전기화학 커패시터 응용을 위한 용액기반의 2차원 소재 제조

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Solution-based Synthesis of Two-dimensional Materials for Electrochemical Capacitors

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초 록

2차원 소재인 그래핀과 이황화몰리브덴(MoS₂)은 슈퍼커패시터 응용을 위한 많은 관심과 무한한 가능성을 보여주었다. 2차원 소재의 슈퍼커패시터 응용성을 높이기 위해서는 2차원 소재 제조를 위한 효율적이면서 친환경적인 저비용 합성법이 개발되어야 한다. 본 논문에서 우리는 최근 개발된 슈퍼커패시터용 용액기반 2차원 소재 제조 기술을 논하고자 한다. 화학적 박리-환원, 화학적 삽입, 액상 박리 기술법들을 소개하고자 한다. 또한 그래핀과 이황화몰리브덴의 전기화학적 특성들을 정리하였다. 용액기반 공정들과 함께 개선되어야 할 나노시트들의 조성, 크기 및 두께 조절 기술 개발을 다룬다.

Abstract

Two-dimensional (2D) materials, especially graphene and MoS₂ sheets, have gained much attention and shown great promise for the application in supercapacitors. To widely use the 2D materials for supercapacitors, highly efficient, low cost, and environmentally friendly synthetic methods for the preparation of 2D materials should be developed. Here, we will review recently developed solution-based processes for preparing 2D materials for supercapacitors. Chemical exfoliation-reduction, chemical intercalation, and liquid phase exfoliation methods will be introduced. Moreover, the electrochemical characteristics of graphene and MoS₂-based electrodes for supercapacitors are summarized. In addition to solution-based processes, other challenges and opportunities are discussed in terms of controlling nanosheet compositions, sizes, and thicknesses.

Keywords: supercapacitor, graphene, MoS₂, solution

1. Introduction

The rapid growth of the global population and economy requires renewable and sustainable energy sources, such as solar cells, fuel cells, batteries, and supercapacitors[1-5]. As one of the major energy storage devices, supercapacitors or electrochemical capacitors (ECs) are emerging, which can provide high power density, fast charge/discharge, and excellent cycle life[6-9]. The energy and power densities of ECs bridge the gap between conventional capacitors and batteries. The gravimetric energy (E) and power (P) densities are indicated by the following equations[8] :

$$E = 1/2C(V_{max})^2 \tag{1}$$

$$P = (V_{max} - V_{drop})^2/4RM \tag{2}$$

where, C is specific capacitance, V_{max} is the cell voltage, R is the internal resistance from IR drop (= $V_{drop}/2I$), and M is the total weight of both electrodes. ECs can be divided typically into two kinds of ECs based on charge storage mechanisms[10]. One is electrical double layer capacitors (EDLCs) that can accumulate charges by ion adsorption from an electrolyte to the surface of carbon-based electrodes (*e.g.*, activated carbons, carbon nanotubes, and graphene). Another is pseudocapacitors, in which energy is stored by fast surface redox reactions in pseudo-capacitive materials, including metal oxides, metal hydroxides, and conducting polymers. Note that the energy and power performances of ECs strongly depend on the features of electrode materials, such as surface area, porous structure, electronic and ionic conductivity, and mechanical properties[11-13].

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Two-dimensional (2D) nanomaterials have been attracted much attention as a great potential as electrode materials for supercapacitors[14-17]. They have a large surface area, ultrathin thickness, reactive basal planes and edges. So far, various 2D nanomaterials, including graphene, transition metal oxides, transition metal dichalcogenides, and transition metal carbides and nitrides (MXenes), have been extensively explored as electrode materials for development of ECs[16]. For instance, graphene, a one-atom-thick 2D single layer of sp^2-bonded carbon, has showed extraordinary electrochemical performances compared to the graphite counterparts. Inspired by the great achievements of graphene-based materials in the past decade, 2D metal dichalcogenides are showing great promise for energy storage applications. In particular, MoS_2 is one of the most common transition metal dichalcogenides for application of ECs. Recently, Chhowalla *et al.* demonstrated that Li-ion intercalated MoS_2 nanosheets, mostly consisted of 1T phase (~70%) delivered as high as 650 F/cm^3 at scan rate of 20 mV/s and excellent cycle life (> 5,000 cycles)[18].

To optimize properties and enhance electrochemical performances in EC applications, rational design and synthesis of 2D nanomaterials should be carefully considered. Until now, 2D nanomaterials can be prepared by various methods, including mechanical exfoliation, chemical vapor deposition (CVD), chemical synthesis, Li-intercalation and exfoliation, chemical exfoliation and reduction, liquid exfoliation, and sonication-assisted exfoliation[15,16,19]. Although mechanical exfoliation and CVD method can yield 2D nanomaterials with high quality, small amounts of their products are limited to the preparation electrode and practical EC devices. Among various methods for preparing 2D nanomaterials, solution-based processes are more suitable for application of ECs because of their high yield, large scale, and facilitated process.

In this review, our aim is to describe the solution-based methods for preparation of 2D nanomaterials for energy storage of ECs. Synthesis methods are focused on graphene and MoS_2 nanomaterials because they are mostly studied for development of high-performance ECs. First, chemical exfoliation and reduction method for graphene nanomaterials are described with supercapacitive properties of graphene-based electrodes. Next, we summarized Li-intercalation and exfoliation, liquid exfoliation, and sonication-assisted exfoliation methods for preparation of MoS_2 nanomaterials with highlights on the outstanding electrochemical performances of MoS_2-based electrodes.

2. Preparation Methods for Graphene

Owing to the high surface area (~2630 m^2/g), high electrical conductivity, and mechanical strength, graphene has been used as one of the most promising electrode materials for ECs. Since Ruoff *et al.* reported great potential of reduced graphene oxide (rGO) for application of ECs, tremendous efforts have been devoted to synthesis of rGO-based electrode materials[20]. The rGO sheets have been synthesized by oxidation-exfoliation-reduction of graphite bulk powders [21,22]. This method renders high yield, easy functionalization, and tunable properties of rGO nanomaterials in solution without the need
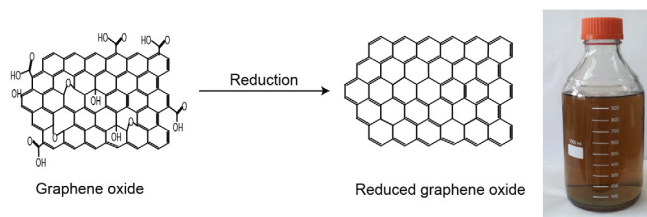

Figure 1. Schematic illustration of GO and rGO sheets obtained from chemical exfoliation-oxidation-reduction process (Photo image is GO dispersion).

for special equipment. During this process, graphene oxide (GO) and rGO sheets were produced. The main challenge in chemical exfoliation and reduction process is to prevent aggregation of rGO sheets originated from interactions and increase electrical conductivity of rGO sheets. In this section, synthesis of GO and rGO sheets obtained from oxidation-exfoliation-reduction of graphite bulk powders was briefly summarized.

2.1. Synthesis of GO

GO materials can be synthesized by exfoliation of graphite oxide prepared by chemical oxidation of bulk graphite using strong oxidants[23-25]. Graphite oxide was usually synthesized by the modified Hummers method. Briefly, graphite powder dispersed in concentrated H_2SO_4 solution was strongly oxidized by adding Na_2NO_3 and $KMnO_4$ [23]. The resulting graphite oxide was obtained by adding H_2O_2. GO sheets dispersed in aqueous solution were obtained by exfoliation of graphite oxide using mild ultrasonication. As-prepared GO solution was purified by centrifugation and dialysis to remove aggregates and impurities. As-synthesized GO contains oxygenated functional groups, such as, hydroxyl, epoxy, carbonyl, and carboxyl groups. Figure 1 shows chemical structure of GO and rGO sheets obtained from chemical exfoliation-oxidation-reduction process. The GO solution is highly stable colloidal suspension (Figure 1).

2.2. Synthesis of rGO

The rGO sheets can be prepared by reducing GO sheets using various reduction methods, such as chemical, thermal, electrochemical, and microwave irradiation reductions. Chemical reduction was widely used to prepare rGO sheets where acidic and alkaline agents were used. In particular, Li and co-workers reported that a stable rGO colloidal suspension is prepared by reduction of GO sheets dispersion in ammonia solution using hydrazine[26]. The residual oxygenated groups effectively prevent re-stacking of rGO sheets and enhance the repulsion force, resulting in good dispersion in aqueous solution. Alternatively, Ruoff *et al.* reported that acidic media of hydriodic acid is employed as reducing agent to prepare rGO sheets[27]. The resulting rGO sheets had a high electrical conductivity of 300 S/cm. This acidic media enabled to produce better graphitization of rGO sheets with lower structural defects compared to the rGO sheets obtained from hydrazine-based reduction process. These chemical reduction methods provide mass production of rGO sheets under solution-based process.

Table 1. Summary of Electrochemical Properties of Graphene and MoS₂ Nanosheets

| Materials	Electrochemical performances	Electrolyte	Configuration	Ref.
rGO	100 F/g	Tetraethylammonium tetrafluoroborate/MeCN	full cell	20
a-MEGO	166 F/g, 70 Wh/kg, 250 kW/kg	[BMIM]BF$_4$/MeCN	full cell	35
N-doped rGO	284 F/g	[Bu4N]BF$_4$/MeCN	full cell	36
3D MnO$_2$/rGO film	389 F/g	1 M H$_2$SO$_4$	half cell	12
N,B-doped rGO	488 F/cm^3	1 M H$_2$SO$_4$	half cell	37
Undoped rGO	181 F/g	1 M H$_2$SO$_4$	half cell	47
3D Fe$_2$O$_3$/rGO	260 F/g	2M LiOH	half cell	31
1T MoS$_2$	650 F/cm^3, 0.11 Wh/cm^3, 51 W/cm^3	1M H$_2$SO$_4$	half cell	18
N-doped MoS$_2$	158 F/g	1M Na$_2$SO$_4$	half cell	44
3D MoS$_2$/rGO aerogel	268 F/g	1M Na$_2$SO$_4$	half cell	45
MoS$_2$ nanosheets	8 mF/cm^2	1M NaOH	half cell	46
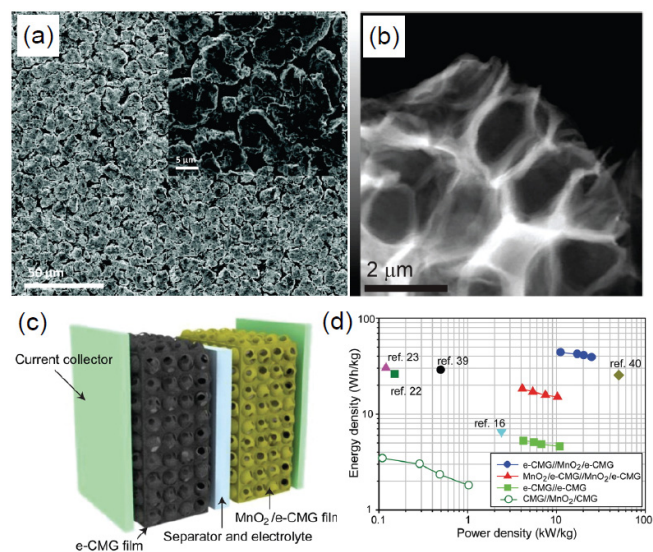
Figure 2. (a) SEM images of rGO particles. (b) HADDF-STEM image of 3D porous rGO film. (c) Scheme of 3D rGO//MnO₂/rGO asymmetric ECs. (d) Raonge plot of asymmetric ECs of 3D rGO//MnO₂/rGO with energy and power densities. (a) Reproduced with permission[20]. Copyright 2008, American Chemical Society. (b-d) Reproduced with permission[12]. Copyright 2012, American Chemical Society.

However, the use of chemical reduction reagents caused several issues of toxic problem and sheet aggregation. To address these issues, more advanced strategies have been suggested to prepare rGO sheets. Hydrothermal and solvothermal reductions have been explored for preparing rGO sheets[28-30]. These methods efficiently remove oxygenated groups from GO and repairing their graphitic structures. In addition, hydrothermal and solvothermal methods using GO dispersion induced 3D architectures of rGO-aerogels and hydrogels. This 3D structure provides graphene materials with high surface area, rapid ion and electron transfer, porous structure, and strong mechanical strength. These unique properties are advantageous in preparation of electrodes for EC applications. Recently, Choi et al. described that the microwave

irradiation allows GO sheets to reduction conversion into exfoliated rGO sheets within a few seconds[31,32].

3. Application of ECs based on rGO Materials

The rGO sheets produced by chemical exfoliation and reduction have been widely explored as electrode materials for constructing EDLCs and asymmetric supercapacitors (ASCs). The rGO sheets can be easily assembled into various promising structures, such as 1D fibers, 2D films, and 3D aerogels and hydrogels, and these structures dramatically enhanced electrochemical performances[33,34]. Previous efforts have been devoted to construction of pore structures for ion transfer and high pathway for electron transfer, leading to high energy and power densities of EC devices. In this section, numerous kinds of rGO-based electrode materials for EC applications are summarized with electrochemical performances.

Ruoff et al. firstly have tried to use rGO sheets as electrode materials for ECs (Figure 2a). The aggregated rGO with microsized ~20 μm had an electrical conductivity of 200 S/m and a specific capacitance of 100 F/g using organic electrolyte[20]. To incorporate pore structure into rGO sheets, same group synthesized KOH-activated graphene sheets with micro- and mesoporosity[35]. The resulting product was introduced by "a-MEGO". The a-MEGO was synthesized by microwave exfoliation of graphite oxide and post-treatment of KOH activation at 800 ℃ under argon gas. As-obtained a-MEGO had high surface are of ~3000 m^2/g and high electrical conductivity of 500 S/m. Using a-MEGO materials, symmetric EDLC devices were constructed and tested using a 1-butyl-3-methyl-imidazolium-tetrafluoroborate (BMIM BF$_4$)/acetonitrile (MeCN) electrolyte in a electrochemical window of 3.5 V. This EDLC delivered as high as gravimetric specific capacitance of 166 F/g, a maximum energy density of 70 Wh/kg, and power density of 250 kW/kg.

On the other hand, 3D porous rGO structures have been suggested to be effective in prevention of restacking of graphene sheets and in facilitating the ion transfer through the pore structure. 3D rGO with various structures, such as hydrogels, aerogels, foams, and 3D films,
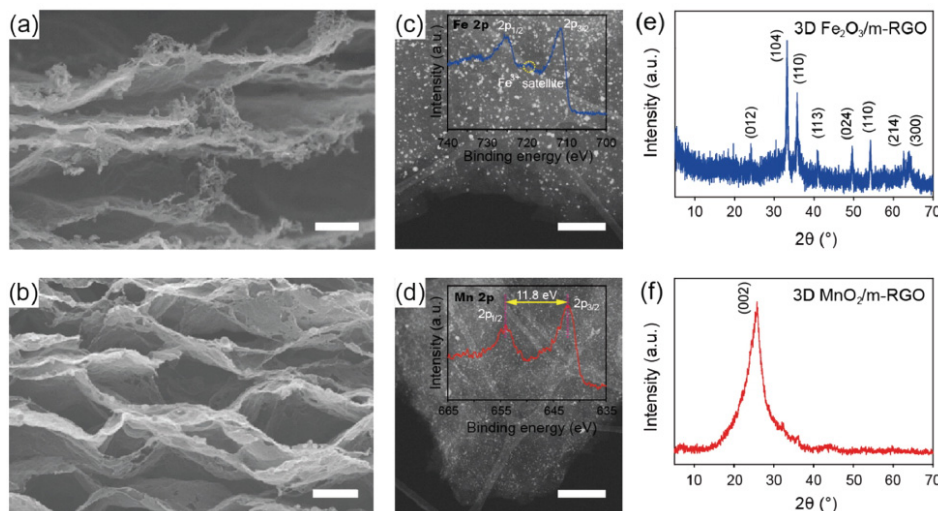
Figure 3. Top and bottom columns are corresponding cross-section SEM images, TEM images, XPS, and XRD patterns of (a, c, and e) 3D Fe₂O₃/rGO and (b, d, and f) 3D MnO₂/rGO films, respectively. (a-f) Reproduced with permission[31]. Copyright 2012, American Chemical Society.

have been extensively explored as electrodes in development of ECs[33,34]. A self-assembled rGO hydrogel was prepared by one-step hydrothermal method. This 3D rGO hydrogel had a high specific surface area of 964 m^2/g and showed a high specific capacitance of 152 F/g[30]. In order to increase capacitance and energy density, various active metal oxides and conducting polymers were incorporated into rGO structures, including MnO_2, polyaniline, polypyrrole, NiO, $Ni(OH)_2$, and Co_3O_4[33,34]. Our group reports 3D rGO films by using polystyrene colloidal particles as sacrificial templates (Figure 2b-2d). This 3D porous film served as mechanical and electrical supports for deposition of active MnO_2 layers onto the surface of 3D rGO films. The resulting 3D MnO_2/rGO composite films showed excellent electrochemical properties, such as a high specific capacitance of 389 F/g, high energy density of 44 Wh/kg, and high power density of 25 kW/kg under an asymmetric full cell. The porous rGO structure with a high surface area facilitates fast ion and electron transport within the entire electrode, leading to the high-performance of ECs[12]. More recently, our group developed fast and simple method for preparation of 3D porous heterostructured films using microwave irradiation[31]. Microwave irradiation enabled exfoliation and reduction of GO sheets into rGO sheets (Figure 3a-3f). In particular, a series of highly pseudocapacitive materials of Fe_2O_3 and MnO_2 were simultaneously synthesized during microwave irradiation. 3D MnO_2/rGO films had a high specific capacitance of 382 F/g at scan rate of 5 mV/s, while 3D Fe_2O_3/rGO films showed 260 F/g. Moreover, when assembling two 3D composite films into asymmetric cells, the asymmetric EC cells had a wide working potential windows of 1.8 V, leading to the high energy density (41.7 Wh/kg) and power density (13.5 kW/kg). A 2 M LiOH electrolyte was used.

Introduction of heteroatoms, such as N, S, O, and P, in rGO sheets can increase specific capacitances because of the enhanced electron donor-acceptor abilities. N-doped rGo sheets were prepared by reaction of GO with cyanamide, followed by thermal treatment[36]. The nitrogen contents of 10 wt% increased dramatically specific capacitance of 284 F/g in a 1 M tetrabutylammonium tetrafluoroborate ([Bu₄N]BF₄)/MeCN

electrolyte. The resulting materials also delivered high rate capability; the original capacitance was still maintained (226 F/g at 10 A/g). Nitrogen and boron co-doped graphene films provided a high volumetric capacitance of ~488 F/cm³[37]. Heteroatom dopping not only facilitate electron transfer by means of change of electronic structure, but also alleviate sheet aggregation, resulting in facilitated ion transfer.

4. Preparation Methods for MoS₂

Inspired by graphene materials, graphene-like other 2D materials have showed a great potential for energy storage applications. Among the 2D materials, MoS_2 is widely investigated in application of ECs. MoS_2 has 2H (semi-conducting), 1T (metallic), both metastable, and 3R (stable at standard conditions) polytypes[38-41]. MoS_2 sheets can be obtained from various methods, such as mechanical exfoliation, chemical intercalation followed by exfoliation, and liquid phase exfoliation by direct sonication[38-41]. Thus, this section introduces preparation methods, particularly solution-based process, for MoS_2. Solution-based exfoliation methods can be divided into three categories: (1) lithium intercalation-exfoliation, (2) liquid exfoliation, and (3) surfactant-assisted exfoliation via ultrasonication, shear force, or ball milling.

4.1. Li intercalation-exfoliation method for MoS₂

To obtain large amounts of MoS_2 sheets, Li intercalation-exfoliation method has been developed, including chemical and electrochemical intercalation process. MoS_2 sheets can be easily intercalated using lithium reactants, typically *n*-butyllithium diluted in hexane. Li slightly intercalated into the MoS_2 sheets during 48 hours at room temperature under argon gas according to the following reaction equation[40] :
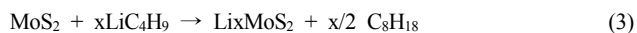
$$MoS_2 + xLiC_4H_9 \rightarrow Li_xMoS_2 + x/2\ C_8H_{18} \qquad (3)$$

Figure 4 shows schematic illustration of lithium intercalation-exfoliation method for preparation of MoS_2 sheets. The electron transfer from

Figure 4. (a) Scheme of lithium intercalation-exfoliation method for preparation of MoS$_2$ sheets. (b) SEM image of exfoliated MoS$_2$ sheets.

butyl to the MoS$_2$ layers indicates the insertion of Li$^+$ in the van der Waals gap. To reduce reaction time of 48 hours, electrochemical Li-intercalation method was also suggested. Using lithium ion battery system, the amount of inserted Li$^+$ was obtained by the discharging. After discharging, single or few layers of MoS$_2$ sheets were obtained by sonicating Li$_x$MoS$_2$ in water or ethanol.

4.2. Liquid exfoliation method for MoS$_2$

Liquid exfoliation method provides versatile, scalable, and sustainable approaches for preparation of 2D nanomaterials. The selection of proper solvent is one of the most important factors for high yield of exfoliation 2D MoS$_2$ nanosheets. Thus, solvents with high boiling points, including *N*-methyl-2-pyrolidone (NMP), dimethylformamide (DMF), and *N*-cyclohexyl-2-pyrrolidone (CHP), have been extensively used to exfoliate MoS$_2$ sheets. In addition, the Hansen solubility parameter has been recognized as key factors for determining dispersive, polar, and hydrogen-bonding components of the cohesive material energy density[42]. These parameters guide proper choice of solvents for exfoliating 2D nanosheets. Liquid exfoliation method is accompanied with centrifugation process to remove unexfoliated 2D bulk materials. Although liquid exfoliation method enabled to exfoliated MoS$_2$ nanosheets in solvents, the yield is relatively low, which limit the scalability of liquid exfoliation method.

4.3. Surfactant-assisted exfoliation for MoS$_2$ nanosheets

As an alternative method to liquid exfoliation method, shear mixing and ball milling process have been developed. These methods allow 2D materials to produce mass production. Shear mixing process up to high sear rates (> 10^4/s) enabled graphite to be effectively exfoliated up to the hundred-liter scale (100 g/h)[19]. In addition, ball milling process provides exfoliated 2D nanomaterials using shear forces and mechanical collisions[43]. The addition of suitable surfactants promotes exfoliation process. Although these methods produce large amounts of 2D nanosheet samples compared to other previous methods, the uncontrollable size and thickness are still big challenges.

5. Application of ECs Based on MoS$_2$ Materials

MoS$_2$ nanosheets have large surface area and active sites for charge storage, leading to the high theoretical specific capacitance (> 1000 F/g). MoS$_2$ can accumulate charges by means of formation of double

layers on inter- and intra-sheet of individual MoS$_2$ and faradic reactions on Mo transition metal centers using a wide range of oxidation states from +2 to +6. However, the MoS$_2$-based materials suffer from poor electronic conductivity and strong tendency of intersheet aggregation. Chhowalla *et al.* synthesized MoS$_2$ sheets using lithium-intercalation-exfoliation method. After collecting 1T phase-MoS$_2$ sheets (~70%), free-standing MoS$_2$ films were prepared by vacuum filtration method[18]. This 1T-MoS$_2$ film high volumetric capacitance up to 650 F/cm^3 at scan rate of 20 mV/s with a good long-term stability (97% retention of original capacitance over 5000 cycles). The maximum energy power densities of 1T-MoS$_2$ films were 0.11 Wh/cm^3 and 51 W/cm^3, respectively. This superior performance was attributed to the enhanced electrical conductivity of 1T phase of MoS$_2$ sheets. In order to increase electrical conductivity of MoS$_2$ sheets, nitrogen-doped carbon layers were coated onto the surface of MoS$_2$ by self-polymerization of dopamine followed by carbonization process[44]. As-synthesized N-doped MoS$_2$ sheets showed high specific capacitance of 158 F/g, high rate capability, and excellent cycling performances when measured in 1 M Na$_2$SO$_4$ electrolyte. These superior electrochemical performances should be attributed to the fast and efficient electron transfer within MoS$_2$ sheets due to the N-doped carbon layers. 3D porous MoS$_2$/rGO aerogels were prepared to increase electrochemical performances of ECs[45]. 3D porous MoS$_2$/rGO aerogels were prepared by a hydrothermal assembly and reduction reaction using a mixture of pre-synthesized GO and MoS$_2$ dispersions. GO dispersion was prepared by modified Hummers method, while MoS$_2$ dispersion obtained from lithium intercalation method. The resulting 3D composite aerogels exhibited superior supercapacitor performances of high specific capacitance (268 F/g), high rate capability, and good cycle life (93% retention for 1000 cycles).

6. Conclusions and Outlook

Solution-based process for 2D nanomaterials, such as chemical exfoliation, lithium intercalation-exfoliation, liquid exfoliation, surfactant-assisted exfoliation methods, allows 2D materials to be effectively exfoliated into stable colloidal dispersions. The stable dispersion enabled to facilitate further processes of vacuum filtration, spin-coating, spray deposition, roll-to-roll process, which are commonly used to fabricate bulk electrodes for application of ECs. Owing to unique properties, 2D nanomaterials, especially when exfoliated to ultrathin nanosheets, demonstrated their extraordinary electrochemical performances for ECs. The composition, shape, size, and thickness of 2D nanosheets significantly influence the electrochemical performances in energy storage systems. In the case of rGO sheets, restacking phenomenon should be addressed in electrochemical energy storage devices. Thus, porous and curved structures are critical points that allow fast ion transport through 2D channels, which are responsible for high energy density of ECs. Drawbacks of 2D MoS$_2$ sheets are intrinsically poor electrical conductivity of MoS$_2$. Control of 1T phase, carbon coating, and hybridization processes have been developed to support electron transfer through MoS$_2$ sheets. Although 2D nanosheets produced by sol-

ution-based processes showed enhanced electrochemical performances in ECs, the synthesis methods should be more improved in terms of control of thickness, size, and yield. Meanwhile, low cost, scalable, environmentally friendly processes must be further developed.

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