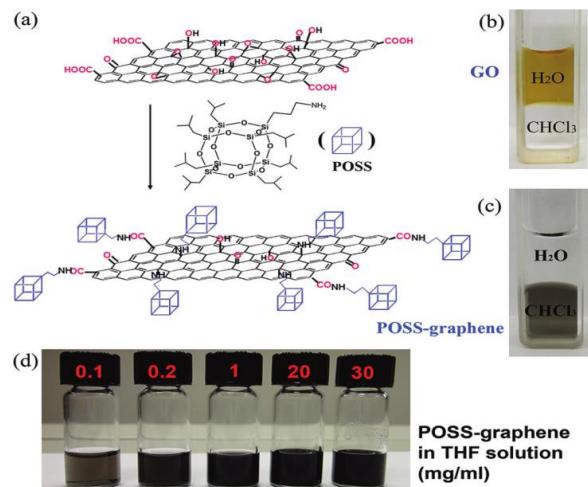


Figure 18 (a) Schematic representation of the route toward POSS-modified graphene (POSS-Graphene), (b) photoimages showing the initial GO in a water phase, which transferred into (c) the CHCl₃ phase after the POSS-Graphene formed, and (d) POSS-Graphene in THF solutions at different concentrations from 0.1 to 30 mg/mL. Reprinted with permission from ref. [127]. Copyright 2012, American Chemical Society

Through a similar approach, -CH₂OH terminated regioregular poly(3-hexylthiophene) (P3HT) was grafted onto the surface of GO by Yu *et al.* [128] The polymer was connected to GO nanoplatelets through ester bonds between the carboxyl groups of the GO nanoplatelets and the OH group of the -CH₂OH terminated P3HT. Fig. 19 depicts the reaction between the GO and CH₂OH-terminated P3HT chains through an esterification reaction. During a typical synthesis of the P3HT-grafted graphene, a dried GO sample was refluxed in thionyl chloride for 24 h; the excess thionyl chloride was removed under vacuum. The CH₂OH-terminated P3HT in THF was added through a syringe to the thionyl chloride-treated GO with stirring, followed by the addition of triethylamine under nitrogen. Due to the large population of hydroxyl groups in the P3HT, the GO-grafted P3HT is soluble in common organic solvents, facilitating materials analysis and device fabrication via solution processing routes.



Figure 19 Schematic representation of the reaction between GO and CH₂OH-terminated P3HT chains through an esterification reaction. Reprinted with permission from Ref. [128]. Copyright 2010, American Chemical Society

Moreover, the authors used the same material when preparing a photovoltaic device using a GO grafted P3HT together with C₆₀, as depicted in Fig 20. The power conversion efficiency improved by almost 200% compared to a pure P₃HT/C₆₀ (0.6%) system, which was a record value. The improved power conversion efficiency has been attributed to the extended electron delocalization that occurred after covalently attaching P₃HT to GO versus pure P₃HT. Similar to the ester linkage between –CH₂OH and GO, the formation of phenyl ester with the carboxyl groups on GO has also been reported. Kumar *et al.* [129] appended 4-amino phenol monomers onto GO through esterification; subsequently, the anchored monomer was polymerized using aniline to synthesize polyaniline-grafted reduced graphene oxide (PANI-g-rGO) composites (Fig. 21). Kothurkar *et al.* [130] have also recently functionalized azo molecules on graphene by ester linkages and observed that the photoluminescence of azo-GO hybrids show a strong

quenching compared with azo molecules due to the photoinduced electron or energy transfer from the azo chromophore to the GO sheets. It also reveals strong electronic interaction between azo and GO sheets with potential for various optoelectronic applications. Wallace *et al.* [131] have covalently linked the polycarbonate to GO using mostly peripheral ester linkages for tissue engineering applications.

The resulting covalently linked composites exhibit far better homogeneity and as a result, both Young's modulus and tensile strength more than double and electrical conductivities increase by ≈ 14 orders of magnitude over the pristine polymer at less than 10% graphene content. *In vitro* cytotoxicity testing of the materials showed good biocompatibility resulting in promising materials for use as conducting substrates for the electrically stimulated growth of cells. Cheng *et al.* [132] presented a novel approach toward fabricating advanced polymeric nanocomposites from poly (vinyl alcohol) (PVA) by incorporating PVA-grafted GO. The mechanical properties of PVA were greatly improved by incorporating PVA-g-GO. For example, the tensile strength and Young's modulus of the PVA nanocomposite containing 1 wt % net GO significantly increased by 88 and 150%, respectively, versus the unfilled PVA. The elongation at break was also increased by 22%, while the elongation at break for the GO-PVA nanocomposite containing 1 wt % pristine GO had decreased by 15%. Therefore, the presence of PVA-g-GO in the PVA matrix could make the PVA stronger and tougher.

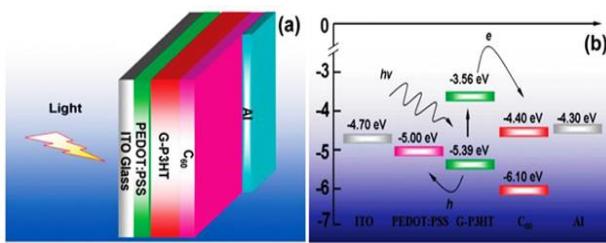


Figure 20 (a) Photovoltaic device schematic diagram prepared using a ITO/PEDOT:PSS/GO-P3HT/C₆₀/Al and (b) Represents energy level diagram of a ITO/PEDOT:PSS/GO-P3HT/C₆₀/Al. Reprinted with permission from ref. [128]. Copyright 2010 American Chemical Society.

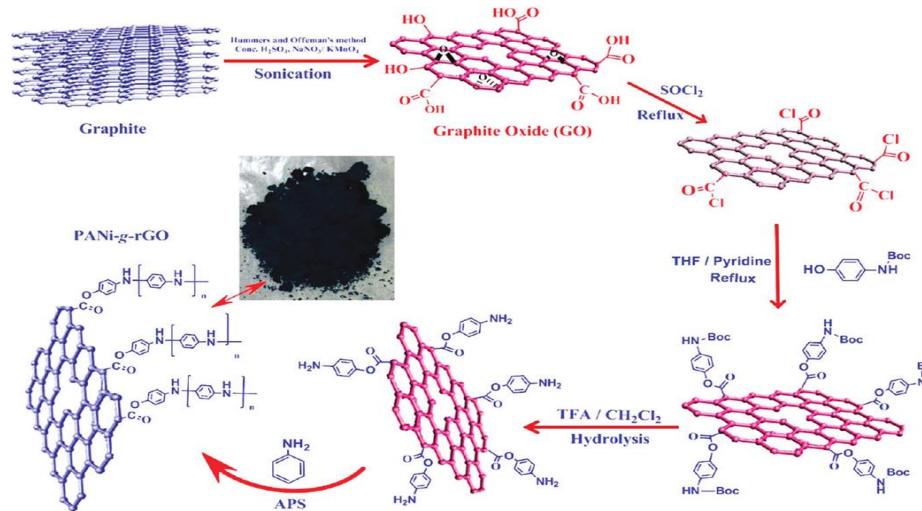


Figure 21 Schematic showing the preparation of PANi-g-rGO with a digital picture of the sample in the middle. Reprinted with permission from ref. [129] Copyright 2012 American Chemical Society.

The strong interfacial adhesion between PVA-g-GO and the PVA matrix was attributed to the good compatibility between the PVA-g-GO and the PVA matrix, as well as hydrogen-bonding. Cheng *et al.* [132] presented a novel approach toward fabricating advanced polymeric nanocomposites from poly (vinyl alcohol) (PVA) by incorporating PVA-grafted GO. The mechanical properties of PVA were greatly improved by incorporating PVA-g-GO. For example, the tensile strength and Young's modulus of the PVA nanocomposite containing 1 wt % net GO significantly increased by 88 and 150%, respectively, versus the unfilled PVA. The elongation at break was also increased by 22%, while the elongation at break for the GO-PVA nanocomposite containing 1 wt % pristine GO had decreased by 15%. Therefore, the presence of PVA-g-GO in the PVA matrix could make the PVA stronger and tougher. The strong interfacial adhesion between PVA-g-GO and the PVA matrix was attributed to the good compatibility between the PVA-g-GO and the PVA matrix, as well as hydrogen-bonding.

Several other functionalized graphene oxides require ester linkages that involve direct substitution of 1-bromobutane [133] or grafting of biodegradable poly (L-lactic acid) [134], glycidyl methacrylate [135], trypsin [136], and phenolic resin [137], etc.

4.1.2.3 Silanization

The GO surface can be silanized using different silylating agents. The R-O-Si bond in silane is very reactive toward protic groups, such as has been widely applied to anchor different silane groups onto carbon surfaces [138]. For example, the silylation of graphite oxide was reported by Matsuo *et al.* in 2004 [139]. Yang *et al.* [140] functionalized GO with 3-aminopropyl triethoxysilane (APTS) through hydrolytic condensation route; the APTS was covalently attached to the GO surface to form silicon-functionalized GO (Si-GO), which enhanced the monolithic silica structure. Moreover, when using silanized GO, several functional groups can be anchored onto the graphene surface.

To improve the stress transfer and distribution of the carbon fiber/epoxy interface, Xu *et al.* [141] introduced a silanized graphene oxide (SGO) as an interphase gradient (Fig. 22). Upon comparison with the base composites without nanosheets, the interfacial shear strength (IFSS), the interlaminar shear strength (ILSS), and the flexural and tensile properties of the hierarchical composites decreased seriously when 0.5 wt% GO was introduced on the carbon fiber surface. However, hierarchical composites containing 0.5 w% silanized GO exhibited a significant increase in the IFSS, ILSS, flexural strength and flexural modulus.

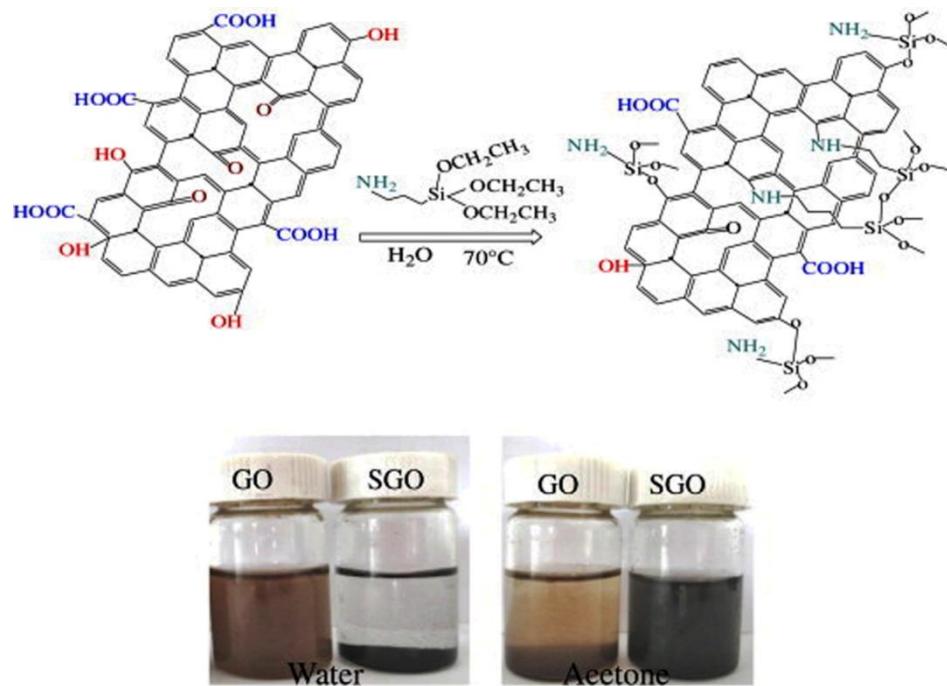


Figure 22 Illustration of the reaction between GO and a silane coupling agent, and photographs of GO and SGO dispersed in water and acetone. Reprinted with permission from ref. [141]. Copyright 2014, Elsevier Ltd.

Similarly, Zang *et al.* [142] used silanized GO with amine-terminated silanes to prepare primary and tertiary amine-bifunctional graphene oxides with excellent catalytic activities and 100% selectivity during a classic synthesis of *trans*- β -nitrostyrene. In addition, highly stable dispersions of silane-functionalized reduced graphene oxides were obtained by silanizing graphene oxide with N-(trimethoxysilylpropyl) ethylenediamine triacetic acid followed a reduction of the silanized GO to produce water-soluble graphene derivatives (EDTA-graphenes) [143]. A covalently bound, polyethylene-grafted graphene oxide hybrid material was also synthesized using aminopropyltriethoxysilane (APTES) [144]. The APTES was first coated onto graphene oxide, and maleic anhydride grafted polyethylene (MA-g-PE) was subsequently grafted to the silanized graphene oxide. The resultant nanocomposite exhibited an improved mechanical performance.

4.1.2.3 Other GO functionalizations

In addition to the classical reactions discussed above, graphene oxide also undergoes several modifications using covalent attachments. Zang *et al.* [145] functionalized GO with phenol formaldehyde through simultaneous reductions that form ether linkages (Fig. 23). The GO is functionalized during a nucleophilic substitution reaction between the epoxide groups of the GO and the hydroxyl groups of phenol under basic conditions. The resulting cured composite exhibited high thermo-mechanical properties. Similar to pristine graphene, graphene oxide also participated in nitrene chemistry. A hydroxylated graphene (G-OH) was prepared utilizing nitrene chemistry by reacting GO with 2-azidoethanol for further functionalization to obtain amphiphilic nanoscale ionic materials (NIM), schematic is depicted in Fig 28. [110, 146].

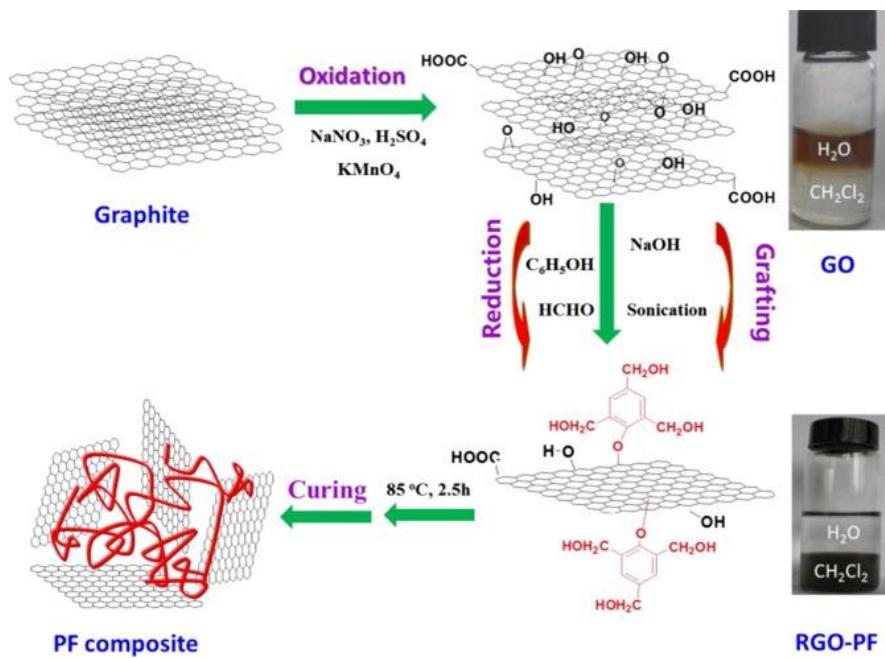


Figure 23 Schematic of the simultaneous reduction and functionalization of GO during the in situ polymerization of a PF composite. Reprinted with permission from ref. [145]. Copyright 2014, Elsevier Ltd.

Similarly, Garcia *et al.* [147] covalently functionalized graphene oxide with phenothiazinyl units and studied its photochemical activity. Zhao *et al.* [148] functionalized graphene oxide using water-soluble pillararenes for in vitro dual-mode Raman and fluorescence bioimaging. Also, an insertion of an aromatic nitrogen moiety in the form of five-membered pyrazole ring was successfully prepared by hydrazine treatment on graphene oxide [149].

4.1.3. Functionalization of partially reduced graphene

As discussed in section 2, a complete reduction of GO to form graphene through different routes, particularly chemical methods, is difficult to achieve because residual epoxy and hydroxyl functional groups always remain on the basal plane of the RGO [150]. Density functional theory (DFT) studies of the graphene structure after deoxygenation confirmed that removing the oxygen functional groups completely from the graphene surface was impossible during chemical or thermal or combination reductions [151, 152]. In a subsequent DFT study, Ghaderi and Peressi confirmed the presence of hydroxyl groups

after a reduction [153].

Iqbal *et al.* [154] reported an uncatalyzed functionalization of thermally reduced graphene (TRG) with 3-aminopropyltriethoxy silane (APTS). The reaction mechanism is based on attaching the silane groups to the TRG surface through the residual, surface-bound phenolic and carbonyl groups, as shown in Fig. 24. Using an organic solvent during the silylation reaction not only increased the grafting yield from 7 to 8 atomic% of Si but also directs APTS groups to the edges of the TRG, as shown through energy filtered TEM elemental mapping (Fig. 25).

Wang *et al.* [155] synthesized hydroxylated GO (G-OH) by reacting partially reduced GO with 2-(4-aminophenyl) ethanol. The G-OH was grafted with a polymerization initiator to graft polymer brushes onto the graphene surfaces. Cornut *et al.* [156] recently discussed a new localized functionalization method using graphene oxide (GO) deposited on a silicon oxide surface (Fig. 26). The functionalization begins by reducing the GO using electrogenerated naphthalene radical anions. Subsequently, the reduced-GO is electrografted with a diazonium salt containing a protonated amino group that can immobilize gold nanoparticles through simple immersion.

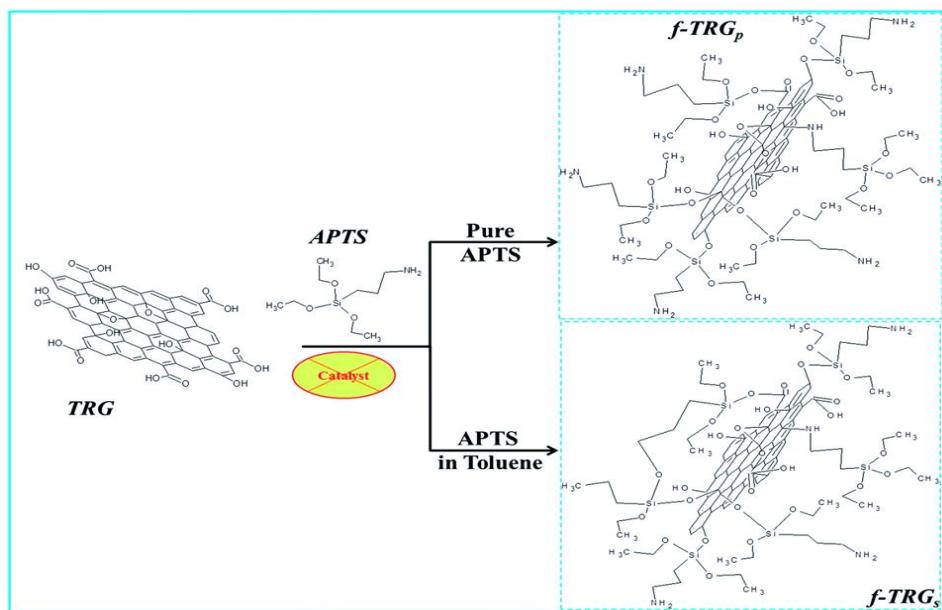


Figure 24 Reaction of APTS with TRG. TRG contains carboxylic functionalities on the sides, while the hydroxyl and epoxy groups are primarily distributed over the surface. Authors own work.

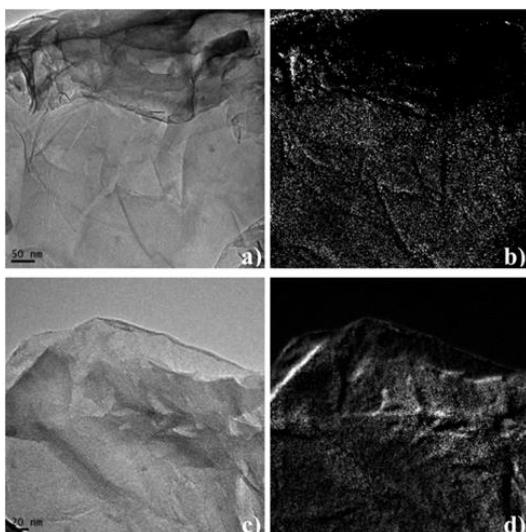


Figure 25 TEM bright field image (a) and corresponding EFTEM maps of silicon (b) for f-TRG_p; TEM bright field image (c) and corresponding EFTEM maps of silicon (d) for the f-TRGs. Authors own work

Similarly, Srinivas *et al.* [157] used partially reduced GO obtained through a solvothermal reduction, which occurred in methanol at 150 °C over 24 h, to generate a graphene organic framework (GOF).

Ajayan *et al.* [158] reported crosslinked 3D networked GO solids, which were called poly GO. These three-dimensionally engineered nanoporous architectures are synthesized by covalently

interconnecting GO via chemical cross-linking and polymerization using glutaraldehyde and resorcinol (Fig. 27). The poly GO sample exhibited good adsorption capacity for CO₂ storage. The chemical functionalization of RGO using residual oxygen groups has been reported by Hsiao and coworkers [159]. This procedure does not create additional defects on the graphene surface compared to the reactions with C=C bonds.

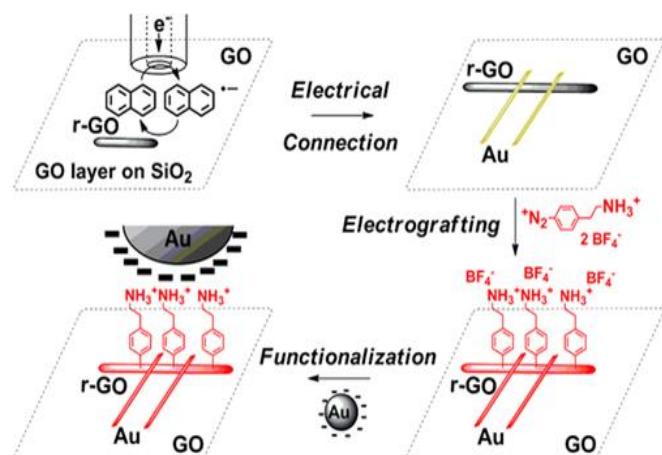


Figure 26 Localized graphene oxide (GO) deposited on a silicon oxide surface using naphthalene radical anions; electrografting reduced-GO with a diazonium salt with immobilize gold nanoparticles. Reprinted with permission from ref. [156]. Copyright 2014, American Chemical Society.

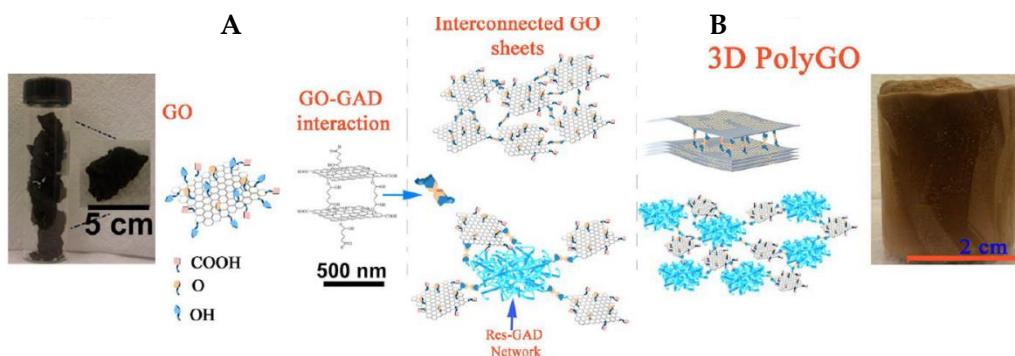


Figure 27 Schematic of the poly-GO synthesis from GO powder. (A) Photograph showing the GO powders synthesized through an improved technique (left); schematic of the GO structure with main functional groups (middle); a possible interaction between the GAD and two neighboring GO sheets via the OH groups in GO is also depicted. (B) Schematic of the two different mechanisms for large-scale GO cross-linking in aqueous solutions via pure GAD (top) and GAD-Res (bottom). (C) Schematic of the 3D networked structure of poly-GO formed through the two different mechanisms. Lyophilization (freeze-drying) of cross-linked solution forms macroscopic solid structures with controllable shapes and sizes. Reprinted with permission from ref. [158]. Copyright 2013 American Chemical Society.

5. Non-covalent modification of graphene

In this section, we will review several procedures developed to form noncovalent interactions between graphene and other molecular species. In particular, the non-covalent functionalization of graphene, including π - π interactions, hydrophobic attraction between a surfactant and graphene and hydrogen bonding interactions are reviewed. Moreover, in certain cases the functional properties of the materials are outlined and prospected. The noncovalent interactions between graphene and organic molecules are of particular interest because these approaches modify the graphene surface without diminishing the outstanding properties of the two-dimensional sp^2 network, as depicted in Fig. 28 [160, 161]. Because subtle changes in the electronic characteristics of the π systems can engenders structural disruption of graphene sheets to cause properties [162, 163]. Therefore, the noncovalent surface modification of graphene by surfactants, ionic liquids or macromolecules was broadly achieved to obtain highly stable dispersions of individual graphene sheets in both aqueous and organic media without altering the structural integrity of graphene. A detailed discussion of noncovalently modifying

graphene surfaces using various chemical species is presented in the following paragraphs.

5.1 Polynuclear aromatic rings

Considering the high affinity for π - π interactions and added functionality, these types of aromatic molecules are frequently used to disperse graphene sheets in aqueous and organic media. In particular, poly-aromatic hydrocarbons, such as aromatic dimers of benzene, naphthalene, anthracene and pyrene functionalized with flexible or possibly polar side chains were effective. The pyrene moiety has a strong affinity toward the basal plane of graphite via π -stacking. Green and co-workers [164] studied several functionalized pyrene derivatives (Fig. 29) and demonstrated that these species could stabilize single- and few-layer graphene flakes in aqueous dispersions. Additionally, the graphene/stabilizer yield obtained through this method is significantly higher than that of conventional nanomaterial stabilizers, such as surfactants or polymers. The mechanism for the stabilization by pyrene derivatives is investigated by studying various parameters. The authors found that a sufficient difference between the polarity of the solvent and the stabilizer is required for adsorption onto the graphene surface.

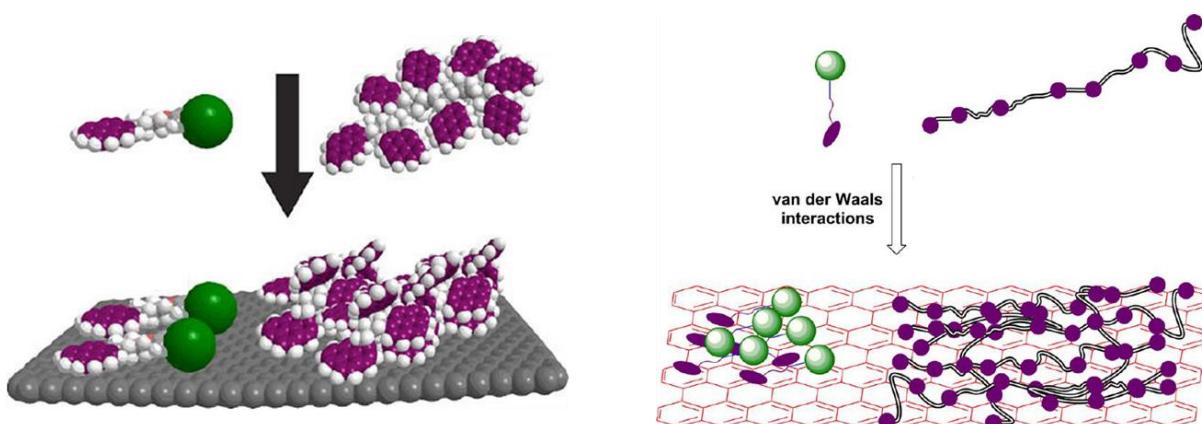


Figure 28 Schematic of the noncovalent functionalization of graphene using polymers and small-molecule adsorbates. Reprinted with permission from ref. [160]. Copyright 2013, American Chemical Society.

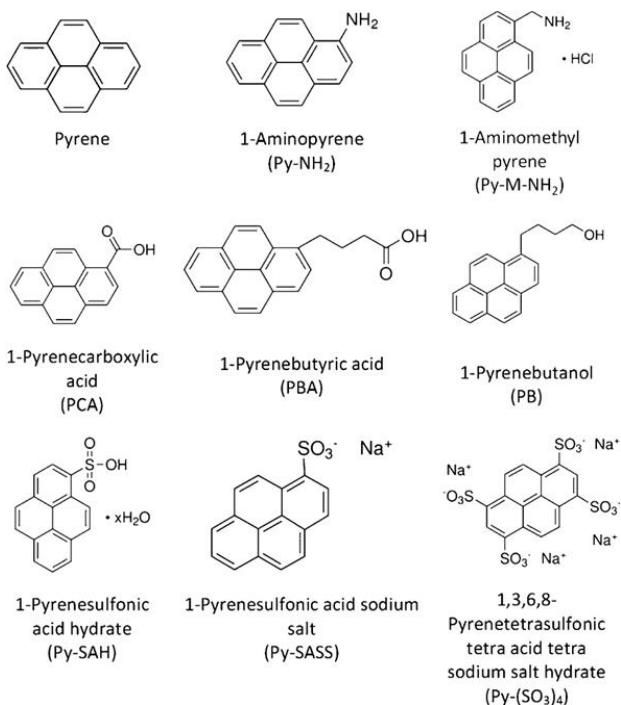


Figure 29 Chemical structure of the pyrene derivatives used for non-covalently modifying graphene. Reprinted with permission from ref. [164]. Copyright 2012, American Chemical Society.

The role of the functional groups on the pyrene derivatives during the stabilization process was also explored; the functional groups with higher electronegativities are more efficient when driving the adsorption of stabilizers onto the graphene layers (Fig. 30).

Mullen and co-workers [165] used the sodium

salt of pyrene-1-sulfonic acid (PyS) as an electron donor, and the sodium salt of 3,4,9,10-perylenetetracarboxylic diimide bisbenzenesulfonic acid (PDI) as an electron acceptor. These authors demonstrated that PyS and PDI have large planar aromatic structures that strongly anchor them onto the hydrophobic surface of graphene sheets through π - π interactions without disrupting the electronic conjugation of graphene. Additionally, the polyaromatic part interacts with the graphene through π - π stacking, while the negatively charged part (the acid) enhances the solubility of the sheet, hindering re-aggregation. Similarly, Xu *et al.* [20] used water-soluble 1-pyrenebutyrate (PB⁻) as a stabilizer when preparing stable aqueous dispersions of graphene nanoplatelets.

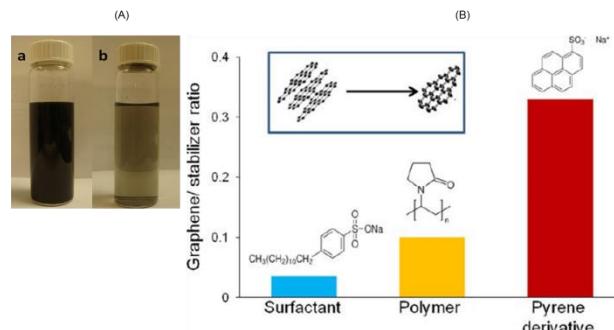


Figure 30 Dispersions of (a) Py-SASS and (b) Py (SO_3)₄ functional graphenes (A) and a comparison of the different functionalities during graphene dispersion (B). Reprinted with permission from ref. [164]. Copyright 2012, American Chemical Society.

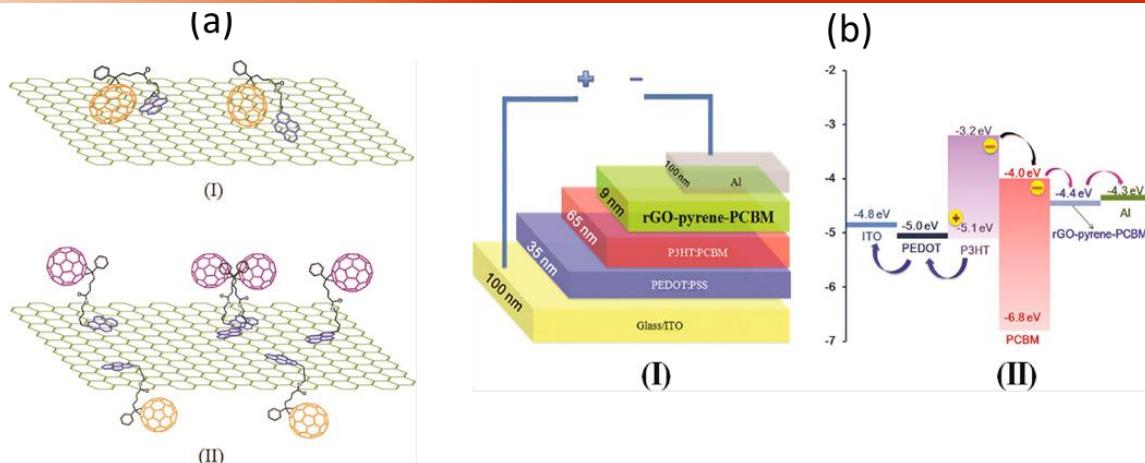


Figure 31 Schematic illustrations of two possible conformations of the rGO-pyrene-PCBM with the orientation of C₆₀ moiety attaching onto (I) or being far from (II) the graphene sheet (left). The schematic architecture (I) and energy level diagram (II) of ITO/PEDOT:PSS/P3HT:PCBM/rGO-pyrene-PCBM/Al BHJ-PSC device with an incorporated rGO-pyrene-PCBM electron extraction layer (right). Reprinted with permission from ref. [170]. Copyright 2013, American Chemical Society.

GO was functionalized with pyrenebutyric acid in the presence of a base, and the resulting product was reduced with hydrazine. The AFM images show GO and functionalized graphene nanoplatelets that are 1.3- and 1.7-nm thick, respectively. The flexible graphene film is 7 times more conductive than the GO precursor. Bose *et al.* [166] described the non-covalent functionalization of graphite by 9-anthracene carboxylic acid (9-ACA) to produce a water-dispersible graphene with excellent electrochemical activities, demonstrating that 9-ACA could attach to the graphite surface through π - π interactions.

Porphyrin-functionalized graphene sheets were suspended in an aqueous medium to fabricate highly conductive graphene films [167]. The attachment of other porphyrin derivatives such as 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin (TPMPyP) [168] and haemin [169] were also reported.

Similarly, Yang *et al.* [170] synthesized a new graphene–fullerene composite (rGO-pyrene-PCBM):[6, 6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) was attached to reduced graphene oxide (rGO) via noncovalent functionalization (Fig. 31). The hybrid structure of the rGO-pyrene-PCBM was confirmed through various spectroscopic techniques. Compared to the pristine rGO, the dispersity of the rGO-pyrene-PCBM in DMF was greatly improved due to the

intramolecular π - π stacking interactions between the graphene sheet and pyrene-PCBM. Finally, rGO-pyrene-PCBM was successfully used as an electron extraction material for P3HT:PCBM BHJ-PSC devices, enhancing the efficiency by ca. 15%. The resulting hybrid shows potential in polymer-based solar cells. Moreover, several other studies used similar polynuclear aromatic derivatives as an efficient non-covalent functionalization tool for various applications [171–175].

Recently, Basiuk *et al.* [176] reported the noncovalent functionalization of a Ni(II) complex containing 5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradeca-3,5,7,10,12,14-hexaene (Ni(II)-tetramethyl dibenzotetraaza annulene, or NiTMTAA) on a graphene surface. This functionalization is a simple model for complex porphyrins and phthalocyanines. Persson and coworkers [177] theoretically demonstrated the adsorption of neutral (poly)-aromatic, anti-aromatic, and more generally π -conjugated systems on graphene through π - π stacking based on Van der Waals density functional theory (Fig. 32). The magnitude of the π - π interactions normalized both per number of total atoms and carbon atoms increases significantly with the amount of hydrogen atoms in the systems.

However, the presence of highly oxidized polyaromatic carboxylated fragments, such as oxidized debris on oxidized graphene surfaces have raised serious concerns [178]. Coluci *et al.* [179] demonstrated that the oxidative debris adsorbed on graphene oxide surfaces are important during the noncovalent interactions between GOs and aromatic compounds, such as 1-nitropyrene (1-NP) the oxidative debris comparable to 1-NP molecules (~ 1 nm) in size obstruct adsorption sites on the GO surface (Fig. 33).

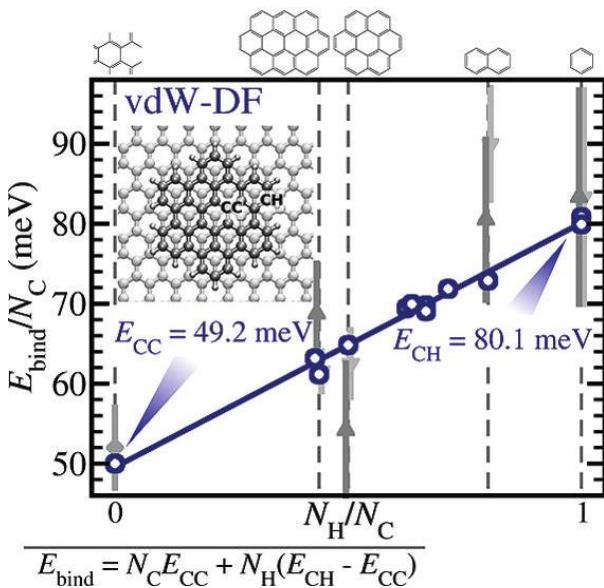


Figure 32 Adsorption of aromatic and anti-aromatic systems on graphene through $\pi-\pi$ Stacking. Reprinted with permission from ref. [177]. Copyright 2010, American Chemical Society

5.1 Surfactants and ionic liquids

Surfactants are commonly used to functionalize various nanoparticles, rendering them more hydrophilic or hydrophobic. Similarly, graphene is functionalized using noncovalent methods, such as wrapping them with surfactants or ionic liquids. Mullen and co-workers [180] described a potentially scalable and environmentally friendly method for producing chloroform-soluble graphene through a surfactant-supported functionalization. For this method, the authors used the salts of amphiphilic molecules, specifically the quaternary ammonium salts of tetradecyltrimethylammonium bromide (TTAB), didodecyldimethylammonium bromide (DDAB), and tetradodecylammonium bromide (TAB) with 1, 2, and 4 alkyl chains, respectively. Moreover, the ionic interactions could preserve the extended aromatic conjugation of the reduced graphene, producing the high conductivity of the cast films. Loyta *et al.* [37] demonstrated a low-cost and scalable process for preparing stable dispersions of graphene at concentrations up to 0.3 mg/mL in the surfactant/water systems. When sodium cholate is used as a surfactant, the dispersed concentration increases sublinearly with the sonication time [181]. Tascon *et al.* [182] measured the ability to stabilize graphene using various surfactants through UV-Vis spectroscopy (Fig. 34). The chemical structures of the surfactants are important Ionic liquids are other prominent candidates for functionalize graphene without compromising their structural integrity.

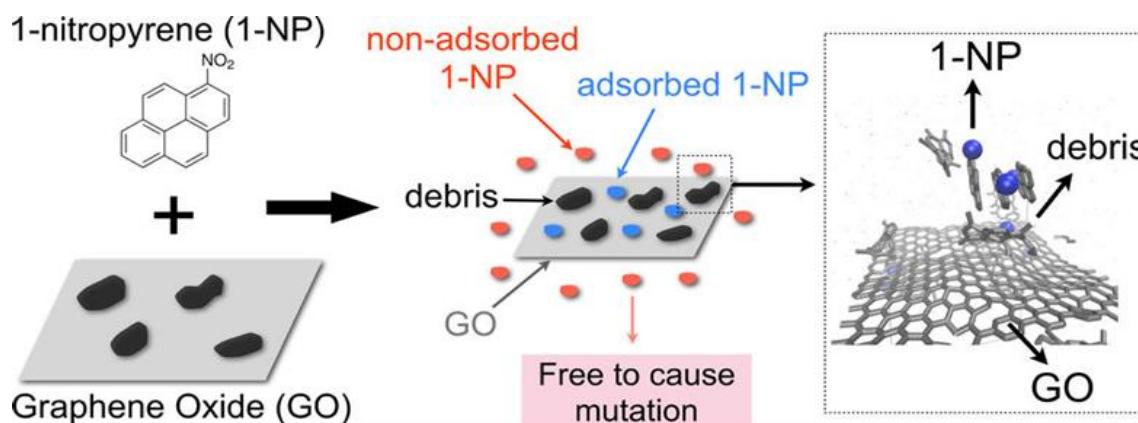


Figure 33 Schematic of the noncovalent interactions between aromatic compounds and graphene oxide, as well as the role of the oxidative debris. Reprinted with permission from ref. [179]. Copyright 2014, American Chemical Society.

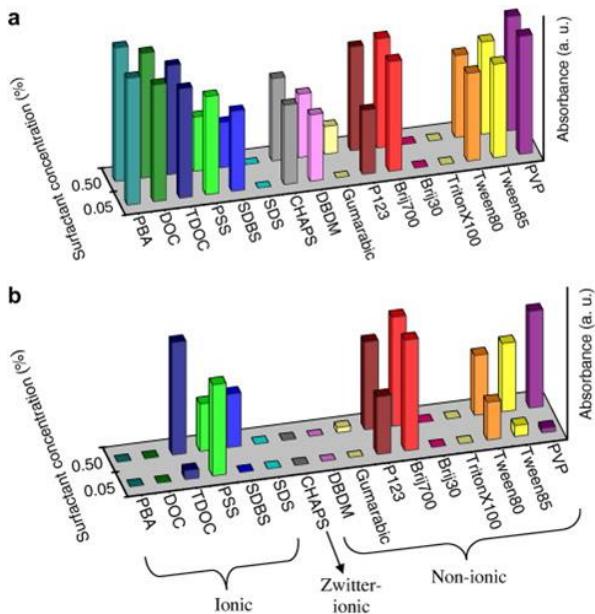


Figure 34 UV-vis absorbance at 450 nm measured in the supernatant of centrifuged ($10,000\text{ g}$, 10 min), surfactant-stabilized 0.1 mg mL^{-1} RGO dispersions in basic (a) and acidic (b) media (pH 12 and 1, respectively). Two surfactant concentrations are shown: 0.05% and 0.50% wt/vol. Reprinted with permission from ref. [182]. Copyright 2012, Elsevier Ltd.

Different ionic liquids was explored as functionalizing agents for graphene toward various applications [183-186]. Lonkar and co-workers [187] used a supramolecular approach based on imidazolium ionic liquids (ILs) to achieve highly organo-dispersible graphenes (Fig 35 A). Moreover,

the hydroxyl functionality from ILs was successfully used as a ring opening polymerization agent to obtain graphene/polymer nanocomposites (Fig 35 B). The resulting nanocomposites exhibited superior thermo-mechanical characteristics. Additionally, the localization of ionic liquids on graphene surface produced a functional hybrid that could be used as a biosensor [188].

5.3 Biomolecules and macromolecules

The stable dispersion of reduced graphene in various organic solvents can also be obtained through noncovalent functionalization with functional polymers. Kim and coworkers [189] exploited organo-dispersed graphene in various solvents mediated by noncovalent functionalization with end-functional polymers. The protonated amine terminal groups of the end-functional polymers interact with the residual oxygenated functionalities on the graphene surface that readily transfer the graphene from the aqueous phase to the organic phase through simple sonication. Yang *et al.* [190] used biopolymers, such as cellulose and lignin, to functionalize graphene forming aqueous-dispersible graphene. Immobilizing enzymes on graphene substrates is also attracting great deal of interest toward improving the enzymatic activities. The enzymes could be immobilized on GO without coupling reagents due to the intrinsic surface functional groups of GO, $\pi - \pi$ stacking, and/or hydrophobic interactions [191, 192].

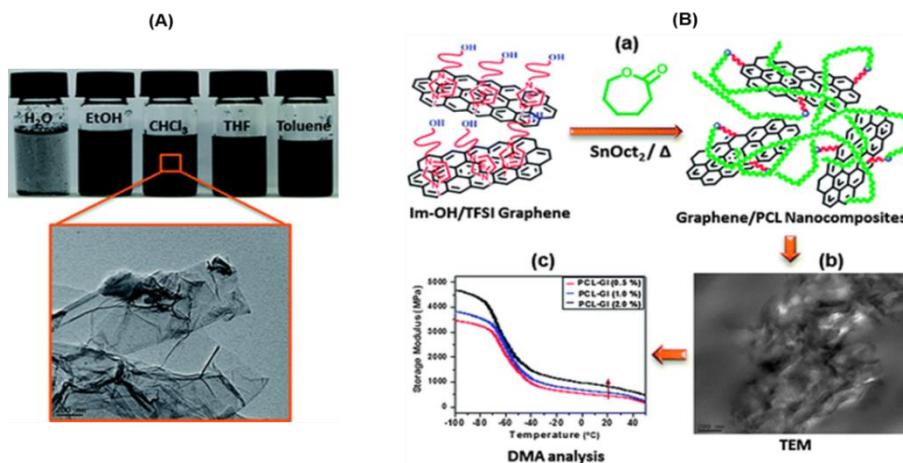


Figure 35 Dispersions of Im-OH/TFSI/graphene in different solvents and a TEM image of the chloroform dispersion (A). Schematic representations, (a) TEM analysis, (b) and dynamic mechanical analysis (DMA) (c) of graphene/PCL nanocomposites (B). Authors own work.

Zhang *et al.* [193] immobilized enzymes without any cross-linking reagents; horseradish peroxidase (HRP) and lysozyme molecules were immobilized onto GO simply by incubating the GO sheets in a phosphate buffer containing the HRP or lysozyme (Fig. 36). Guo and co-workers [194] tested the possible hydrophobic interactions between an enzyme and graphene oxide (GO) that was reduced to different extents to modulate its hydrophobicity.

It was observed that more the GO was reduced, the higher the enzyme loading was, implying that the interaction between the enzyme and CRGO should be dominated by hydrophobic interactions. This result indicates that the hydrophobic interactions between the reduced GO and enzymes are stronger than the electrostatic interaction between the GO and the enzyme.

Recently, the kinetic stability of the tripod monolayers was leveraged to anchor proteins relevant to biosensors on single-layer graphene (SLG) [192].

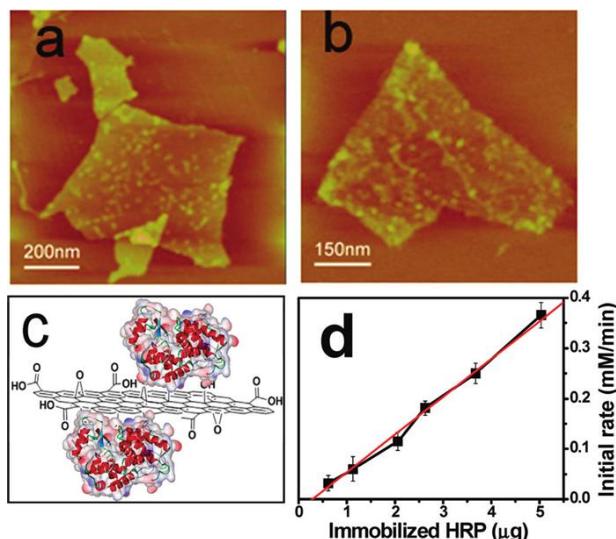


Figure 36 Tapping mode AFM images of the GO-bound HRP with (a) lower and (b) higher enzyme loadings acquired in a liquid cell. (c) Schematic model of the GO-bound HRP. (d) Initial reaction rates of GO-bound HRP versus the HRP concentration. Reprinted with permission from ref. [193]. Copyright 2010, American Chemical Society

An anti-E.coli antibody is readily captured by bare SLG and SLG bearing monolayers of tripod 3 or pyrene butyrate 4, which feature the N-hydroxysuccinimidyl (NHS) esters needed for the bioconjugation reactions. However, only the antibody-functionalized tripod monolayers bind E. coli cells at above background levels, while the antibodies adsorbed on SLG or attached to 4 show levels of E. coli recognition similar to those of a control monolayer containing a mismatched antibody (anti-bovine serum albumin) supported on 3.

Similar findings were observed for the lectin protein Concanavalin A (ConA). Tripod-bound ConA retained its ability to recognize both dissolved oligosaccharides and those found on *Bacillus subtilis* cell walls, while the protein showed no evidence of these actions when adsorbed directly onto single-layer graphene (SLG) [195].

These findings demonstrate the value of robust noncovalent binding groups when preserving the function of proteins on SLG, which are otherwise prone to deleterious denaturation. Similarly, Lee *et al.* [191] reported that heparin could also be absorbed on the graphene surface through hydrophobic interactions, as depicted in Fig. 37. They found that the hydrophobic interaction depends strongly on both the electron density and geometry of the heparin.

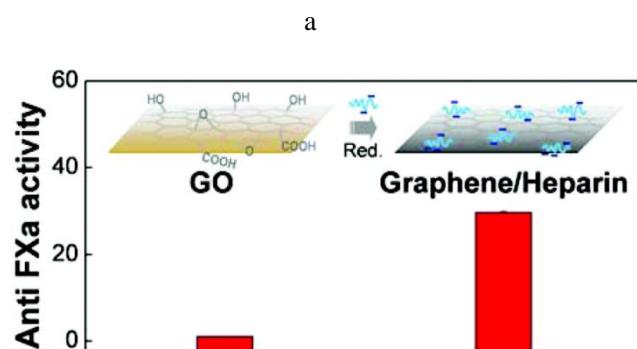


Figure 37 Blood compatible graphene/heparin conjugate formulated through noncovalent interactions between chemically reduced graphene and heparin. Reprinted

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The anti-FXa activity of the graphene/heparin conjugate was significantly higher. Other biomolecules that are immobilized on or interact with graphene surfaces include glucose oxidase [196], chymotrypsin [197], proteins [198] and trypsin [136].

5.4 Attachment of nanoparticles

In addition of surfactants, biomolecules and polymers, nanosized inorganic particles were also attached to the graphene surface through non-covalent modification methods. Most of these methods use bridging molecules that are capable to form π - π , hydrophobic and hydrogen bonding interactions, simultaneously with graphene surface and nanoparticles. Recently, Liu *et. al* [199] used poly (amidoamine) (PAMAM) dendrimer as a bridge to attach silver nanoparticle (AgNP) unto graphene surface using non-covalent interactions. A homogeneous dispersion of AgNP on graphene surface was achieved using PAMAM stabilization. Also, Lu et al. [200] presented a facile non-covalent decoration of graphene using silver nanoparticles. An electrostatic force directed assembly was used under arc plasma at room temperature. Similarly, Fe_3O_4 nanoparticles (NPs) assembled on both sides of reduced graphene oxide (RGO) sheets with tunable density forming two-dimensional NPs composite membranes was reported [201]. The assembly is driven by electrostatic interactions and resulting hybrids exhibit considerable mechanical robustness and sustainable supersonic and solvothermal treatments. Further, the gold nanoparticles decorated GO hybrids were reported, the hybridization was facilitated using anticancer drug doxorubicin through non-covalent interactions [202]. Another examples for such nanoparticle attachments to graphene includes, polyvinylpyrrolidone (PVP) stabilized Fe_2O_3 [203], polyoxyethylene sorbitol anhydride monolaurate (TWEEN 20) stabilized gold nanoparticles [204], PVP stabilized AgNP [205], *p*-phosphonic acid

calix[8]arene stabilized palladium nanoparticles [206] etc.

6. Conclusions and future perspectives

In this review, we have summarized the recent work in the very rapidly growing field of graphene research with a specific emphasis on chemical modification. Evidently, despite having several intriguing properties, potential of graphene for various applications is limited due to difficulties encountered during physical handling. Numerous attempts have been made to stabilize graphene through chemical modification, either covalent or non-covalent. Covalent functionalization primarily involves classical organic reactions, such as diazonium coupling, cycloaddition, substitution, and other reactions. Non-covalent approaches utilize π - π interactions. The anchored functionalities enhance the dispersion of graphene in solvents or polymer matrices while adding new functional properties, revealing new applications for graphene in numerous fields. However, few concerns, such as the interactions between the oxidative debris and functional groups during non-covalent modification must still be addressed. Despite the existing wealth of knowledge regarding graphene functionalization, we anticipate that the newer aspects of the chemical modifications, further studies of graphene reactivity and synthetic control, and improved characterization tools will produce a series of novel materials with highly specific functionalities and enormous potential for targeted applications. We have summarized the recent strategies adopted during the chemical modification of graphene and their impact on the properties of graphene and new activities that they impart. Certain applications, such as gas sensors, biosensors, the adsorption of toxic gases, energy storage, catalysis, and polymer nanocomposites should benefit the most from graphene functionalization.

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