

Functionalization of Graphene for Efficient Energy Conversion and Storage

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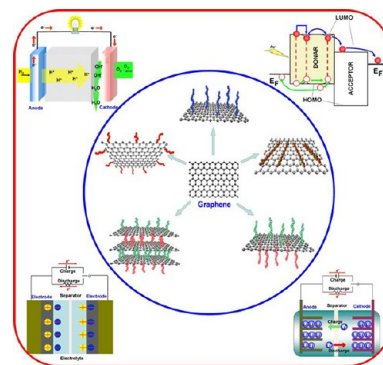
CONSPECTUS

As global energy consumption accelerates at an alarming rate, the development of clean and renewable energy conversion and storage systems has become more important than ever. Although the efficiency of energy conversion and storage devices depends on a variety of factors, their overall performance strongly relies on the structure and properties of the component materials. Nanotechnology has opened up new frontiers in materials science and engineering to meet this challenge by creating new materials, particularly carbon nanomaterials, for efficient energy conversion and storage.

As a building block for carbon materials of all other dimensionalities (such as 0D buckyball, 1D nanotube, 3D graphite), the two-dimensional (2D) single atomic carbon sheet of graphene has emerged as an attractive candidate for energy applications due to its unique structure and properties. Like other materials, however, a graphene-based material that possesses desirable bulk properties rarely features the surface characteristics required for certain specific applications. Therefore, surface functionalization is essential, and researchers have devised various covalent and noncovalent chemistries for making graphene materials with the bulk and surface properties needed for efficient energy conversion and storage.

In this Account, I summarize some of our new ideas and strategies for the controlled functionalization of graphene for the development of efficient energy conversion and storage devices, such as solar cells, fuel cells, supercapacitors, and batteries. The dangling bonds at the edge of graphene can be used for the covalent attachment of various chemical moieties while the graphene basal plane can be modified via either covalent or noncovalent functionalization. The asymmetric functionalization of the two opposite surfaces of individual graphene sheets with different moieties can lead to the self-assembly of graphene sheets into hierarchically structured materials. Judicious application of these *site-selective* reactions to graphene sheets has opened up a rich field of graphene-based energy materials with enhanced performance in energy conversion and storage.

These results reveal the versatility of surface functionalization for making sophisticated graphene materials for energy applications. Even though many covalent and noncovalent functionalization methods have already been reported, vast opportunities remain for developing novel graphene materials for highly efficient energy conversion and storage systems.



1. Introduction

Owing to the rapid economic expansion, increase in world population, and ever-increasing human reliance on energy-based appliances, the global energy consumption has been accelerating at an alarming rate. Consequently, the research and development of sustainable energy conversion and storage technologies have attracted a great deal of interest. Although the efficiency of energy conversion and storage devices depends on a variety of factors, their overall performance strongly relies on the structure and property of

the materials used. Various emerging nanomaterials have been developed for efficient energy conversion and storage. Of particular interest, carbon nanomaterials have been cost-effectively structured into various nanostructures with a high surface area and energy capacity, especially in terms of the ratio of energy/(weight \times cost).¹

As a building block for carbon materials of all other dimensionalities (e.g., 0D buckyball, 1D nanotube, 3D graphite), the two-dimensional (2D) single atomic carbon sheet of graphene has quickly emerged as an attractive

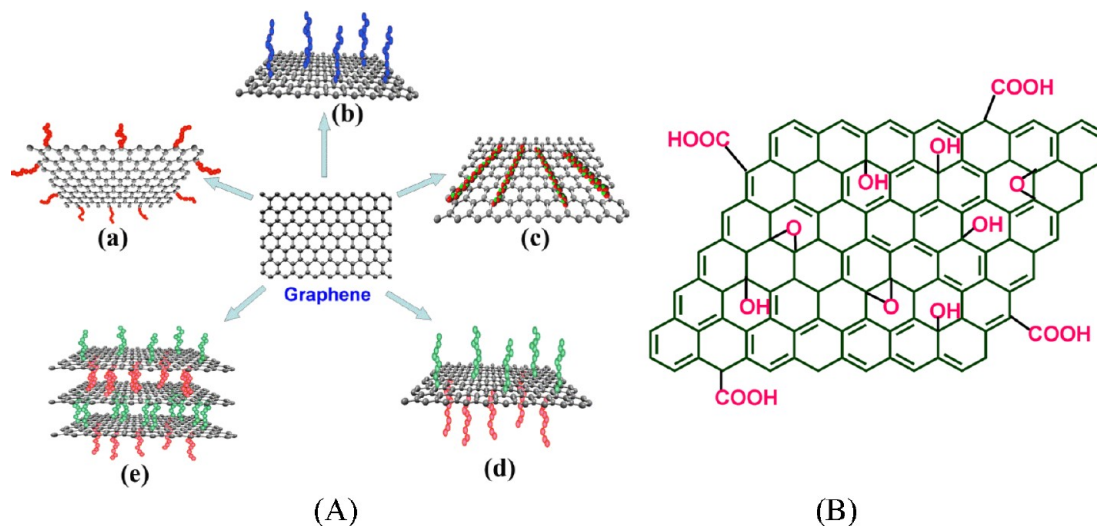


FIGURE 1. (A) Functionalization possibilities for graphene: (a) edge-functionalization, (b) basal-plane-functionalization, (c) noncovalent adsorption on the basal plane, (d) asymmetrical functionalization of the basal plane, and (e) self-assembling of functionalized graphene sheets. (B) Chemical structure of graphene oxide.

candidate for energy applications due to its unique structure and properties, including a large specific surface area ($2630 \text{ m}^2 \cdot \text{g}^{-1}$), excellent electrical conductivity ($10^6 \text{ S} \cdot \text{cm}^{-1}$), good thermal conductivity ($\sim 5000 \text{ W m}^{-1} \cdot \text{K}^{-1}$) and high charge mobility ($200\,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), great mechanical strength (breaking strength of 42 N m^{-1} and Young's modulus of 1.0 TPa), low optical absorbance (2.3%) and density ($< 1 \text{ g} \cdot \text{cm}^{-3}$), and unusual flexibility.^{2–4} Like all other materials, however, it is very rare for a graphene-based material with desirable bulk properties to also possess the surface characteristics required for certain specific applications. Therefore, surface functionalization is essential in making graphene materials of good bulk and surface properties as demanded for efficient energy conversion and storage.

Graphene materials can be prepared via various approaches, including mechanical cleavage of graphite with a Scotch tape,² epitaxial growth on single-crystal SiC,⁵ chemical vapor deposition (CVD) on metal surfaces,^{6,7} chemical coupling reactions,⁸ or exfoliation of graphite powder via solution oxidation,⁹ sonication/intercalation,¹⁰ or ball milling.¹¹ Graphene sheets without functionalization are insoluble and infusible, which have limited their large-scale practical applications. Recent effort has led to solution-processable graphene oxides (GOs) and edge-functionalized graphene (EFG) sheets from exfoliation of graphite powders.^{11,12} The availability of solution-processable GOs and EFGs has not only facilitated functionalization of graphene materials but also allowed for the formation of large-area graphene films through various solution processing methods, followed by reduction of GOs or removal of the edge functionalities of

EFGs. Although the research on functionalization of graphene is still in infancy, some interesting covalent and noncovalent chemistries have been devised for controlled functionalization of the basal plane and/or edge of graphene sheets to impart desirable bulk properties and surface characteristics for many potential applications, ranging from multifunctional composites through bioelectronics to energy devices.

In this Account, I summarize some of our new concepts and strategies for controlled functionalization of graphene for the development of efficient energy conversion (i.e., solar cells, fuel cells) and storage (i.e., supercapacitors, batteries) devices.

2. Functionalization of Graphene

Figure 1A schematically shows the functionalization possibilities for a graphene sheet at both molecular and supramolecular levels. The edge sites of graphene with dangling bonds are more reactive than the basal plane of strong covalent bonding with highly delocalized π electrons over the sp^2 hybridized carbon atoms. Thus, the dangling bonds at the graphene edge can be used for covalent attachment of various chemical moieties (Figure 1A(a)) to impart solubility, film forming capability, and/or reactivity for further chemical functionalization. Unlike the edge modification, covalent functionalization of the graphene basal plane (Figure 1A(b)) could cause significant distortion of the π – π conjugation and the associated physicochemical properties. However, the graphene basal plane structure remains largely unchanged with noncovalent functionalization (e.g., adsorption, Figure 1A(c)). The asymmetric functionalization of the two opposite surfaces of individual graphene sheets

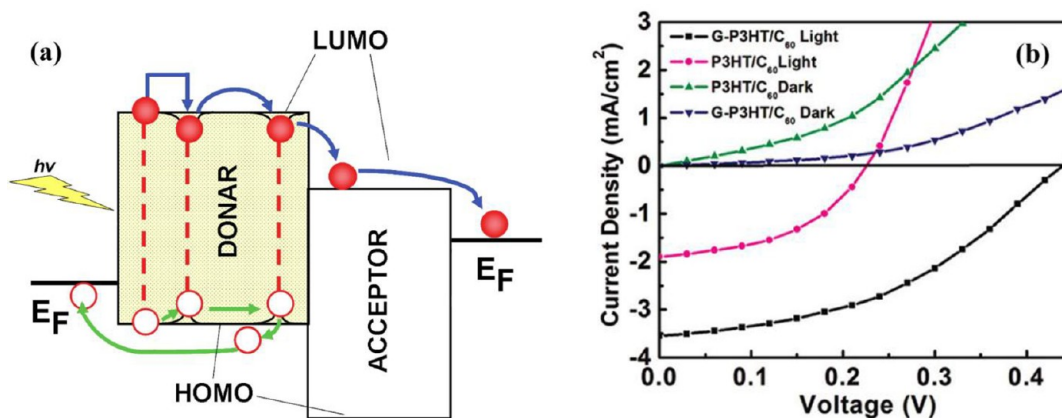


FIGURE 2. (a) Schematic energy level diagram of a PSC. Adapted from reference 13 with permission. Copyright 2005, CRC Press. (b) Current–voltage characteristics of the photovoltaic devices using P3HT/C₆₀ or G-P3HT/C₆₀ as the active layer. Reproduced from reference 17 with permission. Copyright 2010, American Chemical Society.

with different moieties (Figure 1A(d)) could lead to self-assembling of graphene sheets into hierarchically structured materials (Figure 1A(e)) with tunable properties to meet requirements for specific applications. More discussions on the surface chemistry influences on the property changes (i.e., chemistry–property relationships) are made in the context of how they affect applications in the subsequent sections as appropriate.

Functionalization of the pristine graphene sheet (Figure 1A) is very difficult, if not impossible, due to its poor solubility. The solution-processable GO sheet with reactive carboxylic acid groups at the edge and epoxy and hydroxyl groups on its basal plane, derived normally from the solution oxidation of graphite with strong oxidizing reagents (e.g., HNO₃, KMnO₄, and/or H₂SO₄),^{8,9} is one of the most popular starting materials for functionalization of graphene.

3. Functionalization of Graphene for Polymer Solar Cells

Photon absorption by conjugated polymers often creates bound electron hole pairs (i.e., excitons). Charge generation in polymer solar cells (PSCs), therefore, requires dissociation of the excitons at the interface between electron donating and accepting materials (Figure 2a).¹³ To facilitate the charge collection by electrodes, PSCs often employ an electron (hole) extraction layer between cathode (anode) and the active layer (Figure 3).¹⁴ The function of charge extraction layers includes minimizing energy barriers for charge carrier extraction, forming a selective contact for holes and blocking electrons at anode or vice versa at cathode, and modifying the interfaces to alter the active layer morphology. Controlled functionalization of the edge and basal plane of

graphene/GO has been demonstrated to provide various graphene-based materials useful for the active and charge-extraction layers in PSCs, as described below.

3.1. Edge-Functionalized Graphene as Hole-Transporting Material in Active Layer of PSCs. Having the extremely high specific surface area and the highest room-temperature mobility for electron and hole transport among all known carbon nanomaterials,¹⁵ graphene nanosheets have been explored as a new class of charge transport materials in PSCs.^{16,17} In particular, we have chemically grafted CH₂OH-terminated regioregular poly(3-hexylthiophene) (P3HT) onto carboxylic groups of GO via esterification reaction (Scheme 1).¹⁷ A bilayer photovoltaic device based on the solution-cast P3HT-grafted GO sheets (G-P3HT)/C₆₀ heterostructure showed a 200% increase of the power conversion efficiency (PCE = 0.61%) with respect to the P3HT/C₆₀ counterpart under AM 1.5 illumination (100 mW/cm²) (Figure 2b). The significantly improved device performance is attributable to the strong electronic interaction and good bandgap matching between the chemically bonded P3HT and graphene to enhance charge transport.¹⁷ This work indicates that graphene derivatives can be used as an efficient hole transporting material in the active layer of PSCs.

3.2. Edge-Functionalized Graphene Oxide as Electron Extraction Layer in PSCs. GO and reduced GO have been used as a hole extraction layer to show a PCE fairly comparable to that of the state-of-the-art PEDOT:PSS hole extraction layer.^{18,19} Recently, we have found that simple charge neutralization of the periphery –COOH groups of GO with Cs₂CO₃ (Scheme 2) could change the work function of GO and make the cesium-neutralized graphene oxide (GO-Cs) as an excellent electron extraction layer.²⁰ PSCs with GO and GO-Cs as a hole and electron extraction layer (Figure 3),

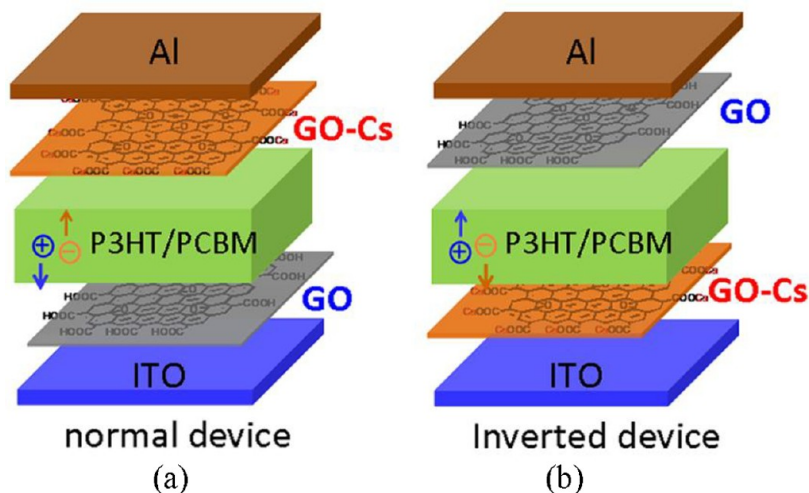
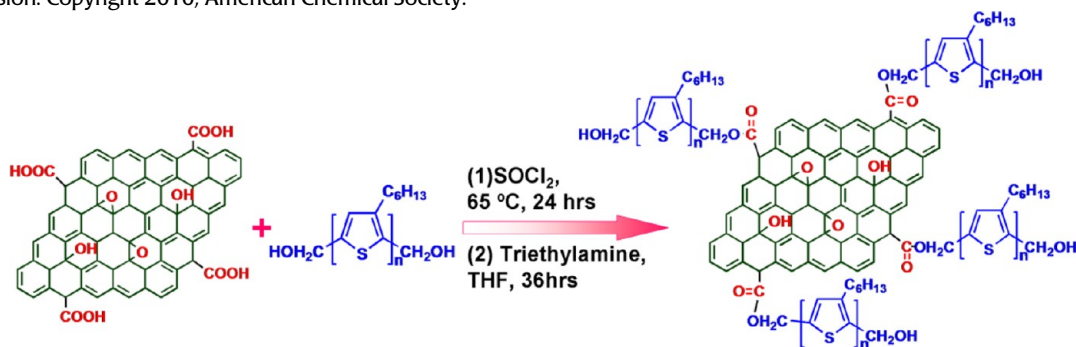
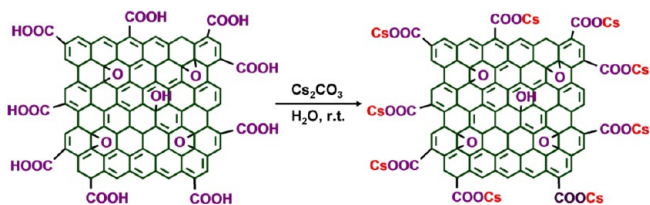


FIGURE 3. Device structure of (a) a normal and (b) an invert PSC with GO as the hole-extraction layer and GO-Cs as the electron-extraction layer. Reproduced from reference 20 with permission. Copyright 2012, John Wiley and Sons.

SCHEME 1. Synthetic Procedure for Chemical Grafting of CH₂OH-Terminated P3HT Chains onto Graphene, Involving the SOCl₂ Treatment of GO (Step 1) and the Esterification Reaction between Acyl-Chloride Functionalized GO and MeOH-Terminated P3HT (Step 2). Reproduced from reference 17 with permission. Copyright 2010, American Chemical Society.



SCHEME 2. Synthetic Route from GO to GO-Cs. Reproduced from reference 20 with permission. Copyright 2012, John Wiley and Sons.



respectively, exhibited a PCE as high as 3.67%. Both the normal (Figure 3a) and inverted (Figure 3b) devices outperformed the corresponding standard bulk-heterojunction (BHJ) solar cells with state-of-the-art hole- and electron-extraction layers.²⁰ These results demonstrated that GO and GO-Cs can act as an excellent hole- and electron-extraction layer, respectively, independent of the anode and cathode materials used in BHJ solar cells. The use of a single material system as both hole- and electron-extraction layers in PSCs could not only simplify

SCHEME 3. Synthetic Route from GO to GO-OSO₃H. Reproduced from reference 22 with permission. Copyright 2012, American Chemical Society.



the materials design and device fabrication but also allow for a precise control of the energy barrier for electron- and hole-extraction by tuning the work function of GO *via*, for example, controlled functionalization (Scheme 2).

Recent work on the edge-functionalization of graphene provides an effective means for the development of functionalized graphene materials with tailor-made chemical structures and electronic properties.^{11,12,21} However, EFGs

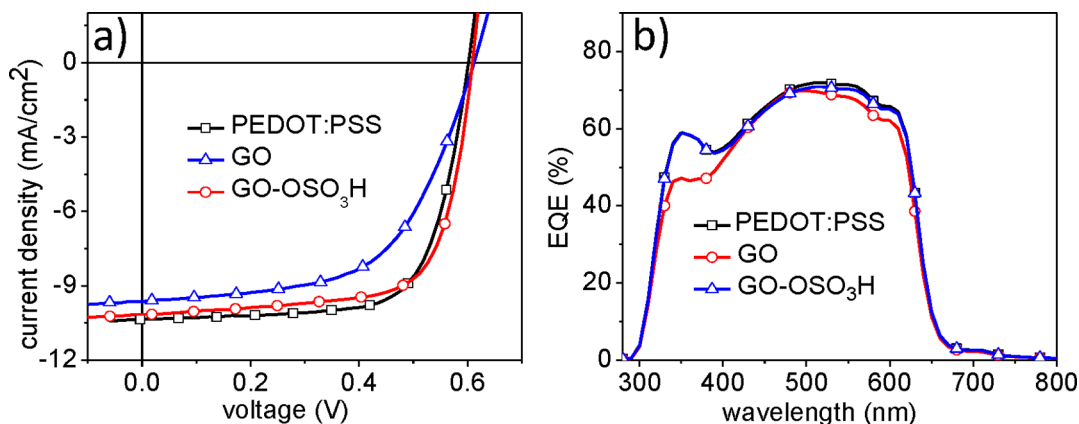
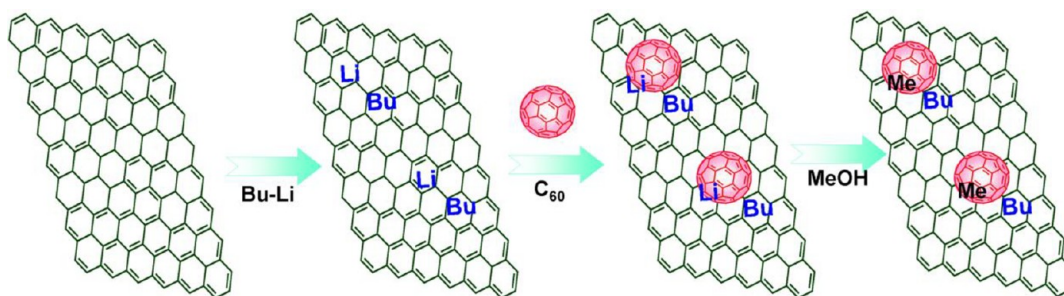


FIGURE 4. J - V curves (a) and the external quantum efficiency (EQE) spectra (b) of the PSC devices with PEDOT:PSS (25 nm), GO (2 nm), or GO-OSO₃H (2 nm) as the hole extraction layer. Reproduced from reference 22 with permission. Copyright 2012, American Chemical Society.

SCHEME 4. Synthetic Route for Grafting C₆₀ onto Graphene through Lithiation Reaction with *n*-Butyllithium. Adapted from reference 24 with permission. Copyright 2011, American Chemical Society.



have hardly been exploited for device applications. The use of GO-Cs, with and without subsequent reduction, as the electron-extraction material in PSCs is just one of a few early examples for applications of EFGs in energy devices,^{20,21} which will surely stimulate further studies on EFGs for device applications.

3.3. Basal-Plane-Functionalized Graphene Oxide as Hole Extraction Layer in PSCs. We have recently synthesized sulfated graphene oxide (GO-OSO₃H) by substituting the in-plane epoxy and/or hydroxyl groups of GO with -OSO₃H groups while largely retaining its -COOH edge groups (Scheme 3).²² The treatment of GO with fuming sulfuric acid could also remove a portion of the epoxy groups and hydroxyl groups on the basal plane to cause the reduction of GO.²²

Compared to GO, the strong acidic -OSO₃H groups in the carbon basal plane of GO-OSO₃H, together with -COOH groups along its edge (Scheme 3), could further impart good solubility for solution processing and enhance the doping of the donor polymer.²² Indeed, a PSC based on a P3HT:PCBM active layer and GO-OSO₃H hole-extraction layer exhibited a fill factor (FF) of 0.71 and PCE of 4.37% (Figure 4),²² both of which are among the highest values reported for P3HT:PCBM devices.²³ Therefore, the *site-selective* functionalization can be

used to tune interfacial and electronic properties of graphene-based charge-extraction materials in PSCs to achieve excellent device performance.

3.4. Basal-Plane-Functionalized Graphene as Electron-Transporting Material in Active Layer of PSCs. In a separate study, we have also developed a simple lithiation reaction (Scheme 4)²⁴ to covalently attach monosubstituted C₆₀ onto a graphene sheet derived from reduction of graphene oxide with hydrazine.²⁵

The above surfactant-free addition of monosubstituted C₆₀ onto graphene (Scheme 4, Figure 5A) provides “clean” all-carbon hybrids attractive for all-carbon devices.²⁶ By using the resultant C₆₀-graphene (C₆₀-G) hybrid as the electron acceptor in the active layer of a P3HT-based BHJ PSC,²⁴ we have demonstrated a 2.5-fold increase in the PCE with a significantly enhanced short-circuit current (J_{sc}) density and open-circuit voltage (V_{oc}), in respect to those of the C₆₀/P3HT system under the same condition, due to improved electron transport via the C-grafted graphene (Figure 5B). Therefore, C₆₀-grafted graphene could act as excellent electron accepting/transporting materials in PSCs and many other optoelectronic devices.

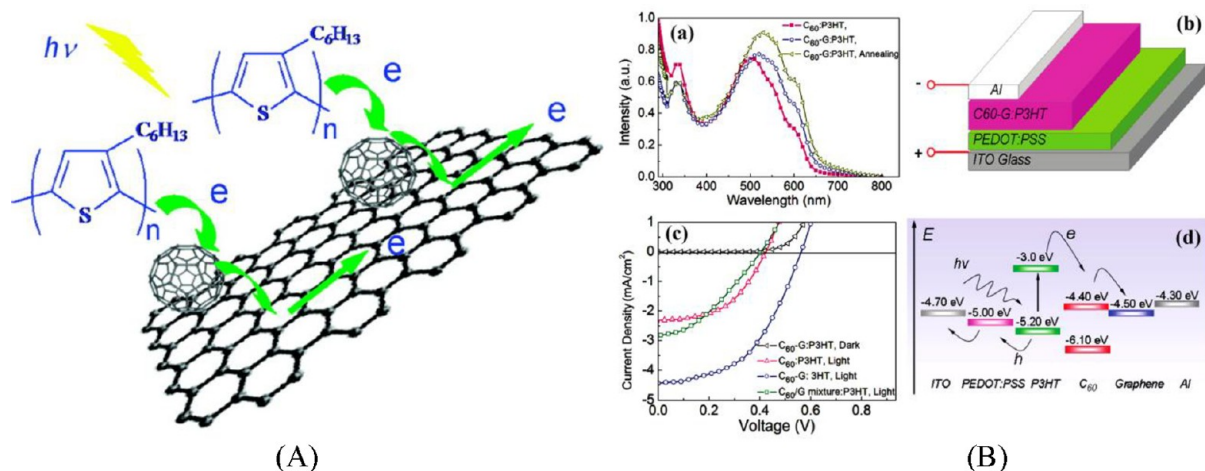


FIGURE 5. (A) Schematic representation of C_{60} -grafted graphene (C_{60} -G) for facilitating the electron transfer and transport in a P3HT-based PSC. (B) (a) Absorption spectra of the C_{60} -G:P3HT (1:1 wt/wt) film before and after annealing (130 °C, 10 min) and the C_{60} -P3HT (1:1 wt/wt) film spin-cast onto quartz plates. (b) Schematic of a PSC with the C_{60} -G:P3HT composite as the active layer. (c) J - V curves of the photovoltaic devices with the C_{60} -G:P3HT (1:1 wt/wt), C_{60} -P3HT (1:1 wt/wt), or C_{60} /G mixture (10 wt % G):P3HT (1:1 wt/wt) as the active layers after the annealing. (d) Energy level diagram for the photovoltaic device with C_{60} -G:P3HT composite as the active layer. Reproduced from reference 24 with permission. Copyright 2011, American Chemical Society.

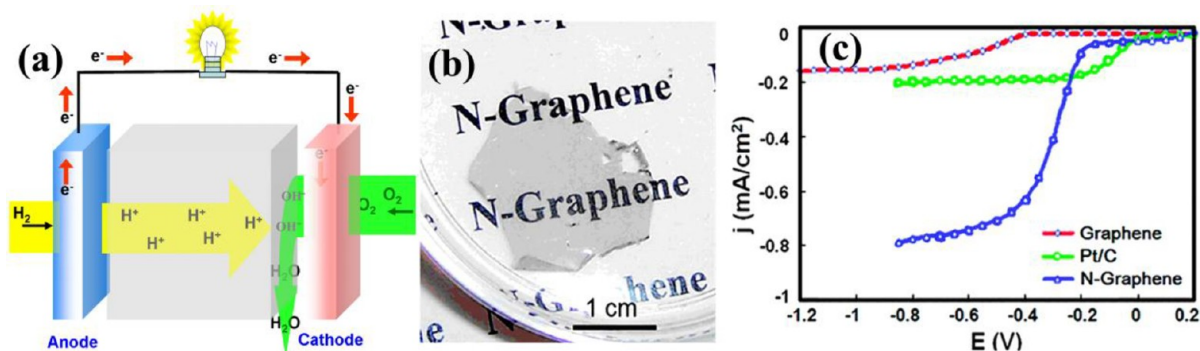
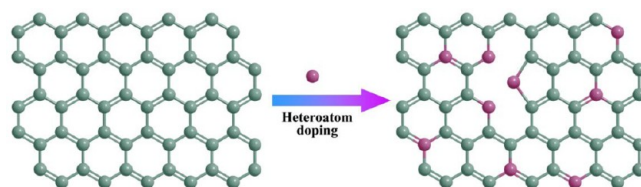


FIGURE 6. (a) Schematic representation and the working principle for a fuel cell. (b) Photo image of a N-doped graphene by CVD. (c) Voltammograms for ORR in air-saturated 0.1 M KOH at the N-doped graphene cathode. Adapted from reference 29 with permission. Copyright 2010, American Chemical Society.

4. Functionalization of Graphene for Fuel Cells

With no moving parts, air pollution, hazardous waste, or noise, fuel cells provide a green solution to directly convert chemical energy into electricity with a high energy conversion efficiency (typically, 40–60% or up to 85% efficiency if waste heat is captured for use) by oxidizing, for example, hydrogen gas into its constituent electrons and protons at anode and reducing oxygen gas at cathode.²⁷ The electrons flow out of the anode to provide electrical power while protons end up at the cathode to combine with the reduced oxygen to form water²⁷ (Figure 6a). The oxygen reduction reaction (ORR) can proceed either through a four-electron process to directly combine oxygen with electrons and protons into water as the end product or through a less efficient two-step, two-electron pathway involving the formation of

SCHEME 5. Doping of Graphene with Heteroatoms (e.g., N)



hydrogen peroxide ions as an intermediate.²⁷ The oxygen reduction would naturally happen very slowly and requires a substantial amount of catalyst (e.g., platinum) on the cathode to speed up the ORR. Although platinum nanoparticles have long been regarded as the best catalyst for the ORR, the high cost of platinum and its scarcity have made these catalysts the primary barrier to mass market fuel cells for commercial applications.

Recent intensive research efforts in reducing or replacing Pt-based electrodes in fuel cells have led to the development of new ORR electrocatalysts based on carbon nanomaterials.²⁸ Of particular interest, functionalized graphene materials have been used as either low cost metal-free catalysts or catalyst supports with outstanding performance.

4.1. Basal-Plane-Doped Graphene as Metal-Free Catalysts in Fuel Cells. In addition to the aforementioned covalent functionalization, the carbon basal plane of graphene can be doped with heteroatoms (Scheme 5) by either in situ doping during the nanocarbon synthesis²⁹ or through post-treatment (i.e., postdoping) of preformed carbon nanostructures with heteroatom-containing precursors (e.g., NH_3 for N-doping).^{29,30} Postdoping of carbon nanomaterials often leads to the surface functionalization only, whereas the in situ doping can incorporate heteroatoms into the entire carbon nanomaterials homogeneously.

The introduction of heteroatom dopants (e.g., nitrogen) into the carbon nanomaterials could cause electron modulation to provide desirable electronic structures for catalytic and many other processes of practical significance.^{29,31} Following our earlier discovery that nitrogen-containing vertically aligned carbon nanotubes (VA-NCNTs) with carbon atoms positively charged by N-doping could catalyze a more efficient four-electron ORR process than commercially available Pt/carbon black catalysts (C2–20, 20% Pt on Vulcan XC-72R, E-TER),³² various new metal-free ORR catalytic materials have been developed for fuel cell and many other applications,²⁸ including N-doped ordered mesoporous graphitic arrays (NOMGAs),³³ N-doped ordered mesoporous carbons (OMCS),³⁴ B-doped CNTs,³⁵ and CNTs codoped with N and B (BCN nanotubes³⁶).

As a building block for carbon nanotubes, graphene is an alternative candidate for metal-free ORR catalyst. Indeed, we have recently demonstrated that N-doped graphene films produced by CVD in the presence of ammonia showed a superb ORR performance without crossover/CO-poisoning effect and with a much higher catalytic activity, lower overpotential, better long-term operation stability than the commercial Pt/carbon black catalysts in alkaline medium (Figure 6b and c).²⁹ N-Doped graphene materials synthesized by other approaches, including nitrogen plasma treated graphene,³⁷ edge-functionalized graphene,²¹ thermal treatment of graphene with ammonia,³⁸ and solvothermal treatment of graphene with tetrachloromethane and lithium nitride,³⁹ have also been demonstrated to show good ORR electrocatalytic activities, suggesting considerable room for cost-effective preparation of

metal-free graphene-based catalysts for efficient oxygen reduction.

Recent work indicated that graphene and its derivatives doped with heteroatoms other than nitrogen could also exhibit improved ORR electrocatalytic activities, as exemplified by P-doped graphite layer⁴⁰ and S-doped graphene.⁴¹ We have successfully produced graphene codoped with N and B (BCN graphene) by simply annealing GO in the presence of boric acid under ammonia and demonstrated a significantly improved ORR electrocatalytic activity, even better than the commercial Pt/C electrode.³⁰ The observed super ORR performance for BCN graphene is attributable to a synergetic charge-transfer effect associated with the N and B codoping of graphene,³⁰ as is the case with the VA-BCN nanotubes.³⁶ However, the observation of ORR activities for graphene doped with S atoms of a similar electronegativity as that of C cannot be explained by the charge-transfer effect.^{32,41} Nevertheless, recent theoretical studies have indicated that doping-induced spin redistribution also plays an important role in regulating the ORR activities of heteroatom-doped graphene materials.⁴²

4.2. Graphene with Its Basal Plane Noncovalently Functionalized by Polymers as Metal-Free Catalysts in Fuel Cells. Apart from the electrocatalytic activity arising from the *intramolecular charge-transfer* induced by heteroatom-doping described above, *intermolecular charge-transfer* via noncovalent functionalization has also been demonstrated to impart ORR electrocatalytic activities to graphene. Noncovalent functionalization involves weak interactions, which cause no change on the basal plane structure of graphene and its electronic properties being largely retained (cf. Figure 1A(c)). We have exploited noncovalent functionalization of graphene by physically adsorbing poly(diallyldimethylammonium chloride) (PDDA) onto the basal plane of all-carbon graphene sheets during the process of reducing GO with sodium borohydride (NaBH_4)⁴³ in the presence of PDDA (Figure 7a).⁴⁴ The resultant PDDA-adsorbed graphene was shown to possess dramatically enhanced electrocatalytic activities toward ORR (Figures 7b) via the intermolecular charge-transfer between the N-free graphene and positively charged PDDA.⁴⁴ Thus, the “intermolecular charge-transfer” provides a simple, low-cost approach to develop carbon-based metal-free ORR catalysts.^{44,45} Although further study on the catalytic mechanism and the long-term performance evaluation in actual fuel cells are still needed, continued research in this embryonic field could give birth to a flourishing advanced fuel cell technology with metal-free ORR catalysts based on graphene materials.

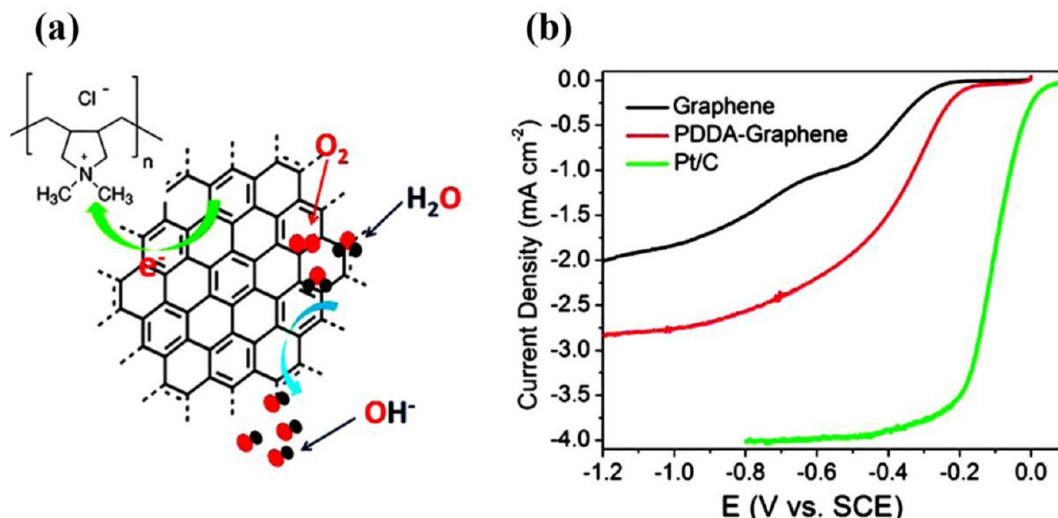
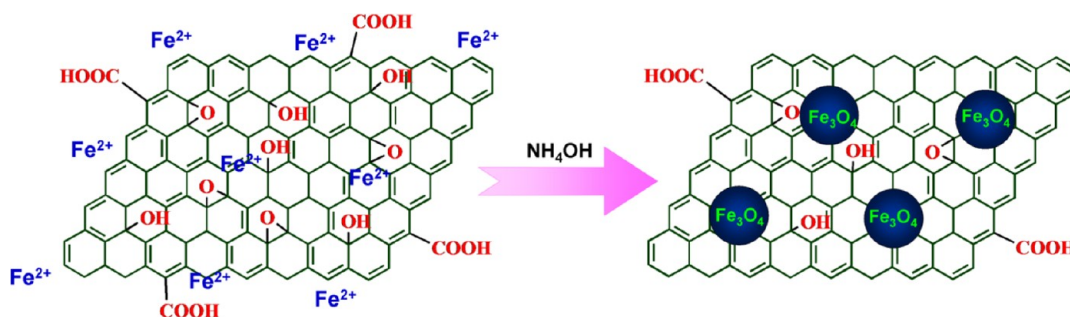


FIGURE 7. (a) Schematic illustration of the ORR catalyst based on the PDDA-adsorbed graphene. (b) Voltammograms for ORR on PDDA-graphene, graphene, and Pt/C electrodes in O_2 -saturated 0.1 M KOH solution. Reproduced from reference 44 with permission. Copyright 2011, American Chemical Society.

SCHEME 6. Synthetic Route to $\text{Fe}_3\text{O}_4/\text{rGO}$ via Redox Reaction between GO and Fe^{2+} Ions. Adapted from reference 50 with permission. Copyright 2011, Royal Society of Chemistry.



4.3. Graphene with Its Basal Plane Noncovalently Functionalized by Metal Nanoparticles as ORR Catalysts in Fuel Cells. Conducting substrates with a high specific surface area has been widely used for noncovalent immobilization of metal nanoparticles to improve the activity and efficiency of metal catalysts.^{46–49} In particular, graphene and N-doped graphene sheets have been used to support Pt^{46,47} or its alloyed nanoparticles⁴⁸ to enhance the ORR activity and stability due to the reduced aggregation of metal nanoparticles on the graphene supports. More recently, we have used GO to oxidize Fe^{2+} cations of FeCl_2 or FeSO_4 into Fe_3O_4 nanoparticles onto the self-reduced graphene oxide (rGO) sheets (Scheme 6).⁵⁰ The resultant $\text{Fe}_3\text{O}_4/\text{rGO}$ hybrid was demonstrated to possess interesting magnetic and electrochemical properties attractive for a large variety of potential applications. This facile approach is of promise to the development of various graphene-supported catalyst nanoparticles for energy-related applications (vide infra).

5. Functionalization of Graphene for Supercapacitors and Batteries

Along with the energy conversion devices (e.g., solar cells, fuel cells) discussed above, energy storage is also of paramount importance, especially for mobile applications.⁵¹ Supercapacitors and batteries are two important electrochemical energy storage devices that have attracted considerable interest. For large-scale practical applications, high energy storage capacity, high power delivery capability, and long cycle life are necessary. Graphene and its derivatives functionalized with metal oxide nanoparticles have recently been used in high-performance supercapacitors and batteries.^{50,51}

5.1. Graphene with Its Basal Plane Noncovalently Functionalized by Metal Oxide Nanoparticles as Electrodes in Supercapacitors and Batteries. Supercapacitors are electrochemical devices that can store energy and release it with high power capability and large current density within a short time interval.⁵² The principle of energy storage in a supercapacitor

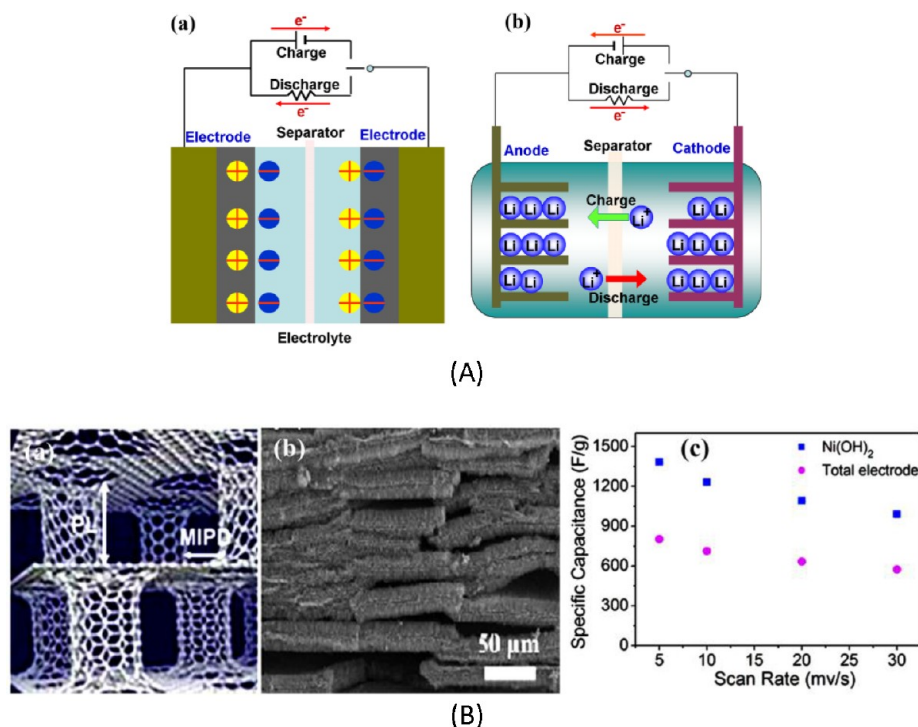


FIGURE 8. (A) Schematic and the working principle for a (a) supercapacitor and (b) battery. (B) (a) Schematic picture and (b) SEM image of a 3D pillared VACNT-graphene nanostructure. (c) Average specific capacitance for the Ni(OH)₂-coated VACNT-graphene pillared electrode at various scan rates. The average specific capacitance was calculated from both the Ni(OH)₂ mass and the total electrode mass. Adapted from reference 55 with permission. Copyright 2011, American Chemical Society.

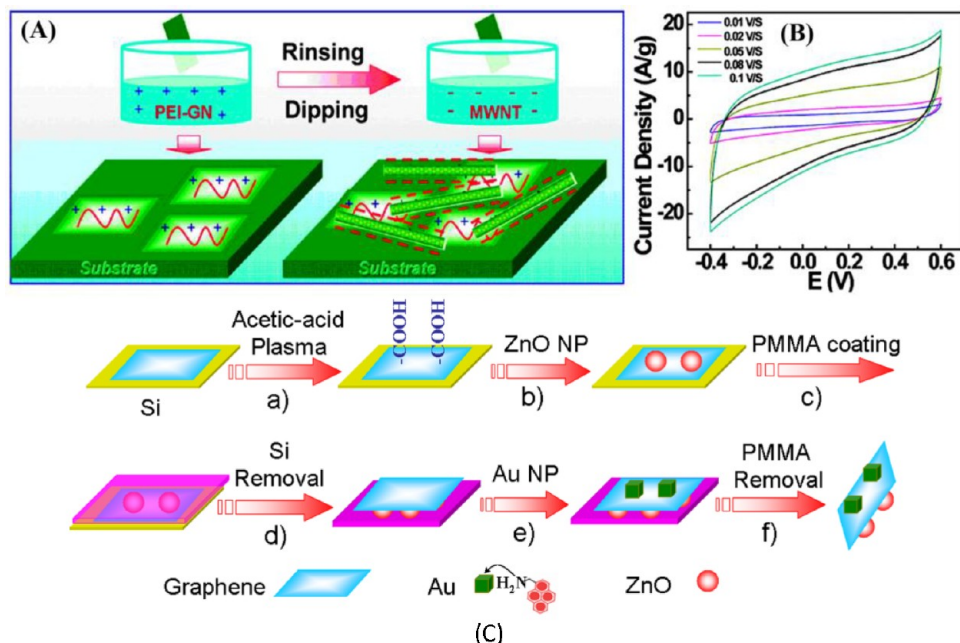


FIGURE 9. (A) Schematic illustration for the preparation of multilayered graphene/MWCNT hybrid electrode. (B) Cyclic voltammograms from the graphene/MWCNT hybrid electrode in 1.0 M H₂SO₄ solution.⁵⁸ (C) Schematic representation for asymmetrical functionalization of the two opposite surfaces of individual graphene sheets with ZnO and Au NPs, respectively.⁵⁹

can be either (i) electrostatic charge accumulation on electrode/electrolyte interface (electrical double layer capacitance,

EDLC) or (ii) transfer a charge to the layer of redox materials (e.g., metal oxide nanoparticles) on the surface of electrode

(pseudocapacitance) (Figure 8A(a)). In practical supercapacitors, the two storage mechanisms often work simultaneously.⁵²

On the other hand, lithium-ion batteries have been regarded as the premier rechargeable battery because of its significantly reduced weight and high energy storage capacity with respect to conventional rechargeable batteries.⁵³ A lithium-ion battery is composed of three essential components, namely the Li⁺ intercalation anode and cathode as well as the electrolyte, in which Li⁺ ions move from the cathode to the anode during charging and back when discharging (Figure 8A(b)).

Traditionally, batteries are high-energy-storage devices with a poor-energy-delivery capability (e.g., low power density, low rate capability), whereas supercapacitors are low-energy-storage devices but with a high-energy-delivery capability. Therefore, supercapacitors are considered to be perfect complement for batteries in various high-rate applications, such as automobiles and high performance portable electronics. The nature and microstructure of the electrode materials are crucial for not only energy and power densities but also for safety and cycle lifetime of both batteries and supercapacitors.^{52,53} Traditional carbon materials (e.g., carbon black, carbon nanofibers, graphite) and metal oxides have been intensively studied as the electrode materials in both supercapacitors⁵² and batteries,⁵³ with a recent focus on graphitic carbon materials to overcome some major drawbacks (e.g., poor electrical conductivity, huge charging-/discharging-induced volume change) associated with the traditional electrode materials.⁵⁴ However, it should be noted that graphene as Li-ion battery electrode still suffers from irreversible reaction with Li, solid electrolyte interface formation, and consequently irreversible performance.

To address the above issues, graphene electrodes hybridized with certain metal or metal oxide nanoparticles of high Li-ion reversible storage capacities have been prepared to exhibit improved performance. To reduce the charging-/discharging-induced volume change, we have prepared 3D pillared graphitic architectures (Figure 8B(a)) by intercalated growth of VA-CNTs into thermally expanded highly ordered pyrolytic graphite (HOPG) (Figure 8B(b)).⁵⁵ The resulting 3D pillared structure hybridized with nickel hydroxide coating showed a high specific capacitance (1065 F/g) with a remarkable rate capability and an excellent cycling ability (Figure 8B(c)).⁵⁵ The obtained specific capacitance (1065 F/g) is about 10 times that of high surface area activated carbons (<100 F/g)⁵⁶ and within the range of 953–1335 F/g for graphene-supported single-crystalline nickel hydroxide hexagonal nanoplates.⁵⁷ In these 3D non-covalently assembled graphene electrodes with a large

surface area, graphene and VA-CNTs can act as not only mechanical supports to relieve the cracking due to the volume change associated with metal oxides but also good conductive paths for electrons and ions, and hence the high capacitance and excellent rate capability.

5.2. Functionalized Graphene Assemblies as Electrodes in Supercapacitors and Batteries. Although graphene sheets with a large surface area are ideal electrode materials for energy storage, much of the graphene surface area is lost due to restacking via the strong π - π interaction. For energy storage applications, therefore, it is highly desirable to physically separate 2D graphene sheets to preserve the high surface area intrinsically associated with individual graphene sheets. In addition to the aforementioned 3D pillared graphene electrode, we have also used a solution layer-by-layer self-assembling approach (Figure 9A) to prepare multilayered hybrid carbon films of poly(ethyleneimine)-modified graphene sheets and acid-oxidized multiwalled CNTs (MWCNTs) for constructing supercapacitors with a relatively high specific capacitance of 120 F/g and rate capability (Figure 9B) as the well-defined interlayers of CNT networks allowed for not only a fast ion diffusion but also efficient electron transport.⁵⁸

In this regard, our recently reported on asymmetric functionalization of the two opposite surfaces of individual graphene sheets with different nanoparticles (Figure 9C),⁵⁹ in either a patterned or nonpatterned fashion, should have great promise for the use of the asymmetrically functionalized graphene sheets to fabricate 3D self-assembled functional electrodes (cf. Figure 1A(e)), including the aforementioned 3D pillared graphene architectures (Figure 8B). These inherently nanoporous 3D architectures with a large surface area and controllable porosity, tunable thermal, mechanical and electrical properties are attractive for many potential applications, including as new efficient electrodes for supercapacitors, batteries, fuel cells, and even solar cells.

6. Concluding Remarks

Graphene shows unique properties attractive for a wide range of potential applications. In order to meet specific requirements demanded for particular applications (e.g., energy conversion and storage), however, the surface functionalization of graphene materials is essential. Various covalent and noncovalent functionalization methods have been developed for preparing graphene materials with appropriate structures and properties. The edge of a graphene sheet has been demonstrated to be more reactive than its basal plane. Judicious application of the *site-selective*

functionalization methods to graphene sheets has opened up a rich field of graphene chemistry. In this Account, I have summarized our recent progress in the research on covalent and noncovalent functionalization of graphene, along with fabrication methods for constructing the functionalized graphene materials into energy conversion and storage devices with desirable characteristics. Even this brief Account has revealed the versatility of surface functionalization for making sophisticated graphene materials for efficient energy conversion and storage. Continued research in this exciting field should be very fruitful.

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FOOTNOTES

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