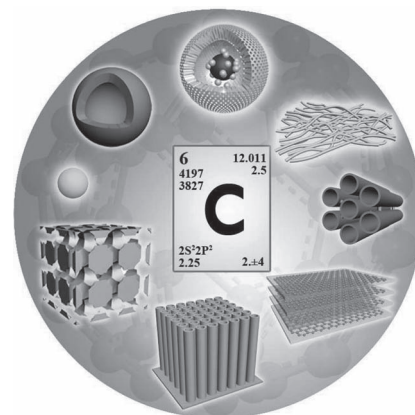


# Chemical Synthesis of Carbon Materials With Intriguing Nanostructure and Morphology

An-Hui Lu,\* Guang-Ping Hao, Qiang Sun, Xiang-Qian Zhang, Wen-Cui Li

In the past decades, carbon materials retain great development because of their indispensable applications in energy storage and conversion, adsorption, catalysis, and others. The evidence is that a number of new structured carbon materials have been synthesized from molecular level, bottom-up strategy. To date, it has been possible to synthesize carbon materials with defined nanostructure and morphology, tunable surface area, and pore size. In this review, we focus on discussing the recent development of chemically synthesized carbon materials with intriguing nanostructure and morphology. For convenience, these materials are grouped into four categories — 0D quantum dots and spheres; 1D fibers, tubes, and wires; 2D films and membranes; and 3D monolithic structure. In each category, materials synthesis strategies are discussed, whereas their applications are briefly touched. In the last section, we made a brief summary and discussed the future perspectives of carbon materials. We expect that this review not only summarizes the main achievements in this area, but also creates interdisciplinary activities in between carbon chemistry and other research areas.



## 1. Introduction

Carbon (from Latin *carbo*, meaning “coal”), the sixth element widely existing in atmosphere and the Earth’s crust, has been one of the most extensively studied elements for materials scientists and organic chemists. Carbon has the ability to form very long chains of interconnecting C–C bonds and can form covalent bonds with other elements, which are strong and stable. Owing to different hybrid orbitals  $sp$ ,  $sp^2$ , and  $sp^3$ , carbon atoms can form pentagonal, hexagonal, and heptagonal carbon rings. These distinctive and diverse properties allow carbon to form an almost infinite number of compounds and build up to various carbon materials.

Humans have been using carbon materials including diamond, graphite, and charcoal since the prehistoric era. Although these materials consist of as simple as only carbon atoms, they can exhibit amazing functions and cover a broad spectrum of properties. For example, diamond is highly transparent and among the hardest materials known, whereas graphite is opaque and black and soft enough to form a streak on paper. Accompanying with the development of modern science and technology, a larger number of new carbon materials with well-controlled and well-defined morphologies and nanostructures have been synthesized by various physical and chemical processes, such as fullerenes, carbon nanotubes (CNTs), graphitic onions, carbon coils, carbon fibers, and so on. Carbon materials have been awarded three times in the last 15 years: fullerenes, the 1996 Nobel Prize in Chemistry; CNTs, the 2008 Kavli Prize in Nanoscience; graphene, the 2010 Nobel Prize in Physics. To date, it is probably fair to say that researches on carbon materials are encountering the most rapid development period (i.e. “the new carbon age”) than ever.

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Nanostructured carbons are versatile materials and can typically be used in the range of nanocomposites, electronics, energy harvesting, storage and conversion, sensing, adsorption, purification, and catalysis. These applications strongly depend on their crystallinity, microstructures, and micromorphologies which, in turn, determine a chemical synthesis methodology. The synthetic strategies toward nanostructured carbon materials rely on protocols such as precursor-controlled pyrolysis, rational synthesis by chemical vapor deposition, templating and surface-mediated synthesis, self-assembly, surface-grafting and modification, and others. Thus, a precise controlled synthesis on carbon nanostructure will provide a promising opportunity to authentically understand their physical and chemical properties of carbon materials from molecular level and thereby efficiently guide practical applications. In this review, special attention has been paid on presenting new developments and future perspectives of novel carbon materials synthesized by chemical methods in turn. For clarity, carbon materials are roughly, according to dimensionality, classified into four groups: 0D quantum dots and spheres; 1D fibers, tubes, and wires; 2D films and membranes; and 3D monolithic structure. It should be pointed out that the dimensionality, we mentioned here, is not the strict definition from viewpoint of physics. The carbon quantum dots and carbon spheres were arranged as the origin of carbon materials to first heave into sight. Gradually, with the extending dimensions and expanding of the sizes, carbon nanofiber, carbon film or membrane, and carbon monolith emerge in the sequence. There are certainly far more references in the literature than we can cover here. Carbons with perfect graphitic crystallinity, such as fullerene and CNT, are not within the scope of discussion in this review.

## 2. Zero-Dimensional Carbon Materials: Carbon Quantum Dots and Carbon Spheres

In this section, we discuss the research progress of carbon quantum dots (CDs) and carbon spheres. They are grouped as zero-dimensional carbon materials because of their spherical morphology. We should point out that the zero dimensionality mentioned here is not the strict definition from viewpoint of physics. Carbon is hardly considered as an intrinsically toxic element. When carbon nanomaterials are prepared small enough, typically with the sizes of 2–10 nm, they become strongly fluorescent. These nanoparticles are called CDs and usually require surface-passivating treatment before they become bright and colorful photoluminescence, physicochemically and photochemically stable, and nonblinking.<sup>[1]</sup> The quantum effect in carbon is extremely important both fundamentally and



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technologically.<sup>[2]</sup> Compared to those metallic quantum dots, CDs are superior in chemical inertness, low cytotoxicity, and excellent biocompatibility.<sup>[3]</sup> Hence, CDs attract grand interest in biological and biomedical research such as optical imaging *in vivo*<sup>[4]</sup> and multiphoton bioimaging.<sup>[5]</sup> These environmentally friendly carbon nanomaterials can be prepared by laser ablation of graphite,<sup>[6]</sup> electrochemical oxidation of graphite,<sup>[7]</sup> chemical oxidation of a suitable precursor,<sup>[8]</sup> proton-beam irradiation of nanodiamonds,<sup>[9,10]</sup> microwave-assisted method,<sup>[11]</sup> and thermal oxidation of suitable precursors.<sup>[12–14]</sup> The carbon particle core could also be doped with an inorganic salt, such as ZnS, before the surface functionalization to significantly enhance the fluorescence brightness.<sup>[4]</sup>

Carbon spheres with tunable size and surface functionality promise wide applications in drug delivery,<sup>[15–18]</sup> active material encapsulation,<sup>[19–22]</sup> gas storage,<sup>[23]</sup> catalyst supports,<sup>[24–37]</sup> and electrode materials.<sup>[38–43]</sup> In early works, many spherically shaped carbon materials have been made, such as carbon bead, carbon onion, carbon ball and carbon black, and so on. Because of the limitation of the synthesis approaches developed previously, the obtained carbon spheres usually tended to agglomerate or bridge to each other to form necklace, bead, or even chain-like structure. Nowadays, a precisely controlled synthesis is able to ensure a production of carbon spheres with high monodispersity, and the word of “sphere” is particularly used as a general term to describe highly monodispersed carbon materials with spherical shape. Taking into the monodispersity as a key target, much effort has been performed on the development of an efficient synthesis of carbon spheres in a controlled manner. A number of methods, including hydrothermal reduction,<sup>[18,30,31,44–50]</sup> emulsion,<sup>[51]</sup> self-assembly,<sup>[17,27,28,52–55]</sup> and templating method,<sup>[33,34,40,41,56–62]</sup> have been developed for the synthesis of carbon spheres as well as metal/carbon composite spheres. In this section, a comprehensive overview of chemical synthesis approaches for various carbon spheres are presented. For clarity, carbon spheres are grouped into solid spheres, hollow spheres, and core-shell structure. Meantime, a discussion of the key applications for the carbon spheres is briefly touched.

## 2.1. Solid Carbon Spheres

The synthesis of highly uniform solid carbon spheres, especially with the size below 200 nm, is extremely difficult and still remains a grand challenge. In the fields of drug delivery,<sup>[63–65]</sup> biodiagnostics,<sup>[66]</sup> catalysis chromatography,<sup>[67]</sup> colloidal catalysts,<sup>[30,31,44,68–72]</sup> particle templates,<sup>[73–82]</sup> photonic crystals,<sup>[83–85]</sup> building complex structures<sup>[83]</sup> and nanodevices,<sup>[86]</sup> a strict control on the monodispersity and particle sizes smaller than 200 nm is of necessity.<sup>[18,87]</sup> That has driven researchers make

long-term unremitting effort in synthesizing monodisperse carbon spheres.

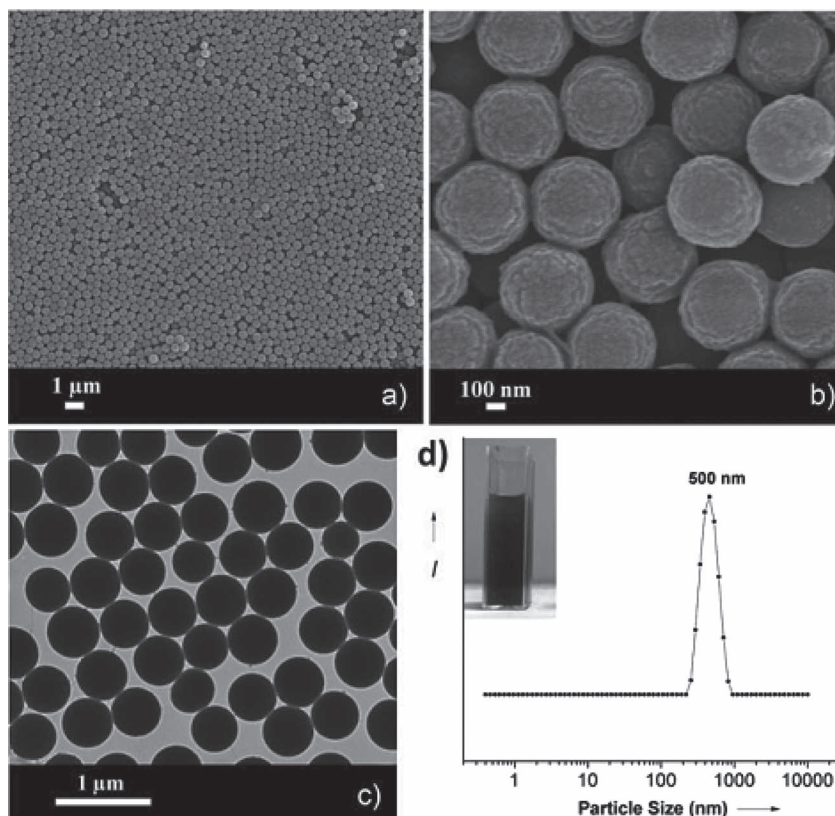
### 2.1.1. Pyrolysis of Carbon-Rich Polymer Spheres (Solution Chemistry)

Carbon-based spheres are usually prepared by carbonization of polymer analogues. In this case, polymer precursors are required to be thermally stable and are able to form carbon residue after a high-temperature pyrolysis. Phenolic resins, derived from the polymerization of phenols (e.g., phenol, resorcinol, and phloroglucinol) with aldehyde (e.g., formaldehyde and furfuraldehyde), are attractive because of their excellent performance characteristics such as high-temperature resistance, thermal abrasiveness, and high yield of carbon conversion. As a result, varieties of chemical syntheses have been reported for the preparation of resin polymer and carbon spheres.<sup>[17,27,38,51,52,88]</sup> In particular, Dong et al.<sup>[52]</sup> reported a simple and low-cost preparation method of carbon nanospheres by carbonization of polymer nanospheres synthesized through polymerization of resorcinol–formaldehyde (RF) in the presence of a basic amino acid, L-lysine, as a catalyst. The diameters of the RF polymer nanospheres can be tuned in the range of 30–650 nm by adjusting the amount of L-lysine and resorcinol. The resulting carbon nanospheres showed surface areas ranging from 330 to 400 m<sup>2</sup> g<sup>-1</sup>.

The synthesis of silica spheres based on the Stöber method involves the condensation of silicon alkoxides [e.g., tetraethyl orthosilicate (TEOS)] in ethanol–water mixtures under alkaline conditions (e.g., ammonia solution) at room temperature. Coincidentally, RF precursors exhibit the structure similarities, that is, coordination sites and tetrahedral building blocks with that of silanes, so their condensation path should be analogous to the hydrolysis and subsequent condensation of silicon alkoxides. Inspiring from this idea and by extension of the Stöber method, Liu et al.<sup>[27]</sup> developed a methodology to synthesize monodisperse RF resin polymer colloidal spheres and their carbonaceous analogues (see Figure 1). Critical to the successful synthesis of such polymer spheres is using ammonia in the reaction system; its role, they consider, lies in not only accelerating the polymerization of RF, but also supplying the positive charges that adhere to the outer surface of spheres to prevent particle aggregation. The particle size of the RF resin colloidal spheres obtained can be finely tuned by changing the ratio of alcohol/water, the amounts of ammonia, and RF precursor, using alcohols with short alkyl chains, or introducing the triblock copolymer surfactant.

It has been known that monodisperse colloidal spheres have the ability to self-assemble into 3D periodic colloidal crystals, only when their size distributions are less than 5%.<sup>[89]</sup> That is a particular challenge to establish a new





**Figure 1.** (a, b) SEM images of RF polymer particles at different magnifications, (c) transmission electron microscope (TEM) image, and (d) DLS plot of the RF resins spheres prepared by the extended Stöber method (Inset: photograph illustrating the dispersivity of the RF resins spheres in ethanol). Reproduced with permission from Figure 1 of ref.[27] Copyright 2011, Wiley-VCH Verlag.

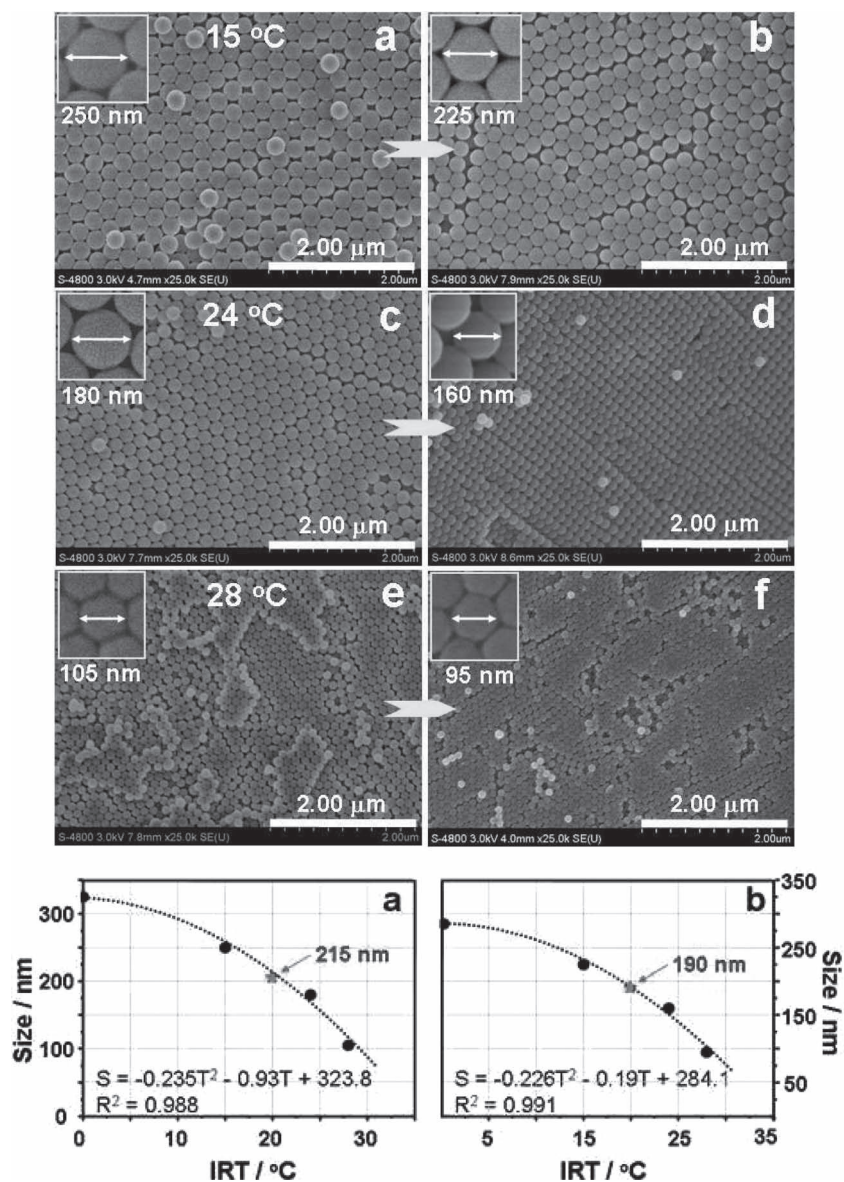
and facile synthesis toward truly monodispersed carbon nanospheres.<sup>[90]</sup> Very recently, Wang et al.<sup>[28]</sup> have established a new synthesis of highly uniform carbon nanospheres with precisely tailored sizes and high monodispersity on the basis of the benzoxazine chemistry. They synthesized polybenzoxazine-based nanospheres under precisely programmed reaction temperatures, using resorcinol, formaldehyde, and 1,6-diaminohexane as the precursors, Pluronic F127 as the surfactant. The sizes of the polymer nanospheres can be precisely adjusted in the range of 95–225 nm by a programmed set of the initial reaction temperature (IRT). Subsequently, the polymer nanospheres can be pseudomorphically and uniformly transferred to carbon counterparts because of good thermal stability and high char yield of such polybenzoxazine-based polymers. It was found that the nanosphere sizes versus IRT fits well with a quadratic function model (see Figure 2). As a result, the size of the polymer and carbon nanospheres can be calculated by the quadratic function. As seen from Figure 2, the as-synthesized nanospheres can be self-assembled into periodic structure with close-packed planes arranged along the [111]

direction. Moreover, the as-prepared polymer nanosphere itself can be the extraordinary building blocks for the preparation of colloidal Pd/carbon catalysts, showing high dispersion of Pd nanoparticles, high catalytic activity, great reusability, and regeneration ability in the selective oxidation reaction of benzyl alcohol to benzaldehyde at moderate conditions.<sup>[28]</sup>

Likewise, the groundbreaking for the synthesis of nanosized mesoporous spheres was recently done by Zhao's group. In their early work, they synthesized 3D cubic single crystals of rhombododecahedron mesoporous carbon (MC) with the uniform size of  $\approx 5 \mu\text{m}$  by an aqueous organic-organic assembly of triblock copolymer F127 and phenol-formaldehyde (PF) resols, and the optimized stirring rate and reaction temperature are  $300 \pm 10 \text{ rpm}$  and  $\approx 66 \text{ }^\circ\text{C}$ , respectively.<sup>[53,54]</sup> Recently, they demonstrate a novel low-concentration hydrothermal route to synthesize biocompatible ordered MC nanospheres with tunable sizes ranging 20–140 nm (see Figure 3). In their synthesis, by using PF resins as carbon precursors, triblock copolymer Pluronic F127 as the structural directing agent, highly ordered body-centered (*Im3m*) cubic MC nano-

particles with spherical morphology and uniform size were obtained.<sup>[17,53,54]</sup> The diameters of the mesophase spheres were tuned by varying the reagent concentration. This synthesis method provides an alternative to “classical” methods for the preparation of carbon nanostructures, which is more applicable to MC nanospheres.<sup>[17]</sup>

Poly(furfuryl alcohol) (PFA) is an alternative high-carbon-yield carbon source. PFA spheres can be synthesized by a two-step polymerization of furfuryl alcohol involving slow polymerization and sphere formation. Then, colloidal carbon spheres were obtained by carbonization of the “nonstick” polymer spheres.<sup>[91]</sup> Alternatively, Nakamura et al.<sup>[92]</sup> have reported a controlled synthesis of highly monodispersed nanoporous carbon spheres using MCM-41-type mesoporous silica as sacrificial template and furfuryl alcohol as carbon source. The diameters of the nanoporous carbon spheres were controlled in the submicrometer range by changing the sizes of silica templates. In addition, the sizes of the resultant spheres were uniform enough to form 3D ordered arrays.<sup>[92]</sup> Recently, Zeng et al.<sup>[56]</sup> demonstrated that carbon spheres can be successfully synthesized by using styrene–divinylbenzene



**Figure 2.** Top: SEM images of the monodisperse polymer nanospheres prepared at different initial reaction temperatures (IRTs): (a) 15, (c) 24, and (e) 28 °C, and their accordingly carbonized analogues CBFS (b), (d), and (f). Bottom: The curves showing the relationship between the IRT and the sizes of polybenzoxazine-based polymer nanosphere (a) and carbon nanosphere (b). Reproduced with permission from Figure 1 and Figure 2a and b of ref.<sup>[28]</sup> Copyright 2011 American Chemical Society.

copolymer as carbon source. The key is to construct intra- and intersphere –CO– cross-linking bridges of the polymer via Friedel Crafts alkylation.

Nitrogen atom doping in carbon materials has been used to tune their physical and chemical properties, that is, chemical reactivity, electrical conductivity, and adsorption properties.<sup>[29,39,55,93–95]</sup> Direct pyrolysis of N-containing polymer can obtain N-containing carbon materials.<sup>[29,39,55,93,94]</sup> For instance, Friedel and co-workers have described a method for the preparation of

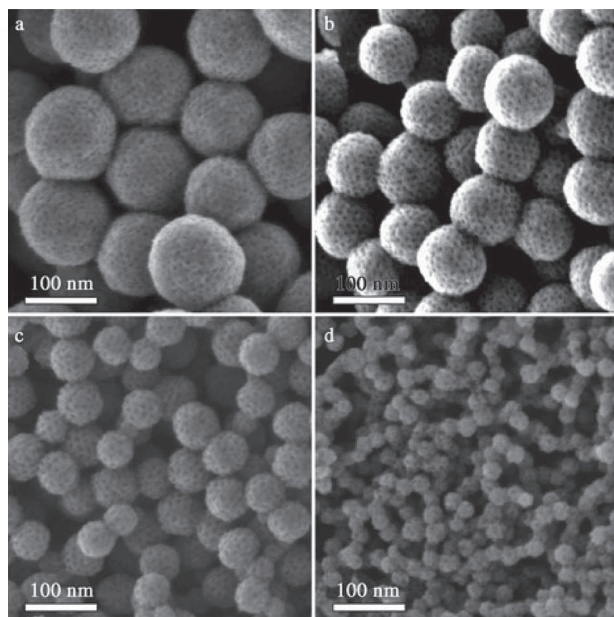
nitrogen-containing carbon spheres derived from melamine–formaldehyde (MF) resin, which was produced through the condensation reaction between melamine and formaldehyde in an aqueous solution.<sup>[55]</sup> As seen in Figure 4, a conversion process on one special batch has been shown for monodisperse MF spheres with an initial diameter of 1.6 μm (as synthesized), which resulted in monodisperse carbon spheres 400 nm in diameter and with smooth surfaces. The nitrogen-rich carbon spheres showed absolutely uniform shrinkage and without any deformation during resin decomposition reactions. This kind of N-containing carbon spheres can be available used in the fields of catalysis<sup>[29]</sup> and electrode materials.<sup>[39,94]</sup>

### 2.1.2. Hydrothermal Carbonization Synthesis of Carbon Spheres

In recent years, the hydrothermal carbonization (HTC) process of biomass (especially isolated carbohydrates) is considered as a facile, low-cost, environmentally friendly, and nontoxic route for the synthesis of novel carbon-based spheres with a wide variety of potential applications.<sup>[45]</sup> The HTC process at a temperature of 160 ≈ 200 °C is in favor of generating colloidal carbonaceous spheres from the carbohydrate sources such as glucose,<sup>[18,30,31,37,46–48,50]</sup> cyclodextrins,<sup>[49]</sup> fructose,<sup>[50]</sup> and sucrose.<sup>[44]</sup> The process of HTC includes four steps: dehydration, condensation, polymerization, and aromatization. The as-synthesized carbonaceous spheres usually have intrinsic porous structures and functional surface groups, which can be used in many potential applications such as catalysis, biomedicine, and nanodevices.

Sun and Li<sup>[30]</sup> have reported a synthesis of monodisperse colloidal carbon spheres (Figure 4) from HTC of glucose. The carbon spheres had hydrophilic surface and showed good stability in an aqueous system. Interestingly, the carbon spheres can be loaded with noble-metal (Ag, Au, Pd, Pt) nanoparticles onto or inside the matrix thus to form hybrid structures. Unsatisfactorily, the resultant carbon spheres had a nonporous structure and relatively large particle size up to micrometers. Recently, Gu et al.<sup>[18]</sup> have reported a hydrothermal synthetic strategy for preparing uniform





**Figure 3.** High-resolution transmission electron microscope (HRSEM) images of the ordered MC nanospheres prepared by a low-concentration hydrothermal method at 130 °C: carbon nanospheres with a diameter of (a) 140; (b) 90; (c) 50, and (d) 20 nm. Reproduced with permission from Figure 1 of ref.<sup>[17]</sup> Copyright 2010 Wiley-VCH Verlag.

MC nanospheres below 200 nm with pore structure complementary, using 3D interconnected MCM-48 mesoporous silica nanospheres as the hard templates. The mesoporous silica nanospheres were first modified with amino functional groups, which provided an electrostatic attraction between the positively charged ammonium cations on the pore surface of the solid template and the negatively charged carbonaceous polysaccharide. The as-prepared MC

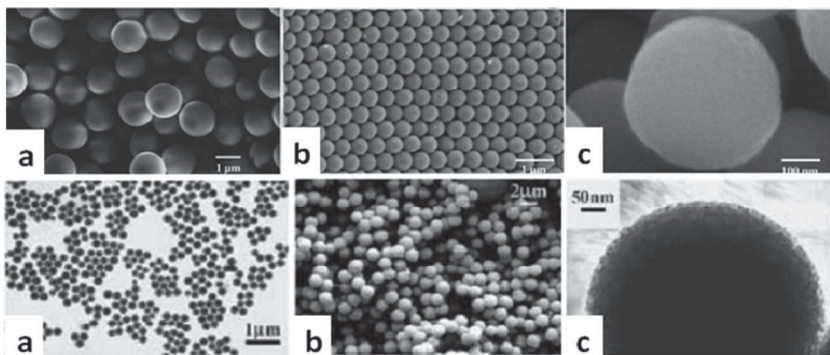
nanospheres served as carriers for camptothecin which efficiently inhibited the growth of MCF-7 (human breast adenocarcinoma) cancer cells after its sustained release therein.<sup>[18]</sup> In addition, Meng and co-workers<sup>[44]</sup> synthesized monodisperse carbon spheres by a modified hydrothermal process. The as-synthesized carbon spheres can be doped with Ag nanoparticles (NPs) via microwave treatment of the suspensions of nanoporous carbon spheres in aqueous  $\text{Ag}(\text{NH}_3)_2^+$  solutions where poly(*N*-vinylpyrrolidone) acted as a reducer. In such way, the fabricated Ag-NP/C composites exhibited an excellent catalytic activity toward the reduction of 4-nitrophenol by sodium borohydride.<sup>[44]</sup> Titirici and co-workers<sup>[46]</sup> have reported the production of carboxylate-rich carbonaceous materials in the presence of acrylic acid by the one-step HTC process of glucose.

## 2.2. Hollow Carbon Spheres

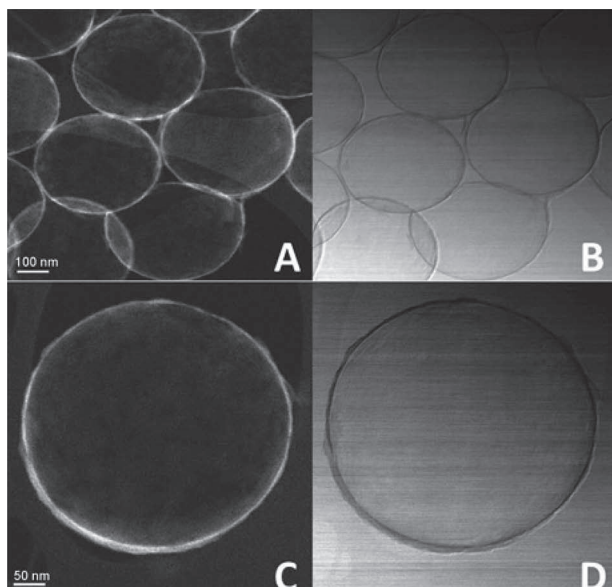
During the last decade, increasing attention has been paid to the hollow carbon spheres because of their superior physical and chemical properties. The hollow cavity in these highly engineered spheres can act as a reservoir or a nanoreactor, whereas the shell provides controlled release pathways for the encapsulated substances and substantial surface area for reactions. As known, templating method is considered to be the most straightforward way to create hollow structure. We broadly divide these approaches into two categories, that is, hard-templating and soft-templating methods, depending on the role of the templates for the formation of a hollow interior. Hereafter, we discuss the synthesis approaches for hollow carbon spheres, and the applications of hollow structures in lithium batteries, catalysis, and biomedical applications.

### 2.2.1. Hard-Templating Method

Preparation of hollow carbon spheres using hard-templating method involves three major processes: (1) synthesis of hard templates, (2) coating the templates with selected carbon source, and (3) removal of the templates to obtain hollow structure. The widely used hard templates include monodisperse silica nanospheres,<sup>[33,48,57–62]</sup> metals or metal compounds particles,<sup>[40,41]</sup> and polymer latex colloids.<sup>[96–98]</sup> These templates are advantageous for several reasons including their narrow size distribution, easy to implement their synthesis using common precursor, and removal of template under mild conditions. Surface coating of the templates with certain carbon source is generally regarded as the pivotal step



**Figure 4.** Top: Scanning electron microscopy (SEM) images of melamine–formaldehyde (MF) microspheres (a) as-synthesized, (b) high monodispersity, and (c) surface condition of carbon spheres prepared after pyrolysis of MF spheres at 900 °C. Reproduced with permission from Figure 2a, e, and f of ref.<sup>[55]</sup> Copyright 2011 Wiley-VCH Verlag. Bottom: (a) SEM image of 200 nm carbon spheres prepared at 0.5 M, 160 °C, 3.5 h; (b) TEM image of 1500 nm carbon spheres prepared at 1 M, 180 °C, 10 h; (c) magnified TEM image of an individual carbon sphere. Reproduced with permission from Figure 1 of ref.<sup>[30]</sup> Copyright 2004 Wiley-VCH Verlag.



**Figure 5.** Scanning transmission electron microscopy images of hollow carbon spheres (a, c) Z-contrast, (b, d) bright field. Reproduced with permission from Figure 1 of ref.<sup>[33]</sup> Copyright 2011 Wiley-VCH Verlag.

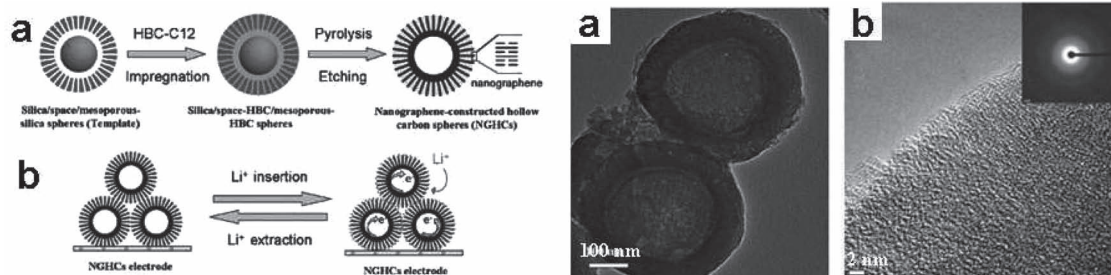
because a facile coating method is required for efficiently creating a shell on a substrate, which might have the sizes in nano- or micrometer range. In most cases, the surface of a template is incompatible with a carbon source. However, this can be overcome by selectively functionalizing or modifying the surface of a template with expected functional groups or electrostatic charges. Moreover, surfactants are occasionally used for assisting surface coating. It should be noted that when removal of the template (core), special care is often taken to retain the perfect shell structure.

In the last decades, much research has been devoted to the synthesis of hollow carbon spheres using hard-templating method. Early in 2002, Yoon et al.<sup>[61]</sup> successfully synthesized carbon capsules with hollow core and mesoporous shell (HCMS) structures using solid core and mesoporous shell silica spheres as the template. The structure of

the HCMS is a replica of the solid core/mesoporous shell silica sphere. The specific surface area and the total pore volume of the HCMS carbon capsules are correspondingly  $1230 \text{ m}^2 \text{ g}^{-1}$ , and  $1.27 \text{ cm}^3 \text{ g}^{-1}$ . Following this pioneer work, the applications of HCMS have been extended to the field of drug delivery,<sup>[16]</sup> electrochemical hydrogen storage,<sup>[23]</sup> enzyme immobilized,<sup>[24]</sup> and catalysis.<sup>[25,32]</sup>

Likewise, Ikeda et al.<sup>[62]</sup> coated a layer of polysaccharide generated by hydrothermal treatment of glucose on amino-functionalized silica spheres, which have a nonporous core and a porous shell. Very recently, as shown in Figure 5, Liu et al.<sup>[33]</sup> have established a versatile and facile method for synthesizing hollow carbon spheres with extremely thin shell (thickness of 4 nm) using dopamine as the carbon source. Dopamine has been found as a powerful surface-coating agent<sup>[99–100]</sup> with high carbon yield. The uniform carbon capsules were obtained easily by a simple immersion of the silica spheres in a dopamine aqueous solution, and subsequent carbonization and template removal.

Graphitic carbon is the most common anode materials in commercial lithium-ion batteries owing to their high electrical conductivity and low cost. Müllen and co-workers<sup>[43]</sup> have synthesized nanographene-constructed hollow carbon spheres (NGHCs) using discotic nanographenes (hexadodecyl-substituted hexa-peri-hexabenzocoronene) as building blocks and silica/space/mesoporous-silica spheres as the template (Figure 6). The as-synthesized NGHCs exhibit uniform size and consist of dual walls, that is, exterior mesoporous shells containing perpendicular nanochannels and interior graphitic solid shells, which is advantageous for lithium-ion diffusion from different orientations, whereas the interior graphitic solid walls can facilitate the collection and transport of electrons during the cycling process. Therefore, high reversible capacity ( $\approx 600 \text{ mA h g}^{-1}$ ) and excellent high-rate capability ( $\approx 200 \text{ mA h g}^{-1}$  at the rate of  $10 \text{ }^\circ\text{C}$ ) were achieved when NGHCs were used as the anode material for lithium-ion batteries.<sup>[43]</sup>



**Figure 6.** Left: (a) Schematic illustration of the fabrication of NGHCs. (b) Diffusion of lithium ions and electrons during the discharge (insertion) and charge (extraction) processes of the NGHCs electrode. Right: (a) TEM and (b) high-resolution transmission electron microscope images of NGHCs (pyrolyzed at  $1000 \text{ }^\circ\text{C}$ ). The inset of (b) is the selected area electron diffraction patterns. Reproduced with permission from Scheme 1 and Figure 2b and d of ref.<sup>[43]</sup> Copyright 2010 Wiley-VCH Verlag.



To save the template removal step in hard-templating process, other than silica nanospheres, polystyrene (PS) nanospheres is an ideal option as hard templates, owing to their thermal volatility. For example, White et al.<sup>[96]</sup> prepared hollow carbon spheres by using glucose as the carbon source and sodium dodecyl sulfate (SDS) as the surfactant under hydrothermal condition, and subsequently removing the polymer template after carbonization the composite upon 500 °C. Yang et al.<sup>[97]</sup> reported a relatively simple method to prepare the hollow carbon spheres using sulfonated PS spheres as templates and polyaniline as carbon source. Following the same method, they also prepared PF composite hollow spheres, and hollow carbon spheres by carbonization of the PF composite hollow spheres at 800 °C in nitrogen.<sup>[98]</sup> Obviously, an inevitable tendency of particles conglutination of carbon nanostructures during high-temperature annealing occurs. The conglutinated carbon nanoparticles demonstrated a limitation in many applications such as colloidal catalysts, drug carriers, nanodevices, and inks. Recently, Lu et al.<sup>[101]</sup> have described a new method referred to as “confined nanospace pyrolysis” for the synthesis of discrete, uniform, and highly dispersible phenolic resin-based hollow carbon spheres with both tailorable shell thickness and cavity size (Figure 7). The crucial importance is to create an inorganic outer silica shell, which was coated on the surface of polymer nanospheres and acted as a nanoreactor providing a confined nanospace for the high-temperature pyrolysis of the PF polymer. Meanwhile, this inorganic shell is also as a boundary to prevent polymer/carbon conglutination during high-temperature treatment. As a result, the approach of Lu et al.<sup>[101]</sup> ensures that even after pyrolysis at a high temperature, the particle coagulation commonly occurred for carbonaceous materials can be

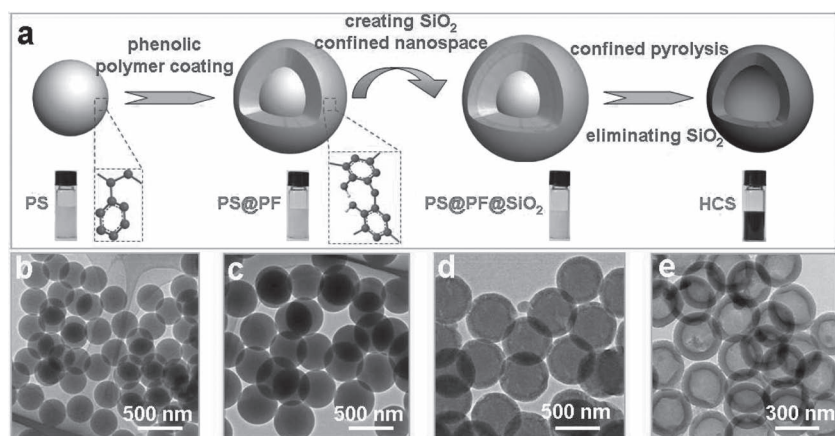
eradicated. This is particularly important in the application fields where a strict control of the monodispersity, particle sizes, and dispersibility of the HCSs is necessary. The HCSs obtained from this method show not only great promise for many applications, such as advanced storage materials, adsorbents, catalyst supports, drug delivery carriers, and templates, but also an ideal basis model system of carbon colloids for exploring their physical and chemical properties.

### 2.2.2. Soft-Templating Method

Although hard templates method is regarded as a powerful tool for the synthesis of HCS with controlled pore structure, it has several intrinsic disadvantages, including low product yields from the multistep synthetic process, lack of structural robustness of the shells upon template removal. Compared to the hard-templating method, soft-templating method using surfactants,<sup>[34,102]</sup> and polymers<sup>[103]</sup> as the structural directing agents, can eliminate the preparation and removal of hard templates steps, and overcome the intrinsic limitations imposed by the hard-templating method. However, the self-assembly ability between the template and polymer precursor is considered as the prerequisite for implementing soft-templating approach, and the template should be chemically stable during the self-assembly process. In the past decade, soft-templating has attracted the greatest attention and made significant progress.

Sun and Li<sup>[102]</sup> have prepared HCS using glucose as carbon source under the assistance of SDS. However, the obtained HCS had wide size distribution ranging from tens of nanometers to several micrometers. More recently, Lu and co-workers<sup>[34]</sup> have established a novel and generalizable hydrothermal synthesis for diverse hollow

nanospheres, which cover polymer, carbon, graphitic carbon, and metal-doped carbon hollow nanospheres. The synthesis principle is based on the weak acid–base interaction ( $-\text{COO}^-/\text{NH}_4^+/-\text{COO}^-$ ) induced assembly. The weak acid–base interaction is created by dihydroxybenzoic acid, ammonium cations, and oleic acid. First, the hollow polymer spheres (HPS) were prepared by ammonia catalyzing polymerization of dihydroxybenzoic acid and formaldehyde, in which the hollow cavity was formed by the emulsion of oleic acid. The diameters and the hollow core sizes of the HPS can be adjusted ranging from 100 to 200 nm and 30 to 80 nm, respectively. It was determined that approximately 61% of added amount of  $\text{NH}_3$  participates is retained in the HPS



**Figure 7.** (a) Schematic illustration of the procedure for the confined nanospace pyrolysis of hollow carbon nanospheres. TEM images of the product obtained from each step: (b) PS, (c) PS@PF, (d) PS@PF@SiO<sub>2</sub>, and (e) HCS; insets are the photographs of the stable aqueous suspensions of these products. Reproduced with permission from Figure 1 of ref.<sup>[101]</sup> Copyright 2011 Wiley-VCH.



product. Owing to the presence of the  $\text{COO}^-$  functional groups, metal cations (e.g.,  $\text{Fe}^{3+}$  and  $\text{Ag}^+$ ) can be introduced into these HPS, so that HPS can then be converted to hollow graphitized nanospheres and Ag doped catalytically active HCS. Noticeably, the HPS can be pseudo-morphologically converted to carbonaceous nanospheres by directly thermal pyrolysis.

Using polymer as template, Xu and co-workers<sup>[103]</sup> have created a novel method to prepare monodisperse carbon nanospheres with a regular round-ball-like shape. Their synthesis route involves three steps: first, to synthesize monodisperse PS spheres by soap-free emulsion polymerization; second, to increase the surface cross-linking degree of PS spheres via Friedel Crafts alkylation as a post-cross-linking reaction; and third, to carbonize the reaction product. By adjusting the post-cross-linking reaction time, the size of hollow core can be finely tuned. This is a novel method in the field of fabrication of carbon spheres.<sup>[56,103]</sup>

The big cavity of a hollow sphere is attractive in guest-host chemistry. To refill the hollow interior with functional species or in situ encapsulation of guest molecules during formation of the shells, though possible, is very challenging. The difficulty has prompted interest in simpler synthetic approaches for producing hollow shells that permit easy encapsulation and release of guest species. Very recently, Lu et al.<sup>[104]</sup> reported a new synthesis of versatile micrometer sized uniform hollow spheres with carbon or graphitized shells, derived from one type of solid polymer spheres which were prepared from lysine-catalyzed polymerization of dihydroxybenzoic acid and formaldehyde in ethanol. It is interesting that a surprisingly simple water washing step can hollow out the solid polymer spheres, which consist of polymer shell and an interior of ion-paired salt-like oligomers, thus to form hollow structures. The as-synthesized polymer spheres can be easily converted into carbon spheres by pyrolysis. In the presence of a graphitization catalyst, graphitized shells are accessible (Figure 8). This synthesis can be called “threefold advantage” as three options of carbonaceous spheres, and is easily scalable to obtain large quantities of product with high purity.<sup>[104]</sup>

### 2.3. Core-shell Carbon-Based Composites

Nobel metals or metal oxides are active agents in many catalysis reactions. Creation of core-shell-structured catalysts consisting of metal nanoparticles entrapped inside a hollow shell is an facile strategy for the fabrication of high-temperature stable and environmentally stable catalysts. As well known, carbonaceous materials are thermally (inert atmospheres) and chemically stable and thus can survive in harsh conditions. On the other hand, a high electrical conductivity of carbon makes it available in electrical devices as electrode materials. Therefore, carbon coating on metal nanoparticles can significantly enhance the electronic conductivity of electrode materials, which results in improved rate performance. The properties of metal nanoparticles were improved. Such composites show unique chemical and physical properties due to their unique structures and components, and may find applications in various fields such as catalysis,<sup>[33,35,36]</sup> lithium-ion batteries,<sup>[40–42]</sup> and biometric applications.<sup>[22]</sup>

Kim et al.<sup>[19]</sup> have reported a synthetic procedure carbon capsules with hollow cores and mesoporous shells containing entrapped Au particles via a replication from solid core/mesoporous shell silica spheres with encapsulated Au seed. The core size, shell thickness, and nanoporosity of the Au-entrapping carbon capsules are tunable by varying the structure of the solid core/mesoporous shell silica spheres. Furthermore, this method should be amenable to a variety of metal particles and inorganic capsule materials. Investigations along this line are currently in progress. Using a similar process, Au@Carbon yolk-shell nanocomposites was obtained by Dai and co-workers,<sup>[33]</sup> and the result nanocomposites showed high catalytic ability and stability in the reduction of 4-nitrophenol.

Other researchers have devoted to the synthesis of core-shell materials by encapsulation metal nanoparticles with carbon materials. For example,  $\text{SnO}_2$ @double-shelled carbon hollow spheres were obtained by Lou et al.,<sup>[40]</sup> using mesoporous  $\text{SnO}_2$  hollow nanospheres as the template. In this synthesis, the carbonization temperature cannot be set exceeding 550 °C because of the

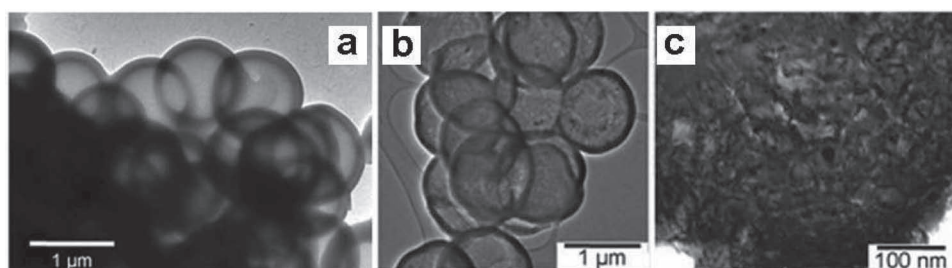


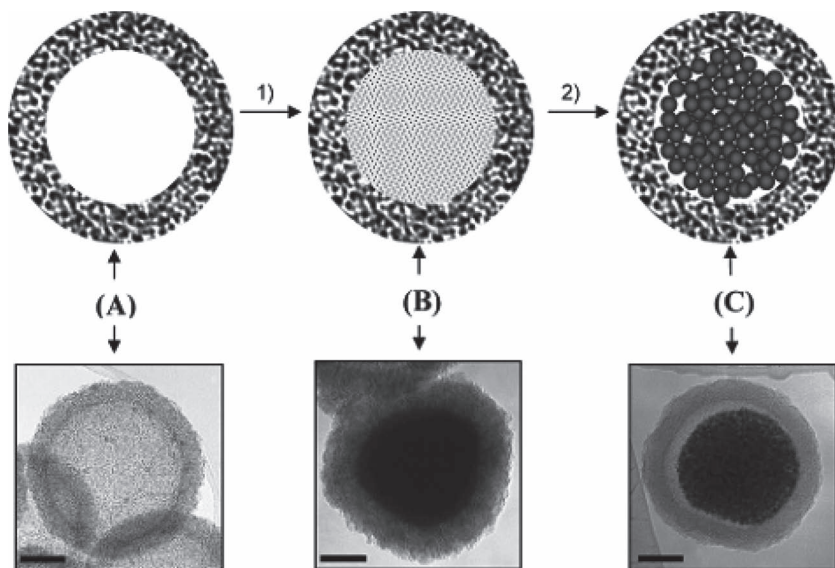
Figure 8. TEM images of (a) the polymer spheres, (b) the resultant hollow graphitic spheres (CS-Fe) after acid leaching. Scanning transmission electron microscopy images of (c) CS-Fe after acid leaching and grinding. Reproduced with permission from Figure 1d and Figure 2b and f of ref.<sup>[104]</sup> Copyright 2010 Wiley-VCH.

reaction between metal oxide and carbon precursor at high temperature, which can destroy the hollow nanostructure. Unusual double-shelled carbon hollow spheres were obtained by selective removal of the sandwiched porous  $\text{SnO}_2$  shells. Lou et al.<sup>[41]</sup> also have synthesized coaxial  $\text{SnO}_2$ @carbon hollow spheres through the coating with glucose-derived polysaccharide by a simple hydrothermal approach on the surface of core/shell silica@ $\text{SnO}_2$  nanospheres. All the  $\text{SnO}_2$ /carbon composites synthesized above showed high reversible capacity, high coulombic efficiency for lithium-ion batteries. Under similar thinking, Zhang et al.<sup>[42]</sup> have synthesized carbon-coated  $\text{Fe}_3\text{O}_4$  nanospindles by partial reduction of monodispersed hematite nanospindles with glucose during a hydrothermal process. The carbon-coated  $\text{Fe}_3\text{O}_4$  nanospindles can serve as a superior anode material for lithium-ion batteries with high reversible capacity, high coulombic efficiency in the first cycle, enhanced cycling performance, and high rate capability compared with bare hematite spindles and commercial magnetite particles.<sup>[42]</sup> Moreover, it can be envisaged that properly tailoring the surface properties of the nanoparticles may allow an extension of a synthesis of other carbon-coated metal oxide, metal, even carbon-coated zeolite, with similar encapsulant structure. Yu et al.<sup>[36]</sup> demonstrated a one-pot route for the fabrication of carbon-coated  $\text{Fe}_x\text{O}_y$  spheres by hydrothermal cohydrolysis-carbonization process using glucose and iron nitrate at a mild temperature. The resultant nanocomposites showed remarkable stability and selectivity in the Fischer–Tropsch synthesis reaction. Moreover, Pd@C core–shell nanoparticles have also been synthesized in a one-step HTC process, which were found to be selective catalysts for the batch partial hydrogenation of hydroxyl aromatic derivatives.<sup>[105]</sup> Interestingly, graphene oxide (GO) sheets and carbon nanotubes (CNTs) can be used as encapsulating agents for the surface coating of poly (glycidyl methacrylate) or PS-based polymer microspheres.<sup>[106,107]</sup>

Impregnation of metal salt solutions into the hollow core of carbon spheres is a straightforward method for the preparation of metal@carbon composites. For example, Fuertes and co-workers have presented a novel and simple synthetic strategy for fabricating core-shell materials made up of magnetic nanoparticles confined within a hollow MC shell.<sup>[22]</sup> This methodology has been expanded to encapsulate a variety of magnetic nanoparticles such as  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{LiCoPO}_4$ , NiO, and

$\text{Cr}_2\text{O}_3$ . As seen in Figure 9, the inner macroporous core can be filled by nanoparticles to a great extent, and the pores of the carbon shell hardly contain deposited nanoparticles. The authors demonstrated an application of such composites for the immobilization of an enzyme (lysozyme) and easy manipulation by means of an external magnetic field.<sup>[22]</sup>

The successes in synthesis of diverse carbon-based spheres have provided opportunities to tune their physical and chemical properties. These advances have in turn promoted exploration in a growing list of applications, such as environmental, catalytic, electronic, sensing, and biological applications. However, it should be noted that high-quality (e.g., monodisperse, uniform, controlled size, and tunable surface property) carbonaceous spheres are more desirable in many cases for both fundamental researches and practical applications. A survey of literature shows that methods for producing such high quality carbon-based spheres are still very limited, even if a small number of products are finely controllable synthesis. In addition, many of the processes for synthesis of carbon-based spheres are based on solution synthesis, in which the yield is very low. Nevertheless, the great challenge in scaling-up of these lab-scale syntheses is to produce industrial-scale quantities of such carbon spheres meanwhile retaining their size and morphology. Addressing these challenges and problems in the future will further facilitate and strengthen the capability for rational design of a variety of carbon spheres and extended practical applications.

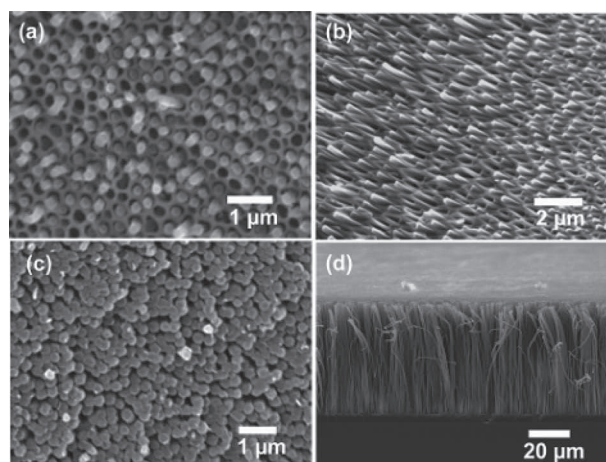


**Figure 9.** Illustration of the synthesis procedure. (a) Carbon capsule; (b) carbon capsule loaded with the inorganic precursor; (c) inorganic nanoparticles encapsulated within the MC shell. (1) Filling of the carbon capsule with the inorganic precursor; (2) conversion of the inorganic precursor into inorganic nanoparticles. Bar scale = 100 nm. Reproduced with permission from Figure 1 of ref.<sup>[22]</sup> Copyright 2007 American Chemical Society.

### 3. One-Dimensional Carbon Materials

When we talk about 1D carbon materials, CNTs are probably the easiest ones to jump up for imagination. Since the first synthesis of CNTs via arcing between graphite-like electrodes by Iijima in 1991,<sup>[108]</sup> 1D carbon materials have been extremely researched because of their outstanding properties such as excellent chemical and thermal stability, high surface area, unique electronic properties and potential applications in electronics, adsorption, water purification, catalysis, and so on.<sup>[109–116]</sup> So far, chemical vapor deposition (CVD)<sup>[117,118]</sup> and the electrospinning technique<sup>[113,119]</sup> have been widely used in production of 1D carbon materials. However, it is very difficult to achieve precise control of the properties of the resulting carbon materials in terms of surface area, pore size, and surface functionality. There are quite number of research articles and comprehensive reviews for CNTs. Herein, we will not discuss CNTs, instead, mainly focus on newly synthesized 1D carbon materials using chemical synthesis methods, such as hydrothermal method, self-assembly approach, and template process.<sup>[88,114–116,120–122]</sup>

Template method is of the widely used approaches for preparation of 1D carbon materials. For example, anodic aluminum oxide (AAO),<sup>[120,123–125]</sup> mesoporous silica,<sup>[122]</sup> and Te nanowires<sup>[114]</sup> have been successfully used for synthesis of carbon tubes, fibers, and wires. As pioneered by Kyotani et al.,<sup>[124]</sup> uniform and straight CNTs and submicron-tubes can be prepared through the pyrolytic carbon deposition from propylene on the pore walls of an AAO film followed by template removal with HF washing. By this templating process, well-aligned free-standing arrays of MC nanofibers have been fabricated on silicon wafers by Holmes and co-workers in 2007.<sup>[125]</sup> Figure 10 shows the SEM images of arrays of MC nanofibers after being calcined at 600 °C. Subsequently, Steinhart et al.<sup>[120]</sup> reported a direct and solvent-free approach to the synthesis of MC nanowires and microwires with high aspect ratios and low defect density. In this strategy, porous alumina as template was first infiltrated by a treated precursor mixture (F127, phloroglucinol, formaldehyde, and traces of HCl), and subsequent carbonized at a moderate temperature of 500 °C.<sup>[120]</sup> Recently, a novel highly ordered MC nanofiber arrays were fabricated by combining surfactant templating (self-assembly of organic resol) with a natural crab shell templating process in which the crab shell was used as a hard template for the generation of the nanofiber arrays, and triblock copolymer Pluronic P123 was used as a soft template for the organization of mesopores.<sup>[123]</sup> By using a mesoporous silica nanofiber template, Chae et al.<sup>[122]</sup> has successfully fabricated the 1D MC nanofiber. The obtained nanofibers mainly consisted of carbon nanoclusters with the internal mesostructure of circularly wound nanochannel alignment. Recently, Liang



**Figure 10.** Scanning electron microscope images of arrays of MC nanofibers after being calcined at 600 °C for 3 h: (a) top and (b) side views of MC nanofiber arrays within the pores of AAO membranes; (c) top and (d) side views of nanofiber arrays prepared on a silicon wafer by a supercritical CO<sub>2</sub> drying process following the dissolving of AAO membrane. Reproduced with permission from Figure 1 of ref.<sup>[125]</sup> Copyright 2007 American Chemical Society.

et al.<sup>[114]</sup> have synthesized a free-standing fibrous membrane using the so-called HTC process from Te nanowires and glucose with subsequent removal of Te cores by H<sub>2</sub>O<sub>2</sub>. The obtained carbon nanofibers were flexible and mechanically robust enough for filtration and separation of nanoparticles with different sizes from a solution.<sup>[126]</sup>

To date, several groups have reported the direct synthesis of porous carbon nanotube films (CNFs) through carbonization of 1D polymers, but the fibers so produced always possess small pore sizes and low surface area.<sup>[127,128]</sup> Very recently, Zhao and co-workers<sup>[116]</sup> fabricated CNFs using a novel self-template strategy based on a solution growth process using ethylene glycol (EG) as the carbon precursor and Zn(CH<sub>3</sub>COO)<sub>2</sub> as the structural constructor as well as the porogen, wherein the initially formed zinc glycolate acted as the build-in template during the subsequent carbonization process. The fibers possessed a well-designed 1D nanostructure and a 3D interconnected mesoporous texture, uniformly sized mesopore and high surface area, and plentiful oxygen functional groups on the surface, which gave rise to excellent performances as an electrode material for electrochemical capacitors (ECs). To create porosity in carbon nanofibers, Fu et al.<sup>[129]</sup> fabricated uniform porous carbon nanofibers by fabricating and then carbonizing the cross-linked polyphosphazene nanofibers. In this synthesis, the pores were created in the direct pyrolysis process without the need of an additional activation step.

Furthermore, Jang and Bae<sup>[130]</sup> synthesized polyacrylonitrile (PAN) nanofibers and carbon nanofibers with a high aspect ratio by using a salt-assisted microemulsion polymerization and carbonization process. Fujikawa et al.<sup>[88]</sup>



demonstrated that monodisperse carbon nanowires and spheres with high surface areas can be obtained from resin polymer nanowires and spheres. In the synthesis, 1,3,5-trimethylbenzene (TMB) and *t*-Butyl Alcohol (*t*BuOH) were used as cosurfactants and the shape of the obtained materials can be tuned from spheres to wires with the variation of the amount of *t*BuOH. By Pt-catalyzed pyrolysis of cellulose diacetate (CDA) nanofibrils, Nam and co-workers<sup>[131]</sup> has synthesized a well-developed carbon nanorod structure via the anisotropic catalytic activation of Pt nanoparticles. The resulting carbon/Pt aerogel exhibited an MC structure with a large surface area ( $311 \text{ m}^2 \text{ g}^{-1}$ ) and provided a high loading content of Pt up to 56 wt%, which shows great potential for applications in various catalytic and electrochemical systems.

So far, although extensive efforts have been devoted to producing porous carbon nanofibers, it is still a great challenge to develop a facile method for the synthesis of carbon nanofibers with high surface area, large pore size, and rich surface functionalities.

#### 4. Two-Dimensional Carbon Materials: Membranes and Films

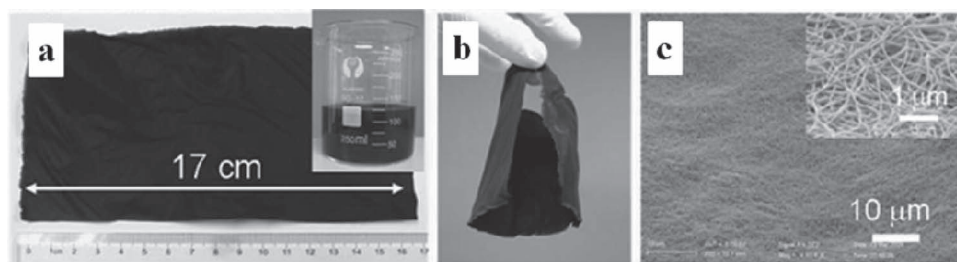
Two-Dimensional carbon materials, often referred to carbon thin films and membranes, are interesting materials because of their special physicochemical and mechanical properties that facilitate various applications in purification and separation, electrochemical energy storage, lithium-ion batteries, cell electrodes, and catalyst supports. Carbon films or membranes can be synthesized by hard- and soft-templating, pyrolysis of organic polymer precursors, chemical and physical vapor deposition, and electrochemical methods.<sup>[132]</sup> Recently, several reviews have reported for the preparation and application of carbon films.<sup>[132–134]</sup> Herein, the latest development on CNT-based films, free-standing carbon fiber-based membranes, stretchable graphene films, and other films are discussed.

Recently, a new class of carbon films composed of CNTs, which can be used as supercapacitors, transistors, and

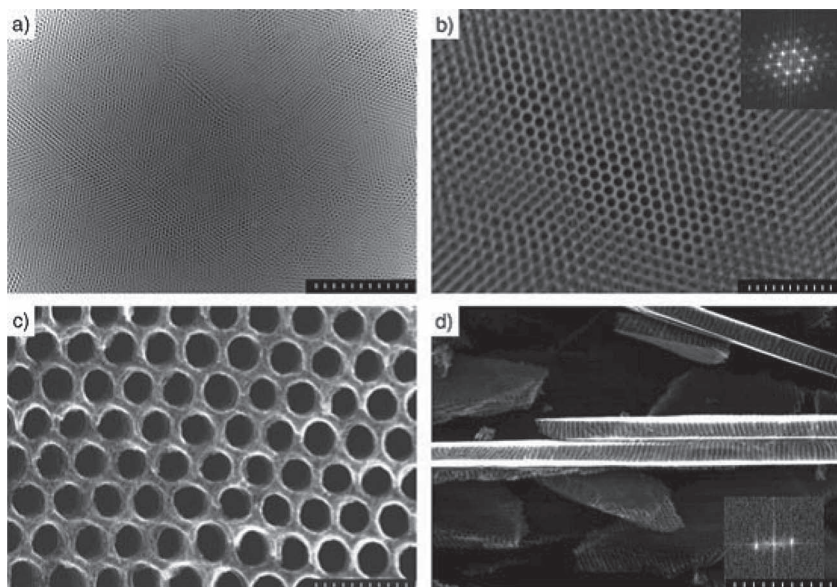
transparent electrodes, have received increasing attention. Through a CVD process, uniform films of vertically aligned nanotubes were grown on silicon substrates.<sup>[135,136]</sup> By using single-walled carbon nanotube (SWNT) ink and via a “dipping and drying” process, Cui and co-workers<sup>[137]</sup> produced highly conductive textiles with outstanding flexibility and stretchability, demonstrating strong adhesion between the SWNTs and the textiles of interest. Another category of synthesis is solution-based processes which can prepare energy-storage devices by integrating single-walled CNTs with metal nanowires.<sup>[138]</sup> On the excellent properties of these CNTs films or CNT composites, supercapacitors, electrodes, and other devices have been successfully fabricated.<sup>[139]</sup>

Transformation of fibers into membranes without any binders has attracted tremendous interest. Recently, Yu and co-workers<sup>[14]</sup> have constructed the free-standing membrane using the highly uniform glucose-based carbonaceous nanofibers through a solvent-evaporation-induced self-assembly (EISA) process. A typical quadrate free-standing CNF membrane  $17 \text{ cm} \times 9 \text{ cm}$  in size is shown in Figure 11. The membrane with a controllable cutoff size exhibits high flux and excellent size-selective rejection properties, and can be used to filter and separate nanoparticles with different sizes from solution by a simple filtration process. By Pt-catalyzed carbonization of cellulose fibers, Kunitake and co-workers<sup>[140]</sup> fabricated the composite of platinum nanoparticles and amorphous carbon film, using a piece of lint-free cellulose paper (PS-2, Bemcot, 100% cellulose) as the starting matrix. Then the Pt/cellulose composite was placed in a quartz tube furnace under nitrogen atmosphere and carbonized at  $400 \text{ }^\circ\text{C}$ . This process facilitates designed fabrication of various carbon-based functional materials with catalytic metal nanoparticles (e.g., catalysts).

In the template methods for the synthesis of nanoporous carbon materials, the composite consisting of carbon precursors and solid templates (e.g., zeolite, silica, polymer, etc.) is produced either by dispersing the solid template in a solution of carbon precursor or by impregnating the carbon precursor into a solid template. By carbonization of a thin layer of phenolic resin on the suitable



**Figure 11.** (a, b) Optical images of the flexible CNF membrane, the inset in (a) shows the optical image of the CNF solution used for casting the membrane. (c) Low and high (the inset) magnification SEM images showing surface morphology of the CNF-50 membrane. Reproduced with permission from Figure 1 of ref.<sup>[14]</sup> Copyright 2010 Wiley-VCH Verlag.



**Figure 12.** Electron microscopy images of the carbon film. (a) Z-contrast image of the large-scale homogeneous carbon film in a 4 mm × 3 mm area. The scale bar is 1 mm. (b) Z-contrast image showing details of the highly ordered carbon structure. The scale bar is 300 nm. (c) HRSEM image of the surface of the carbon film with uniform hexagonal-pore array. The pore size is  $33.7 \pm 2.5$  nm and the wall thickness is  $9.0 \pm 1.1$  nm. The scale bar is 100 nm. (d) SEM image of the film cross-section, which exhibits all parallel straight channels perpendicular to the film surface. The scale bar is 100 nm. Reproduced with permission from Figure 4 of ref.<sup>[143]</sup> Copyright 2004 Wiley-VCH Verlag.

templates, Gierszal and Jaroniec<sup>[141]</sup> reported a synthesis of one kind of uniform carbon film with large pore volumes, uniform pore sizes, and controlled thickness. A uniform polymeric film is first formed on the pore walls of silica colloidal crystals or colloidal silica aggregates, and subsequently, carbonization and template dissolution are carried out, obtaining the carbon film product.

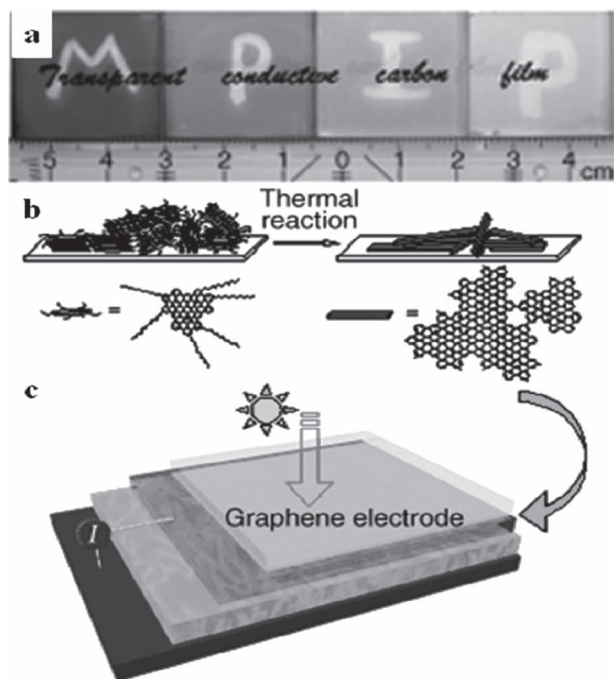
The large-scale alignment of the carbon films is still a big challenge. Noticeably, highly ordered MC with cubic  $Im\bar{3}m$  symmetry has been synthesized successfully via a direct carbonization of self-assembled F108 ( $\text{EO}_{132}\text{PO}_{50}\text{EO}_{132}$ ) and RF composites obtained in a basic medium of nonaqueous solution.<sup>[142]</sup> Liang et al.<sup>[143]</sup> demonstrated a stepwise self-assembly approach to the preparation of large-scale, highly ordered nanoporous carbon films (see Figure 12). The synthesis of well-defined porous carbon films involves four steps: (1) monomer–block copolymer film casting, (2) structure refining through solvent annealing, (3) polymerization of the carbon precursor, and (4) carbonization. Very recently, Zhao and co-workers<sup>[144]</sup> reported the fabrication of free-standing MC thin films with highly ordered pore architecture via a simple coating–etching method. The MC films were first synthesized by coating a resol precursors/Pluronic copolymer solution on a preoxidized silicon wafer, forming highly ordered polymeric mesostructures based on organic–organic self-assembly, followed by carbonizing at 600 °C, and, finally, etching of the native

oxide layer between the carbon film and the silicon substrate. Mild reacting conditions and wide composition ranges are the obvious advantages of this method over the techniques previously reported.<sup>[145–147]</sup>

The emergence of graphene nanosheet has opened up an exciting new field in the science and technology of 2D nanomaterials.<sup>[134]</sup> Recently, much effort has been made for the assembly of graphene nanosheets into membrane-shaped macrostructures or fabrication of novel composite materials.<sup>[148–152]</sup> Yang and co-workers<sup>[153]</sup> produced free-standing GOs membranes through a self-assembly process at the liquid–air interface and the membranes are thickness controllable and area adjustable. In recent years, Müllen and co-workers<sup>[154–157]</sup> have made great contribution in fabricating transparent graphene films and graphene-based composite films and/or sheets. For example, they presented a new bottom-up chemical approach toward the synthesis of transparent graphene-

constructed films (TGFs) which have been achieved by the thermal reaction of synthetic nanographene molecules of giant polycyclic aromatic hydrocarbons (PAHs) (see Figure 13).<sup>[154]</sup> The as-synthesized films show superior electrical conductivity, excellent mechanical flexibility, and good optical transparency, which render them good performance in electronics applications, including lithium-ion batteries,<sup>[158]</sup> field effect transistors,<sup>[156,159]</sup> and so on. Luong et al.<sup>[160]</sup> fabricated a kind of graphene/cellulose nanocomposite paper with high mechanical and electrical performances by mixing reduced GO and amine-modified nanofibrillated cellulose. Furthermore, reduced GO platelets can be self-assembled into highly ordered, mechanically flexible carbon films with tunable porous morphologies through the spontaneous bottom-up organization of preexisting components into patterned structures.<sup>[161]</sup> Further nitrogen doping enhanced the electrical properties and supercapacitor performances of the carbon-based assemblies, and provided chemical functionality.

Carbide-derived carbon film is another attractive film produced by hydrothermal decomposition of carbide precursors on various substrates and then selectively etching metals from metal carbides using chlorine at elevated temperature. These films always have high specific surface area and high specific capacitance.<sup>[162–164]</sup> Porous carbon film synthesized from this approach has a great potential for integrated supercapacitors due to no polymer binder,



**Figure 13.** (a) 30, 22, 12, and 4 nm thick TGFs on quartz ( $2.5 \text{ cm} \times 2.5 \text{ cm}$ ) with letters M, P, I, and P inside, erased from the film before heat treatment. (b) Illustration of the mechanism of the intermolecular condensation of nanographene (PAHs) into graphitic networks. (c) Illustration of the solar cell; the four layers from bottom to top are Ag—a blend of P<sub>3</sub>HT and PCBM, TGF, and quartz, respectively. Reproduced with permission from Figures 1–3 of ref.<sup>[154]</sup> Copyright 2008 Wiley-VCH Verlag.

reduced macropore volume, and good adhesion between current collector and active material.<sup>[165]</sup>

To summarize, various kinds of carbon films have been so far synthesized using methods such as templating, controlled pyrolysis of organic polymer films, and chemical and electrochemical approaches. Because structures and properties of the films determine their efficiency, the development of novel nanostructured carbon films and investigation of their characteristics will continue. Considering the ever-increasing demands for electrical energy storage and separation, it is urgent and crucial to develop simple and efficient techniques to create new type of porous carbon films with controlled porosity and architectures. A possible solution is to take element strategy to introduce foreign atoms in the carbon nanostructures and on the surface, thus to improve the performance in according applications.

### 5. Three-Dimensional Carbon Materials: Monoliths

Porous carbons are a versatile material that possesses a wide range of morphologies not only on the microscopic

level but also on the macroscopic level. Macroscopically, a monolith generally shows wide flexibility of operation in contrast to its powder counterparts.<sup>[166]</sup> Microscopically, monolithic structure is characterized by its 3D bicontinuous hierarchical porosity, which usually leads to several distinct advantages such as low pressure drop, fast heat and mass transfer, high contacting efficiency, easy to deal with, and so on.<sup>[167–169]</sup>

The synthesis of monolithic carbons generally rely on the means including sol–gel method, nanocasting pathway and self-assembly approach.<sup>[170,171]</sup> In recent years, much efforts have been devoted to create new types carbon monoliths with enhanced functions, these are as follows: developing new polymerization systems (solvents and/or precursors), precise pore engineering toward to multimodal porosities, and targeted surface/bulk functionalization.<sup>[172–176]</sup> This part highlights the recently developed chemical synthesis of carbon monoliths with interconnected pores and some of their applications are briefly discussed.

#### 5.1. Sol–Gel Method

##### 5.1.1. New Synthesis Approaches

The sol–gel method is one of the most conventional methods to prepare bulk carbon materials with fully interconnected pores. Carbon aerogels are the representative monolithic materials, whose synthesis generally involves the transformation of molecular precursors into highly cross-linked organic gels based on sol–gel chemistry.<sup>[177]</sup> Since the pioneering work of Pekala,<sup>[178]</sup> the polymer based monolithic carbons have scored remarkable achievements in the new polymerization system and further surface/bulk functionalization. Fairén-Jiménez et al.<sup>[179]</sup> synthesized carbon aerogels with monolith density ranging from 0.37 to 0.87 g cm<sup>-3</sup> by carbonization of organic aerogels deriving from RF polymer prepared in various solvents such as water, methanol, ethanol, tetrahydrofuran, or acetone solution. They found that the samples with a density higher than 0.61 g cm<sup>-3</sup> had micropores and mesopores but no macropores. Using ionic liquids (deep eutectic solvents) either as solvents, or as carbonaceous precursors and structure-directing agents, Monte's group and Dai's group prepared carbon monoliths with high yield (80%) and tailored mesopore diameters.<sup>[180–182]</sup> Sotiriou-Leventis and co-workers,<sup>[183–185]</sup> in recent years, have developed several new polymerization systems such as isocyanate-cross-linked RF gels, polyurea (PUA) gels, polyimide gels, and so on, which offer a high degree of flexibility in producing polymer aerogels and the monolithic carbons. The carbon products show interconnected hierarchical pore networks and 3D bicontinuous morphology, high surface area and large pore volume. For example, PUA gels, which eventually convert to highly porous (up to 98.6% v/v) aerogels

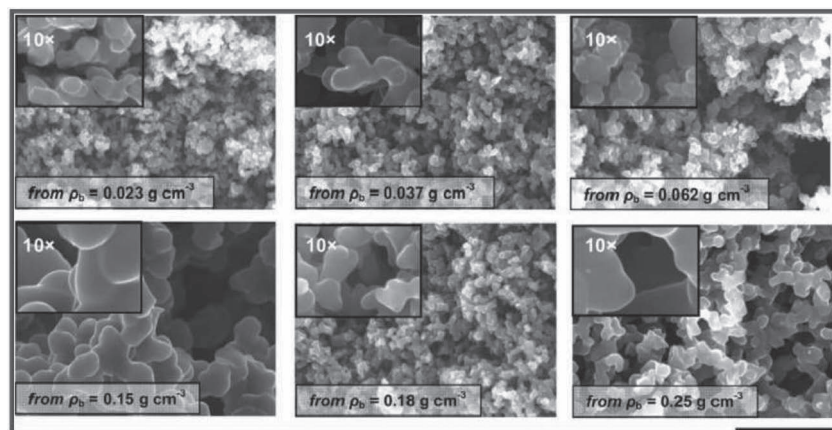


over a very wide density range, can be prepared by carefully controlling of the relative Desmodur RE (isocyanate)/water/triethylamine (catalyst) ratios in acetone (Figure 14). It is worthy of exploration of their applications as catalyst supports, adsorbents, and electrodes in the forthcoming research.

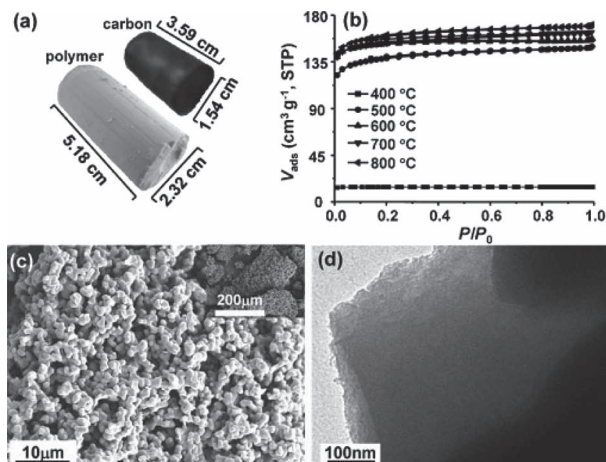
Alternatively, the copolymerization and/or cooperative assembly between carbon precursors, and one or more additional modifiers (i.e. heteroatom-containing components) can be used to directly synthesize functional carbons.<sup>[186]</sup> Sepehri et al.<sup>[187]</sup> synthesized a series of nitrogen–boron codoped carbon cryogels by homogenous dispersion of ammonia borane in RF hydrogel during solvent exchange and followed by freeze drying and pyrolysis. The nitrogen–boron codoping results in a big change of porous structure, and improves electrochemical properties as compared to the nonmodified carbons. Recently, Lu and co-workers<sup>[95]</sup> reported a time-saving synthesis toward to a new-type nitrogen-doped carbon monolith through a sol–gel copolymerization of resorcinol, formaldehyde, and L-lysine (Figure 15). The monolithic carbon shows a highly interconnected macroporosity and an abundant microporosity, which allow a high performance in CO<sub>2</sub> capture with the capacity of 3.13 mmol g<sup>-1</sup> at 25 °C.<sup>[95]</sup>

### 5.1.2. Functionality Integration

Postmodification is a versatile method for the preparation of advanced carbons with powerful functions through processes such as CVD,<sup>[188,190]</sup> impregnation,<sup>[191–193]</sup> metal transfer reactions.<sup>[194]</sup> García-Martínez et al.<sup>[195]</sup> reported a solvent-free, liquid-phase synthesis of self-assembled carbon foams, which can be prepared in variable shapes



**Figure 14.** SEM of carbon aerogels derived from PUA aerogels made of Desmodur RE triisocyanate. Densities (inset) are those of the parent PUA aerogels. Scale bar: 5 μm. Densities of the actual C samples (from left to right): top row, not measured (sample broke to pieces);  $0.29 \pm 0.06 \text{ g cm}^{-3}$ ;  $0.40 \pm 0.02 \text{ g cm}^{-3}$ ; lower row,  $0.62 \pm 0.08 \text{ g cm}^{-3}$ ;  $0.72 \pm 0.03 \text{ g cm}^{-3}$ ;  $0.78 \pm 0.01 \text{ g cm}^{-3}$ . Reproduced with permission from Figure 15 of ref.<sup>[184]</sup> Copyright 2010 American Chemical Society.



**Figure 15.** (a) Photograph of as-made polymer monolith and its carbonized product. (b) N<sub>2</sub>-sorption isotherms of the obtained carbon monolith pyrolyzed at different temperatures ( $P/P_0$  is the relative pressure). (c) SEM image of sample RFL-500 (the inset shows an overview of the macroscopic structure). (d) TEM image of sample RFL-500. Reproduced with permission from Figure 1 of ref.<sup>[95]</sup> Copyright 2010 Wiley-VCH Verlag.

and morphologies without the need of any binders. After loading with palladium catalyst by vapor grafting procedure, the Pd/carbon foams composite exhibit high activity even after multiple runs in the Heck reaction. They believed that the unique features including semicrystalline and conductive framework, high surface area and interconnected porous structure allow a high dispersion of Pd clusters without growth and agglomeration. Long et al.<sup>[196]</sup> prepared carbon aerogels by sol–gel polymerization of phenol, melamine and formaldehyde, followed by subsequent carbonization process. The carbon aerogel monolith impregnated with Na<sub>2</sub>CO<sub>3</sub> may act as an active catalyst for low-temperature oxidation of H<sub>2</sub>S. The catalytic results showed that the impregnated carbons exhibited very high activity (up to 3 g sulfur per gram of catalyst) and high selectivity due to the large pore size, 3D mesoporosity, and large pore volume, which allow easy diffusion of reactants and products, and served as the reservoir for the elemental sulfur. Using similar procedure, Nielsen et al.<sup>[197]</sup> prepared 2LiBH<sub>4</sub>-MgH<sub>2</sub>/carbon aerogel systems as hydrogen storage materials through the nanoconfined chemistry. In this designed composite, LiBH<sub>4</sub> and MgH<sub>2</sub> nanoparticles are embedded in a nanoporous carbon aerogel scaffold with pore size of 21 nm and react during release of hydrogen and form MgB<sub>2</sub>.

Incorporation of additives has also been extensively investigated with the aim to enhance the catalytic, electrical, thermal, and mechanical properties, and to enrich the active sites of composite materials. A direct copolymerization is suitable not only for introduction of molecular functional groups to the carbon products, but also allows well dispersion of nanoparticles throughout the carbon framework. Researchers from Lawrence Livermore National Laboratory have made major advances in synthesis and functionalization of monolithic carbon aerogels.<sup>[198,199]</sup> Recently, they reported TiO<sub>2</sub>/C, TiCN/C, ZnO/C composites aerogels by carbothermal reduction of the titania (or ZnO) coated carbon aerogels. The resulting monoliths consisted of nitrogen-rich titanium carbonitride (TiC<sub>1-x</sub>N<sub>x</sub>,  $x = 0.90$ ) nanocrystals or well-crystallized ZnO nanoparticles exhibited a surface area of 1838 m<sup>2</sup> g<sup>-1</sup> and 1500 m<sup>2</sup> g<sup>-1</sup>, respectively. Also, they successfully integrate CNTs or graphene sheets into the sol-gel reaction, leading to the formation of the advanced monolithic carbons with significantly improved mechanical and electrical properties.<sup>[200–203]</sup> This strategy has used the organic RF binder that is reducible concurrently with the GO or CNTs to thus produce carbon cross-links in the graphene or CNTs network which are virtually indistinguishable from those in the graphene sheets or CNTs networks.

As mentioned above, Worsley et al.<sup>[203]</sup> prepared carbon/graphene composite aerogels through sol-gel polymerization of resorcinol and formaldehyde in an aqueous suspension of GO, and followed by the carbothermal reduction of GO to graphene during pyrolysis at 1050 °C (Figure 16). Alternatively, Zhang et al.<sup>[204]</sup> reported an easy method to create graphene aerogels from graphene hydrogel precursors which were obtained by chemical reduction of GO using L-ascorbic acid as a reducing agent. The resulting graphene aerogels show low density (12–96 mg cm<sup>-3</sup>),

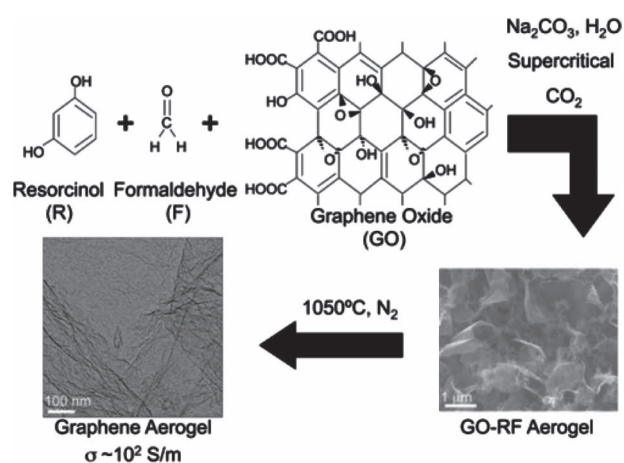


Figure 16. The synthesis procedure for the GO-RF aerogel and graphene aerogel. Reproduced with permission from the ToC figure of ref.<sup>[201]</sup> Copyright 2010 American Chemical Society.

high conductivity ( $\approx 10^2$  S m<sup>-1</sup>), and developed porosity (Brunauer-Emmett-Teller (BET) surface area of 512 m<sup>2</sup> g<sup>-1</sup> and pore volume of 2.48 cm<sup>3</sup> g<sup>-1</sup>). It is worth while to note that such graphene aerogel can support more than 14 000 times its own weight. (Figure 17) The recent intensive work has revealed that the self-assembly method is also a practical way to prepare bulk graphene or GO macroassemblies. For example, Tang et al.<sup>[205]</sup> reported the controlled assembly of single-layered GO into 3D macrostructures promoted by a noble-metal nanocrystal (Au, Ag, Pd, Ir, Rh, or Pt, etc.). The macroassemblies show very low density (0.03 g cm<sup>-3</sup>) and good mechanical properties (compressive strength of 0.042 MPa and compress modulus of 0.26 MPa), and have been utilized as fixed-bed catalysts for a Heck reaction resulting in both 100% selectivity and conversion.<sup>[205]</sup> Similarly, Yang and co-workers<sup>[206]</sup> reported a novel 3D graphene macroassembly with a core-shell structure starting from reduced GO by a one-pot self-assembly process under below 100 °C at atmospheric pressure in presence of KMnO<sub>4</sub>, which is believed to play a key role in the self-assembly process. They also report an interesting GO-derived solid-liquid interfacial phenomenon where aqueous-dispersed GO strongly interacts with a hydrophilic porous media, that is, anodic aluminium oxide (AAO), to form a hydrogel-like GO-based macrostructure.<sup>[207]</sup> One step further, Xu et al.<sup>[189]</sup> developed a novel and facile 3D self-assembly method to prepare GO/DNA composite hydrogels. This work provided a new way for the assembly of GO-based building blocks and

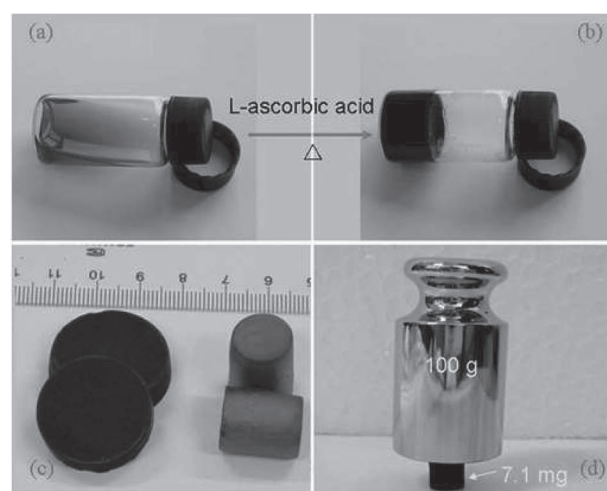


Figure 17. Digital photos of the aqueous suspension of GO (a), the graphene hydrogel (b) in a vial prepared by heating the mixture of GO and L-ascorbic acid without stirring, the supercritical CO<sub>2</sub> dried (left) and freeze-dried (right) graphene aerogel (c), and a 7.1 mg graphene aerogel pillar with the diameter of 0.62 cm and the height of 0.83 cm supporting a 100 g counterpoise, more than 14 000 times its own weight (d). Reproduced with permission from Figure 1 of ref.<sup>[204]</sup> Copyright 2010 Royal Society of Chemistry.

other molecules or units, which is beneficial for rational design of hierarchical graphene-based materials. Cheng and co-workers<sup>[208]</sup> demonstrated a direct synthesis of 3D foam-like graphene macrostructures, namely, graphene foams (GFs), using nickel foams as templates through a CVD process. The GF/poly(dimethyl siloxane) composite product, even with a GF loading as low as  $\approx 0.5$  wt%, shows a very high electrical conductivity of  $\approx 10$  S cm<sup>-1</sup>, which is significantly higher ( $\approx 6$  orders of magnitude) than chemically derived graphene-based composites. The authors believed that the remarkable improvement may arise from highly interconnected graphene networks, which act as the fast transport channel of charge carriers for high electrical conductivity.

Recently, Leventis et al.<sup>[209]</sup> reported a one-pot synthesis of interpenetrating inorganic–organic networks of CuO/RF aerogels as nanostructured energetic materials, in which the catalytic role of CuO was demonstrated. In a similar manner, ferromagnetic nickel particles,<sup>[210]</sup> Pt catalyst,<sup>[211]</sup> ZnO nanoparticles can be uniformly incorporated into the 3D carbon matrix. Li et al.<sup>[212]</sup> reported a gas-bubble-assisted synthesis of mesoporous MnO<sub>2</sub>/carbon aerogel composites by electrochemical deposition. The homogeneously scattered MnO<sub>2</sub> nanoparticles improve the electronic and ionic conductivity of this MnO<sub>2</sub>/carbon composite, and thereby maximize the performance as a supercapacitor electrode.

Sol–gel method is indeed a simple and direct approach for the synthesis of bulky carbons, and is already widely used both in laboratory and in industry. The major disadvantage associated with this method is the long synthesis period and the rigorous drying process of the wet gel (i.e., solvent exchange or supercritical drying), in which slight variations may cause drastic variations in the structural features, and hence properties.<sup>[213]</sup> In addition, pore blocking and sometimes uncontrolled dispersion of active sites both on the surface of and in carbon pore walls remain to be solved.

## 5.2. Nanocasting Pathway

Nanocasting is a process in which a mold (may be called as hard template, scaffold) over nanometer scale is filled with a precursor, and after processing, the initial mold is afterward removed. In this way, the space once occupied by the host mold is thus transferred into pores of the final carbon products, and the carbon in the original template pores is released as a continuous carbon framework. Nanocasting usually involves the following steps: (1) preparation of a porous template with controlled porosity; (2) introduction of a suitable carbon precursor into the template pores through techniques such as wet impregnation, CVD, or their combination; (3) polymerization and carbonization of the carbon precursor to generate an organic–inorganic

composite; and (4) removal of the inorganic template. In the past decades, nanocasting pathway has been demonstrated as a controllable method in preparing carbon monoliths with tailorable pore size over several length scales. The keys rely on preparing a template monolith with accessible porosity and a thermal stable carbon precursor such as phenolic resin, sucrose, furfuryl alcohol, acrylonitrile, acetonitrile, mesophase pitch, and so on. In the following, we discuss the detailed synthesis principle based on several representative examples.

### 5.2.1. Carbon Monolith Replicated from Silica Monolith

Thanks to the contribution of Nakanishi and Tanaka<sup>[214]</sup> in developing silica monolith with designed pore architecture, a series of carbon monoliths with a variety of structures have been synthesized. The replication of silica monolith results the carbon monolith with the following unique features: positive replicas of the silica framework at the micrometre level, but negative replicas on the nanometer scale. Using the hierarchical silica monolith possessing fully interconnected mesopores and abundant macropores, Lindén and co-workers prepared hierarchical porous monolithic carbon containing worm-holelike mesopores and macropores (Figure 18).<sup>[170,215–217]</sup> In a similar way, Shi et al. prepared carbon monoliths with co-continuous structure and trimodal pores using a hierarchical silica monolith as the template.<sup>[218]</sup> Hu et al. synthesized hierarchically porous carbon monoliths with a relatively higher graphite-like ordered carbon structure by using meso-/macroporous silica as a template and using

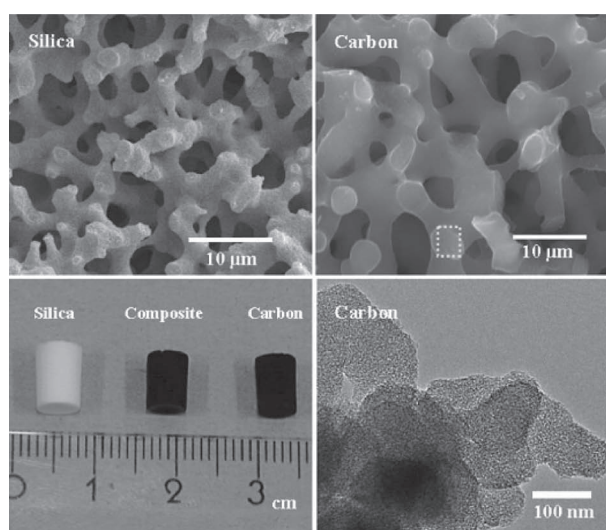


Figure 18. Scanning electron microscopy (SEM) images (upper), photograph (lower, left), and TEM image (lower, right) of silica and carbon monoliths. Reproduced with permission from Figure 7 of ref.<sup>[170]</sup> Copyright 2006 Wiley-VCH Verlag.



mesophase pitch as a precursor.<sup>[219]</sup> Owing to the high porosity and good electronic conductivity ( $\approx 0.1 \text{ S cm}^{-1}$ ), such carbon monoliths show high reversible capacity and superior high-rate performance in rechargeable lithium batteries. A short time later, researchers in the same group took this a step further by potentiostatic deposition of aniline on the nanocast carbon monolith, resulting in high-performance polyaniline electrode in supercapacitors which showed a capacitance of  $2200 \text{ F g}^{-1}$ , a power density of  $0.47 \text{ kW kg}^{-1}$  and an energy density of  $300 \text{ Wh kg}^{-1}$ .<sup>[220]</sup> Recently, Paraknowitsch et al.<sup>[221]</sup> synthesized a nitrogen doped monolithic carbon with bicontinuous meso-/macroporous porosity through a nanocasting pathway using the carefully selected ILS (3-methyl-*N*-butyl-pyridinium-dicyanamide and *N,N*-ethylmethylimidazolium-dicyanamide) as carbon precursors. Due to the structural features in term of hierarchical porosity and nitrogen-doped surface chemistry, this kind of monoliths are suitable as electrode materials.<sup>[221]</sup>

Brun et al.<sup>[222]</sup> reported an interconnected macro-/microporous carbon monolith with a surface area of  $\approx 600 \text{ m}^2 \text{ g}^{-1}$  synthesized using macrocellular silica foams as the hard templates. The carbonaceous monoliths show good cyclability when tested as a lithium-ion negative electrode.<sup>[222]</sup> Meso-/macroporous carbon foams can be prepared through a two-step nanocasting approach, in which a PS foam was first used to prepare silica foam which was then used as the template for the fabrication of carbon foam.<sup>[223]</sup> Gross and Nowak<sup>[224]</sup> synthesized hierarchical carbon foams with independently tunable mesopore and macropore size distributions by fluidic templating in high internal phase emulsions (HIPE). The HIPE consists of an internal oil phase that controls the macropore dimensions and an aqueous RF precursor solution external phase that directs the mesopore size distribution. The advantage of such synthesis is that it avoids the use of solid templates, thus the template removal process is omitted.<sup>[224]</sup>

It is easy to image that when a parent template with periodic porosity is used, the obtained carbon monolith usually inherits the periodicity of the pores. Because the synthesis of silica monolith with various ordered symmetry has become mature, the templated carbons with ordered mesoporosity appear successively. Yang et al.<sup>[225]</sup> synthesized a monolithic carbon with a bicontinuous cubic structure (*Ia3d* symmetry) by using mesoporous silica monoliths with the same periodic symmetry. Lu et al. reported a new interesting synthesis toward hierarchically structured carbon monoliths, in which the mixing and shaping of SBA-15/PFA composites with small particle NaCl was introduced and subsequent through the self-binding and salt templating process.<sup>[226]</sup> This strategy is general, and can be extended to prepare other macro-/mesoporous carbon monoliths using properly selected silica template such as M41S, SBA-*n* series

and so on. Similarly, Feng and co-workers<sup>[190]</sup> reported the synthesis of hierarchical porous carbon monoliths with either hexagonal or cubic mesostructures starting from ordered mesoporous silica SBA-15 or KIT-6 powders by integration of gel casting and impregnation technique. A secondary loading of carbon by a CVD method conduces to a control over the hierarchical porosity of the carbon monoliths. Xia and Mokaya<sup>[227]</sup> have prepared ordered MC monoliths with amorphous feature using mesoporous silica monoliths (SBA-15) as template via CVD. This type of carbon monolith exhibited considerable hydrogen uptake capacity of 3.4 wt% at 20 bar and  $-196 \text{ }^\circ\text{C}$ .

### 5.2.2. Carbon Monoliths Replicated from Colloidal Crystals

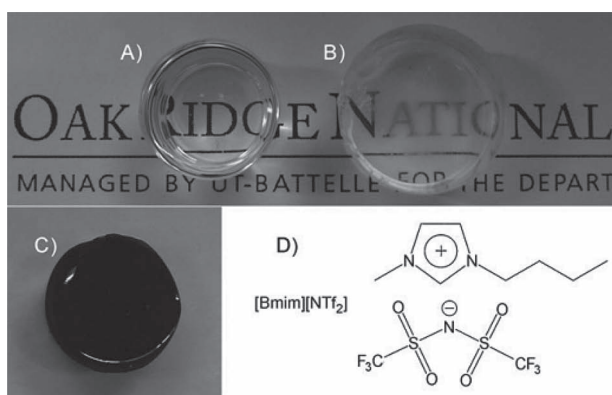
Colloidal crystals are the self-assembly periodic structures consisting of close packed uniform particles. Replication of a colloidal crystal (colloidal silica/polymer sphere) in most cases leads to a high degree of periodicity in three dimensions. Removal of the crystal template leads to a replica with 3D ordered macroporous (3DOM) structures. The groups of Stein, Velez, and Lenhoff have independently achieved many great results in the field of colloidal crystal and their related areas.<sup>[76,175,228,229]</sup> Here we only discuss a small aspect that templating of colloidal crystal is an effective path to get monolithic carbons with highly ordered macroporosity. For example, Lee et al.<sup>[228]</sup> synthesized 3DOM monoliths of hard carbon via an RF sol-gel process using poly(methyl methacrylate) (PMMA) colloidal-crystal templates. The features of well-interconnected pore and wall structures with controlled thicknesses improve the rate performance of lithium-ion secondary batteries. Adelhelm et al.<sup>[230]</sup> also synthesized a hierarchical meso- and macroporous carbon using mesophase pitch as precursors and PS or PMMA as templates through spinodal decomposition.

### 5.2.3. One-Step Nanocasting Technique

Although the above-mentioned classical nanocasting method was far more successful, the multisteps and long synthesis period it involved are impressive. To simplify the tedious procedures, researchers made massive efforts. Han et al.<sup>[231]</sup> developed a one-step nanocasting technique to synthesize micro-/mesoporous carbon monoliths with very high BET surface area ( $\approx 1970 \text{ m}^2 \text{ g}^{-1}$ ) and  $\approx 2 \text{ nm}$  mesopores by the cocondensation of  $\beta$ -cyclodextrin with tetramethylorthosilicate. Recently, Zhang et al.<sup>[232]</sup> presented a one-pot method to synthesize hierarchically bimodal ordered porous carbons with interconnected macropores and mesopores, via in situ self-assembly of colloidal polymer (280, 370, and 475 nm) and silica spheres (50 nm) using sucrose as the carbon source. Compared with the classical

nanocasting procedure, this approach is veritably simple; neither presynthesis of crystal templates nor additional infiltration is needed, and the self-assembly of polymer spheres into the crystal template and the infiltration are finished simultaneously in the same system.<sup>[232]</sup> Similarly, a hierarchically porous carbon with multimodal (macro-pore and mesopore) porosity have also been prepared by using dual-template (PS/colloidal silica and PMMA/colloidal silica), where PS (or PMMA) is for creating 3D ordered macropores, colloidal silica is responsible for creating spherical mesopores. This type of carbon has been tested as an anode for lithium-ion batteries, exhibiting enhanced performance particularly in cycling performance and rate capability. This is mainly attributed to the superb structures, that is, the open larger mesopores located in the ordered macropores. This unique structure allows efficient Li storage and acts as buffer reservoirs for volume change during the charge–discharge cycling.<sup>[233,234]</sup>

Very recently, functionalized porous carbon monolith has been synthesized using heteroatoms incorporated ionic liquids (ILs) such as nitrogen- or boron-containing ILs as precursors through a one-step nanocasting process (Figure 19). Dai and Wang<sup>[235]</sup> proposed confined carbonization method to prepare ILs-based carbons, that is, carbonization of ILs trapped within a silica matrix and subsequent silica removal process produced carbon frameworks with continuous pores. Such one-step synthesis method, using the mesophases of silica/surfactant as starting materials, represents a cost-effective strategy, as it needs fewer synthesis steps, and in particular does not require the mesophases to be calcined prior to use as template. One major challenge as to this method is the uncontrollable formation of the mesophase of the template, which leads to more unpredictable variables in precise pore engineering.



**Figure 19.** Transparent monolithic silica gels containing different amounts of [Bmim][NTf<sub>2</sub>] [ $x = 0.3$  and  $2.0$  for (a) and (b), respectively]. After heat treatment under N<sub>2</sub>, the clear monolith (a) turned black (c). (d) Structure of [Bmim][NTf<sub>2</sub>]. Reproduced with permission from Figure 1 of ref.<sup>[235]</sup> Copyright 2010 Wiley-VCH Verlag.

### 5.3. Self-Assembly Approach for the Preparation of Carbon Monoliths

In the past few years, great progress has been achieved on the direct synthesis of porous carbon materials, especially for ordered MCs in the form of particle and film, by self-assembly of copolymer molecular template and carbon precursors. This paves the way to prepare porous carbon materials with fewer steps and therefore shorter synthesis duration. However, it remains a great challenge to synthesize monolithic carbons with highly developed porosity, especially for generating mesoporosity in regular arrangement, due to the strict requirements. Firstly, a perfect matching interaction between the carbon-yielding precursors and the pore-forming component is required, which allows self-assembling of a stable micelle nanostructure; Secondly, the micelle structures should be stable during sustaining the temperature required for curing a carbon-yielding component, but can be readily decomposed during carbonization; Thirdly, the carbon-yielding component should be able to form a highly cross-linked polymeric material that can retain its nanostructure during the decomposition or the extraction of the pore-forming component. In order to achieve a monolithic carbon with well-developed mesoporosity, not a single one of these conditions can be dispensed with.

Dai and co-workers<sup>[143]</sup> first synthesized highly ordered MC film through a solvent annealing accelerated self-assembly method using PS-block-poly (4-vinylpyridine) (PS-P4VP) as soft templates and *N,N*-dimethylformamide (DMF) as the solvent. Since then, using self-assembly method to prepare porous carbons has been extensively investigated. At present, the products are mostly in a form of powder or film. For example, Valkama et al.<sup>[236]</sup> reported a soft template method to achieve carbon products in any desired shape, and the porosity can be tuned from mesoporous to hierarchically micro-/mesoporous simply by varying pyrolysis conditions for the cured block-copolymer phenolic resin complexes.

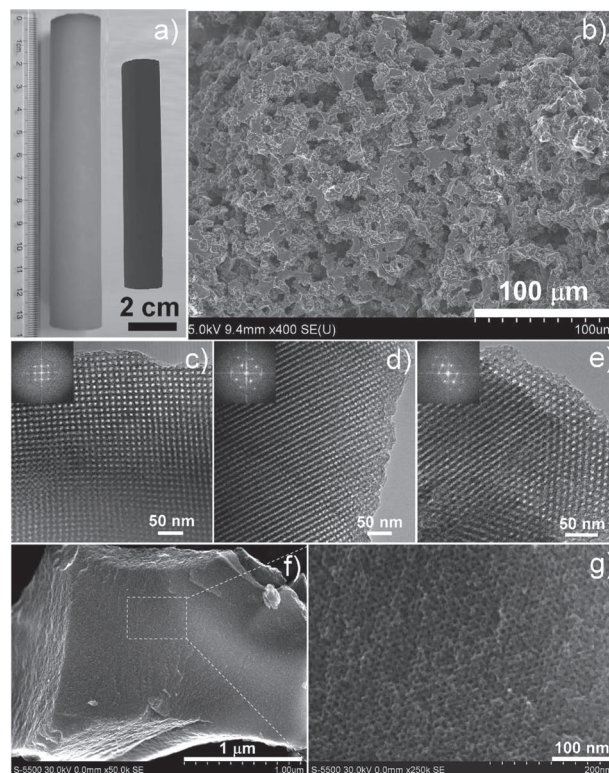
Recently, based on the soft-templating principle, Dai and Liang<sup>[146]</sup> reported a versatile synthesis of porous carbons (monolith, film, fiber, particle) by using phenol-, resorcinol-, and phloroglucinol-based phenolic resins as carbon precursors and triblock copolymer (F127) as the template. They found that due to the enhanced hydrogen bonding interaction with triblock copolymers, phloroglucinol with three hydroxyl groups is an excellent precursor for the synthesis of MCs with well-organized mesostructure.<sup>[146]</sup> Later, they prepared monolithic carbons with ordered mesopores based on self-assembly approach of RF polymer and block copolymers under strong acidic conditions, and by subsequent centrifugation and shaping techniques. The I<sup>+</sup>X<sup>-</sup>S<sup>+</sup> mechanism and hydrogen bonding are believed to be the driving force for self-assembly between

the RF resol and F127 template.<sup>[237]</sup> The polymerization-induced spinodal decomposition in glycolic solutions of phloroglucinol/formaldehyde polymers and block copolymers also lead to successful formation of the bimodal meso-/macroporous carbon monoliths.<sup>[238]</sup>

Zhao and co-workers<sup>[239]</sup> developed a hydrothermal synthesis by using F127 and P123 as double templates and PF as the carbon precursor (molar ratio between phenol and surfactant about 46: 1), followed by hydrothermal aging at 100 °C for 10 h. A short time later, Xiao and co-workers also reported a hydrothermal synthesis at even higher temperature and longer time (i.e. 260 °C for more than 17 h) to prepare carbon monoliths with well-ordered hexagonal or cubic mesopore systems.<sup>[240]</sup> Meanwhile, Gutiérrez et al.<sup>[241]</sup> synthesized a very light and highly conductive (2.5 S cm<sup>-1</sup>) monolithic carbon exhibiting a 3D continuous micro- and macroporous structure, which derived from a PPO<sub>15</sub>-PEO<sub>22</sub>-PPO<sub>15</sub> block-copolymer-assisted RF polymerization. The resulting monolith products were used as electrodes of electric double layer capacitors, with remarkable specific mass capacitance of up to 225 F g<sup>-1</sup>.

Zhang and co-workers<sup>[242]</sup> reported an organic-organic aqueous self-assembly approach to prepare B-/P-doped ordered MCs using boric acid and/or phosphoric acid as B- or P-heteroatom source, RF resin as the carbon precursor and triblock copolymer Pluronic F127 as the mesoporous structure template. Lu and co-workers<sup>[243]</sup> established a rapid and scalable synthesis of crack-free and nitrogen-doped carbon monoliths with fully interconnected macropores and an ordered mesostructure through the soft-template method. The monoliths are achieved by using organic base lysine as a polymerization agent and mesostructure assembly promotor, through rapid sol-gel process at 90 °C. Very recently, the same group reported a new-type porous carbon monolith, which was synthesized through a self-assembly approach based on benzoxazine chemistry.<sup>[244]</sup> The obtained carbon monoliths show crack-free macromorphology, well-defined multilength scale pore structures, a nitrogen-containing framework, and high mechanical strength (Figure 20). As expected, with such designed structures, the carbon monoliths show outstanding CO<sub>2</sub> capture and separation capacities even in the presence of moisture, high selectivity, and facile regeneration at room temperature.

To date, the hydrogen-bonding interactions have been extensively explored as the self-assembly driving force between block copolymer surfactants and carbon precursors. As viewed from the current research, the success of hydrogen-bonding induced self-assembly is only in the small mesopore range (3–10 nm). The groundbreaking achievements in achieving well-ordered porosity in either micropore scale (<2 nm) or larger mesopore range (10–50 nm) are still grand challenges. Moreover, the common features of most current syntheses are that they



**Figure 20.** Photograph of the synthesized polymer (a) and carbon monolith (b); TEM images (c, d, and e: images viewed in the [100], [110], and [111] direction; the insets are the corresponding fast Fourier transform (FFT) diffractograms) and HRSEM images (f, g) of the carbon monolith HCM-DAH-1. Reproduced with permission from Figures 1 and 2 of ref.<sup>[244]</sup> Copyright 2011 American Chemical Society.

usually take a day long, or even longer, and use inorganic catalysts (HCl or NaOH) for the polymerization and self-assembly. Hence, to explore new polymerization systems (new carbon precursors and organic catalysts) that are more time effective is an exciting research area. More desirably, hierarchical structured monolithic carbons with multimodal porosity would be more suitable for applications in catalysis, separations, and energy storage and conversion.

#### 5.4. Dual Template to Hierarchical Carbon Monolith: A Combination of Nanocasting and Self-Assembly

Because of the high precision in pore engineering by nanocasting pathway and the great variety of the micelle nanostructure deriving from soft-templating, many researchers try to combine both techniques into an interdependent and interactive module with the aim of achieving porous carbons with controlled pore structure in a cost-effective manner. Wang et al.<sup>[229]</sup> prepared 3D ordered macro-/mesoporous porous carbons by combining colloidal crystal templating with surfactant templating through a gas-phase process. In a vapor phase infiltration, the wall thickness and



window sizes of carbons are controllable through the variation of the infiltration time. Hierarchically ordered macro-/mesoporous carbon was prepared by dual templating with a hard template (silica colloidal crystal) and a soft template (Pluronic F127), using PF precursors dissolved in ethanol.<sup>[245]</sup> Zhao and co-workers<sup>[246]</sup> reported a mass preparation of hierarchical carbon–silica composite monoliths with ordered mesopores by using polyurethane (PU) foam as a sacrificial scaffold. The macroporous PU foam provides a large, 3D, interconnecting interface for EISA of the coated phenolic resin–silica block-copolymer composites, thus endowing composite monoliths with a diversity of macroporous architectures.<sup>[246]</sup> Recently, the same group reported a direct synthesis of transparent ordered mesostructured resin–silica composite monoliths with uniform rectangular shape through the EISA process by copolymerization of TEOS and resol in the presence of triblock copolymer Pluronic F127 as a template.<sup>[247]</sup> The key factor of this synthesis is the good interoperability and compatibility of the plastic organic resin polymers and the rigid silica skeleton. As a result, multiple choices of the products (ordered MC or silica monoliths with integrated macroscopic morphologies similar to the original composite monoliths) can be realized by either removal of silica in HF solution or elimination of carbon by simple combustion.

Monolithic carbons obtained through the above mentioned methods, in most cases, have the amorphous carbon walls, which contain either adventitious micropores or templated open mesopores. Because of the long-range random arrangement of the primary carbon fragments, the amorphous carbon possesses abundant active sites and displays various kinds of porosity, thus leading to a high surface area. These properties endowed by the amorphous feature, combined with the ease of handling, amorphous carbon monoliths are widely used in many fields such as catalysis, adsorption/separation, hydrogen storage, desalination, and so on.

Porous carbons with highly crystalline features show superior popularity when high electronic conductivity required. Currently, it is challenging to produce graphitic porous carbons at low pyrolysis temperature (e.g., lower than 900 °C), under which usually lead to a serious shortage of ordering at the atomic scale. Though high-temperature thermal treatments above 2000 °C can facilitate the transition to graphitization phase; unfortunately, it often results in a partial or total collapse of the pore structures and reduces the accessible surface areas. By employing graphitization catalysts (i.e. Fe or Co salt),<sup>[248]</sup> one can obtain graphitic porous carbons, in which an additional leaching process is required to remove the final metal oxide derived from the catalyst precursors. Liang et al.<sup>[249]</sup> report a synthesis of monolithic graphitic carbon column with bimodal pores, which was prepared by pyrolyzing a rod made of a copolymer of a resorcinol/iron(III)

complex and formaldehyde in the presence of silica beads through a nanocasting process. Very recently, Dai and co-workers<sup>[250]</sup> pioneered a “brick-and-mortar” self-assembly approach toward ordered graphitic MC nanocomposites with tunable mesopore sizes below 850 °C without using graphitization catalysts or high-temperature thermal treatments. In this strategy, phenolic resin-based MCs act as mortar, whereas the highly conductive carbon blacks or carbon onions were introduced as bricks that are responsible for the graphitic domains of the pore walls. Because of the greatly improved electric conductivity, the obtained nanocomposites show well electrochemical performance.<sup>[250]</sup> This breakthrough provides a new approach to the synthesis of porous carbons with high level of graphitization under a facile condition.

## 6. Summary and Outlook

In summary, carbon-based nanostructured materials have encountered a rapid development era since 1980s. Various kinds of new carbon materials have been synthesized, such as fullerene, CNTs, carbon nanofibers, CDs, graphene, and so on. Nowadays, the synthesis of carbon materials with defined nanostructure and morphology, tunable surface area, and pore sizes in a controlled manner has become possible. In this paper, we have reviewed the recent development of carbon materials with intriguing nanostructure and morphology, which were mainly prepared by chemical synthesis approaches. These materials are summarized based on their dimensionality, such as 0D quantum dots and spheres; 1D fibers, tubes, and wires; 2D films and membranes; and 3D monolithic structure. The synthesis strategies toward these carbon materials generally include precursor controlled pyrolysis, chemical vapor deposition, sol–gel process, self-assembly, nanocasting, and various surface modification or grafting methods. This provides an opportunity for fundamentally understanding the physical and chemical properties of carbon materials from molecular level. It, in turn, facilitates wilful design and synthesis of high-quality carbon nanostructures to meet practical applications. Carbon materials have demonstrated their grand capability in the application areas of energy harvesting, storage and conversion, adsorption and separation, catalysis, nanocomposites materials. Considering the ever-increasing demands for energy and environmental concerns, it is urgent and crucial task for scientists to develop simple, efficient, and innovative techniques to create high-performance nanostructured carbon materials. A feasible solution is to utilize element strategy to introduce foreign atoms selectively decorated either in carbon frameworks, or on carbon surfaces, or combining both, thus to create new functional composites or hybrid materials. Certainly, carbon chemistry strongly requires interdisciplinary

know-how input, by profiting knowledge from other disciplines such as organic synthesis, polymer chemistry, solid state-chemistry, and so on. We have reason to believe that along with the development of carbon chemistry and modern characterization techniques, the designed synthesis of carbon materials with particular nanostructures and properties can be realized in the near future.

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