Review Article

Graphene-Based Carbon Materials for Electrochemical Energy Storage

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Because of their unique 2D structure and numerous fascinating properties, graphene-based materials have attracted particular attention for their potential applications in energy storage devices. In this review paper, we focus on the latest work regarding the development of electrode materials for batteries and supercapacitors from graphene and graphene-based carbon materials. To begin, the advantages of graphene as an electrode material and the existing problems facing its use in this application will be discussed. The next several sections deal with three different methods for improving the energy storage performance of graphene: the restacking of the nanosheets, the doping of graphene with other elements, and the creation of defects on graphene planes. State-of-the-art work is reviewed. Finally, the prospects and further developments in the field of graphene-based materials for electrochemical energy storage are discussed.

1. Introduction

During the past decade, the successful fabrication of graphene has opened an astonishing new field for materials science and technology [1–5]. Graphene was originally defined as a 2-dimensional (2D) monolayer sheet of sp^2-bonded carbon; however, all members of the family of graphene-related materials consisting of structural or chemical derivatives of graphene are commonly called "graphene" by the research community. These materials include double- and few-layer graphene and chemically reduced graphene oxide (reduced GO or RGO) [6]. Inspired by their many fascinating features, researchers have focused their attention on the scientific and technical issues of graphene. Graphene possesses unique optical, electrical, mechanical, and electrochemical properties. The surface area of graphene is calculated to be $2630 \, m^2 \, g^{-1}$, and graphene exhibits high structural stability and electrical conductivity and is a good carrier for other molecules; all these characteristics are highly favorable for energy storage applications [7, 8].

In current Li-ion battery (LIB) technology, graphite is widely used as a commercial anode material because of its safety and low cost [9, 10]. However, because of its tightly stacked layered structure, graphite can only form LiC_6 structures with a limited theoretical capacity ($372 \, mAhg^{-1}$) and poor rate performance; graphite therefore cannot satisfy the high energy and power density demands of modern electronic devices [11]. The emergence of graphene provides an opportunity to use carbon materials to construct a nanostructure that has better electrochemical performance than bulk graphite. In individual defect-free graphene sheets, LiC_3 structures can be formed in which lithium is stored on both sides of the graphene sheet, and the theoretical capacity of these sheets is $744 \, mAhg^{-1}$ [12]. Graphene has already surpassed many carbon materials in the field of energy storage because of its large open surface area and high conductivity; however, problems still remain. In particular, full utilization of the potential of graphene is difficult because graphene nanosheets (GNS) tend to aggregate during the preparation and application processes; this aggregation causes the loss of many of the properties of individual GNSs and generates discontinuous channels that retard fast ion transport [13].

Graphene, with its high surface area and high conductivity, is also an ideal candidate for use in supercapacitor electrodes because the electric double-layer capacitance (EDLC)

of a material is directly proportional to its surface area. The application of graphene as a supercapacitor electrode was first explored by Ruoff and coworkers [14], who found that chemically derived graphene powder exhibits specific capacitances of 135 and 99 Fg^{-1} in aqueous and organic electrolytes, respectively; different forms of graphene with improved performance have since been reported [15]. The different values obtained with different forms of graphene also primarily depend on the stacking and the surfaces of the graphene nanosheets because only surface areas accessible to the electrolyte can contribute to the specific capacitance.

Therefore, the performance of graphene as an electrochemical energy storage material strongly depends on the manner in which the individual sheets are arranged. Effective prevention of intersheet restacking or the creation of fast ion/electrolyte transport paths is essential to enhance the performance of graphene in electrochemical energy storage applications and to generate more electrochemically active sites.

In this review paper, we focus on recent developments in graphene and graphene-based carbon materials for electrochemical energy storage, including LIB and supercapacitor applications. The following discussion is categorized into three sections based on the different strategies used to improve the performance of graphene as an electrode material; these strategies are preventing the restacking of nanosheets, doping the graphene with other elements, and creating defeats on the graphene planes. The applications of LIBs and supercapacitors are discussed simultaneously because of the numerous similarities between these applications from the perspective of materials science.

2. Preventing Restacking of Graphene Nanosheets

The control of assembly manner of GNSs in their bulk form is of significant importance for tuning their properties, and, when used in electrochemical energy storage devices, preventing the restacking of graphene nanosheets and increasing surface area of electrode are usually an efficient strategy to improve their performance. Some reports have shown that the introduction of foreign nanoparticles (such as metals and metal oxides) as spacers can partially prevent the restacking of GNS and that some of these foreign components also exhibit electrochemical activity [16–19]. However, the introduction of foreign components often leads to a more complex charge/discharge process, which is not favorable for practical applications. Therefore, better choices are the use of nanocarbon as a spacer or the modification of graphene itself to control the stacking of GNS.

Chen et al. [20] reported the fabrication of nanostructures constructed from GNS and in situ carbonized amorphous carbon anchored on the nanosheets. This carbon material is formed from an aqueous suspension of GO and a linear polymer (polyvinyl alcohol, PVA, 10 wt% in the starting material). The polymer is rich in hydroxyl groups that can interact with the oxygen-containing groups (mostly hydroxyl and carboxyl groups) on the GO plane to form a stable network in which
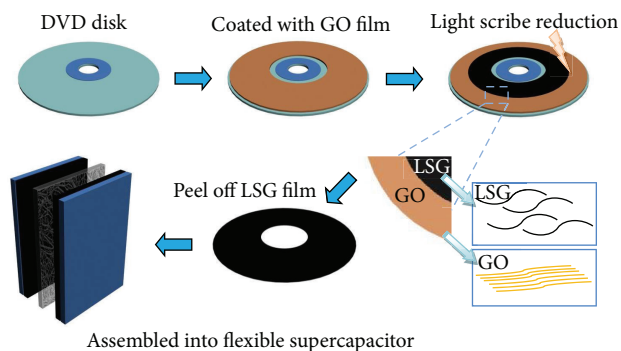

FIGURE 1: Schematic illustration of the fabrication of laser scribed grapheme- (LSG-) based electrochemical capacitors [21].

the PVA chains align along the GO plane to prevent the restacking of the GO nanosheets during the drying process. In addition, after the carbonization process, a graphene-based carbon nanostructure with expanded channels is formed, and most of the PVA was removed during the pyrolysis process, and the rest transformed into amorphous carbon. This carbon material exhibits better cycling stability and rate performance than GNS as a LIB anode material; the specific discharge capacity of this material is approximately 480 $mAhg^{-1}$ at 500 mAg^{-1}, 320 $mAhg^{-1}$ at 2 Ag^{-1}, and 235 $mAhg^{-1}$ at 5 Ag^{-1} after 100, 200, and 300 cycles, respectively. The improved performance of this graphene material can be attributed to structural factors. The skeleton of the graphene layers provides a continuous conductive network for fast electron transfer. In contrast, the expanded channels provide open channels for fast ion transport. Furthermore, for the commercialization of graphene-based electrochemical energy storage devices, the method provided here has the advantage of cheap, simple, and suitable for mass production.

Rapid expansion is another effective technique for the exfoliation of stacked graphene sheets. High-temperature treatments can reduce graphene oxide and can simultaneously generate space between GNS because of the release of a tremendous quantity of gaseous species. El-Kady et al. [21] have presented a strategy for the fabrication of flexible graphene electrodes for supercapacitors via a simple laser-scribing approach that avoids the restacking of GNS. This process is illustrated in Figure 1. In this rapid reduction process, the closely stacked GO sheets can be well exfoliated to form porous laser-scribed graphene (LSG) sheets. When two LSG films were directly used as supercapacitor electrodes without any binders or conductive additives, a specific capacitance of 3.67 $mFcm^{-2}$ was achieved in an aqueous electrolyte of 1.0 M H_3PO_4 (4.04 $mFcm^{-2}$ in an aqueous electrolyte of 1.0 M H_2SO_4) with a current density of 1 Ag^{-1}. Even when the electrodes were tested at a high charge/discharge rate of 1000 Ag^{-1}, the specific capacitance remained 1.84 $mFcm^{-2}$, which indicates the high rate capability of these electrodes. The high performance of the LSG electrodes can be attributed to the porous structure of the graphene film; this structure provides an electrolyte reservoir to facilitate ion transport and minimizes the diffusion distance to the interior surfaces.
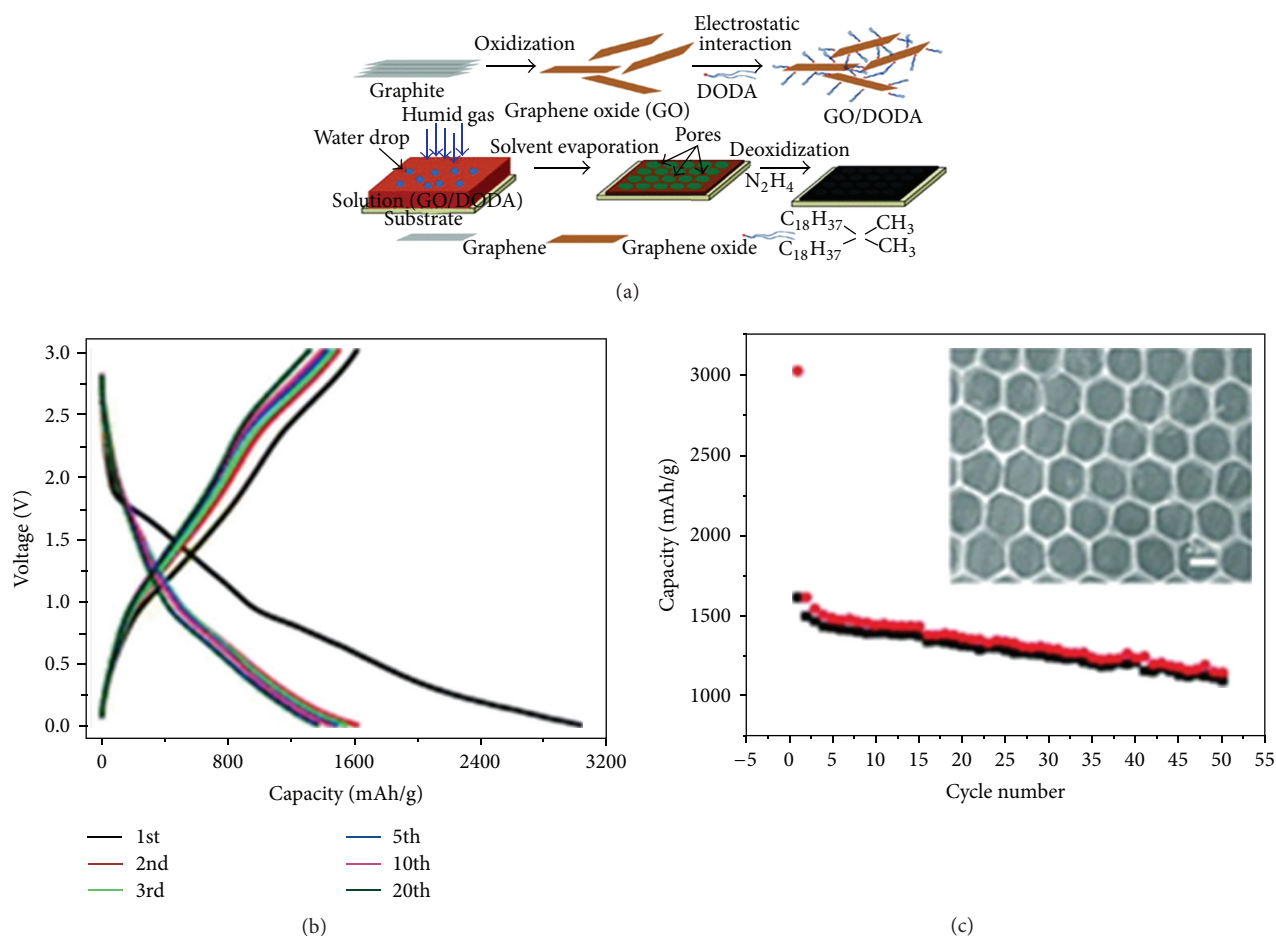
(a)

(b)

(c)

FIGURE 2: (a) Schematic drawing of the preparation of the honeycomb structured film based on graphene oxide; (b) charge and discharge cycle curves of the honeycomb patterned film as anode in lithium cells at a current density of 50 mA/g; (c) capacity versus cycle number for the honeycomb film at a current density of 50 mA/g [22].

To generate highly porous graphene electrodes, Yin et al. [22] developed an self-assembly strategy to create bio-inspired honeycomb hierarchical structures composed of functionalized graphene sheets. The principle behind their method is the "breath figure" method, as shown in Figure 2(a). The presence of cationic surfactants (dimethyl-dioctadecylammonium bromide, DODA·Br) during this process not only helps GO disperse in the organic media but also prevents the aggregation of adjacent graphene layers when the GO is reduced to graphene. The hierarchical graphene films exhibit novel multilevel architectures that range from nanosheets to nanopores to three-dimensional microscale porous structures with interconnected active and passive components that simultaneously optimize ion transport and capacity. When tested as a LIB anode, a large specific capacity of approximately 3025 mAhg^{-1} and a reversible capacity of approximately 1612 mAhg^{-1} were obtained at a current density of 50 mAg^{-1} (potential window of 0.01 to 3.00 V relative to Li/Li$^+$, Figure 2(b)). The reversible capacity of the rGO/DODA honeycomb electrodes remained 1300 mAhg^{-1} during the initial 25 cycles and was 1150 mAhg^{-1} after 50 cycles (Figure 2(c)).

Liu et al. [23] have developed a novel graphene aerogel pressing approach to fabricate graphene paper with folded, structured graphene sheets; these sheets can generate fast ion/electrolyte diffusion paths when used in an electrode. The structure is shown in Figures 3(a) and 3(b). The first discharge and charge capacities of this graphene paper as an LIB anode are 1091 and 864 mAhg^{-1} at a current density of 100 mAg^{-1}; these values give an initial Coulombic efficiency of 79.2% (Figure 3(c)). The discharge and charge capacities are as high as 815 mAhg^{-1} and 806 mAhg^{-1} in the second cycle, and these values are much higher than those of regular graphene paper obtained by vacuum filtration (84 mAhg^{-1}), in which the GNSs are subject to close stacking. Such graphene paper also possesses high rate capability and cycling stability; at current densities of 200, 500, 1000, and 1500 mAg^{-1}, the corresponding reversible specific capacities are 557, 268, 169, and 141 mAhg^{-1}, respectively. In addition, a capacity of 568 mAhg^{-1} can still be attained after 100 cycles at 100 mAg^{-1} (Figure 3(d)). The high performance obtained here can be attributed to the non-closely stacking graphene sheets, and such structures can provide slightly increased intersheet distance and more active sites when used as LIB anode, which
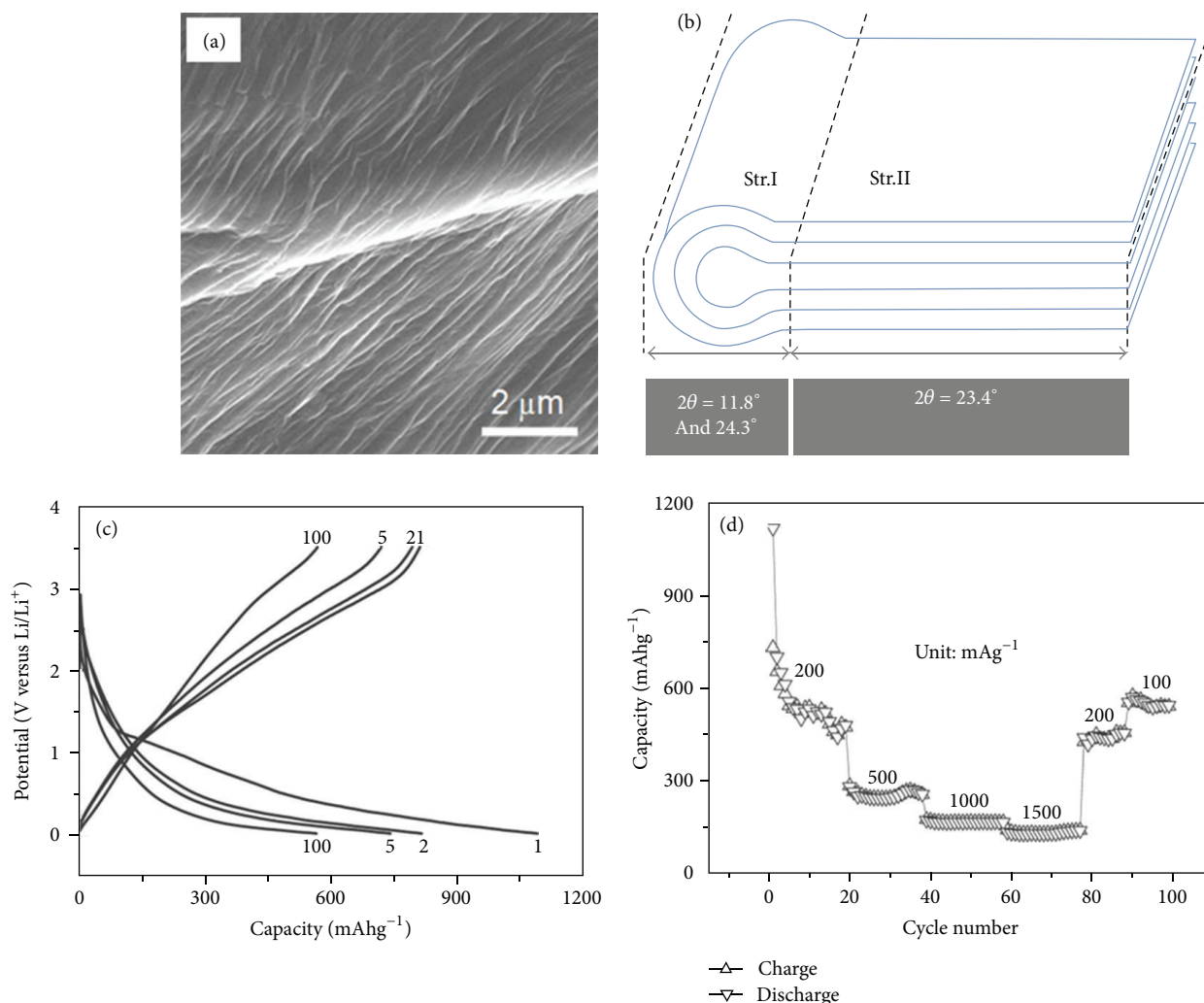
FIGURE 3: (a) SEM image and (b) structure illustration of folding graphene sheets; (c) discharge/charge profiles (1st, 2nd, 5th, and 100th cycles) of the as-prepared graphene paper at the current density of $100\,mAhg^{-1}$ as LIB anode; (d) cycle performance of the graphene paper as LIB anode at different current densities [23].

can facilitate Li-ion diffusion and solid-electrolyte interface (SEI) formation, leading to higher reversible capacity and Coulombic efficiency.

3. Doping Graphene with Other Elements

The chemical doping of graphene is another effective method for manipulating the physical and chemical properties of graphene because the introduction of suitable reactive sites can improve graphene's electrochemical properties [24]. Among these materials, nitrogen-doped graphene has attracted a great deal of attention because theoretical studies have shown that nitrogen doping can drastically alter the electronic performance, can introduce additional active sites, and can enhance the interaction between the carbon structure and the lithium and electrolyte; thus, the kinetics for ion

diffusion and transfer is improved [25, 26], and this kinetics is essential to the electrochemical performance.

As an example, Wu et al. [27] reported LIB anode materials with very high rate capabilities prepared from heteroatom (N, B)-doped chemically derived graphene. The N-doped graphene was prepared at $600°C$ in a mixed gas of NH_3 and Ar, whereas the B-doped graphene was prepared at $800°C$ in a mixed gas of BCl_3 and Ar. At a low charge/discharge rate of $50\,mAg^{-1}$, the doped graphene electrodes exhibited high capacities of $1043\,mAhg^{-1}$ for N-doped graphene and $1549\,mAhg^{-1}$ for B-doped graphene; these capacities are much larger than that of undoped graphene. More importantly, the doped graphene showed greatly improved rate performance. At a high charge/discharge rate of $25\,Ag^{-1}$, the electrodes still exhibited capacities of $199\,mAhg^{-1}$ for N-doped graphene and $235\,mAhg^{-1}$ for B-doped graphene (Figure 4). These results indicate the strong potential of
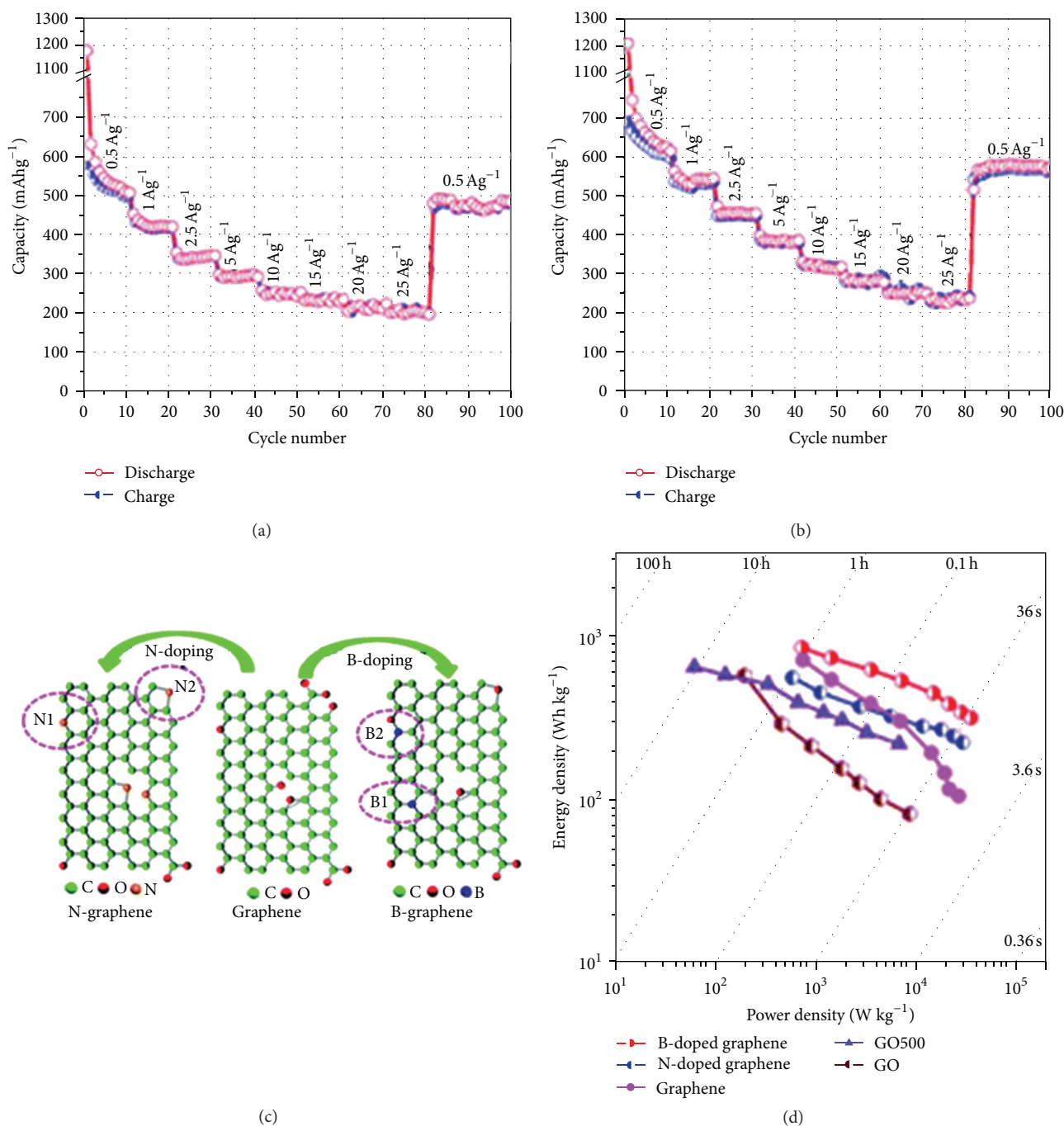
(a)

(b)

(c)

(d)

FIGURE 4: (a) N-doped and (b) B-doped graphene electrodes obtained over a wide range of current densities, from 0.5 to 25 Ag^{-1}; (c) schematic structure of the binding conditions of N and B in a graphene lattice; (d) Ragone plots for the pristine graphene, N-doped grapheme, and B-doped grapheme [27].

chemically doped graphene as a high-performance anode material in LIBs.

Chemical doping can also combine with microstructure control to further improve the performance of graphene. Wen et al. [28] developed an efficient and facile strategy for the fabrication of highly crumpled nitrogen-doped graphene nanosheets (C-NGNSs) that combine the advantages of high surface area and nitrogen doping. Figures 5(a)–5(d) describe

the entire procedure for the preparation of C-NGNSs; this procedure employs cyanamide (NH_2CN) as a nitrogen source. Cyanamide can be deposited onto the GO surface during the drying process because of hydrogen bonding and electrostatic interactions. The resulting GO-NH_2CN product was then transformed to a thin C_3N_4 polymer layer on the surface of the GO after being heated at 400°C to induce polymerization. Further calcination at 750 or 900°C resulted
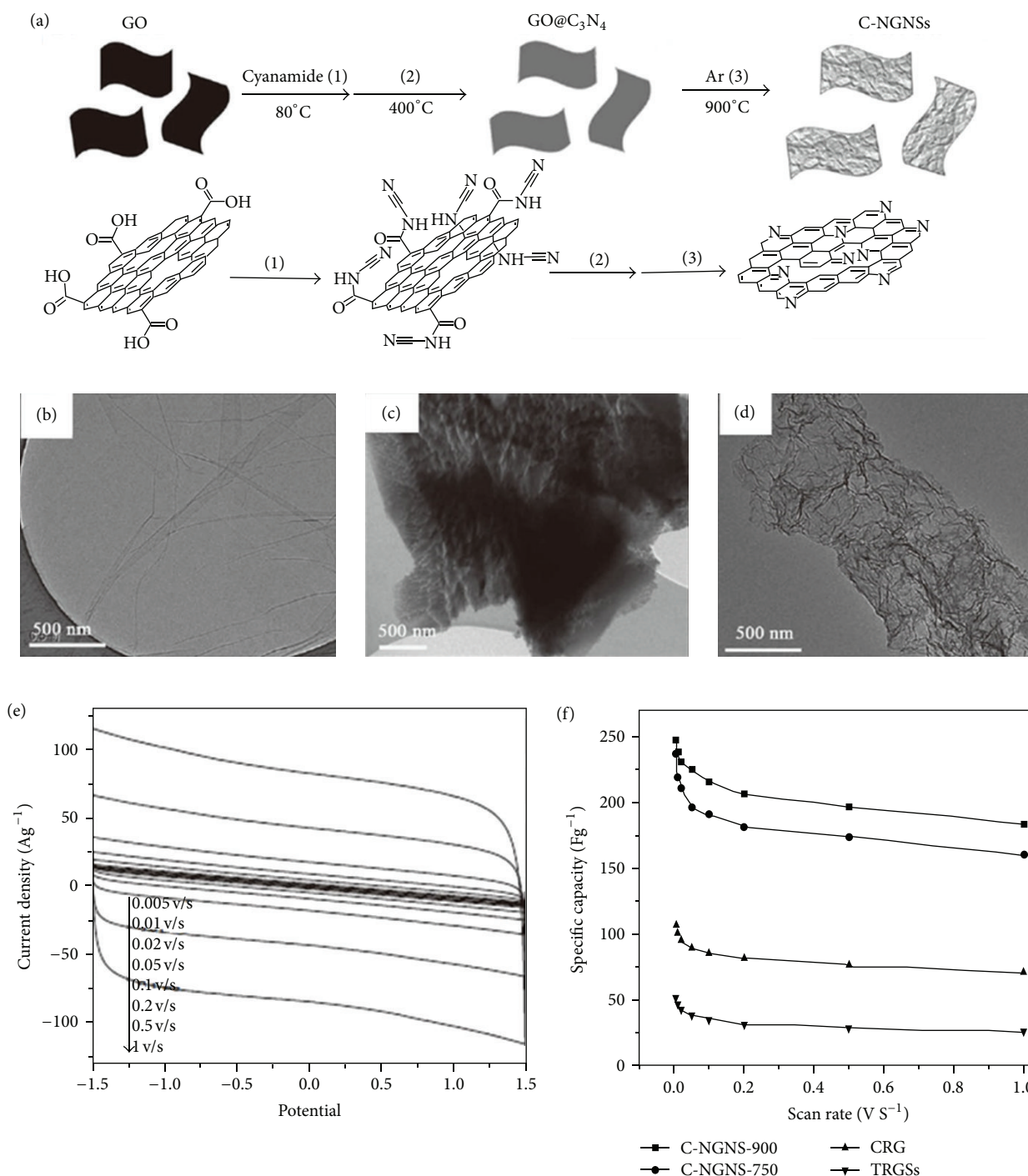
FIGURE 5: (a) Schematic illustration for fabricating crumpled nitrogen-doped graphene; TEM images of (b) GO, (c) GO-C_3N_4, and (d) C-NGNSs; (e) CVs of C-NGNSs-900 supercapacitors in 1.0 M [Bu_4N]BF_4 acetonitrile solution between −1.5 and 1.5 V at different scan rates; (f) specific capacitance dependence on potential sweep rates in different graphene-based supercapacitors with 1.0 M [Bu_4N]BF_4 acetonitrile solution as electrolyte [28].

in the preparation of crumpled nitrogen-doped graphene nanosheets. The C-NGNSs exhibited significant improvements in capacitance and rate performance; when tested in a two-electrode system with an electrolyte of 1.0 M [Bu_4N]BF_4 in acetonitrile, specific capacitances of 245.9, 238.8, 233.3, and 226.5 Fg^{-1} were obtained at current densities of 1.0, 2.0, 5.0, and 10.0 Ag^{-1}, respectively, (Figures 5(e) and 5(f)). This high performance can be attributed to the abundant wrinkled structures, the high pore volume, the nitrogen doping, and the improved electrical conductivity of the C-NGNSs.
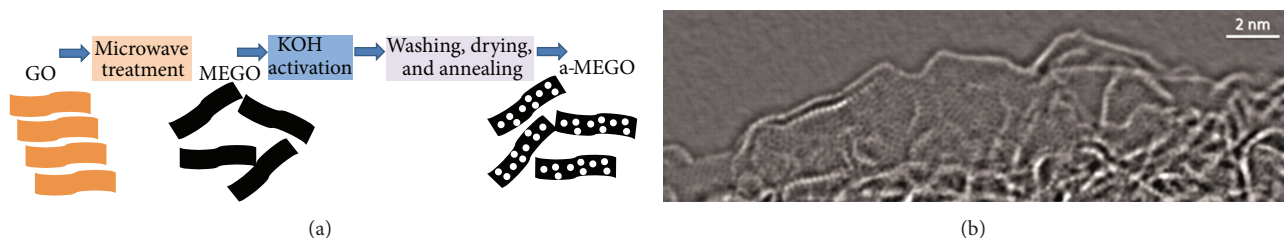
(a)

(b)

FIGURE 6: (a) Schematic showing the microwave exfoliation/reduction of GO and the following chemical activation of MEGO with KOH that creates pores while retaining high electrical conductivity. (b) High-resolution phase contrast electron micrograph of the thin edge of an actived MEGO chunk [29].
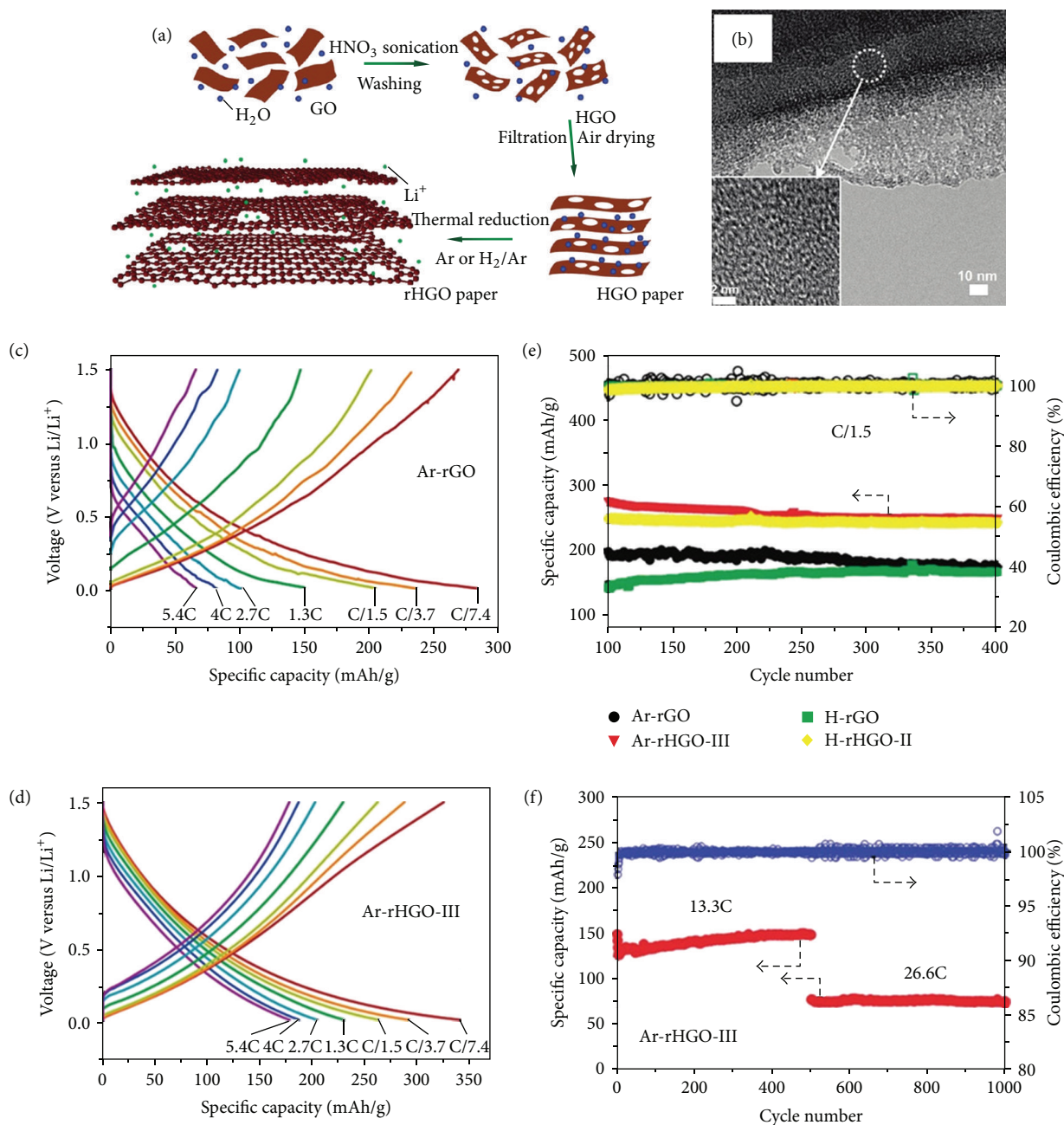

FIGURE 7: (a) Schematic illustration and TEM images of graphene sheets with plane defects (holes) fabricated by acid oxidation; ((c)–(f)) test as LIB anode in the potential range of 0.01 to 1.5 V versus Li/Li$^+$ [30].

TABLE 1: Summarization of the LIB performances of grapheme-based electrodes mentioned in this review paper.

| Material form	Reversible capacity ($mAhg^{-1}$)	Cycling stability ($mAhg^{-1}$/Cycles)	Reference number
PVA carbon inserted graphene	480 (500 mAg^{-1}) 235 (50 Ag^{-1})	480/100	[20]
Honeycomb graphene film	1612 (50 mAg^{-1})	1150/50	[22]
Folded structured graphene paper	864 (100 mAg^{-1}) 169 (1000 mAg^{-1})	568/100	[23]
N-doped graphene	1043 (50 mAg^{-1}) 199 (25 Ag^{-1})	~500/100	[27]
B-doped graphene	1549 (50 mAg^{-1}) 235 (25 Ag^{-1})	~600/100	[27]
Holey graphene paper	454 (50 mAg^{-1}) 178 (2000 mAg^{-1})	~450/400	[30]
Mesoporous graphene	1040 (100 mAg^{-1}) 255 (5 Ag^{-1})	833/60	[31]
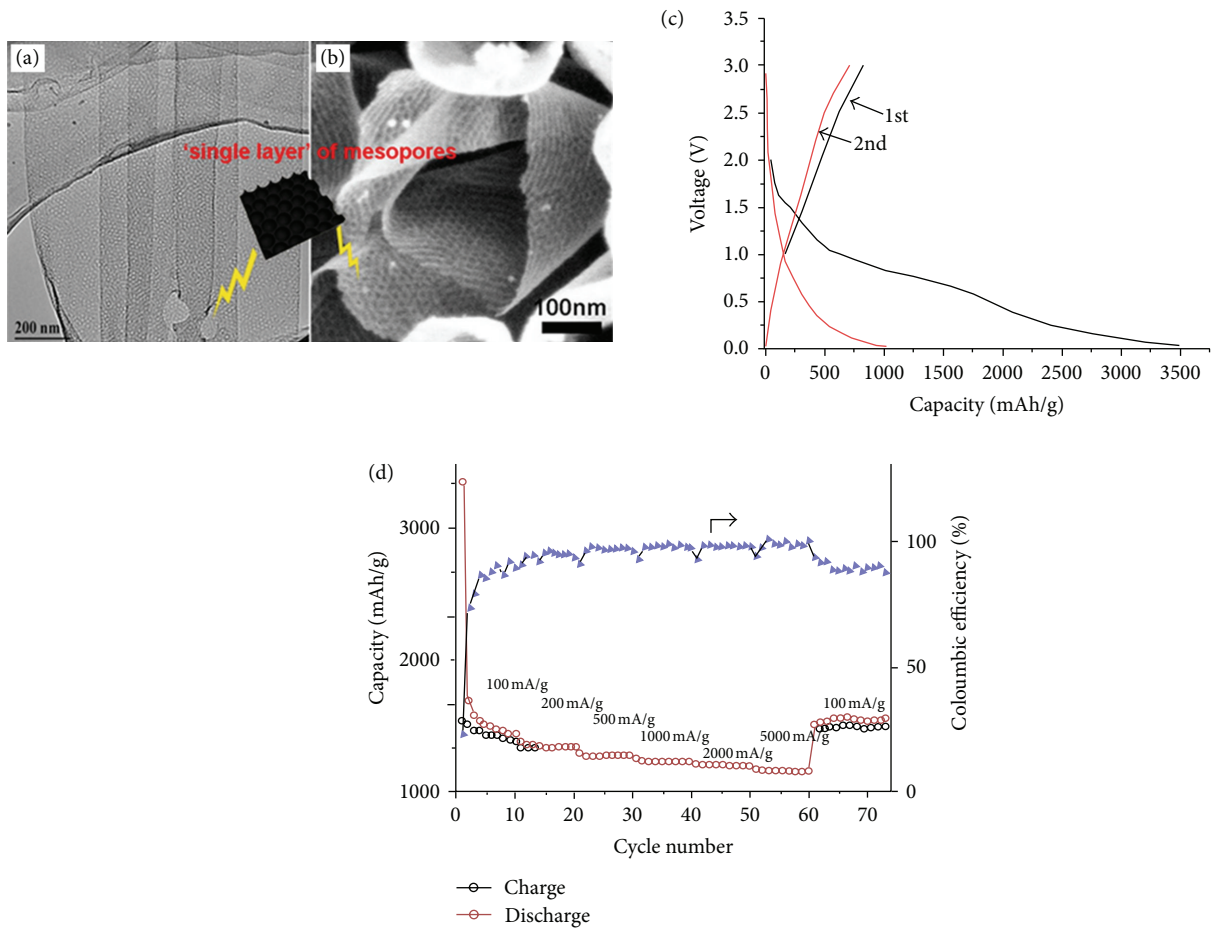
FIGURE 8: (a) TEM and (b) SEM images of the mesoporous graphene nanosheets; (c) first and second cycles of galvanostatic discharge/charge curves of the mesoporous graphene nanosheets; (d) cycling performance at different current densities [31].

4. Creating Defects on Graphene Planes

In addition to the two previously discussed methods, the generation of defects on graphene planes is another approach to improving the electrode performance of graphene. The existence of defect sites on graphene can enhance the performance of graphene from several aspects. Holes on graphene can act as fast ion/electrolyte transport paths, alleviating the closely stacking problem of GNSs; defect holes also bring more edge sites, which are more chemically active than pristine grapheme; such sites can store extra Li, leading to a specific capacity even higher than the theoretical value; Furthermore, holey structure can increase the surface area of graphene, which is highly desired for supercapacitor

TABLE 2: Summarization of the supercapacitor performances of grapheme-based electrodes mentioned in this review paper.

Graphene form	Cell configuration Electrolyte	Specific capacitance (Fg^{-1})	Reference number
Laser-scribed graphene	Two-electrode $(1\,M\,H_3PO_4\,aq)$ Two-electrode $(1\,M\,H_2SO_4\,aq)$	$3.67\,mFcm^{-2}\,(1\,Ag^{-1})$ $1.84\,mFcm^{-2}\,(1000\,Ag^{-1})$ $4.04\,mFcm^{-2}\,(1\,Ag^{-1})$	[21]
Folded structured graphene paper	Two-electrode $(1\,M\,H_2SO_4\,aq)$	$172\,(1\,Ag^{-1})$ $119\,(100\,Ag^{-1})$	[23]
Crumpled nitrogen-doped graphene nanosheets	Two-electrode $(1\,M\,[Bu_4N]\,BF_4\,acetonitrile)$	$245\,(1\,Ag^{-1})$ $226\,(10\,Ag^{-1})$	[28]
Porous graphene	Two-electrode $((BMIMBF_4)/AN)$	$166\,(5.7\,Ag^{-1})$	[29]

application. For example, Zhu et al. [29] reported that KOH activation can generate holes or defects on the surface of graphene. The activation step was performed through treatment of microwave exfoliated GO (MEGO) with KOH under flowing argon at 800°C for 1 h (Figure 6). The surface area of the active product can be as high as $3100\,m^2\,g^{-1}$, which is much higher than that of theoretical value of pristine graphene due to the existence of abandon holes or defects. When the performance of the product was measured with a two-electrode symmetrical supercapacitor cell using 1-butyl-3-methyl-imidazolium tetrafluoroborate $(BMIMBF_4)/AN$ as an electrolyte, the specific capacitances were calculated to be 165, 166, and $166\,Fg^{-1}$ at current densities of 1.4, 2.8, and $5.7\,Ag^{-1}$, respectively. The high performance of this material is closely related to its highly interconnected porous structure and its short diffusion pathways, which favor fast ion transport.

Zhao et al. [30] also reported the introduction of in-plane carbon vacancy defects (pores) into graphene sheets through a more facile solution-based method. As illustrated in Figure 7(a), in-plane defects can be introduced into the basal planes of GO via ultrasonic-assisted treatment in hot HNO_3. Under such conditions, sections of GO can be transformed into soluble polyaromatic hydrocarbons, and a holey GO sheet (HGO) is thus formed. Subsequent thermal reduction can convert the HGO sheet into electrically conductive holey graphene sheets. The in-plane porosity can provide a high density of cross-plane ion diffusion channels that facilitate ion transport and energy storage at high rates. When the electrochemical performance of holey graphene papers with a thickness of $\sim 5\,\mu m$ was tested as LIB anodes (Figures 7(c)–7(f)), reversible capacities of 454 and $178\,mAhg^{-1}$ were obtained at current densities of $50\,mAg^{-1}$ and $2000\,mAg^{-1}$, respectively; these capacities were obtained in the potential range of 0.01 to 1.5 V relative to Li/Li^+.

As an alternative approach, Fang et al. [31] fabricated novel mesoporous graphene from mesoporous carbon nanosheets. Two-dimensional-ordered mesoporous carbon materials were first obtained by carbonization of low-concentration, close-packed assemblies of monomicelles on a substrate surface (AAO template) at 400°C. After carbonization, these carbon nanosheets were converted into mesoporous graphene nanosheets by further treatment at

700°C under Ar. The obtained 2D mesoporous nanosheets had thicknesses of approximately 1 nm and offered a unique combination of flat graphene layers with large surface areas and abundant ordered mesopores as efficient ion transport pathways (Figures 8(a) and 8(b)). When used as an LIB anode material, the mesoporous graphene nanosheets exhibited an ultrahigh initial discharge capacity of $3535\,mAhg^{-1}$ at $100\,mAg^{-1}$, and a reversible capacity of $1040\,mAhg^{-1}$ was obtained (Figures 8(c) and 8(d)). The capacity loss during the first cycle can be attributed to the decomposition of the electrolyte and the formation of SEI on the surface of the electrode materials. Even at a high current density of $5\,Ag^{-1}$, a reversible capacity of $255\,mAhg^{-1}$ could still be obtained, and, when the current density was reset to $100\,mAg^{-1}$ after 60 cycles at various current densities, the capacity of $833\,mAhg^{-1}$ was retained.

5. Conclusions and Outlook

Graphene has attracted much attention in the field of electrochemical energy storage because of its unique atom-thick 2D structure and excellent electrical, thermal, mechanical, and chemical properties. Furthermore, graphene may be produced on a large scale at low cost in the near future [32, 33]. Here, we have reviewed some recent work on the modification and application of graphene as an electrode material for LIBs and supercapacitors. The performances of the graphene-based electrodes mentioned in this review chapter are summarized in Tables 1 and 2. From what shown in these tables, specific capacities, specific capacitances, and current densities of up to $1600\,mAhg^{-1}$, $245\,Fg^{-1}$, $25\,Ag^{-1}$ (for LIB), and $1000\,Ag^{-1}$ (for supercapacitor) have been reported for devices based on different types of graphene. These values indicate that graphene-based LIBs and supercapacitors can indeed compete with many other energy storage devices.

Although considerable progress has been achieved, studies in this field are in their initial stages, and several challenges still remain. For example, the chemical and physical stabilities of graphene-based materials still need improvement, and the lithium storage capacity of graphene still decreases during long-term cycling. Furthermore, the mechanisms of the graphene-based materials in energy storage systems are not

completely clear, and the explanations for lithium storage in different forms of graphene are still confusing. Nevertheless, graphene-based materials have already provided numerous opportunities to improve the performance of LIBs and supercapacitors. After fully exploring the potential of graphene through the multidisciplinary efforts of chemists, physicists, and materials scientists, we believe that many applications of these materials will become realized in the near future.

Acknowledgment

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