



Modification and Functionalization of Graphene /Graphene oxide

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Abstract:

Graphene is a material that has generated enormous research interest and activity in the past few years due to its remarkable properties and wide applications in fields, such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors, hydrogen storage, transparent conductors and energy storage materials. (Reduced) graphene oxide have a great potential as a functional chemical building block in fabrication of various carbon-based nanostructures and their composites, for which chemical functionalization of the materials is critically important. Functionalization of graphene is one of the key topics in graphene research. Graphene has found to be the best known transparent conductor or semiconductor. The graphene was synthesized by using chemical methods. This article aims to provide broad-based coverage on the recent solution-based functionalization methods of graphene in a concise and mechanistic manner. We focus on the reactions of the graphene sp^2 backbone, such as nucleophilic addition, cycloaddition, free radical additions, substitutions and rearrangement, and reduction of graphene oxide and its various environmental applications.

Introduction:

Graphene is a one-atom-thick planar sheet consisting of sp^2 carbon atoms that are densely packed in a honeycomb crystal lattice [1]. Graphene has many unique properties such as high surface area, high electronic conductivity, high Young's modulus, high thermal conductivity and high optical transmittance [2,3]. Thus, graphene is considered a versatile building material for fabrication of electrochemical devices. Ever since the mechanical exfoliation of single-layer graphene from graphite succeeded in 2004, graphene has been receiving extensive research interest in EECS. The introduction of graphene brings some innovative properties to the electrochemical devices. Many review papers have focused on this topic [2,4,5]. Functionalization of graphene is one of the key topics in graphene research. Generally, there are two main categories of functionalization: chemical and nonchemical. Chemical functionalization is realized through the formation of new covalent bonds between the atoms native to RGO/GO and the guest functional groups; in contrast, nonchemical functionalization is mainly based on π interaction between guest molecules and RGO/GO, i.e., mainly a physical interaction. Both types of functionalization can induce some property changes for graphene, but the chemical routes are more effective. So far, various chemical routes have proposed, which successfully incorporate a large number of





different atoms/organic groups into graphene, including heterogeneous atoms doping, diazonium coupling, amidation, silanization, esterization, substitution, cycloaddition, etc. The research also demonstrates that the size of graphene (particularly the thickness of the ribbons) strongly affects the reactivity of graphene and the application of the functionalized graphene [6,7]. Graphene oxide (GO) has attracted increasing interest due to its distinct advantages, such as the abundance of different oxygenated species. GO contains many hydroxyl, carboxylic acid and other reactive groups amenable to ligand conjugation, cross-linking and other modifications. The incorporation of graphene oxide into polymers has drawn much attention as a route to obtaining new 25 materials with new structural and functional properties [8]. Chemical modified graphenes (CMGs) are provided by the addition of functional groups to GO platelets using various chemical reactions. A wide range of reactions utilizing carboxylic acids have been developed and applied to modify GO [9-11]. Moreover, the GO platelets contain reactive epoxy groups on their basal planes, which can be easily modified through ring-opening reactions under various conditions [12,13].

Methods:

Covalently functionalized graphene oxide reduction:

Green reduction with various Stoichiometry: The chemical reduction of GO has attracted the most interest as a route for industrial production [14-16], the toxicity driven limitations of hydrazine-based reducing agents generated the introduction of new reducing agents e.g. an environmentally friendly ascorbic acid under mild conditions [17]. A. Pruna and coworkers explored the properties of graphene materials by a functionalization approach of GO with varying stoichiometry by employing carbodiimide chemistry [18] while sodium bisulfite is proposed as toxicity-free reducing agent. It is demonstrated that GO and functionalized GO (fGO) have been successfully reduced and the proposed approach presents great potential for production of graphene-based composites [19]. Various reducing agents have been reported for the reduction of GO, including hydrazine and ascorbic acid. Pruna and coworkers demonstrate that sodium hydrosulfite can be used to reduce GO; the short time required for the reducing process could be the best advantage of such a reducing agent. Nevertheless, several factors could improve its reduction efficiency, such as the proportioning of reducing agent, use of catalysers or the reduction temperature [20]. While the preparation of graphite oxide was first carried out 150 years ago, attempts to remove the oxygen functionalities on the surface of graphite oxide via chemical means did not occur until approximately another 80 years later. A record by Brauer in 1963 noted the treatment of graphite oxide with hydrazine, hydroxylamine, hydroiodic acid, iron (II) and tin(II) ions for reduction [21]. Chung and co-workers recently introduced ammonia borane (NH_3BH_3) in aqueous and organic solvents to reduce graphene oxide [22]. Ammonia borane is a mild reducing agent with a similar reactivity to sodium borohydride and exhibits potential as a material for hydrogen storage [23]. Lithium aluminium hydride is one of the strongest reducing agents in synthetic chemistry. Its reduction capability surpassed that of borohydride salts whereby more oxidised groups such as carboxylic acids and esters could be reduced



to the corresponding hydroxyl groups. It was thus applied on graphene oxide in conjunction with sodium borohydride and hydrazine reducing agents for comparison purposes [24]. Hydrohalic acids such as HI, HBr, and HCl are often utilized in synthetic chemistry for electrophilic addition and nucleophilic substitution reactions. The halides are nucleophilic in nature, with increasing nucleophilicity from $\text{Cl}^- < \text{Br}^- < \text{I}^-$, and react via both the $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ pathway depending on the reacting substrates. On top of that, the hydrohalic acids are capable of opening epoxides as well. These reactivities rendered hydrohalic acids excellent candidates for removing the abundant hydroxyl and epoxide functionalities found on graphene oxide. Although hydrohalic acid has been previously applied for the reduction of graphite oxide, it has resurfaced for the reduction of graphene oxide in recent years, as achieved by Lee and co-workers [25].

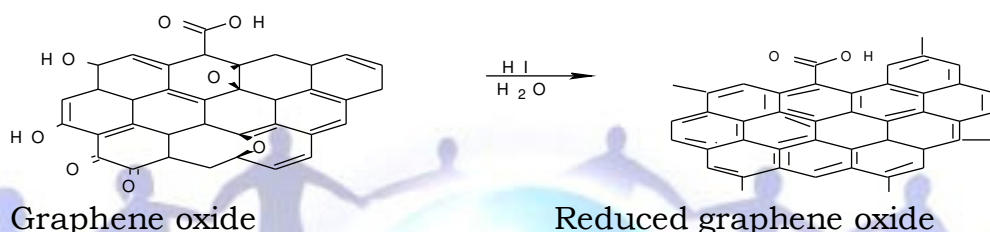


Fig.1: Mechanism for the reduction of epoxide and hydroxyl group

Sulphur-containing reducing agents: The usage of conventional reducing agents for graphene oxide may be preferred, unconventional reducing agents could potentially provide comparable efficiencies as well. Fugetsu and co-workers reported similar reduction capability of thiourea in alkaline (i.e. NaOH) conditions [26]. Consequently, Guo and co-workers reported the usage of thiourea dioxide as a reducing agent for graphene oxide while replacing NaOH with NH_3 to achieve an alkaline condition [27]. The resulting graphene showed a C/O ratio is less than the previous graphene oxide.

Covalent functionalization on graphene carbon network: Nucleophilic addition: The halide-malonate moiety is typically generated in situ in a mixture of tetrahalomethane and a base. The base abstracts a proton from the halide-malonate to provide an enolate which subsequently nucleophilically attacks a C=C bond on the graphene carbon framework. Based on the Bingel cyclopropanation reaction, Tagmatarchis and co-workers successfully introduced cyclopropane adducts onto the exfoliated graphene sp^2 carbon network with microwave irradiation as shown in Fig.2 [28]. In this work, the hybrid graphene materials were reported to be functionalized up to 23% and shows good dispersibility in organic solvents.

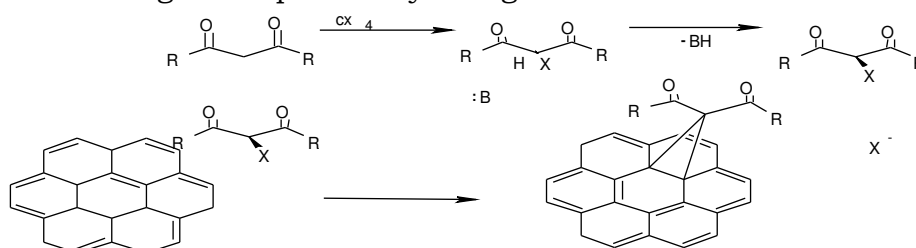


Fig.2 Mechanism of the (top) formation of halide derivative of enolate (bottom) addition of halide derivative of enolate onto graphene.

Cycloaddition on graphene network: Cycloaddition is one of the earliest adopted methods to functionalize the graphene sp^2 carbon network. There are generally two

main approaches in this category, mainly the cycloaddition towards the formation of cyclopropane or aziridine adducts. The cyclopropane adduct is achieved via dichlorocarbene insertion reaction, whereas the nitrene moiety is utilized as an intermediate towards the formation of an aziridine adduct [29]. Carbene in the form of dichlorocarbene has been introduced on the graphene sp^2 carbon network. Carbene formation was achieved by the conventional α -elimination method from a mixture of chloroform in strong base (NaOH). Such grafting of dichlorocarbene on chemically reduced graphene, by utilizing a mixture of chloroform with sodium hydroxide and triethylbenzylammonium chloride as a phase transfer catalyst, was demonstrated by Pumera and co-workers (Fig. 3).[30]. The group established the formation of the hybrid graphene material by HRXPS.

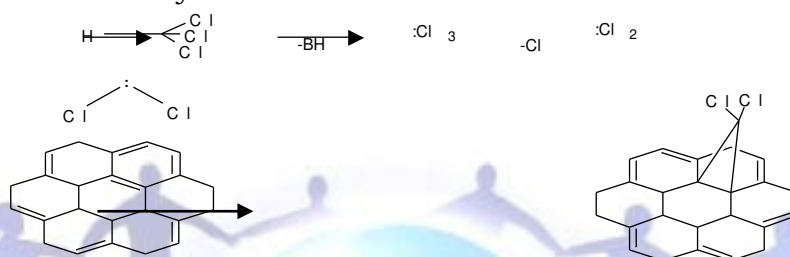


Fig.3 Mechanism of the (top) formation of dichlorocarbene with chloroform and base, and (bottom) cyclopropanation of graphene with dichlorocarbene

The introduction of aziridine adduct onto the graphene sp^2 carbon network is usually achieved via a nitrene intermediate, which is an analogue of carbene. The addition of aziridine adducts onto epitaxial graphene sp^2 carbon network was first illustrated by Kim and co-workers in 2009 [31]. The group reported the addition of azidotrimethylsilane onto an epitaxial graphene, with a reactive nitrene radical intermediate generated by thermal treatment. The addition of aziridine adducts through thermal photochemical activation techniques were also highlighted by Yan and co-workers (Fig. 4).[32-33].



Fig.4 Mechanism of the (top) formation of nitrene from the decomposition of azide and (bottom) cycloaddition of nitrene onto graphene.

Free radical addition: Functionalization of carbon nanomaterials via a free radical addition has been previously achieved on fullerene, graphite, and carbon nanotubes. The methodology has been successfully applied on graphene nanomaterials to promote band gap opening and tweaking of solubility. The functionalization of graphene via free radical addition approach has been achieved by both thermal and photochemical treatments. To this aim, the most common adduct utilized is aryl diazonium salts, apart from other organic free radicals. M. B. Smith and coworkers explain the covalent bonding of aryl group directly on the graphene sp^2 carbon network has been widely accomplished with aryl diazonium salts such as diazonium tetrafluoroborate derivatives. In acidic environments, the diazonium salt is

ionic and undergoes a polar reaction which results in an aryl cation. However, under neutral or basic conditions, the reaction mechanism goes through a free radical step (fig.5) [34]. The addition of aryl diazonium salts onto graphene was first introduced by Tour and co-workers, where the group ascertained the successful functionalization of graphene with chlorobenzene, nitrobenzene, methoxybenzene and bromobenzene moieties on chemically reduced graphene [35].

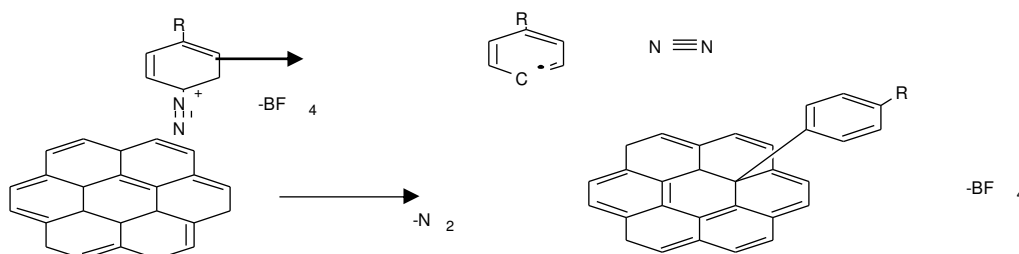


Fig.5 Mechanism of the free radical addition for derivatives of phenyl onto graphene.

Substitution Reaction on graphene: The functionalizations of graphene carbon networks based on electrophilic substitution reactions have been reported as well owing to the electron rich nature of graphene. Therefore graphene shows strong reactivity towards electrophiles. The acylation of graphene via Friedel–Crafts reaction has been successfully performed by Pumera and co-workers [36] based on a mild reaction condition introduced by Baek and co-workers [37]. The acylation was achieved with 4-aminobenzoic acid in the presence of PPA/P₂O₅ (Fig. 6). They evaluated hybrid graphene material using HRXPS which highlighted a new peak corresponding to C=O in the C1s core level spectrum. This was further supported by FTIR study as well.

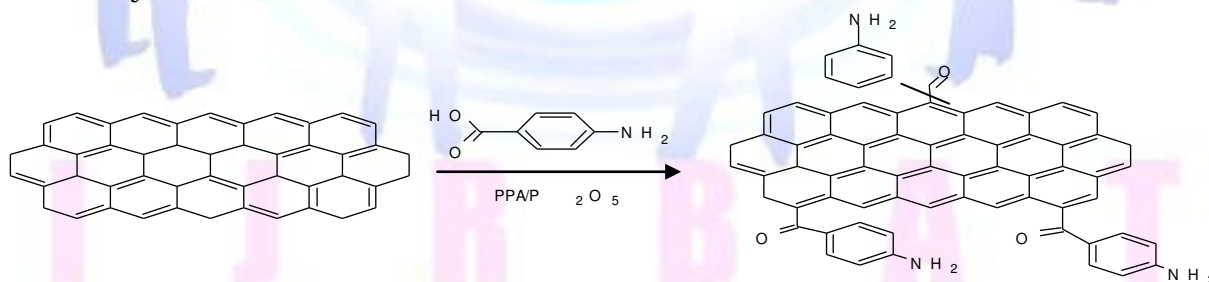


Fig.6 Functionalization of graphene via Friedel–Crafts acylation with PPA/P₂O₅.

Conclusion:

We have so far covered the common functionalization methods used for the chemical modification of graphene mainly over the past 5 years. New methodology has been developed in environmental and electrochemical aspect. Apart from developing new methodologies, it is equally important to improve current methods to increase the ease of functionalization as well as to reduce possible chemisorbed or physisorbed contaminants from the introduction of new functional adducts. Lastly, the improvement in synthetic modifications on graphene is definitely here to stay and to bring promising opportunities to graphene.



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