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Recent Advances on Multi-Dimensional Nanocarbons for Superapacitors: A Review

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ABSTRACT

In general, the charge storage characteristics and overall performance of electrochemical energy devices (such as lithium-ion batteries and supercapacitors) significantly depends on the structural and geometrical factors of the electrodes' active materials. The most widely used active materials of electrochemical energy storage devices are based on carbons of various forms. Each carbon type has drawbacks and advantages when used as the electrode material. Studies have been recently carried out to combine different types of carbons, in particular nanostructured carbons, in order to overcome the structure-originated limitations and thus enhance the overall electrochemical performances. In this feature article, we report the recent progress on the development of this novel class of materials (multidimensional nanocarbons), and their applications for supercapacitors. Multidimensional nanocarbons include graphenes/carbon nanotubes (CNTs), CNTs/carbon films, CNTs/fullerenes, and ternary carbon nanostructures. Various applications using these multidimensional nanocarbons have been proposed and demonstrated in the literature. Owing to the recent extensive studies on electrochemical energy storage devices and considering that carbons are their most fundamental electrode materials, the number of reports on nanocarbons employed as electrodes of the electrochemical energy storage devices is rapidly increasing. Recently, numerous multidimensional nanocarbons have been designed, prepared, and utilized as electrodes of electrochemical capacitors or supercapacitors, which are considered next-generation energy devices owing to their unique merits compared to the conventional structures. In this review, we summarize the basic motivations, preparation methods, and resultant supercapacitor performances of each class of multidimensional nanocarbons published in the literature, focusing on recent reports.

Keywords : Multi-dimensional, Nanocarbons, Graphenes, Carbon nanotubes, Fullerenes, Supercapacitors

1. Introduction

An increasing number of studies on a new class of carbon nanomaterials (nanocarbons) have been recently reported. These novel nanocarbons are referred to as multidimensional carbons. Carbon is one of the most fundamental and versatile elements on earth, the 15th most abundant element in the Earth crust, and the most common element in organic life forms. The carbon atoms bond together in various structural forms with sp^2 and sp^3 bondings. The resulting allotropes of carbons can be categorized into bulk phases (graphite, diamond, and amorphous carbon) and nanoscale low-dimensional carbons, i.e., nanocarbons. Since the discovery of zero-dimensional (0D) carbons (fullerenes) in 1985, several nanocarbons such as carbon nanotubes (CNTs, one-dimensional (1D)) and graphene (two-dimensional (2D)) were discovered and intensively investigated owing to their remarkable physical, chemical, and mechanical properties.

Each nanocarbon has unique characteristics. CNTs exhibit high electrical conductivity, very large thermal conductivity, high mechanical resilience, and open tubular structures. Graphene is a 2D single-layered sp^2 carbon [1], with a large surface area (larger than 2600 m^2 g^{-1} [2]) as well as high electrical and thermal conductivities. Fullerenes have the form of hollow spheres consisting of sp^2-hybridized

carbon atoms, which were discovered by Kroto et al. in 1985 [3]. Fullerenes can be used to form endohedral species, where metal atoms are trapped inside cage of a fullerene.

Recently, considering the energy crisis, environmental issues, and development of portable electronics, there has been an increasing demand for storage technologies. Batteries and supercapacitors have attracted the most attention among the various energy storage devices. Supercapacitors hold considerable potentials as the next generation storage devices owing to their advantages, including high power densities, rapid charging and discharging capabilities, long life-cycles (>100,000 cycles), and environmental friendliness [4-7]. It is well-known that supercapacitors can be classified into electrical double-layer capacitors (EDLCs) and pseudocapacitors based on their charge storage mechanisms [8]. EDLCs store the electrical charge by separation of charge in the Helmholtz double layer, whose mechanism is electrostatic. Pseudocapacitors utilize the reversible Faradaic redox reactions, providing higher capacitances and energy densities than those of EDLCs [9-11]. At present, major commercial supercapacitors are EDLCs, in which the electrode materials are carbons mainly activated carbons which have merits of extremely high surface areas and low costs. Recently, nanocarbons have been extensively studied as electrodes of supercapacitors due to their unique potentials as the electrodes exhibiting also high surface areas to enable an efficient charge transport at the electrode-electrolyte interface [1].

"Multidimensional" nanocarbons are defined as carbons formed by combining nanocarbons with different dimensions (0D, 1D, 2D and 3D). Most common forms of such multi-dimensional nanocarbons appeared as incorporating CNTs (1D nanocarbons) into graphenes (2D nanocarbons). There are numerous advantages of designing the multi-dimensional nanocarbons for their applications as electrodes of electrochemical energy storage devices. First, we can expect a significant enhancement in the active electrode materials' surface area by combining 1D or 2D nanocarbons. Second, in the case of employing 2D carbons such as graphenes, additional nanocarbons (e.g. CNTs) can be used as pillars or spacers to avoid aggregation of 2D nanocarbons (e.g. graphenes). The spacers could provide efficient channels for the electrolyte ions to enhance the charge-discharge characteristics of the energy devices [12]. Considering the overall capabilities of supercapacitors or lithium-ion batteries are significantly affected by the geometrical and structural properties of the carbon electrode materials and each nanocarbon has their own pros and cons, the structure-related limitations cab be overcome by combining different types of nanocarbons [1].

In this review, we will overview and summarize recent advances on this emerging new class of materials, i.e., multi-dimensional nanocarbons and their applications for supercapacitors.

Table 1 Different carbon structures used in EDLCs with onion-like carbon, carbon nanotube, graphene, activated carbon, carbide-derived carbon, and template carbon

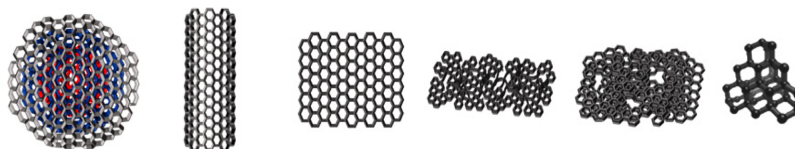| Material	Carbon onions	Carbon nanotubes	Graphene	Activated carbon	Carbide derived carbon	Templated carbon
Dimensionality	0D	1D	2D	3D	3D	3D
Conductivity	High	High	High	Low	Moderate	Low
Volumetric capacitance	Low	Low	Moderate	High	High	Low
Cost	High	High	Moderate	Low	Moderate	High
Structure						

Fig. 1. Various carbon nanostructures to form the multi-dimensional nanocarbons. Redrawn from reference 2.

2. Various multi-dimensional nanocarbons for supercapacitor applications

2.1 Graphene/CNTs hybrid films

Various studies have been performed to combine 1D and 2D carbon nanostructures. Among various 1D carbon allotropes, CNTs (1D) have been extensively employed for incorporation into 2D nanocarbons. To date, CNTs have been extensively studied as the electrodes of EDLCs. CNTs have a high mechanical resilience and open tubular structure, making them promising as electrodes of high power energy devices. In addition, their tubular geometries provide good scaffolds or supports for other active materials. One of the main drawbacks of CNTs is their relatively small specific surface area (smaller than 500 m^2 g^{-1} [2]) compared to those of other large-surface-area carbons (e.g. activated carbons), which hinders their applications in high-energy EDLCs.

Graphene was often chosen as a 2D nanocarbon for the electrodes of electrochemical energy storage devices due to its excellent properties including very high electrical and thermal conductivities, tunable bandgap, large surface area, and very high mechanical strength [13]. CNTs were combined with graphene for the electrode materials of rechargeable lithium-ion secondary batteries [14] and transparent electrodes [1]. The first graphene-based EDLCs were reported by Ruoff et al. [15]; the specific capacitance of the graphene-based supercapacitor was up to 135 F g^{-1} in an aqueous electrolyte.

The main advantage of the incorporation of CNTs into graphene can be explained as follows. The performance of the graphene-based supercapacitor is limited owing to restacking of graphene during the processing. Therefore, the actual surface area of the graphene electrode is usually significantly smaller than the theoretical surface area (larger than 2600 m^2 g^{-1}) [16]. The addition of CNTs between graphene sheets provides spacers: thus, minimizing the restacking.

There have been numerous reports on explicitly employing CNTs as spacers to prevent the restacking of graphene. Cheng et al. [17] reported a graphene and single-walled CNT (SWCNT) composite film prepared by a blending process. The supercapacitors using graphene/SWCNT as electrodes exhibited very high specific capacitances of 290.6 F g^{-1} and
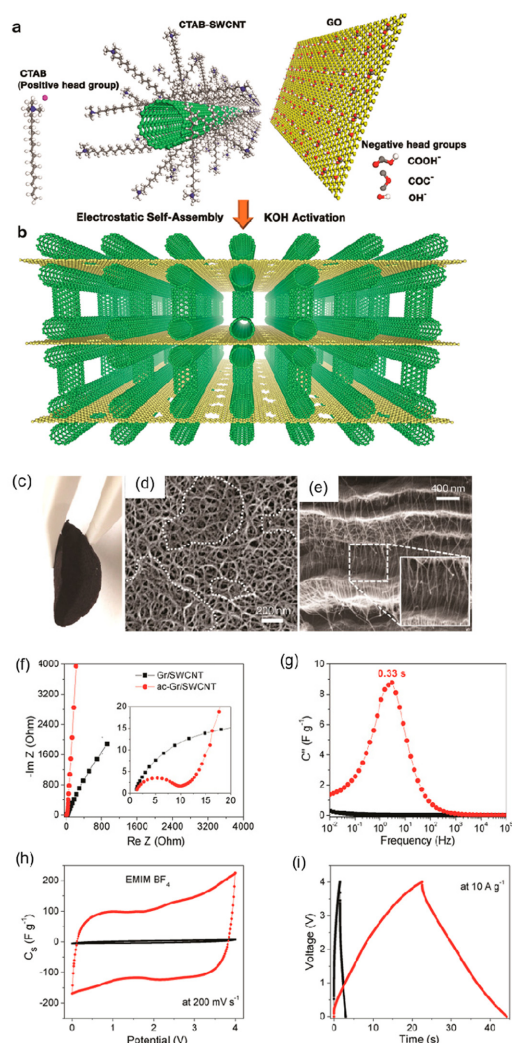

Fig. 2. Schematic for fabricating the ac-Gr/SWCNT hybrid nanostructure. (a) The CTAB-grafted SWCNTs are positively charged, and the GO layers are negatively charged due to their functional groups. (b) Schematic of the 3D SWCNT-bridged graphene block. (c) Optical micrograph showing the free-standing and flexible film. (d) Top-view SEM image showing the porous SWCNT network and remaining graphene flakes (dotted lines). (e) Crosssectional SEM image containing dangling SWCNTs (magnified in the inset). Electrochemical performance of the optimized ac-Gr/SWCNT electrode. The nonactivated Gr-SWCNT sample is shown as a reference. (f) Nyquist plot revealing the nearly ideal capacitive behavior of the cell. The inset shows a magnified view of the high-frequency region. (g) Plot of the imaginary capacitance versus the frequency showing the low relaxation time, 0.33 s, which indicates rapid ion diffusion. (h) CV curves at a scan rate of 200 mV s1 with a nearly rectangular shape, indicating an efficient EDLC. (i) CD curves at a current density of 10 A g^{-1}. Reprinted from reference 21 with the permission.

201.0 F g^{-1} in aqueous and organic electrolytes, respectively. It is reported that the addition of SWCNTs, which acted as a conductive additive, spacer, and binder, increased the energy density by 23% and power density by 31% compared to those of the graphene electrodes. Yang et al. [18] reported that the stacking of individual graphene sheets was effectively inhibited by introducing CNTs to form a 3D hierarchical structure. The specific capacitance of CNT/graphene was significantly higher than that of graphene (326.5 F g^{-1} vs. 83 F g^{-1}). Preventing graphene sheets from restacking by use of hydrothermally introduced CNTS as spacers showed a high specific capacitance of 318 F g^{-1}[19]. Recent studies have been performed on the applications of CNTs as spacers including nitrogen-doped graphene/CNTs [20], chemical-free synthesis of graphene/CNTs (for lithium-ion batteries), graphene layers pillared with SWCNTs [21], flexible nitrogen-doped graphene/CNT papers [22], and NiOH$_2$-graphene/CNTs [23].

Hybrid films of graphene and CNT were reported before the recent development of multi-dimensional nanocarbons. In 2008, Cai et al. reported the fabrication of conductive CNT films hybridized with graphitic oxide nanoparticles used as a carrier [24]. Tung et al. demonstrated nanocomposite comprised of chemically converted graphene and CNTs without surfactant to preserve the intrinsic electronic and mechanical properties of both components [1]. In a more recent report, an in situ reduction of exfoliated graphite oxides (GOs) in the presence of cationic poly(ethyleneimine) (PEI) was employed to perform self-assembly of multi-walled (MW) CNTs forming the hybrid films [25]. The sequential self-assembly of functionalized 2D graphene sheets and 1D CNTs through electrostatic interactions were reported to be suitable for the electrochemical measurements. In another recent study, a novel graphene foam was employed to make hybrid film of graphene foam/CNTs for flexible asymmetric supercapacitors [26].

Many approaches have been performed to prepare the desired graphene/CNT multi-dimensional nanocarbons, including microwave irradiation, solution based process, and CVD method. Each preparation method has advantages and disadvantages. In applications as electrodes of supercapacitors and batteries, a strong bonding of CNTs on graphene is important. In order to address the bonding issue, reports on direct growth of CNTs typically through the CVD method are increasing. Yu et al. reported a direct CNT growth on the graphene nanoplatelets (GNPs) via a thermal CVD process [27]. Vertical
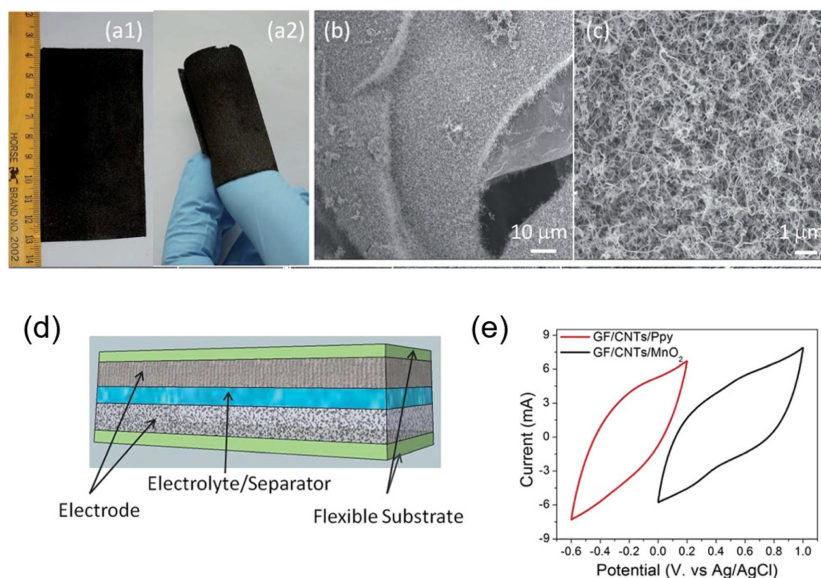

Fig. 3. (a1 and a2) Representative photograph showing the large-size and flexibility of the film. (b, c) Typical FESEM images of the GF/CNT hybrid film. (d) Schematic illustration of an ASC that consists of the GF/CNT/MnO$_2$ positive electrode, electrolyte-soaked separator and GF/CNT/Ppy negative electrode. (e) CV curves of GF/CNT/MnO$_2$ and GF/CNT/Ppy half cells in 0.5 M Na$_2$SO$_4$ solution at a scan rate of 20 mV s^{-1}. Reprinted from reference 26 with the permission.
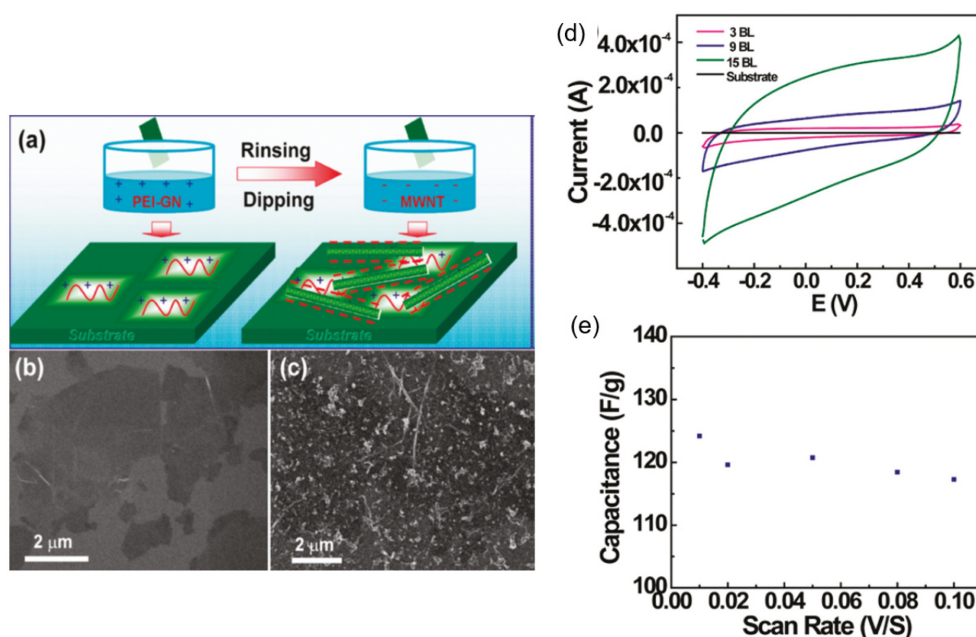
Fig. 4. (a) Illustration of positively charged PEI-GN and negatively charged MWNT film deposition process on an appropriate substrate (e.g., silicon wafer, ITO glass). SEM images of (b) the first layer PEI-GN and (c) the first bilayer [PEI-GN/MWNT-COOH]₁ film deposited on a silicon substrate. (d) CVs at a scan rate of 0.05 V/s in 1.0 M H2SO4 at room temperature obtained from heat-treated [PEI-GN/MWNT-COOH]n films with bilayer number n = 3, 9, 15. (e) Specific capacitance at scan rates of 0.01, 0.02, 0.05, 0.08, and 0.1 V/s from [PEI-GN/MWNT-COOH]₉ film in 1.0 M H_2SO_4 at room temperature. Reprinted from reference 25 with permission.

growths of CNTs on patterned grahenes were performed, yielding good flexibility and electrical conductivity [28]. Similar direct growths on graphenes or graphene-related nanocarbons were carried out by CVD method as the preparation method of CNT/graphenes.

Beidaghi et al. reported graphene/CNT composite micro-supercapacitors through electrostatic spray deposition. Their supercapacitors exhibited a high volumetric capacitance with a low RC time constant (4.8ms) [16].

CNTs and graphenes were combined to prepare the transparent conductors and electrode materials for lithium ion batteries [1]. CNTs and graphene sandwich structures with CNT pillars were fabricated by CVD for the electrodes in supercapacitors [1]. Graphene nanoplatelets were combined with CNTs without any buffer layers to improve both in- and through-plane thermal conductivities [1].

As graphenes are very thin and highly conductive, they are increasing employed as electrodes of flexible supercapacitors, which also formed another emerging field. The addition of CNTs into graphenes is beneficial as CNTs are highly conductive and porous, thus enhancing electronic and ionic tranports [29].

2.2 CNTs/carbon films

Another class of multi-dimensional nanocarbons are CNTs on various carbon films. Early demonstrations of CNTs on carbon films include an aligned growth of CNTs on graphitic substrates through plasma-enhanced CVD [30-32], supergrowth of aligned CNTs directly on carbon papers [33], and vertically aligned CNT growth on glassy carbon films by thermal CVD for cyclic voltammetry study [34]. The carbon films in these studies have several merits and advantages as the electrodes. For example, graphitic carbons are inexpensive and simple to handle. An early growth of CNTs showed low degree of alignment, while more recent works provided highly aligned or even vertically aligned CNTs on carbon films. In a study by Liu et al., vertically aligned CNTs were successfully formed on the substrates and their electrochemical properties as voltammetric elec-
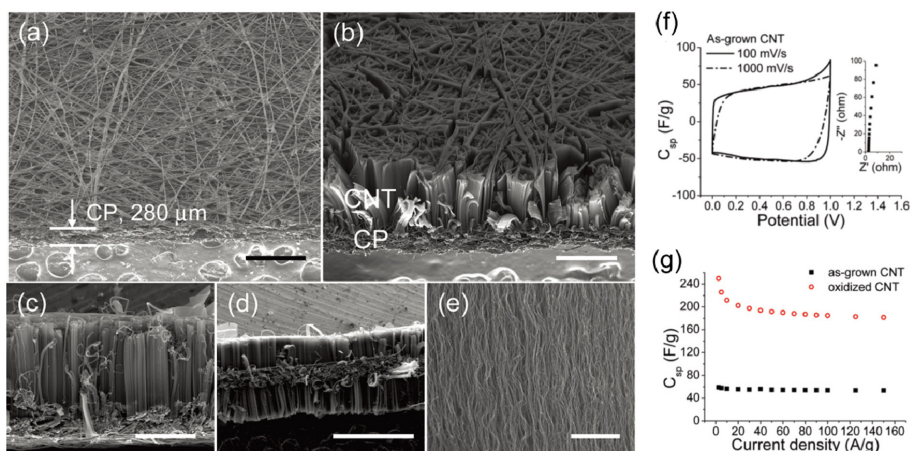
Fig. 5. Scanning electron microscopy (SEM) images of tilted views of (a) a carbon paper (CP) and (b) carbon nanotubes (CNTs) synthesized on the CP (scale bars) 500 μm). (c) SEM images of a side view of the CNTs on a CP (scale bar) 300 μm) and (d) the CNTs grown on both sides of a CP (scale bar) 1 mm). (e) Zoom-in SEM image of aligned CNTs (scale bar) 2 μm). Electrochemical properties measured in 1 M H2SO4 aqueous solution. Cyclic voltammograms of (f) as-grown CNTs. (g) Specific capacitance vs current density plot. Reprinted from reference 33 with the permission.
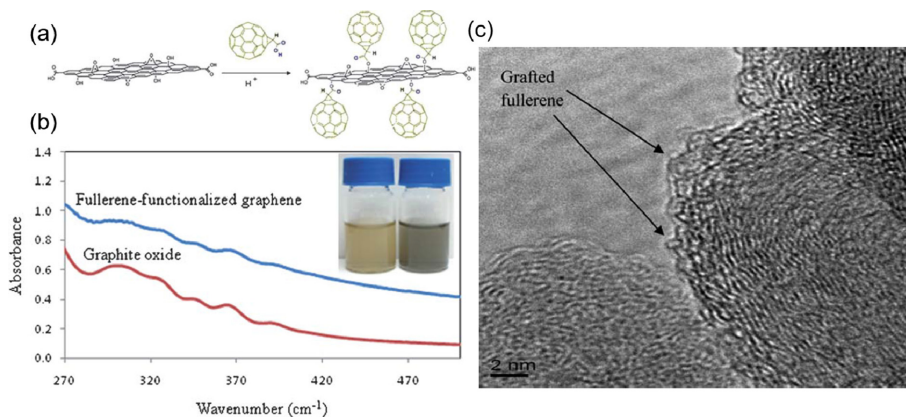

Fig. 6. (a) Functionalization of the graphite oxide via the Fisher esterification. UV–Vis spectra of graphite oxide and fullerene-functionalized graphene. Inset: a photograph of graphite oxide (left) and fullerene functionalized graphene (right) dispersion at the same concentration (100 mg L^{-1}). (c) High resolution transmission electron microscopy image of fullerene-functionalized graphene compound. Reprinted from reference 36 with the permission.

trodes were evaluated by obtaining cyclic voltammograms.

2.3 Fullerene-based supercapacitors

Fullerenes and their derivatives are considered promising as electrodes of supercapacitors because of their reversible redox charge storage and large surface areas (1100-1400 m^{2}g^{-1} [35]. However, reports on supercapacitors based on fullerenes or fullerenes combined with other carbon allotropes are limited in the literature mainly owing to the low specific capacitances [13].

However, numerous studies have been performed on multi-dimensional carbons combining fullerenes and other nanocarbons. For example, covalent bonding of 0D fullerenes onto 2D graphene oxide surface was achieved by Zhang et al. [36]. In their study, the functionalization of the graphite oxide was realized by fullerene insertion and chemical reaction through Fisher esterification, in which the esterifica-
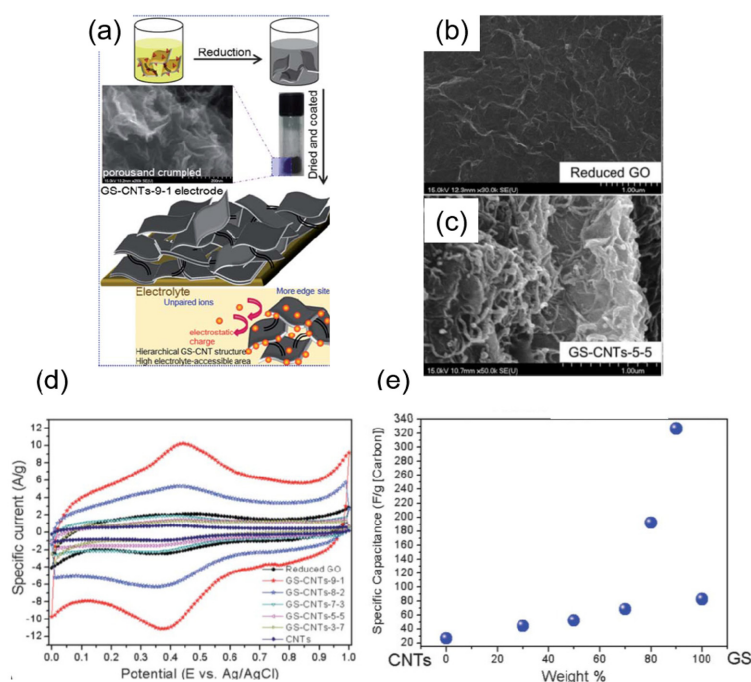
Fig. 7. Scheme for preparing (a) GS-CNTs-9-1 electrode. Fiele emission scanning electron microscopy (b) reduced GO, (c) GS-CNTs-9-1. (d) CV curves measured at 20 mV s^{-1} in 0.5M H$_2$SO$_4$ for carbon composites with various ratios of reduced GO and CNTs. (e) The dependence of CS on composition for all composites. Reprinted from ref. 18 with the permission.

tion took place between the hydroxyl groups of the graphite oxide and the carboxyl groups of the fullerenoacetic acid.

Various electrochemical sensors can be fabricated on composites of fullerenes and various carbonaceous materials. A fullerene-C$_{60}$-modified edge plane pyrolytic graphite electrode was demonstrated to electrochemically investigate prednisone [37]. Dopamine sensors were fabricated using C$_{60}$-functionalized MWCNT films [38]. The C$_{60}$-MWCNTs film showed special selectivity and sensitivity for detection of dopamine than those of a bare MWCNT film. In another study, fullerenes were supported on graphene oxide through noncovalent conjunction through facile grinding method [39]. A phosphotungstic acid-graphene oxide-fullerene film was prepared to fabricate an electrode, which exhibited showed catalytic activity for redox of biomolecules.

The successful demonstrations of fullerenes-based nanocarbons, particularly for applications in the electrochemical sensors, suggest that supercapacitor electrodes made of fullerene nanocarbons could be feasible.

2.4 Ternary carbon nanostructures

Despite their excellent chemical, physical, and electrochemical properties, graphenes naturally aggregate and stack to multilayers during the drying process in the electrode fabrication. Multilayered graphenes exhibit worse physical and chemical properties than those of the monolayer state [40,41]. In order to avoid the agglomeration, it was proposed that metal oxides such as SnO$_2$ or MnO$_2$ were inserted into the interlayers of graphene. The metal oxide "spacers" demonstrate another advantage of pesudocapacitances originating from metal oxides leading to the increase of the total capacitances. SnO$_2$-loaded CNTs were used as spacers in graphenes [42]. γ-MnO$_2$ nanoflowers were anchored onto CNTs combined with graphene nanosheets formed the flexible electrodes [40]. The ternary components (γ-MnO$_2$-CNTs-graphenes) are reported to double the specific capacitance compared to that of the graphene-only electrodes, and the capacitance is the highest reported for symmetric supercapacitors containing MnO$_2$ and graphenes [40]. Similar structure, multilayer nanoflake structure composed of

MnO_2/grapehene oxide with 3D hierarchical porous structure was reported as supercapacitor electrodes with enhanced stability [43]. In more recent applications, nitrogen-doped graphene foam/carbon nanotube/manganese dioxide were fabricated via chemical vapor deposition and hydrothermal method [44]. While MnO_2 has been extensively employed as the spacers, Rakhi et al. reported recently crystalline RuO_2 nanoparticles loaded to carbon nanocoils as spacers in reduced graphene oxide [45]. The RuO_2-based ternary electrode exhibited a high specific capacitance of 725 F g^{-1} at a scan rate of 20 mV s^{-1}. The ternary electrodes were also employed as electrodes of lithium ion batteries. Si is one of the highest specific capacity anode materials but generally, it has poor cycle performance due to its significant volume expansion during the charging and discharging. In order to overcome this problem, ternary Si-based composite electrodes were demonstrated, in which Si nanoparticles were coated on a thin carbon layer and encapsulated in a graphene framework [46].

3. Conclusions and Outlook

In this review, we summarized the recent progress preparation methods of multi-dimensional nanocarbons and their applications for supercapacitor electrodes. To date, various and almost all the morphologies of nanostructured carbon have been combined to prepare the multidimensional nanocarbons. We also observed that the synthesis and preparation methods to produce each nanocarbons were employed to result in the desired multidimensional nanocarbons. Since the electrochemical energy storage devices such as supercapacitors and batteries employ carbon as active material of the electrode, these novel nanocarbons have found their immediate applications in the electrodes of supercapacitors. The nanocarbons were used as active materials for supercapacitor electrodes exhibiting high electrochemical performances. It was often demonstrated that the electrochemical characteristics of resultant multidimensional nanocarbons were much enhanced compared to those of each nanocarbon comprising them. The enhancement was attributed to the hierarchical porous channels, structural interconnectivity, improved electrical conductivity, and interconnected meso- and micropores in the electrode materials [2].

Despite the increasing number of reports on multi-dimensional carbons for energy storages, this novel research field is still in the initial stage of development. There are much room for fundamental and technological studies to further develop the multidimensional nanocarbons particularly for supercapacitor applications. As can be seen in the recent reports on ternary nanocarbon-metal oxides, it is noteworthy that various non-carbons, particularly pseudocapacitve metal oxide nanomaterials are tested to be combined with the multi-dimensional nanocarbons mainly for the purpose of increasing energy densities of supercapacitors. Due to the purely EDLC charge storage mechanism, carbonaceous materials including the multi-dimensional nanocarbons inherently exhibit limited capacitances and energy densities.

Acknowledgment

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