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Diatom-Templated Synthesis of Ordered Meso/Macroporous Hierarchical Materials

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Ordered meso/macroporous hierarchical silica materials have been prepared using block copolymer P123 (EO_{20}-$PO_{70}EO_{20}$) and an inverse carbon replica of diatom as templates. The silica wall of the diatom was replaced by ordered mesoporous silica, while the micron-sized diatom architecture was replicated by using an inverse carbon replication technique. The mesoporous silica was found to have macroporous structures of both columnar and discoid diatom templates. The presence of hierarchical meso/macroporous systems was confirmed by the results from scanning and transmission electron microscopy, powder X-ray diffraction, and nitrogen adsorption–desorption studies. The materials with columnar and discoid morphologies have BET surface areas of about 400 $m^2 g^{-1}$.

Introduction

In recent years hierarchical porous materials with two or more levels of porosities have attracted much attention owing to their potential applications in catalysis, separation, and ion-exchange.[1–7] Such materials improve the diffusion of the guest molecules through the inorganic network of pores and channels, because larger pores allow for better molecular accessibility while the smaller pores provide high surface areas and large pore volumes.[8] Zhao et al. reported that sponge-like silica membranes with 3D mesoporous/macroporous structures were obtained by a multiphase process of acid-catalyzed silica sol–gel chemistry.[9] Wood cells were used to prepare micro/macroporous materials by a zeolite-seeded growth method.[10] Many nonsiliceous hierarchical porous materials, for example carbon or metal oxide monoliths, were replicated from porous silica monoliths by Smått et al.[11] During the preparation of hierarchical porous materials, the simplicity of the synthesis and abundance of raw materials are important considerations. For example, a micro/macroporous composite material was prepared readily with the use of abundant diatomaceous earth.[12]

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Diatoms are microscopic aquatic, single-celled algae.[13] Diatomaceous earth, the residue of decayed diatoms, largely consists of amorphous silica with a macroporous architecture.[14] Diatomaceous earth is extremely abundant and available at low cost.[15] It is commonly used in sound and heat insulation, abrasives, filters, absorbents, and explosives.[16] The introduction of mesoporosity or microporosity to macroporous diatom architecture may extend or improve their use in many applications. Diatom zeolitization is a method of obtaining micro/macroporous hierarchical materials.[12,17] A meso/macroporous material with a BET surface area of 284 $m^2 g^{-1}$ has been prepared using hexadecyltrimethylammonium bromide (CTAB) (C_{16}TMABr) as the template in a previous investigation.[8] The technique of introducing ordered mesoporosity into the macrostructure of diatoms is based on "pseudomorphic synthesis", which has been utilized by Di Renzo and co-workers to prepare discrete micrometer-sized spherical particles of MCM-48, MCM-41, and large-pore micelle-templated silica (MTS).[18–20] However, when it was used to rearrange the silica wall of diatoms, both ordered and disordered mesostructures co-existed.[8]

Carbon is often used as the hard template to prepare zeolite or mesoporous materials because of its easy removal. Zeolite hollow fibers have been prepared by employing carbon fibers as the hard template.[21–23] Carbon nanofibers and carbon black aggregates were also capable of acting as a template for preparing mesoporous materials.[24,25] ZSM-5 zeolite/porous carbon composite has been prepared from carbonized rice husk.[26] Carbon aerogel was employed as the template to produce zeolite of mesoporous channels.[27,28] Zeolite single crystals of mesoporous channels were synthesized by using carbon particles as the tem-

plate.[29] Activated carbon is another template for making nanoporous silica.[30]

Since ordered mesoporous carbons were prepared by Ryoo et al.,[31] many ordered mesoporous silica materials and zeolites have been prepared using mesoporous carbon as the hard template.[32–36] However, to the best of our knowledge, there has been no report in the literature on the use of carbon replicas of biomaterials as templates. Here, we present the first synthesis of ordered meso/macroporous hierarchical materials using carbon replicas of biomaterials as hard templates for macroporosity and a block copolymer as the templating surfactant for mesoporosity. The nonionic block copolymer and the inverse carbon replica of diatom are used as direct templates under acidic conditions. Although the diatom is an indirect template, it is vital for keeping the microscopic morphology of the hierarchical materials. In this process the silica wall of the diatom is replaced by ordered mesoporous silica completely and the near perfect macroporous diatom architecture is well replicated.

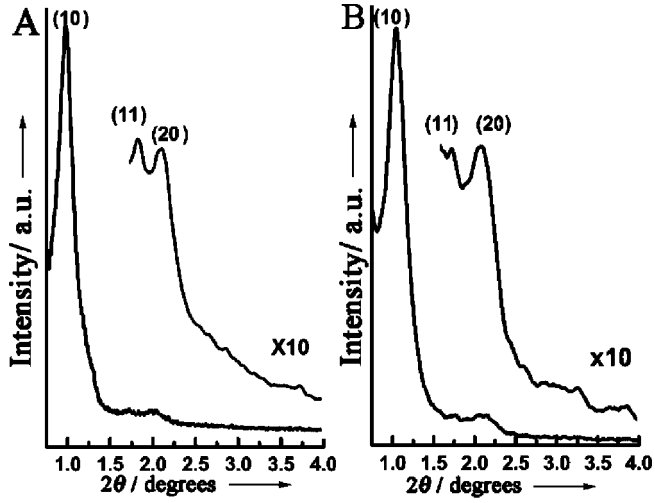


Figure 1. Powder XRD patterns of hierarchical porous materials templated by the diatoms with (A) columnar and (B) discoid morphologies.

Results and Discussion

The preparation of ordered meso/macroporous hierarchical materials with carbon replicas of diatoms as templates is achieved as follows: sucrose was first introduced in the macropores of the diatom; after carbonizing the sucrose and etching the diatom, the carbon replica of the diatom was prepared; using the carbon replica of the diatom as the hard template, a solid product with both carbon and silica was obtained through the solvent evaporation technique.[39] After removing the carbon replica and the organic template, the ordered meso/macroporous hierarchical materials were finally prepared.

Figure 1 shows small-angle X-ray diffraction (XRD) patterns for the hierarchical porous materials that were prepared using columnar and discoid diatoms as templates. Three resolved peaks appearing at low angles in Figure 1 A and Figure 1 B can be indexed as 10, 11, and 20 reflections associated with two-dimensional hexagonal pore ordering in the *p6mm* space group.[37] The morphologies of the initial diatoms were revealed by scanning electron microscopy (SEM). Figure 2 shows the diatoms with columnar and discoid morphologies. The columnar diatoms have a diameter of about 7 μm and a length of about 15 μm (Figure 2 A). A high-magnification image (Figure 2 B) shows that the diameter of subpores is about 0.6 μm. The top of the hollow columnar diatom presents a hole with a diameter of about 5 μm, as shown in Figure 2 C. Low-magnification images display the discoid diatoms with a diameter of about 30 μm (Figure 2 D). From high-magnification observations of the surface, the subpore sizes range from approximately 350 to 550 nm (Figure 2 E). The thickness of the discoid diatom is about 5 μm, as identifiable from the side view in Figure 2 F. There is a cavum in each type of diatom. Part of the diatom wall is represented in Scheme 1 a.

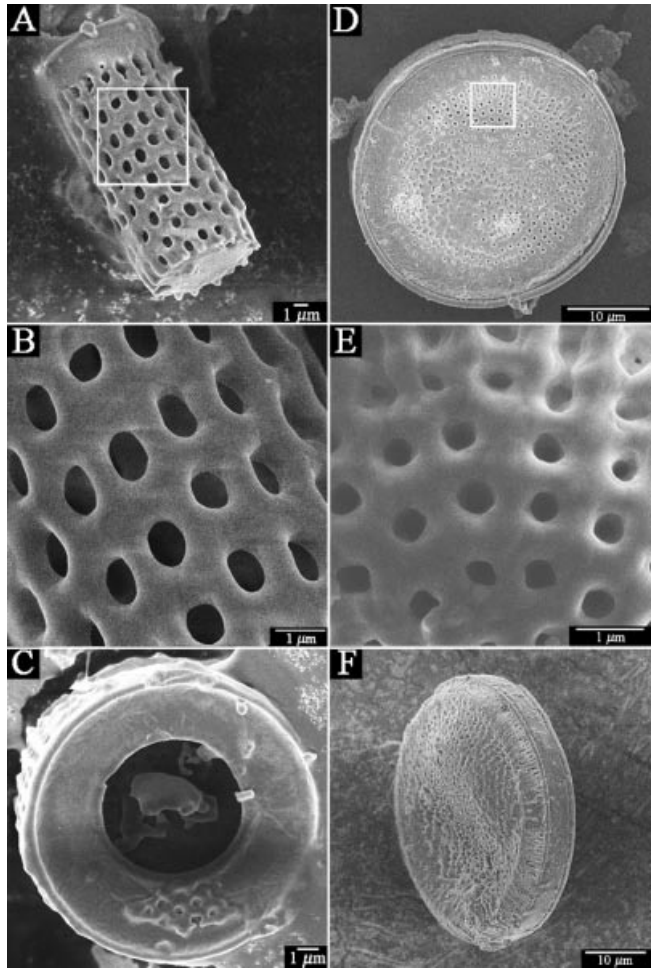
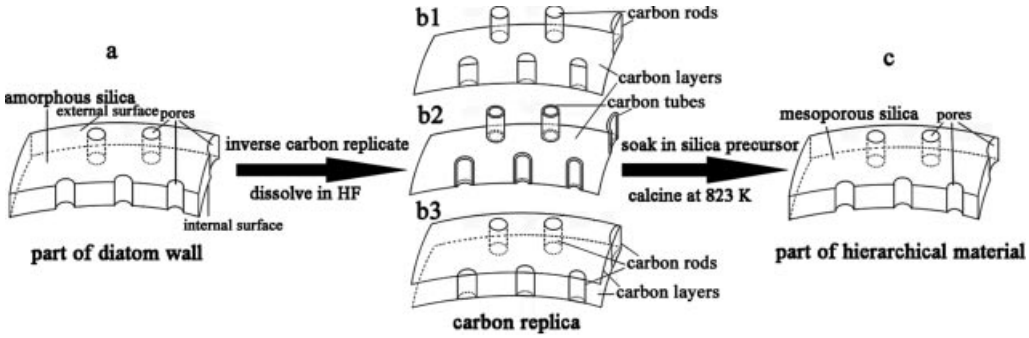


Figure 2. SEM images of initial diatoms with (A, B, C) columnar and (D, E, F) discoid morphologies.

The extent of carbonization depends on the amount of sucrose adsorbed on the inner surface of the diatom. After the diatom was dissolved in HF solution, a carbon frame-



Scheme 1. Schematic illustration of the preparation of the meso/macroporous hierarchical porous materials.

work as an inverse replica of the diatom was obtained, as shown in Figure 3. Figure 3 A–C show the inverse carbon replicas of columnar diatoms, while Figure 3 D shows the carbon replica of the discoid diatom. At a high weight ratio of sucrose/diatom, it is a carbon rod that inversely replicates the subpores of diatoms (Figure 3 A–C), which is illustrated in Scheme 1 b1. When the sucrose is in large excess, the carbon layers are formed not only on the internal surface but also on the external surface of the diatoms (Figure 3 C), which is represented in Scheme 1 b3. When the weight ratio of sucrose/diatom is low, insufficient sucrose is absorbed on the surface of the subpores, which is transformed not to carbon rods but carbon tubes (Figure 3D), as illustrated in Scheme 1 b2.

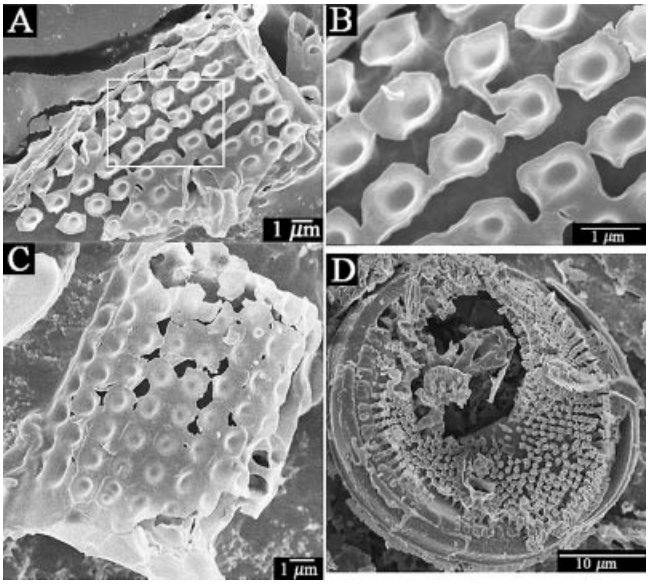


Figure 3. SEM images of inverse carbon replicas of diatoms with (A, B, C) columnar and (D) discoid morphologies.

After the inverse carbon replicas were immersed in the silica reaction mixture, they were coated with mesoporous silica upon evaporation of ethanol. When the carbon and the surfactant were removed by calcination, the diatom-replicated silica framework possessing an ordered mesostructure was obtained as depicted in Scheme 1 c and evidenced by SEM images (Figure 4) for the resultant mesoporous silicas with columnar (Figure 4 A and B) and discoid (Figure 4 C and D) morphologies. It is apparent that both the macroporous structure and the morphology of the initial diatom can be replicated by this method. As observed from the TEM images in Figure 5, the wall of the above final

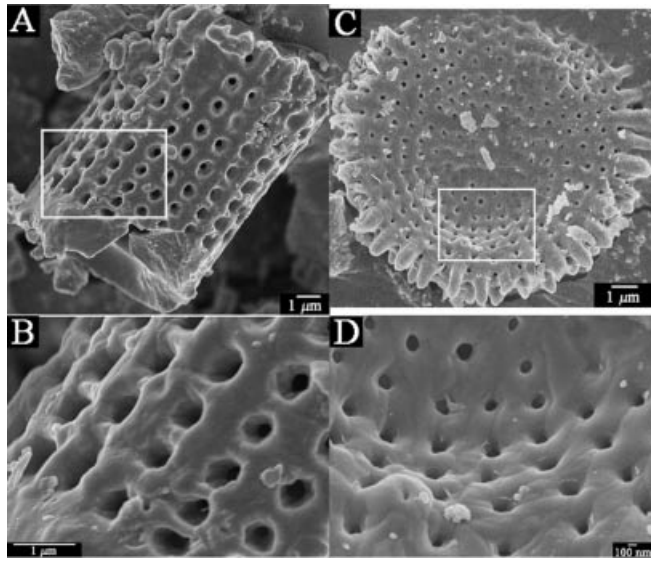


Figure 4. SEM images of hierarchical porous materials templated by diatoms with (A, B) columnar and (C, D) discoid morphologies.

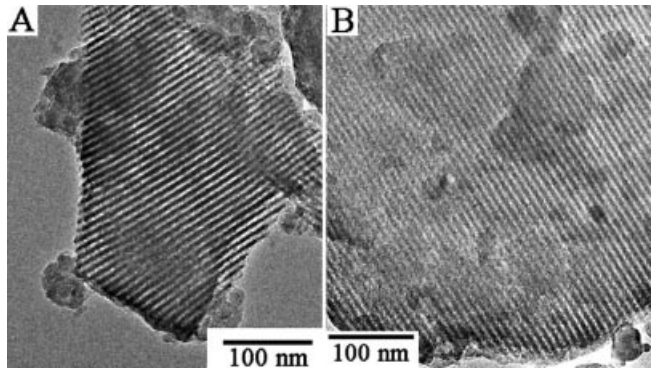


Figure 5. TEM images of hierarchical porous materials templated by diatoms with (A) columnar and (B) discoid morphologies.

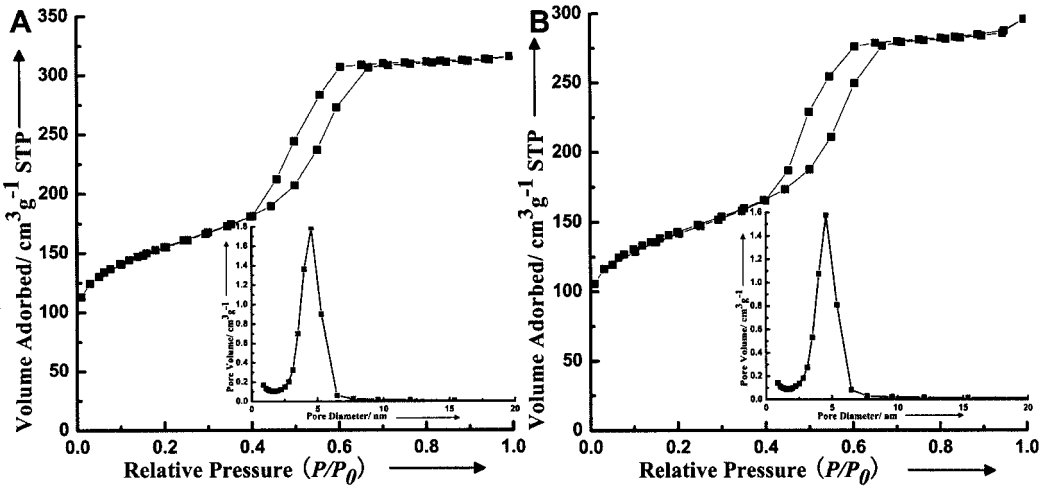


Figure 6. N_2 adsorption–desorption isotherms and pore-size distribution (inset) of hierarchical porous materials templated by diatoms with (A) columnar and (B) discoid morphologies.

hierarchical porous silica possesses ordered mesopores, which is in agreement with results of powder X-ray diffraction (Figure 1).

Nitrogen adsorption–desorption isotherm measurements were performed on both columnar (Figure 6 A) and discoid (Figure 6 B) hierarchical porous silica materials. In both cases, type IV isotherms with large hystereses were obtained, which are characteristic of mesoporous materials. The BET surface areas of the columnar and discoid hierarchical porous materials are 405 and 381 $cm^2 g^{-1}$ and the pore volumes are 0.41 and 0.37 $cm^3 g^{-1}$, respectively. It is noted that the BET surface area of about 400 $m^2 g^{-1}$ as obtained here because of the presence of mesoporosity is much higher than that of previously reported materials templated by diatoms.[8] The average pore diameter of both hierarchical materials is about 4.5 nm, as calculated from the BJH method of mesopore size analysis on the adsorption branch of the N_2 isotherms.

Conclusions

We have demonstrated the synthesis of ordered hierarchical porous silica using block copolymer P123 and a carbon replica of a diatom as dual templates. The P123 functions as a soft template for the formation of mesoporosity and the inverse carbon replica as a direct hard template for macroporous structures. The macrostructure of the diatom is inversely replicated by the carbon replica. The weight ratio of sucrose/diatom was found to be important for the preparation of carbon replicas. High sucrose/diatom ratios lead to the formation of carbon layers on both internal and external surfaces of diatoms and of carbon rods in the subpores of diatoms; while low ratios resulted in the formation of a carbon layers only on the internal surface and of carbon tubes in pores. SEM results show that hierarchical materials with macropores 350–550 nm in diameter exhibit columnar and discoid morphologies. Nitrogen sorption studies indicate that the materials have high BET surface areas of about 400 $m^2 g^{-1}$. Powder XRD and TEM results indicate that the mesopore in the hierarchical structure has a two-dimensional hexagonal pore ordering. These ordered hierarchical porous materials have the advantages of both mesoporosity and macroporosity, which may find a broad range of potential applications in catalysis, adsorption, and separation.

Experimental Section

Two types of diatomaceous earth (consisting of columnar and discoid diatoms) were purchased from Aldrich (Celatom FW80) and Tianjin Chemical Graduate School, respectively, and were purified further by sedimentation and ultrasonication. A sedimentary method in deionized water was used to remove the mixed scrappy mineral and ultrasonication in ethanol solution was performed to separate the clay from the diatom. The inverse carbon replication technique that was used in this work was adopted from the literature.[38] Thus, the purified diatom was impregnated with an aqueous solution of sucrose in the presence of sulfuric acid, and then the resulting mixture was dried and carbonized at 373 K and subsequently at 433 K. Diatom silica was removed by HF. The detailed procedure is as follows: purified diatom (1 g) was added to a solution obtained by dissolving sucrose (0.6 g) and H_2SO_4 (0.14 g) in H_2O (5 g). The mixture was placed in a drying oven at 373 K for 6 h, and subsequently the oven temperature was increased to 433 K for another 6 h. After dissolving the diatom in an aqueous solution of HF for 12 h, the inverse carbon replica was obtained. A silica reaction mixture was prepared as follows:[39] P123 (0.3 g) was dissolved in ethanol (4.5 g), followed by addition of an aqueous HCl solution (0.03 g, 2 M), deionized water (0.24 g), and tetraethyl orthosilicate (TEOS) (0.7 g), whilst stirring. The mixture was stirred at room temperature for 2 h. Inverse carbon replica (0.23 g) was added to the above reaction mixture under agitation and the whole mixture was transferred to an uncovered vessel until the air bubbles in the solution disappeared. The volatiles were evaporated under a flow of air after almost 12 h. The black solid was isolated after the weight of the mixture had lost about 60% by evaporation of ethanol and was dried at 373 K; it was then calcined at 823 K for 5 h to remove the inverse carbon replica and surfactant. The final product was a white powder. We also employed other silica sources,

including water glass, silica sol, and fumed silica, and so forth, but so far no good results have been obtained under the same experimental conditions. When triblock copolymer F127 (EO_{106}-$PO_{70}EO_{106}$) was used instead of P123, meso/macroporous hierarchical materials could also be prepared and the mesoporous structure had a cubic *Im*3*m* space-group symmetry with a pore size of 5–6 nm. X-ray diffraction (XRD) measurements were conducted with a Siemens D5005 diffractometer using Cu-K_α radiation (λ = 1.54 Å). Transmission electron micrograph was obtained with a JEM-3010 using a copper grid-type sample holder. Scanning electron microscopy was performed with a JSM-6700F. Nitrogen adsorption–desorption isotherms were measured at the temperature of liquid nitrogen using a Micromeritics ASAP 2010 system. The samples were degassed at 573 K for 10 h before the measurements.

Acknowledgments

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