
Chemically Functionalized Graphene and Their Applications in Electrochemical Energy Conversion and Storage

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1. Introduction

Electrochemical energy conversion and storage (EECS) is one of the important strategies to address the strong demand on clean energy supply. Rechargeable batteries, fuel cells (FC) and supercapacitors are the typical electrochemical devices. Now, the challenge for the EECS is to make these devices bear enough capacities so as to fulfill the demand of the emerging markets, particularly, transportation applications and portable smart electronics. In this regard, the limitation of graphite, which has been a key component in the existing electrochemical devices, is seen. Much effort is being made toward exploring new morphologies for carbon, which are expected to provide some novel properties that would overcome the drawbacks of graphite. Among these, success in exfoliation of graphene from graphite has broken the ground.

Graphene is a one-atom-thick planar sheet consisting of sp^2 carbon atoms that are densely packed in a honeycomb crystal lattice [1], as shown in Fig. 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].

Pristine graphene, which is composed of only sp^2 carbon atoms, is a zero-gap semiconductor, and its Fermi level exactly crosses the Dirac point. For practical application, an energy gap is essential and thus, it is necessary and crucial to develop new methods to precisely control the

carrier type and concentration in graphene for further development of graphene-based devices. Normally, graphene has two oxidation states: graphene oxide (GO) and reduced graphene oxide (RGO). GO is water soluble with low electronic conductivity, while RGO reveals good conductivity but poor solubility in water. The excellent solubility of GO in aqueous solution is primarily due to its rich oxygen-containing and hydrophilic groups, such as hydroxyl, epoxide, carboxyl and carboxylic. Upon reduction, most of the oxygen-containing groups, in particular the hydroxyl, epoxide and carboxyl, will be completely removed. Thus, GO will then be converted to π -conjugation-rich graphene, i.e., RGO. The π -conjugation in graphene sheets (GNS) can restore the conductivity of graphene but reduces its solubility in water and other organic solvents. The decline in solubility may inevitably reduce processability of graphene and therefore limit its applications. All these render functionalization of graphene highly desirable.

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]. The thinner the ribbons, the more reactive they are. Moreover, it is also confirmed that carbon atoms on the ribbon edge are more reactive than those in the middle of the ribbon [6,7]. The chemical functionalization greatly alters the electric conductivity of graphene and introduces some defect sites, significantly affecting the application of the functionalized graphene in EECS applications. So far, heterogeneous atoms doping evidently improves the electric conductivity of graphene and hence, the resulting functionalized graphene is widely investigated [8,9]; on the other hand, incorporation of organic groups into graphene reduces the electric conductivity, preventing its electrochemical applications. Nevertheless, such functionalized graphene finds more extensive application in polymer science and technology, a topic that is not the focus of this chapter.

In this chapter, we review the chemical routes for functionalizing graphene and summarize the advances in the applications of the functionalized graphene in EECS, including FCs, lithium ion batteries (LIBs) and supercapacitors. Noticeably, chemical functionalization of graphene is a big field that involves organic chemistry/polymer chemistry. Various kinds of organic molecules have been chemically anchored onto graphene. It is impossible for us to list all kinds of molecules in this short review; instead, we address this in term of what kind of typical organic reaction is adopted for the functionalization. The organic reactions in this chapter are easy to understand and follow. For each reaction, the most original and representative studies are selected for review. Moreover, a large number of references are involved in

this topic, which can not be listed totally due to the page limit. Hence, only the references that are strictly about functionalized graphene and their applications are provided here. Finally, research in this field is advancing quickly, thus, some new results might not be addressed.

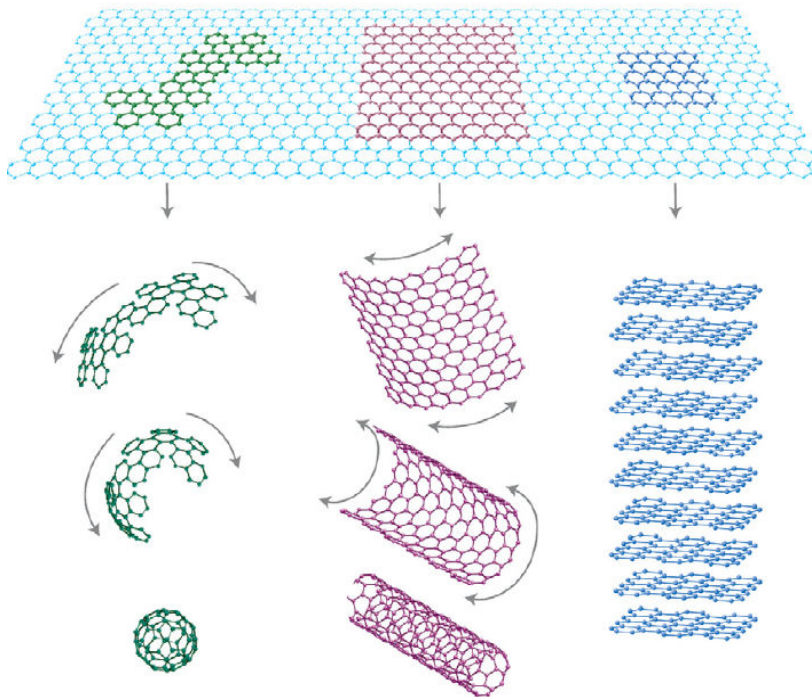


Figure 1. Schematic diagrams of graphene and graphene-based 0D, 1D and 3D structured carbon (Nature Mater. 2007;6(3) 183-191.)

2. Chemical functionalization of graphene

Generally, the functionalization is realized in two ways. The first is to dope heterogeneous atoms onto the basal plane (form covalent bond directly with C atoms of graphene), mainly tuning the electronic structure and introducing defect sites; the second is to establish covalent bond between the functional group native to GO and the guest functional group. Various kinds of functional groups have been chemically anchored onto graphene, giving rise to a diversity of graphene based nanocomposites that were widely investigated in various applications. In this part, we will provide a comprehensive picture for this subject in term of how the covalent bonds are formed.

2.1. Characterization of the functionalized graphene

Chemical functionalization is a chemical (or electrochemical) process that proceeds at an atomic/molecular level. Raman, Infra red spectroscopy (IR), X-ray photoemission spectrometry (XPS), High resolution transmission electric microscopy (HRTEM), Atomic force microscopy (AFM), and Cyclic voltammetry (CV) are the typical instruments that are widely employed for understanding the properties resulting from the functionalization. Raman and IR are sensitive to the formation and change of chemical bonds, helping to determine whether chemical functionalization is successful. Moreover, they also allow semi-quantity analysis. XPS is the powerful instrument for functionalized graphene characterization in terms of both qualification and quantization. For example, XPS can provide decisive information on how many N atoms are doped into graphene and the types of the doped N atoms. HRTEM can tell how the morphology and structure changes following chemical functionalization. AFM can show the thickness and the morphology of graphene. CV measurement is a direct electrochemical method for understanding the electrochemical properties resulting from the functionalization, a topic of the focus in this chapter.

Guest functional group	Chemical process	References
N atoms	CVD	[13-16]
	N-plasma or N ⁺ -ion irradiation	[17,18]
	Arc discharge	[19,20]
	Electrothermal reactions	[22]
B atoms	Chemical synthesis	[23-25]
	CVD	[20,26]
S atoms	Chemical synthesis	[27]
	Pyrolysis	[28,67]
F atoms	Arc discharge	[29]

Table 1. A summary of the chemical routes for functionalization of graphene by heterogeneous atoms doping

2.2. Heterogeneous atoms doping

Heterogeneous atoms doping is one of the most important approaches to chemically functionalize graphene, and such an approach mainly alters the electric properties of graphene. Understanding the electric properties of the doped graphene is a hot topic in physics and semiconductors, for which the studies usually take a combination of experimental measurement and computer simulation. As a typical example, Novoselov and Geim, the two Nobel Prize laureates in 2010 because of graphene, did some pioneer research on this topic. In 2008, they chose the NO₂ system providing both open-shell single molecules and closed-shell dimers N₂O₄ to study the doping due to adsorbates by combining ab initio theory with transport measurements [10]. A general relation between the doping strength and whether adsorbates are open- or closed-shell systems is demonstrated with the NO₂ system: The single, open shell NO₂ molecule is a strong acceptor (attracts electrons from graphene), whereas its closed shell dimer N₂O₄ causes only weak doping. This effect is pronounced by graphene's peculiar density

of states (DOS), which provides an ideal situation for model studies of doping effects in semiconductors.

Strictly speaking, GO, which contains a variety of heterogeneous atoms or groups such as -O, -COOH, and -OH, is a typical functionalized graphene. But due to the low electronic conductivity, their application in EECs is limited and hence, there are few studies focusing on GO in this field. Nevertheless, these functional groups play important roles in the chemical functionalization of graphene. Considering these, in this chapter, we will take GO as graphene. Doping atoms, such as N, B, P and S and chlorides, into graphene is highly desired because the doping effectively converts graphene from gapless structure to semiconductor. The resultant functionalized graphenes are either p-type or n-type, depending on the electronic structure of the guest atoms. Moreover, the doping also induced more defect sites that facilitate deposition of other electrochemically functional components (e.g., growth of Pt on graphene) and stabilize them. Theoretically, all these atoms can be covalently bonded to graphene. However, in practice, doping N is much easier than doping other elements, and has received more extensive attention. Success in B, S and F doping is reported recently. To make this part more understandable, Table 1 summarizes the most typical chemical approaches adopted in the existing studies.

2.2.1. N-doped graphene

N doping gives rise to n-type (negative) graphene. The well-bonded nitrogen atoms improve the electronic conductivity and offer more active sites (defects). Nitrogen doping has proved to be an effective method to improve both the microstructure and the electrochemical properties of graphene. So far, many chemical routes have been developed for synthesis of N-doped graphene (N-graphene), including chemical vapour deposition (CVD), N-plasma treatment, arc discharge, electrothermal reaction, electrochemical reaction, chemical synthesis, etc. Now, CVD and chemical synthesis are more widely adopted for large-scale production.

2.2.1.1. CVD method

Chemical incorporation of nitrogen atoms into graphite by CVD method was first reported by Johansson, et al., in 1990s. Now, CVD has become one of the important methods for synthesizing carbon based nanomaterials including the graphene and N-graphene. A typical CVD process involves three key components, i.e., catalyst, reactants and high temperature. The mechanism can be expressed as following [11-13]: (I) at high temperature (e.g., >800 °C) the catalyst (transition metals) is liquidized, acting as the catalytic sites for absorption and dissociation of the gas reactants including N-containing reactant (mainly NH₃), (II) the catalyst becomes saturated with the atoms/fragments from the dissociation of the reactants and hence; (III) solid graphitic carbon (graphene layers) grows from the saturated catalyst by means of precipitation, with the adsorbed N atoms precipitating into the graphitic lattice, giving rise to N-doped carbon. The CVD synthesis of N-graphene succeeded in 2009 [13]. In principle, a Cu film grown on a Si substrate was employed as the catalyst. The substrate was placed in a quartz tube with a flow of hydrogen and argon. When the center of the furnace reached 800 °C, CH₄ and NH₃ were introduced into the flow as the carbon source and nitrogen source respec-

tively, and then the substrate was rapidly moved to the high temperature region. After 10 min of growth, the sample was cooled to room temperature under H_2 ambient. Most of the products are few-layer graphene, and single-layer graphene can be occasionally found. The doped N atoms are localized in three different sites, i.e., the well-known graphitic N, pyridinic N and pyrrolic N, respectively. Their configurations are schematically described in Fig. 2. The typical TEM images are shown in Fig. 3. Atomic percentage of N in the sample is about 8.9 %. Following this pioneer work, many modified CVD methods have been developed, of which, annealing graphene in NH_3 stream is relatively easier to achieve [14-16].

2.2.1.2. Nitrogen plasma or N^+ -ion irradiation

Nitrogen plasma is another important method for the N doping in the earlier period of N-graphene research. Typically, graphene was first synthesized on Si substrate using CH_4/N_2 plasma at 800 W on microwave plasma enhanced CVD (MPECVD) system [17]. Further N_2 plasma treatment of the as-synthesized graphene was carried out using in situ electron cyclotron resonance (ECR) plasma at a low-pressure and room-temperature. For N doping, a working pressure of ~ 0.025 Pa and a microwave power of 150 W were applied for 5 min. N content varies from approximately 0.7 at% to nearly 6.3 at% (following ECR plasma treatment). N^+ -ion irradiation synthesis involves N^+ -ions bombardment of graphene and subsequently annealing of the bombarded graphene in NH_3 [18]. To achieve this goal, N^+ -ion irradiation (30 KeV) was first carried out on the mechanically exfoliated single-layer graphene grown on a 300 nm SiO_2/Si substrate at room temperature in a vacuum chamber. The bombardment introduces defects into the plane of the graphene. The defect-possessing graphene was then annealed in NH_3 atmosphere at 1100 °C for 30s, resulting in restoration of some defect sites and N doped into the plane. N atoms exist mainly as graphitic N.

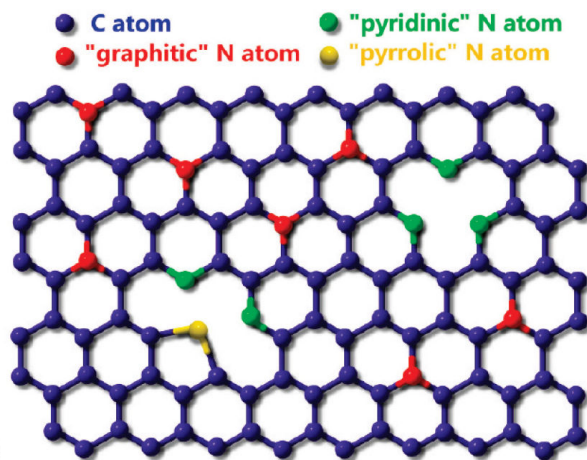


Figure 2. Schematic diagram of the three types of doped N atoms in N-graphene (Nano Lett. 2008;9(5) 1752-1758.)

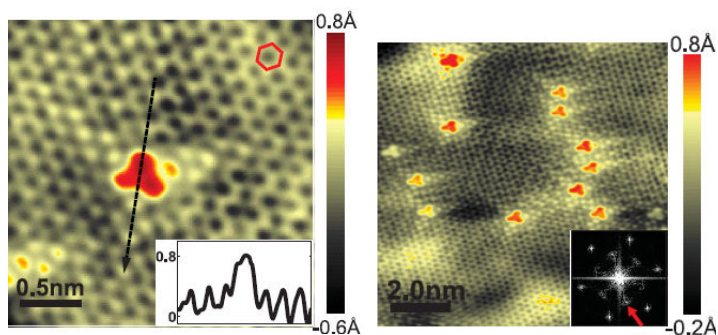


Figure 3. TEM images of N-doped graphene on copper foils: Left, with a single graphitic N dopant; right, with 14 graphitic N dopants and strong intervalley scattering tails. (Science 2011;333, 999-1003.)

2.2.1.3. Arc discharge

The most typical study focusing on fabrication of N-graphene by arc discharge was reported by Li, et al., a method that allows large scale synthesis of N-doped multi-layered (2-6 layers) sheets [19]. In detail, direct current (DC) arc-discharge was carried out in a water-cooled stainless steel chamber. Two electrodes were both $\Phi 8$ mm pure graphite rod. The current was held at 120 A. As the rods were brought close together, discharge occurred resulting in the formation of plasma. The anode was vaporized in He and NH_3 mixing atmosphere of 760 Torr. As the anode was consumed, the rods were kept at a constant distance of about 1 mm by rotating the cathode. When the discharge ended, the soot generated was collected under ambient conditions. The condition that is favorable for obtaining N-doped multi-layer graphene is the high proportion of NH_3 (above 50%, by volume). However, no information on how many N atoms can be incorporated into the plane was provided. Rao et al., [20] modified this method using H_2 +pyridine or H_2 +ammonia as starting materials, making use of the fact that in the presence of hydrogen, GNS do not readily roll into nanotubes. The result N-graphene only contains about 1 at% of N. It should be mentioned that there is a major drawback in using arc discharge for carbon materials synthesis (including graphene). This process gives rise to a large amount of unwanted products; in other word, the selectivity is lower. As a result, the process requires complicated and well controlled purification steps [21].

2.2.1.4. Electrothermal reactions

Electrothermal reaction is relatively more complicated and of higher cost. It was developed in Dai's lab [22]. This method involves high-power electrical joule heating of GNS in ammonia gas. To achieve this goal, they first fabricated a field emission like device using graphene nanoribbons. The graphene nanoribbon device was then e-annealed in a ~ 1 torr NH_3 /Ar environment with carefully designed sequences and control experiments. In NH_3 , they applied similar e-annealing sequences as in vacuum. After e-annealing, the chamber was pumped down to base pressure to fully remove physisorbed NH_3 molecules. It is proposed that chemical

reactions between graphene nanoribbons and NH_3 lead to nitrogen functionalization, most likely take place at the more reactive edge carbon atoms.

2.2.1.5. Chemical synthesis

Irrespective of the progress made on N-graphene synthesis, continuous pursuing in this area is still highly demanded. Future applications of N-graphene rely on easy-to-operate methods, which can deliver products in a reasonably large quantity and at obviously reduced cost. On this aspect, chemical synthesis has drawn much attention. The first attempt for this is the synthesis using embedded carbon and nitrogen sources in metal [23]. First, boron and nickel layers were sequentially deposited on SiO_2/Si substrate by electron beam evaporation, where a trace amount of nitrogen species were incorporated into the boron layer spontaneously. Then, the sandwiched $\text{Ni}(\text{C})/\text{B}(\text{N})/\text{SiO}_2/\text{Si}$ substrate was vacuum annealed at a desired temperature (800-1100 °C) at a slow rate of 15-20 °C min^{-1} . The samples were maintained at a desired temperature for 0-60 min with a pressure of 10^{-3} - 10^{-4} Pa, and then cooled down to room temperature at a rate of 2-50 °C min^{-1} . Typically, the N/C atomic ratios, estimated by XPS, range from 0.3 to 2.9 at%. Later, a novel method was developed for one-pot direct synthesis by the hydrothermal reaction of lithium nitride with tetrachloromethane under mild conditions (in a stainless steel autoclave in nitrogen with temperatures below 350 °C), allowing fabrication in gram scale [24]. The nitrogen content varies in the range of 4.5-16.4 at% with the aid of cyanuric chloride. This method also allows adjusting the ratio of nitrogen species (graphitic N, pyrrolic N and pyridinic N). Except the high cost of the starting material (Li_3N), this method is indeed suitable for massive N-graphene synthesis. Recently, N-graphene with the nitrogen level as high as 10.13 at% was synthesized via a simple hydrothermal reaction of graphene oxide (GO) and urea [25]. N-doping and reduction of GO were achieved simultaneously under the hydrothermal reaction. In the fabrication, the nitrogen-enriched urea plays a pivotal role in forming the N-graphene nanosheets with a high nitrogen level. During the hydrothermal process, the N-doped urea could release NH_3 in a sustained manner, accompanied by the released NH_3 reacting with the oxygen functional groups of the GO and then the nitrogen atoms doped into graphene skeleton, leading to the formation of N-graphene. The nitrogen level and species could be conveniently controlled by tuning the experimental parameters, including the mass ratio between urea and GO and the hydrothermal temperature.

2.2.2. B-doped graphene

B doping gives rise to P-type (positive) graphene. As compared to N doping, B doping is harder to achieve. So far, to our knowledge, there are only a couple of research groups reporting successful synthesis of B-graphene. Rao et al., are the first group that succeeded [20]. Typically, they used two methods for the synthesis. For the first, B-graphene was prepared by performing the arc discharge of graphite electrodes in the presence of hydrogen, helium, and diborane (B_2H_6). B_2H_6 vapor was generated by the addition of BF_3 -diethyl etherate to sodium borohydride in tetraglyme. B_2H_6 vapor was carried to the arc chamber by flowing hydrogen and subsequently He through the B_2H_6 generator. For the second, B-graphene was prepared by carrying out the arc discharge using boron-packed graphite electrodes (3 at% B) in the presence

of H₂ and He. XPS results indicated that B content could be 3.1 at%. Wang, et al., [26] explored a more novel method. B-graphene was prepared by reacting CCl₄, K and BBr₃ at 160 °C for 20 h in a sealed teflon-lined stainless steel autoclave, i.e., a typical solvent thermal process. The content of boron was determined to be 1.1 at% based on the XPS intensity measurement.

2.2.3. S-doped graphene

For S doping, the S atoms exist either as thiophene S (One S atom bonded to two C atoms of graphene) and SO_x. Sulfur doped graphene (S-graphene) was reported successful only recently [27]. The doping proceeds through thermal treatment of GO and benzyl disulfide (BDS) in Ar. In detail, GO and BDS were first ultrasonically dispersed in ethanol for about 30 min. The resulting suspension was spread onto an evaporating dish and dried, forming a uniform solid mixture. The mixtures were placed into a quartz tube in Ar atmosphere and were annealed at 600-1050 °C. The contents and bonding configurations of sulfur in the resultant S-graphene can be adjusted by adjusting the mass ratio of GO and BDS as well as the annealing temperatures. This approach gives rise to a highest S content of ~1.53 wt%. Another typical method involves pyrolysis of sulphur-containing liquid precursor [28]. Sulfur powder was dissolved in hexane under ultrasound to form a transparent liquid, which was used as the growth precursor. Cu foil was placed in a quartz tube, and the whole system was pumped down to 10⁻² Torr. The substrate was heated up with a flow of hydrogen and argon mixture. When the temperature reached 950 °C, the H₂-Ar flow was shut off and S-hexane mixture vapor was introduced into the reaction chamber. After 2.5 min of growth, the sample was rapidly cooled down to 800 °C, and then the whole system was cooled down to room temperature within the hydrogen and Ar atmosphere. The doping is about 0.6 at% as estimated by XPS.

2.2.4. Fluorine doped graphene

Fluorine-doped GNS (F-graphene) were synthesized by arc discharge [29]. The arc-discharge process for preparing GNS was carried out in a water-cooled chamber and graphite rods with purity of 99.99% were used as the cathode and anode. After the pressure in the chamber reached 1 Pa, the chamber was filled by H₂ and He. During the discharge, the current was maintained at 140 A. For preparing F-graphene, a hollow graphite rod filled with powdery graphite fluoride (fluorine content is 60 wt%) was used as the anode. The as-obtained powders were collected only in the inner and top wall of the chamber in order to exclude relatively heavy products (such as unexfoliated graphite or graphite fluoride) dropped to the bottom of the chamber during the arc discharge process. The functionalized GNS contain about 10 wt% F and are highly hydrophobic.

2.3. Chemical functionalization of graphene with organic groups

As compared to element doping, the functionalization with more complicated organic groups is an easier procedure. The functionalization usually takes advantage of some typical organic reactions, through which a wide spectrum of functional groups has been chemically anchored onto graphene. Besides the evidently different electrical properties from undoped graphene, such kind of functionalization also brings about some other intriguing properties, such as

thermal stability, mechanical strength, high processability, etc, and makes a platform for fabricating 3D materials. There are a huge number of papers published. In this section, we will review the related studies in this area in detail. Considering the major diversity of the organic groups, the review is run in term of how the covalent bonds are formed between graphene/GO and the functional groups, including diazonium coupling, amidation, silanization, esterization, substitution, cycloaddition, etc. The organic molecules that chemically bonded to graphene are listed in Table 2.

2.3.1. Electrochemical reaction

Electrochemical reaction is a powerful method to functionalize graphene with inert precursors, e.g., H_2 . In 2009, Zhang's group reported direct electrochemical reduction of single-layer graphene oxide (GO) and subsequent functionalization with glucose oxidase [30]. This approach involves several key steps (as shown in Fig. 4), i.e., adsorption of graphene on the surface of a glassy carbon electrode (GCE), formation and reduction of GCE-APTES-GO (APTES stands for 3-aminopropyltriethoxysilane), electrografting of N-Succinimidyl Acrylate (NSA) on the surface of GCE-APTES-rGO, and anchoring glucose oxidase (GOx) on the surface of GCE-APTES-rGO-pNSA. Most recently, Daniels, et al., reported electrochemical graphene functionalization and its substrate dependence [31]. For this purpose, nanocrystalline graphene layers grown on non-polar faces of SiC were used as control samples for the functionalized graphene on Si-face. Atomic hydrogen was generated using a home-built electrochemical setup, with current applied through a 10% H_2SO_4 acid solution. A 99.6% Pt wire and exposed graphene (approximately a 4 mm diameter circular area) were used as the anode and cathode, respectively. With this setup, under applied voltage, H^+ cations are attracted to the negatively charged graphene cathode electrostatically where they can be reduced by addition of an electron, leading to current flow. Oxidation occurs at the Pt anode during this process. A voltage <1.2 V was used to prevent the splitting of H_2O which causes the formation of H_2 bubbles.

2.3.2. Diazonium coupling

The reduction of diazonium salts has been widely employed for grafting aryl groups to the surface of sp^2 -hybridized carbon materials including glassy carbon, HOPG, and carbon nanotubes. The sp^2 atoms of graphene are prone to react with diazonium salts. Recently, this type of chemistry has also been applied to chemically functionalize graphene in several research groups, who also investigated the generated unique properties [32-36]. Haddon, et al., are one of the several groups early reporting success in this study [32]. The surface modification with nitrophenyl groups was achieved through the spontaneous reaction of the diazonium salt (4-nitrophenyl diazonium tetrafluoroborate, denoted as 4-NPD) with the graphene layer, as illustrated in Fig. 5. Intrinsically, the reaction is a result of spontaneous electron transfer from the graphene layer and its substrate to the diazonium salt. The functionalization changes the electronic structure and transport properties of the epitaxial graphene from near-metallic to semiconducting. Following this work, later, the same group [33] further proved that aryl-radical functionalization of epitaxial graphene not only changes the

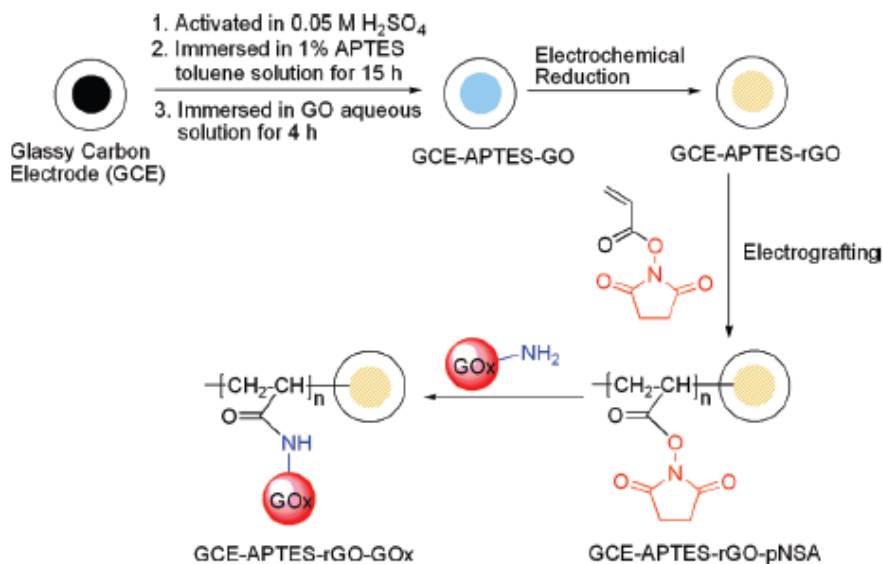


Figure 4. A schematic diagram for the direct electrochemical reduction of single-layer graphene oxide (GO) and subsequent functionalization with glucose oxidase (J. Phys. Chem. C 2009, 113, 14071-14073.)

electronic properties but leads to disordered magnetism in the sheet, which consists of a mixture of ferromagnetic (ferromagnetic), superparamagnetic, and antiferromagnetic regions.

The diazonium coupling reaction of graphene is strongly dependent on graphene layers. Strano, et al., found that single GNS are almost 10 times more reactive than bi- or multilayers of graphene [6]. More interestingly, the reactivity of edges is at least two times higher than the reactivity of the bulk single GNS. This suggestion is supported by the research by Lim [7] and Sinitskii, et al [34].

Besides the aryl groups, through the diazonium reduction chemistry, more complicated organic groups, e.g., polymers, were also reported to be chemically anchored onto graphene, a strategy for fabricating graphene based polymer nanocomposites. Nutt, et al., reported grafting of polystyrene chain on a single-layer GNS [35]. Grafting density and polystyrene chain lengths are controlled by modulating the concentrations of diazonium compound and the monomer of target polymer during the grafting reaction of the initiator and the succeeding atomic transfer radical polymerization. Polystyrene chains grafted on the surface of single-layer GNS exhibited remarkably confined relaxation behavior. An increase in the glass transition temperature (T_g) of up to 18 °C is observed for high grafting density, low molecular weight polymer-grafted graphene samples. The low grafting density, high molecular weight sample shows an increase in T_g of ~9 °C, which is attributed to superior heat conduction efficiency. The measured thermal conductivity for the polystyrene composite film with 2.0 wt % single-layer GNS increases by a factor of 2.6 compared to that of the pure polystyrene.

For practical uses, an easy-access approach was developed to functionalize individually dispersed, highly soluble, and conductive GNS by diazonium reduction chemistry [36]. Typically, requisite amounts of GO and NMP were placed in a flask fitted with a condenser. The mixture was treated within an ultrasonic bath for 1 h and then placed on a magnetic stirrer with an oil bath. After the mixture was bubbled with nitrogen, a given amount of azide compounds (e.g., Az-OH, Az-COOH, Az-NH₂, Az-Br, Az-C16, Az-PEG, Az-PS) was added. The reaction mixture was then heated and maintained around 160 °C in a nitrogen atmosphere under constant stirring. After being cooled to room temperature, the mixture was separated by repeated centrifugation and washed, affording the final product of functionalized graphenes.

2.3.3. Chemical functionalization of GO

Compared to graphene, there are many heterogeneous atoms or atom groups on GO, such as OH, O, O-O, COOH, etc, which are covalently bonded to the C atoms (sp³) of graphene. These groups are relatively more reactive than C atoms of GNS and therefore, are considered the predominating sites to which the functional groups are bonded. In this section, we will summarize the research aiming at chemically functionalizing GO. Noticeably, no matter how complicated a functional group is, the functionalization generally takes place through typical organic reactions, such as silanization, amidation, esterization, substitution, cycloaddition, etc. The review of this part also follows this line. Such an approach may not be able to comprise all the papers but is effective enough for the readers to understand the chemistry and therefore to explore new methods for the functionalization of graphene.

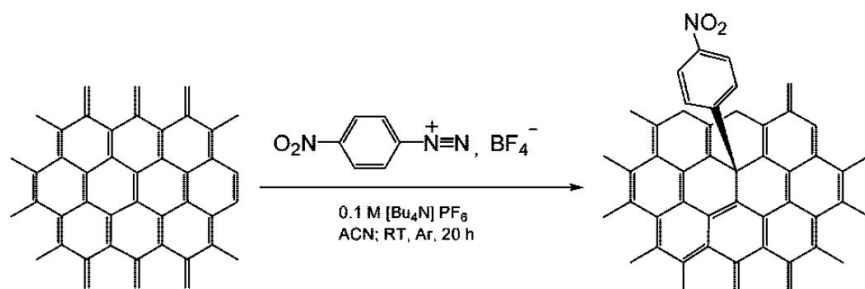


Figure 5. Schematic diagram for the functionalization of graphene using diazonium reduction reaction (*J. Amer. Chem. Soc.* 2009;131(4) 1336-1337.)

2.3.3.1. Silanization

R-O-Si bond in silane is very reactive toward protic group, i.e., OH. This chemistry has been widely applied to anchor silane groups onto carbon surface. Introduction of silane into GO has also succeeded. In 2010, Hou, et al., reported chemical functionalization of GNS with N-(trimethoxysilylpropyl) ethylenediamine triacetic acid (EDTA) [37]. As described in Fig. 6, the reaction is assumed to proceed through two steps: (1) hydrolysis of the trialkoxy groups of

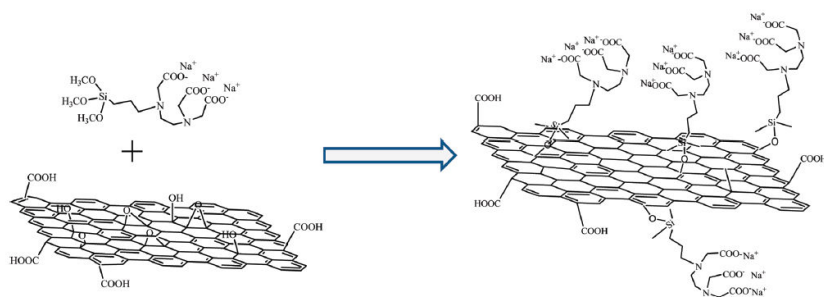


Figure 6. Schematic diagram for the functionalization of graphene using silanization reaction (J. Phys. Chem. C 2009;114 (35), 14915-14921.)

silane generates -Si-OH groups; and (2) the reaction between Si-OH and C-OH of graphene links EDTA to the graphene surface through Si-O-C bond. One CH₄ is released. The silanized GO sheets were further reduced with hydrazine to produce graphene derivatives (EDTA-graphene). The EDTA-graphene showed improved dispersion in water. A relatively simpler method was developed with quaterthiophene molecules (T4-Si) functionalizing using microwaves [38]. GO dispersed in dimethylformamide (DMF) were introduced in a microwave oven reactor and irradiated at 80 °C (100 W) for 40 min. The chemical tethering to GO hinders T4-T4 electronic interactions and aggregation.

2.3.3.2. Amidation

On GO, amidation proceeds mainly through the reaction between the -COOH group native to GO and the -NH₂ group of the functional molecule, or vice versa. Amidation is a most effective way to chemically functionalize graphene, and is more widely employed than other methods. Various -NH₂ terminated functional groups have been anchored onto graphene [39-44]. The most typical example is Xu's study in 2009 [39]. They synthesized porphyrin-graphene nanohybrid through 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) functionalization of GO. The synthesis procedure is shown in Fig. 7. TPP-NH₂, as the reaction precursor, was first synthesized. GO was refluxed in SOCl₂ in the presence of DMF at 70 °C for 24 h under Ar atmosphere. In the presence of triethylamine (Et₃N), the above product was allowed to react with TPP-NH₂ in DMF at 130 °C for 72 h under Ar. The product was isolated by filtration and washed thoroughly. Attachment of TPP-NH₂ significantly improves the solubility and dispersion stability of the graphene-based material in organic solvents. In this donor-acceptor nanohybrid, the fluorescence of photoexcited TPP-NH₂ is effectively quenched by a possible electron-transfer process.

2.3.3.3. Esterization

The presence of -COOH groups native to graphene renders functionalization of GO with CH₂OH-terminated functional groups feasible, i.e., esterization. There are a number of studies addressing this process [45,46]. As a typical molecule that possesses CH₂OH-terminated group,

poly(3-hexylthiophene) (P3HT) has been employed to chemically modify GO [45]. End-functionalized regioregular P3HT with methylene hydroxy groups was first synthesized. In a typical experiment for the synthesis of the P3HT-grafted graphene, dried GO sample was refluxed in thionyl chloride for 24 h, followed by the removal of excess thionyl chloride under vacuum. CH_2OH -terminated P3HT in THF was then added through a syringe to the thionyl chloride treated GO under stirring, followed by the addition of triethylamine in nitrogen atmosphere. After sonication, the reaction mixture was vigorously stirred, leading to a dark suspension. The solid in the suspension was removed by centrifuging, and the solvent in the clear solution thus prepared was partially removed by evaporation. It was further purified by precipitating in methanol, filtering, and solvent-washing thoroughly to remove the excess triethylamine.

This reaction also allows fabrication of more complicated graphene based nanocomposites. Pham, et al., explored a facile strategy for covalent functionalization of GO with polyglycerol and used the resultant composites as templates for anchoring magnetic nanoparticles [46]. Pristine graphite was firstly oxidized to obtain GO with hydroxyl functional groups. Then, the covalent grafting of polyglycerol onto the surface of GO was carried out based on *in situ* ring-opening polymerization of glycidol. For the construction of novel hybrid nanostructure, Fe-core/Au-shell nanoparticles were functionalized using 4-mercaptophenylboronic acid through the well-developed Au-S chemistry. Subsequently, magnetic nanoparticles were anchored on the surface of polyglycerol-grafted graphene nanosheets via boroster bonds. The synthesized novel hybrid nanostructures could be stably dispersed in water over 3 months.

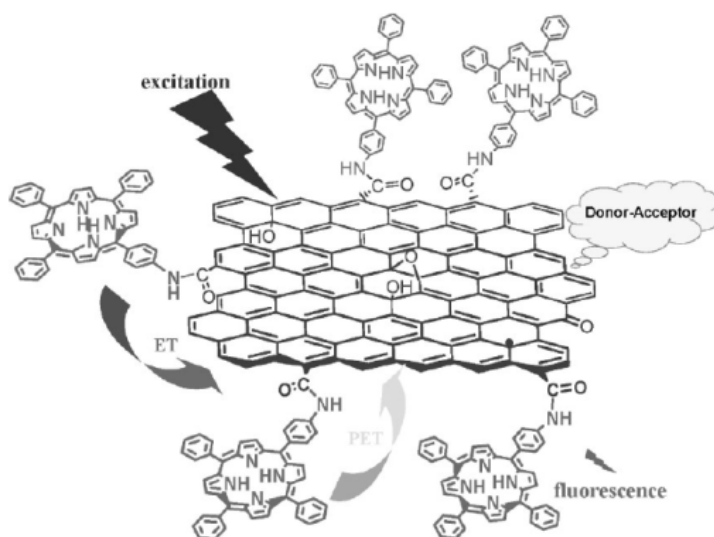


Figure 7. Chemical functionalization of graphene using amidation reaction (Adv. Maters. 2009;21(4) 1275-1279.)

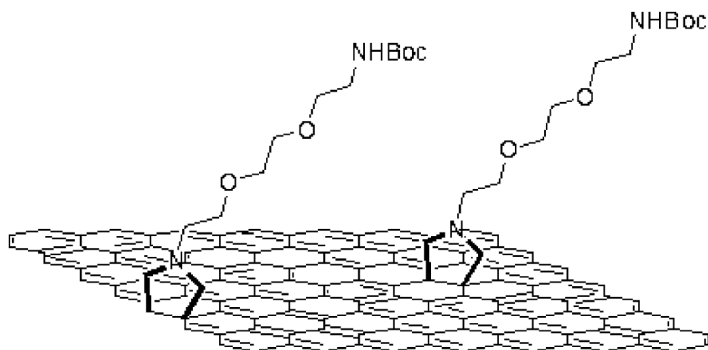


Figure 8. Chemical functionalization of graphene using cycloaddition reaction (ACS Nano 2010;4(6) 3527-3533.)

2.3.3.4. Substitution

Chloride atoms, either bonded to graphene or to functional group, can be substituted by OH group, a reaction that is an alternative route for chemical functionalization. Shen, et al., [47] report a scalable, fast, and easy method for preparation of organophilic chemically functionalized GNS. The basic strategy involved the complete exfoliation of graphite oxide into GO sheets, followed by reacting with 1-bromobutane. The resulting organic dispersions are homogeneous, exhibit long-term stability, and are made up of graphene sheets a few hundred nanometers large. Pramoda, et al., describes a new route to chemically bonded polymer-graphene nanocomposites and the subsequent enhancement in thermal and mechanical properties [48]. At first, the graphite oxide is functionalized with octadecylamine (ODA). The ODA functionalized graphite oxides are reacted with methacryloyl chloride to incorporate polymerizable -C=C- functionality at the nanographene platelet surfaces, which were subsequently employed in *in situ* polymerization of methylmethacrylate to obtain covalently bonded poly(methyl methacrylate) (PMMA)-graphene nanocomposites. The obtained nanocomposites show significant enhancement in thermal and mechanical properties compared with neat PMMA. Even with 0.5 wt % graphene nanosheets, the T_g increased from 119 °C for neat PMMA to 131 °C for PMMA-graphene nanocomposite, and the respective storage modulus increased from 1.29 to 2 GPa.

2.3.3.5. Cycloaddition

Arynes are recognized as useful reactive intermediates during nucleophilic aromatic substitution in organic synthesis and are frequently used in a variety of reactions. To date, quite a few attempts at aryne cycloaddition have been performed for carbon nanomaterials, demonstrating that fullerenes and derivatives can be successfully functionalized. Recently, chemical modification of graphene by aryne cycloaddition has been reported by several groups. Zhong, et al., developed a novel and convenient approach to chemically functionalize graphene by

this reaction with benzene precursors [49]. Commercial GNS from the arc-discharge method were used. 2-(Trimethylsilyl) phenyl triate was employed as the functional group. A typical procedure for preparing aryne-modified graphene sheets is given in Fig. 8. On the basis of weight loss, it is estimated that the degree of functionalization is approximately over 1 functional group per 17 carbon atoms. The resultant graphene shows remarkable solubility and thermal stability. The functionalized graphene is stable at temperature high to 500 °C. With the similar reaction, chemical functionalizations using the 1,3-dipolar cycloaddition of azomethine ylides and cyclopropanated malonate also succeeded[50,51].

Chemical process	Organic group	References
Diazonium coupling	Nitrophenyl	[6,7, 32-34]
	Polystyrene chain	[35]
	C ₁₆ H ₃₄ , Polyethylene glycol	[36]
Silanization	EDTA	[37]
	Quaterthiophene	[38]
Amidation	Porphyrin	[39]
	Zinc phthalocyanine	[41]
	Oligothiophene	[40]
	Poly(N-vinylcarbazole)	[42]
	2-amino-4,6-didodecylamino-1,3,5-Triazine	[44]
	Chitosan	[43]
Etherization	poly(3-hexylthiophene) (P3HT)	[45]
	Polyglycerol	[46]
Substitution	1-bromobutane	[47]
	Methacryloyl chloride	[48]
Cycloaddition	2-(Trimethylsilyl) phenyl triate	[49]
	Azomethine ylides	[50]
	Cyclopropanated malonate	[51]

Table 2. A summary of the chemical functionalization of graphene with organic groups

3. Chemically functionalized graphene for electrochemical energy conversion and storage

Although a wide spectrum of functional groups (from single atoms to polymers) has been chemically grown onto graphene, it is a fact that for EECS, only element doped graphene has been widely investigated on EECS devices including FCs [16, 17, 29, 52-61], LIBs [14, 62-67]

and supercapacitors [27, 68, 69]. The related studies are tabulated in Table 3. This is because the covalent bonding with most of the organic groups frequently damages the inherent properties of graphene, especially the electronic conductivity significantly, resulting in decline in the electron transfer and hence decay of electrochemical performances. In this section, we will comprehensively outline all the characteristic research in this area, emphasizing on FCs, LIBs and then supercapacitors.

3.1. Fuel cells

A major impediment to the commercialization of proton exchange membrane fuel cells (PEMFC) is the high cost and the stability of Pt-based electrocatalysts (Pt/C). Much effort is focusing on seeking either new support materials to improve the distribution of Pt and hence to lower its loading or non-noble metal electrocatalysts to decrease the cost. Nitrogen doped carbon material is recognized as a good support for Pt based catalyst. The doped nitrogen atoms not only provide the anchoring sites for the metal particles, but also act as chemically active sites for catalytic reactions. Moreover, recent intense research has found that nitrogen-doped carbon materials (especially, vertically aligned nitrogen-containing carbon nanotubes, nitrogen doped ordered mesoporous graphitic carbon and silk-derived carbon (0.8% nitrogen in the carbon network) could act as effective non-noble metal-free electrocatalysts. The real active sites of nitrogen-doped carbon materials in such applications remain unclear, but the doped nitrogen atoms are believed to (such as graphite-like, pyridine-like, pyrrole-like, and quaternary nitrogen atoms, see Fig. 2) play a crucial role for oxygen reduction reaction (hereafter denoted as ORR). Usually, the greater the extent of graphitization of the carbon material, the longer the durability is. The existing data prove that N-graphene exhibit high electrocatalytic activity and long-term operation stability for the ORR. Besides N doping, S-graphene is also investigated for FCs application. The related research is reviewed in two separate parts here.

3.1.1. Chemically functionalized graphene as a catalyst support

Wu, et al., reported identification of the nitrogen species on N-graphene layers and the performance of Pt/NG (Pt/N-graphene) composite catalyst in direct methanol fuel cells (DMFC) [16]. The N-graphene was synthesized through thermal-treatment of GO in ammonia stream at various temperatures, offering various distributions of nitrogen species. In electrochemical tests, Pt/NG, Pt/graphene and Pt/CB (carbon black, Vulcan XC 72) composites were investigated in anodic half-cell reaction in DMFC. A Pt/NG-800 composite, for which the graphene was treated in NH_3 flow at 800°C , exhibits outstanding electrocatalytic activities for methanol oxidation. The mass specific oxidation current for Pt/NG-300, Pt/G-300 and Pt/G-800 is 40, 41 and 34 mA mg^{-1} , respectively. In sharp contrast, the methanol oxidation current of Pt/NG-800 (135 mA mg^{-1}) is three times higher than the other three composites and the commercial Pt/CB (27 mA mg^{-1}). The higher methanol oxidation activity from Pt/NG-800 is assumed to be associated with (1) the high dispersion state of the Pt nanoparticles facilitated by the pyridinic nitrogen doped in the carbon network; and (2) higher conductivity as a result of reduced defect sites by the higher temperature treatment. Ramaprabhu compared the activities

of Pt nanoparticles supported on graphene nanoplatelets and N-graphene nanoplatelets, respectively, as catalysts for ORR in PEMFC [52]. Nitrogen plasma treatment created pyrrolic nitrogen defects, which act as good anchoring sites for the deposition of platinum nanoparticles. Pt was dispersed over these support materials using the conventional chemical reduction technique. A maximum power density of 440 mW cm^{-2} was obtained with the Pt loaded N-graphene, and 390 mW cm^{-2} for the Pt loaded graphene nanoplatelets, respectively. The improved performance of FCs with N-graphene as catalyst supports was attributed to the increased electrical conductivity and the enhanced carbon-catalyst binding.

Enhanced electrochemical sensitivity of bimetal PtRh electrodes coated with N-graphene (PtRh@N-graphene) was reported by Wang, et al [53]. Deposition of N-graphene onto the surface of a metal electrode (PtRh alloy mesh) was performed by dipping the mesh into the dispersion and withdrawing. The suspended GNS was thus deposited onto the surface of the PtRh alloy mesh. The coating effectively improves the electron transfer kinetics. Nanoflower-like N-graphene with pure sp^2 hybridized carbon and designed nitrogen types was synthesized by a low temperature solvothermal process [54]. The product consists of many N-graphene sheets with about 6-10 graphitic layers. The sheets are rich of pyridine-like and quaternary nitrogen atoms, and possess high graphitized structure and ultra-micropores. As such, electrochemical test showed that N-graphene has a much higher durability as a Pt support for FCs than commercial carbon black (Vulcan XC-72).

A MnCo_2O_4 /N-graphene hybrid material was developed as highly efficient ORR electrocatalyst in alkaline conditions [55]. The covalent coupling between MnCo_2O_4 nanoparticles and N-graphene sheets offers much higher activity and stronger durability than the physical mixture of both components. At a same mass loading, the MnCo_2O_4 /N-graphene hybrid can outperform Pt/C in ORR current density at potential $<0.75 \text{ V vs RHE}$. The stability is also superior to that of the Pt/C. Semi-quantitatively, an optimum range of MnCo_2O_4 content between 65 and 80 wt % was found to give similarly high ORR performance from carbon fiber paper measurements. Out of this range, too low a MnCo_2O_4 content could lead to fewer ORR active sites in the hybrids, while too high a MnCo_2O_4 content could result in aggregation of nanoparticles and even free growth, which were less active than the nanoparticles directly grown on GNS.

3.1.2. Chemically functionalized graphene as a catalyst

3.1.2.1. Nitrogen-doped graphene

N-graphene as metal-free electrocatalyst for FCs is drawing rapidly increasing attention. Plausible electrocatalytic activities were observed. Dai, et al., are the first group reporting the use of N-graphene as metal-free catalysts for ORR [56]. N-graphene was synthesized by CVD of methane in the presence of ammonia. For comparison, electrocatalytic selectivities of the N-graphene electrode were tested against the electro-oxidation of various commonly used fuel molecules, including hydrogen gas, glucose and methanol. The N-graphene electrode demonstrated a stronger and more stable amperometric response from the ORR than the Pt/C catalyst does. The current remained unchanged after the addition of hydrogen gas, glucose, and methanol. They ascribed the high selectivity of the N-graphene electrode and remarkably

good tolerance to crossover effect to the much lower ORR potential than that required for oxidation of the fuel molecules. Moreover, the N-graphene electrode was insensitive to CO, but the Pt/C electrode was rapidly poisoned under the same conditions. Continuous potential cycling test indicated that for the N-graphene electrode, no obvious decrease in current was observed after 200000 continuous cycles between -1.0 and 0 V in air-saturated 0.1 M KOH. Shao, et al., synthesized N-graphene by exposing graphene to nitrogen plasma and carried out detailed studies on its electrochemical activities [17]. The N-graphene exhibits much higher electrocatalytic activity toward ORR and H_2O_2 reduction than graphene does, and much higher durability and selectivity than the Pt/C. The ORR kinetic currents for graphene, N-graphene and Pt/C (ETek, 20 wt%) at -0.03 V (Hg/HgO) are ~1, 65 and 255 μA , respectively. The ORR over-potential is greatly decreased on the N-graphene in comparison with graphene. After accelerated degradation test, the N-graphene exhibits a slight increase in ORR activity; however, Pt/C degraded by ~85%. Moreover, when performing in O_2 -saturated 0.1 M KOH, no changes in surface chemistry of the N-graphene were observed. The ORR on N-graphene is not influenced by the fuel molecules (e.g., methanol). Geng, et al., reported high ORR activity and durability of N-graphene synthesized by the thermal treatment of graphene with ammonia at different temperatures [57]. 2.8 at% nitrogen was introduced for the N-graphene (900 °C), which also exhibits a highest ORR activity in alkaline solution. The onset potentials for ORR (E_{ORR}) of graphene, N-graphene (800), N-graphene (900), and N-graphene (1000) were 0.046, 0.184, 0.308, and 0.204 V, respectively. N-graphene (900) catalyst was assumed to effectively promote the desired $4e^-$ ORR activity in alkaline solution. Only quaternary type nitrogen species plays the most important role for the ORR. In comparison to the commercial Pt/C catalyst ($4.85 \mu\text{gPt cm}^{-2}$), the electrochemical performance of the N-graphene (900) catalyst is also better, as shown in Fig. 9. Besides the higher onset potential (0.308 V), oxygen-reduction half-wave potential is 43 mV more positive on the N-graphene catalysts. Almost no change in the voltammetric charge was found after 5000 cycles of the potential sweep for the N-graphene, however, the current density for Pt/C dropped dramatically.

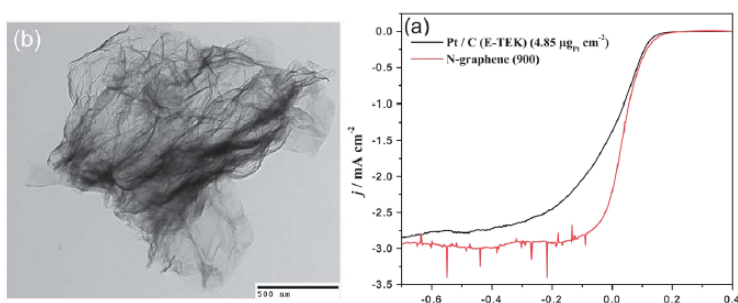


Figure 9. TEM image of nitrogen doped graphene and its electrochemical performance as a metal free catalyst for ORR. (Energy & Environ. Sci. 2011;4(3) 760-764.)

ORR on N-graphene was also tested in acid media [58]. The mass activity of the N-graphene catalyst ($1234 \text{ mA g}^{-1}_{\text{catal}}$) is about 35 times higher than that of the Vulcan carbon ($35 \text{ mA g}^{-1}_{\text{catal}}$).

This activity is about 50% lower than that of Pt/C catalysts ($2791 \text{ mA g}^{-1}_{\text{catal}}$). High electric conductivity, high surface area, large amount of edge sites and pyridinic N site in reduced graphene sheets are assumed to make major contribution to the high ORR activity. Lee, synthesized N-doped carbon nanosheets from pyrolysis of collagen at $800 \text{ }^\circ\text{C}$, which possesses a surface area of $695 \text{ m}^2 \text{ g}^{-1}$ and nitrogen content of $\sim 1\%$ [59]. With the contribution of N-doped structures, the carbon nanosheets showed a specific capacitance of 102 F g^{-1} at 25 mV s^{-1} , and 80% capacitance retention in $0.5 \text{ M H}_2\text{SO}_4$ at 1000 mV s^{-1} . In comparison with a commercial electrocatalyst, 20% Pt on Vulcan XC-72, the carbon nanosheets display a positive shift in the onset potential and superior electrocatalytic activity toward the ORR. The onset potential of the ORR for the N-doped carbon nanosheets is 0.95 V (the commercial Pt electrocatalyst is 0.83 V). The significant catalytic activity toward the ORR of the N-doped carbon nanosheets is assumed to mainly come from the contribution of pyridinic-N and quaternary-N, which change the adsorption of the oxygen molecule on carbon materials from end-on to side-on type, thus weakening the O-O bond to facilitate the ORR. On the other hand, Luo, et al., was focused on exploring the contribution of different doped N atoms to the ORR reaction of the N-graphene [60]. For this purpose, single layer graphene doped with pure pyridinic N was synthesized by CVD of hydrogen and ethylene on Cu foils in the presence of ammonia. By adjusting the flow rate of ammonia, the atomic ratio of N and C can be modulated from 0 to 16%. The pyridinic N efficiently changes the valence band structure of graphene, including the increase in the density of π states near the Fermi level and the reduction of work function. Interestingly, on the base of the $2e$ reduction mechanism of ORR on the resultant CN_x graphene revealed by rotating disk electrode voltammetry, they suggested that the pyridinic N may not be an effective promoter for the ORR activity of carbon materials as previously expected. Obviously, this question remains open for further investigation.

3.1.2.2. S-doped graphene

S-graphene as catalysts for PEMFC was first reported by Mullen's group [61]. The S-graphene was synthesized by annealing graphene in H_2S at temperatures from 500 to $1000 \text{ }^\circ\text{C}$. S exists as thiophene like S and oxidized S. A highest S content is obtained in the sample doped at $900 \text{ }^\circ\text{C}$ (1.7%). The electrocatalytic activity was investigated via RRDE linear sweep voltammetry at a scan rate of 100 mV s^{-1} in O_2 and Ar-saturated 0.1 M KOH solution as well as O_2 -saturated 0.1 M KOH solution with 3M methanol. The S-graphene sheets exhibit good electrocatalytic activity, long durability and high selectivity when employed as metal-free catalysts for ORR, depending on the annealing temperature. As the annealing temperature increases from 500 to $900 \text{ }^\circ\text{C}$, the electron transfer number of S-graphene slightly decreases from 3.5 to 3.2 , a result of the reduction of the amount of sulfur (from 1.7% to 1.2%), because the S-C bonds play a key role to affect the catalytic process of S-graphene for the ORR. Moreover, the S-graphene and commercial Pt/C were further compared by separately introducing O_2 and fuel molecules (e.g., methanol) into the electrolyte to examine their possible selectivity and crossover effects via chronoamperometric measurements. The S-graphene also outperforms the commercial Pt/C. Similarly, it was reported that S-graphene through thermal treatment of graphene oxide (GO) and benzyl disulfide (BDS) in Ar showed higher electrocatalytic activity than Pt/C catalysts do [29].

3.2. Lithium ion batteries

The research on the application of chemically functionalized graphene to LIBs is also developing rapidly. For LIBs, the functionalized graphene is used both as anode materials and as a doping composite. In both cases, improved lithium storage capacities were observed.

3.2.1. N-doped graphene as anode materials

In 2010, Reddy, et al., published the first paper about N-graphene for LIB application [62]. Few layers of graphene and N-doped graphene films on Cu substrate were synthesized by CVD technique using hexane and acetonitrile precursors, respectively. For the half cell measurements, an electrochemical test cell was assembled using the graphene/N-d-graphene as working electrode, lithium metal foil as the counter/reference electrode and 1 M solution of LiPF_6 in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte. Through introduction of surface defects and pyridinic N atoms into the graphene structure, intercalation of Li-ion in N-graphene electrode was obviously enhanced. Reversible discharge capacity of N-graphene remains beyond 0.6 mAh cm^{-1} after 50 cycles, while that of pristine graphene is $\sim 0.48 \text{ mAh cm}^{-1}$. Cho, et al., [63] deposited N-graphitic layers on silicon nanowires by CVD for LIB anode. Graphite-like and pyridine-like structures were selectively chosen for 3 and 10% N doping, respectively. Increasing the thickness of the undoped graphitic layers from 20 to 50 nm led to an increase in the charge capacity from 800 to 1040 mAh g^{-1} after 45 cycles. Graphite-like 3% N-doping in the 50 nm-thick shell increases the charge capacity by 21% (i.e., to 1260 mAh g^{-1}), while pyridine-like 10% N-doping in the 20 nm-thick shell increases it by 36% (i.e., to 1090 mAh g^{-1}). This suggests that both pyridine- and graphite-like structures can be effective for lithium intercalation.

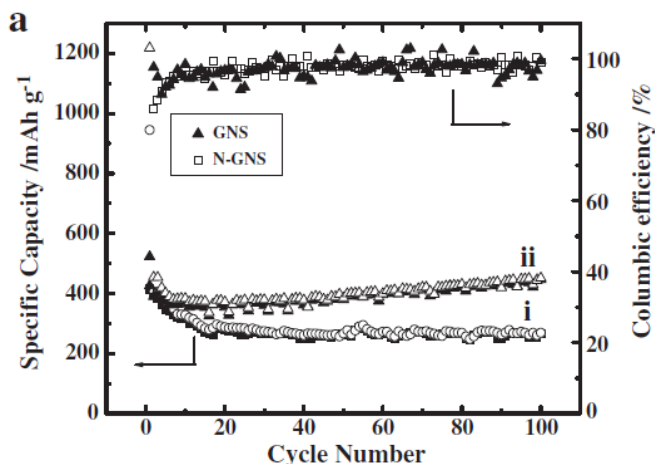


Figure 10. Electrochemical performances of nitrogen doped graphene as anode for LIBs (Electrochem. Comm. 2011;13(8) 822-825.)

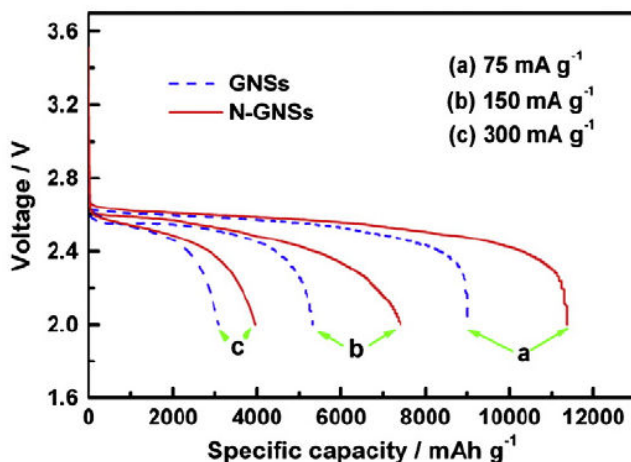


Figure 11. Electrochemical performances of nitrogen doped graphene as cathode for lithium oxygen batteries (Electrochem. Comm. 2011;18(1) 12-15.)

Powder based N-graphene with excellent lithium storage was also reported by Cui and Li respectively [14, 64]. In Cui's research, the N-graphene nanosheets were prepared by heat treatment of graphite oxide under an ammonia atmosphere at 800 °C for 2 h. The doping level is about 2% nitrogen, where the N binding configuration of the graphene includes 57.4% pyridinic, 35.0% pyrrolic and 7.6% graphitic N atoms. The N-graphene nanosheets exhibited a high reversible capacity (900 mAh g^{-1} at 42 mA g^{-1}), excellent rate performance (250 mAh g^{-1} at a current density of 2.1 A g^{-1}), and significantly enhanced cycling stability. The doped graphene in Li's study was obtained by high-temperature annealing graphene in NH_3 . Interestingly, the specific capacity of the doped graphene evidently increases with charge/discharge cycles. As shown in Fig. 10, after 100 charge-discharge cycles, the specific capacity was $\sim 480 \text{ mAh g}^{-1}$ for the N-graphene, while only 290 mAh g^{-1} for the undoped graphene. The obtained significant improvement is attributed to the incorporated nitrogen to graphene planes with a result of more structural defects during cycling, as indicated by Raman analysis.

N-graphene also indicates excellent performances when used as cathode for Li air batteries. Sun's research group fabricated nonaqueous lithium-oxygen battery with N-graphene nanosheets as cathode materials, which delivered a discharge capacity of 11660 mAh g^{-1} , as shown in Fig. 11 [65]. This capacity is about 40% higher than that with the pristine GNS. The excellent electrochemical performance of N-graphene is attributed to the defects and functional groups as active sites introduced by nitrogen doping.

3.2.2. N-doped graphene as an electrode composite

Wang, et al., synthesized N-graphene- SnO_2 sandwich papers as anode for LIBs through a complicated procedure [66]. The materials show excellent electrochemical performances. The

N-doped G-SnO₂ paper delivered an initial reversible capacity of 918 mAh g⁻¹, which is higher than those obtained for both pure SnO₂ nanoparticles (881 mAh g⁻¹) and graphene paper (548 mAh g⁻¹). Moreover, the N-doped G-SnO₂ papers also exhibited enhanced rate capacities. The specific capacity was maintained at values as high as 683 mAh g⁻¹ and 619 mAh g⁻¹ after the current density was increased to 1000 mA g⁻¹ and 2000 mA g⁻¹, respectively. Even at a current density of 5000 mA g⁻¹, the material still delivered a capacity of 504 mAh g⁻¹.

3.2.3. S-doped graphene as cathode for lithium oxygen batteries

Recently, Sun's research group reported the use of S-graphene as cathode for lithium oxygen batteries [67]. The S-doped graphene was obtained through pyrolysis of p-toluenesulfonic acid. The initial discharge capacity of S-graphene electrode is about 4300 mAh g⁻¹, which is lower than that of the pristine graphene electrode (~8700 mAh g⁻¹). However, the initial charge capacity of the S-graphene electrode is about 4100 mAh g⁻¹, but it is only ~170 mAh g⁻¹ for the undoped graphene electrode. Moreover, the discharge capacities in the second cycle of the S-graphene and undoped graphene electrodes are 3500 and 220 mAh g⁻¹, respectively. Importantly, S-doping in graphene results in morphological change of reaction products from nanoparticles to nanorod-like.

Guest functional group	Electrochemical devices	References
N atoms	Fuel cells	[16,17,52-60]
	Lithium ion batteries	[14,62-66]
	Supercapacitors	[27,68,69]
B atoms	Fuel cells	[70]
S atoms	Fuel cells	[29,61]
	Lithium ion batteries	[67]

Table 3. A summary of the functionalized graphene applied in EECS.

3.3. Supercapacitors

Although various carbon nanomaterials including activated carbon, carbon nanotubes and graphene have demonstrated high-performance for supercapacitors, the capacitances they can hold are still much lower than the demanded. It is a challenge to research and development of qualified materials for high-performance supercapacitors. Application of N-graphene in supercapacitors slightly falls behind FCs and LIBs [27,68,69]. The first report concerning N-graphene for supercapacitor appeared in May 2011 by Hyung, et al., [68]. The N-graphene was produced by a simple plasma treatment of graphene. The N-graphene supercapacitors gave rise to a highest capacitance of ~280 F/g_{electrode}, which is about 4 times larger than those of undoped graphene based counterparts. Moreover, the supercapacitors also demonstrated excellent cycle life (>200000), high power capability (a power density up to ~8 × 10⁵ W kg⁻¹ and an energy density up to ~48 Wh kg⁻¹), and compatibility with flexible substrates. In the same

study, using local N-configuration mappings during plasma treatment along with side binding energy calculated by density functional theory, they also articulated that the origin of the improved capacitance is a certain N-configuration at basal planes. N-graphene nanosheets with the nitrogen level as high as 10.13 at% were synthesized from GO and urea in a hydrothermal process [27]. The N-graphene has a large surface area of $593 \text{ m}^2 \text{ g}^{-1}$, and exhibits excellent capacitive behaviors (326 F g^{-1} , 0.2 A g^{-1}), superior cycling stability (maintaining initial capacity even) and high coulombic efficiency (99.58%) after 2000 cycles. An energy density of 25.02 Wh kg^{-1} could be achieved at power density of 7980 W kg^{-1} by a two-electrode symmetric capacitor test. Both the N-content and the N-type are very significant for the capacitive behaviors. In more detail, the pyridinic-N and pyrrolic-N play main roles for improving pseudo-capacitance by the redox reaction, while quaternary-N could enhance the conductivity of the materials which is favorable to the transport of electrons during the charge/discharge process.

4. Conclusion

Chemical functionalization of graphene is one of the key subjects in graphene science and technology, and has been extensively studied. The functionalization proceeds mainly through chemical atom doping, diazonium coupling, silanization, amidation, etherisation, substitution and cycloaddition, etc. Various innovative properties have been brought about and therefore the functionalized graphene exhibits potential application in a wide spectrum of fields. In electrochemical energy storage and conversion, graphene doped with N, S and B has shown plausible performances and has been widely investigated. Nitrogen doped graphene was used either as a support for Pt or as a metal-free catalyst for fuel cells. Its application in lithium ion batteries and supercapacitors also offers higher lithium storage capacities and rate capability and higher capacitance. S doped graphene also results in improved oxygen reduction reaction and lithium storage capacities for lithium oxygen batteries. This subject is still under rapid development. B doped graphene also improved oxygen reduction reaction. However, functionalized graphene with complicated organic molecules has yet been applied to this field due to the lower electronic conductivity. An atomic understanding of interaction between functional group and graphene, the change in the property of the functionalized graphene during performance, etc., should be pursued in the future studies.

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