Nanostructured Carbon

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Mesoporous Carbon Materials: Synthesis and Modification

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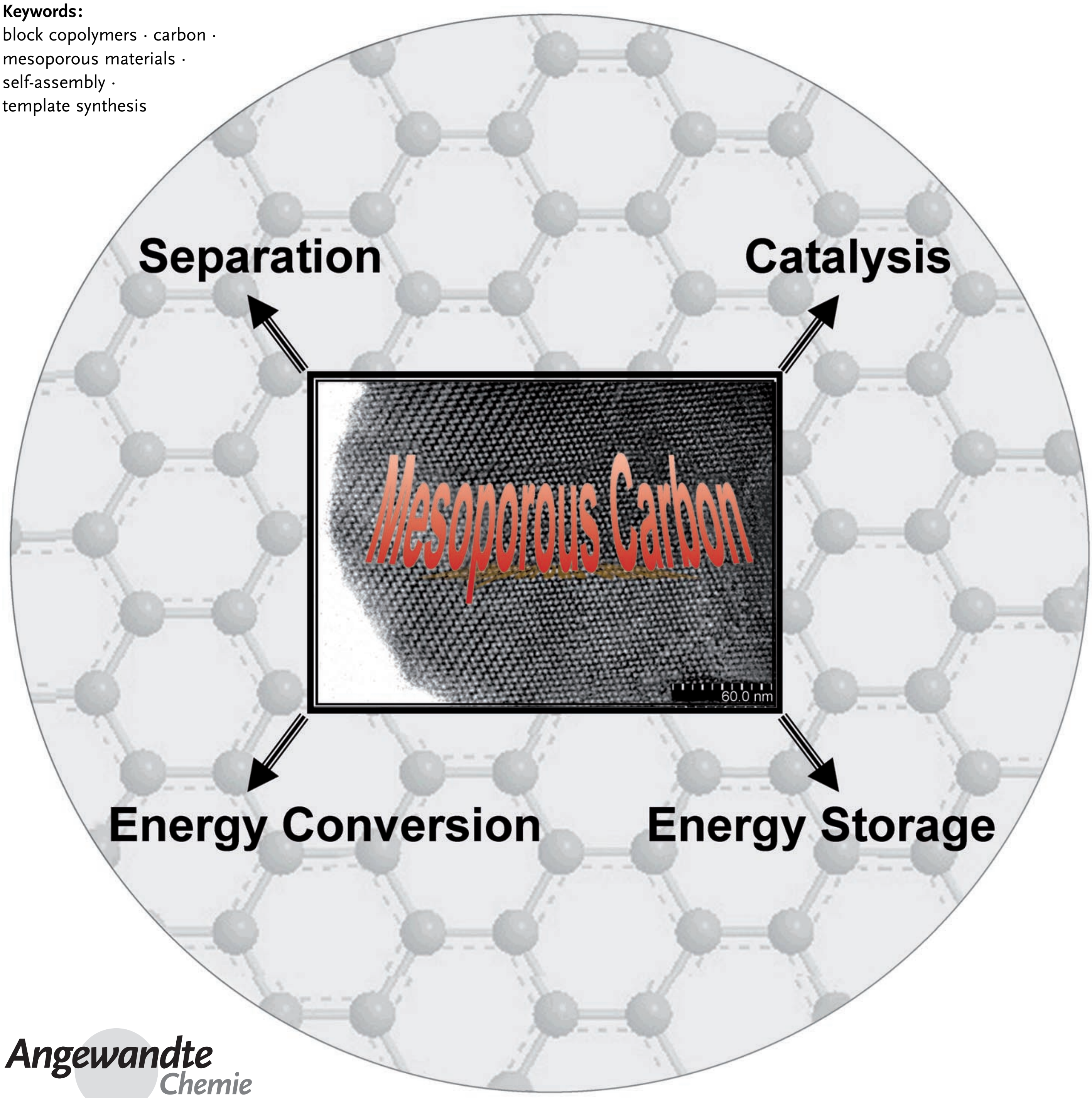

Porous carbon materials are of interest in many applications because of their high surface area and physicochemical properties. Conventional syntheses can only produce randomly porous materials, with little control over the pore-size distributions, let alone mesostructures. Recent breakthroughs in the preparation of other porous materials have resulted in the development of methods for the preparation of mesoporous carbon materials with extremely high surface areas and ordered mesostructures, with potential applications as catalysts, separation media, and advanced electronic materials in many scientific disciplines. Current syntheses can be categorized as either hard-template or soft-template methods. Both are examined in this Review along with procedures for surface functionalization of the carbon materials obtained.

From the Contents

1. Introduction

Porous carbon materials are ubiquitous and indispensable in many modern-day scientific applications. They are used extensively as electrode materials for batteries, fuel cells, and supercapacitors, as sorbents for separation processes and gas storage, and as supports for many important catalytic processes. Their use in such diverse applications is directly related not only to their superior physical and chemical properties, such as electric conductivity, thermal conductivity, chemical stability, and low density, but also to their wide availability. Many advances have been made in carbon technology in recent years, both through continued improvement of existing fabrication methods and through the development and introduction of new synthetic techniques. Porous carbon materials can be classified according to their pore diameters as microporous (pore size < 2 nm), mesoporous ($2 \text{ nm} < \text{pore size} < 50$ nm), and/or macroporous (pore size > 50 nm). Conventional porous carbon materials, such as activated carbon and carbon molecular sieves, are synthesized by pyrolysis and physical or chemical activation of organic precursors, such as coal, wood, fruit shell, or polymers, at elevated temperatures.[1–3] These carbon materials normally have relatively broad pore-size distributions in both micropore and mesopore ranges. Activated carbons and carbon molecular sieves have been produced in large quantities, and are used widely in adsorption, separation, and catalysis applications.

Key advances in the activation synthesis of microporous carbon materials include (a) the use of potassium hydroxide for the synthesis of supermicroporous carbon materials (with surface areas as high as 3000 m^2g^{-1}),[4,5] and (b) the selective reaction of carbides with halogen gases for the generation of carbon materials with controlled microporosity.[6] The latter method uses carbides as the carbon source, and the metal ions are selectively removed by reaction with halogen gas. This chemical-etching method generates micropores with a very narrow size distribution. The microporosity of these carbon materials affords high specific surface areas, large pore volumes, and large adsorption capacities for gaseous or liquid adsorption. Despite the wide applications of microporous materials in adsorption, separation, and catalysis applications, they suffer some limitations arising from the methods used in their production. The key drawbacks associated with activated microporous carbon materials are (a) slow mass transport of molecules because of space confinement imposed by small pore sizes, (b) low conductivity arising from of the presence of enormous surface functional groups and defects, and (c) collapse of porous structures during high-temperature treatments or graphitization.

To overcome these limitations, efforts have been directed toward other synthetic methods, which include the following: (a) a high degree of activation by physical or combined physical/chemical methods,[1,7–9] (b) carbonization of carbon precursors composed of one thermosetting component and one thermally unstable component,[10,11] (c) catalyst-assisted activation of carbon precursors with metal (oxides) or organometallic compounds,[9,12–14] (d) carbonization of aerogels or cryogels,[15,16] (e) replication synthesis with presynthesized hard templates through impregnation, carbonization, and template removal,[17,18] and (f) self-assembly using soft templates through cocondensation and carbonization.[19–21] Methods a) to d) only result in mesoporous carbon materials with broad pore-size distributions (PSD) and considerable microporosity.[9,22] Accordingly, these methods are less attractive.

The focus of this Review concerns methods e) and f), which are related to recent developments in synthesizing mesoporous carbon materials with well-controlled mesopores. Method e), involving the use of presynthesized organic or inorganic templates, is also called a hard-template synthesis method.[23] The templates mainly serve as molds for replication of mesoporous carbon materials, and no significant chemical interactions take place between templates and carbon precursors. The corresponding porous structures are predetermined by the templates, which have well-defined

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nanostructures. Conversely, method f) involves soft templates, which generate the nanostructures through self-assembly of organic molecules. The corresponding pore structures are determined by synthetic conditions, such as mixing ratios, solvents, and temperatures. Although the term “soft template” has not been formally defined, soft templates refer in this Review to self-assembled templates. They differ from hard-template synthesis by the self-assembly of organic templates, in which molecules or moieties are manipulated at the molecular level and spatially organized in nanospaces by hydrogen bonding, hydrophobic/hydrophilic interactions, ion pairing, and/or dative interactions. The chemical interactions between templates and carbon precursors play a key role in the success of the soft-template synthesis.

Owing to the intensive research on mesoporous inorganic materials conducted over the past decade,[24–27] the synthetic methods involving hard and soft templates have proven to be the most successful methods for the preparation of mesoporous carbon with well-defined pore structures and narrow pore-size distributions. The hard-template synthesis approach to mesoporous carbon materials is reviewed in Section 2, with special emphasis on developments in methodology. The soft-template method is discussed in Section 3. Information on porous carbon materials prepared using other methods can be obtained from related reports and recent reviews.[9,22,28,29] The chemical modification of mesoporous carbons is covered in Section 4.

2. Hard-Template Synthesis of Mesoporous Carbon Materials

Microporous activated carbon has long been produced in large quantities, and used as adsorbent in gaseous or liquid adsorptions. However, the synthesis of carbon materials with mesoporous structure by the templating method was not accomplished until early 1980s, when Knox and co-workers reported the synthesis of mesoporous carbon using spherical solid gel as the template.[17,18] Their approach includes the following steps, which are often used today in the hard-template synthesis of mesoporous carbons with well-defined mesoporous structure: a) preparation of silica gel with controlled pore structure, b) impregnation/infiltration of the silica template with monomer or polymer precursors, c) cross-linking and carbonization of the organic precursors, and d) dissolution of the silica template. The space once occupied by the host silica materials is thus transferred into the pores in the resulting carbon materials, and the carbon in the pores of the host silica becomes the continuous carbon framework. Knox et al. synthesized rigid mesoporous carbon using a phenol–hexamine mixture as the carbon precursor. Polymerization, followed by carbonization of the resulting phenolic resin inside the pores of spherical silica gel, and then dissolution of the silica template resulted in rigid, spherical mesoporous carbon material with a Brunauer–Emett–Teller (BET) surface area of 460–600 $m^2 g^{-1}$. The complementary micropores in the resulting carbon material were removed by a graphitization process conducted at 2500 °C in an inert atmosphere, and the final specific surface area was about 150 $m^2 g^{-1}$. Carbon material synthesized by this method was later commercialized under the name “Hypercarb”, and these graphitized, mesoporous carbon spheres exhibit unique retention characteristics in liquid chromatographic separations.[17,18]

Research into the template synthesis of porous carbon materials, and especially materials with ordered porous structures, has continued since the pioneering work of Knox’s group. Kyotani and other researchers synthesized porous carbon and polymer materials using zeolites as the template materials. However, the fine crystalline structure of zeolites was not replicated in the templated porous materials after dissolution of the zeolite frameworks.[30–32] Recently, Kyotani et al. developed a two-step synthetic approach (impregnation followed by chemical vapor deposition), and successfully synthesized a microporous carbon with an X-ray diffraction (XRD) peak at $2\theta = 6.26°$.[33,34] The resulting carbon showed a surprisingly high surface area of 3600 $m^2 g^{-1}$, and micropore volume of 1.52 $cm^3 g^{-1}$.[34] The same group also reported carbon materials templated with β- and L-zeolite.[35] The ordered microporous carbon material synthesized using zeolites as templates has great applicative potential in energy storage devices.

2.1. Ordered Mesoporous Carbon Materials

Interest in the synthesis of ordered mesoporous carbon materials became apparent in the late 1990s, after considerable experience had been accumulated in developing mesoporous molecular sieves with uniform pore size and ordered structure using ionic surfactants, block coploymers, and neutral amines as structure-directing agents.[24,26,27,36,37] To

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Chengdu Liang received his Ph.D. from University of Tennessee, Knoxville in 2005, where he worked with Georges Guiochon and Sheng Dai on novel separation media. After a brief postdoctoral study with Sheng Dai at Oak Ridge National Laboratory, he accepted a joint appointment at the Center for Nanophase Materials Sciences and Chemical Science Division at Oak Ridge National Laboratory in 2006. His current research program focuses on the synthesis of nanostructured materials and the design of novel catalyst systems.

our knowledge, the first ordered carbon material in ordered silica pores was achieved by Wu and Bein,[38] who were studying the conducting properties of carbon inside the hexagonally structured cylindrical mesopores of MCM-41. However, the first self-supported highly ordered mesoporous carbon material was reported in 1999 when Ryoo et al. synthesized mesoporous carbon materials of ordered structures, CMK-1, by employing the ordered aluminosilicate MCM-48 as a hard template.[39] Three months later, Hyeon et al. reported the synthesis of an ordered mesoporous carbon material, SNU-1, by also employing MCM-48 as the template, and with phenolic resin as the carbon precursor. The performance of SNU-1 in an electrochemical double-layer capacitor was also evaluated.[40]

In the synthesis developed by Ryoo's group,[39] the mesopores of the cubically structured aluminosilicate MCM-48 (*Ia*3*d*) were impregnated with solutions of sucrose and sulfuric acid. The acid acts as a catalyst during carbonization at temperatures of up to 1073–1373 °C. The silica framework was finally removed with a hot ethanolic solution of NaOH. This synthetic process resulted in a cubically structured mesoporous carbon, CMK-1, with an average pore size of circa 3 nm. The nitrogen or argon adsorption isotherms of CMK-1 featured a sharp adsorption step owing to the capillary condensation of adsorbate molecules inside these uniform mesopores.[39,41,42] Figure 1 shows a transmission electron microscope (TEM) image of the CMK-1 carbon material, and the corresponding XRD patterns. CMK-1 has a periodic mesoporous structure with a unit-cell size of about 9 nm, that is, a mesoporous molecular sieve carbon material with an amorphous, microporous pore-wall structure.[22,39] One interesting phenomenon is the structure transformation of CMK-1 with respect to the MCM-48 silica template (see Figure 1). CMK-1 is not a true inverse replica of the MCM-48 ordered silica; MCM-48 has a cubic structure of *Ia*3*d,* whereas CMK-1 has a cubic structure of $I4_1/a$.[43] This structural change was explained in terms of the displacement model, or the change in the relative position of the two non-interconnecting mesopore systems filled with carbon in MCM-48 after the silica template was removed.[43]

Carbon materials synthesized using MCM-48 as the template and chemical vapor deposition (CVD) resulted in different XRD results. Ryoo, Terasaki et al. reported that CMK-4 prepared using the CVD method showed the same XRD patterns as the MCM-48 silica template used,[43] and Vix-Guterl et al.[44] reported that carbon material produced by the CVD approach had XRD patterns similar to that of the impregnated samples in Figure 1. Interestingly, structural transformation was also observed in the silica replica of the CMK-1 carbon material using tetraethylorthosilicate (TEOS) as a precursor. The replica had a cubic structure with ordered pores of 4.2 nm, which is neither like the MCM-48 silica nor the CMK-1 carbon.[45]

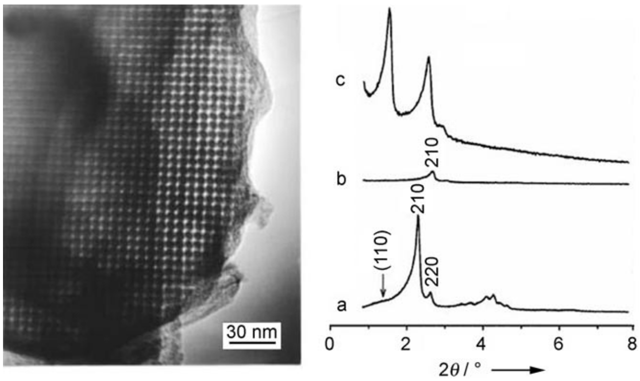

Figure 1. Left: TEM view of the ordered carbon molecular sieve CMK-1. Right: Changes in powder X-ray diffraction patterns during synthesis of the carbon molecular sieve CMK-1 with its silica template MCM-48. (a) The silica mesoporous molecular sieve MCM-48, b) the carbonized carbon/MCM-48 composite, and c) CMK-1 after dissolution of the template.[39]

Recently, our group synthesized an ordered carbon "C48" using MCM-48 silica as the template and mesophase pitch as the carbon precursor. The C48 material exhibited XRD patterns similar to that of CMK-1.[46,47] The high strength and conductivity of pitch-based carbon material enabled us to obtain the first high-resolution scanning electron microscopy (SEM) image of the material (Figure 2). The framework of the C48 carbon network is composed of carbon nanorods of 1.5–2-nm length interconnected in three-dimensions, whereas the mesopores in the MCM-48 template have a system of pores about 2.5 nm in diameter interconnected in three dimensions. Based on the SEM analysis, we suggested that the structure transformation is probably caused by the structural shrinkage and/or the preferred positioning of the formed carbonaceous mesophase in MCM-48 pores during heat

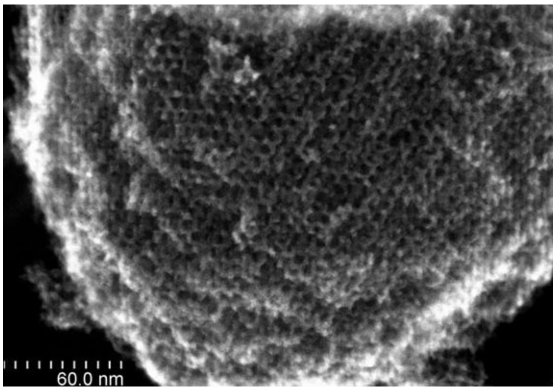

Figure 2. High-resolution SEM image of C48 templated with MCM-48 ordered silica and using mesophase pitch as the carbon precursor.[46]

Zuojiang Li received his Ph.D. from Kent State University in 2003, where he worked with M. Jaroniec on novel columns for chromatographic separations. Later he joined Sheng Dai's group as a postdoctoral fellow at Oak Ridge National Laboratory working on nanostructured materials. His research interests include development, surface modification, and advanced applications of porous adsorbents and carbon materials.

treatment.[46] The higher structural shrinkage during carbonization would permit a higher degree of freedom in orientation of the carbon nanorods. A similar process probably took place during formation of the silica replica of CMK-1 using TEOS as a precursor.[45] However, Parmentier et al. showed that, in addition to the temperature during the process, the presence of steam during carbonization has a significant impact on the stability of MCM-48.[48] Further experimentation and theoretical simulations are needed to clarify this structure transformation phenomenon.

It is generally accepted that the interconnected, three-dimensional porous structure of the templating material is essential for the successful synthesis of porous carbon materials using the hard-template method. For example, ordered mesoporous carbons cannot be successfully synthesized using the MCM-41 silica as the template, which exhibits hexagonally arranged, one-dimensional cylindrical pores.[49] However, Tian et al. successfully synthesized an ultrathin carbon nanowire array by introducing a microwave digestion procedure to the preparation of MCM-41 ordered silica, which led to interconnectivities between the one-dimensional cylindrical pores in MCM-41 silica materials.[50] These interconnected pores make it possible to synthesize self-supported carbon nanowires of 2–2.4-nm length. It is of interest to note that the XRD pattern of the resultant carbon material differs from that of the MCM-41 template, probably owing to structural shrinkage during carbonization. Lee, Hyeon et al. reported the synthesis of a mesoporous carbon (SNU-2) using hexagonal mesoporous aluminosilicate (Al-HMS) as the template and phenolic resin as the carbon precursor.[49] HMS was synthesized using a primary alkylamine as the structure-directing agent and TEOS as the silica source and has a uniform pore size of circa 3 nm and a reflection in the XRD pattern at $2\theta = 2°$.[36,51] Al-HMS was generated by treating HMS with aluminum(III) chloride without changing the mesostructure. The SNU-2 carbon material thus synthesized has a uniform pore size of 2 nm and a reflection in the XRD pattern at $2\theta = 2.18°$. The TEM analysis of Al-HMS and its SNU-2 replica was very helpful in clarifying the three-dimensional interconnected worm-like hexagonal structure of HMS as opposed to a straight-channel model.[51]

Shortly after SNU-2 was synthesized, a highly ordered, hexagonally structured mesoporous carbon, CMK-3, was produced by Ryoo's group[52] using the hexagonally structured SBA-15 silica mesoporous molecular sieve as the template. SBA-15 was synthesized using triblock-copolymer surfactant poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO-PPO-PEO, Pluronic P123) as the structure-directing agent.[26,27] SBA-15 was initially believed to possess a hexagonal structure with disconnected cylindrical pores, similar to MCM-41 silica. However, subsequent nitrogen adsorption studies showed that there are connecting micropores or small mesopores between the primary cylindrical pores in SBA-15.[53] A possible explanation for the formation of these complementary pores is as a result of penetration of poly(ethylene oxide) chains of the triblock copolymer surfactant within the silica pore walls during synthesis of SBA-15. The structure of SBA-15 silica was further confirmed by its carbon replica CMK-3, which is a real inverse replica of the SBA-15 template. CMK-3 is composed of carbon nanorods arranged in a hexagonal pattern, with connecting bridges between them. As for CMK-1, there is a considerable number of complementary micropores in the pore wall structure of CMK-3, resulting in a much higher specific surface area than calculations indicated for CMK-3 composed of nonporous pore walls. The synthesis of CMK-3 with SBA-15 as template confirmed the existence of interconnecting micropores and small mesopores among the primary hexagonal pores in SBA-15 silica.[54]

The pore size of an ordered carbon material synthesized with a hard template is primarily determined by the pore wall thickness of the inorganic templates, which can be tailored by the synthetic conditions.[27] Ryoo et al. systematically synthesized a series of SBA-15-type ordered silica materials with tailored pore wall thicknesses of 1.4–2.2 nm by controlling the ratio of hexadecyltrimethylammonium bromide (HTAB) to the poly(oxyethylene hexadecyl ether) surfactants ($C_{16}EO_8$) in the surfactant mixture. With these silica templates, they were able to synthesize CMK-3 materials with a tailored mesopore size of 2.2–3.3 nm.[55]

Yu et al. reported the synthesis of a rod-like, hexagonally ordered CMK-3-type mesoporous carbon material by employing a rod-shaped SBA-15 template. This template morphology was made available by incorporating the inorganic salt KCl into the synthesis of SBA-15 silica.[56] Kim and Pinnavaia reported an ordered mesoporous carbon material with pore sizes of about 4 nm, named C-MSU-H, using MSU-H silica as the template. MSU-H is very similar to SBA-15, but is synthesized under near-neutral conditions and using sodium silicate as the silica source.[57] Efforts have also been made to directly convert the triblock copolymer (e.g., Pluronic P123) in the as-synthesized silica/triblock copolymer nanocomposites into ordered carbon material by direct carbonization and template removal.[58,59] Hyeon's group used sulfuric acid to treat the as-synthesized SBA-15 silica/triblock copolymer nanocomposite and successfully synthesized ordered mesoporous carbon materials with narrow pore-size distributions maximized at about 3 nm. Sulfuric acid is essential as a catalyst in the dehydration and carbonization of triblock copolymer surfactant. Without sulfuric acid treatment, ordered mesoporous carbon materials cannot be obtained directly from the as-synthesized SBA-15-type silica.

Another significant advancement on the development of mesoporous carbon materials by Ryoo's group is the synthesis of a nanopipe-like ordered mesoporous carbon material, CMK-5, that has a hexagonally ordered array of amorphous carbon nanopipes.[60,61] During synthesis, aluminum was incorporated onto the surface of SBA-15 ordered silica to introduce acidic sites that would catalyze the polymerization of furfuryl alcohol on the pore walls. The partial impregnation of furfuryl alcohol onto the SBA-15 pores is critical for the successful synthesis of CMK-5. It was later found that repetitive impregnation of furfuryl alcohol and carbonization under vacuum can improve the quality of the CMK-5.[61] The carbon nanopipes are connected to each other at some points owing to the presence of complementary micropores/mesopores in the SBA-15 template. Because of this unique structure, the CMK-5 carbon material has XRD patterns similar to those of CMK-3 but shows two maxima in pore-size distributions, one at 5.9 nm from the pores inside the cylindrical channels, and another at 4.2 nm from the pores formed between the adjacent cylinders.[60] In CMK-5, the outside diameter of the cylindrical pores is controlled by the selection of a SBA-15 template with a suitable pore diameter, whereas the inside diameter and the wall thickness are controlled by the amount of furfuryl alcohol polymerized onto the pores. As for CMK-3, the pore wall of CMK-5 is microporous, which explains its high surface area of circa 2000 $m^2 g^{-1}$ and total pore volume of about 1.5 $cm^3 g^{-1}$.[61] Figure 3 shows a TEM image of the CMK-5 ordered carbon material comprised of uniformly sized carbon nanopipes.[60,62]

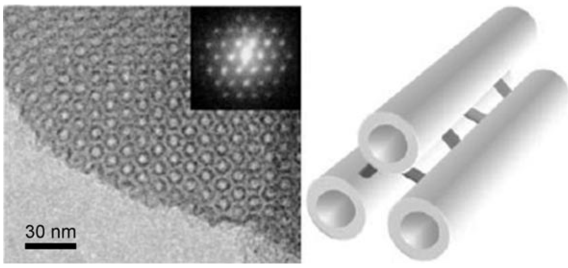

Figure 3. Left: TEM image of CMK-5 viewed along the direction of the nanopipes and the corresponding Fourier diffractogram. Right: Schematic model for the structure of CMK-5.[60]

Recently, Lu, Schüth et al. synthesized a "NCC-1" carbon with a bimodal pore-size distribution and a structure similar to CMK-5, further confirming the composite mesoporous system composed of pores from the dissolution of the pore walls of SBA-15 silica and the pores from the inner carbon nanopipes.[63]

Chemical vapor deposition (CVD) has also been applied to the synthesis of ordered mesoporous carbons. Ryoo's group reported a CVD approach to prepare ordered mesoporous CMK-4 at 1073 K using the aluminosilicate MCM-48 as template and acetylene as carbon precursor.[43] Vix-Guterl et al. used 2.5 vol % propylene as carbon precursor, and the CVD of propylene in MCM-48 at 1020 K led to an ordered carbon material with XRD patterns similar to those of CMK-1.[44] Zhang et al. reported a catalytic CVD method to synthesize CMK-5-type hexagonal arrays of carbon nanopipes, using cobalt-incorporated SBA-15 silica as template and ethylene gas as carbon precursor. They found that sufficient deposition time was required for successful synthesis of high-quality ordered arrays of carbon nanopipes.[64] Xia and Mokaya reported that the CVD of styrene on SBA-15 at higher temperatures generated a hollow spherical mesoporous carbon material after the template was removed.[65]

Parallel to the intensive studies of templated carbon materials with diverse structures, great efforts have been made to synthesize silica materials with the cubic *Ia*3*d* structure, which has larger ordered mesopores and unit-cell dimension, owing to their potential application as catalyst or catalyst support. Unlike SBA-15, it was difficult to change the pore wall thickness of MCM-48 to prepare ordered carbon materials with tailored pore size by a templating method.[42] Recent accelerated research on the ordered mesoporous materials has made it possible to synthesize silica materials with an *Ia*3*d* structure and large meospores from 3 to over 10 nm using the triblock copolymer P123 as the structure-directing agent.[66–69] Liu, Zhao et al. synthesized large-pore 3D bicontinuous mesoporous silica (FDU-5) by solvent evaporation using P123 as the template and organosiloxane (3-mercaptopropyl)trimethoxysilane as a modifier.[67] Using cubically structured large-pore silica as the template, rod-like[70] and tube-like[66] mesoporous carbons with bicontinuous cubic *Ia*3*d* symmetry were synthesized. High-quality cubic mesoporous silica KIT-6 (*Ia*3*d*) with a tunable pore size (4–12 nm) was hydrothermally synthesized by Klietz, Ryoo et al. using butanol as a modifier, and the rod-type and tube-type carbon replica were synthesized by employing KIT-6 as the template.[68,69] In contrast to CMK-1, carbon materials synthesized using FDU-5 and KIT-6 as templates show the same symmetry as their parent silica materials. This structure retention was explained by Zhao et al. as being the result of a rigid carbon framework that prevents the symmetry change owing to the larger pore size of FDU-5 compared to MCM-48.[67] The prevention of symmetry change is due to the rigid carbon network that was templated by the larger pore size. Ryoo et al. believed the presence of porous bridges between the channel-like enantiomeric systems of the cubic KIT-6 were responsible for structure retention. As in the case of CMK-3, the structure retention was due to the interconnecting micropores/small mesopores among the hexagonal cylindrical pores of SBA-15 silica.[52]

Thanks to rapid progress made in the synthesis of ordered silica materials with diverse structures, ordered mesoporous carbon materials with a variety of structures have been synthesized using silica templates. These materials include a) a cubic structure with symmetry $I4_1/a$,[39] b) a two-dimensional hexagonal structure with symmetry *P*6*mm*,[52,60] c) a cubic structure with symmetry *Ia*3*d*,[39,43,70] d) a body-centered cubic structure with symmetry *Im*3*m*,[71] e) a face-centered structure with symmetry *Fm*3*m*,[71] and f) a cubic structure with symmetry *Pm*3*n*.[22] It is anticipated that ordered mesoporous carbon materials will be synthesized with novel structures and symmetries, given the current intensive research on porous silica materials.

The molecular structure of carbon precursors has a great impact on the structure and pore size of mesoporous carbon materials synthesized using hard-template synthetic approaches. The employment of carbon precursors with loose molecular structures, such as sucrose, sugar, and furfuryl alcohol, often results in mesoporous carbons with complementary micropores on the pore walls.[22,39] For example, CMK-1 and CMK-3 synthesized using sucrose as the precursor have primary ordered mesopores with microporous wall structure.[39,60,61] The presence of micropores in the carbon framework is responsible for the high BET surface area and large pore volume of these templated materials. In contrast, mesoporous carbon material synthesized using a fused aromatic precursor, such as mesophase pitch, acenaphthene, and pyrene, show high mechanical strength and smaller BET surface areas and pore volumes.[72–75] Using ordered or disordered silica gel[73,76] or silica sol[72,77] as templates, and mesophase pitch or polyacrylonitrile as carbon precursors, Li and Jaroniec synthesized mesoporous carbon materials with negligible microporosity.[77] The pore size of ordered mesoporous carbon material from mesophase pitch is smaller than those synthesized from precursors containing less aromatic structures because the structural shrinkage in carbonization process was dramatically reduced. Carbon materials synthesized with precursors containing fused aromatic structures have relatively smaller pore size, lower surface area and pore volume, and higher mechanical strength.[72,73,76,77]

2.2. Ordered Mesoporous Carbon Materials with Graphitic Pore-Wall Structure

Ordered mesoporous carbon materials with graphitic pore wall structure were also pursued recently by several research groups,[75,78–82] because of their great potential in various applications, such as fuel cells and double-layer capacitors. Carbon materials with a well-developed pore structure have an amorphous pore-wall structure instead of graphitic crystallinity. Three approaches have been used to synthesize ordered mesoporous carbon with graphitic structure: 1) using carbon precursors with fused aromatic structures, 2) synthesis by CVD at high temperature (> 900 °C), and 3) treating carbons with amorphous pore walls at temperatures over 2000 °C to induce a graphitization process.

Kim, Ryoo et al. synthesized a CMK-3-type ordered mesoporous carbon with graphitic frameworks at 900 °C using acenaphthene as carbon precursor and alumina-incorporated SBA-15 as the template.[75] The carbon frameworks are composed of discoid graphene sheets that had self-aligned perpendicularly to the template walls during synthesis. This novel carbon material showed high mechanical strength and thermal stability in air. Kim, Lee, and Pinnavaia[78] compared the effects of carbon precursors, such as naphthalene, anthracene, pyrene, and benzene, on the graphitic structure and pore size of mesoporous carbon material templated with the hexagonal MSU-H silica [83]. They found that carbon materials from pyrene and naphthalene showed a higher degree of graphitic structure, whereas the material from benzene showed the highest degree of conductivity owing to the catalytic carbonization/graphitization of the iron nanoparticle incorporated on the MSU-H surface. In any case, the conductivity of the mesoporous carbon materials from these precursors was at least one order of magnitude higher than that of the materials synthesized using sucrose as the precursor.

Ordered mesoporous carbons with two-dimensional hexagonal *p6mm* or cubic *Ia3d* symmetry were synthesized by Yang, Zhao et al. using pitch as the precursor.[79] They found that the carbon (002) plane is vertical to the long axis of carbon nanorods. Xia and Mokaya developed a CVD method to synthesize nitrogen-doped graphitic mesoporous carbon materials using acetonitrile as the carbon precursor.[80,81] Fuertes and Alvarez also reported ordered mesoporous carbons, using polyvinylchloride as the carbon precursor and SBA-15 and MSU-1 as templates. The graphitization treatment (2300 °C) of these carbon materials resulted in mesoporous materials with high electrical conductivity (0.3 $\mathrm{S\,cm^{-1}}$), broad pore distributions, and a lower degree of structure ordering.[84] The same group later reported a $FeCl_3$-catalyzed graphitization of ordered carbon from pyrrole at a lower temperature of 900 °C.[85]

2.3. Disordered Mesoporous Carbon Materials with Uniform Mesopores

In addition to rapid development in the syntheses of ordered mesoporous carbon materials having differing structures using ordered silica as templates, a variety of approaches have been developed for the synthesis of disordered mesoporous carbon materials with uniform pores. These approaches include templating with silica nanoparticles or crystals,[72,77,86–91] anodic alumina,[92–95] silica gel, or alumina–silica[17,18,73,96,97] and copolymerization of carbon precursors with alkoxide inorganic precursors such as tetraethylorthosilicate (TEOS).[98–102] Mesoporous carbon materials with a variety of hierarchical pore structures and/or interesting morphologies are thus synthesized.

2.3.1. Mesoporous Carbon Materials from Copolymerization/Cocondensation

Kawashima and Kyotani et al. synthesized mesoporous carbon material from carbon/silica nanocomposite, which was obtained through the copolymerization reaction of TEOS and furfuryl alcohol (FA). The mesopore size in the resulting material is greatly affected by the FA/TEOS ratio.[98] A similar technique was adopted by Pang, Lu et al. to prepare mesoporous carbon films.[101] Han et al. developed a one-step nanocasting technique to synthesize carbon materials with circa 2-nm mesopores by the cocondensation of β-cyclodextrin with tetramethylorthosilicate. The carbonization of the transparent cyclodextrin/silica composite and subsequent silica dissolution resulted in a mesoporous material in granular or monolith form, depending on the synthetic conditions.[102]

2.3.2. Mesoporous Carbon Materials Templated with Colloidal Silica Particles

Han, Sohn, and Hyeon synthesized a mesoporous carbon using silica nanoparticles of 12-nm size as a template. First resorcinol/formaldehyde was polymerized in the presence of these nanoparticles to give a carbon/silica nanocomposite. The pore size of the resulting carbon has a relatively broad pore-size distribution (PSD) after the dissolution of the silica nanoparticles.[103] They also found that the silica/resorcinol ratio had a great impact on the PSD of the resulting carbon material. The same group later improved the synthesis by stabilizing the silica nanoparticles with cetyltrimethylammonium bromide (CTAB) to avoid the agglomeration of silica nanoparticles, and the resulting carbon show a narrow PSD with a maximum at about 10 nm corresponding to the size of the initial silica nanoparticles.[87]

Jang and Lim also reported a technique to prepare porous carbon using surfactant-modified silica and constrained polymerization of divinylbenezene on the silica surface.[88] Hampsey, Lu et al. recently reported a spherical mesoporous carbon material formed by atomizing a silica nanoparticle/sucrose mixture, followed by solvent evaporation.[90] Gierszal and Jaroniec recently reported a carbon with an extremely large volume (ca. 6 cm^{3}g^{-1}) of uniform mesopores by the formation of a uniform carbon film of the controlled thickness on the pore walls of colloidal silica crystal.[104] SEM images of carbons templated with colloidal silicas are shown in Figure 4.[105]

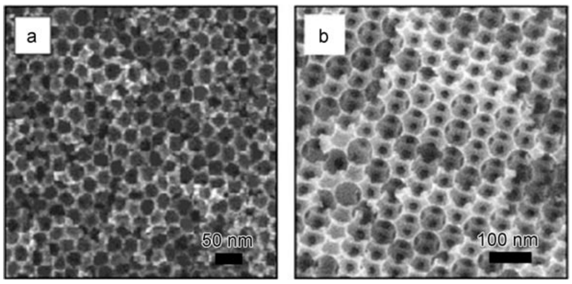

Figure 4. SEM of mesoporous carbon materials (pore sizes of 25 nm (a) and 68 nm (b)) synthesized using colloidal silica particles as templates.[105]

Li and Jaroniec developed a colloidal-imprinting technique to synthesize mesoporous carbon with uniform mesopores.[72] Mesophase pitch was employed as the carbon precursor, and commercial colloidal silicas were used as templates. The resulting carbon showed a uniform mesopore size of 13 and 24 nm, respectively, caused by the dissolution of the corresponding colloidal spheres. The maximum BET surface area of the resulting carbon is in good agreement with calculations based on a model of nonmicroporous pore wall structure. Li, Jaroniec et al. also reported the first graphitized mesoporous carbon with uniform and well-controlled pore size, high surface area, and homogeneous surface.[106] However, owing to structure shrinkage upon graphitization, the pore size changed from 24 to 16 nm. Figure 5 shows the nitrogen adsorption isotherms and the corresponding pore-size distribution for the colloidal-imprinted mesoporous carbon materials before and after graphitization at 2400 °C.

Fuertes reported a mesoporous carbon material with particle sizes in three length scales of 2–8 μm, 0.2–0.5 μm, and 10-20 nm that could be controlled by the conditions for the synthesis of the mesostructured silica template.[107] Mesoporous/macroporous carbons with uniform pore size were also synthesized using colloidal silica crystals as templates by impregnation[105,108–111] and CVD methods.[112] It is not uncommon that, in the synthesis of marcoporous silicas, a sintering step is carried out to create connections among silica spheres prior to the impregnation procedure.[91] Hyeon et al. reported a bimodal mesoporous carbon in which circa 4-nm framework mesopores and circa 30-nm textural pores were synthesized using a silica template composed of 30–40-nm nanoparticles with about 3.5-nm, three-dimensionally interconnected mesopores.[113] Gierszal and Jaroniec also reported a mesoporous carbon with bimodal distributions, using a mixture of ordered SBA-15 and colloidal silica spheres as templates.[114]

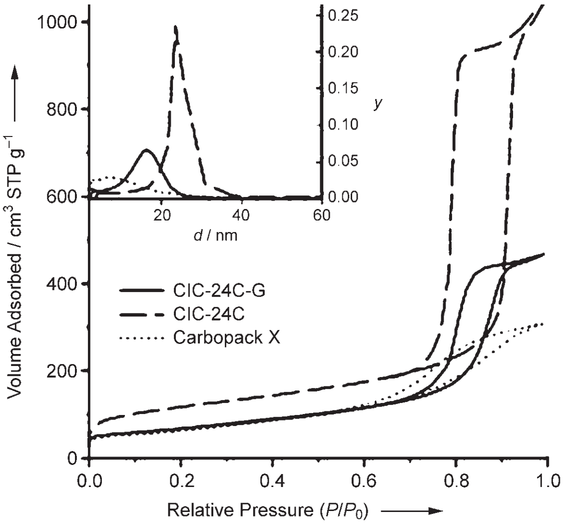

Figure 5. Nitrogen adsorption/desorption isotherms and corresponding pore-size distributions (*d*: pore diameter, *y*: pore-size distribution in cm^{3}g^{-1}nm^{-1}) before (dashed lines) and after (solid lines) graphitization at 2400 °C.[106]

2.3.3. Mesoporous Carbon Materials Templated with Silica/Aluminosilicate Gels

Lee, Sohn, and Hyeon synthesized a mesocellular carbon foam with uniform mesopores by partially impregnating the mesocellular aluminosilicate foam with phenol/formaldehyde, followed by carbonization and template removal.[96] The silicate foam has uniformly sized cells and opening windows, with some complementary mesopores (ca. 3.5 nm) in the cell walls.[96,115] During the synthesis, the carbon precursor was impregnated into the complementary mesopores; the filling of the primary cellular space should be avoided. The resultant cellular carbon foam shows a primary cell dimension of 27 nm and window openings of about 11 nm. In Figure 6, a schematic structure of mesocellular foams is shown.[96] Oda, Tatsumi et al. also reported mesocellular carbon foams of similar structure but with closed cells, using a two-step repetitive impregnation technique and sucrose as the carbon precursor.[97] Hyeon et al. also reported another mesostructured carbon material, HMMC, composed of mesocelluar pores of about 40 nm and mesopores of circa 4.7 nm resulting from the dissolution of silica walls. This mesoporous carbon material shows a lower degree of ordered structure.[96,116,117]

Hollow macroporous core/mesoporous shell-type carbon materials have also been synthesized using a silica template with a solid core/mesoporous shell structure.[118,119] Monolithic mesoporous carbon materials have been synthesized using a monolithic silica or colloidal silica as a template.[70,120–124] Notably, Feng and co-workers[122] have successfully synthesized a monolithic mesoporous carbon material using a

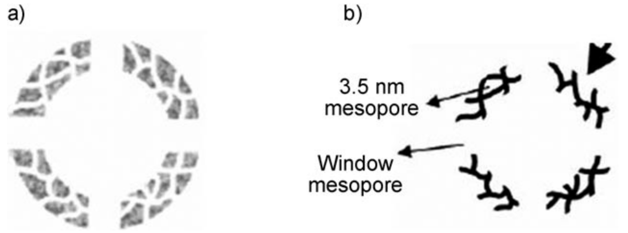

Figure 6. Structural models of a) the mesocellular silica and b) the resultant templated mesocellular carbon using phenol resin as the carbon source.[96]

monolithic mesoporous silica formed with the sol–gel process as the template.

2.3.4. *Mesoporous Carbon Materials Templated with Anodic Aluminum Oxide*

Anodic aluminum oxide (AAO) is normally composed of a one-dimensional hexagonal array of individual cylindrical channels ranging in diameter from 20 nm to several micrometers. The pore size and the interpore distance can be controlled by the oxidation voltage and time. The AAO membrane has been used to produce the crystalline carbon nanotubes and amorphous carbon nanopipes.[92,93] Kyotani et al. reported the synthesis of carbon nanotubes with a diameter of about 30 nm using AAO as a one-dimensional template, and propylene or furfuryl alcohol as the carbon precursor.[92] Other groups have also reported templated carbon nanotubes from AAO membrane.[94,95] Nevertheless, in many cases, the diameter of the templated carbon nanotubes or nanopipes is greater than 50 nm, and no nitrogen adsorption data are reported, probably because of a lack of samples.

2.3.5. *Mesoporous Carbon Materials Templated with Polymer Beads*

Organic polymer spheres, such as polystyrene spheres, have been used as the template in the synthesis of macroporous ordered carbon material cavities connected with mesoporous windows. Formation of a phenolic-type resin on these spheres followed by template dissolution with toluene and heat treatment gives rise to an ordered macroporous carbon with cavities of circa 100 nm and interconnections mesopores of about 6 nm.[124] Use of polymer beads as templates may eliminate the dissolution step, which is an indispensable step when inorganic templates were used, owing to the ready thermal decomposition of the polymer beads along with the carbonization of the carbon precursors.

3. *Soft-Template Synthesis of Mesoporous Carbon Materials*

Amphiphilic molecules, such as surfactants and block copolymers, have been extensively employed as soft templates in the synthesis of ordered mesoporous oxides. Since the first report of mesoporous silica by researchers at the Mobil Company in 1992,[24] ordered inorganic oxides have appeared frequently in nanomaterial research. Ordered polymeric mesoporous materials, though less popular than their inorganic cousins, have been studied for almost two decades since the first ordered organic nanoporous materials were reported in 1988.[125] The emergence of ordered mesoporous carbon is a natural development in the area of mesoporous materials because of the unique physicochemical properties of porous carbon materials, which can fill technological gaps in numerous applications that neither oxide nor polymer mesoporous materials are able to fill. However, the synthesis of ordered mesoporous carbon materials by the self-assembly approach is difficult to achieve for several reasons.[29,126]

There are four key requirements for the successful synthesis of mesoporous carbon materials using soft templates: 1) the ability of the precursor components to self-assemble into nanostructures, 2) the presence of at least one pore-forming component and at least one carbon-yielding component, 3) the stability of the pore-forming component that can sustain the temperature required for curing the carbon-yielding component but can be readily decomposed with the least carbon yield during carbonization, and 4) the ability of the carbon-yielding component to form a highly cross-linked polymeric material that can retain its nanostructure during the decomposition or the extraction of the pore-forming component. So far only a few materials meet these requirements. Although some of the research activities summarized in the following sections are related to the soft-template synthesis of polymeric structures, they are included because the fundamental principles behind the synthesis of these self-assembled nanostructures are very similar to those behind the synthesis of mesoporous carbons, and can shed light on the future development of new synthetic stategies for mesoporous carbons.

3.1. *Synthesizing Mesoporous Carbons Using Amphiphilic Molecules*

The first attempt to synthesize ordered mesoporous carbon material using micelle templates was reported by Moriguchi et al.[127] Inspired by the synthesis of MCM-41, they used the surfactant cetyltrimethylammonium bromide (CTAB) as a template and successfully assembled mesophases of phenolic resin and surfactant. The Coulombic interaction between the positively charged surfactant head and the negatively charged phenolic resin was proposed as a driving force for the self-assembly of the surfactant/phenolic resin complex. By varying the ratio of phenol to CTAB from 1:1 to 6:1, lamella, hexagonal, and disordered mesophases have been synthesized. The d spacing of the mesophase depends on the length of the alkyl chain of the template surfactant: octadecyltrimethylammonium (C18), hexadecyltrimethylammonium (C16), and tetradecyltrimethylammonium (C14) bromides led to mesoscopic materials with d values of 37, 35, and 29 Å, respectively. However, the mesophases collapsed after aging at 200 °C, and unfortunately no porous carbon was obtained.

The use of CTAB as a soft template for the synthesis of mesoporous carbon materials has also been explored by our group.[128] The carbon precursor used in our investigation was a solubilized pitch material which has negatively charged terminal groups; an interesting carbon material with vesicular, hierarchical structure was synthesized by this micelle-templating strategy. However, no ordered mesoporous carbon materials were obtained. Another attempt to synthesize mesoporous carbon material using surfactants based on alkyl chains was reported by Zhao et al. in 2006.[129] They used commercial Brij surfactants with the formula $C_nH_{2n+1}(EO)_x$ (EO = ethyleneoxy). Although highly ordered mesophases were achieved using Brij surfactants as the soft templates and phenolic resin as the carbon source, the carbonized materials did not have any mesoporous structure, probably because of the high carbon yield of the templating surfactants containing alkyl chains. Therefore, the complete decomposition of the templates with the lowest possible carbon yield is highly desirable in the synthesis of mesoporous carbon material using soft templates. Ideal templates are amphiphilic molecules whose pyrolyzed products are gaseous. Although successful in the synthesis of metal oxides, the alkyl-chain-based surfactants are not likely to directly template the synthesis of mesoporous carbon because of the charcoal residue arising from pyrolysis of the alkyl chains. This residual carbon can occupy the spaces intended for the generation of mesopores. The alkyl-chain-based surfactants should be able to be used for the synthesis of mesoporous carbons as long as the surfactant templates can be removed by solvent extraction before carbonization.

3.2. *Carbon Nanostructures from the Self-Assembly of Block Copolymers*

Block copolymers are fascinating because of their rich phase behaviors and tunable properties that result from the self-assembly nature of various macromolecular architectures.[130–133] Nevertheless, most block copolymers are not suitable for the direct synthesis of carbon nanostructures. This inability is due to two factors: 1) the structural instability of nanostructures assembled by linear block copolymers under carbonization temperatures (> 450 °C), and 2) the low carbon yield of most block copolymers. To produce carbon nanostructures using block copolymers, a maximum charring contrast of the carbon-yielding to pore-forming moieties is highly desirable.

Several research efforts were made to synthesize mesoscopic carbon structures through the direct carbonization of self-assembled block copolymers. Notably, Matyjaszewski et al. attempted to synthesize carbon nanostructures by carbonization of a self-assembled structure derived from a triblock copolymer of acrylonitrile (AN) and *n*-butyl acrylate (BA), with an average composition $(AN)_{45}$-$(BA)_{530}$-$(AN)_{45}$.[11] The difference between the carbon-yielding (AN) to the pore-forming (BA) blocks in charring were maximized through thermal stabilization, a industrial method for manufacturing carbon fibers from polyacrylonitrile homopolymers.[11] The block copolymer was first cast into a very thin film, forming a well-defined nanostructure. A large ratio of BA to AN was used to ensure spherical domains of AN after microphase separation. The AN block was further cross-linked by oxidation, resulting in a ladder-like polymer which stabilized the nanostructure. The BA block was decomposed upon carbonization of the cross-linked AN block. Spherical carbon arrays were produced in the form of supported films (Figure 7).

An alternative approach was reported for the synthesis of spherical carbon nanoparticle films by stabilizing the micelle structures by cross-linking of shells, thus forming shell cross-linked knedels (SCKs).[134] A water-soluble diblock copolymer, poly(acrylic acid)-*b*-poly(acrylonitrile), or PAA-*b*-PAN, was prepared by the hydrolysis of the BA block of a diblock PBA-PAN copolymer. The PAA-*b*-PAN formed spherical micelles in water with PAN as the core and PAA as the shell. By cross-linking the PAA shell with the diamine 1,2-bis(2-aminoethoxy)ethane, the micelles were converted into covalently stabilized SCK nanoparticles. The carbon nanoparticles were produced by pyrolysis of the SCK nanoparticles (Figure 8). These research activities reveal that block copoly-

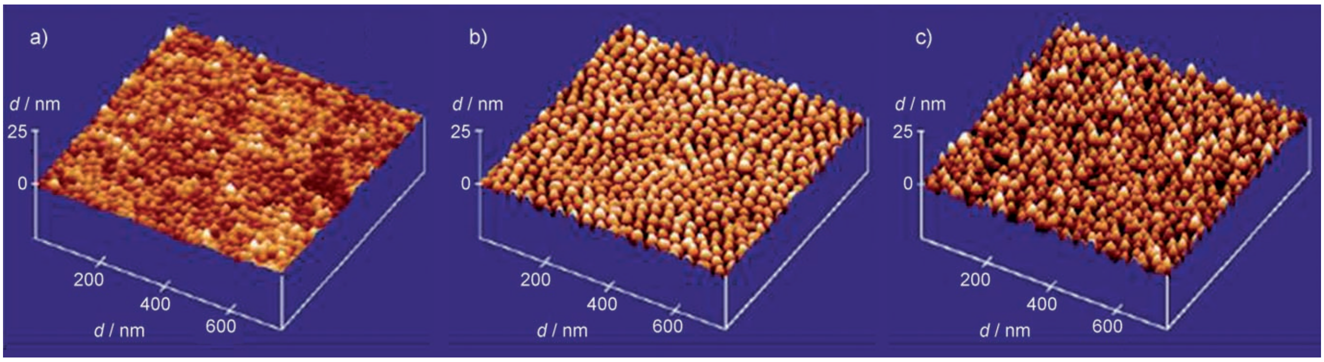

Figure 7. Tapping-mode atomic force microscopy (AFM) images illustrating the effect of thermal treatment on the evolution of nanoscale morphology of ultrathin ($d < 50$ nm) films of $(AN)_{45}$-$(BA)_{530}$-$(AN)_{45}$ block copolymer spin-coated onto a silicon wafer. The sample was a) vacuum annealed for 2 h at 220 °C to equilibrate the morphology, and b) sample heated under nitrogen at 20 °C min^{-1} from room temperature to 600 °C and c) to 1200 °C.[11]

mers with a carbon yielding block and a sacrificial block are alone able to produce carbon nanostructures by self-assembly. Unfortunately, no mesoporous carbon materials have been reported based on these block copolymer systems.

3.3. Ordered Mesoporous Carbon Materials from the Self-Assembly of Block Copolymers

Unlike the synthesis of oxide mesoporous materials, the synthesis of carbon material more closely resembles that of macromolecules. Up until the final carbonization reaction, the self-assembled nanostructures of carbon precursors are pure organic phases (more specifically, highly cross-linked organic polymers). The first report on the synthesis of highly ordered mesorporous carbon materials through soft templates appeared in 2004.[19]

3.3.1. The Polystyrene-b-poly(4-vinylpyridine) (PS-P4VP)/Resorcinol–Formaldehyde System

To our knowledge, the PS-P4VP/resorcinol–formaldehyde system was the first report of soft-template synthesis of highly ordered mesoporous carbon materials.[19] Hydrogen bonding was utilized to preferentially organize the resorcinol polymer precursor into the P4VP domain. Resorcinol was then polymerized with formaldehyde to form a carbon precursor with a high carbon yield. The carbonization yield was confirmed by thermogravimetric analysis (TGA). The four steps involved in the synthesis are summarized in Figure 9: the first step involves forming the macromolecular assembly of PS-P4VP through hydrogen bonding and film casting, the second step controlled solvent evaporation to direct the orientation of the microphase-separated nanostructure, the third polymerizing resorcinol localized in the P4VP domains through the gas–solid reaction with gaseous formaldehyde, and the fourth step carbonizing the polymer complex assembly to the corresponding porous carbon film.

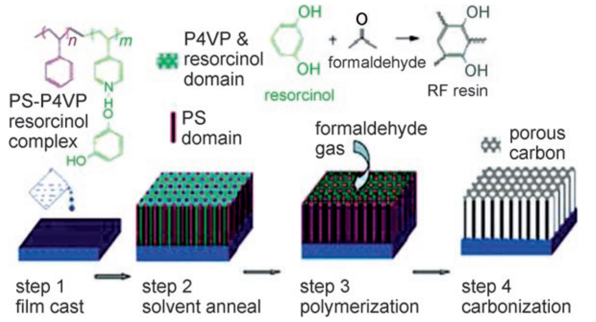

Figure 9. Schematic representation of the synthetic procedure used to prepare well-defined carbon nanostructures using the PS-P4VP/resorcinol–formaldehyde system.[19]

Because the carbon yield of organic compounds depends on their chemical and spatial environments, the pyrolysis of organic templates in nanocomposites usually has higher carbon yields than the pyrolysis of the same templates alone. Nanoconfinement may play a role in determining carbon yields during pyrolysis processes. For example, as discussed in Section 3.1, the alkyl-chain-based surfactants, such as CTAB and Brij series of surfactants, give a low carbon yield when pyrolyzed alone. However, if these surfactants are confined to the nanospace of a polymer complex, the corresponding carbon yield can increase significantly.[57,59] In the PS-P4VP/resorcinol–formaldehyde system, PS-P4VP contributed only 1.05 wt% of the carbon in the final film, as

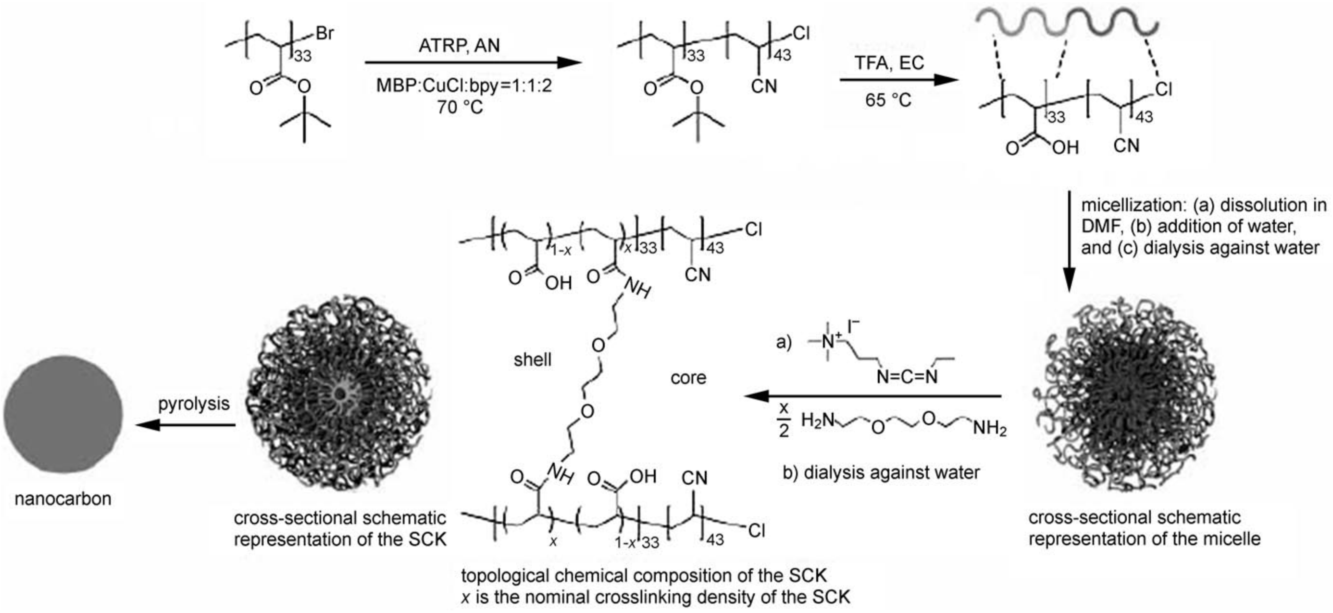

Figure 8. Illustration of the five-step synthesis of carbon nanoparticles from a block copolymer alone: 1) formation of a diblock copolymer PBA-*b*-PAN by atom-transfer radical polymerization (ATRP), 2) formation of the amphiphilic diblock copolymer PAA-*b*-PAN, 3) formation of polymer micelles by self-assembly, 4) formation of SCKs by cross-linking of the shell layer of polymer micelles, 5) formation of nanostructured carbon particles by pyrolysis. MBP = methyl 2-bromopropionate, bpy = 2,2′-bipyridine, TFA = trifluoroacetic acid.[134]

determined by TGA.[19] To obtain a stable structure that can survive the high temperature of carbonization, the mesophases usually have to be stabilized by cross-linking. However, cross-linking limits the mobility of the polymer chains, which is needed for the formation of mesophases by microphase separation. In the PS-P4VP/resorcinol–formaldehyde system, this dilemma was overcome using a multistep reaction that allows the fine adjustment of microphase separation prior to the polymerization of the carbon precursor. Highly ordered carbon film with pore diameters (33.7 ± 2.5) nm and wall thicknesses of (9.0 ± 1.1) nm was obtained after solvent annealing (Figure 10).

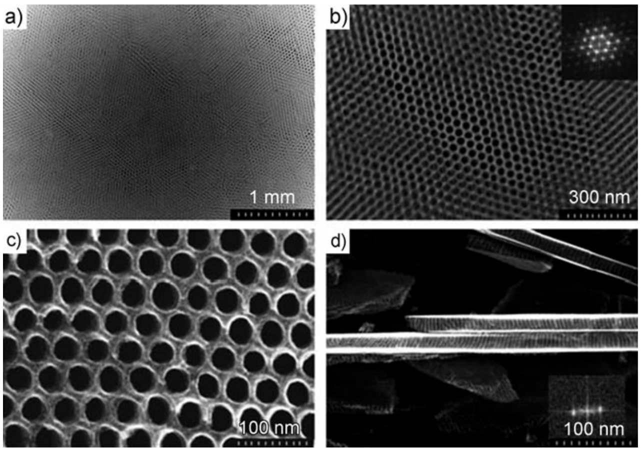

Figure 10. Electron-microscopy images of the carbon film obtained using the PS-P4VP/resorcinol–formaldehyde system. a) Z-contrast image of the large-scale homogeneous carbon film in a 4×3 μm area. b) Z-contrast image showing details of the highly ordered carbon structure. The inset shows a Fourier transform (FT) of the image shows a pattern with multiple reflections, which is characteristic of a highly ordered hexagonal array. c) High-resolution SEM image of the surface of the carbon film with uniform hexagonal-pore array. d) SEM image of the film cross-section, which has all-parallel straight channels perpendicular to the film surface. Inset: FT of the cross-section image. The FT pattern shows the reflections of the periodic parallel channels.[19]

The PS-P4VP/resorcinol–formaldehyde system established a set of principles for the soft-template synthesis of ordered mesoprorous carbon material. First, unlike carbon nanostructures made directly from block copolymers (see Section 3.2), which were employed as both sacrificial and carbon-yielding components, the PS-P4VP/resorcinol–formaldehyde system uses a binary molecular system, which consists of a block copolymer as the pore-forming and structure-directing reagent and a highly cross-linked carbon-yielding reagent as the carbon precursor. Second, the thermosetting property of the carbon precursor is one of the key factors in the survival of the mesostructures upon the high-temperature pyrolysis. Third, the interaction between template and carbon precursor molecules (e.g., hydrogen bonding) is the driving force for the self-assembly process.

Kosonen et al. have also developed a similar strategy toward the synthesis of porous polymeric nanostructures through self-assembly and pyrolysis.[135] Self-assembly was achieved by mixing uncured phenolic resins and PS-P4VP block copolymers. Again, hydrogen bonding is the driving force for this self-assembly process. The phenolic resins were successfully cured and the self-assembly was preserved. A hierarchical pore structure was observed for these materials, and the use of these porous materials as advanced sorbent materials has been demonstrated. Later, the same research group demonstrated the feasibility of using this synthetic method for synthesizing bulk materials with highly ordered pore structures.[136] The curing agent used for cross-linking in both cases is hexamethylenetetraamine, which exhibits some advantages in terms of cross-linking uniformity.

*3.3.2. The Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO)/Resorcinol–Formaldehyde System*

Although PS-P4VP is an excellent soft template for synthesizing mesoporous carbons, its limited commercial availability limits its wide use in the large scale synthesis of mesoporous carbon materials. This deficiency prompted our group[137] and other groups[20,119] to search for alternative and less expensive template systems. Although our group patented the synthesis of mesoporous carbons based on the triblock-copolymer soft templates of PEO-PPO-PEO (Pluronic surfactants) in 2004,[137] Tanaka et al. were the first to report the successful synthesis of ordered porous carbon films (named COU-1) using a Pluronic surfactant template (F127).[20] Resorcinol–formaldehyde copolymer and triethyl orthoacetate (EOA) were proposed as coprecursors for the carbon material. Although there was no evidence to support EOA contributing to the carbon content of the final porous carbon material, EOA was shown to enhance the periodicity of the porous carbon film. Hexagonal carbon nanostructures were reported with a *d* spacing ranging from 7.0 to 9.2 nm.

Tanaka et al. analyzed the elemental content of carbon films made at 400, 600, and 800 °C, showing the presence of C, H, and O.[20] If the films were carbonized at 400 °C, the weight percentage of C and H is 66.4 wt % and the oxygen content is calculated to be as high as 33.6 %, which is close to the composition of resorcinol/formaldehyde copolymers. Therefore, 400 °C is insufficient for carbonizing the resorcinol–formaldehyde resin, and the porous films made at 400 °C are most likely polymer films. It was subsequently confirmed by Zhao's group that mesoporous polymers instead of mesoporous carbon materials were produced at this low temperature.[138] The formation of mesopores results from pyrolysis of PEO-PPO-PEO templates.[129,138] The carbon content increased to 72.9 and 82.6 wt % at 600 and 800 °C, respectively. Thus, even at 800 °C, the carbon film still contained 17.4 wt % of oxygen. If the pyrolysis temperature was increased from 400 to 800 °C, the pore sizes dropped from 7.4 nm to 5.9 nm, and the surface area increased from 624 to 1354 $m^2 g^{-1}$. Micropores account for the increase in surface area when the carbonization temperature increases from 400 to 600 °C. Although the carbon films continued to lose weight up to 800 °C, the micropore volume and surface area of the resulting mesoporous carbon materials did not increase when they were heated above 600 °C. However, as can be seen in the field-emission electron micrograph (FE-SEM) images in Figure 11, the structure of the sample carbonized at 800 °C is inferior to that of the sample carbonized at 600 °C. Clearly, a more systematic investigation is needed to determine the formation mechanisms of these mesostructures.

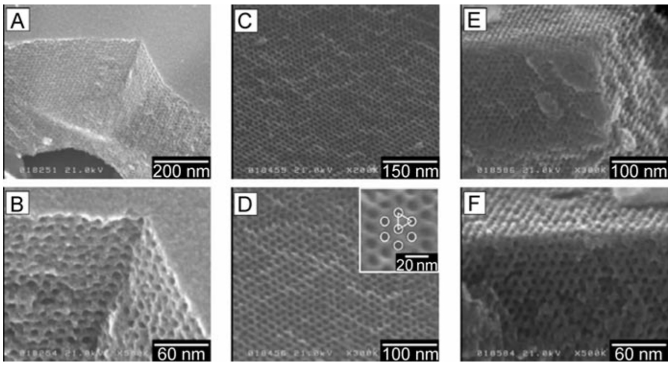

Figure 11. FE-SEM images of carbonized COU-1. The carbonization temperatures were: A, B) 400 °C, C, D) 600 °C, and E, F) 800 °C.[20]

*3.3.3. **The PEO-PPO-PEO/Resol System***

Major advances have been made by Zhao's group in the soft-template synthesis of mesoporous carbons with PEO-PPO-PEO templates. They reported the self-assembly of PEO-PPO-PEO and resol mixtures and successful removal of the template (F127, F108, and P123) at a series of temperatures to produce mesoporous polymers and carbon materials.[119,129,138,139] Resol is a low-molecular-weight phenolic resin produced by reacting phenol and formaldehyde in a mole ratio of 1:1 with a base catalyst. After neutralization with an acid, the multiple hydroxy groups of resol provide hydrogen bonding with the PEO moieties of the template. As a result of microphase separation, highly ordered mesoporous carbon materials were obtained in the form of thin films and particles after the pyrolysis of the self-assembled organic composites. In Figure 12, a hypothetic mechanism is shown for the formation of FDU-14, a self-assembled triblock copolymer and resol composite.

In a recent publication, Zhao et al. summarized the five steps involved in the synthesis of ordered mesoporous carbon using resol as carbon precursor (Figure 13):[129] 1) the synthesis of resol, 2) formation of a surfactant/resol complex and assembly of mesostructures, 3) curing of resol by thermopolymerization, 4) removal of the template, and 5) carbonization. Three factors that affect the morphologies of the final mesostructures are: 1) the volume ratio of PEO to PPO in block polymer surfactants, 2) the mixing ratio of carbon precursors to surfactants, and 3) the carbonization conditions. By varying the mixing ratios of resols to surfactants and the use of surfactants with different ratios of PEO to PPO, highly ordered carbons were successfully synthesized with symmetries of two-dimensional hexagonal *p6m*, three-dimensional bicontinuous $Ia\bar{3}d$, and body-centered cubic $Im\bar{3}m$ symmetries (Figure 14). Polymer composites with a lamellar structure were also synthesized, but the structure collapsed after the removal of the template. Apart from the removal of templates by thermal decomposition under an inert gas, Zhao et al.also reported the solvent extraction of surfactants by 48 wt % sulfuric acid, which resulted in a thick and condensed wall of porous carbons. It should be noted that the symmetries of the carbon structures prepared from the same compositions changed when a low percentage of oxygen was used for assisting the removal of templates. The presence of 2.4 % of oxygen by volume in the carbonization atmosphere changed

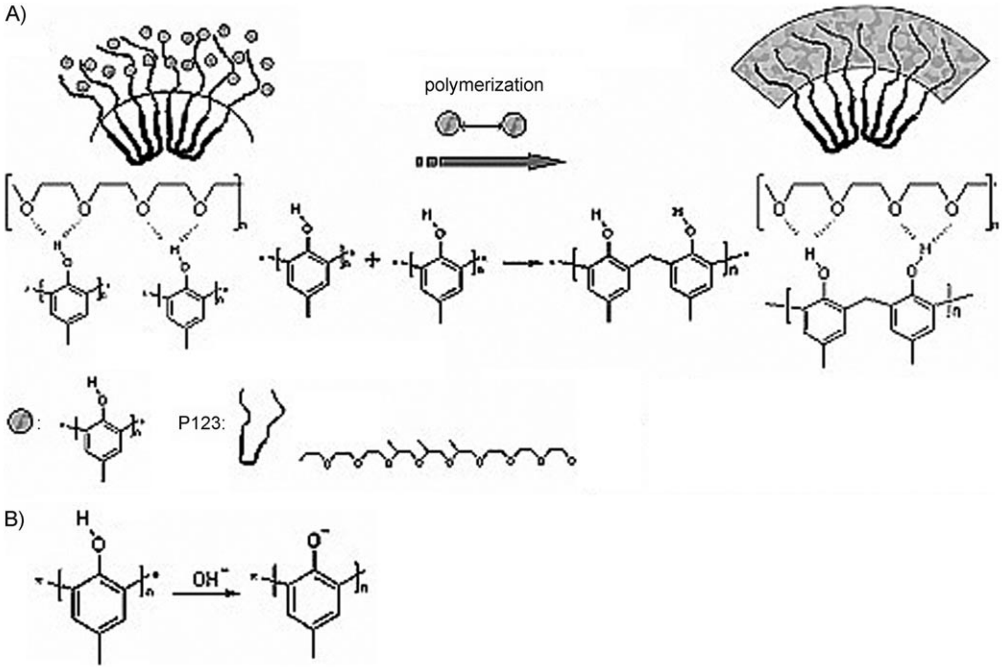

Figure 12. A) Possible mechanism for FDU-14 formation. B) Resol anions formed in strong basic media.[119]

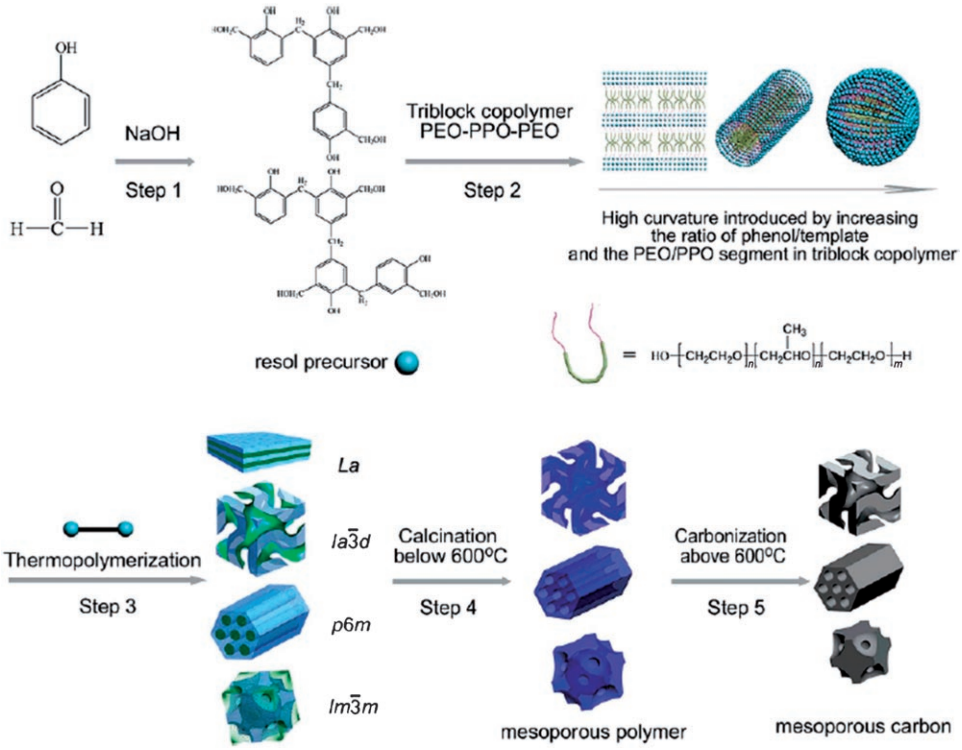

Figure 13. Preparation of ordered mesoporous polymer resins and carbon frameworks with resol as carbon precursor.[129]

the hexagonal structure of FDU-15 to a cubic structure of FDU-16.

3.3.4. *The PEO-PPO-PEO/Phenol–Formaldehyde Resin/Silica System*

Lin and his coworkers[140] were the first to explore the soft cosynthesis (coassembly) of mesoporous carbon/silica composites using F127 templates. The carbon precursor used in this approach was a phenol–formaldehyde (PF) resin with a molecular weight M_w of ca. 96000. The cross-linking of the PF resin was achieved by high-temperature treatment before carbonization. Mesoporous carbon/silica composites with highly ordered mesostructures were also obtained by carbonization of the corresponding F127/resol/silica mesoscopic composites.[141] Zhao and his coworkers[141] conducted a systematic investigation concerning the effect of various synthetic conditions on the formation of mesophases. Highly ordered composite films were obtained by evaporation-induced self-assembly (EISA).[142] These binary systems are interesting in terms of their multiple functionalities.

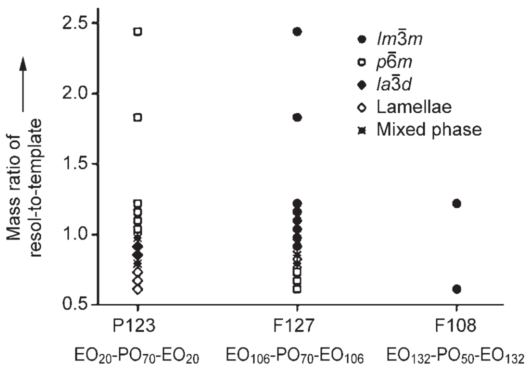

Figure 14. Symmetries of freshly synthesized mesostructured materials depending on the resol/surfactant and the PEO-PPO-PEO ratio. [129]

3.3.5. *The PEO-PPO-PEO/Phloroglucinol/Formaldehyde System*

As pointed out in Section 3.3.1, hydrogen bonding between soft templates and carbon precursors is the key to the successful self-assembly synthesis of highly ordered mesoporous carbon materials in the PS-P4VP/resorcinol–formaldehyde system. This consideration led us to investigate alternative carbon precursors with enhanced hydrogen-bonding capabilities in the synthesis of mesoporous carbon materials using F127 as a template. A comparative experiment was conducted using three phenolic resin monomers: phenol, resorcinol (1,3-dihydroxybenzene), and phloroglucinol (1,3,5-trihydroxybenzene). These three monomers can form single, double, and triple hydrogen bonds to the PEO chains of F127 and thereby allow the study of the hydrogen-bonding effect on self-assembly.[21] The pyrolysis of the polymer made from phenol, a monodentate hydrogen-bonding reagent, yielded a carbon material with a very low surface area. The use of resorcinol, a bidentate hydrogen-bonding reagent as the carbon precursor yielded a carbon material with a considerably increased surface area but a poor mesostructure. Highly ordered carbon mesostructures were produced when phloroglucinol, a tridentate hydrogen-bonding reagent, was employed as the carbon precursor.

A possible mechanism that leads to these highly ordered carbon mesostructures is given in Figure 15. All three hydroxy groups of phloroglucinol interact with the PEO moieties of the block copolymers, giving rise to the cross-linking of the intra- and interpolymer chains by hydrogen bonding. The interpolymer-chain hydrogen bonding "cross-links" the triblock copolymer templates and thereby stabilize the micelle structures in which phloroglucinol was enriched inside the PEO domains. The polymerization of phloroglucinol and formaldehyde was then localized in the PEO domains. The polymerization of phloroglucinol and formaldehyde caused the self-assembled polymer composite to separate from the

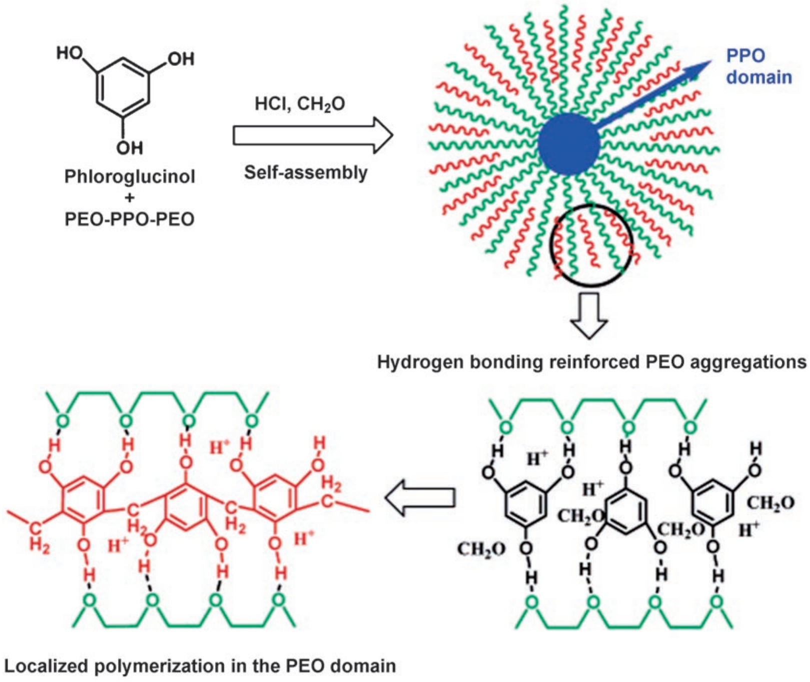

Figure 15. Schematic illustration of the localized polymerization of phloroglucinol and formaldehyde in the synthesis of mesoporous carbon materials with the template F127.[21]

solvent as a polymer phase. The composite was further processed as mesoporous carbon material in the form of film, monolith, fiber, and particles.

With this method, the large-scale synthesis of ordered mesoporous carbon material is viable. The periodicity and pore-size distribution of the resulting carbon materials depend on the processing conditions of the phase-segregated polymer phase. If the polymer is cured too fast and microphase separation has not reached its equilibrium, a wormy structure is obtained. If directional forces are applied to the polymer, microphase separation could be facilitated, and highly ordered structures are obtained by controlled solvent evaporation or a shear force. A hexagonal structure was reported and confirmed by the corresponding XRD pattern. The tuning of pore sizes in the range of 5 to 10 nm was also demonstrated. Figure 16 shows the morphologies of the porous materials that have been made from resorcinol and phloroglucinol in the forms of monolith, film, and fiber.

3.3.6. *The PS-P4VP/Carbohydrate System in Confined Space*

The multiple hydrogen-bonding capabilities of carbohydrates make them good candidates for the synthesis of ordered mesoporous carbon by the self-assembly of block copolymers driven by hydrogen bonding. Fan et al. used PS-P4VP and PS-P2VP as templates, and turanose, raffinose, and glucose as carbon precursors in the confined space of porous anodic aluminum oxide (AAO).[143] The carbohydrates interacted with PVP moieties of the diblock copolymers over multiple hydrogen bonds and thus were enriched in the PVP domains after microphase separation. The PS domains decomposed during carbonization of the carbohydrates at 460 °C, which is a relatively low temperature for carbonization. The elemental composition of the resulting carbons was not provided. After release from the AAO hard template by chemical etching, porous carbon nanotubes were obtained. The tubular structure was given by the AAO channels, and the mesopores on the wall of the carbon nanotubes were attributed to the decomposition of the block copolymers. The hexagonal symmetry of the mesopores was shown by a TEM image of the carbon nanotubes. A disordered structure was formed when PS-P2VP was used as the template. A diameter of 200 nm for the carbon nanotubes was reported, which is consistent with the channel size of the AAO templates. The mesopore diameter was around 16 nm, and the resulting carbon has a surface area of 130 $m^2 g^{-1}$ (Figures 17 and 18).

3.4. *Mesoporous Carbon Films*

Over the last two decades, the formation of block copolymer thin films by self-assembly has been intensively studied. It is not a coincidence that ordered mesoporous carbons initially synthesized with soft templates are in the form of thin films.[19–21,129,138] The self-assembly of block copolymers can be promoted or refined by a number of directional forces originating from shearing,[144,145] temperature gradients,[146] concentration gradients,[147] crystallization,[148] electric fields,[133,149] graphoepitaxy,[150,151] and controlled interfacial interactions.[152] In the following sections, we briefly review the techniques that have been used for the synthesis of highly ordered mesoporous carbon films.

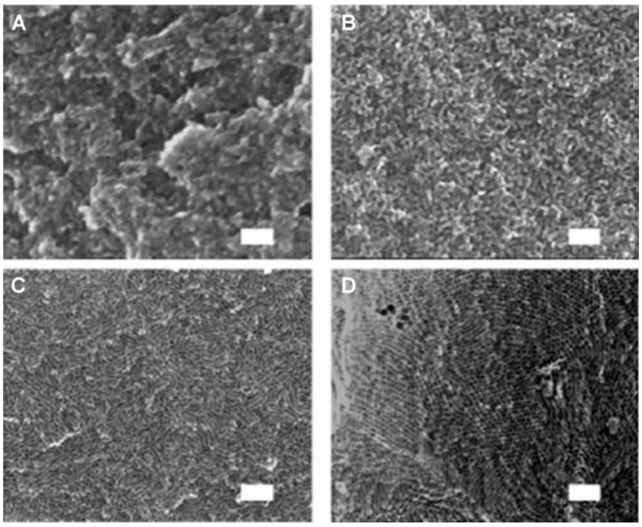

Figure 16. High-resolution SEM images of carbon materials synthesized from resorcinol and phloroglucinol: A) monolith from resorcinol, B) monolith from phloroglucinol, C) film from phloroglucinol, and D) fiber from phloroglucinol. The scale bars are all 100 nm.[21]

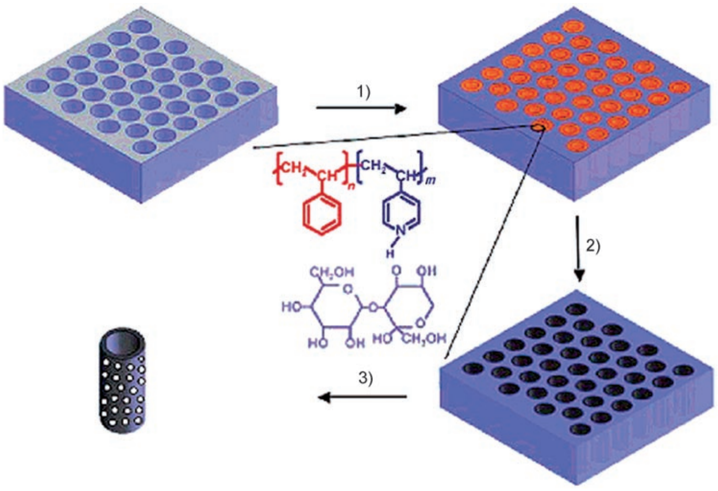

Figure 17. Schematic illustration of the synthesis of nanoporous carbon nanotubes by AAO-confined hydrogen-bonding self-assembly. 1) AAO loading, 2) carbonization, and 3) removal from AAO.[143]

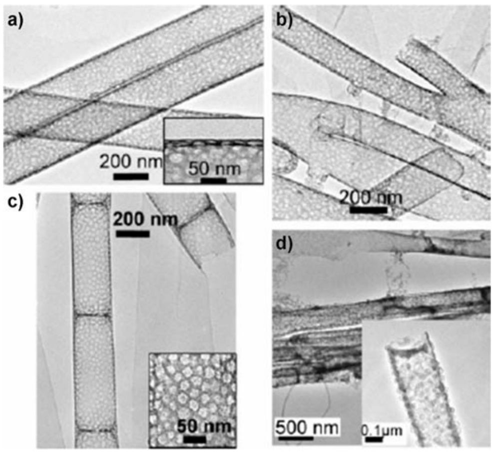

Figure 18. TEM images of nanoporous carbon nanotubes. a) The same sample as in Figure 1. Inset: Magnified image over a nanotube wall, showing the nanoporous feature within the tube wall. b) Branched nanotubes. c) Bamboo-like nanotubes. Inset: Hexagonal arrays of pores on the tube wall. d) Carbon nanotubes prepared using PS-P2VP. Inset: High-resolution TEM image of the same sample.[143]

3.4.1. *Solvent Annealing in the Synthesis of Oriented Mesoporous Carbon Film*

Solvent annealing is a thin-film technique that has been developed for the synthesis of highly ordered block copolymer films with oriented nanostructures. The most critical aspect of solvent annealing is the utilization of a strong directional force parallel to the direction of the solvent concentration gradient to drive the self-assembly of block copolymers in a particular direction. As depicted in Figure 19, solvent evaporation induces the ordering at the surface of the thin film.[147] With the further evaporation of the solvent, the ordering front propagates through the entire thickness of the thin film. The solvent concentration is lowest at the surface, and the block copolymer undergoes an ordering or microphase separation. A gradient in the concentration of the solvent, as a function of depth *r*, is established normal to the film surface. As the solvent evaporates, an ordering front propagates through the film, similar to zone refinement, producing a highly ordered and oriented array of cylindrical microdomains of the film.[147] The solvent plays two roles in solvent annealing: one is to provide directional force for the alignment of the microphase-separated domains, and the other is to impart mobility to the polymer chains.

An elegant example of synthetic control of highly ordered block copolymer films by solvent evaporation is the orientation switching of the nanodomains of the supramolecular assembly (SMA) of PS-P4VP and 2-[(4-hydroxyphenyl)azo]benzoic acid (HABA) by using different solvents.[153] A hexagonal phase of the SMA parallel to the substrate formed in a chloroform solution, whereas a hexagonal phase of the SMA perpendicular to the substrate formed in a 1,4-dioxane solution. The orientations can be switched back and forth by annealing the film in different solvents. Hydrogen-bonding capabilities of the solvents account for the alignment of nanodomains in a certain direction (Figure 20).

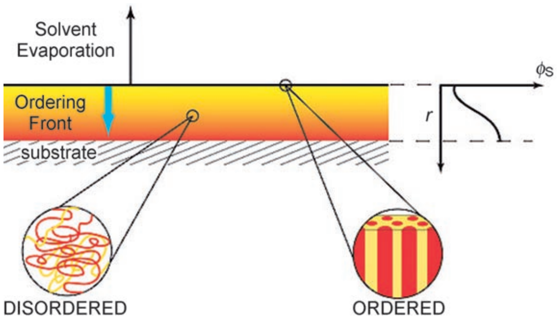

Figure 19. Solvent annealing in a thin block copolymer film, and the gradient of solvent concentration ϕ_S as a function of depth *r*.[147]

Our group was the first to utilize the solvent-annealing strategy for the soft-template synthesis of oriented mesoporous carbon films.[19] As shown in Figure 10, the channel-like nanopores are aligned normal to the substrate surface with a highly ordered, hexagonal symmetry. The solvent annealing of the preorganized PS-P4VP/resorcinol complex by the vapor of the benzene/dimethylformamide mixture aligned the microphase separation of the carbon precursor. It is worth noting that the mobility of the PS-P4VP/resorcinol complex is the key factor in achieving the alignment of the mesophase.

3.4.2. *EISA for Self-Assembly of Ordered Mesoporous Carbon Films and Spherical Carbon Particles*

Evaporation-induced self-assembly (EISA) is a robust and versatile method for the synthesis of ordered mesoporous films and particles, in particular for oxides. As ordered mesoporous oxides are beyond the topic of this review, details

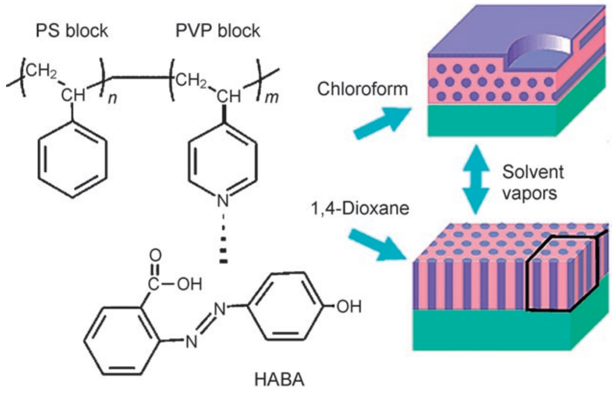

Figure 20. Switching of SMA orientations resulting from changing the solvent for annealing.[153]

of EISA are available in a review by Brinker and co-workers.[142] EISA was used in the synthesis of highly ordered mesoporous carbon by Zhao et al.[129,138] Lu and co-workers[154] have utilized an EISA-based aerosol process to synthesize the multicomponent assembly of silica and carbon materials using the F127 template. Mesoporous composite particles successfully obtained through this aerosol process were tested as carbon electrodes for fuel-cell applications. The EISA process utilizes a concentration gradient to induce the ordering of precursors around templates, which, to some extent, resembles the solvent-annealing process. The key difference lies in the reversibility of the initial self-assembly process. The EISA process during the casting of the film is irreversible, whereas a reversible process is used in solvent annealing. Precursor molecules are cross-linked concomitantly with solvent evaporation in the EISA process. Therefore, the mobility of the precursors is lost after the evaporation of the solvents, and there is no mechanism to remove defects generated during the EISA process. However, the thin-film synthesis based on the solvent annealing process decouples the self-assembly process from that of cross-linking, thereby allowing the refinement of self-assembled structures.

4. *Surface Modification of Mesoporous Carbon Materials*

As discussed in the previous sections, mesoporous carbon materials with a variety of structures have been synthesized using different inorganic or organic templates, carbon precursors, and synthetic strategies. The applications of these highly ordered mesoporous carbon materials in separation, catalysis, and electronics require surface modification. Nevertheless, the chemical modification of carbon surface is difficult, owing to the low reactivity of carbon. One technique to functionalize the carbon surface involves oxidizing it with acids or ozone, through which oxygenated functionalities, such as carboxylic acids, esters, or quinones are generated. The subsequent reaction of thionyl chloride with carboxy groups makes it possible to further refine the surface properties.[155] However, the drawbacks of this method lie in the low bonding densities, and damage to the carbon surface or pore structure during oxidative treatment.[156,157]

Ryoo and co-workers[158,159] functionalized ordered mesoporous carbon materials by a controlled impregnation with organic monomers. The monomers were subsequently converted into cross-linked polymers. Functional groups can be introduced through the choice of organic monomers. The resulting structures have the bifunctionality of mesoporous carbons (electrical conductivity) and of organic polymers. Carbon structures are retained during polymerization, which is a key advantage of this functionalization method.

Our group functionalized ordered mesoporous carbon materials by using a solvent-free technique,[160–163] in which diazonium compounds were generated in situ and reacted with carbon surfaces.[46,47] Aryl groups substituted at the 4-poisiton (ArR, R = Cl, CO_2R', alkyl) were covalently grafted onto the surface of ordered mesoporous carbon materials, which were synthesized using ordered silica SBA-15 or MCM-48 as templates. The presence of these functional groups on the modified carbons was confirmed with infrared spectroscopy, thermogravimetric analysis, electron microscopy, and nitrogen adsorption. A high grafting density of 0.9–1.5 $\mu mol\,m^{-2}$ was accomplished on these ordered porous carbons. We compared the surface functionalization process on different ordered mesoporous carbon materials, and found that the density of grafted functional groups was related to the specific surface area arising primarily from mesopores.[46] The covalently bonded functional groups considerably decreased the primary mesopore width by 1–1.5 nm, though both mesostructure and unit parameter of ordered mesoporous carbon material were retained. For carbon materials templated with MCM-48 and SBA-15, the functionalization process provided carbons with micropores, whereas mixed micropores and small mesopores were observed for the CMK-5 carbon material after modification. The BET surface area and pore volume were also reduced because of functionalization. Thus, surface functionalization can also be used as a technique to manipulate the pore size for ordered mesoporous carbons.

Li et al. observed the unsymmetrical degradation of XRD patterns for carbon materials templated with the MCM-48 silica after functionalization, which might be caused by the preferred adsorption/reaction in pores of C48. Figure 21 shows thermogravimetric profiles in nitrogen for modified and unmodified ordered carbon templated with the SBA-15 silica using mesophase pitch as the precursor. The weight loss in the temperature range of 200–600 °C corresponds to the loss of bonded functional groups. The changes in nitrogen adsorption isotherms at 77 K and the shrinkage in pore-size distribution are shown in Figure 22. Wang, Feng et al. recently functionalized the ordered mesoporous carbon CMK-5 with sulfonic acid-containing aryl groups via reduction of diazonium salt. The resulting material acts as a stable and highly active protonic acid catalyst for reactions such as esterification and condensation.[164]

In addition to grafting organic functional groups, fluorination is another important strategy to modify graphite, activated carbon, and carbon nanotubes for their application as a lubricant or as an electrode in lithium batteries.[165] Our

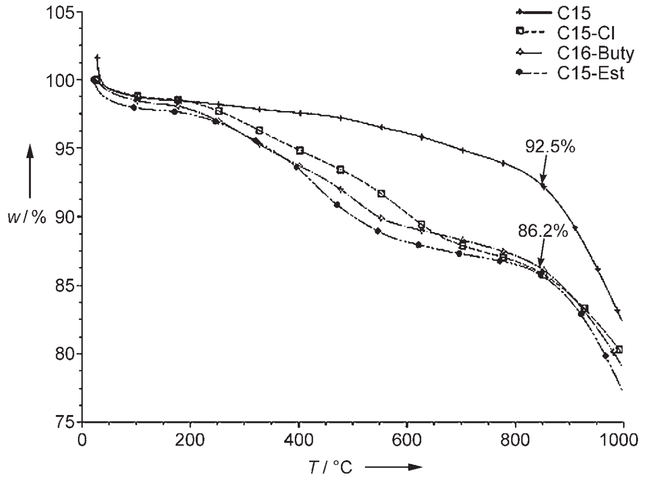

Figure 21. Thermogravimetric profiles in nitrogen for the unmodified carbon material C15 and the modified samples containing Cl (C15-Cl), ester (C15-Est) , and alkyl groups (C15-Buty).[47]

group recently reported the fluorination and concomitant structural change of a highly ordered mesoporous carbon material templated with MCM-48 silica. This ordered mesoporous carbon was treated in diluted fluorine gas (4 vol% in helium) for 4 days at room temperature or moderately elevated temperatures. Gradual structure degradation was observed, and the color of the fluorinated carbon material changed from black to brown to white as the reaction temperature increased. The ordered mesoporous structure was retained for the carbon material fluorinated at room temperature, though apparent structural expansion was observed. On the other hand, the sample fluorinated at higher temperature lost its ordered pore structure. The structural expansion or degradation of ordered carbon materials could be ascribed to the strong reactivity of fluorine, which reacts with both saturated or unsaturated carbon materials.[166] In Figure 23, a fluorinated mesoporous carbon with an ordered structure is shown.

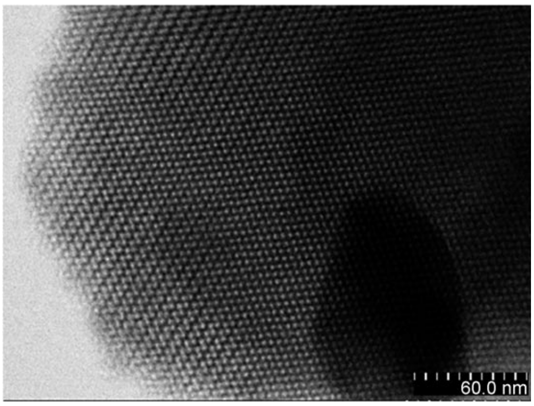

Figure 23. TEM image of a fluorinated mesoporous carbon material prepared at room temperature. The ordered pore structure was retained.[165]

Another interesting advance in the functionalization of mesoporous carbons is the development of superhydrophobic material based on ordered mesoporous carbon materials.[167] Superhydrophobic materials generally have a water contact angle larger than 150° and have great application potentials.[168–170] In addition to a hydrophobic surface, the contact area between water and the surface should be minimized, whereas the contact area between water and air should be maximized, and that the air trapped in the trough area contributes greatly to the increase in hydrophobicity.[170] Accordingly, superhydrophobic materials based on the rough surfaces of silica and other nanostructured materials have been accomplished by bonding fluorine-rich organic groups to such surfaces.

Jiang et al. reported that both superhydrophobicity and hydrophilicity can be achieved on anisotropically aligned carbon nanotube (ACNT) films by varying the structural parameters without altering the chemical composition. This effect was attributed to the coexistence of the horizontal and vertical ACNT arrays.[169] More recently, Xiao, Jiang et al. reported that superhydrophobicity can be achieved for

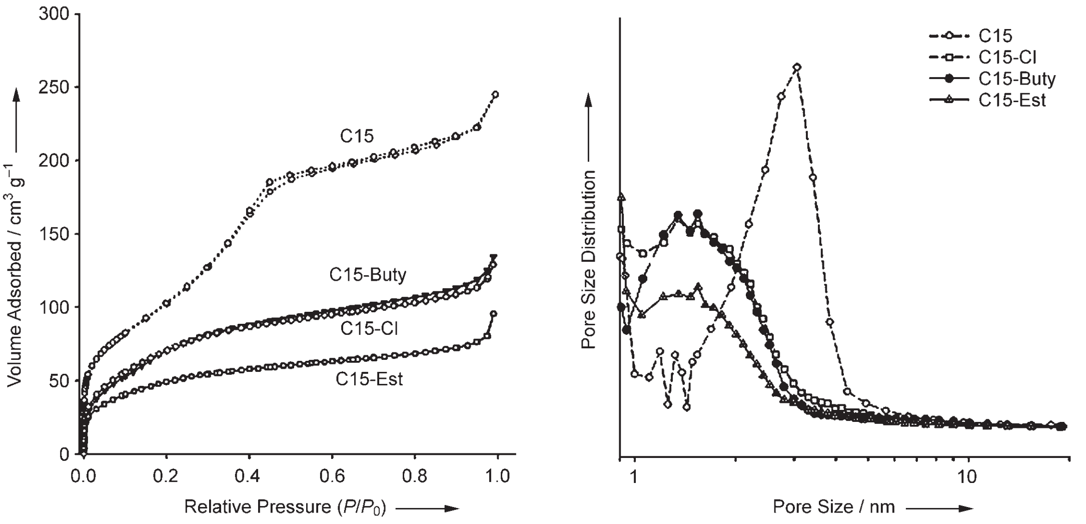

Figure 22. The change in nitrogen adsorption isotherms and the corresponding pore-size distributions arising from surface functionalization.[47]

ordered mesoporous carbon materials by treating the ordered mesoporous carbon material with concentrated nitric acid and sulfuric acid, followed by modification with fluoroalkylsilane $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$ (FAS-17).[167] The modified carbon material exhibited a water contact angle of 150.2 °C, and the ordered mesostructure was retained. In Figure 24 photographs are shown of a water droplet on the modified and unmodified ordered mesoporous carbon material. The surface roughness of ordered mesoporous carbon is essential for the superhydrophobic effect.[167]

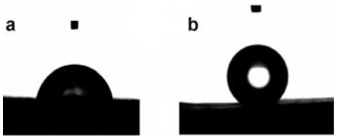

Figure 24. Photographs of a water droplet on the mesoporous carbon monolith a) before and b) after modification with fluoroalkylsilane FAS-17.[167]

Electrochemically assisted modification of carbon material have been studied over a decade ago based on nonporous carbon materials of both glassy carbon and graphite.[171–176] The first application of electrochemically modified porous carbon was reported by Porter's group in 2001.[176] Porous graphitized carbon (PGC) was packed as a column, which was then used as the working electrode of electrochemically modulated liquid chromatography apparatus. Diazonium salts in acetonitrile were percolated through the column while a negative voltage was applied to reduce the diazonium salts on the carbon surface. The electrochemical reduction of diazonium salts produced radicals that were attached to the carbon surface through carbon–carbon bond linkage. The covalently modified PGC particles were employed as reverse-phase media for chromatographic separations. Liang et al. modified the porous carbon rods by using a diazonium-based ionic liquid [*p*-butylbenzenediazonium][bis(trifluoromethanesulfonyl)amide].[177] The ionic liquid was used as both reactant and solvent. The functionalization densities of 3.38 μmol m^{-2} and 6.07 μmol m^{-2} were achieved on the carbon surface through chemical and electrochemical reactions, respectively.

5. Summary and Outlook

In this review, an overview was provided of the template-assisted synthesis and chemical modification of mesoporous carbon materials. Since the inception of the hard-template synthesis of PGC in 1980, this approach has proven to be the only method that can be used for the production of spherical mesorporous carbon particles. The success of the hard-template synthesis lies in its simplicity and fidelity in replicating the structures of templates. The technique has recently enjoyed an exciting resurgence as a "nanocasting" method by interfacing it with newly developed nanostructured templates.[23,29] The key to this resurgence is related to the availability of a large pool of hard templates with periodic porous structures generated by sol–gel chemistry and soft-template synthesis. Given the numerous demonstrations of replicating templates with various structures, pore sizes, and symmetries, the hard-template synthesis is regarded as a hallmark for the controlled synthesis of mesoporus carbon materials. This hard-replication process is, however, not thermodynamically driven. Few chemical interactions between hard templates and carbon precursors occur during the replication process. Accordingly, the hard-template synthesis suffers from its intrinsic limitations in the sacrificial use of hard templates, insufficient stabilities of replicated mesostructures, and difficulties of synthesis of large film and monolithic structures.

Recent developments in the soft-template synthesis of mesoporous carbon materials create new possibilities in overcoming the intrinsic limitations imposed by the hard-template method.[19,21,119,129,138,139,178] The soft-template method relies on supramolecular assemblies, which template the polymerization processes of carbon polymeric precursors. The synthesis is thermodynamically driven, and therefore depends on the chemical interactions between supramolecular templates and carbon precursors. Although extensive methods of soft-template synthesis have been developed to control mesoscopic architectures and surface properties for silica and metal oxide materials, similar methodologies for mesoporous carbon materials are still in their early stages of development. To date, only hydrogen-bonding interactions between soft templates and carbon precursors have been exploited for the production of mesoporous carbon materials. Other chemical interactions, such as Coulombic[179] and/or dative forces,[180] have not been fully explored. Numerous opportunities exist for future research in this area. With the emergence of diverse synthetic pathways, new pairs of templates and precursors will be explored, and the use of these non-hydrogen-bonding interactions to organize the self-assembly of the carbon precursors is only a matter of time.

Currently, block copolymer templates have dominated the soft-template synthesis of mesoporous carbons because of their facile processing characteristics. However, there is a threshold of the pore size that block copolymers can template (minimum size ca. 3 nm). Small amphiphilic template molecules, such as CTAB and Brij surfactants, could fill the current gap in mesopore sizes from 2 nm to 3 nm. Unfortunately, all reported attempts to use small surfactant molecules in the synthesis of mesoporous carbon have met with limited success. Pursuing various driving forces for self-assembly holds promise for the bridging of the pore size range from 2 nm to 3 nm and for the diversification of the soft-template synthesis of mesoporous carbon materials as well.

Synthesis of bimodal porous carbon material that has both mesoporosity and macroporosity will be another exciting research area owing to the application potential of these bimodal porous materials in catalysis, separations, and energy storage and conversion. The macroporosity of bimodal porous carbon materials adds structural complexity to the mesoporous carbon materials. The combination of hard and soft templates will be a viable approach.[143,181] Microphase separation in tandem with spinodal decomposition will be another possible approach to the soft-template synthesis of such hierarchically porous carbon materials.

The control of interfacial properties through tunable surface functionalities is essential in the development of functional mesoporous carbon sorbents. The chemical modification of the novel carbon structures has already been explored with applications in mind, revealing that the chemical inertness of carbon materials imposes some difficulties in the covalent attachment of functional groups to them. Creating functionalities on carbon surfaces through oxidation requires extremely harsh chemical treatments, which can damage the integrity of both chemical and porous structures. The functionalization of carbon surfaces by either chemical or electrochemical reduction of adsorbed diazonium salts presents an alternative approach. This approach confers a high coverage of functional groups on carbon surfaces. Electrochemical reduction of the diazonium salt is appealing because of the high functionalization yield. Pinhole-free monolayer coverage of functional groups on carbon surfaces has been demonstrated.

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