

# Preparation of Porous Graphene-Based Nanomaterials for Electrochemical Energy Storage Devices

Yuanzhe Piao

**Abstract** Graphene-based nanostructures exhibit good mechanical strength, high porosity, outstanding electrical conductivity, and excellent thermal and chemical stability, which in addition to its low cost, versatile functionalization chemistry, and relative ease of large-scale preparation make it ideally suited to serve as a key component for the development of new electrode materials. Recently, a wide variety of methods have been developed for the formation of porous graphene architectures to further improve the performances. Porous graphene provides abundant pathways for rapid ion diffusion and high accessible surface area. In this chapter, the recent continued breakthroughs in the preparation of porous graphene-based nanoarchitectures as well as their applications as electrode materials for electrochemical energy storage devices are introduced.

**Keywords** Graphene · Porous · Electrochemistry · Electrochemical energy storage · Nanostructures · Lithium-ion rechargeable batteries · Supercapacitors

## 1 Introduction

Graphene is an atomic single layer of honeycomb carbon lattice. Recently, graphene and graphene-based nanomaterials have attracted increased attention because of their unique properties and great potential for numerous applications [3, 14, 21, 33, 36–38, 51, 63]. In particular, research on graphene-based nanomaterials for electrochemical energy storage has progressed rapidly during recent years due to the increasing demand for the development of these storage devices with improved performance including high energy, power density, and excellent cycle stability,

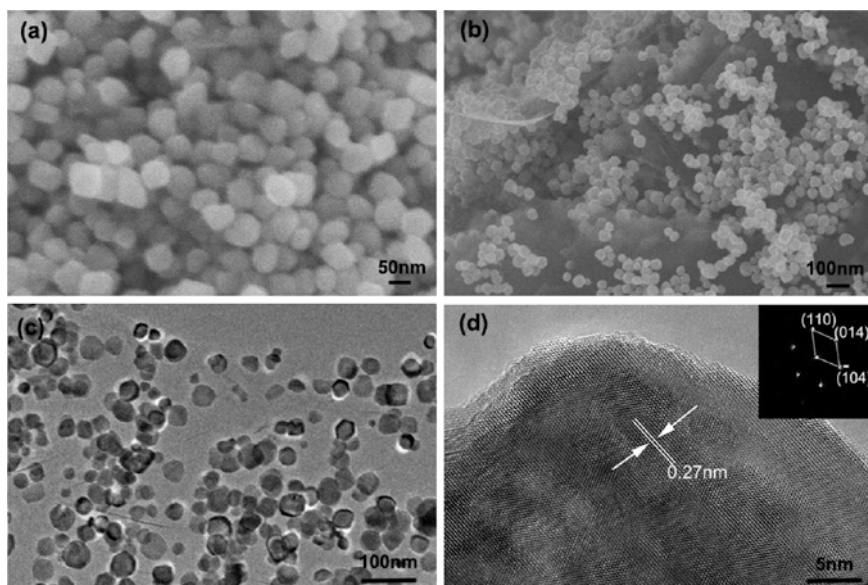
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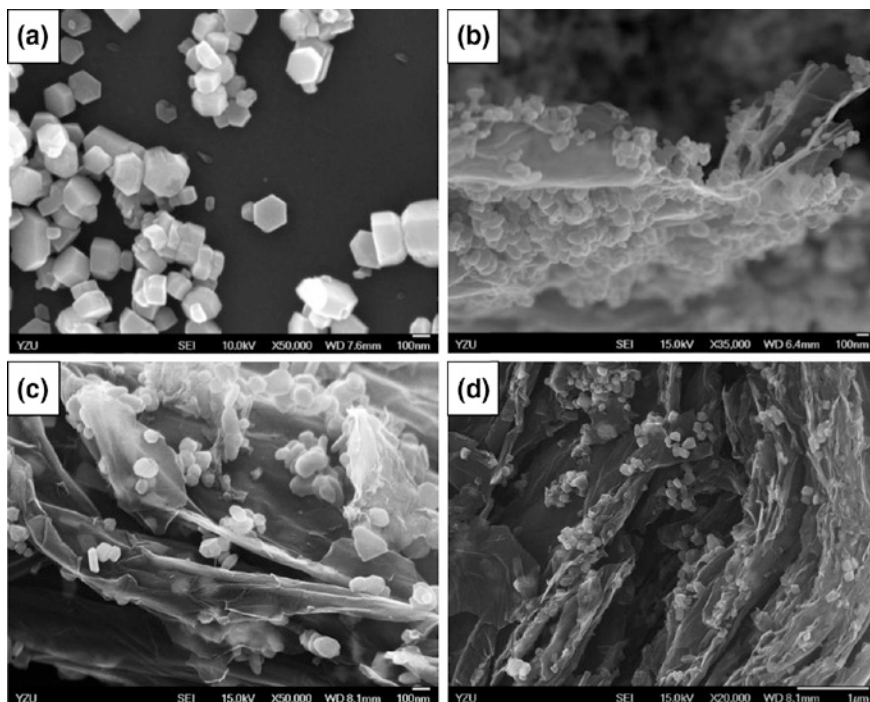
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while maintaining low production cost [15, 43, 44, 71, 76, 83, 92]. Among various carbon materials, graphene has awakened a tremendous interest because of its superior electronic conductivity, large theoretical specific surface area, and physicochemical stability [22, 30, 52]. These interesting properties make graphene and graphene-based nanomaterials promising electrode materials for various electrochemical energy storage devices (e.g., supercapacitors and batteries), which have a wide range of applications from microelectromechanical systems to portable electronic devices, and to electric vehicles.

Graphene-based nanomaterial from graphite oxide is being manufactured in large scale at relatively low cost [58]. During the past decade, various graphene-based nanomaterials (Figs. 1, 2, and 3) have been investigated as potential electrode materials with high specific capacity and long cycle stability [26, 29, 31, 40–42, 46, 48, 53, 62, 82]. However, in spite of the previous efforts to prepare better electrochemical energy storage devices by using graphene, market demand for higher performances of these devices are ever increasing. For lithium-ion batteries, since lithium ions cannot pass through the carbon atomic arrays in 2D sheets of graphene, therefore, lithium ions have to tortuously detour to reach the electrolyte. This results in a longer diffusion distance and slow charge–discharge rate in lithium-ion battery systems [35, 65]. Supercapacitors, also called ultracapacitors or electrochemical capacitors, store electrical charge on high-surface-area conducting materials. Their widespread use is limited by their low energy storage density and



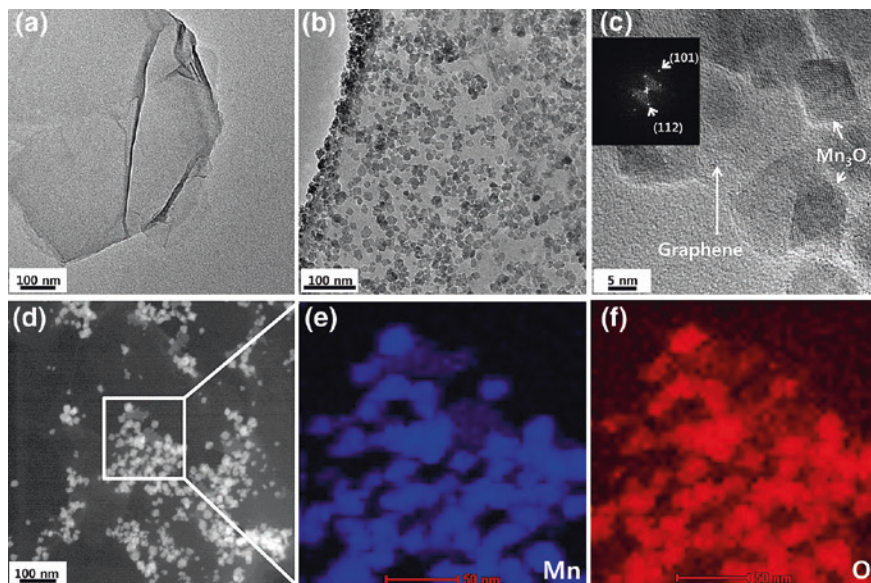
**Fig. 1** a SEM image of  $\text{Fe}_2\text{O}_3$ ; b SEM image of  $\text{Fe}_2\text{O}_3/\text{graphene}$ ; c TEM image of  $\text{Fe}_2\text{O}_3/\text{graphene}$ ; d TEM image of  $\text{Fe}_2\text{O}_3/\text{graphene}$  in high resolution. Reproduced from Ref. [82] with permission from Elsevier



**Fig. 2** FE-SEM photographs of **a** ZnO nanocrystals and different types of ZnO@GN hybrids, **b** ZnO@GN-1, **c** ZnO@GN-2, and **d** ZnO@GN-3. Reproduced from Ref. [26] with permission from Elsevier

relatively high effective series resistance. As previously reported, the theoretical specific surface area of a single graphene sheet is extremely high ( $\sim 2600 \text{ m}^2 \text{ g}^{-1}$ ) [64]. However, the real accessible surface areas of graphene-based materials are far below this value, mainly due to the strong aggregation tendency of graphene sheets (Fig. 4).

To surmount these challenges, graphene sheets were further treated into porous structures which mean abundant pathways for rapid lithium-ion diffusion [79] and to achieve higher accessible surface area [90]. Due to its unique structural and electronic characteristics, a porous graphene opens up new opportunities for the development of electrode materials with novel nanoarchitectures in electrochemical energy storage devices. In this chapter, recent advances and novel strategies in the preparation of porous graphene architectures as well as their applications as electrode materials for electrochemical energy storage devices are introduced. Finally, the future prospects in the development of graphene-based nanocomposite materials with improved energy storage performances are discussed.



**Fig. 3** TEM images of **a** GO before the one-step in-situ transformation reaction, and **b**  $\text{Mn}_3\text{O}_4/\text{GNS}$  composite after the one-step in-situ transformation reaction. **c** HRTEM image of individual  $\text{Mn}_3\text{O}_4$  nanoparticle in  $\text{Mn}_3\text{O}_4/\text{GNS}$  composite; the inset shows the electron diffraction pattern of  $\text{Mn}_3\text{O}_4$  nanoparticle in  $\text{Mn}_3\text{O}_4/\text{GNS}$  composite. **d** HAADF-STEM image of  $\text{Mn}_3\text{O}_4/\text{GNS}$  composite and EDS element mapping results for **e** Mn and **f** O species of  $\text{Mn}_3\text{O}_4/\text{GNS}$  composite. Reproduced from Ref. [48] with permission from Elsevier

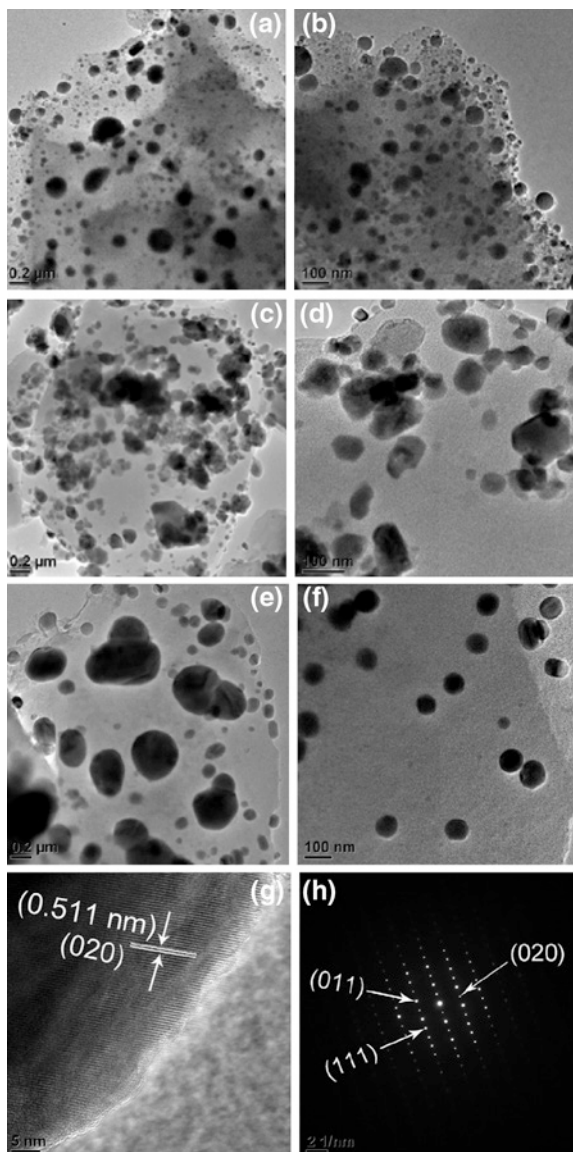
## 2 Strategies to Buildup Porous Graphene

A wide variety of strategies have been developed for the formation of porous graphene architectures as outlined in Table 1. These can be roughly divided into two categories. One is the in-plane generation of defective pores into the graphene sheets and the other is the out-of-plane generation of 3D graphene-based porous superstructures (Scheme 1) (Figs. 5 and 6).

### 2.1 Generation of Defective Pores into the Graphene Sheets

When etching of graphene is performed under appropriate acid/oxidizer solution, carbon erosion will occur. Accordingly, porous graphene is produced when graphene oxide dispersed in water is treated with acid/oxidizer solution under sonication [84] or microwave irradiation [18].  $\text{HNO}_3$  and  $\text{KMnO}_4$  are typical examples of acid and oxidizer used.

**Fig. 4** TEM images of **a** and **b** LFP/CA-1, **c** and **d** LFP/CA-2, and **e** and **f** LFP/CA-3. And **g** HRTEM image and **h** SAED pattern of the  $\text{LiFePO}_4$  particle in LFP/CA-3. Reproduced from Ref. [79] with permission from Elsevier

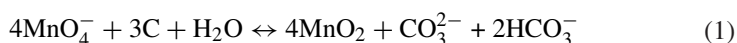


Fan et al. [18] investigated the preparation of porous graphene using  $\text{KMnO}_4$  as oxidizer under microwave irradiation (Fig. 7). The obtained porous graphene revealed a pore size of approximately 3 nm and a specific surface area of  $1374 \text{ m}^2 \text{ g}^{-1}$ .

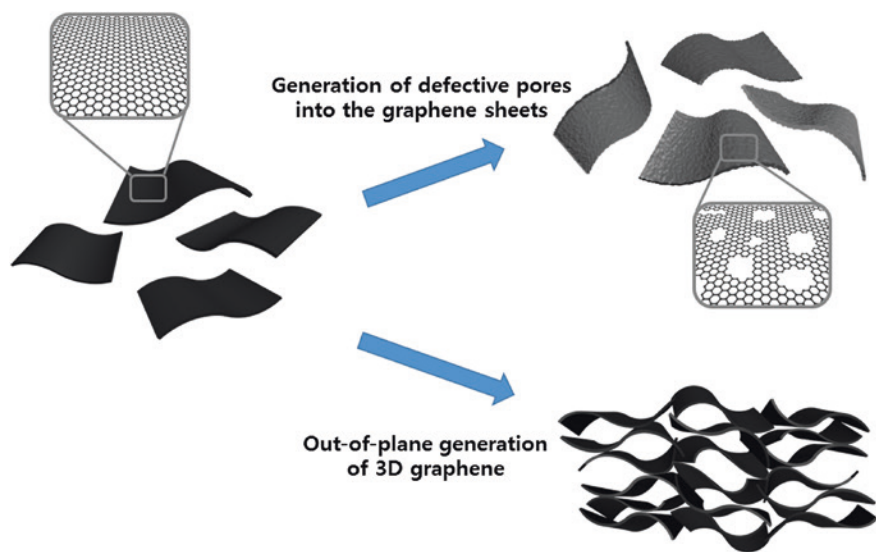
**Table 1** Typical strategies for the formation of porous graphene

Method	Detail	Pore	Pore size	Specific surface area	Example
Acid/oxidizer	HNO <sub>3</sub> , microwave	meso/macro	7–600 nm	15–25 m <sup>2</sup> /g	[88]
	HNO <sub>3</sub> , microwave	macro	100–1000nm	784 m <sup>2</sup> /g	[84]
	KMnO <sub>4</sub> , microwave	meso	3 nm	1374 m <sup>2</sup> /g	[18]
	KMnO <sub>4</sub> , HCl, H <sub>2</sub> O <sub>2</sub>	meso	–	81 m <sup>2</sup> /g	[11]
Base	KOH	micro/meso	0.6–5 nm	3100 m <sup>2</sup> /g	[90]
	KOH	micro/meso	~5 nm	2400 m <sup>2</sup> /g	[86]
	KOH	micro/meso	1–10 nm	3523 m <sup>2</sup> /g	[87]
Hard template	Silica	meso	32.5 nm	851 m <sup>2</sup> /g	[27]
	Silica	macro	140 nm	412 m <sup>2</sup> /g	[2]
	PMMA	macro	107.3 nm	128.2 m <sup>2</sup> /g	[9]
	SPS, PVP, Ni foam	micro/meso/ macro	–	70 m <sup>2</sup> /g	[68]
	PS	macro	2000 nm	–	[13]
	Ice template	macro	–	–	[66]
	Ice template	macro	–	–	[17]
Deposition	Chemical vapor deposition	macro	~100 μm	670 m <sup>2</sup> /g	[56]
	Chemical vapor deposition	macro	–	–	[8]
	Chemical vapor deposition	macro	–	1654 m <sup>2</sup> /g	[50]
	Electrochemical deposition	macro	100–1000nm	1000 m <sup>2</sup> /g	[10]
Hydrothermal	Hydrothermal	meso	20 nm	–	[24]
	Hydrothermal	meso	9 nm	281 m <sup>2</sup> /g	[20]
	Hydrothermal	macro	~1000 nm	–	[67]
	Hydrothermal	macro	–	–	[74]
	Hydrothermal	macro	–	–	[1]
Others	Polymer, thermal decompose	micro/meso	30 nm	1720 m <sup>2</sup> /g	[77]
	Self-assembly	macro	1000 nm	–	[39]

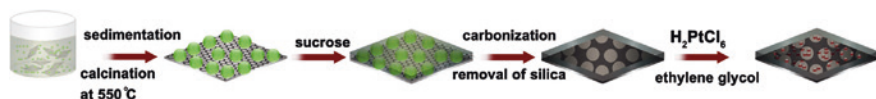
The following equation shows the reaction of carbon with KMnO<sub>4</sub>:



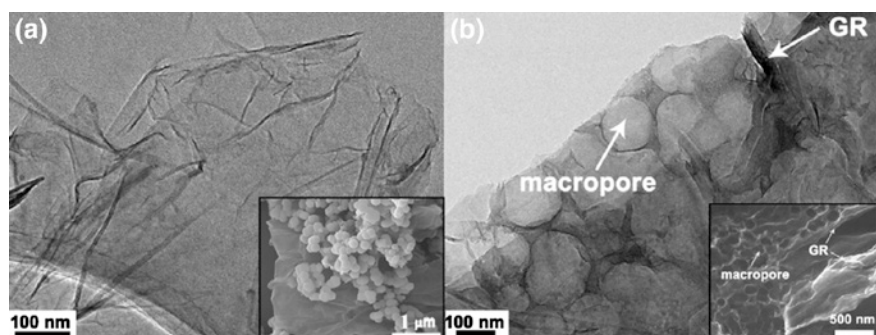
Porous graphene could also be produced by using a strong base. Romanos et al. [57] presented nanospace engineering of KOH-activated carbon. It is reported that



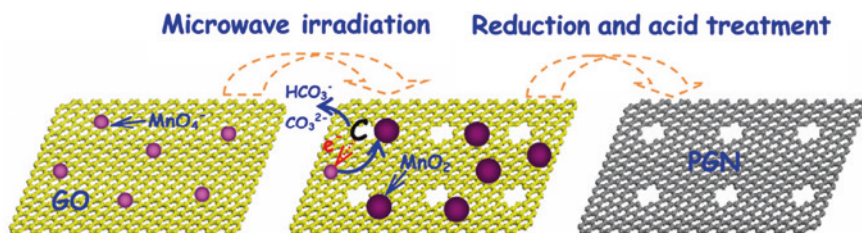
**Scheme 1** Schematic illustration of in-plane generation of defective pores into the graphene sheets and out-of-plane generation of 3D graphene-based porous superstructures



**Fig. 5** Preparation pathway of the MC-GR and Pt/MC-GR composites. Reproduced from Ref. [2] with permission from Elsevier



**Fig. 6** **a** TEM image of GR. Inset shows SEM image of SiO<sub>2</sub>-GO after calcination. **b** TEM image of MC-GR. Inset shows SEM image of MC-GR. Reproduced from Ref. [2] with permission from Elsevier



**Fig. 7** Illustration of the formation of porous graphene material with pores on the surface of sheet. Reproduced from Ref. [18] with permission from Elsevier

high specific surface areas, porosities, subnanometer (<1nm), and suprananometer (1–5 nm) pore volumes could be quantitatively controlled by a combination of KOH concentration and activation temperature. Recently, the chemical process was used to prepare chemically activated graphene. Typical examples of these bases are KOH and NaOH. After chemical activation, the specific surface area of the porous graphene is increased to become closer to the theoretical value [86, 90].

## 2.2 Out-of-Plane Generation of 3D Graphene-Based Porous Superstructures

Besides the in-plane generation of defective pores into the graphene sheets, 3D graphene-based out-of-plane porous superstructures could be built up. Using the hard template approaches, graphene layers were deposited on inorganic/organic particles larger than 50 nm or in situ grown on metallic porous frameworks followed by the elimination of template that can result into graphene-based materials with 3D porous structures.

Using uniform polymethyl methacrylate (PMMA) latex spheres as hard templates, Chen et al. [9] prepared a controllable 3D macroporous bubble graphene film with tailorable microstructure. Zhao et al. [27] developed a novel hydrophobic interaction-driven hard templating approach for the rational designed preparation of nanoporous graphene foams with controlled pore size, high surface area, and ultra-large pore volume. Monodisperse silica particles were used as the templates to prepare nanoporous graphene foams. The generated graphene foams show the highest total pore volume value in all the reported porous graphene materials. Additionally, they demonstrated that metal oxide nanoparticles can be easily decorated on the pore walls, due to the ultra-large open-porous feature and the homogeneous hydrophobic surface nature. Huh et al. [13] built a 3D macroporous structure that consists of chemically modified graphene by using polystyrene particles as a sacrificial template. Furthermore, for further capacitance boost, a thin layer of MnO<sub>2</sub> was additionally deposited onto the embossed chemically modified graphene. The porous graphene nanostructure shows a large surface area facilitates fast ionic transport



within the electrode while preserving decent electronic conductivity and thus endows the composite electrodes with excellent electrochemical properties. Using sulfonated polystyrene (SPS) sphere as hard template, Zhang et al. [68] also prepared porous graphene electrode by an in situ constructing strategy.

Chemical vapor deposition and electrochemical deposition were used to prepare graphene-based materials with 3D porous structures using Ni foam, porous MgO, etc., as templates. Zhang et al. [4] prepared a novel 3D porous graphene networks by the scalable ethanol-chemical vapor deposition method. They demonstrated that the 3D graphene network can be used as a good platform to construct graphene/metal oxide composites for supercapacitor applications.

3D porous graphene-based composite materials were prepared by electrochemical deposition [10]. 3D graphene porous material is prepared electrochemically by reducing a concentrated graphene oxide dispersion. Subsequently, the second component is electrochemically deposited onto this 3D matrix, yielding graphene-based 3D porous composite material. The prepared graphene-based composite materials have a conductive graphene network as the matrix, onto which the second component is homogeneously coated.

Sun et al. [67] reported a hydrothermal approach to prepare nitrogen-doped graphene in various forms, including a stable dispersion, a hydrogel and an aerogel of nitrogen-doped graphene. The stable dispersion mainly consists of single-sheet graphene and the hydrogel is physically cross-linked to be quite strong.

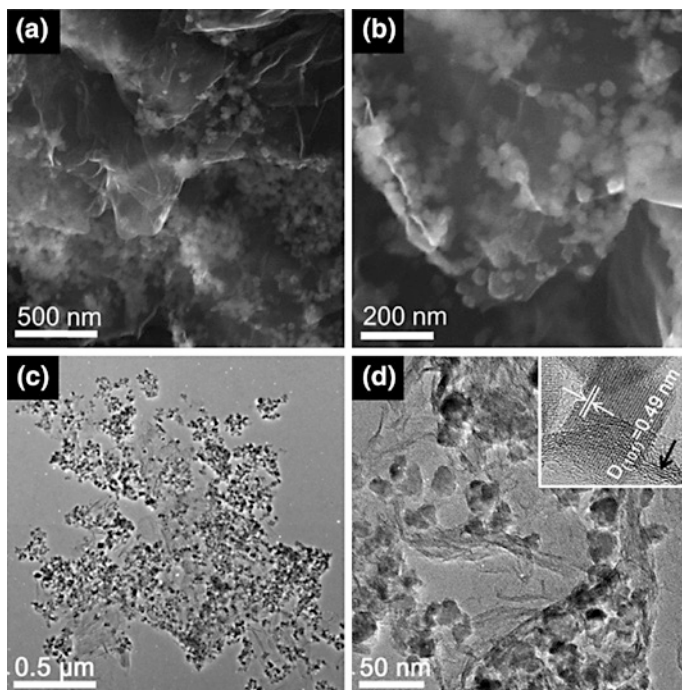
### 2.3 Other Methods

Ogale et al. reported a one-step, catalyst-free process for the preparation of single-layer-graphene-assembled porous carbon by a polymer pyrolysis route [77]. The surface area of the single-layer-graphene-assembled porous carbon was found to be  $1720 \text{ m}^2 \text{ g}^{-1}$ . The nanomaterial was tested as a supercapacitor and showed a high capacitance value of ca.  $154 \text{ F g}^{-1}$  in an aqueous electrolyte in a typical electrochemical cell.

Zhu et al. reported a simple approach to transform the CVD graphene films through self-assembly into porous and continuous fibers with tunable diameter, pore distribution, and high electrical conductivity [39]. Graphene is first self-assembled from a 2D film to a 1D fiber-like structure in an organic solvent and then dried to give the porous and crumpled structure.

## 3 Applications in Lithium-Ion Rechargeable Batteries

Due to their attractive advantages over other types of batteries, lithium-ion batteries have been widely used as power sources for various portable electronic devices. More recently, they have attracted growing attention as power supplies



**Fig. 8** **a, b** SEM images and **c, d** TEM images of M-NG composite (inset: HRTEM image of  $\text{Mn}_3\text{O}_4$  nanoparticle on the graphene sheet). Reproduced from Ref. [54] with permission from Elsevier

for electric vehicles and hybrid electric vehicles. Intensive research has been performed to develop new electrode materials with improved performance for lithium-ion batteries. Accordingly, a great deal of effort has been made to find alternative electrode materials with improved electrochemical performance for lithium-ion batteries. To improve lithium storage capacity, the most promising carbon is disordered partially graphitic carbon from both a technological and scientific point of view, since defects provide large excess capacities [32]. Among the various novel nanostructured electrode candidate materials, graphene-based electrode materials (Fig. 8) are of particular interest due to their high surface area and good conductivity [54, 85].

### 3.1 Porous Graphene-Based Anode Materials

Porous graphene nanostructure could provide more space to accommodate the volume change of the active materials during the charge–discharge to enhance the electrochemical stability of the electrodes. Accordingly, porous graphene-based

materials hold promise as novel electrode materials to further improve the performance of lithium-ion batteries.

Feng et al. presented a bottom-up approach to the large-scale production of 2D sandwich like graphene-based mesoporous carbon [80]. Their high surface area, thinness, and numerous mesopores are favorable for the accessibility of the electrolyte, rapid diffusion of lithium ions, and host uptake. Additionally, the graphene layers can act as mini-current collectors dispersed in the electrode, which facilitates the fast transport of electrons during the charge–discharge cycling due to its high electrical conductivity. When the porous nanocomposite material is used as an anode material for lithium-ion batteries, the nanostructured electrode material exhibits a first discharge capacity of  $915 \text{ mA h g}^{-1}$ , which rapidly stabilizes and remains at  $770 \text{ mA h g}^{-1}$  even after 30 cycles, when cycled at a rate of C/5.

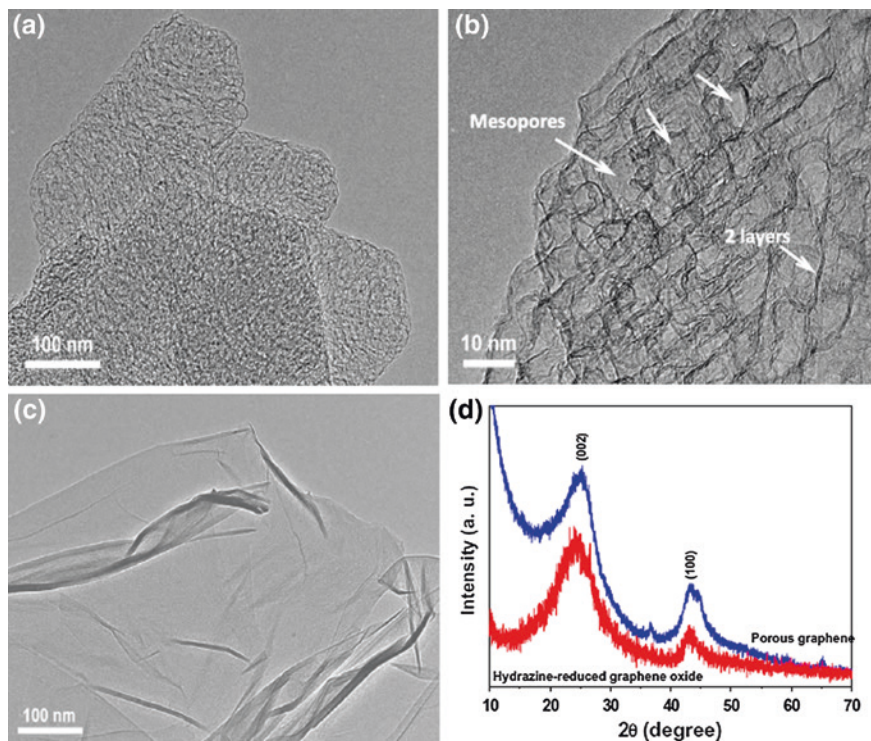
Graphene-based 3D macroporous materials are favorable electrode candidates for lithium-ion batteries. Yan et al. reported a simple method for the preparation of 3D graphene/Fe<sub>3</sub>O<sub>4</sub> architectures by a mild chemical reduction of graphene oxide in the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles [7]. The obtained superparamagnetic, porous, and lightweight material shows good electrochemical performance as anode material in lithium-ion battery.

Using porous MgO sheets as a template, Fan et al. reported a simple CVD approach for scalable preparation of porous graphene materials (Figs. 9, and 10) [19]. The resulting porous graphene networks exhibit a high reversible capacity of  $1723 \text{ mA h g}^{-1}$ , and excellent high rate capability and cycling stability for Li-ion batteries.

A 3D porous architecture of Si/graphene nanocomposite was rationally designed and constructed through an in situ magnesiothermic reduction of SiO<sub>2</sub>/graphene oxide composites series and spray-drying with additional graphene [73]. The porous nanoarchitected composite has superior electrochemical stability and the 3D graphene network shows enhanced electrical conductivity as well as improves rate performance. Furthermore, the 3D nanoarchitected structure can be cycled at extremely high Li<sup>+</sup> extraction rates.

3D graphene foams cross-linked with Fe<sub>3</sub>O<sub>4</sub> nanospheres were prepared by hydrothermal treatment [70]. The Fe<sub>3</sub>O<sub>4</sub> nanospheres are wrapped by graphene sheets and further confined within continuous graphene networks. Such hierarchical Fe<sub>3</sub>O<sub>4</sub>/graphene hybrids provide double protection against the volume changes of Fe<sub>3</sub>O<sub>4</sub> nanospheres during electrochemical processes. The graphene shells suppress the aggregation of Fe<sub>3</sub>O<sub>4</sub> nanospheres and buffer the volume expansion, while the interconnected 3D graphene networks act to reinforce the core–shell structure of Fe<sub>3</sub>O<sub>4</sub>@graphene shell (Fe<sub>3</sub>O<sub>4</sub>@GS) and thus enhance the electrical conductivity of the overall electrode. As a result, 3D graphene foams cross-linked with Fe<sub>3</sub>O<sub>4</sub> nanospheres (Fe<sub>3</sub>O<sub>4</sub> NSs) encapsulated with graphene (Fe<sub>3</sub>O<sub>4</sub>@GS/GF) delivers a high reversible capacity of  $1059 \text{ mA h g}^{-1}$  over 150 cycles, and excellent rate capability, thus exhibiting great potential as an anode material for lithium storage.

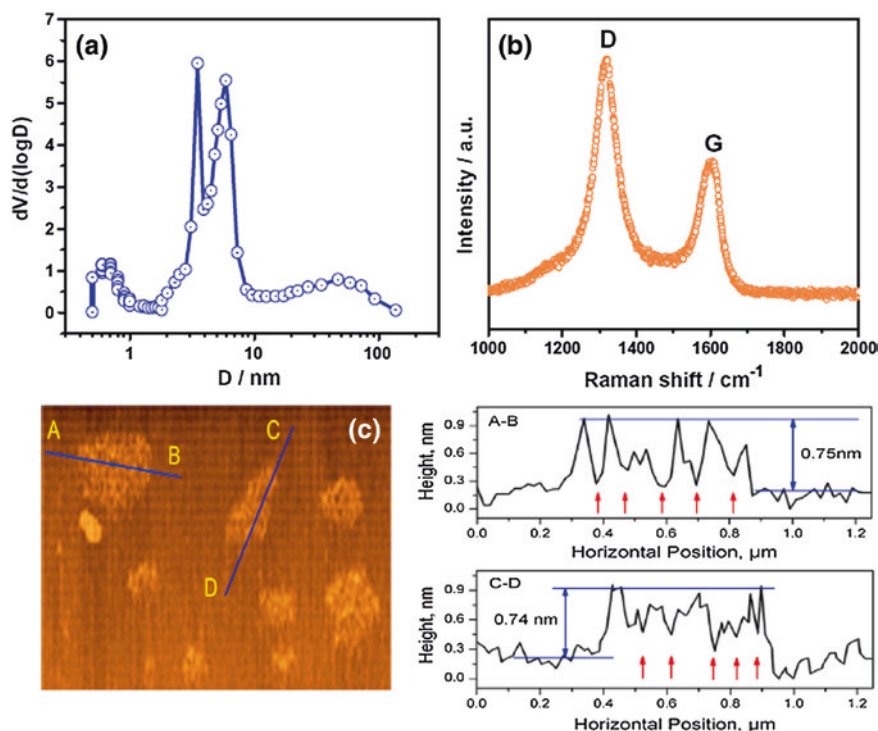
Fan et al. reported a bottom-up strategy assisted by atomic layer deposition to graft bicontinuous mesoporous nanostructure Fe<sub>3</sub>O<sub>4</sub> onto 3D graphene foams and



**Fig. 9** TEM images of porous graphene (a) and (b), and hydrazine-reduced graphene oxide (c). XRD patterns of porous graphene and hydrazine-reduced graphene oxide (d). Reproduced from Ref. [19] with permission from Elsevier

directly use the composite as the lithium-ion battery anode [45]. This electrode exhibits high reversible capacity and fast charging and discharging capability. A high capacity of  $785 \text{ mA h g}^{-1}$  is achieved at 1 C rate and is maintained this high capacity up to 500 cycles. Moreover, the rate of up to 60 C is also demonstrated, rendering a fast discharge potential. For the first step, graphene foam was grown on Ni foam by CVD and then Ni was etched away by a mixture of  $\text{FeCl}_3$  and HCl solution. In the second step, a layer of ZnO was coated onto the graphene foam by atomic layer deposition.

A facile and general method was reported to prepare ordered porous binder-free 3D porous graphene–metal oxide@carbon electrodes at a large scale [91]. Viscous precursor paint was prepared by mixing graphene oxide slurry, polystyrene aqueous solution and metal salt. The ordered porous binder-free electrodes were obtained after heat treatment of the paint at  $400^\circ\text{C}$  under Ar for 60 min. The overall framework is macroporous structure and made of metal oxides or a mixture of graphene and metal oxides. There are secondary pores in the walls of the porous electrode with size in the range of 5–10 nm. The macropores are derived from the



**Fig. 10** **a** Pore size distribution and **b** Raman spectra of the porous graphene. **c** AFM image of the porous graphene, the arrows indicate the existence of pores in graphene sheet. Reproduced from Ref. [19] with permission from Elsevier

duplication of sacrificing polystyrene spheres, while the mesopores are generated from the gas release during decomposition of precursors. The preparation process allows the adjustment of the selected components, the amount of graphene added, the thickness of the electrodes. Such ordered porous binder-free electrodes demonstrated superior Li storage properties. For example, graphene- $\text{Fe}_3\text{O}_4$ @C binder-free electrode depicts high capacities of 1123.8 and 505  $\text{mAh g}^{-1}$  at current densities of 0.5 and 10  $\text{A g}^{-1}$ , respectively. It shows that the surface Li storage mechanism contributes significantly to the total capacities in such 3D porous binder-free electrodes.

A novel composite,  $\text{MoS}_2$ -coated 3D graphene network, is synthesized by a facile CVD method [5]. The 3D graphene network serves as a template for the deposition of  $\text{MoS}_2$  and provides good electrical contact between the current collector and deposited  $\text{MoS}_2$ . As proof of concept, the nanocomposite shows excellent electrochemical performance as an anode material for lithium-ion batteries, which exhibits reversible capacities of 877 and 665  $\text{mA h g}^{-1}$  during the 50th cycle at current densities of 100 and 500  $\text{mA g}^{-1}$ , respectively, indicating its

good cycling performance. Furthermore, the nanocomposite also shows excellent high-current-density performance.

Ultrahigh rate capabilities of transition metal oxide-based electrodes were derived from the design of ordered hierarchically porous 3D electrodes with entrapped active nanoparticle configuration [28]. In contrast to previous reports on hierarchically porous electrodes from irregular self-assembly or post-incorporation of active nanoparticles, the strategy relies on in situ formation and entrapment of active nanoparticles inside the simultaneously formed ordered hierarchically 3D porous carbon, in which the periodic macroporous-mesoporous carbon was directly integrated with the open-porous Ni foam current collector without organic binder, and the electrode active nanoparticles were spatially entrapped inside the periodic porous carbon. Based on the unique electrode configuration, the as-prepared ordered hierarchically porous 3D electrodes show extraordinary rate capabilities.

Zhang et al. developed a simple method for the preparation of metal-oxide coated 3D graphene composites through a facile two-step annealing process [6]. The metal-organic frameworks that served as the precursors of the metal oxides were first synthesized on the 3D graphene networks. The desired nanocomposites were then obtained by a two-step annealing process. The method is expected to be used for synthesis of other metal oxide/graphene composites with 3D structures.

### ***3.2 Porous Graphene-Based Cathode Materials***

Porous graphene-based cathode materials were also studied. Yang et al. reported a composite of chemically activated carbon and  $\text{LiFePO}_4$  as a cathode active material. KOH activation was conducted to construct a 3D structure allowing for diffusion of lithium ions. The porous structure of chemically activated carbon is advantageous to lithium-ion diffusion due to its high rate capability [79]. A composite of chemically activated porous graphene and  $\text{LiFePO}_4$  was developed to improve the speed of charging-discharging and the cycling stability of lithium-ion batteries using  $\text{LiFePO}_4$  as a cathode material [23]. Chemically activated porous graphene was synthesized using KOH. Electrochemical properties have also been investigated after assembling coin cells with the porous graphene/ $\text{LiFePO}_4$  composite as an active material. The composite electrode exhibited better electrochemical properties than the conventional graphene/ $\text{LiFePO}_4$  composite as well as bare  $\text{LiFePO}_4$ , including exceptional speed of charging-discharging and excellent cycle stability. The porous graphene in the electrode composite provides abundant porous channels for the diffusion of lithium ions. Moreover, it acts as a conducting network for easy charge transfer and as a divider, preventing the aggregation of  $\text{LiFePO}_4$  particles.

## 4 Applications in Supercapacitors

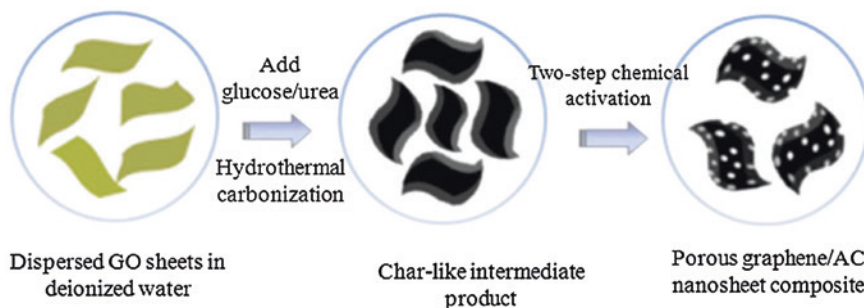
Electrochemical supercapacitors store energy using either ion adsorption or fast surface redox reactions [60]. Electrochemical capacitors are also promising energy storage devices due to the advantages of short charging times, a long cycle, and high power density [47, 49, 61]. However, current commercial electrochemical supercapacitors have much lower energy density than lithium-ion batteries. Design of a desirable, low-cost electrode material with a longer cycling lifetime and higher energy density is imperative for electrochemical capacitor. The performance of electrode materials for supercapacitors is dependent on the accessible specific surface area and the pore structure. The control over structure and morphology of carbon electrode materials is therefore an effective strategy to render them high surface area and efficient paths for ion diffusion. Accordingly, porous graphene-based materials have been proved favorable electrode candidates for supercapacitors due to their open-porous structure that allows electrolytes access more easily to the surface of frameworks.

### 4.1 Activation of Graphene for Supercapacitors

Defective pores could be generated on graphene by chemical methods to prepare activated graphene. Zhu et al. synthesized chemically activated graphene (CA-graphene) with a 3D morphology via KOH activation for application to supercapacitors. The extremely high energy and power density for supercapacitors were possible due to the large surface area from the abundant pore systems [33].

Hierarchical porous carbons are promising electrode materials in high-power supercapacitors. Kim et al. demonstrate the fabrication of highly porous graphene-derived carbons with hierarchical pore structures in which mesopores are integrated into macroporous scaffolds [34]. The macropores were introduced by assembling graphene-based hollow spheres, and the mesopores were derived from the chemical activation with KOH. The unique 3D pore structures in the graphene-based carbons give rise to a BET surface area value of up to  $3290 \text{ m}^2 \text{ g}^{-1}$  and provide an efficient pathway for electrolyte ions to diffuse into the interior surfaces of electrode particles. These carbons exhibit both high gravimetric ( $174 \text{ F g}^{-1}$ ) and volumetric ( $\sim 100 \text{ F cm}^{-3}$ ) specific capacitance in an ionic liquid electrolyte in acetonitrile. The energy density and power density of the cell assembled with this carbon electrode are also high, with gravimetric values of  $74 \text{ Wh kg}^{-1}$  and  $338 \text{ kW kg}^{-1}$  and volumetric values of  $44 \text{ Wh L}^{-1}$  and  $199 \text{ kW L}^{-1}$ , respectively. The high supercapacitor performance achieved with these graphene-based carbons is attributed to their unique pore structure and makes them potentially promising for various energy storage devices.

Zheng et al. synthesized porous graphene/activated carbon composite by hydrothermal carbonization and subsequent two-step chemical activation with KOH



**Fig. 11** Schematic illustration showing the experimental steps of preparing porous graphene/AC nanosheet composite. Reproduced from Ref. [89] with permission from Elsevier

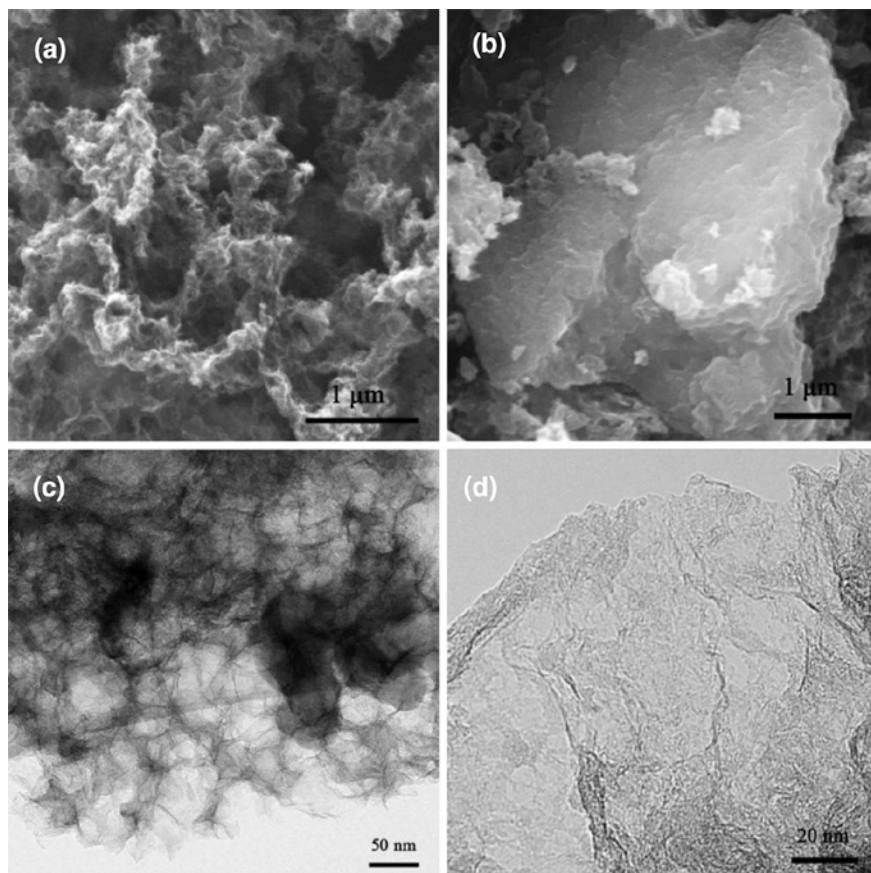
(Fig. 11) [89]. The composite has a relatively high packing density and large specific surface area of  $2106 \text{ m}^2 \text{ g}^{-1}$ , as well as containing plenty of mesopores (Fig. 12). As supercapacitor electrode material, it exhibits specific capacitance up to  $210 \text{ F g}^{-1}$  in an aqueous electrolyte and  $103 \text{ F g}^{-1}$  in organic electrolyte, respectively. The specific capacitance decreases by only 5.3 % after 5000 cycles. In this composite material, a layer of porous activated carbon coats on graphene improves dispersion of graphene sheets and increases its packing density. The graphene integrated into activated carbon matrix also increases conductivity. Additionally, the nanosheet-like electrode material has a short diffusion pathway, which facilitates rapid transport of the electrolyte ions. Three-dimensional graphene-based frameworks are also fabricated by hydrolysis of TEOS with graphene aerogel as support and CTAB as soft template [72]. The resulting hierarchical macro- and mesoporous structures exhibit narrow mesopore size distribution (2–3.5 nm), high surface area, and low mass density. Benefiting from the integration of meso- and macroporous structures, the material manifests outstanding specific capacitance ( $226 \text{ F g}^{-1}$ ), high rate capability, and excellent cycling stability when it is applied in electrochemical capacitors.

## 4.2 3D Graphene-Based Porous Materials for Supercapacitors

Many research works have been published on 3D graphene-based porous nanostructures for supercapacitors. Here, some selected studies on this research field are reviewed.

Zhang et al. present a simple, green, and efficient approach using two standard and simple industry steps to make 3D graphene-based porous materials at bulk scale, with ultrahigh specific surface area ( $3523 \text{ m}^2 \text{ g}^{-1}$ ) and excellent bulk conductivity [87]. The good properties of these materials are demonstrated by their





**Fig. 12** **a** SEM image of char-like intermediate product, **b** SEM image of graphene/AC nanosheet composite, **c**, **d** TEM images of graphene/AC nanosheet composite. Reproduced from Ref. [89] with permission from Elsevier

superior supercapacitor performance in ionic liquid with specific capacitance and energy density of  $231 \text{ F g}^{-1}$  and  $98 \text{ Wh kg}^{-1}$ , respectively.

A self-assembled macrostructured graphene architecture was prepared by a convenient one-step hydrothermal method [74]. The self-assembled graphene hydrogel is electrically conductive, mechanically strong, and thermally stable and exhibits a high specific capacitance. The self-assembled graphene hydrogel as a 3D supercapacitor electrode material exhibits high specific capacitance ( $175 \text{ F g}^{-1}$ ) in an aqueous electrolyte.

Freestanding, lightweight, ultrathin, highly conductive, and flexible 3D graphene networks, loaded with  $\text{MnO}_2$  by electrodeposition, were prepared as the electrodes of a flexible supercapacitor [25]. The 3D graphene networks showed an ideal supporter for active materials and permitted a large  $\text{MnO}_2$  mass loading of

9.8 mg cm<sup>-2</sup>, leading to a high area capacitance of 1.42 F cm<sup>-2</sup> at a scan rate of 2 mV s<sup>-1</sup>. The MnO<sub>2</sub> content with respect to the entire electrode was further optimized and a maximum specific capacitance of 130 F g<sup>-1</sup> was achieved. The excellent electrochemical performance of a symmetrical supercapacitor consisting of a sandwich structure of two pieces of 3D graphene/MnO<sub>2</sub> composite network separated by a membrane and encapsulated in polyethylene terephthalate membranes was explored.

A hybrid structure of ZnO on 3D graphene foam has been synthesized by CVD growth of graphene followed by a facial in situ precipitation of ZnO nanorods under hydrothermal conditions [16]. The results show that the ZnO nanorods have high crystallinity and cluster uniformly on graphene skeleton to form flower-like nanostructures. It is found that the graphene/ZnO hybrids display superior capacitive performance with high specific capacitance of ~400 F g<sup>-1</sup> as well as excellent cycle life, making them suitable for high-performance energy storage applications.

3D graphene architectures in the macroworld can in principle maintain all the extraordinary nanoscale properties of individual graphene flakes. However, current 3D graphene products suffer from poor electrical conductivity, low surface area, and insufficient mechanical strength/elasticity; the interconnected self-supported reproducible 3D graphenes remain unavailable. A sugar-blowing approach based on a polymeric predecessor to synthesize a 3D graphene bubble network was reported [69]. The bubble network consists of mono- or few-layered graphitic membranes that are tightly glued, rigidly fixed, and spatially scaffolded by micrometer-scale graphitic struts. Such a topological configuration provides intimate structural interconnectivities, freeway for electron/phonon transports, huge accessible surface area, as well as robust mechanical properties. The graphene network thus overcomes the drawbacks of presently available 3D graphene products and opens up a wide horizon for diverse practical uses, for example, high-power high-energy electrochemical capacitors, as highlighted in this work.

Fan et al. demonstrated the fabrication of functionalized graphene nanosheets via low temperature thermal treatment of graphite oxide with a slow heating rate using Mg(OH)<sub>2</sub> nanosheets as template [78]. Because of its dented sheet with high surface area, a certain amount of oxygen-containing groups, and low pore volume, the as-obtained graphene delivers both ultrahigh specific gravimetric and volumetric capacitances of 456 F g<sup>-1</sup> and 470 F cm<sup>-3</sup>, almost 3.7 times and 3.3 times higher than hydrazine-reduced graphene, respectively. The assembled supercapacitor exhibits an ultrahigh volumetric energy density of 27.2 Wh L<sup>-1</sup>, which is among the highest values for carbon materials in aqueous electrolytes, as well as excellent cycling stability with 134 % of its initial capacitance after 10,000 cycles.

Mitlin et al. employed a microwave synthesis process of cobalt phthalocyanine molecules templated by acid-functionalized multiwalled carbon nanotubes to create 3D sponge-like graphene nanoarchitectures suited for ionic liquid-based electrochemical capacitor electrodes that operate at very high scan rates [75]. The 3D nanoarchitectures are able to deliver an energy density of 7.1 Wh kg<sup>-1</sup> even at an extra high power density of 48 kW kg<sup>-1</sup>. In addition, the ionic liquid supercapacitor based on this material works very well at room temperature due to its fully

opened structures, which is ideal for the high-power energy application requiring more tolerance to temperature variation. Moreover, the structures are stable in both ionic liquids and 1 M H<sub>2</sub>SO<sub>4</sub>, retaining 90 and 98 % capacitance after 10,000 cycles, respectively.

Porous yet densely packed carbon electrodes with high ion-accessible surface area and low ion-transport resistance are formed by capillary compression of adaptive graphene gel films in the presence of a nonvolatile liquid electrolyte [81]. This simple soft approach enables subnanometer-scale integration of graphene sheets with electrolytes to form highly compact carbon electrodes with a continuous ion-transport network. Electrochemical capacitors based on the resulting films can obtain volumetric energy densities approaching 60 Wh L<sup>-1</sup>.

### ***4.3 Flexible Supercapacitors Using 3D Graphene-Based Porous Materials***

There has been much research interest in the development of flexible supercapacitors over the past few years due to their high mechanical compliance. Li et al. reported that the combination of graphene chemistry with ice physics can lead to the formation of ultralight and superelastic graphene-based cellular monoliths [55]. Chi et al. reported the preparation of freestanding paper-like electrode materials have triggered significant research interest for their practical application in flexible and lightweight energy storage devices [12]. The utilization of 3D porous graphene scaffold to load nanostructured polyaniline dramatically enhances the electrical conductivity, the specific capacitance, and the cycle stability of the graphene–polyaniline nanocomposite. Shao et al. demonstrated a simple method for preparing high-performance flexible asymmetric supercapacitors based on 3D porous graphene/MnO<sub>2</sub> nanorod and graphene/Ag hybrid thin-film electrodes [59]. These graphene hybrid films, which accelerate ion and electron transport by providing lower ion-transport resistances and shorter diffusion-distances, exhibit high specific capacitances and power performances, and excellent mechanical flexibility. These results suggest that such asymmetric graphene/MnO<sub>2</sub> nanorod and graphene/Ag hybrid thin-film architectures are promising for next-generation high-performance flexible supercapacitors.

## **5 Future Perspectives**

To overcome the limitations of conventional materials, numerous novel nanocomposite materials have been prepared by combining different types of nanomaterials with porous graphene for various electrochemical energy storage devices. The major challenges for the preparation of porous graphene-based nanocomposite materials include the preparation of nanostructures with precisely controlled of

complex and hierarchical pore morphology as well as the designed fabrication of nanocomposite materials with novel compositions.

Porous graphene, as a new platform for nanocomposite materials, provides new possibilities to the nanodevices. Although there has been rapid growth in the development of porous graphene-based nanocomposite materials as promising candidate electrode materials for electrochemical energy storage application in the past few years, as evidenced by the sharp increase in research work published in this area, there remain several challenges needed to be overcome. In order for them to be used in real energy storage devices in the future, several issues including the production cost, scalable synthesis, and long-term mechanical stability of the nanocomposite materials need to be addressed. To study the performance of a porous material for electrochemical energy storage, more reliable parameter, such as the volumetric energy and power density against the whole electrochemical energy devices, should be measured. Nevertheless, we envisioned that numerous well-designed porous graphene-based novel nanocomposite materials with improved energy storage performances will be developed by using new preparation methods and novel compositions. These nanocomposite materials will provide many new chances for efficient electrochemical energy storage devices in the future.

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