

Graphene-based hybrid materials and their applications in energy storage and conversion

ZHOU Ding^{1,2}, CUI Yi^{1,2} & HAN BaoHang^{1,2*}

¹ National Center for Nanoscience and Technology, Beijing 100190, China;

² State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Shanghai 200050, China

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Graphene attracts more and more scientists and researchers owing to its superior electronic, thermal, and mechanical properties. For material scientists, graphene is a kind of versatile building blocks, and considerable progress has been made in recent years. Graphene-based hybrid materials have been prepared by incorporating inorganic species and/or cross-linking of organic species through covalent and/or noncovalent interactions. The graphene-based hybrid materials show improved or excellent performance in various fields. In this review, we summarize the synthesis of graphene and graphene-based hybrid materials, and their applications in energy storage and conversion.

graphene, hybrid material, energy storage, energy conversion

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Graphene is a kind of two-dimensional (2D) carbon nanomaterials, and possesses a large theoretical specific surface area of about $2600 \text{ m}^2 \text{ g}^{-1}$, superior electronic and thermal properties. Since its experimental realization in 2004, graphene became a famous star for the scientists in various fields, therefore, graphene-based materials and devices have been widely investigated [1]. In the material view, graphene has been considered as a kind of versatile and unique building blocks for functional materials [2]. Graphene-based hybrid materials have been fabricated by the cross-linking of graphene or graphene oxide (GO) through various kinds of inorganic or organic species, i.e. inorganic nanoparticles, polymers, multifunctional organic molecules, and metal ions/complexes [3]. The graphene-based inorganic or organic hybrid materials have been extensively investigated in various energy storage and/or conversion related fields [4].

1 Synthesis and modification of graphene

The synthesis of graphene is still a bottleneck for the com-

mercial application of graphene-based materials and devices. Various methods have been developed to prepare graphene so far, which can be divided into chemical vapor deposition of graphene layers, micromechanical exfoliation of graphite using peel-off method with Scotch-tape, epitaxial growth of graphene films, bottom-up synthesis of graphene from organic molecules, and reduction/deoxygenation of GO sheets [5]. In these methods, reduction of GO is a most common method to obtain graphene with high-volume production, which can be achieved through chemical, thermal, or electrochemical reduction pathways [5]. A wide variety of reductants, such as hydrazine, sodium borohydride, hydroquinone, and aqueous alkaline solution have been used to reduce GO [6]. Meanwhile, the oxygen-containing groups could be easily removed by chemical, electrochemical or thermal methods, however, after the removal of oxygen-containing groups of GO, graphene sheets suffer from very limited dispersibility and even irreversible agglomeration due to the increase in the π - π stacking interaction and van der Waals forces between graphene sheets [5]. Therefore, modification and/or stabilization of graphene are needed, which have been realized through covalent or noncovalent

*Corresponding author (email: hanbh@nanoctr.cn)

modification [5–7].

There are many oxygen-containing groups on the surface and edges of GO sheets, which make it easier to be covalent and noncovalent modified [6,7]. The most popular method for the modification of graphene and fabrication of graphene-based materials is noncovalent modification of graphene or GO sheets through different interactions, i.e. π - π , hydrophobic, electrostatic and chemisorption interaction. Many kinds of stabilizer have so far been employed, such as polyelectrolyte [8], pyrene derivative [9] and amphiphilic polymers [10]. Meanwhile, the oxygen containing groups, which could react with many groups, such as amido, hydroxyl, and isocyanato groups, provide a wide variety of reactions for covalent modification of graphene [11,12]. Furthermore, covalent surface functionalization of graphene could be realized through diazonium and azide reaction with the C=C bond of graphene [7,13]. On the basis of the modification methods, graphene-based hybrid materials have prepared by incorporating and crosslinking graphene or GO by the multifunctional inorganic or organic crosslinkers.

2 Preparation of graphene-based hybrid materials

Various kinds of graphene-based hybrid materials have been fabricated through the crosslinking or assembling of graphene or GO sheets by covalent or noncovalent methods [14–16]. According to the crosslinker used in the fabrication of graphene-based hybrid materials, they could be divided into two catalogs: graphene-based inorganic materials and graphene-based organic materials. Graphene-based inorganic hybrid materials are fabricated by incorporating inorganic species between graphene sheets, such as inorganic nanostructures and metal ions; while for graphene-based organic hybrid materials, organic molecules are used as crosslinkers through noncovalent and covalent interactions.

2.1 Graphene-based inorganic materials

Inorganic materials, such as metal and metal oxides showed wide applications in electrode materials and catalysis [2,4]. In recent years, various kinds of graphene-inorganic hybrid materials were fabricated by incorporating the inorganic nanostructure between graphene sheets through the driving force of chemisorption interaction. The methods for the synthesis of graphene-based inorganic hybrid materials could be classified into two categories: (i) assembly of graphene (oxides) with synthesized inorganic nanostructures, and (ii) one-pot synthesis and assembly of graphene and inorganic nanostructures. In the first method, inorganic nanostructures are prepared and then mixed with graphene or GO dispersion. However, in the second method, graphene and inorganic species are obtained *in situ* and then assemble together in one-pot reaction.

Several groups have extensively investigated the second strategy, i.e. metal or metal oxide nanoparticles are mixed with GO or graphene dispersion to fabricate functional materials. SnO₂-graphene was prepared through assembling of graphene sheets and SnO₂ nanoparticles in ethylene glycol to fabricate porous electrode materials with delaminated structure [17]. Scheuermann et al. [18] synthesized palladium nanoparticle-graphene composite and investigated its catalytic activity in Suzuki-Miyaura coupling reaction. Pd²⁺ was immobilized on GO sheets by ion exchange method, and then the obtained GO-Pd²⁺ precursor was reduced through thermal expansion, hydrogen, or hydrazine reduction. Polyoxometalate (POM) nanoparticles are incorporated between graphene sheets by reduction of the mixture of GO and POM. GO and POM are both negatively charged, therefore, the mixture are homogeneous without aggregation. After the addition of hydrazine into the mixture, GO was reduced into graphene, which assembled with POM through the driving force of chemisorption interaction into three-dimensional (3D) porous structures [19].

On the basis of the chemical routes developed for the preparation of graphene and inorganic materials, various kinds of graphene inorganic hybrid materials with unique performances are designed and fabricated. Besides metals, metal oxides, graphene-based hybrid materials containing different inorganic species, such as metal nitride [20], and metal sulfide [21], metal selenide [22], metal telluride [23], metal antimonide [24], and multi-element compounds have been prepared for the application in the energy storage and conversion materials. Hydro- or solvo-thermal process is a simple method for the preparation of graphene-based inorganic materials [4,25], in which GO could be reduced into graphene and the metal ions precursors would be transformed into metal or metal oxide species, therefore, the inorganic species could be incorporated into the graphene matrix. Novel metal and metal oxide nanoparticles promoted assembly of graphene with low density and tunable macro and microstructures are achieved successfully by using a hydrothermal method [26]. In a solvothermal reaction, graphene-CdS composite material with good structural and optoelectronic properties has been successfully and directly synthesized from the mixture of GO and Cd²⁺ in the solvent of DMSO [21] (Figure 1).

Further thermal treatment of graphene-metal oxide composites could also result in other kinds of graphene-based materials. GO-V₂O₅ was synthesized through a sol-gel method, and was thermally annealed at 800°C in the atmosphere of ammonia. In the thermal annealing process, V₂O₅ transformed into vanadium nitride and GO was reduced and N-doped, therefore N-doped graphene-vanadium nitride (GVN) composite could be obtained [20]. Furthermore, when thermally treated in H₂S or H₂, the metal oxides would be transformed into metal sulfide or reduced into metal. In this way, graphene-metal sulfide or graphene-metal hybrid materials could be obtained [4].

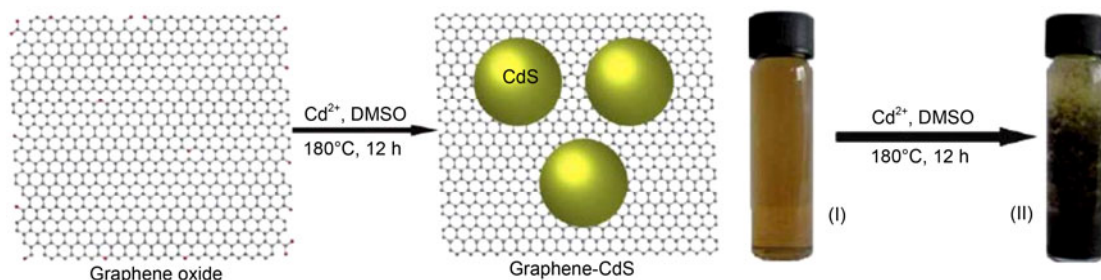


Figure 1 (Color online) Solvothermal synthesis of graphene-CdS hybrid material. Reprinted from ref. [21] with permission from the Wiley-VCH.

2.2 Graphene-based organic materials

Graphene-based organic materials have been constructed through covalent linkage and noncovalent crosslinking of the graphene or GO sheets. For the covalent linking method, bi- or multi-functional molecules are used as crosslinkers, in which the functional groups could react with the oxygen-containing groups and the carbon skeletons. For the non-covalent crosslinking method, the interactions between GO and polymers, i.e. hydrogen bonding, π - π stacking, hydrophobic interaction, electrostatic interaction, and chemisorption, perform as the driving forces for the formation of the graphene-based organic hybrid materials [6,7].

Graphite oxide hybrid porous materials (GHPMs) were prepared through the crosslinking of GO sheets with organic diisocyanates by using the reaction of diisocyanate with the carboxyl and hydroxyl groups on both sides of the sheets (Figure 2). The obtained graphite oxide hybrid porous materials exhibit a much enhanced porosity ($168 \text{ m}^2 \text{ g}^{-1}$) compared with the powdery GO [27].

This versatile functionalization of graphene with organic molecules allows it to act as building blocks in designing metal-organic framework (MOF) hybrids or other porous materials. MOF nanowire on benzoic acid-functionalized graphene was fabricated as shown in Figure 3. The hybrid material possesses a specific surface area of $810 \text{ m}^2 \text{ g}^{-1}$ [28].

Besides the increase in the porosity, the crosslinking would also enhance the mechanical and thermal stability of the hybrid material. GO paper is exposed in the glutaraldehyde (GA) vapor to prepare GA crosslinked GO paper. As a consequence of better interlayer adhesions, the mechanical property of the GA-treated GO paper has an average modulus of about 30.4 GPa and strength of about 101 MPa, which are about 190% and 60% higher than that of the as-received GO paper [29]. Zu et al. [30] employ triblock copolymers (PEO-*b*-PPO-*b*-PEO) as the stabilizer for chemically exfoliated graphene oxide, and supramolecular hydrogel are formed with α -cyclodextrins through the penetration of PEO chains into the cyclodextrin cavities (Figure 4).

3 Application of graphene-based hybrid materials

3.1 Supercapacitor

Owing to its high power density, long cycle life, and small

size, supercapacitor is considered to be one of the most attractive and promising electrochemical energy storage systems [31]. In general, there are two kinds of energy storage mechanisms for supercapacitor: (i) electrical double-layer capacitance and (ii) pseudocapacitance. Carbon material is a kind of electrical double-layer capacitor and widely used as electrode materials for supercapacitor because of its good stability and low cost [32,33]. Pseudocapacitor electrode materials, like conducting polymers and transition metal oxides, exhibit a higher capacitance due to the reversible Faradic redox reaction. Hybridization of the two kinds of capacitor material would possibly obtain a synergistic effect, which would result in an increase in the performance of the hybrid capacitor. In order to improve the electrochemical performance, many attempts have been devoted to the hybridization of different components and optimization of the nanostructures [34].

Graphene synthesized by different methods has been investigated as the electrode materials for supercapacitor, and it exhibits a good stability and a specific capacitance of about $100\text{--}264 \text{ F g}^{-1}$ [4,33]. Introducing functional species into graphene matrix could improve the electrochemical stability and rate performances. Graphene-based organic hybrid materials containing conducting polymers, such as polyaniline (PANI), polypyrrole, and poly(ethylenedioxythiophene) (PEDOT), exhibit a specific capacitance of about $300\text{--}1500 \text{ F g}^{-1}$ [35–37]. Graphene-PANI composite film prepared by filtration of the mixture of graphene and PANI showed a specific capacitance of about 210 F g^{-1} [35]. Morphology-controlled synthesis of functional species on GO or graphene sheets would also increase the electrochemical performances. Through the *in situ* polymerization method, PANI nanowire arrays have been uniformly aligned on GO sheets (Figure 5(A)). The specific capacitance of the PANI-GO composites can reach as high as 555 F g^{-1} at a discharge current density of 0.2 A g^{-1} (Figure 5(B)). Meanwhile, owing to the synergistic effect of GO and PANI nanowire, the capacitance retention of PANI-GO nanocomposite still kept 92% of its initial capacitance (Figure 5(C)), while pristine PANI kept only 74% of its initial capacitance [36,38].

In the meanwhile, many efforts have been put into the fabrication of graphene-metal oxides hybrid materials. Transition metal oxides, especially, ruthenium oxide (RuO_2) and

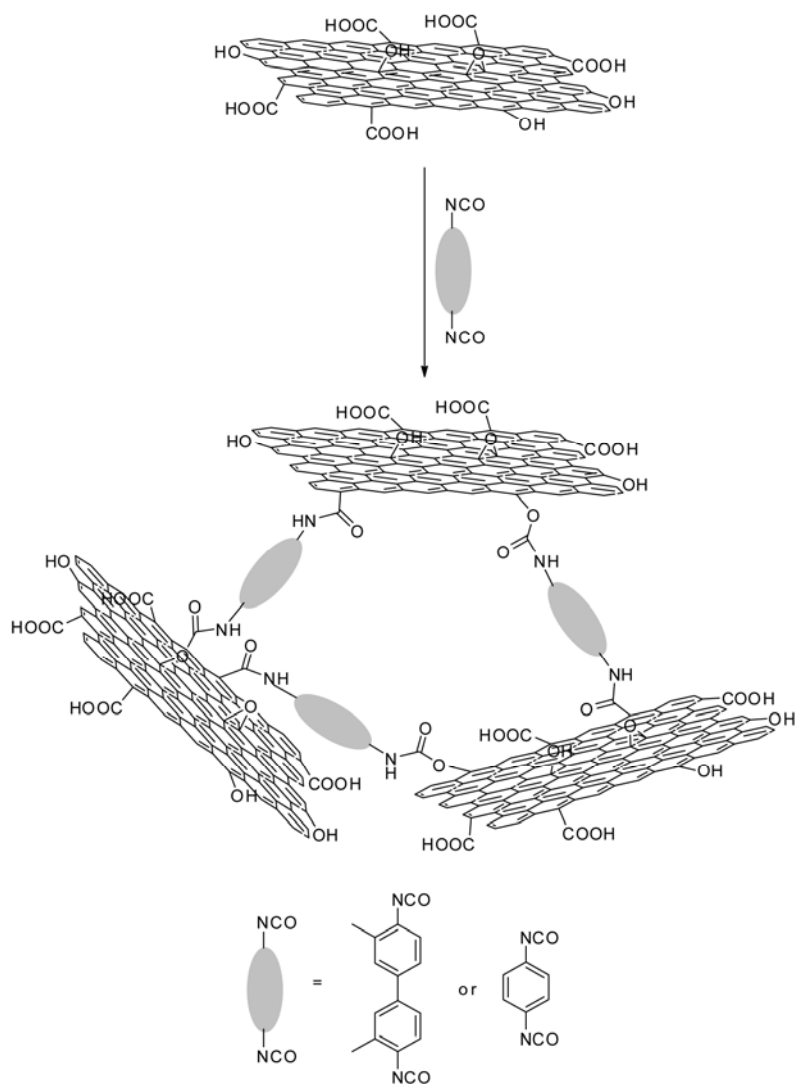


Figure 2 Scheme of the construction of GHPMs through crosslinking GO sheets with organic diisocyanates. Reprinted from ref. [27] with permission from the Elsevier B.V.

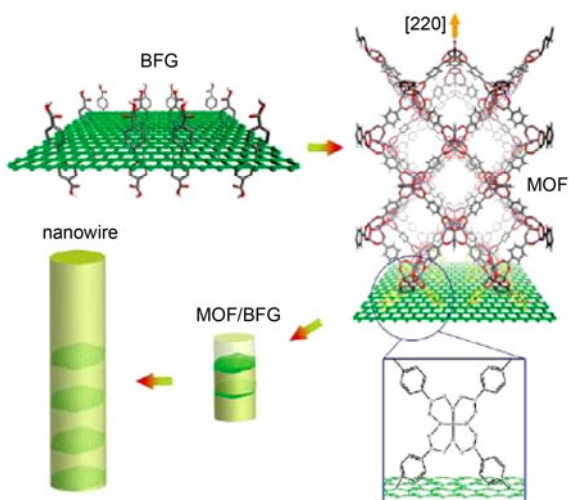


Figure 3 (Color online) Schematic of proposed bonding between functionalized graphene and MOF via $-\text{COOH}$ groups. Reprinted from ref. [28] with permission from the American Chemical Society.

manganese oxide (MnO_2), are considered as the most promising materials offering a high specific capacitance with an excellent cyclability [32,33]. Graphene- RuO_2 hybrid materials reported by Cheng's group [39,40] showed an excellent electrochemical stability (97.9% retention after 1000 cycles). The specific capacitance of graphene- MnO_2 composites could reach up to 300 F g^{-1} [41]. Up to date, the largest specific capacitance of graphene-based inorganic material is reported by Dai's group [42] for the graphene- $\text{Ni}(\text{OH})_2$, in which $\text{Ni}(\text{OH})_2$ hexagonal nanoplates were grown on low-oxidation graphene sheets (Figure 6(a)). The specific capacitance of the graphene- $\text{Ni}(\text{OH})_2$ hybrid material is about 1335 F g^{-1} and is comparable to the graphene-conducting polymer hybrid materials. The high specific capacitance and remarkable rate capability are promising for the applications in supercapacitors with both high energy and power densities (Figure 6(b) and (c)).

The performance of graphene-based supercapacitor could

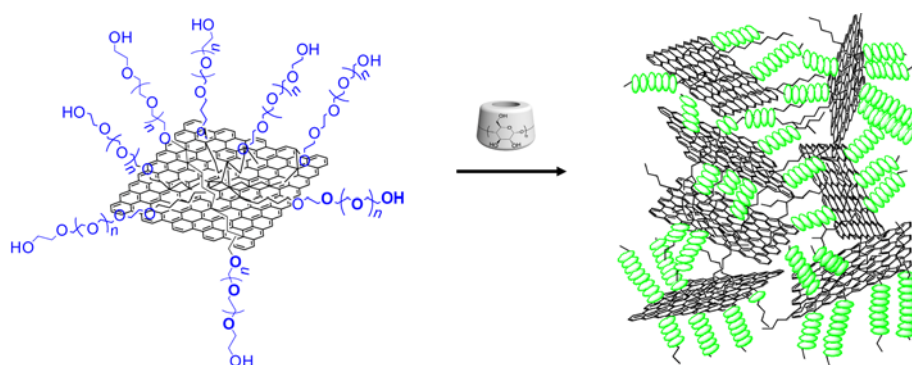


Figure 4 (Color online) Proposed structure of the copolymer coated graphene and the formation of the supramolecular hybrid hydrogel. Reprinted from ref. [30] with permission from the American Chemical Society.

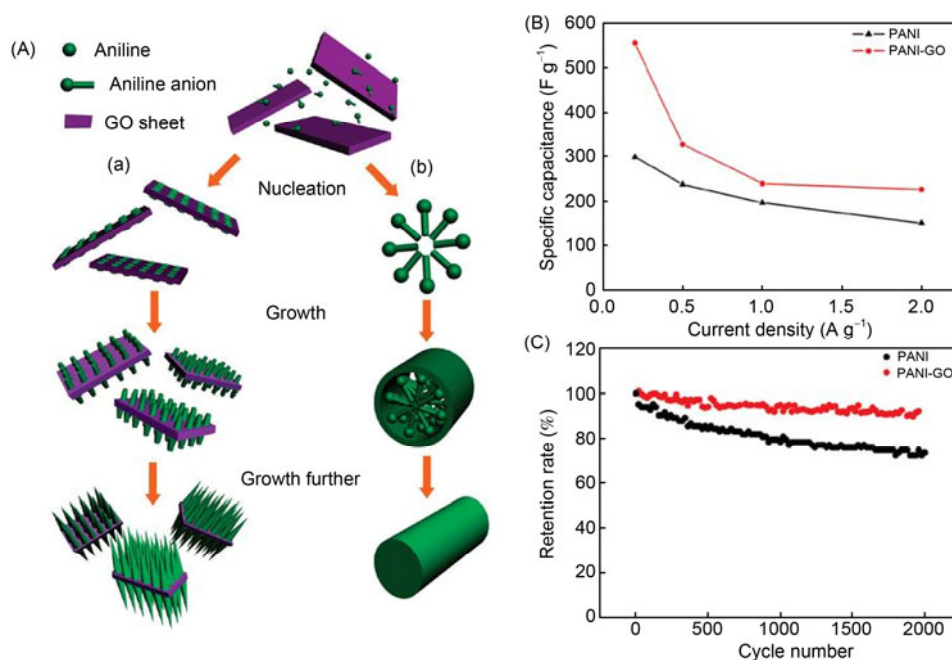


Figure 5 (Color online) (A) Schematic illustration of nucleation and growth mechanism of PANI nanowires: (a) heterogeneous nucleation on GO nanosheets; (b) homogeneous nucleation in bulk solution. (B) Specific capacitance of PANI and PANI-GO at different current densities. (C) Stability of PANI and PANI-GO. Reprinted from ref. [36] with permission from the American Chemical Society.

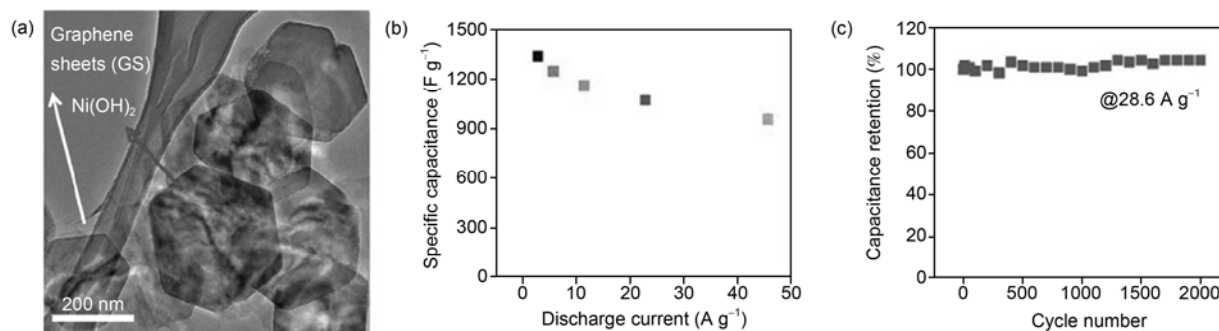


Figure 6 TEM image (a), specific capacitance (b), and capacitance retention (c) of graphene-Ni(OH)₂. Reprinted from ref. [42] with permission from the American Chemical Society.

be improved by increasing its electrical double-layer capacitance and pseudocapacitance. For electrical double-layer capacitance, one effective method is to increase the surface

area and optimize the porosity in the materials. Whereas, introducing of functional species with redox ability would increase the pseudocapacitance and even produce synergistic

benefits on the performance.

3.2 Lithium ion battery

Lithium ion battery (LIB) is an electrochemical energy storage device based on intercalation and deintercalation of lithium ions, and generally fabricated by an anode, cathode electrode, and electrolyte (separator) [43]. The performance of lithium ion batteries is largely depending on the physical and chemical properties of the cathode and anode materials [44]. Metals, (lithium containing) metal oxide and carbon materials are widely investigated as LIB electrode materials [32,33]. Graphene or graphene-based materials were investigated as electrode materials in recent years [45,46]. The lithium storage properties of graphene were investigated by Yoo et al. [47], and it shows higher capacity (about 540 mA h g^{-1}) than that of graphite (about 372 mA h g^{-1}). After incorporating CNT and C_{60} between graphene sheets, the capacities increase up to 730 and 784 mA h g^{-1} , respectively.

Graphene would increase the performance of the LIB electrode from two aspects, one is the capacitance and the other one is stability. Graphene- SnO_2 hybrid material is firstly reported by Honma's group [17] and it was then investigated as the LIB anode material. The obtained graphene- SnO_2 exhibits a reversible capacity of 810 mA h g^{-1} , while that of the bare SnO_2 nanoparticle on the first charge was 550 mA h g^{-1} . Furthermore, the cycling performance also improved, the charge capacity of graphene- SnO_2 still remained 70% (570 mA h g^{-1}) of the reversible capacity after 30 cycles, in comparison, bare SnO_2 nanoparticle decreased dramatically from 550 mA h g^{-1} on the first charge to 60 mA h g^{-1} only after 15 cycles (Figure 7).

Lithium containing metal oxides (i.e. LiFePO_4 , LiMn_2O_4) are widely used as cathode materials for LIB, but the main limitation for applications is their poor conductivity and lithium ion diffusion. In order to solve this problem, doping with foreign atoms, decreasing the particle size, and coating with electronically conductive materials are three common pathways [43,44]. Inspired by the excellent conductivity

and large theoretical surface area of graphene, LiFeO_4 nanoparticles are modified on graphene sheets. The capacity and cycle performances of LiFePO_4 could be improved considerably by the addition of graphene, and the hybrid cathode possesses an initial discharge capacity of 160 mA h g^{-1} at 0.2 C and the capacity retained 110 mA h g^{-1} even at high rate of 10 C with only 1.5 wt% of graphene [48].

Nanostructured composites can often produce synergistic benefits on the performance of the LIB electrode materials [32,33]. Graphene-PEDOT- MnO_2 composites with hierarchically nanostructure are fabricated by combining one-dimensional (1D) rod-like MnO_2 and 2D graphene nanosheet. PEDOT was grown on graphene matrix by *in-situ* polymerization, and the 1D rod-like MnO_2 was then grown on the graphene-PEDOT composites (Figure 8(b)). Owing to the high specific surface area, redox ability of the conjugating polymer and MnO_2 , and good conductivity, graphene-PEDOT- MnO_2 composite shows a significantly improved performance and stability. Graphene-PEDOT- MnO_2 exhibits a large first discharge capacity of 1835 mA h g^{-1} and retains 948 mA h g^{-1} after 15 cycles; while for graphene- MnO_2 , the capacity is about 1180 mA h g^{-1} at the first cycle and decreases to 421 mA h g^{-1} after 15 cycles [49] (Figure 8(a)).

Porosity is an important factor influencing the performance of the electrode materials. Graphene provides a large surface area for the deposition or growth of functional species, which would optimize the porosity of the hybrid materials. The porosity would also increase the flow of electrolyte, which is beneficial for the charging and discharging of the battery system. Meanwhile, the electron interactions between the components and graphene would also have an impact on the electrochemical performances.

3.3 Hydrogen storage

Hydrogen storage is one of the main issues for the realization of fuel cell powered vehicles using hydrogen as the energy carrier, and carbon based nanomaterials are the ideal media for hydrogen storage due to their highly porous

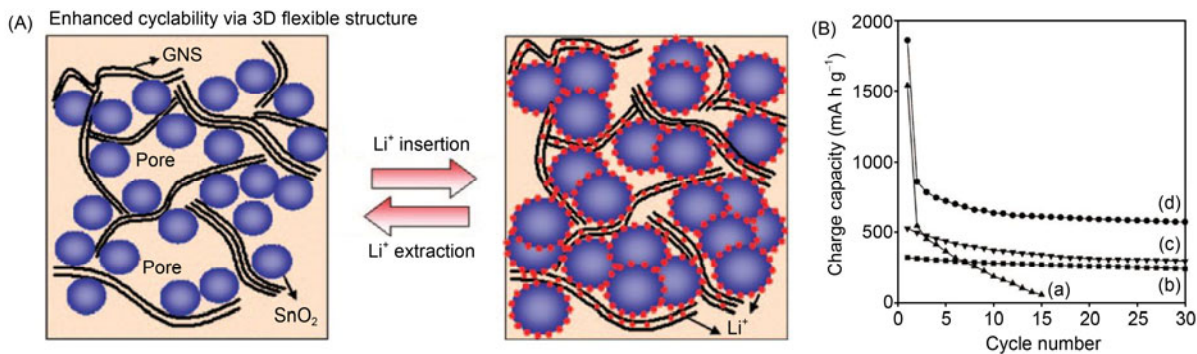


Figure 7 (Color online) (A) Scheme of the insertion and extraction of the Li^+ ions in the graphene- SnO_2 , and (B) the cyclic performances for (a) bare SnO_2 nanoparticle, (b) graphite, (c) graphene, and (d) graphene- SnO_2 composites. Reprinted from ref. [17] with permission from the American Chemical Society.

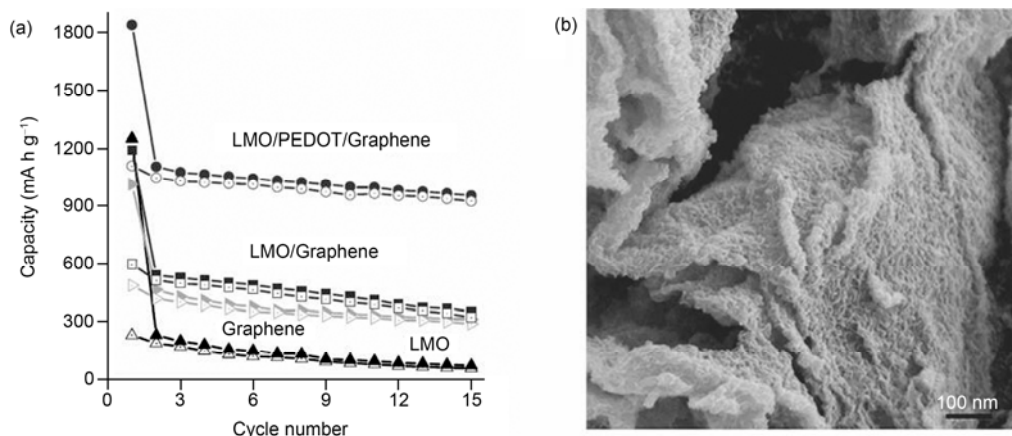


Figure 8 Cyclic performance (a) and SEM image (b) of graphene-PEDOT-MnO₂. Reprinted from ref. [49] with permission from the Wiley-VCH.

structure, low density, high stability, and large surface area. Porous graphene materials are theoretically investigated as gas separation membrane [50] or hydrogen purification membrane [51,52]. Meanwhile, in the study of graphene-based porous material, gas sorption and separation properties are investigated. Owing to the large theoretic surface area and the 2D structure of graphene, graphene-based porous materials are fabricated by incorporating inorganic nanoparticles and crosslinking of bifunctional material. The attempts focus on increasing the surface area, optimizing the porosity and doping of other atoms or ions [4].

Inorganic nanoparticles are using as the spacer to increase the distance between graphene sheets in order to construct 3D graphene structure with high porosity. As shown in Figure 9, POM nanoparticles are incorporated between graphene sheets to prepare graphene-POM (GPOM), which was then oxidized into o-GPOM due to the redox ability of the POM. Owing to the changes in micropores and electron distribution, the hydrogen uptake increases from 0.8 wt% of GPOM to 1.3 wt% of o-GPOM. Inspired by the redox ability of POM, controllable hydrogen adsorption-desorption ability could be achieved by tuning the redox

state of POM [19].

Although the space between graphene sheets could be increased by the inorganic nanoparticles, but the specific surface area values are usually lower than the reduced-GO owing to the large density of the inorganic nanoparticles [53]. Rigid bifunctional molecules would also serve as the crosslinker through covalent binding. The graphene-based organic hybrid materials possess lower density, which is beneficial for obtaining larger specific surface area. Srinivas et al. [54] synthesized the porous GO frameworks (GOFs) by expansion of GO sheets with various linear boronic acid pillaring units in a solvothermal reaction. The GOF structures develop through boronate-ester formation as a result of B-O bonding between boronic acids and oxygen functional groups on the GO layers. The obtained frameworks possess a specific surface area of 470 m² g⁻¹ and H₂ uptake capacities of 1.2 wt% at 10.0 bar (1 bar=10⁵ Pa), and 77 K.

3.4 Solar cells

Graphene is considered as a promising next-generation conducting material and possible to replace the indium tin oxide

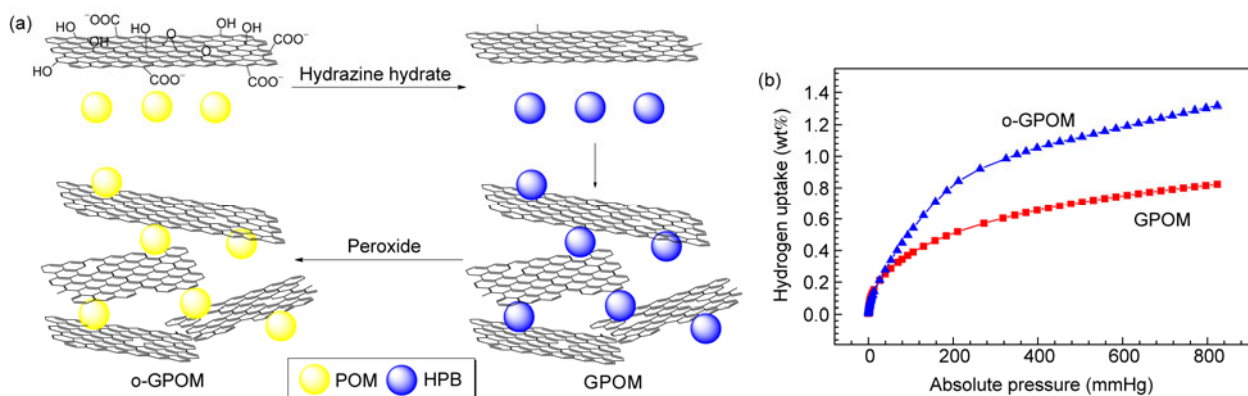


Figure 9 (Color online) Scheme of the formation process (a) and the hydrogen uptake isotherms (b) of GPOM and o-GPOM. 1 mmHg=1.33 × 10² Pa. Reprinted from ref. [19] with permission from the Wiley-VCH.

and fluorine tin oxide in optoelectronic devices owing to its high electron mobility, high thermal stability, and flexibility [4,5]. Graphene films are fabricated because of the solution processable operation of (functionalized) graphene sheets, such as the spinning coating methods [55,56].

The most important reason for graphene-based materials being used as electrode materials in the organic photovoltaic devices is the high electron mobility of graphene, which increases the charge separation and hole transportation in the organic photovoltaic devices. Graphene was incorporated into TiO₂ nanostructure anode in dye-sensitized solar cells (DSSCs). In the hybrid anode, graphene could be considered as a bridge for the photoelectrons, thus enhances the charge transport rate and prevents the charge recombination. Meanwhile, the light collection efficiency of the hybrid anode also increased, therefore, the photoelectrical conversion efficiency is improved [57] (Figure 10).

Vertically aligned carbon nanotubes (VACNTs) are growing directly onto a freestanding graphene paper by using chemical vapor deposition method, and the composite paper

was then investigated as the counter electrode of the DSSCs. Owing to the VACNTs growing on the graphene paper could provide the shortest transportation paths for the electrons, the composite paper exhibits an improved conversion efficiency as the counter electrode of about 6.05%, which is about 83% of that with a Pt film electrode [58].

Functionalized graphene material have been investigated as electron-accepter material in the bulk heterojunction photovoltaic devices with P3OT and P3HT as donor material. The interaction between graphene and P3OT/P3HT makes this composite work well as the active layer in bulk heterojunction-organic photovoltaic devices and the best power conversion efficiency of could be obtained at 1.4% under sun light illumination from a filtered Xenon lamp [55] (Figure 11).

3.5 Fuel cells

Catalyst shows a crucial effect on both the cost and durability of fuel cells. In order to improve the catalytic efficiency, a

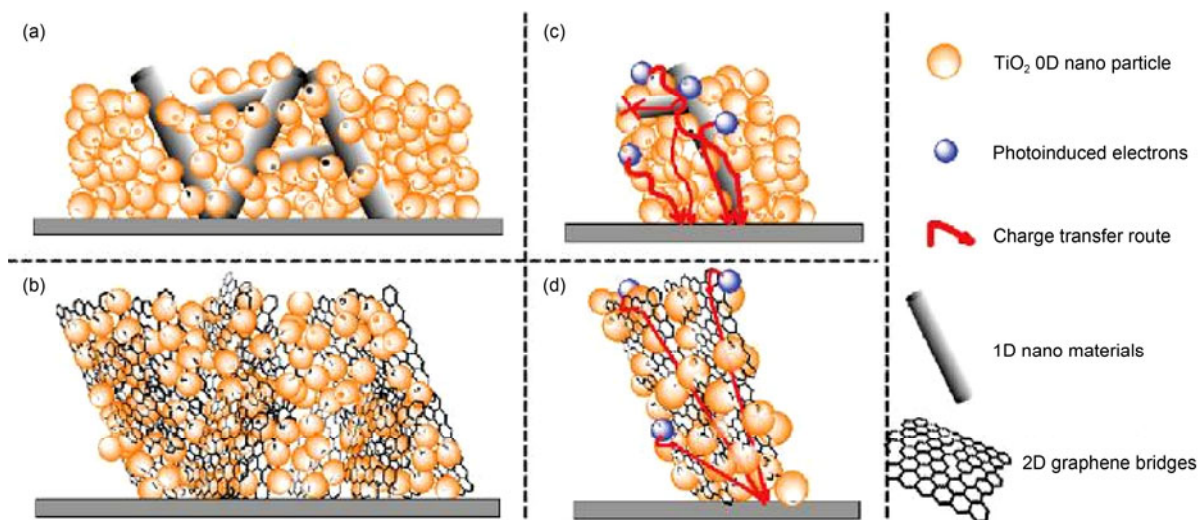


Figure 10 (Color online) Scheme of the improved electron bridge effect of the graphene-TiO₂ electrode. Reprinted from ref. [57] with permission from the American Chemical Society.

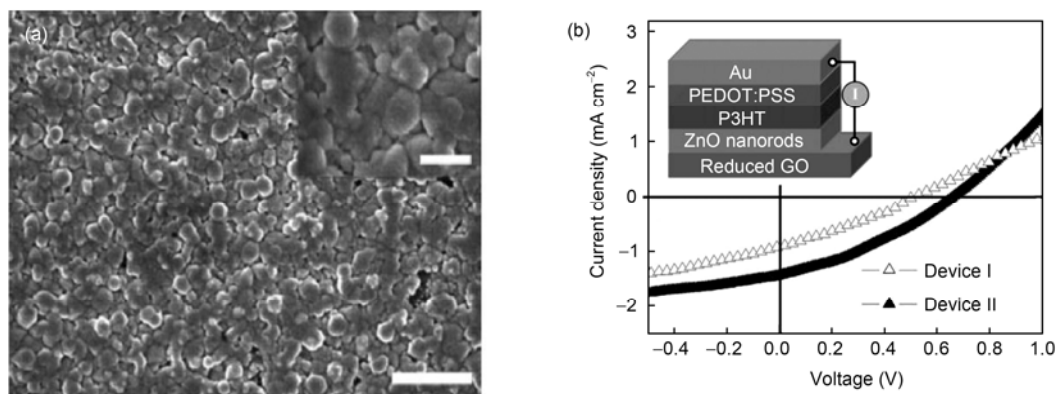


Figure 11 (a) SEM images of electrochemically deposited ZnO on rGO films (scale bars: images (2 μm) and inset (600 nm)), and (b) *I*-*V* curves for ZnO/P3HT hybrid solar cells under simulated globe sun illumination. Reprinted from ref. [55] with permission from the Wiley-VCH.

carbon material is widely used as the supporting material for catalyst nanoparticles due to its high surface area and stability [4]. As a 2D structured carbon material, graphene has a large surface area and both sides of the sheets can be used to support catalyst. Furthermore, due to its mechanical, structural, and electronic properties, graphene exhibits an outstanding performance as the support material for fuel cells since its discovery [59–61].

Platinum-based (Pt-based) electrocatalysts have been widely used as the electrocatalysts in direct methanol fuel cells for the respective methanol oxidation and oxygen reduction reaction. Pt nanoparticles are deposited on or incorporated between graphene sheets to fabricate graphene-Pt hybrid electrode for fuel cell. The hybrid electrode shows a much higher catalytic activity, better stability and tolerance toward CO. The maximum power density of graphene/Pt catalyst is 260 mW cm^{-2} at 540 mV, which is higher than that of the commercial Pt/C catalyst (139 mW cm^{-2} at 540 mV) [62]. PtRu/graphene catalyst was prepared and compared with PtRu/MWCNTs catalysts in the application in direct methanol fuel cells, in which the current value of PtRu/graphene catalyst is about 2.5 times higher than that of the PtRu/MWCNTs catalyst. Furthermore, the PtRu/graphene catalyst exhibits a better tolerance to poisoning species in methanol [63,64].

Functionalized GO-Nafion nanocomposite has been prepared and investigated in the application of proton exchange membrane fuel cell. The addition of graphene offers substantial proton exchange membrane fuel cell performance improvements at elevated temperatures. The composite displays a peak power density of 0.042 W cm^{-2} , and a significant proton conductivity improvement (four times) in comparison with Nafion at a low humidity value and high temperature [65].

3.6 Water splitting

Hydrogen energy has been considered as a renewable and clean energy, which solves the future energy and environmental problems. To produce hydrogen, an ideal way is the water splitting under visible light irradiation with the assistance of photocatalyst. Semiconductor photocatalysts, such as TiO_2 , CdS, have been developed for the photocatalytic reaction [66,67]. Graphene can create a 2D conductive support path for charge transport and collection, which can be used to enhance electron transport properties of semiconductor photocatalyst [68].

CdS clusters were decorated on graphene nanosheets through a one-step solvothermal method and were investigated as visible-light-driven photocatalysts. Graphene serves as the electron collector and transporter that efficiently lengthen the lifetime of the photogenerated charge carriers from CdS nanoparticles (Figure 12(a)). As a result, the graphene-CdS composite exhibits a high H_2 -production rate of 1.12 mmol h^{-1} , which is about five times higher than that of pure CdS nanoparticles. Meanwhile, its apparent quantum efficiency (QE) is 22.5% at wavelength of 420 nm (Figure 12(b)) [69].

Besides the traditional metal-containing semiconductor photoconductor, a metal-free polymeric photocatalyst, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has been developed in recent years [70]. Owing to its high thermal, chemical stability and interesting electronic properties, $\text{g-C}_3\text{N}_4$ showed a good photocatalytic performance for hydrogen or oxygen production via water splitting under visible-light irradiation. Furthermore, graphene- $\text{g-C}_3\text{N}_4$ hybrid material shows high conductivity and photocatalytic properties compared to pure $\text{g-C}_3\text{N}_4$. With the optimized content of graphene (sample GC1.0, 1.0 wt%), the corresponding H_2 -production rate of graphene- $\text{g-C}_3\text{N}_4$ was $451 \mu\text{mol h}^{-1} \text{ g}^{-1}$, which is more than 3.07 times of the value of pure $\text{g-C}_3\text{N}_4$ (Figure 13) [71].

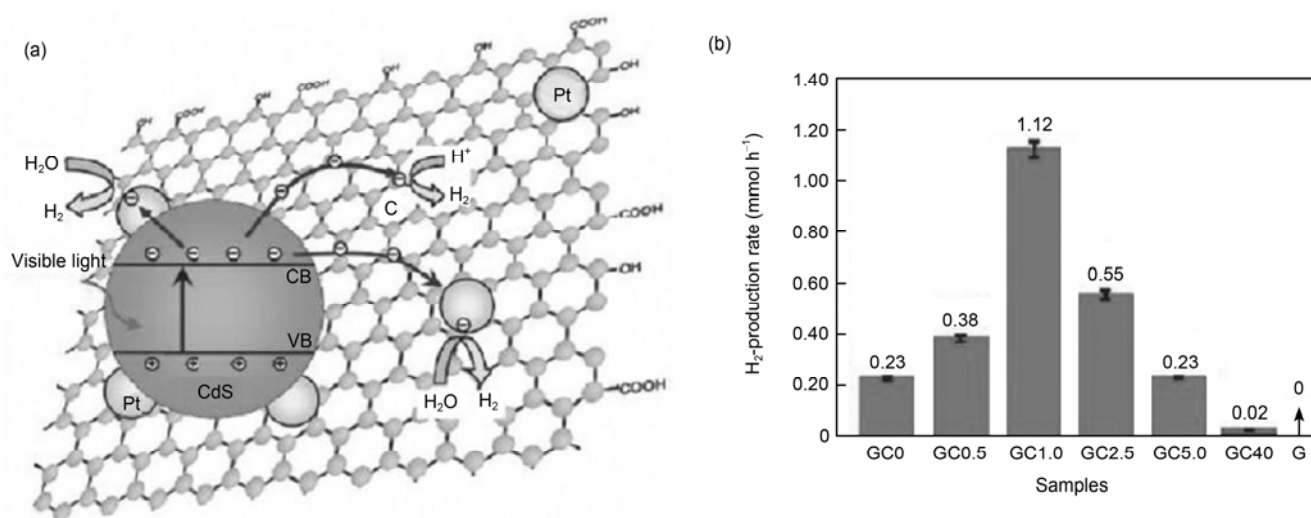


Figure 12 Proposed mechanism for the enhanced electron transfer in the graphene-CdS composites (a) and comparison of the photocatalytic activity of the samples with different contents of graphene (b). Reprinted from ref. [68] with permission from the American Chemical Society.

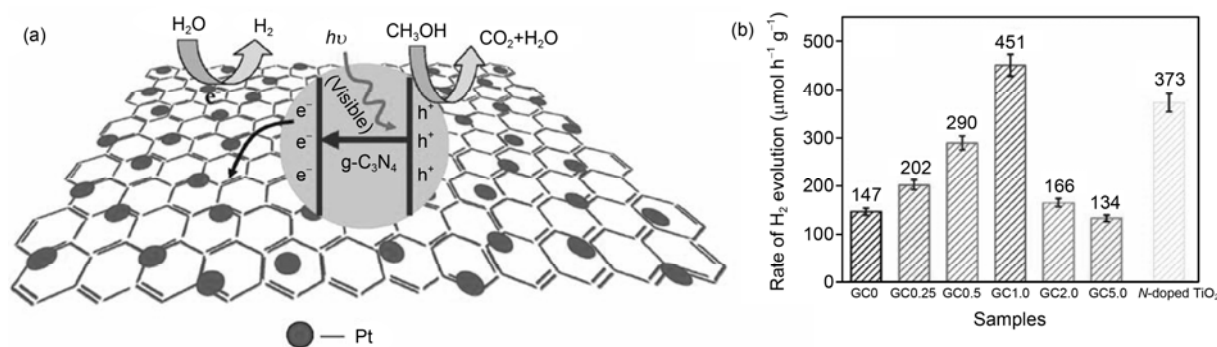


Figure 13 Proposed mechanism for the enhanced electron transfer in the graphene-g-C₃N₄ composites (a) and comparison of the photocatalytic activity of the samples with different content of graphene (b). Reprinted from ref. [70] with permission from the American Chemical Society.

4 Conclusions

Graphene, as a 2D material with unique properties, attracts more and more scientists to seek the solutions and answers in various fields. Triggered by the energy and environmental need, graphene-based hybrid materials for energy storage and conversion are widely investigated. In most of the graphene-based hybrid materials, graphene serves as the building block, conductive support, or additive with larger surface area, high flexibility and stability. Although the study of the graphene-based hybrid materials has achieved much progress, there are still many challenges in this field. Further development and study of graphene-based hybrid material in the views of science and technology are still needed to commercialize the application.

In the science view, graphene field developed only for several years, the understanding of graphene in the material and molecule view is limited. Therefore, systematic study of the assembly behavior, interaction and reaction mechanism of graphene/GO is fundamental for the controllable design and fabrication of the high performance graphene-based material. In the technology view, new techniques for the production of graphene in both quality and quantity should be developed. Traditional chemical reduction method for graphene is still not realistic for the commercial production and application. On the basis of the further understanding and proficient technology, graphene-based hybrid material would be a promising candidate for the application in energy storage and conversion fields.

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