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Hierarchically Porous Silica with Ordered Mesostructure from Confinement Self-Assembly in Skeleton Scaffolds

Chunfeng Xue, Jinxiu Wang, Bo Tu,* and Dongyuan Zhao*

Department of Chemistry, Shanghai Key Lab of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People's Republic of China

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Hierarchically porous silica materials have been synthesized through a confinement self-assembly approach in the skeletal scaffolds of commercial polyurethane (PU) foams. Macroporous/mesoporous silica materials with a well-ordered two-dimensional (2-D) hexagonal ($p6mm$) mesostructure have been synthesized in an acidic solution using tetraethoxysilane as a precursor, triblock copolymer Pluronic P123 as a mesostructural template, and PU foams with three-dimensional (3-D) interconnecting strut networks as a macrostructure scaffold. By controlling the volume ratio of the cast silica sol to the PU foam scaffolds, hierarchically porous silica monoliths with various macropore structures can be obtained. The porous silica monoliths can be disassembled into uniform polyhedron-like particles. The porous silica polyhedrons exhibit macropores 100–500 μm in diameter, adjustable uniform mesopores (6.5–9.3 nm in diameter), high surface areas (340–780 m^2/g), and large pore volumes (0.48–1.16 cm^3/g). The resulting macroporous/mesoporous silica polyhedrons show an excellent adsorption and remove capability of Microcystin-LR in wastewater.

1. Introduction

Hierarchical pore structures in nature such as stems of plants, bones of animals, etc. are common and play important roles in mass transfer.¹ Materials organized with such macropore structures can also minimize the channel blocking for fast diffusion of bulky molecules in industrial catalysis, adsorption, separation and waste-disposing processes, etc., because they can effectively access the mesopores and/or micropores interconnected by macropores, especially in sticky systems.^{2–8} Mesopores can provide selective or active sites for reactants, whereas the existence of macropores can offer a highway for reactants accessing the sites with small pressure drops and benefit for obtaining intermediate product. For example, macroporous/mesoporous silica monoliths have been used in chromatographic separation systems.⁹ For

actually useful materials, the fabrications of hierarchically porous materials with required morphology, as well as having control of pore structures and compositions are much important. Bulk monolithic materials such as columns are generally designed for macromolecular separation in regular towers. The hierarchically porous particles such as spheres can fill various shapes, even for twisted or snakelike reactors.

Many approaches for the fabrication of hierarchically porous silica have been proposed, including solid biology templates,⁶ ice-crystal templating,¹⁰ dual templates,^{9,11–14} etc. Generally, a controllable dual-templating method can combine two different soft templates or soft templates with hard ones. For instance, macroporous–mesoporous silica monoliths can be obtained from silica-based sol–gel in the presence of copolymer Pluronic P123 and swelling agent (1,3,5-trimethylbenzene, TMB); however, probably because of the effect of the swelling agent on the mesostructure assembly, disordered small pores are formed and the corresponding mesopore size distribution is also broad.⁹ For other examples, hierarchically porous silica can be prepared by combining resolvable homopolymer

*Author to whom correspondence should be addressed. E-mail: botu@fudan.edu.cn (B.T.); dyzhao@fudan.edu.cn (D.Z.).

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poly(ethenlene glycol) (PEG) with cationic surfactant (cetyltrimethylammonium bromides),¹⁵ the obtained mesostructure is disordered. Stein and co-workers successfully prepared macroporous/mesoporous silica materials by combining the hard and soft templating methods, using the water-insoluble polystyrene (PS) microsphere as a macropore template and amphiphilic surfactant as a mesostructural template.^{13,14} Ordered mesoporous silica materials with a well-defined macropore structure were obtained by directly introducing a mixed sol of prehydrolyzed silica precursors and surfactant into voids of the colloidal spheres. By controlling the packing and size of latex colloidal beads and the assembly of surfactants and silicate oligomers, oriented mesopore channels of variable macropore size and window connection can be formed.^{16–19} However, the inverse macrophase replication requires many colloidal templates, which are tedious and difficult to prepare in large scale, and their surface modifications are usually required. Obviously, it is not an economical approach for the preparation of multilevel porous materials. Thus, it is challenge to prepare hierarchically porous silica materials via an economical pathway.

Commercial polyurethane (PU) foams have controllable skeleton macrostructure and many large voids, which is significantly different from the stacks or arrays of colloid microbeads. Its interconnectivity of the macropores is perfect well for macrocasting (coating) and the self-assembly for the highly ordered mesostructure. The assembly cannot only occur in the large voids, but also along the interface formed by the interconnective struts and the network. What is most important is the fact that the obtained macropore cells of the target materials have excellent interconnectivity, which are much better than windows replicating from necks of polymethyl methacrylate (PMMA) or polystyrene (PS) microspheres arrays. PU foams with the diverse porosities (10–400 pores per linear inch, ppi) can be used as scaffolds for different materials, especially for pore with micrometer level (60–2500 μm). Coincidentally, the commercial PU foams containing a small amount of silica (5 wt %) have good compatibility for casting silica precursors. PU foam has been used as scaffolds or substrates for the fabrication of microporous/macroporous silica materials.^{20–22} Recently, a strategy toward polymer-based skeleton monoliths with mesoporosity/macroporosity has been further developed basing on the commercial PU foam scaffolds.^{23,24} Ordered mesoporous carbonaceous polymer and carbon

composites with different symmetries are fabricated by filling and coating the three-dimensional (3-D) skeleton networks of PU foams. This PU foam sacrificial scaffold process is a simple and economic pathway for the mass production of porous materials. Herein, the approach is extended for the preparation of hierarchically porous silica materials with ordered mesostructures. Interestingly, the silica sols with amphiphilic surfactant can not only cast the PU foam skeletal networks to yield macroporous/mesoporous silica monoliths with variable morphologies, but also assemble in confinements of PU foams' 3-D interconnected struts. Instead, after breaking down the skeleton monoliths, uniform polyhedron-like mesoporous silica particles can be obtained. Both silica monoliths and polyhedral particles exhibit a well-ordered 2-D hexagonal mesostructure templated from amphiphilic triblock copolymer Pluronic P123 under acidic conditions and a hydrothermal treatment at 100 °C. Furthermore, the porous silica polyhedrons exhibit hollow macropores with a diameter of 100–500 μm , adjustable uniform mesopores (6.5–9.3 nm), high surface areas (340–780 m^2/g), and large pore volumes (0.48–1.16 cm^3/g). They are also used to efficiently adsorb and remove Microcystin-LR in wastewater.

2. Experiments

2.1. Chemicals. Polyether polyol-based polyurethane (PU) foam was an industrial product with porosities of 50 ppi (pores per linear inch) and purchased from the Shanghai Changda Foam Factory. The density of the commercial PU foam was 0.02 g/cm^3 . The triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, with an average molecular weight of $M_{\text{av}} = 5800$) was purchased from Aldrich. Microcystin-LR (MC-LR) (HPLC purity of >95%) was provided by Beijing Express Technology Co., Ltd. Other chemicals, including absolute ethanol (EtOH), concentrated hydrochloride acid (HCl, 36.5 wt %), and tetraethoxysilane (TEOS) were purchased from the Shanghai Chemical Co., Ltd. All chemicals were used as received without further purification.

2.2. Synthesis. Hierarchically porous silica monoliths were prepared by the confinement self-assembly approach, which combined a macrocasting of PU foam skeletal scaffolds with an evaporation-induced inorganic–organic cooperative assembly. The initial sol mixture composed of prehydrolyzed silica precursor from TEOS and Pluronic P123 as a mesostructural template was used to macrocast the PU foam as a macroporous scaffold. For a typical procedure,²⁵ 10 g of Pluronic P123 was dissolved in a mixture of 10 g of 0.2 M HCl and 100 g of ethanol with stirring at 30 °C for 2 h. Then, 20.8 g of TEOS was added and stirred for another 1 h, and a homogeneous sol solution was obtained. Fifty milliliters of the sol was cast into the PU foam with a total volume of 100 cm^3 . To achieve uniform macrocasting, the air bubbles in PU foam scaffolds were

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continuously squeezed out. After the solvent was evaporated completely at 25–30 °C in air, the sample was hydrothermally treated in water at 100 °C for 2 days in an autoclave. After being filtrated and dried at 80 °C in air, the hierarchically porous silica (named as HPS-50) was finally obtained. Calcination of as-made samples was performed at 550 °C for 6 h in air to remove all the organic templates. The heating rate of the muffle oven was 1 °C/min. The term “HPS-*x*” denotes the hierarchically porous silica monolith, where *x* represents the volume ratio of the cast sol to PU foam scaffolds.

2.3. Adsorption. Aqueous solutions of MC-LR with different concentrations (0.4, 0.6, 1.25, 2.5, 5, and 10 µg/mL) at pH 4 were prepared. Ultraviolet–visible light (UV–vis) spectrometry was used to determine the absorbency at a wavelength of 238 nm. A plot of the absorbency, relative to the toxin concentration, was fit with the linear regression function to get a standard curve, $Y = 0.01645 + 0.03756X$, and the correlative coefficient, $r = 0.9987$ ($R^2 = 0.9974$). Four milliliters of the MC-LR solution (10 µg/mL) was added into each of nine 5.0-mL-capacity tubes containing 100 mg of calcined hierarchically porous silica HPS-50. The mixture was then shaken at room temperature for 5, 10, 15, 20, 25, 30, 40, 50, and 60 min. After centrifugation, the residual MC-LR concentrations (c_t) of the supernatants were determined by UV–vis spectrometer. The amount (q_e) of MC-LR removed from the solution related to one microgram of the porous silica sample was calculated by the formula $q_e = V(c_0 - c_t)/W$, where V represents the volume of the solution (in milliliters), W represents the mass of the porous silica sample (in milligrams), and c_0 represents the initial concentration of MC-LR solution (given in units of µg/mL). The equilibrium adsorption isotherms for MC-LR on the obtained porous silica samples were determined at room temperature (25 °C). One hundred milligrams of the porous silica samples were added into 4 mL of MC-LR solution at pH 4. The mixture was shaken for 10 min and centrifuged. The residual MC-LR concentration of the supernatant was determined by UV/vis spectrometry.

2.4. Characterization. Small-angle X-ray scattering (SAXS) data were collected on a Nanostar U small-angle X-ray scattering system using Cu K α radiation at 40 kV and 35 mA. The d -spacing values were calculated from the formula $d = 2\pi/q$. The unit-cell parameters of ordered mesostructures were calculated using the formula $a = 2d_{10}/(\sqrt{3})$, where d_{10} represents the d -spacing values of the 10 diffraction of a two-dimensional (2-D) hexagonal mesostructure. Transmission electron microscopy (TEM) experiments were performed on a JEOL Model 2011 microscope operated at 200 kV. The ground samples for TEM measurements were suspended in ethanol and supported onto a carbon-coated copper grid. Scanning electron microscopy (SEM) images were collected with Philips XL30 electron microscope operated at 20 kV. A thin gold film was sprayed on the samples before SEM measurements. Field-emission scanning electron microscopy (FE-SEM) images were collected on the Hitachi Model S-4800 field emission scanning electron microscope and the samples without further gold-spraying treatment were used for

the observations. N₂ sorption isotherms were measured with a Micromeritics Model Tristar 3000 analyzer at 77 K. Before the measurements, all samples were degassed at 180 °C under vacuum for at least 6 h. Using the Barrett–Joyner–Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms. The Brunauer–Emment–Teller (BET) method was utilized to calculate the specific surface areas. The thermal decomposition behavior and weight changes of the samples were monitored using a Mettler–Toledo Model TGA-SDTA851 analyzer from 25 °C to 900 °C in air with a heating rate of 5 °C/min. A Jasco Model V-550 UV–Vis spectrometer (Japan) was used to measure the concentration of MC-LR.

3. Results and Discussion

3.1. Fabrication of Hierarchically Porous Silica. A hierarchically porous silica with an ordered mesostructure can be prepared via a confinement self-assembly approach that combines macrocasting skeletal scaffolds with a surfactant-templating mesostructure process. The commercially available PU foam was used as a macrostructural sacrificial scaffold for the macrocasting. The prehydrolyzed silica sol containing triblock copolymer Pluronic P123 as a mesostructural template can be impregnated in the macropore voids of the foam driven by capillary force. With the solvent evaporation, the confinement self-assembly of the triblock copolymers with silica oligomers and cross-linking of silica precursors are performed in the PU networks. The mesostructured silica was coated and formed on/around the interconnected struts, which was dependent on the volume ratio of the silica sol to PU foam. After the copolymer template and PU foam scaffolds are completely removed by calcination, the ordered mesopores are exposed and the macroporous skeleton of the sacrificial scaffold is replicated. The hierarchically porous silica monoliths with ordered mesostructure can be obtained.

Here, we use the hierarchically porous silica monolith HPS-50 that was prepared by macrocasting with the sol to PU foam (volume ratio of 50%) as an example. The as-made HPS-50 monolith composite, after the macrocasting and drying, shrinks by 6.5% in the linear dimensions and by 18% in volume, compared to the original PU foam scaffolds; the shrinkage is attributed to the cross-linking stress of silica species during the aging process (see Figure 1a). The brown–yellow color of the as-made monolith is due to the commercial PU foam, implying a transparent macrocast Pluronic P123-silica composite layer. After calcination at 550 °C in air, the PU foam scaffold and the copolymer surfactant are completely removed, and the calcined hierarchically porous silica monolith (HPS-50) retains the foamlike macrostructural architecture (see Figure 1b). It shrinks by 28% in the linear dimensions and by ~63% in volume, which is similar to that for the porous carbon monoliths prepared using the PU foam as a macrostructural sacrificial scaffold (~27% in the linear dimensions).^{23,24} The similar

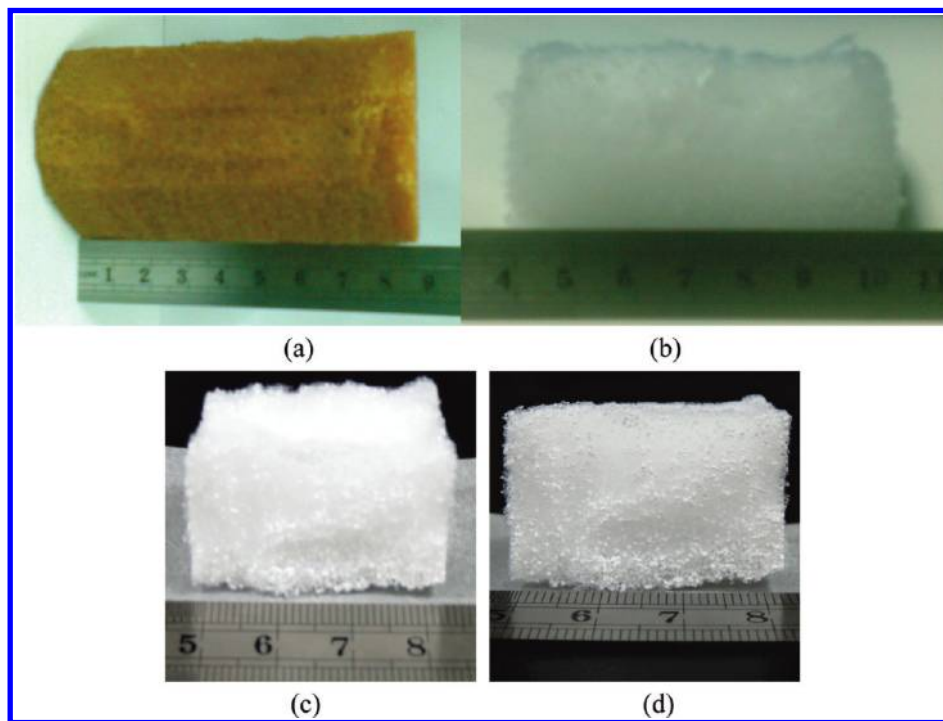


Figure 1. Photographs of hierarchically porous silica monoliths: (a) as-made HPS-50, (b, c) calcined HPS-50, and (d) calcined HPS-25.

macrostructure shrinkage is mainly related to the meso-structural constriction of the rigid silica framework caused by the condensation and hollow struts structure, because of the removal of PU foam scaffolds during the heating process. Similar to the mesoporous silica monoliths prepared by the liquid paraffin covering method,²⁶ the obtained hierarchically porous silica monolith is semitransparent, different from the white mesoporous silica powders.²⁷ The continuous coating of ordered mesostructure and thin layers of highly polymerized amorphous silica frameworks from the sol–gel process may lead to the semitransparent texture. Scaffolds with different shape can also be used as a macrocasting template for the confined assembly of the silica mesostructure. After being calcined at 550 °C in air for 6 h to remove all the organic templates, a uniform shrinkage is also observed and a silica monolith also can be obtained (see Figure 1c). The well-retained morphology (see Figure 1c) shows good replication of the macroporous architecture and a good thermal stability. In case the volume ratio of the cast sol to PU foam scaffolds is 25%, the calcined hierarchically porous silica monolith HPS-25 (see Figure 1d) also has a similar shrinkage ratio as the calcined HPS-50 (~30% in the linear dimensions, ~66% in volume), suggesting that it is mainly related to that of mesostructured silica but less related to the shape and thickness of the coatings.

SEM images of the commercial PU foam scaffolds show the smooth inverse-sphere surface of irregular quasi-prism struts (see Figure 2a). The three-dimensional

(3-D) interconnected struts build a cellular structure with the pore diameter of ~100–500 μm . When the volume ratio of the cast sol to PU foam scaffolds is 25%, SEM measurements show that the calcined HPS-25 silica monolith have 3-D skeletal structure with the pore width of ~450 μm (see Figure 2b), similar to that of the PU foam scaffolds, indicating a faithfully replication of the skeletal macrostructure. The results suggest that a small amount of silica sol can only coat the struts. The triarris tubular structure replicated from the quasi-prism structure of the PU foam scaffolds is formed. The cross-section SEM image of the silica struts clearly shows a hollow triangle, which is molded by the struts (see Figure 2c), because the PU foams are burned out and the voids are left after the rigid silica frameworks are formed. The calcined hierarchically porous silica monolith (HPS-25) is too fragile to be subjected to the hardness measurement but can be disassembled into irregular skeleton-like particles (see Figure 2d). SEM images show that the particles have the smooth outside surfaces, which are molded and peeled from the PU foam struts (see Figure 2d). When the volume ratio of the cast sol to PU foam scaffolds is as high as 50%, silica precursors can form a cell membrane based on the adjacent struts during the solvent evaporation, suggesting that the silica sols not only coat the 3-D struts of PU foams, but the superfluous sols also can accommodate the cellular cavities constructed by the 3-D struts for the confined assembly. In addition, a fully connected macroporous architecture with windows of 400 μm was obtained with the cellular silica membranes sharing the interconnected struts (see Figure 2e). The calcined hierarchically porous silica monolith (HPS-50) can be disassembled into polyhedron powders with uniform size (~500 μm ; see Figure 2f). The windows and

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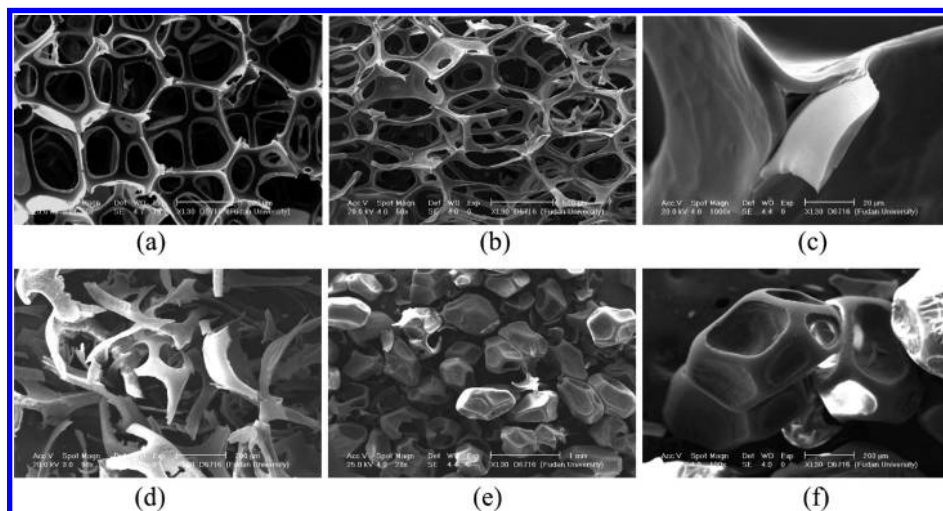


Figure 2. SEM images of (a) the commercial PU foam scaffolds, (b, c, d) calcined hierarchically porous silica HPS-25, and (e, f) calcined HPS-50.

hollow structures are formed during the solvent evaporation process. SEM images show that the cellular cavity polyhedrons are $\sim 500 \mu\text{m}$ in diameter, which matches well with the skeletal macropores built with adjacent struts of the PU foam scaffolds. The results show that the formation of the porous silica polyhedrons is based on the macropore architecture of the PU foam scaffolds (see Figures 2e and 2f), suggesting confinement growth. SEM images also show that the arris and vertexes of polyhedrons are smooth and spherical, implying that they are formed on the interface of the PU foam struts and partially replicated them (see Figure 2f). On the other hand, the cellular window surface is coarse, different from that for the arris and vertexes (see Figure 2f), suggesting that it is formed on the air interface during the solvent evaporation process.

3.3. Mesostructure. After calcination at 550°C for 6 h, small-angle X-ray scattering (SAXS) patterns of the hierarchically porous silica (HPS-50) prepared with a high ratio of silica sol to PU foam show three well-resolved scattering peaks (see Figure 3a), which can be indexed as the 10, 11, and 20 reflections of the 2-D hexagonal mesostructure.²⁷ The unit-cell parameter (a_0) is calculated to be $\sim 11.1 \text{ nm}$. The results clearly indicate that the calcined silica monolith (HPS-50) has an ordered mesostructure with a symmetry (space group $p6mm$) similar to that of mesoporous silica SBA-15.^{26,27} This also confirms that an ordered silica mesostructure is successfully formed through inorganic–organic self-assembly in the confined cavities of the organic PU scaffolds. In the case of low volume ratio of the cast sol to PU foam scaffolds (25%), the hierarchically porous silica monolith (HPS-25) obtained after the removal of all the organic templates also shows the resolved SAXS pattern, corresponding to a 2-D hexagonal mesostructure (see Figure 3b). Moreover, its unit-cell dimension (a_0) is also $\sim 11.3 \text{ nm}$, which is very close to that of HPS-50, implying that the mesostructure assembly is not related to the PU foam scaffolds. SAXS patterns of the hierarchically porous silica samples without aging treatment also show well-resolved scattering peaks of 2-D hexagonal

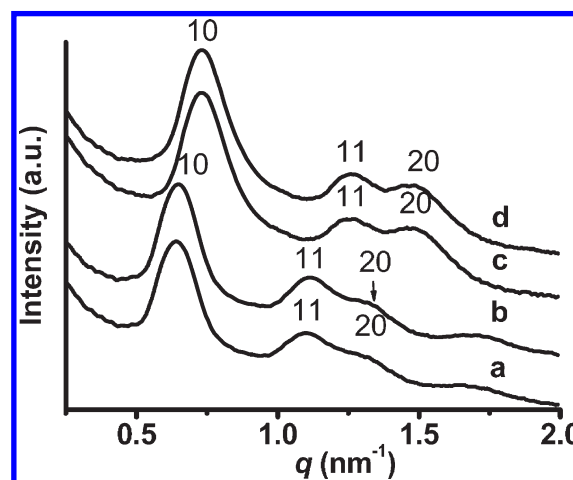


Figure 3. Small-angle X-ray scattering (SAXS) patterns of the calcined hierarchically porous silica prepared with the aging treatment (HPS-50 (spectrum a) and HPS-25 (spectrum b)) and without the aging treatment (HPS-50 (spectrum c) and HPS-25 (spectrum d)).

mesostructure at higher angles (see Figures 3c and 3d), indicating smaller unit-cell parameters ($\sim 10.2 \text{ nm}$).

Transmission electron microscopy (TEM) images of the hierarchically porous silica (HPS-50) after calcination at 550°C in air show large domains of typical striplike patterns, viewed from the $[110]$ direction (see Figure 4a). The typical hexagonally arranged patterns are also observed in the TEM image viewed from the $[001]$ direction (see Figure 4b). All the results further confirm the ordered 2-D hexagonal mesostructure of the HPS-50 silica monolith. The lattice parameter (a_0) estimated from the TEM images is $\sim 11.0 \text{ nm}$, in accordance with the values from the SAXS patterns. It further confirms that the ordered mesostructure silica assembled in the confined cavities of the skeletal PU foam scaffold is thermally stable. It is interesting that high-resolution field-emission scanning electron microscopy (FE-SEM) images of the polyhedron-like silica (HPS-50) particles broken down from the monoliths reveal ordered 2-D hexagonal mesochannel arrays on the top planes (see Figures 4c and 4d). Careful observation shows that all the cell membranes of the

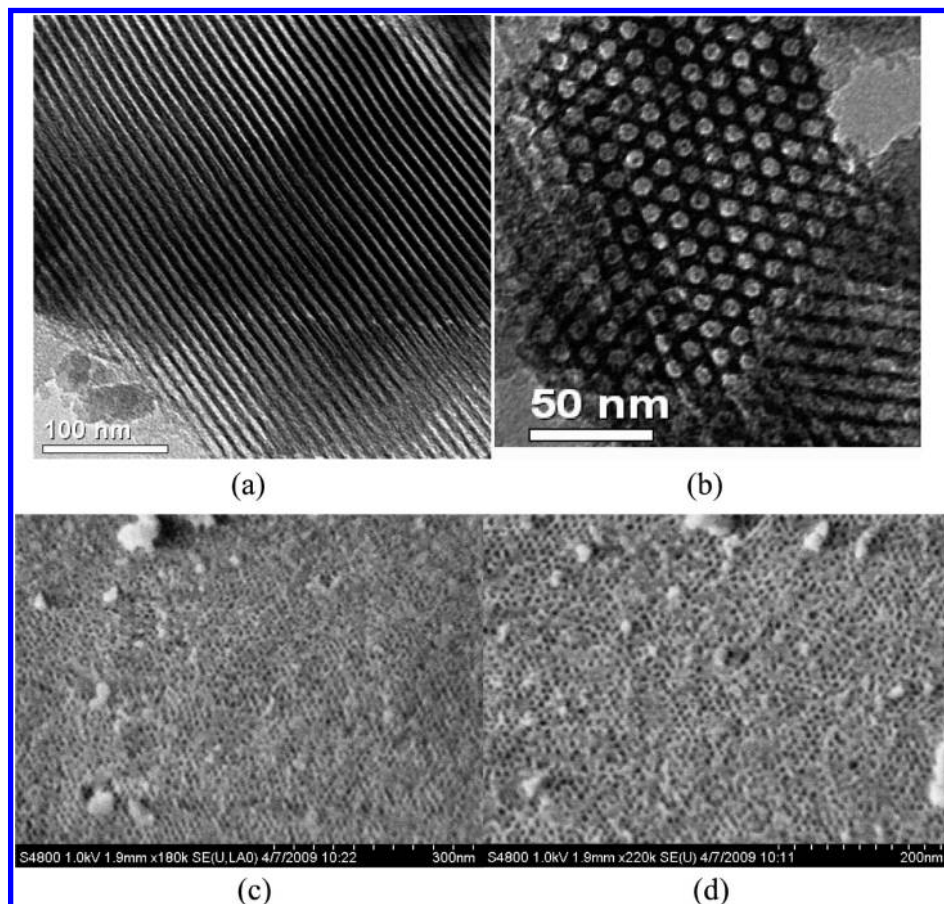


Figure 4. Transmission electron microscopy (TEM) images of the calcined hierarchically porous silica HPS-50 along (a) the [110] direction and (b) the [001] direction; panels (c) and (d) show FE-SEM images for the cellular membranes of the calcined porous silica HPS-50.

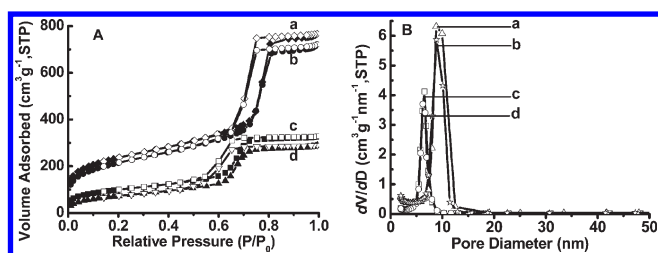


Figure 5. (A) N_2 sorption isotherms and (B) pore size distributions of the calcined hierarchically porous silica prepared with the aging treatment (HPS-50 (isotherm a) and HPS-25 (isotherm b)) and without aging treatment (HPS-50 (isotherm c) and HPS-25 (isotherm d)).

polyhedron-like silica cellular cavities have an ordered mesostructure. All the results show that the walls of cellular cavities are composed of an ordered mesostructure silica with the [001] mesochannels exposed.

3.4. N_2 Sorption Isotherms. N_2 sorption isotherms of the calcined hierarchically porous silica (HPS-50) exhibit typical type-IV curves (isotherm a in Figure 5A), similar to that for the ordered mesoporous silica reported previously.^{26,27} An obviously capillary condensation step at a relative pressure of $P/P_0 = 0.65\text{--}0.82$ is observed, suggesting a uniform pore size distribution. No steep adsorption is observed at relative pressures of $P/P_0 > 0.9$, suggesting that the macropores are too large to be measured in the N_2 sorption isotherms. It is not surprising that the macropore size is $\sim 400\text{ }\mu\text{m}$, based on the SEM observations. According to the BJH model, the

Table 1. Data from N_2 Sorption Isotherms of Hierarchically Porous Silica

sample	S_{BET} (m^2/g)	S_{Micro} (m^2/g)	pore width (nm)	pore volume (cm^3/g)
Subjected to the Aging Process				
HPS-50	777	125	9.3	1.16
HPS-25	772	121	9.1	1.12
Not Subjected to the Aging Process ^a				
HPS-50	357	44	6.5	0.51
HPS-25	334	40	6.5	0.48

^a The hierarchically porous silica without the aging process before the calcinations in air.

pore size distribution calculated from the adsorption branch has a mean value of 9.3 nm (see isotherm a in Figure 5B). H_1 -type hysteresis loops for hierarchically porous silica HPS-50 are observed, suggesting uniform cylinder mesochannels. This result is in good agreement with ordered mesostructure confirmed by the SAXS and TEM measurements. The total pore volume and BET surface area for the silica monolith HPS-50 sample are calculated to be $1.16\text{ cm}^3/\text{g}$ and $780\text{ m}^2/\text{g}$, respectively. The surface area derived from micropores is calculated from t -plots to be $\sim 125\text{ m}^2/\text{g}$ (see Table 1), suggesting few microporosities in the pore walls that are due to the high polymerization of silica frameworks. As the volume ratio of the cast sol to PU foam scaffolds decreased to 25%, N_2 sorption isotherms of the obtained hierarchically

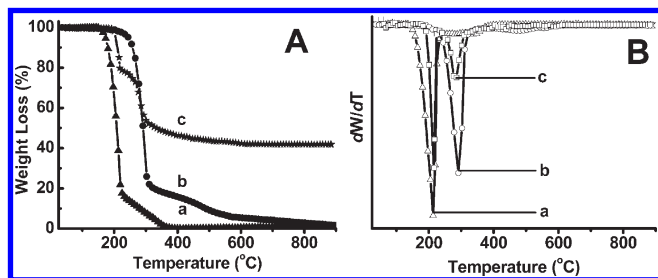


Figure 6. (A) Thermogravimetric analysis (TGA) and (B) differential thermal gradient (DTG) curves in air of the triblock copolymer P123 (curve a), the commercial PU foam scaffold (curve b), and the as-made hierarchically porous silica monolith HPS-50 (curve c).

porous silica HPS-25 also exhibit typical type-IV curves (see isotherm b in Figure 5A). The corresponding pore size distribution (isotherm b in Figure 5B), BET surface area, and total pore volume of HPS-25 are very similar to those of HPS-50 prepared with the high volume ratio of the cast sol to PU foam scaffolds (see Table 1). The results further confirm that the ratio of the silica sol to PU foam scaffolds have no distinct influences on the mesostructural self-assembly and porosities. N_2 sorption isotherms of the hierarchically porous silica without the aging treatment also exhibit typical type-IV curves and H_1 -type hysteresis loops, suggesting the uniform cylinder mesochannels (see isotherms c and d in Figure 5A). An obviously capillary condensation step at relative low pressure ($P/P_0 = 0.55\text{--}0.75$) is observed, suggesting a uniform but small pore size distribution (6.3 nm) (see isotherms c and d in Figure 5B). The total pore volume and BET surface area for the silica materials are summarized in Table 1. The BET surface area and pore volume increase after the aging treatment, while the thickness of the pore walls decreases by ~ 1 nm, because of further crosslinking of the silica species. These results further show that the aging treatment can improve the mesoporosity.

3.5. Thermogravimetric Analysis (TGA) Curves. The TGA curve in air for pure triblock copolymer Pluronic P123 shows a notable weight loss of $\sim 80\%$ at $\sim 210^\circ\text{C}$ and $\sim 20\%$ in the range of $210\text{--}370^\circ\text{C}$ (see Figure 6a), suggesting that it can be completely removed by calcination at 550°C . Two weight losses of the PU foam scaffolds occurred at $\sim 300^\circ\text{C}$ and in the range of $300\text{--}550^\circ\text{C}$, respectively, which corresponds to a total weight loss of 95% below 550°C (see Figure 6b). The results suggest that the PU foam scaffolds can be removed by the decomposition at 550°C in air. Compared to that of the Pluronic P123 template, the decomposition temperature of the PU foam scaffolds is slightly higher. Four weight-loss steps for the as-made hierarchically porous silica monolith HPS-50 are observed, at 210 , $220\text{--}270$, 280 , and $310\text{--}550^\circ\text{C}$ (see Figure 6c). The former two losses are mainly contributed from the decomposition of the triblock copolymer P123 and the latter two from the PU foam scaffolds, suggesting that P123 template is more prior than the PU foam scaffolds to be removed during the calcination. The weight loss for the HPS-50 sample is $\sim 58\%$ below 550°C . The minor weight loss ($< 1\%$) at $550\text{--}800^\circ\text{C}$ mainly ascribes to the removal of hydroxyl group and further crosslinking of silica species.

3.6. Formation of Hierarchical Structures. Based on the above observations, a confinement self-assembly route of silicate species and triblock copolymers in the skeletal PU foam scaffold cavities is proposed for the preparation of hierarchically porous materials, as shown in Figure 7. First, the sol solution containing the silica oligomers and triblock copolymers can be infused into the skeletal network of PU foam scaffolds with the aid of capillary forces. As the ethanol evaporated, the silica precursors continuously hydrolyze, cross-link, condense, and self-assemble with the triblock copolymers on the interface of PU foam scaffold struts, resulting in a coated layer of silica-triblock copolymer composites on the struts. The 3-D interconnected struts of PU foam serve as a porous substrate for the assembly of silica hexagonal mesostructure. After being dried, the swollen PU foam recovers its original shape and size. When the volume ratio of the cast sol to PU foam scaffolds is as low as 25% , the silica species and triblock copolymers self-assemble on the hydrophilic interface of the struts to form layered composite mesostructure, but are insufficient to weave the cell membranes between the adjacent struts except forming a 3-D skeleton macrostructure. A skeletal cablelike PU@Meso-SiO_2 structure is finally formed; here, the core is composed of the 3-D interconnected strut networks and the mesostructured silica-triblock-copolymer composites serve as the shell. During the aging process, the mesostructured silica shells are further cross-linked and condensed, resulting in minor shrinkage (6.5% in the linear dimensions and 18% in volume); however, the mesopore aperture and the silica lattice parameter become larger (by 1 nm) than the corresponding ones. In addition, the aging treatment improves the assembly of the mesostructure, improving the regularity and resulting in a thin silica pore wall.²⁸ During the calcination process at 550°C in air, the amphiphilic triblock copolymer templates are removed first, prior to that for the PU foam scaffolds; therefore, the silica frameworks become rigid and mesochannels are exposed and accessible. During this process, the uniform shrinkage of silicates along every direction occurs and ensures a faithful replication of the skeletal macroarchitecture. With continued heating at 550°C for 6 h in air, the PU foam struts are removed, and triaxial tubular hollow cavities are formed. Finally, the hierarchically porous silica monolith with ordered mesoporous structure and replicated macropore morphology from the foams is obtained. Because of the hedge of the struts, the silica linkage is not strong enough along the frameworks of struts, resulting in low mechanical stability of the monolith. The mesostructured silica shells can probably split along the three ridges of the PU foam struts into pieces. The irregular skeleton particles are obtained from the disassembled monoliths. Both surface sides of the clapperlike particles are different: one is smooth and replicated from the foam scaffolds, and the other is coarse and formed from the air/silicate sol interface.

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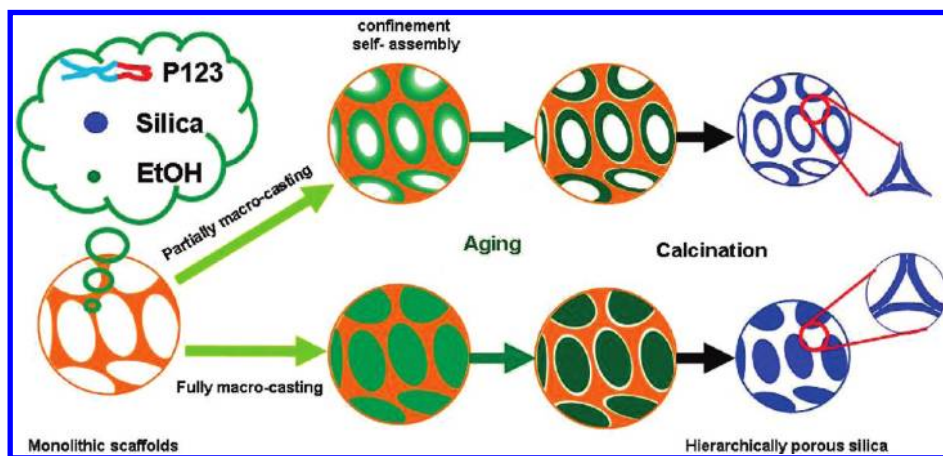


Figure 7. Schematic representation for the formation of hierarchically porous silica monoliths via confinement self-assembly in the skeleton scaffolds.

In the case of a high volume ratio of the sol to PU foam scaffolds, the silica sol is plentiful, which can cast all of the macropore cells of the PU foams, in addition to coating the foam struts. Because of the hydrophilic surface of the PU foams and the low surface tension with amphiphilic copolymer Pluronic P123, the sol can cover the entire surface of the macropore cells $\sim 100\ \mu\text{m}$ in size, resulting in the formation of the cellular silica membranes. The extra silica sols can be accommodated as drops in the cellular cavities for further confined assembly. Similarly, during the evaporation process, the silica precursors can self-assemble with block copolymers Pluronic P123 under the confinement of PU foams to form mesostructured silica–copolymer composite layers. The mesostructured silica not only coats the strut networks, but also forms cell membranes on the adjacent struts. The cellular cavities with one or two windows are fabricated with the silica cell membrane sharing the connected struts of PU foam scaffolds. A stacked “lantern@cage” structure is finally formed, where the lanterns are decorated by the white mesostructured silica cellular cavities (polyhedrons) and the strut networks of PU foam scaffolds serve as the cages. The silica membranes, like semitransparent cells, are fabricated and bridged the both sides of the cellular cavities. The cages of the “lanterns” are partially filled by mesostructured silica composites, depending on the concentration of the sols. Thousands of “lantern@cages” interconnect and pack to hierarchically porous silica monolith. During the aging process, minicracking between cellular cavities and PU struts is caused by the further crosslinking of silica species and the shrinkage of PU struts. After the Pluronic copolymer templates and the PU foam scaffolds are removed by calcination at $550\ ^\circ\text{C}$ in air, the hierarchically porous silica monoliths with ordered mesostructure are obtained. Because of the removal of the struts network, the silica monoliths are not mechanically stable and can be disassembled along the ridges of the shared struts into polyhedron-like particles with cellular cavities, which are molded by the skeletal cell of PU foam. Interestingly, FE-SEM images show that ordered mesochannels of hierarchically porous silica particles are accessible and

aligned vertically, relative to the macropore walls. The special structure benefit the molecules pass through the macropore wall along the mesochannels.

In summary, the approach of confined self-assembly in the skeletal scaffolds is simple and facile to construct hierarchically porous materials. The sizes and morphologies of macropore cells or polyhedrons are controlled in the “confinement” space. However, the “confinement” of the macropore skeleton scaffolds is weak to confine the self-assembly of ordered mesostructures, because the macropores are large as several hundred micrometers. The thickness of the macropore walls is mainly dependent on the cast amount of the silica precursors. Our approach has following features: (i) the PU foam used here contains much-larger voids that formed from colloid PS or PMMA spheres, which slightly affect the assembly of the silica mesostructure (therefore, highly ordered mesostructures can easily be obtained); (ii) depending on the coating amount and surface tension, the silicate oligomer–surfactant sols can not only be coated on the PU foam struts, but also the strut networks to form ordered mesostructured silica membranes with oriented mesochannels. After disassembled, irregular skeleton-like and polyhedra mesoporous silica particles can be obtained; (iii) the PU foam is commercially available and much less expensive than PS or PMMA colloid beads; (iv) PU foams with diverse properties (including porosity, texture, compatible surface and morphology) can be used as scaffolds to prepare different target materials. In combination with the diversity of PU foam scaffolds, the skeleton-templating strategy can provide control over the shape and self-assembly of the ordered mesostructure, such as metal oxides, transition-metal oxides, etc.

3.7. Removal of MC-LR. Microcystins (MCs), which are hepatotoxic cyclic peptides, are produced by cyanobacterium and can cause poisoning of animals and present health risks to humans. MCs are extremely stable and can persist for months or years in natural water.²⁹ Cyclic heptapeptide MCs consist of five invariant amino acids and X-, Z-variable amino acids. There are more than

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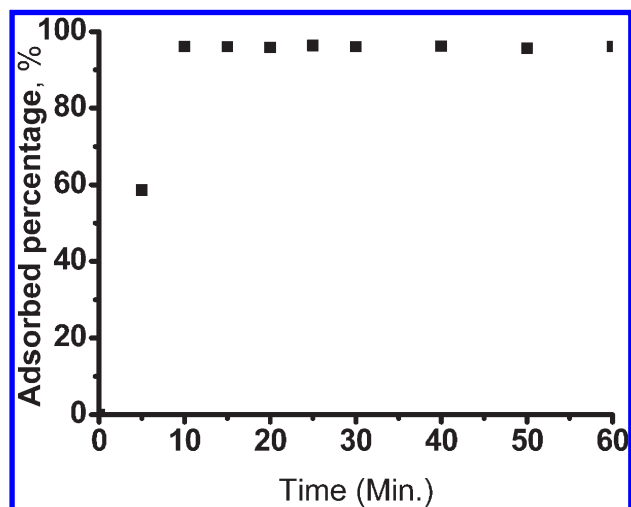


Figure 8. Percentage of MC-LR adsorbed on the calcined hierarchically porous silica polyhedron-like monoliths HPS-50 functioned with the contact time in acidic media (pH 4) at 25 °C.

60 types of MCs, as a result of the two variable amino acids.³⁰ MC-LR, RR, and YR are the dominant types of MCs, and MC-LR has the most toxicity. Many methods have been used to remove MCs from water, such as sand filtration, chlorination, ozone treatment, photoirradiation, active carbon adsorption, etc.^{31–35} However, the micropores of active carbon are not large enough to accommodate MC-LR molecules, which is ~1.9 nm and the adsorption mainly is dependent on the mesopores and the macropores.^{36,37}

Here, the obtained hierarchically porous silica monoliths were used as adsorbents to remove the MC-LR in acidic media (pH 4) under static conditions. Figure 8 shows the batch kinetic removal curves, presented by the percentage adsorbed versus contact time. Approximately 60 wt % of the MC-LR can be adsorbed by calcined HPS-50 sample in 5 min, and 96 wt % in 10 min. With the time prolonged up to 60 min, the adsorption percentage almost keeps constant, suggesting that a contact time of 10 min is sufficient for attaining the adsorption equilibrium. The residual MC-LR concentration (0.4 $\mu\text{g/mL}$) of the supernatant is higher than the standard concentration (0.001 $\mu\text{g/mL}$) of safe drinking water, which is proposed by the World Health Organization.³² Our results show that the calcined hierarchically porous silica polyhedrons (HPS-50) can adsorb ~96 wt % of MC-LR, while only

Table 2. Hierarchically Porous Silica Materials for the Adsorption of MC-LR

silica materials	q_c ($\mu\text{g}/\text{mg}$)	adsorbed percentage (wt %)
Subjected to the Aging Process		
HPS-50 polyhedron	0.48	96
HPS-50 powder	0.45	89
Not Subjected to the Aging Process ^a		
HPS-50 polyhedron	0.31	61
HPS-50 powder	0.44	88

^a The hierarchically porous silica without aging process before the calcinations in air.

89 wt % adsorption is observed for the ground HPS-50 sample (see Table 2). We determined that the hierarchically porous silica monoliths (or polyhedrons) not only have a larger adsorbed amount of MC-LR than the powder, but also better stability than the latter against the runoff in practice. The enhanced adsorption efficiency may be attributed to the macropores, which provides large pathways to access the silica mesochannels for MC-LR molecules. After it is ground to a powder, the macropores and hierarchical porosity are destroyed, and, thus, the adsorption efficiency decreases. Under the same conditions, the polyhedron-like sample HPS-50 without the aging treatment can adsorb only 61 wt % of the MC-LR, whereas ~88 wt % for the treated sample. The improved adsorption efficiency is probably related to the exposition and accessibility of more mesochannels after the aging treatment.

4. Conclusions

A confinement self-assembly approach for the synthesis of macroporous/mesoporous silica materials is demonstrated using skeletal-structured polyurethane (PU) foam as macrostructure scaffolds and triblock copolymer Pluronic P123 as a mesostructure template. Hierarchically porous silica monoliths are obtained through a macrocasting of PU foam skeletons with the sol solution containing prehydrolyzed silicate precursors and Pluronic P123. The volume ratio of the casting sol to PU foam scaffolds has great influence on the morphological fashion of porous silica, which is not related to the mesostructural assembly. When the ratio is low (~25%), mesostructured silica-copolymer composites can coat the PU foam struts, and the macropore structure with the size of ~400 μm is faithfully replicated from PU foam scaffolds. When the volume ratio is higher than 50%, the silica sol can not only coat the struts, but also cover the entire surface of macropore cells to form the cellular silica membranes and further grow inside the cellular cavities, resulting in a stacked “lantern@cage” structure. The silica monoliths can be disassembled, and mesoporous polyhedron-like particles with cellular cavities are obtained. The hierarchically porous silica has an ordered two-dimensional (2-D) hexagonal mesostructure with space group of $p6mm$. The mesochannels are aligned vertically, relative to the macroporous wall of cellular cavities with a diameter of ~500 μm . They have uniform mesopore size (6.5–9.3 nm),

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high surface area (340–780 m²/g), and large pore volume (0.48–1.16 cm³/g). The hierarchically porous silica polyhedrons with exposed mesochannels can effectively remove (>96 wt %) microcystin-LR (MC-LR) in water.

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