

Tailoring Carbon Nanostructures for Energy Applications

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Abstract: Carbon nanostructures have become one of the most exciting and rapidly expanding research topics since the discoveries of fullerene and carbon nanotubes. In particular, carbon nanotubes, graphene, and mesoporous carbons are the most important classes of carbon nanostructures in terms of synthesis and practical applications. Due to their excellent chemical, physical, mechanical, and electrical properties, carbon nanostructures have been considered as promising candidate materials for energy devices. Therefore, it is important to summarize and review the previous research on carbon nanomaterials in energy storage, conversion, and generation. Herein, the typical fabrication procedures for carbon nanostructures, and the characteristics and performances of those carbon nanomaterials as major components in energy devices are briefly described. The wet-type approaches to carbon nanomaterials are discussed extensively because the chemical vapor deposition and template methods have already been reported frequently. In addition, recent research on the improvement of batteries, capacitors, and solar cells will be concisely reviewed.

Keywords: Carbon nanostructures, energy, battery, capacitor, solar cell.

1. INTRODUCTION

Carbon materials have been popular for over ten centuries due to their usefulness in purifications, deodorants, and structural hybrid composites [1]. The impact has been given through the discovery of C₆₀ fullerene by famous researchers, Kroto and Smalley [2]. Their discovery extended beyond the academia and marked the beginning of a new era in carbon science. Subsequently, carbon nanotubes (CNTs), the most important fruit of carbon research, were discovered by Iijima and co-workers [3]. These “molecular carbon fibers” consist of tiny cylinders of graphite that are closed at each end with caps and contain precisely six pentagonal rings [2]. Since the discovery of these alluring carbon nanostructures, research on carbon nanomaterials has been expanding rapidly and includes the development of numerous carbon nanostructures for example, nanospheres [4-7], nanocapsules [8-11], nanofibers [12-14], and mesoporous carbons [15-18]. The above-mentioned carbon nanostructures must exhibit not only the inherent advantages of carbons but also the intriguing characteristics of nanoscale substances, which differ from conventional bulky materials. The functionalizations and diversifications of numerous carbon nanomaterials have captured ever-increasing interest from scientists.

On the other hand, the carbon nanomaterial fabrication strategies have also progressed rapidly to keep up with

the increasing demands for tailored carbon nanostructures. The typical preparation methods include chemical vapor depositions (CVDs) [3], template approaches [19], and wet-type methods [20]. CVD methods provide the most reliable synthetic method of generating carbon nanostructures, while template methods are suitable for nanoporous or mesoporous carbon materials. The newly developing wet procedures for carbon nanostructures have potential advantages such as simplicity, wide selection of intermediate compounds, use of nontoxic chemicals, and easy modification of reaction media. Jang and colleagues have conducted extensive studies on the realizations of novel carbon nanostructures using surfactant-mediated methodologies [4-18].

Regardless of the fabrication method, carbon nanostructures can be applied in most areas of science and technology, ranging from conventional carbon fibers to state-of-the-art electronic devices. Among these emerging applications, the most important and urgent challenge for researchers is to resolve the low efficiency in energy collection, storage, and conversion systems. Therefore, researchers and scientists from all fields are now endeavoring to construct highly efficient energy management systems with a relatively low cost. Novel types of batteries, capacitors, and solar cells are strong alternatives for resolving these energy problems. As expected, carbon nanostructures have been exploited in these devices as electrodes, matrices, and transporting media, resulting in the improvements of performance and efficiency [21].

Therefore, herein, wet methods for carbon nanostructures are discussed extensively, because the CVD and template approaches have been discussed more frequently and in more detail. In addition, the significant research on the incorporation of carbon nanostructures into batteries,

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supercapacitors, and solar cells will be highlighted succinctly in Section 3. It is expected that this article will provide an overview of essential information concerning the use of carbon nanostructures in energy devices.

2. FABRICATIONS OF CARBON NANOMATERIALS

2.1. Wet Methods

Wet methods can produce diverse carbon nanostructures with unique morphologies such as nanoparticles, nanofibers, nanotubes, hollow capsules, and mesoporous materials. Most of wet methods for the preparation of carbon nanomaterials use various types of surfactants for precursor formation, because the surfactants can generate micelles with diverse morphologies. Therefore, the typical preparation method, emulsion system is introduced (Section 2.1.1) first. Subsequently, the wet fabrication methods of representative carbon nanomaterials with diverse morphologies are briefly described (Section 2.1.2~2.1.6).

2.1.1. Emulsion Systems

A representative wet method is an emulsion system which is a heterogeneous system consisting of at least one immiscible liquid dispersed in another in droplet form with sizes of tens of nanometers to micrometers [22]. The emulsion process possesses several distinct advantages:

1. The physical state of the emulsion system enables easy control of the process.
2. Thermal and viscosity problems are much less significant than in bulk polymerizations.
3. The product referred to as latex can be used directly without further purification.
4. It is possible to obtain both a high molecular weight and a high reaction rate.

In contrast, microemulsions are macroscopically homogeneous mixtures of oil, water and surfactants, which consist of individual domains of oil and water separated by a monolayer of amphiphile at a microscopic level [22]. The traditional concept of the structure was that of an emulsion with very small droplets. However, the concept of microemulsion was modified by later research. Thus, there are significant differences between emulsion and microemulsion caused by the much larger amount of emulsifier in the microemulsion process. However, microemulsions should not be regarded as emulsions with very small droplet sizes; microemulsions and conventional emulsions are fundamentally different. The microemulsion polymerization allows the preparation of polymer latexes with very high

particle interface areas and narrow particle size distributions [4]. The reaction in the microemulsion occurs in a large number of isolated loci dispersed in the continuous aqueous phase. While an emulsion system exhibits three rate intervals, only two are observed in microemulsion. First, the polymerization rate increases rapidly with the reaction time and then decreases steadily over time. In summary, the essential features of microemulsion polymerization are as follows:

1. The polymerization reaction proceeds under non-stationary state.
2. The size and particle concentration increase throughout the duration of the polymerization.
3. The chain-transfer to monomer/exit of the transferred monomeric radical/radical re-entry is operative.
4. The molecular weight is independent of the conversion and the distribution of resulting polymer is very broad.

Recently, microemulsion polymerization has become a simple method to produce polymeric nanomaterial precursors. It is thermodynamically stable and thus creates robust micelles. The enormous number ($\sim 10^{15}$ /mL) of micelles has been useful as nanoreactors for preparing polymer nanostructures as precursors for carbon nanostructures. Table 1 compares the conventional emulsion and microemulsion in oil-in-water (O/W) systems.

2.1.2. Fabrications of Carbon Nanospheres

Remarkable progress has been made by Jang and colleagues in the synthesis of carbon nanospheres [4]. They reported the selective fabrication of amorphous polypyrrole (PPy) nanoparticles as small as 2 nm in diameter, using microemulsion polymerization at low temperatures [4, 23]. In addition, they have also described the novel fabrication of graphite nanoparticles with dimensions less than 2 nm, using ultra small amorphous PPy as the carbon precursor (Fig. 1). It was demonstrated that the graphite nanoparticles, when blended with polycarbonate, have improved transparent conducting performance compared with carbon nanotubes. They also reported a novel top-down approach to fullerenes with PPy nanoparticles as precursors.

A similar approach was used to fabricate polyacrylonitrile nanoparticles with average diameters of 5 nm to 30 nm. The subsequent carbonization produced amorphous carbon nanoparticles [39].

The large-scale manufacture of nanomaterials with well-defined sizes and functionalities remains a significant challenge in contemporary nanoscopic research. Thus, such nanomaterials have been restricted in their practical

Table 1. Comparison Between Conventional and Micro-emulsion in Oil-in-water (O/W) Systems [22]

	Conventional	Microemulsion
Emulsifier (wt %)	1~3	15~30
Droplet size (nm)	> 500	10~100
Appearance & Stability	Milky & phase separated	Stable & transparent

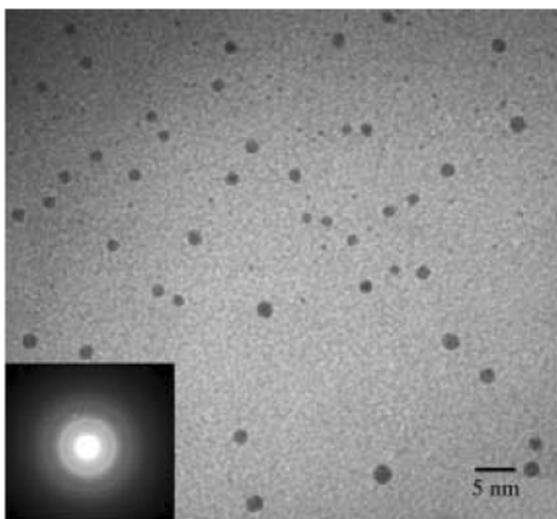


Fig. (1). TEM image and nanobeam electron diffraction pattern of graphite nanoparticles fabricated by the carbonization of PPy nanoparticles [4].

applications, due to the lack of a simple and reproducible synthetic method that allows the production of pure and uniform nanoparticles in bulk quantities. The fabrication of PPy nanoparticles and magnetic carbon nanoparticles with uniform diameters is critical, because the characteristics of these nanoparticles are dependent on their dimensions. Jang and Yoon described a reliable method for producing monodispersed PPy nanoparticles in multigram scale and they also reported a breakthrough in fabricating large quantities with uniform sizes [6, 7].

In addition, numerous carbon nanoparticles have been prepared using the wet-method [24-28]. Well-defined carbon nanoparticles were developed through the pyrolysis of shell cross-linked poly (acrylic acid)-*b*-poly (acrylonitrile) nanoparticles prepared *via* the micellization and crosslinking of amphiphilic block copolymers in aqueous systems [24]. A novel carbon with a vesicular, hierarchical structure was synthesized using a direct, micelle templating method. The vesicular carbon exhibits a wormlike morphology with very thin shells (5–30 nm) and mesopores of 2–4 nm within the shell that are perpendicular to the walls of the carbon vesicles [25]. Furthermore, highly luminescent graphitic carbon quantum dots (GQDs) have been synthesized using reverse micelles as nanoreactors [26]. The amphiphilic poly (vinyl alcohol)-*b*-poly (acrylonitrile) block copolymer dispersed in water can be easily loaded with gold nanoparticles through the addition of chlorauric acid followed by reduction using sodium borohydride. After the deposition of the loaded micelles onto silicon wafer, followed by an appropriate thermal treatment, the poly (acrylonitrile) core of the micelles is carbonized leading to gold encapsulated in the carbon nanoparticles [27]. Kim and Chang prepared carbon nanospheres through the pyrolysis of core cross-linked diblock copolymer micelles [28].

2.1.3. Fabrication of Carbon Nanocapsules

Carbon nanocapsules have the unique feature of encapsulating nanometer-sized materials in their cores. They

also provide remarkable properties of high specific surface areas, large pore volumes, chemical inertness, and good mechanical stability [29]. Therefore, hollow carbon nanocapsules are useful in numerous areas of modern science and technology, including the delivery and protection of proteins and enzymes, the protection of magnetic particles from oxidation, and the design of radioactive nanoparticles for radiology, radiation therapy, sensing, and storage. The growing demand for carbon nanocapsules has motivated the development of various fabrication methods. Jang and Ha reported the fabrication of carbon nanocapsules with an average diameter of ca. 15 nm using polymer core templating (Fig. 2) [9]. In this methodology, it is unnecessary to etch the polymer core part to fabricate ultrafine carbon hollow spheres. When the core/shell polymer nanomaterial is carbonized, the polymer core section is eliminated, and the shell is transformed into a carbon nanocapsule during the carbonization process. This demonstrates that carbon nanocapsules can be fabricated without an additional core etching procedure [9]. In addition, Jang and Bae reported the selective synthesis of PAN nanocapsules and nanotubes using cyclodextrin-mediated microemulsion polymerization. In this process, cyclodextrin functions as a nanoporogen and iron(III) chloride (FeCl_3) was used as a structure-directing agent to prepare the polymer nanotubes. In addition, the average pore sizes of the polymer nanocapsules and nanotubes could be conveniently tailored through the amount of cyclodextrin used in the process [30]. Jang and Bae also showed a novel surfactant-mediated interfacial polymerization (SMIP) method that selectively fabricated PEDOT nanocapsules and mesocellular foams. This represents the first demonstration of a selective fabrication process for conducting-polymer nanostructures through controlling the surfactant concentration. Furthermore, the electrochemical performance of the PEDOT nanomaterials has been evaluated to investigate their capabilities as supercapacitors [31]. Diverse hollow carbon nanostructures have also been fabricated using the modified methods [32-35].

2.1.4. Fabrications of Carbon Nanofibers and Nanotubes

Among the various types of nanomaterials, nanofibers have attracted considerable attention due to their intriguing

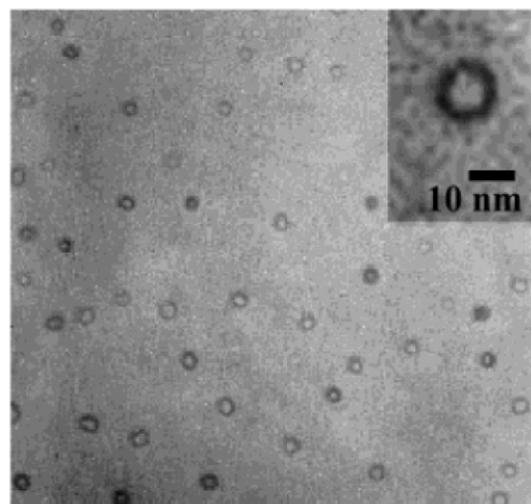


Fig. (2). TEM image of carbon nanocapsules [9].

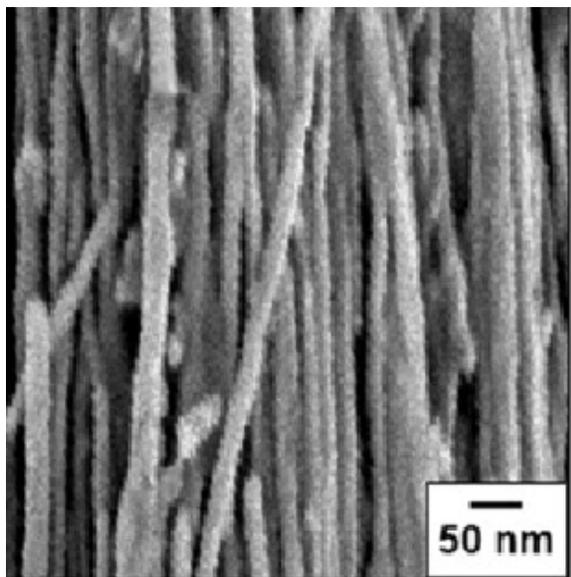


Fig. (3). SEM image of carbon nanofibers prepared by microemulsion polymerization [39].

chemical and physical properties [36]. To date, microemulsion polymerization has been considered to be a simple process for the production of polymer nanomaterials as reviewed by Antonietti and co-workers [37]. Jang and Bae demonstrated that novel polyacrylonitrile (PAN) nanofibers and carbon nanofibers with a high aspect ratio could be fabricated using a salt-assisted microemulsion polymerization. In this work, iron(III) chloride (FeCl_3) was used as a structure-directing agent, it formed a coordination-complex with PAN nanoparticles during the polymer nanofiber formation, and it functioned as a catalyst for the conversion

of the polymer into carbon nanofibers (Fig. 3). The salt-assisted sphere-to-cylinder micelle transformation is the crucial step in the nanofiber formation [38]. The detailed formation mechanism of polymer nanofibers has been examined by the same group in the subsequent research. The effects of the surfactant properties such as the concentration, chain length, and ionic character as well as the monomer structure and polymerization temperature on the structure of the resulting polymer nanofibers were also investigated extensively. Importantly, the PAN nanofibers exhibited novel photoluminescence (PL), which was observed for the first time. The PL of the PAN nanofibers differed significantly from that of the PAN nanoparticles. The PAN nanofibers were also used as precursors for carbon nanofibers. The carbonization temperature of the PAN nanofibers has a significant effect on the degree of crystallinity of the resulting carbon nanofibers [39].

A typical fabrication procedure for magnetic carbon nanotubes is exhibited in Fig. (4) [14]. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was used as the surfactant. When the aqueous iron chloride solution was added to the AOT/isooctane mixture, the surfactants in the isooctane could generate cylindrical micelles. Then the pyrrole monomers were introduced into the reverse microemulsion polymerization and polymerized using Fe ions along the exterior of the micelles. The PPy nanotubes were converted to the corresponding carbon nanotubes *via* carbonization.

2.1.5. Fabrications of Mesoporous Carbons

The diversity of potential applications of mesoporous polymer materials such as adsorption of large molecules, purification, energy storage, and batteries has motivated the development of various fabrication methods for tailored mesoporous polymers with tunable pore sizes [40]. Most

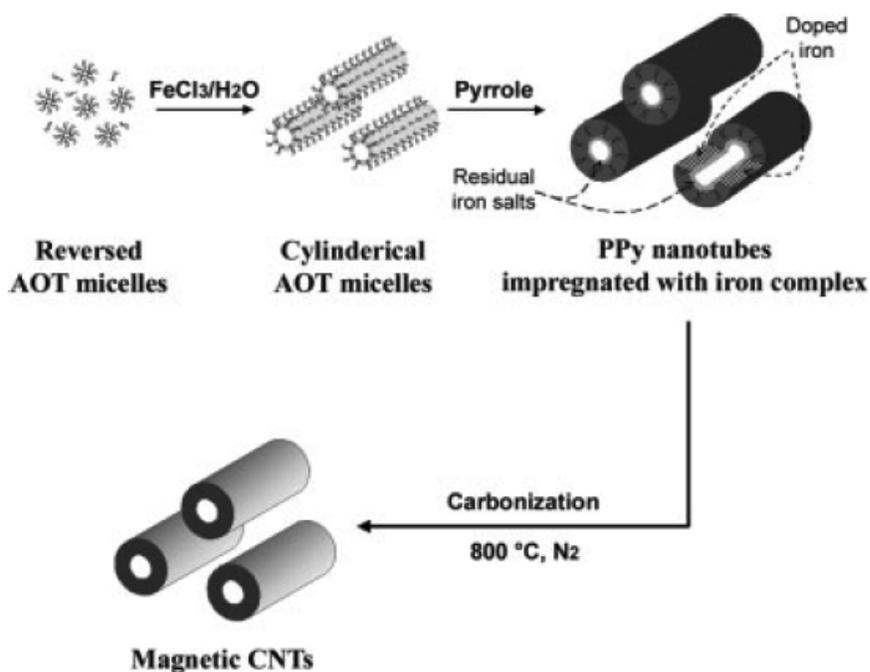


Fig. (4). Typical fabrication procedure for magnetic carbon nanotubes by reverse microemulsion polymerization [14].

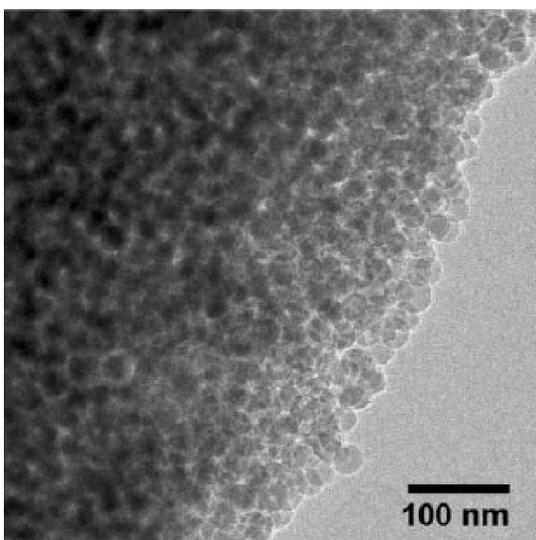


Fig. (5). TEM image of mesoporous carbon [42].

synthetic strategies for mesoporous polymers are related to the hard template technique such as silica or block copolymers, and it is unavoidable to use toxic chemicals such as hydrofluoric acid to generate well-ordered mesopores by removing the templates [41]. Therefore, there have been significant efforts regarding the simple fabrication of mesoporous polymer materials. The concept of “micelle templating” with self assembled surfactants, has provided a simple and reliable synthetic tool for tailoring mesoporous materials. Jang and Bae reported on the novel fabrication of micelle polymer (polyacrylonitrile, PAN) precursors in reverse microemulsion systems and mesoporous polymers derived from micelle/polymer precursors using self-assembled spherical micelles as porogens [42]. On the other hand, a mesoporous polymer/silica hybrid was fabricated using a surfactant-mediated sol-gel method. The acrylonitrile (AN) monomer was located on the micelle exterior and the sol-gel reaction of tetraethyl orthosilicate (TEOS) proceeded concurrently with the polymerization reaction of the AN monomer. That is, the micelle/polyacrylonitrile/silica precursor was synthesized through the radical polymerization accompanied with a hydrolysis/condensation single reaction in a reaction system. The pore diameter of the mesoporous polymer/silica hybrid could be tuned through varying the spacer length and concentration of surfactants [43]. In addition, various emulsion routes to mesoporous carbon (Fig. 5) structures have been addressed [44-47].

2.1.6. Encapsulation of carbon nanotubes via Emulsion

Apart from the bulk and solution processes, the functionalization of the CNTs has also been conducted using the emulsion process. This approach is based on earlier studies that found that stable suspensions of individual CNTs could be produced effectively with the assistance of a sodium dodecylbenzene sulfonate (SDBS) surfactant [48]. Li and co-workers functionalized vinylated single-walled CNTs (SWCNTs-v) with PMMA *via* emulsion polymerization [49]. Several studies have been conducted on the encapsulation of carbon nanotubes by emulsion systems [50-55].

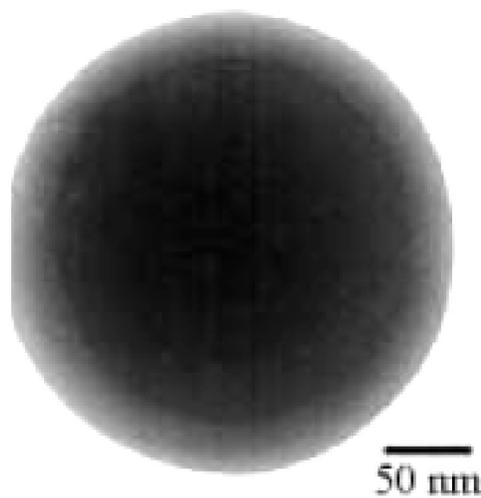


Fig. (6). TEM image of silica nanoparticles coated with PMMA by vapor deposition method [8].

2.2. Fabrications of Carbon Nanostructures by Chemical Vapor Deposition

The CVD synthesis of carbon nanotubes and graphene is well known. Herein, we discuss the use of chemical vapor deposition method for the realizations of diverse carbon nanostructures. While vapor deposition polymerization (VDP) has been performed on metals and semiconductors with macroscopically flat surfaces *via* radiation-induced polymerization, considerably less attention has been brought to the coating of inorganic colloids with polymers. Jang and Lim reported a simple fabrication method for various inorganic colloid-vinyl polymer core-shell nanostructures (Fig. 6) using a one-step VDP. Having demonstrated the feasibility of the approach, it was applied to encapsulate silica and titania nanoparticles with poly(methyl methacrylate) (PMMA) and polydivinylbenzene (PDVB) [8]. Using this method, it was possible to selectively produce carbon foam and nanocapsules [56, 57].

2.3. Fabrications of Carbon Nanostructures by Template Methods

Anodized aluminum oxide (AAO) membranes and mesoporous silicas have been used extensively as templates for carbon nanostructure preparations [13, 58]. Jang and Oh revealed a template-mediated VDP technique that was simple and effective method for the fabrication of polymer and carbon nanotubes. The vapor phase polymerization provided a highly uniform nanotubular surface as well as easier control over the wall thickness [13].

3. APPLICATIONS OF CARBON NANOSTRUCTURES FOR ENERGY DEVICES

3.1. Supercapacitors

Since the discovery of carbon nanotubes, their properties as supercapacitor electrodes have been investigated [59-64]. Iijima and his colleagues presented a rational and general method for the fabrication of a densely packed and aligned

single-walled carbon-nanotube (SWNT) material by using the zipping effect of liquids to draw the carbon nanotubes together. This bulk carbon-nanotube material retained the intrinsic properties of individual SWNTs, such as high surface area, flexibility, and electrical conductivity. The dense SWNT material is advantageous for numerous applications, its use as flexible heaters as well as supercapacitor electrodes for compact energy-storage devices has been demonstrated [59]. The electrochemical behavior of the PEDOT-carbon colloidal sphere composite was examined. The results demonstrated the feasibility of using monodisperse colloidal microparticles containing conjugated polymers as electrode materials for high-energy and high-power-density supercapacitors [65].

In addition to carbon nanotubes, graphenes are also available in supercapacitors [66-72]. Supercapacitors with graphene-based electrodes have been found to exhibit a specific energy density of 85.6 Wh/kg at room temperature and 136 Wh/kg at 80 °C (based on the total electrode weight), and were measured at a current density of 1 A/g. These energy density values are comparable with those of the Ni metal hydride battery, and the supercapacitor has a significant advantage of being able to be charged and discharged in seconds or minutes [66].

Mesoporous carbons are considered to be the strongest candidate for capacitors due to their high surface area [73-78]. A mesoporous carbon with regular three-dimensionally interconnected 2 nm pore arrays using AIMCM-48 as a template has been synthesized; the mesoporous carbon exhibited excellent performance as an electrochemical double layer capacitor [73]. Oh *et al.* developed a new mesoporous carbon (NMC), and its performance in an electric double-layer capacitor (EDLC) was compared with that of a conventional carbon (a molecular-sieving carbon, MSC25). The effects of the pore size and pore connection pattern on the EDLC performance were demonstrated. NMC had three-dimensionally interconnected mesopores (2.3 nm average diameter), but randomly connected cage-like micropores (<2.0 nm) were dominant in the MSC25. The difference in the pore size and pore connection pattern between the two carbons caused a remarkable difference in their EDLC performances. The NMC exhibited a smaller specific capacitance (about 120 F/g) than MSC25 as a result of its smaller surface area, but it also exhibited a higher critical scan rate than the MSC25 electrode due to its smaller resistance-capacitance (RC) time constant [74].

3.2. Lithium Ion Batteries

Secondary batteries are developing fast due to the active scientific and industrial research. Carbon materials, for example graphite have been primarily employed as anodes in lithium ion batteries [79]. Numerous studies have been conducted on the incorporation of CNT and related materials to replace the conventional graphite [80-86]. Ajayan and researchers have presented coaxial manganese oxide/carbon nanotube (CNT) arrays deposited inside porous alumina templates used as cathodes in lithium batteries. The excellent cyclic stability and capacity of the MnO₂/CNT coaxial nanotube electrodes resulted from the hybrid nature of the electrodes with improved electronic conductivity and the

dual mechanism of lithium storage. The reversible capacity of the battery was increased by one order compared with template-grown MnO₂ nanotubes, which renders them suitable electrodes for advanced Li ion batteries [80]. Lee *et al.* reported an alternative approach based on the redox reactions of functional groups on carbon nanotube surfaces. Layer-by-layer techniques are used to assemble an electrode that consists of additive-free, densely packed and functionalized multiwalled carbon nanotubes. The electrode can store lithium up to a reversible gravimetric capacity of similar to 200 mAh/g (electrode) while also delivering 100 kW/kg(electrode) of power and providing lifetime excess of thousands of cycles both of which are comparable with electrochemical capacitor electrodes [82]. Wang and Wallace suggested flexible, aligned carbon nanotube/conducting polymer electrodes for a lithium-ion battery [83]. Kang and Jung published the fabrication and characterization of highly porous, stretchable, and conductive polymer nanocomposites embedded with carbon nanotubes (CNTs) for application in flexible lithium-ion batteries [86].

The lithium storage properties of graphene nanosheet (GNS) materials as high capacity anode materials for rechargeable lithium secondary batteries (LIB) were investigated by Honma and scientists [87]. Graphite is a practical anode material for use in LIBs, as a result of its capability of reversible lithium ion intercalation in the layered crystals, and the structural similarities of GNS to graphite may provide another type of intercalation anode compound. The specific capacity of GNS is 540 mAh/g, which is considerably larger than that of graphite. Numerous researches have been performed for performance improvements of secondary batteries and their studies are reviewed continuously [88-91]. Three-component hybrids such as Sn@CNT-graphene have also been introduced into batteries systems [91].

Nanoporous carbons are very useful as electrode materials in lithium ion batteries [92-96]. Cho and co-workers have developed mesoporous Si@carbon core-shell nanowires with diameters of approximately 6.5 nm as lithium battery anode materials using a mesoporous silica (SBA15) template. The as-synthesized nanowires demonstrated an excellent first charge capacity of 3163 mAh/g with a Coulombic efficiency of 86% at a rate of 0.2 C (600 mA/g) between 1.5 and 0 V in coin-type half-cells. Moreover, the capacity retention after 80 cycles was 87% and the rate capability at 2 C (6000 mA/g) was 78% of the capacity at 0.2 C [92]. Dai *et al.* fabricated mesoporous carbon with homogeneously dispersed multiwalled carbon nanotubes (MWNTs) *via* a one-step "brick and mortar" soft-templating approach. The nanocomposites exhibited a reversible lithium storage capacity of 900 mAh/g and a good rate performance. Such homogeneous nanocomposites are ideal candidates for electric vehicle applications where high power and energy density are critical requirements [94]. A mesoporous Li₄Ti₅O₁₂/C nanocomposite was synthesized using a nanocasting technique with the porous carbon material [97]. Recently, emerging materials such as vanadium-based materials receive significant attention as potential electrodes for energy storage systems particularly in LIBs and supercapacitors.

3.3. Photovoltaics

Photovoltaic (PV) is an emerging field of energy research. Fullerene has been considered as an ideal material for PV devices. Since then, numerous studies have been conducted to add elegant carbon nanostructures such as CNT [98-105], graphene [106-112], and mesoporous carbon [113-116] into PV devices. The advantages of combining carbon nanotubes with conjugated polymers for high-efficiency photovoltaic devices are explored by Schaffer [98]. The preparation and optical properties of a composite of multiwalled carbon nanotubes (MWNTs) and poly(p-phenylene vinylene) (PPV) have been reported and the efficiency of a photovoltaic device fabricated from the composite has been investigated. When used as conducting scaffolds in TiO₂ semiconductor-based electrochemical cells, the single wall carbon nanotube (SWCNT) architecture can boost the photoconversion efficiency by a factor of 2 [101]. Unalan described the use of single-wall carbon nanotube (SWNT) thin films as transparent and conducting electrodes for hole collection in poly(hexyl)thiophene-[6-6]phenyl-C-61-butyric acid methyl ester (P3HT-PCBM) organic photovoltaics [102]. The single-walled carbon nanotubes (SWNTs) were determined to have significant interaction with poly(3-hexylthiophene) (P3HT) [103].

Transparent, conductive, and ultrathin graphene films have been demonstrated as alternatives to the metal oxides window electrodes for solid-state dye-sensitized solar cells [106]. These graphene films are fabricated from exfoliated graphite oxide, followed by thermal reduction. The obtained films exhibit a high conductivity of 550 S/cm and a transparency of more than 70% over 1000-3000 nm. Solution-processable functionalized graphene (SPF Graphene) has also been used as an electron-accepting material in organic photovoltaic (OPV) devices [107]. It has become possible to synthesize solution-processable, black graphene quantum dots with uniform sizes through solution chemistry, and it has been shown that these QDs can be used as sensitizers in solar cells [112].

The mesoporous carbons have been prepared through the carbonation of a triblock copolymer F127/phloroglucinol-formaldehyde composite that self-assembles in an acid medium and have been used as a catalyst for triiodide reduction in dye-sensitized solar cells (DSCs) [113]. Ramasamy and Lee reported that a counter-electrode comprised of large-pore sized mesoporous carbon exhibits low charge transfer resistance in iodide/triiodide redox electrolyte, thus liquid and quasi-solid dye sensitized solar cells have shown 8.18% and 3.61% solar to electric energy conversion efficiency, respectively [114-115]. Joo and Cheon reported the preparation of highly interconnected and ordered mesoporous carbon-carbon nanotube nanocomposites that exhibit Pt-like dye-sensitized solar cell (DSSC) efficiency and remarkable long-term durability as DSSC counter electrodes [116].

3.4. Nanofluidics

It is well known that graphitic materials contain higher thermal conductivity (~ 2500 W/mK) than metallic materials [117]. The carbon nanomaterials composed of graphitic structures such as carbon nanotubes or nanofibers can be

excellent candidates for nanofluidic systems. The nanofluid pioneered by Choi *et al.* has been the most promising method of meeting the requirements for efficient thermal equipment [118]. The nanofluid is a liquid suspension of nanometer-sized solid particles and fibers [119]. The diameter of the ultrafine filler dispersed in the nanofluid is typically submicrometer and the thermal conductivity (TC) of the nanofluid is noticeably higher than those of commercial coolants, such as water and ethylene glycol [120]. In addition, the nanofluid has an enhanced TC compared with the theoretical predictions based on the Maxwell equation for a well-dispersed particulate composite model. Various metallic and nonmetallic materials could be adapted by developing synthetic methods of nanosized materials in nanofluid systems [121]. Lee and Jang described a simple and efficient method for preparing water-dispersible carbon nanofibers suitable as nanofluid fillers. Oxygen plasma treatments enable the generation of the hydrophilic functionality on the surface of CNFs without any deterioration of the intrinsic properties, and enable the reduction of the bundling or surface defects of CNFs [122].

4. CONCLUSIONS

In this article, wet synthetic methods for fabrication of carbon nanostructures have been summarized and it is clear that carbon nanostructures have a diversity of uses in energy devices due to their excellent properties. In particular, it is important to know that the carbon nanostructures are attracting ever-increasing interest from researchers and scientists. Thus this article provides essential information on the synthesis and use of carbon nanostructures in energy devices.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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The authors reviewed previous literatures and manuscript. KJL collected references on the fabrication of carbon nanostructures. JP summarized previous reports on batteries and JB collected information on wet type fabrication methods and energy applications other than batteries. KJL and JB wrote manuscript draft and JP edited extensively.

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