POROUS CARBON MATERIALS FOR CLEAN AND SUSTAINABLE ENERGY

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ABSTRACT

Carbon materials mostly involved in new alternative clean and sustainable energy technologies have been playing more and more significant role in energy storage and conversion systems, especially for the carbon porous materials, because carbon porous materials with structures can provide large surface areas for reaction, interfacial transport, or dispersion of active sites at different length scales of pores and shorten diffusion paths or reduce diffusion effect. Therefore, the soft, hard templated and hierarchically ordered strategies employed to fabricate porous carbon materials are marked along with the relevant advantages and disadvantages aim to provide the vital information about the growing field for future energy to minimize the potential environmental risks. Carbon porous materials with attractive structures as ideal candidates for the versatility and feasibility of application to energy storage and conversion should not only be realized, but also much effort has to be devoted to systematic studies on the relationship between physicochemical properties of these materials and their performances in energy conversion and storage to more efficiently stimulate further developments in this fascinating area, alongside eco-technologies that will ensure minimal environmental impact.

Contribution/Originality: This study contributes in the existing literature of carbon porous materials with attractive structures ordered by various techniques for future eco energy.

1. INTRODUCTION

Technologies in an urgent attempt to alleviate fossil fuel usage and CO_2 emissions, fuels, heat or electricity must be economic, energetically efficient, environmentally friendly and not competitive with food production due to unsustain of the current fossil fuel usage and its successive greenhouse gas production. Carbon materials, especially for porous carbon materials and nanostructured materials, with hierarchically ordered porosity and structures have been heavily involved in newly developed energy storage and conversion systems. With meticulous design and ingenious hierarchical structure of porosities by mimic nature, hierarchically structured porous carbon materials can provide large surface areas for reaction, interfacial transport, and dispersion of active sites at different length scales of pores to shorten the diffusion lengths as well as to increase the diffusion rate. It can be also widely used in in energy storage devices such as supercapacitor and lithium ion battery.

To date, several researches on state-of-the-art carbons and porous carbon materials with well-controlled porosity including micropore, mesopore, and macropore, have wide variety of applications in environmental remediation (separation science and water purification), heterogeneous catalyst supports, sensing devices, and the developing areas of electrochemical energy conversion and storage devices.

Moreover, a tremendous wave of interest in elucidating the relationship between performance and their physicochemical properties including surface area, porosity, surface property, electrical conductivity, and chemical

stability has been illustrated. It shows that the porous structure of porous carbon materials can play a crucial role in determining and optimizing the performance in the abovementioned applications. It is also noteworthy that the required disruptive improvement in energy and environmental science has motivated the design of the structure, porous architecture and surface functionality/polarity of porous carbon materials through the aid of suitable templates (soft-templates and hard-templates) and pore surface modification.

2. STRATEGIES FOR ORDERED POROUS CARBONS

2.1. Soft Templated Porous Carbons

The porous material can be defined as a solid matrix permeated by an interconnected network of pores such as cavities and channels being deeper than their width. Three classes of porous materials are defined according to their pore sizes, namely microporous (pore size <2 nm), mesoporous (2 nm < pore size <50 nm), and macroporous (pore size >50 nm) [1]. Porous carbon materials of designed porosities and tunable properties, with high surface area, tunable porosity and surface property, good electrical conductivity, high chemical stability, have attracted intense interests in separation science and water purification, stationary phase materials, heterogeneous catalyst supports, sensing devices, and energy generation and storage applications (fuel cells, batteries, solar cells, and supercapacitors) [2-6].

According to the requirements of disruptive improvement in energy and environmental science, the design of the pore architecture and surface functionality/polarity of porous carbon materials is therefore proposed with the aid of suitable templates (soft-templates, hard-templates), along with the pore surface modification.

Templating is one of the most frequently used methods for synthesis of uniformly and hierarchically porous carbon materials. In the templating synthesis of materials, the template plays the most important role in controlling the types of porous networks as well as the sizes and shapes of pores [7, 8]. The templates in the broader sense can be classified into two categories. The first one is the common "soft-template" which the organic molecules or supramolecular aggregates are used as soft-templates to impart structural features to the porous carbons. The second type of templates uses porous solids as templates (hard templates) to structure the porous carbon, often being inverse replicas of the template. The soft and hard templates can come in a variety of forms including organic molecules, ionic surfactants, block copolymers, nanoparticles, colloids, colloidal crystals, and even biological materials.

Generally, the use of ordered mesoporous silicates as the hard template makes the procedures complicate, time-consuming, and unsuitable for mass production. Moreover, a toxic chemical of hydrofluoric acid is needed for the removal of silicates.

Therefore, soft templating techniques using surfactants and biomolecules as the templates have been developed for the production of ordered mesoporous carbon materials. It is well known that one of the major advantages of soft templating method is the use of all commercially available and low-cost raw materials to prepare the highly ordered mesoporous carbon materials [7, 9, 10].

Unfortunately, some mesoporous carbon materials cannot offer any macropore character (pore size >50 nm), and soft templating process is a versatile method and the selection of soft templates is often flexible, but is also complicated and unpredictable. The obtained mesostructures from the self-assembly of soft templates is highly dependent on many parameters such as temperature, solvent, concentration, hydrophobic/hydrophilic properties, interface interaction, and ion strength. Astonishingly, a significant progress in soft-templating method has been achieved on the direct synthesis of ordered mesoporous carbon materials proposed by Liang, et al. [11] with self-assembly of copolymer molecular arrays and carbon precursors to realize the efficient synthesis of mesoporous carbons with controllable pore structures. It first reported the preparation of highly ordered and well-oriented mesoporous carbon thin films through the carbonization of a nanostructured phenolic resin and polystyrene-b-poly(4-vinylpyridine) (PS-P4VP) composite as shown in Figs. 1 and 2. Two important

roles of the block copolymers in the synthesis are: (1) directing the formation of the phenolic resin nanostructure, and (2) serving as templates for nanopores. Resorcinol monomers interact with the P4VP segment of the copolymer via hydrogen bonds, and are preorganized into well-ordered mesostructured films assisted with amphiphilic PS-P4VP self-assembly through spin coating and solvent annealing followed by *in situ* polymerization to form the carbon precursor in the presence of formaldehyde vapor. After carbonization under N_2 atmosphere, ordered mesoporous carbon films with a hexagonal structure and large pore size of *ca.* 34 nm were obtained.
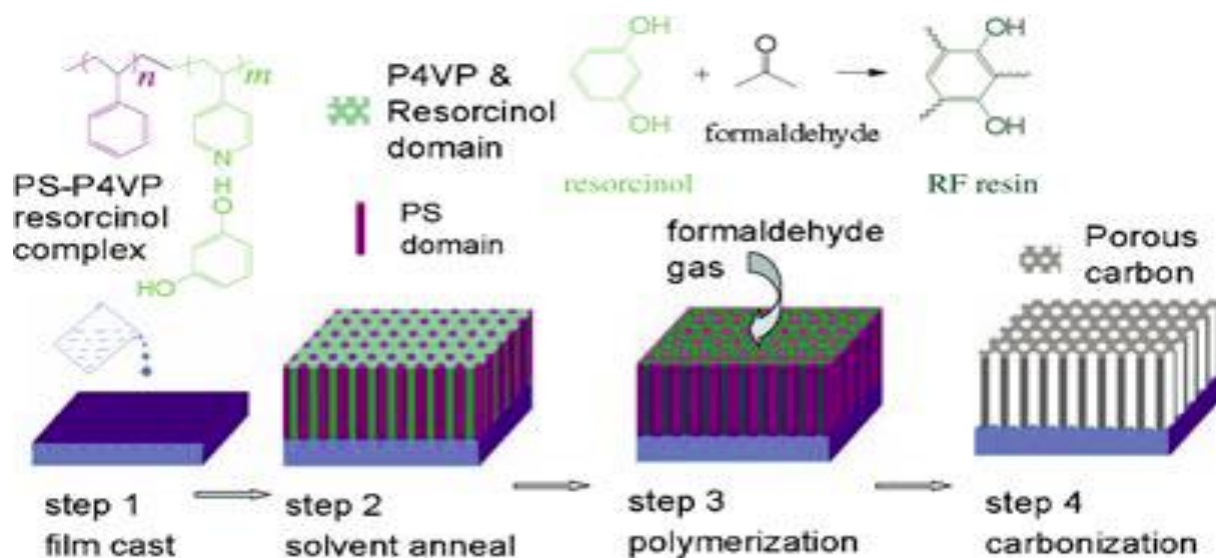

Fig-1. Schematic representation of the synthesis protocol used to prepare well-defined carbon nanostructures [11].
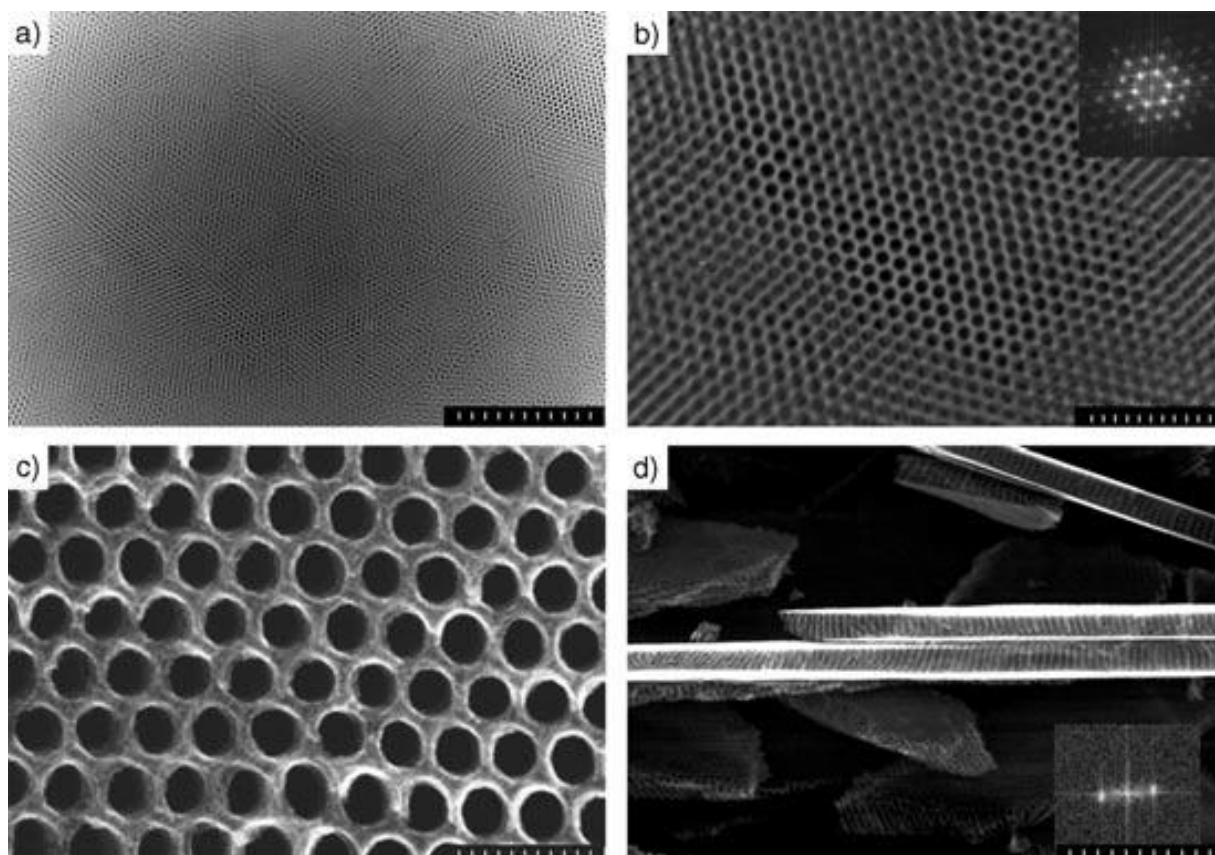

Fig-2. Electron microscopy images of the carbon film [11].

To date, the ordered mesoporous carbons can be fabricated using solvent evaporation-induced self-assembly (EISA) synthesis procedure in the presence of resol and copolymers. Low-molecular-weight and water-soluble resol, which is from the polymerization of phenol and formaldehyde under an alkaline condition, was first mixed with PEO-PPO-PEO triblock copolymer in an ethanol. The homogenous solution is poured into dished to evaporate the solvent. It induces the organic-organic self-assembly of phenolic resin with amphiphilic block copolymers by hydrogen-bonding interaction to form ordered mesostructure. The polymerization of phenolic resins is carried out at 100 °C. Due to the difference in chemical and thermal stability between the phenolic resin and the triblock copolymer, the template can be removed either by pyrolysis at 350 °C under an inert gas atmosphere or by extraction with sulfuric acid solution, and results in the formation of ordered mesoporous polymers. Heating at a high temperature above 600 °C under N_2 or Ar atmosphere can transform the polymer into corresponding carbon frameworks. The family members include two-dimensional hexagonal (space group, *p6m*), three-dimensional bicontinuous (*Ia3d*), body-centered cubic (*Im3m*), and lamellar mesostructures, which can be controlled through simply adjusting the ratio of phenolic resin/template or choosing different block copolymers. The carbon mesostructures are highly stable and can be retained at temperatures up to 1400 °C under nitrogen atmosphere.

2.2. Hard- Templated Porous Carbons

In the hard templating process, a liquid or a fluid material is poured into a template, which contains a hollow cavity of the desired shape, and is then allowed to solidify. Templating is most frequently used for making complex shapes that would be otherwise difficult or uneconomical to produce by other methods [12].

The hard templating process mainly includes three steps: (1) impregnation of carbon precursor (monomer and polymer) into solid template of mesoporous silica, (2) polymerization followed by carbonization of the precursor in the pore system resulting in a carbon-silica composite, and (3) removal of mesoporous silica template via chemical reaction. Various carbon precursors such as sucrose, furfuryl alcohol, phenolic resin, benzene, poly-vinyl chloride, pitches, acenaphthene, propylene, and acetonitrile can be utilized as the carbon precursors. The mesopore structures of the hard template acting as a nanoreactor have a significant influence on the size and structure of resultant cast replicas. Theoretically, replicated mesostructures with different symmetries can be obtained by choosing proper templates. The pore connectivity of the hard templates directly affects the structures of mesoporous replicas. When the template consists of a fully continuous solid phase and a connected pore channel system, 3D pore structures of resulting materials can be easily retained.

2.2.1. Ordered Mesoporous Silica-Templated Ordered Porous Carbons

Conventionally, mesoporous carbons are usually prepared by catalytic activation and carbonization of organic gels (carbon aerogel) with high mesoporosity. In 1986, Knox, et al. [13] first synthesized the rigid mesoporous carbon materials which exhibited unique retention characteristics in liquid chromatographic separation using spherical solid silica gel with controlled pore structure as the template and a phenol-formaldehyde resin as the carbon precursor. However, the concept of nanocasting in mesoporous materials was proposed after more than 10 years [14]. After that, many unique carbon materials with disordered structures have been synthesized by the hard-templating approach using silica as template. Unfortunately, the mesopores are still not well-organized in an ordered form. But with exhilarating news, only after one year, the hard-templating mesoporous carbon with an ordered pore structure was synthesized successfully [15].

Since then, various studies have been carried out to synthesize ordered mesoporous carbon with different mesopore structures. Until now, it is well-accepted that the structure of the resultant mesoporous carbon is indeed determined by that of the parent template. In the cases of preparing cubic phase mesoporous

carbons, MCM-48 silica was first used as a template. The polymerization of sucrose in the pore space of MCM-48 silica catalyzed by sulfuric acid and carbonization leads to the formation of mesoporous carbon of CMK-1 type after the removal of the silica. Interestingly, the structure of the mesoporous carbon replica can be easily be tuned by varying the filling amount of carbon precursor. Up to now, the ordered mesoporous silicates as hard templates with the nanocasting strategy for the synthesis of ordered mesoporous carbons have been applied successfully.

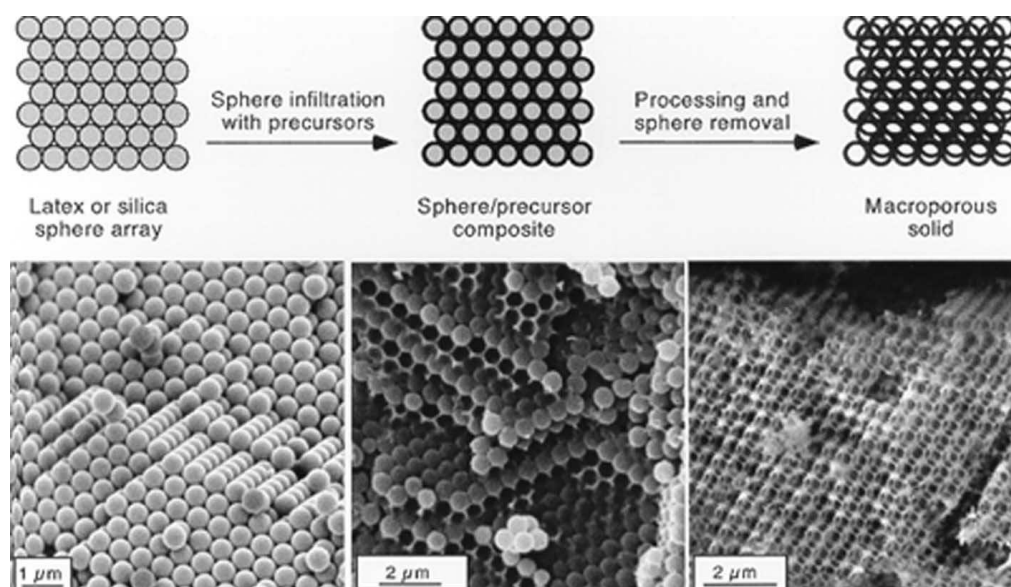**2.2.2. Colloidal Crystal-Templated Ordered Porous Carbons**

Fig-3. General synthesis scheme for periodic macroporous solids and the corresponding SEM images for a PS/Silica system prepared with TEOS [16].

Ordered macroporous carbons are prepared via the replication of ordered array structures, which are assembled by spherical and monodispersed colloidal spheres of sub-micrometer size including silica and polymer latex (e.g. polystyrene (PS) and poly(methyl methacrylate) (PMMA)) [16-18]. The pore size of the ordered macroporous solid is controllable by tuning the size of the spherical silica or polymer latex. The hard-templating approach is illustrated in Fig. 3. It can be seen that the colloidal crystals are first formed by packing uniform spheres into arrays, then the interstitial voids of the colloid crystals are filled with liquid precursor, and subsequently converted into a solid skeleton. Removal of the colloidal spheres leads to the generation of a solid skeleton in the location of the former interstitial spaces and interconnected voids where the spheres are originally located. It also shows that the morphology of macroporous carbon materials is actually largely dependent on the extent of void infiltration of template.

Besides spherical silica, organic polymer microspheres (e.g. PS or PMMA) are also been used as the templates for the synthesis of ordered macroporous carbon materials with mesoporous windows. The use of polymer beads as templates may eliminate the dissolution step, which is an indispensable step when inorganic templates (silica sphere) are used, because of the ready thermal decomposition of the polymer beads along with the carbonization of the carbon precursors.

2.2.3. Zeolite-Templated Ordered Porous Carbons

The major approaches to prepare microporous carbons are the pyrolysis of carbon precursor (such as glucose) [19] and the modification of existing pore structures of microporous carbons by chemical vapor deposition (CVD) [20] and the carbide-derived carbons (CDC) produced by high-temperature chlorination of

metal carbides. Xia, et al. [21] explored nitrogen–doped, microporous carbon materials using zeolite EMC-2 as a hard template and acetonitrile as the carbon source by chemical vapour deposition (CVD) in the temperature range 700–950 °C. Figure 4 illustrates carbons prepared at 700–900 °C display solid core disc-like particles, while the sample prepared at 950 °C exhibits broken hollow sheet-like particles. The morphology of the zeolite EMC-2 template was clearly transferred to the carbon materials, which is consistent with a templating mechanism whereby the carbon is predominantly nanocast either within the pore channels of the zeolite EMC-2 (700–900 °C) or on the surface of the zeolite particles (CEMC950).
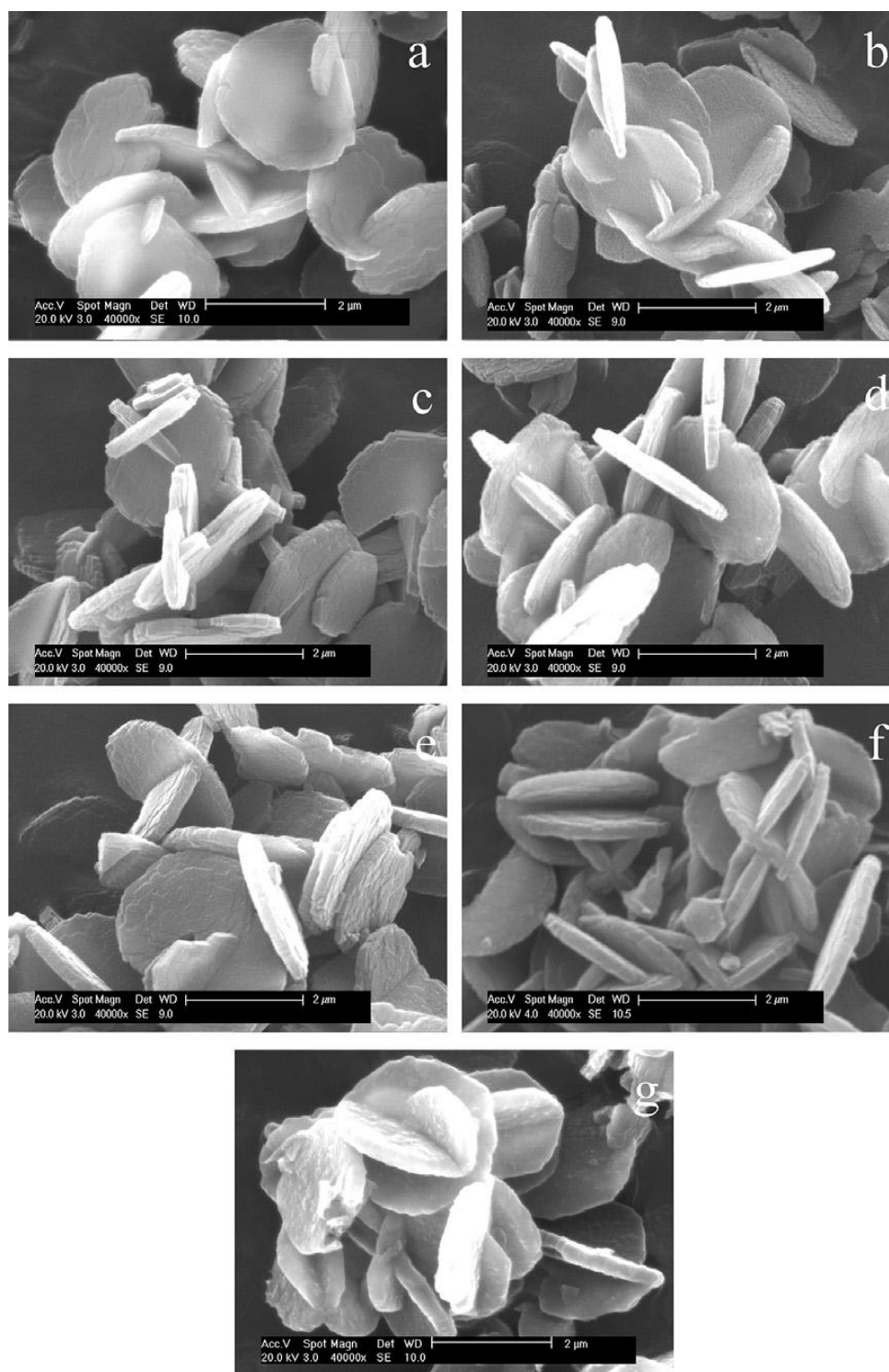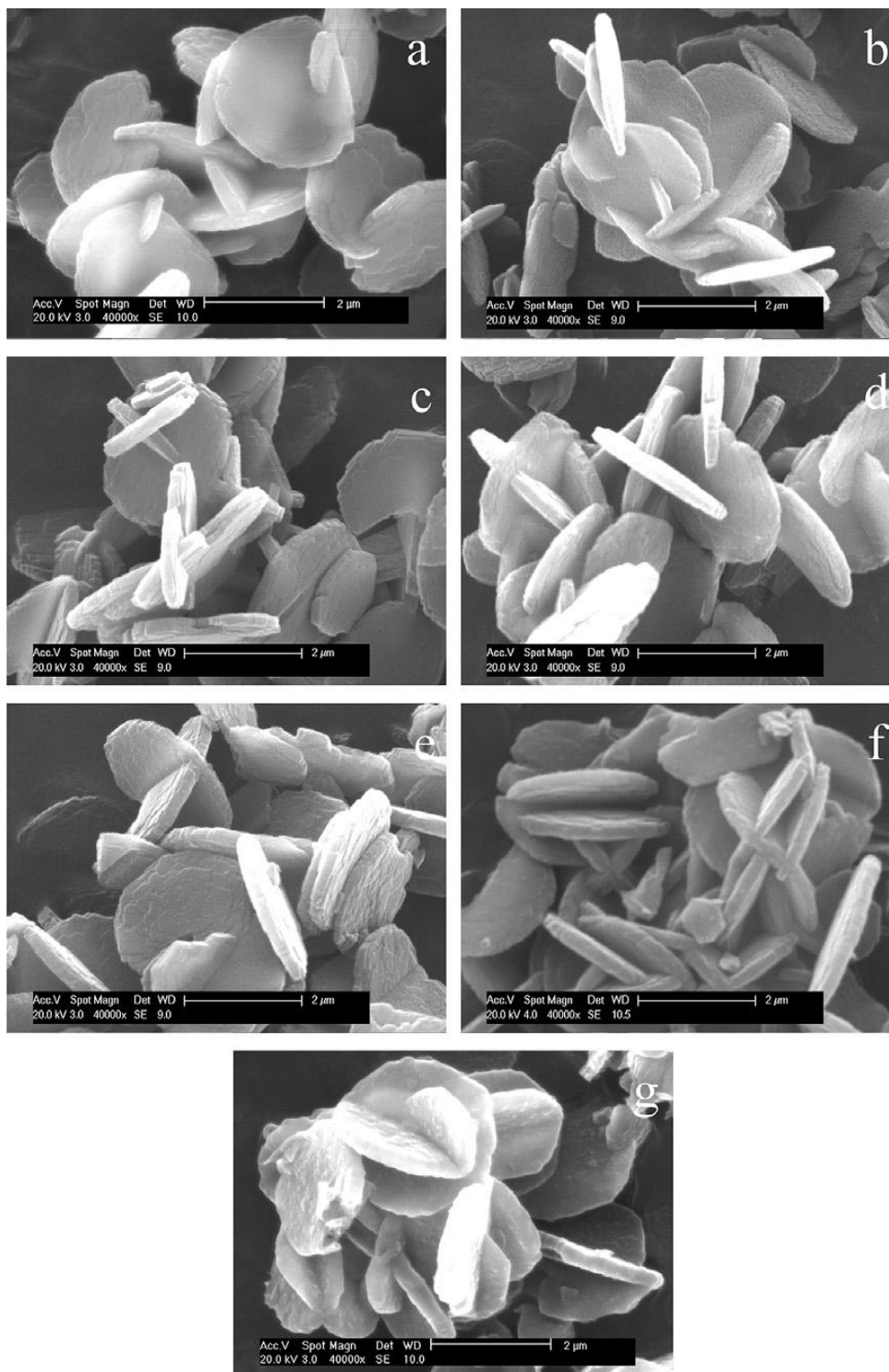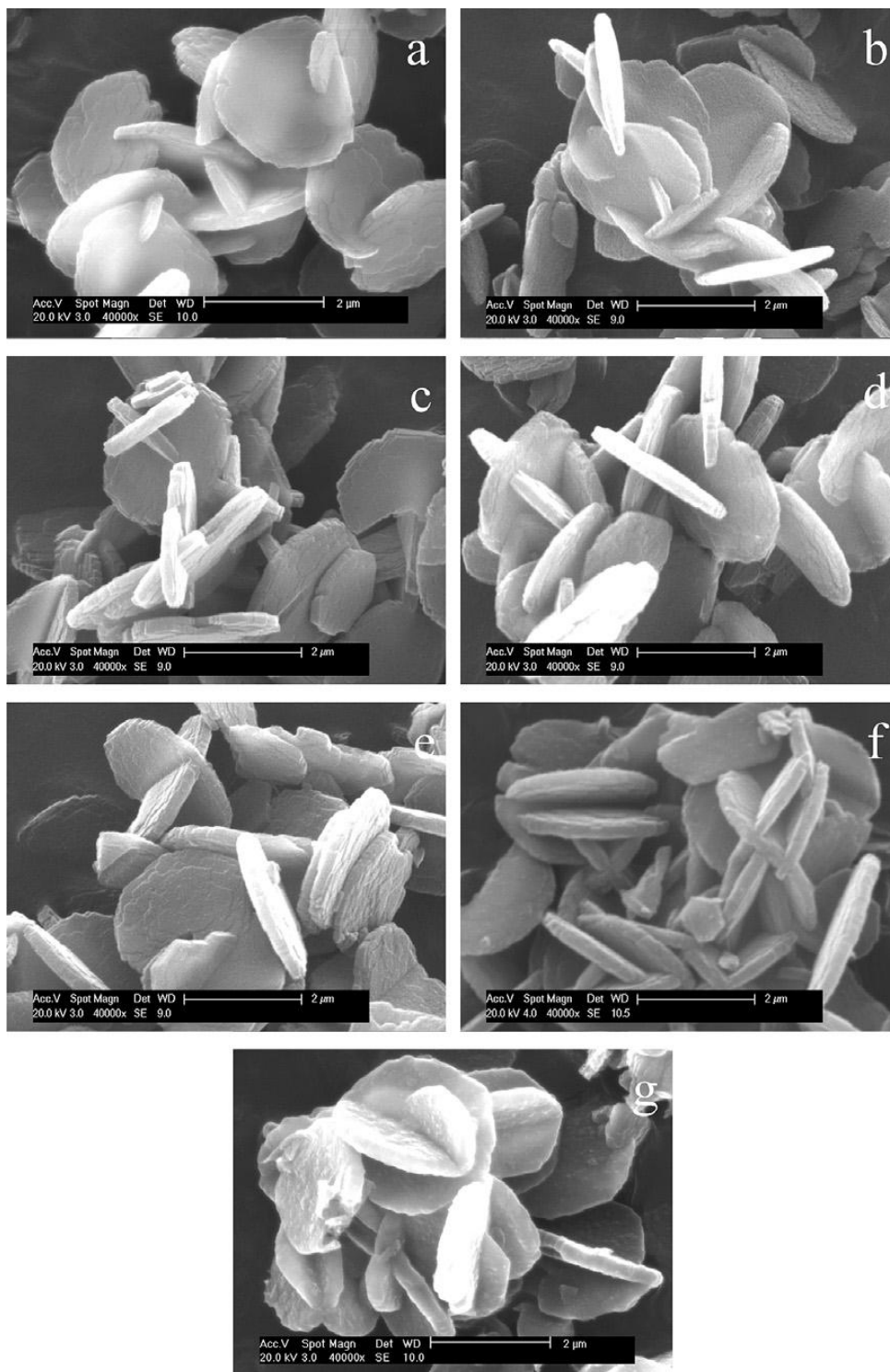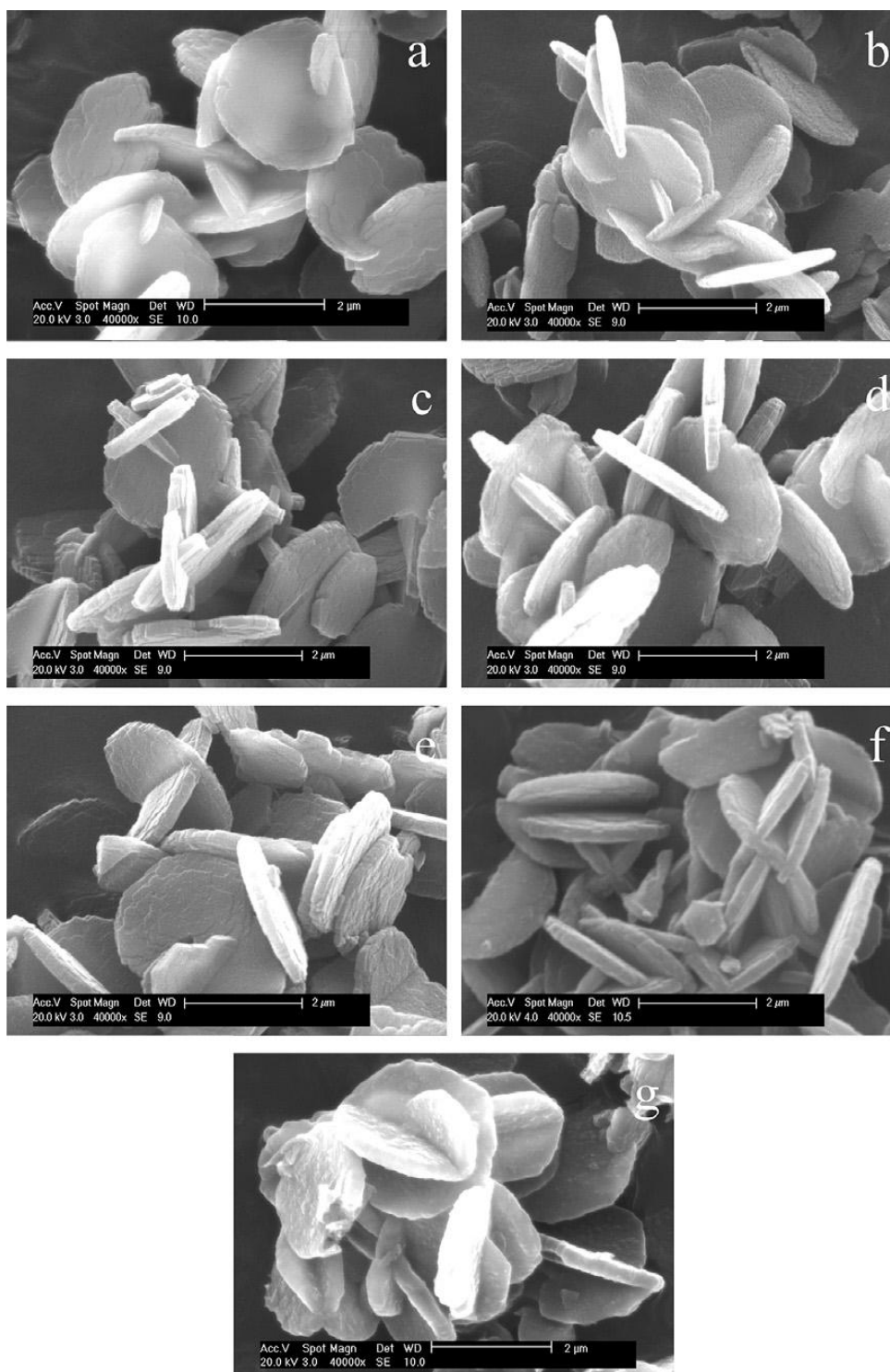
Fig-4. Representative SEM images of zeolite EMC-2 (a) and zeolite-templated carbons prepared at (b) 700 °C (CEMC700), (c) 750 °C (CEMC750), (d) 800 °C (CEMC800), (e) 850 °C (CEMC850), (f) 900 °C (CEMC900) and (g) 950 °C (CEMC950) [21].

In principle, the specific surface area of colloidal-crystal-templated macroporous carbon structures is relatively low due to the presence of large pores. However, macroporous carbons with high surface area are usually desirable when these materials are designed for serving as adsorbents, catalyst supports and electrode materials. To create a high surface area and maintain their pores in an ordered structure, a solution method is normally used to generate secondary porosity in the macropore frameworks [22].

The advantage of hard template is that the synthesis process is more easily controlled and predicted, because the hard-templated structures are already fixed by nanoscale pore architectures. Therefore, the framework and

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morphology of the replicas are under control. However, the use of ordered mesoporous silicates as hard templates makes the procedures complicated and time-consuming, and the mesopore size obtained from the hard templating are relatively small, which is not easy tunable. It is noteworthy that the hard templates are actually produced from the soft templating process, which means that hard-templating method would be unsuitable for mass production. In addition, toxic chemical such as hydrofluoric acid (HF) is needed for removal of silicates templates and HF itself is very toxic and harmful to the human body.

3. HIERARCHICALLY ORDERED POROUS CARBONS

The soft-templating methods have been proven to successfully prepare both the ordered macroporous and mesoporous carbons. However, the surface area of ordered macroporous carbon is usually lower than that of ordered mesoporous carbon. Therefore, the porosity in macroporous carbon materials can be tuned by introducing micro- and mesoporosity into the macropore wall to increase the specific surface area. The use of dual-templating strategy, which combines multiple hard- and soft-templating approaches, to synthesize three-dimensional hierarchically porous carbon materials with designed porosity on multiple length scales has been explored. In this case, the two templates play different roles: the hard template is used to control the macroscopic structures, while the other which may be hard or soft template is employed for self-assembly of structurally ordered mesopores [23].

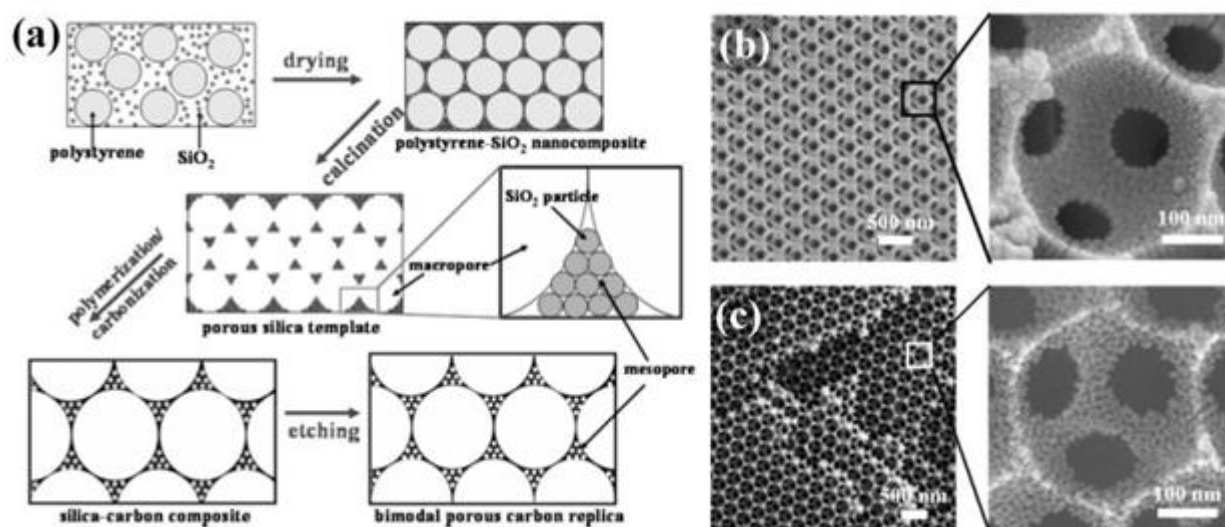### 3.1. Polymer Sphere/SiO2 Sphere For Ordered Porous

Fig-5. (a) Schematic illustration of the synthesis of a periodically ordered macroporous carbon framework with mesoporous walls. SEM images at different magnifications of (b) the silica template composed of silica nanoparticles in the walls and macropores of about 330 nm, and (c) the resulting bimodal porous carbon replica composed of macropores of about 317 nm connecting with small mesopores of about 10 nm [22].

Chai, et al. [22] proposed a dual-templating method by co-precipitation of colloidal crystals (polystyrene sphere and silica particles) with ordered arrays for fabrication of hierarchically porous carbon as shown in Fig. 5. The 3D ordered interconnected macropores were generated from the PS spheres, and the matrix was composed of silica particles. After impregnation of divinylbenzene together with free-radical initiator (azobisisobutyronitrile) into voids of matrix followed by polymerization, carbonization and HF etching, the ordered macro-/mesoporous carbon materials containing 330 nm of macropores and 10 nm of mesopores were

obtained. The specific surface area of the ordered macro-/mesoporous carbons could be up to 465 m^2g^{-1} with

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the pore volume of 1.32 cm^3g^{-1}. Although the synthesis of hierarchical carbon materials is more complicated, time-consuming, and more expensive, the morphology can be easily tailored, especially compared with the traditionally nancasting mesoporous carbons.

A one-pot synthesis of hierarchically ordered porous carbons with interconnected macropores and mesopores has also been proposed by an *in situ* self-assembly of colloidal polymer and silica spheres with sucrose as the carbon source [24]. Compared with the other techniques, this procedure is simple, environmentally friendly, and can be used for mass production of hierarchically ordered porous carbon. Neither pre-synthesis of the macropore/mesopore or crystal templates nor additional infiltration is needed, and the self-assembly of polymer spheres into the crystal template as well as the infiltration can be completed in the same system. The sizes of macropores and mesopores can be independently tuned by simply selecting the sizes of polymer (280-475 nm) and silica spheres (9-50 nm), respectively.

3.2. Polymer Sphere/Triblock Copolymer For Ordered Porous

In addition to the inorganic SiO_2, organic polymers such as poly(methyl methacrylate) (PMMA) and polystyrene can be used as the templates for macropores. Wang, et al. [25] also found that hierarchically ordered macroporous polymer and carbon monoliths with walls containing face-centered cubic or 2D-hexagonal mesopores could be synthesized via a facile dual-templating technique using both PMMA colloidal crystals and amphiphilic triblock copolymer surfactants F127 as templates. A bimodal mesostructure could be conveniently controlled by the concentration ratio of F127 and phenolic resin. Starting from the PMMA templates, four processing stages including precursor infiltration, solvent removal, thermal curing, and carbonization were involved in preparing the bimodal porous carbon materials. A two-step thermal curing method was utilized to improve the robustness of the products. The growth of mesopores was significantly influenced by the confinement effect of the colloidal crystal template. Both spherical and cylindrical mesopores were aligned parallel to the surface of PMMA spheres. Therefore, the obtained mesostructures exhibited apparent curvatures near the surface of macropore walls. On the basis of nano-indentation measurements, it demonstrates that the carbon products were mechanically more stable than that of hierarchically porous carbon monoliths synthesized by nanocasting method, and the product with the cubic mesopore structure was even more stable than 3D-ordered macroporous carbon lacking of any templated mesopores in the wall skeleton. Compared with the conventional nanocasting strategies, this method avoids the use of hazardous hydrofluoric acid required to remove a silica template, and therefore the synthesis procedure is more environmentally benign.

3.3. Hierarchical Ordered Porous Structure from Biological Templates/Triblock Copolymer Templates

Compared with traditionally artificial templates, the attractive characteristics of biological templates are generally abundant, renewable, inexpensive and environmentally benign. Biological templates are not only inherently hierarchical and complex, but also different from species to species, even within the same biology, making it possible that the obtained biomimetic materials have unique multilevel structures and morphologies Zhou, et al. [26]. Liu, et al. [27] have used a natural crab shell, which contains a number of relatively uniform ellipse-type macropores with dimensions of *ca.* 1×0.5 μm, as a confined space for Pluronic P123-templated self-assembly of phenolic resin. The obtained mesoporous carbon nanofiber arrays (MCNAs) retained an interpenetrated ordered array that was replicated from the crab shell hard-template and all the carbon nanofibers were composed of ordered mesopores with close to 2D hexagonal structures. MCNAs contained three types of pores in the materials, namely, 11 nm mesopores originated from P123 templates, 70 nm void pores formed between the nanofibers, and 1 μm macropores between nanofiber arrays. The unique

structure consisting of ordered mesopores, macroporous voids and partially graphitic framework provides a more favorable path for electrolyte penetration and transportation, good electronic conductivity as well as a large specific surface area (1270 m^{2}g^{-1}) and more vacancies or defects in a graphite plane, which facilitates uniform distribution of metal nanoparticles and a synergistic effect between the nanoparticles and MCNAs for serving as a promising electrocatalytic support for Pt in direct methanol fuel cells.

4. CONCLUSION

The advantages of soft templating strategy are that the templates can be of low cost, and the procedure is relatively easy and can be carried out under mild conditions, and various mesoporous structures are possible, depending on synthesis parameters such as mixing ratios, solvents, and temperatures. The self-assembly between templates and carbon precursor plays a key role in the success of soft templating synthesis. In addition to the ability of self-assembly between templates and carbon precursors, two key requirements should be concerned: (1) the stability of the template that can sustain at the temperature required for polymerization of carbon precursor but will be readily decomposed during carbonization and (2) the ability of the carbon precursor to form a highly cross-linked polymeric material that can retain its porous structure during the removal of templates. At present, block copolymers are the dominant templates used in the soft templating strategy for ordered mesoporous carbon. Pursuing the suitable templates for self-assembly holds promise for controlling the uniform mesopore size in the range of $2\square\square0$ nm as well as for diversification of soft-templated mesoporous carbons. Moreover, soft templating offers the chance to synthesize porous carbon materials with particular structures such as nanospheres, vesicles, and hierarchical structure, which are difficult to fabricate through the hard templating method.

The success of the hard templating method lies in its simplicity and fidelity in replicating the porous structured templates. The corresponding microporous, mesoporous, and macroporous structures can be controlled by choosing inorganic solids such as zeolite, ordered mesoporous silicas, and colloidal silicas as hard templates. However, it is still complicated because several processes including the complete filling of pore in the template by liquid impregnation, carbonization in the template channels, and separation of the obtained carbon from template by costly chemical etching using dangerous reagents HF are essential. This is not desirable for a large-scale production of ordered porous carbon. In addition, the ordered structure in the carbon cannot be retained after removal of the template when the filling of carbon precursor is not enough. Furthermore, few undesired chemical reactions between silica templates and carbon occur during the carbonization at high temperature, such as the formation of SiC or SiOC. Besides the inorganic solids, some organic polymers such as PS and PMMA spheres have been used as hard templates for the synthesis of ordered macroporous carbons with pore sizes ranging from 50 nm to several hundred nanometers. These templates can be removed by dissolution with organic solvent or thermal decomposition along with the carbonization of carbon precursor.

Ultimately, the use of dual-templating strategies, which combine multiple hard- and soft-templating approaches, to synthesize three-dimensional hierarchically porous carbon materials with designed porosity on multiple length scales will be an impressively exciting research area in the near future, especially coupled with the nanotechnology.

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