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Chapter 9

Porous Graphene Materials for Energy Storage and Conversion Applications

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Additional information is available at the end of the chapter

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Abstract

Porous graphene materials possess a unique structure with interconnected networks, high surface area, and high pore volume. Because of the combination of its remarkable architecture and intrinsic properties, such as high mechanical strength, excellent electrical conductivity, and good thermal stability, porous graphene has attracted tremendous attention in many fields, such as nanocomposites, lithium batteries, supercapacitors, and dye-sensitized solar cells. This chapter reviews synthesis methods, properties, and several key applications of porous graphene materials.

Keywords: porous graphene, synthesis, surface area, Li batteries, supercapacitors

1. Introduction

Porous materials are generally referred to materials containing pores or voids with different shapes and sizes. These porous structures have demonstrated unique properties and emerged as attractive candidates for a wide range of applications in medicine, catalysis, sensors, adsorbents, and energy storage and conversion [1–10]. Particularly, porous carbon is an exceptional material with a low density and high specific strength. It is also capable of bonding with other atoms through its sp, sp^2, and sp^3 hybrid orbitals. Among various carbon materials, graphene has received enormous attention because of its high surface area (2630 m^2/g), exceptional thermal conductivity (5000 W/m.K), high Young's modulus (1.0 TPa), and chemical stability. Studies have shown that it has a high intrinsic carrier mobility of 2×10^5 $cm^2/V.s$ and an excellent electrical conductivity of 10^6 S/cm at room temperature [11–13]. Graphene is a

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two-dimensional hexagonal lattice of sp^2 hybridized carbon atoms and since its discovery in 2004, significant efforts have been put in exploring its potential applications. Various synthesis methods have been developed to produce graphene including epitaxial growth of graphene on metal or SiC substrates [14, 15], chemical vapor deposition (CVD) [16–18], chemical reduction [19, 20], thermal reduction [21, 22], electrochemical synthesis [23, 24], and liquid phase exfoliation [25, 26]. However, because of the strong π-π stacking and van der Waals interactions between graphene sheets, the experimentally obtainable surface area is far below the theoretical value. To overcome this problem, increasing effort has been put to transforming graphene into porous structures to achieve higher surface area [27–29]. Along with the inherent properties of graphene, porous graphene has a clear edge over other porous carbon materials. For example, the excellent electrical conductivity can be used as a perfect current collector for the rapid diffusion of electrons/ions while its high mechanical strength provides mechanical stability to the porous framework. These unique properties make porous graphene a highly promising material for energy storage and conversion applications like lithium-ion batteries (LIBs), lithium-sulfur (Li-S) batteries, supercapacitors, the dye-sensitized solar cells (DSSCs), and fuel cells.

2. Synthesis of porous graphene

According to the standard specified by the International Union of Pure and Applied Chemistry (IUPAC), microporous materials have pore diameters of less than 2 nm, mesoporous materials have pore diameters between 2 and 50 nm, and macroporous materials have pore diameters of greater than 50 nm. There are basically two main methods, which can be used to fabricate porous graphene materials. These are the template and template-free methods, which will be described in greater details below.

2.1. Template approach

Template synthesis is an effective method for the transformation of graphene into porous graphene. It uses various inorganic and organic structures as templates for the transformation. Depending on the required size and morphology of pores, the appropriate template could be selected. This method can be divided into two categories: (1) soft-template method and (2) hard-template method.

2.1.1. Soft-template methods

Different kinds of amphiphilic molecules, such as surfactants and copolymers are used as structure directing agents under mild operating conditions in the soft-template methods. A bottom-up approach has been used for the preparation of mesoporous materials with two-dimensional (2D) sandwich structure consisting of graphene layers and mesoporous silica with the use of cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) [30]. The presence of oxygen functionalized groups makes graphene oxide (GO) sheets negatively charged. CTAB has the capability of electrostatically adsorbing and self-assembling onto the surface of negatively charged GO in alkaline solution. The GO-based silica hybrid is formed after the

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hydrolysis of silicon precursor, tetraethylorthosilicate (TEOS), and removal of CTAB. Thermal annealing at high temperature gives graphene-based silica sheets. The adsorption data have indicated a high specific area of 980 m^2/g. In another method, mesostructured graphene-based SnO_2 composite is prepared by hydrothermally treating a suspension of GO, CTAB, and $SnCl_4$ [31].

Two-dimensional ordered mesoporous carbon nanosheets have been prepared by low molecular weight phenolic resols on graphene sheets using a triblock copolymer called Pluronic F-127 as the structure-directing agent [32]. After mixing an aqueous GO dispersion with the above prepolymer, hydrothermal treatment and further thermal annealing were carried out to prepare mesoporous carbon/graphene composite. It was reported that, Brunauer-Emmett-Teller (BET) surface area decreases with increase in the GO ratio in the composite. In another case, the same hydrothermally driven low-concentration micelle assembly approach was used with the help of anodic aluminum oxide (AAO) membranes to provide a large surface area [33]. After the hydrothermal treatment, AAO membrane was carbonized at 400–500°C for 2 h in argon atmosphere, followed by further carbonization at 700°C for 2 h in the same environment. Finally, mesoporous graphene sheets were obtained by dissolving the AAO substrate (**Figure 1**). The TEM images suggest that these nanosheets displayed ordered mesostructures, having an average pore size of 9 nm and wall thickness of 4 nm. Wen et al. [34] used a dual template method with Pluronic F-127 as the soft template and SiO_2 as the hard template to fabricate three-dimensional graphene-based hierarchically porous carbon (3DGHPC). Carbonization was carried out to convert the layer of coated polymers on SiO_2 spheres to carbon phase and simultaneously reduce GO. Finally, the 3DGHPC was obtained by treating as-prepared composite with 10% HCl to remove the SiO_2 template followed by plenty of washing with Deionized (DI) water and drying at 50°C for 24 h. The as-prepared 3DGHPC displayed a specific area of 384.4 m^2/g with a pore volume of 0.73 cm^3/g.

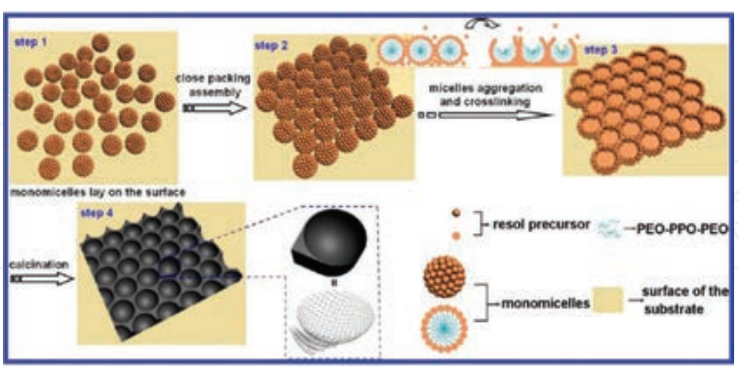


Figure 1. Schematic representation of the formation of ordered mesoporous graphene nanosheets [33]. Reprinted with the permission of the American Chemical Society.

2.1.2. Hard-template methods

When preparing porous graphene by hard template method, the template should initially be prepared. This includes the preparation of hard template itself and functionalization of its

surface to get the required properties. Then, depending on the requirement, the template should be coated with graphene or GO. The final step is the selective removal of the template without destroying its structure.

Huang et al. [35] used methyl group grafted silica spheres as a hard template to prepare nanoporous graphene foams. These graphene foams had pore sizes of 30–120 nm and ultrahigh pore volumes of 4.3 cm^3/g. The surface area was reported to be 851 m^2/g. Hydrophobic surface of methyl group grafted silica spheres interacts with the hydrophobic basal planes of GO to induce self-assembled lamellar like structures. Choi et al. [36] were able to use polystyrene (PS) colloidal particles as sacrificial templates to synthesize macroporous embossed chemically modified graphene (CMG) sheets with an average pore size of 2 μm. Initially, free-standing PS/CMG film was made by vacuum filtration of a mixed suspension of CMG and PS. PS particles were then removed to generate 3D macropores. Three-dimensional macroscopic graphene foams (GFs) were made by the chemical vapor deposition (CVD) method using nickel (Ni) foam as the 3D scaffold template followed by the removal of the template by hot HCl [37–43]. In 2011, Cheng et al. [44] reported a flexible 3D GF using template directed CVD. The as-prepared GF had a specific surface area, up to 850 m^2/g, corresponding to an average number of layers of ~3. Poly methyl methacrylate (PMMA) can be used as a hard template to prepare macroporous graphene materials. Chen et al. [45] fabricated macroporous bubble graphene film by PMMA directed ordered assembly method. GO was mixed with the PMMA suspension and vacuum filtration was conducted to make a sandwich type assembly of the PMMA spheres and GO. Composite film was then peeled off from the filter, air dried and calcinated at 800°C to remove the template and reduce GO. As-prepared macroporous graphene film has a specific surface area of 128.2 m^2/g with an average pore diameter of 107.3 nm.

2.2. Template-free approach

In the template-free approach, defects are introduced in the graphene basal planes by different methods. Chemical etching or chemical activation is one such method which had been used extensively to prepare porous carbon materials. It is an effective and relatively easy method to fabricate porous graphene sheets without using any template.

Zhu et al. [46] produced porous carbon by a simple activation with KOH of microwave exfoliated GO (MEGO) and thermally exfoliated GO (TEGO). A mixture of the MEGO and KOH was thermally treated for 1 h at 800°C in a tube furnace in argon atmosphere at a pressure of 400 torr. Pores ranging from ~1 to ~10 nm were generated in the carbon matrix by the activation with KOH. The activation of carbon with KOH proceeds as, $6KOH + C \leftrightarrow 2K + 3H_2 + 2K_2CO_3$, followed by the decomposition of K_2CO_3 and reaction of $K/K_2CO_3/CO_2$ with carbon [46, 47].

Porous graphene hybrids can also be produced by thermally treating a mixture of graphene and porous components [48–55]. Rui et al. [48] produced a V_2O_5/rGO composite by thermal pyrolysis of a hybrid of vanadium oxide (VO) and rGO at the temperature of 350°C for 30 min under a heating rate of 10°C/min in air. In the thermal pyrolysis process, reduced VO (rVO) is converted into polycrystalline V_2O_5 porous spheres ranging from 200 to 800 nm.

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Apart from using organic and inorganic species to carry out the template-free approaches to produce porous graphene, the amphiphilic nature of GO itself can also be used to fabricate foam-like structures of macroscopic graphene. The pore sizes of these 3D macroscopic structures are in the range of submicrometer to several micrometers. Because of macroscopic nature, they possess high mechanical strength, compressibility, excellent conductivity, and adsorption characteristics [56–59]. Xu et al. [60] prepared a self-assembled graphene hydrogel (SGH) by heating the GO dispersion sealed in a Teflon-lined autoclave at 180°C for 12 h. The hydrothermally reduced GO had a well-defined 3D interconnected porous network (**Figure 2**). The framework of SGH was assembled on partial overlapping of flexible graphene sheets because of π-π stacking interactions. The as-prepared SGH showed excellent mechanical strength and a good electrical conductivity of 5×10^3 S/cm. Later, the same research group reported a highly conductive graphene hydrogel which was reduced by hydrazine hydrate or hydrogen iodide to improve the conductivity by further removing its residual oxygenated groups [61].

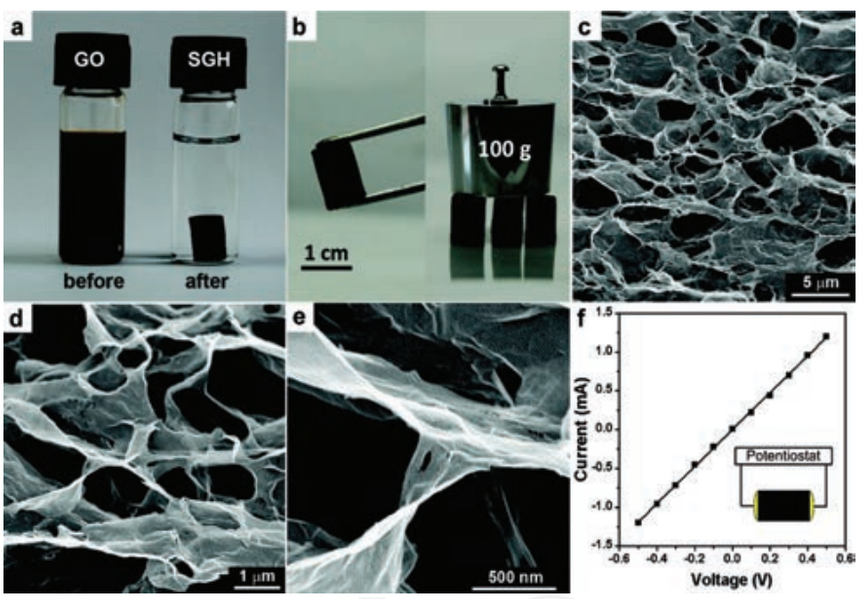


Figure 2. (a) Photographs of a 2 mg/ml homogeneous GO aqueous dispersion before and after hydrothermal reduction at 180°C for 12 h; (b) photographs of a strong SGH allowing easy handling and supporting weight; (c-e) SEM images with different magnifications of the SGH interior microstructures; (f) room temperature *I-V* curve of the SGH exhibiting Ohmic characteristic, inset shows the two-probe method for the conductivity measurements [60]. Reprinted with the permission of the American Chemical Society.

3. Applications of porous graphene materials

Unique porous structure of graphene along with its superior properties makes graphene a potential candidate for energy storage and conversion applications. The following sections review several key applications of porous graphene in LIBs, Li-S batteries, supercapacitors, and the dye-sensitized solar cells.

3.1. Lithium-ion batteries

Lithium-ion battery has a widespread increasing demand because of its high energy density, flexibility, low maintenance, and longer lifespan compared with other battery technologies [62]. To further increase the energy density, charging efficiency, and cycle life of lithium-ion batteries, it is essential to look at new electrode materials that have good lithium storage capability. Porous graphene with exceptional properties holds a great potential as an electrode material for the lithium-ion battery. The high surface area of graphene can significantly increase the diffusion of lithium ions and electrons. Furthermore, the superior electrical conductivity provides a good conductive network within the electrodes. Graphene can construct a 3D framework with a strong tolerance to the volume change of electrochemically active materials during charge-discharge cycles [63].

An anode material for Li-ion battery was made by hierarchical mesoporous and macroporous carbon using the spinodal decomposition of a mesophase pitch (MP) carbon precursor and polystyrene as a soft template [64]. Scanning Electron Microscope (SEM) images of this structure revealed a 3D bicontinuous network of macropores and according to Hg porosimetry the average macropore size was recorded as 100 μm. The first reversible capacity of 470 mAh/g was recorded at a discharge-charge rate of C/5. When discharge-charge rates were increased to 1 and 5 C, reversible capacities of 320 and 200 mAh/g were obtained. Yang et al. [30] managed to synthesize a graphene-based mesoporous carbon anode which performed better than previous graphitic anode. Two-dimensional sandwich like graphene structure increases the surface area while each nanosheet acts as a mini-current collector. They facilitate the rapid transportation of electrons during charge-discharge cycles. At the rate of C/5, its reversible capacity stabilized at 770 mAh/g. When the discharge-charge rates were increased to 1 and 5 C, the reversible capacities recorded 540 and 370 mAh/g, respectively.

Graphene materials loaded with macroporous structures have shown positive results as anode materials for the Li-ion batteries. Mn_3O_4-graphene [65], Co_3O_4-graphene [66], and Fe_3O_4-graphene [67–69] have been studied extensively as potential anode materials for Li-ion materials. Chen et al. [69] reported a 3D graphene-Fe_3O_4 hybrid prepared by chemical reduction of the GO in the presence of Fe_3O_4 nanoparticles. The as-prepared hybrid was tested as an anode material for LiBs and exhibited capacities of 990 and 730 mAh/g at current densities of 800 and 1600 mA/g, respectively.

3.2. Li-sulfur batteries

For more than 20 years, the Li-ion battery has dominated the rechargeable battery market for portable devices and it is still the best choice for electric vehicles. But, when it comes to the electrical performance, a significant improvement is less likely as the performance of the Li-ion battery has almost reached its theoretical limits [70, 71]. Therefore, Li-S battery is considered as one of the potential candidates to replace the Li-ion battery as the next generation rechargeable battery. Sulfur is considered as the 10th most abundant element in the Earth. When employed as a cathode, it has a high specific capacity of 1675 mAh/g and it can deliver a specific energy of 2600 Wh/kg. However, several key issues have prevented the practical applications of Li-S batteries so far. The issues which need to be addressed are (i) poor electrical

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conductivity of sulfur and its final discharge products (Li_2S/Li_2S_2); (ii) large volume change of sulfur electrode during electrochemical cycling; and (iii) dissolution of polysulfides, intermediate reactant products in the organic electrolyte leading to deposition of Li_2S_2/Li_2S at the electrode interface. To overcome these drawbacks, extensive researches have been carried out to use graphene materials as scaffolds for cathodes in Li-S batteries [72–76].

For the first time, Wang et al. [77] synthesized a sulfur-graphene (S-GNS) composite by heating a mixture of graphene nanosheets and elemental sulfur. The electrochemical performance of the battery was unsatisfactory as S-GNS electrode contained only 17.6 wt% sulfur. Wang et al. [78] improved the performance of this cathode by increasing the sulfur content up to 44.5 wt % using the same synthesis method. The reversible capacities of the electrode were recorded as 662 mAh/g at 1 C and 391 mAh/g at 2 C after 100 cycles.

Kim et al. [79] produced mesoporous graphene-silica composite (m-GS) as a cathode structure to host sulfur for Li-S batteries. With the help of the ternary cooperative assembly of triblock copolymer (P123), silica precursor and graphene, porous silica structure was made parallel to graphene sheets. Sulfur was infiltrated into the mesoporus structure by melt diffusion at 155°C for 12 h. S intercalated graphite oxide cathode was made by in situ sulfur reduction and intercalation of graphite oxide [80]. By heating a mixture of S_8 and graphite oxide at 600°C under vacuum, would break large molecules of S_8 into S_2 and in the meantime reduce graphite oxide to graphene. Interplanar distance of the carbon matrix allows S_2 to intercalate into GO. To minimize the capacity decay, surface S_8 could be removed by CS_2. This specified cathode was able to maintain a reversible capacity of 880 mAh/g after 200 cycles.

To obtain better electrochemical performance, Zhang et al. [81] created dense nanopores on the surface of graphene nanosheets by chemically activating hydrothermally reduced graphene oxide (rGO). Sulfur was infiltrated into the KOH-activated graphene hydrogels by the melt diffusion method (**Figure 3**). The rGO hydrogel served as a trap for soluble polysulfides.

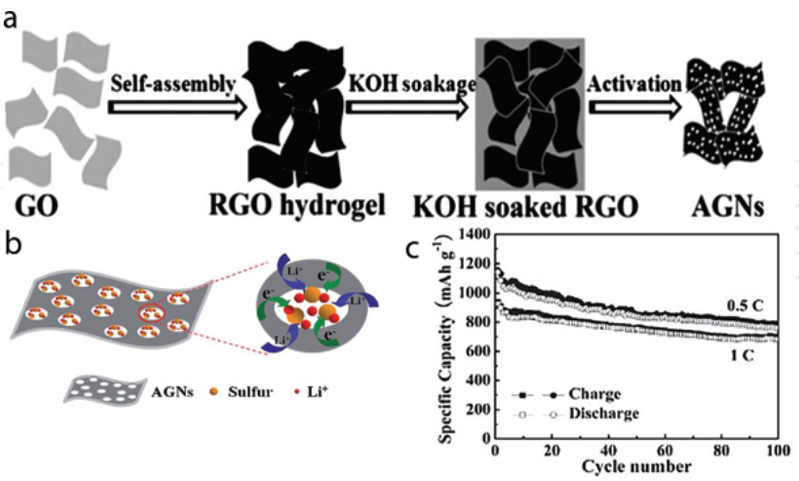


Figure 3. (a) Schematic representation of the preparation route of activated graphene nanosheets through self-assembly of GO, ion diffusion and chemical activation strategy. (b) Proposed scheme for the constrained electrochemical reaction process of the graphene/sulfur composite. (c) Cycling performances of graphene/sulfur composite electrode at 0.5 C and 1 C [81]. Reprinted with the permission of the Royal Society of Chemistry.

According to results from nitrogen sorption measurements, the surface area of the mesoporous system was 2313 m^2/g and the mean value of nanopores was 3.8 nm. At 0.5 C and 1 C, the graphene/sulfur composite electrode delivered high reversible capacities of 1143 and 927 mAh/g, respectively.

Evers and Nazar [82] prepared a graphene-sulfur cathode material with a sulfur loading of 87 wt% by a simple one pot method. A mixture of GO and soluble polysulfide was oxidized *in situ* as a one pot reaction. Because of the formation of insulating Li_2S layer, the initial discharge capacity of 705 mAh/g at 0.2 C decreased drastically after 50 cycles. S/rGO composite material for Li-S battery cathode was made by concurrently oxidizing sulfide and reducing GO [83]. In this method, Na_2S and Na_2SO_3 were mixed with the GO solution. The composite material is obtained by the reduction of GO by Na_2S. The composite with a sulfur loading of 63.6 wt% delivered a reversible capacity of 804 mAh/g after 80 cycles at 0.186 C and 440 mAh/g after 500 cycles at 0.75 C. Gao et al. [84] prepared a sulfur cathode composed of sulfur nanoparticles wrapped in graphene by using $Na_2S_2O_3$ as a precursor of sulfur. In acidic medium, $Na_2S_2O_3$ can also serve as a reducing agent of GO. Polyvinylpyrrolidone (PVP) was used to prevent the S particles from aggregation and to keep the sulfur particles at submicrometer range. By using $(NH_4)_2S_2O_3$ as a sulfur precursor, Xu et al. made a graphene-encapsulated sulfur composite. In this synthesis method, a mild reducing agent, urea, was used to reduce GO.

3.3. Supercapacitors

Supercapacitor is another major alternative solution for the energy storage applications. Supercapacitors have higher power densities than batteries and also higher energy densities than dielectric capacitors [46, 85–88]. The first attempt to use graphene as a supercapacitor was done by Rouff et al. [89] in 2008. In that method, GO was reduced by using hydrazine hydrate and the surface area as measured by BET method was 705 m^2/g. Specific capacitances of 135 and 99 F/g were obtained in aqueous and organic electrolytes, respectively. However, strong π-π stacking and van der Waals attractions among inter layers cause irreversible agglomeration to form graphite, resulting a decrease in surface area which may hinder the diffusion of the electrolyte. Therefore, making graphene in to a highly open porous structure is an effective way to increase the accessible surface area and the specific capacitance.

Zhu et al. [46] were able to make a carbon based supercapacitor by chemically activating the microwave exfoliated GO (MEGO) and thermally exfoliated GO (TEGO) using the KOH to obtain surface area values up to 3100 m^2/g and a high electrical conductivity of 500 S/m with a C/O atomic ratio of 35 . The specific capacitance values calculated from the charge-discharge curves were 165, 166, and 166 F/g at current densities of 1.4, 2.8, and 5.7 A/g, respectively.

Chen et al. [90] discovered a route to convert noncovalent functionalized graphene to a graphene-activated carbon composite by chemically activating with the KOH, which consisted of a specific surface area of 798 m^2/g. Stable graphene colloids absorbed by oligomers of p-phenylene diamne (PPD) were converted to a graphene-activated carbon composite by the KOH activation annealing method. The KOH activation created micro/mesopores in the

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activated carbon covered on graphene whereas pores in activated carbon also contributed the high surface area of the composite. The as-prepared graphene composite exhibited a specific capacitance of 122 F/g and energy density of 6.1 Wh/kg in aqueous electrolyte. Maximum energy density values of 52.2 and 99.2 Wh/kg were obtained in 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) electrolyte at room temperature and 80°C, respectively.

Zhang et al. [91] introduced a method to produce porous 3D graphene-based bulk materials with ultrahigh specific area of 3523 m^2/g and excellent bulk conductivity (up to 303 S/m) by *in-situ* hydrothermal polymerization/carbonization of a mixture of industry carbon sources and the GO followed by KOH activation (**Figure 4**). The carbon sources used in this method were biomass, phenol-formaldehyde (PF), polyvinyl alcohol (PVA), sucrose, cellulose, and lignin. Graphene-PF composite material gave the highest specific capacitance values of 202 F/g in 1 M $TEABF_4$/AN and 231 F/g in neat $EMIMBF_4$ electrolyte systems, respectively.

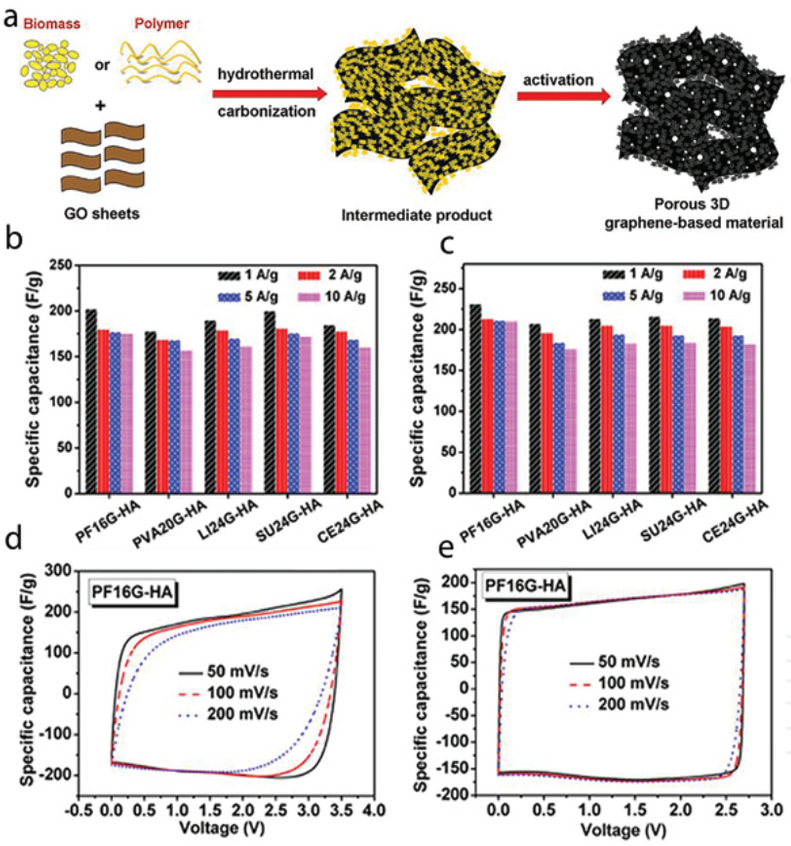


Figure 4. (a) Schematic representation of the synthesis procedure of the porous three-dimensional graphene-based materials. Galvanostatic charge/discharge test results of supercapacitors based on the optimized porous 3D graphene-based materials in (b) 1 M $TEABF_4$/AN and (c) neat $EMIMBF_4$ electrolytes under different current densities. CV curves of PF16G-HA based supercapacitor under different scan rates in (d) 1 M$TEABF_4$/AN and (e) neat $EMIMBF_4$ electrolyte. Reproduced with permission [91], Copyright 2013 NPG.

The electrochemical performance of carbon based materials can be enhanced by doping carbon network with nitrogen and boron [92–95]. Nitrogen and boron co-doped 3D graphene aerogel

(BN-GA) was fabricated by using the GO and ammonia boron trifluoride (NH_3BF_3) [96]. The interconnected framework of graphene nanosheets had a surface area of 249 m^2/g with a macroporous structure. BN-GAs were directly processed into thin electrodes without destroying the 3D continuous frameworks and used in all-solid-state supercapacitors (ASSSs). Because of the unique structure and strong synergetic effects of nitrogen and boron co-doping, a specific capacitance of 62 F/g and energy density of 8.65 Wh/kg were obtained. 3D graphene aerogels with mesoporous silica frameworks (GA-SiO_2) were fabricated by the hydrolysis of TEOS with graphene aerogel and CTAB as the soft template [97]. Graphene aerogel-mesoporous carbon (GA-MC) with a surface area of 295 m^2/g was generated by infiltrating a sucrose solution into the GA-SiO_2 followed by carbonization at 700°C for 3 h in argon. The as-prepared GA-MC exhibited a specific capacitance of 226 F/g when it was used as a supercapacitor.

3.4. Dye-sensitized solar cells

The dye-sensitized solar cells are among third generation photovoltaic devices that are cost-effective and highly efficient. It consists of a mesoporous TiO_2 photoanode with a dye to increase light absorption, a counter electrode (CE), and electrolyte. The CE should reduce redox species, which are used to regenerate the sensitizer after electron ejection. To increase the efficiency of DSSC, it is essential to select a CE material with low sheet resistance, high catalytic activity for the reduction of redox species, excellent chemical stability, and low cost. Recently, graphene-based CEs have been studied extensively as a potential cost-effective replacement for platinum based CEs.

Compared with other graphene-based materials, functionalized or doped graphene exhibits exceptional electocatalytic activity. In 2012, Xu et al. prepared Hemin, an iron-containing porphyrin functionalized rGO by microwave irradiation [98]. The Hemin-rGO hybrid exhibited a power conversion efficiency (PCE) value of 2.45 %. Yen et al. [99] reported a nitrogen-doped graphene prepared using a hydrothermal method. The nitrogen-doped domains on the graphene surface act as electroactive sites, which have selectivity for redox species in the reduction reaction. The as-prepared nitrogen-doped graphene CE exhibited the PCE value of 4.75%. Xue et al. [100] managed to prepare 3D nitrogen-doped graphene foams with a nitrogen content of 7.6% freeze drying the GO foams followed by annealing at 800°C in ammonia/argon mixture for 1 h. Because of the high content of nitrogen, the PCE value of 7.07% was obtained.

4. Conclusion

In conclusion, owing to its high surface area, unique pore structure, and remarkable electrochemical performances, porous graphene has attracted great attention in the fields of energy storage and conversion. However, there are several key issues, which need to be addressed. The precise control of pore size, pore morphology, and wall thickness is necessary for the assembly of hierarchically structured porous graphene materials. Introduction of different sizes of pores into graphene matrix is essential to produce porous graphene materials to obtain

synergic effects of different pores. With increasing research efforts in the field, we believe that there would be significant advances in the synthesis and application of porous graphene in the near future, benefiting development of high performance energy conversion and storage devices. This research was partially supported under the Australian Research Council Discovery Project (DP150101717). Kimal Chandula Wasalathilake acknowledges the QUTPRA scholarship from the Queensland University of Technology.

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