Morphological Control of Highly Ordered Mesoporous Silica SBA-15

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Mesoporous materials are of great interest to the materials community because their pore structures as well as catalytic, adsorbed, conductive and magnetic properties can readily be tailored.[1−8] Recently, a highly ordered large mesoporous silica SBA-15 was synthesized by using amphiphilic triblock copolymers as the structure-directing agents.[5,6] It is now apparent that morphology and texture of mesoporous silica are extremely important for industrial applications,[2−6,8−19] and by use of acid-based synthesis,[7,20] mesoporous silica films, spheres, hollow spheres, and fibers have been synthesized for this purpose.[10,13−19] There have also been several reports that describe methods to control the shapes of smaller mesoporous particles.[14,15,18,21−23]

We previously reported synthesis of spongelike meso−macroporous silica membranes by the multiphase assembly and inorganic salts (such as NaCl, LiCl) as the macroporous structure templates.[23] Lin et al.[22] have synthesized hollow mesoporous silicate spheres with hierarchically ordered structures by using butanol as a cosurfactant. Recently, Shio et al.[21] have described the synthesis of fine and rodlike mesoporous silica powder from completely dissolved aqueous solutions of sodium metasilicate and cationic surfactants. In this communication, we report a morphological control approach using block copolymers, cosurfactants, cosolvents, or the additive of strong electrolytes to selectively form micrometer-sized hard sphere-, fiber-, doughnut-, rope-, egg-sausage-, gyroid-, and discoidlike mesoporous silica SBA-15 with highly ordered large mesopore hexagonal structures.

Fiberlike mesoporous SBA-15 was synthesized by using tetramethyl orthosilicate (TMOS) as a silica source and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, $M_{\text{avg.}} = 5800$, $EO_{20}PO_{70}EO_{20}$, P123) as the structure-directing agent.[5,6] In a typical synthesis, 2.0 g of P123 block copolymer was dissolved with stirring in a solution of 45.0 g of water and 30.0 g of HCl (4 M), and then 3.1 g of TMOS was added with stirring at 40 °C. After being stirred for 20 h at 40 °C, the gel solution was transferred into a Teflon bottle and heated at 100 °C for 24 h without stirring. After being cooled to room temperature, the solid product was recovered by filtering without washing and was dried at room temperature in air.

Doughnutlike mesoporous SBA-15 powder was prepared by using *N*,*N*-dimethylformamide (DMF) as a cosolvent according to above procedure except that tetraethyl orthosilicate (TEOS) was used as the silica source. A typical reaction composition was 2.0 g of P123: 30 g of H_2O:15 g of DMF:30 g of (4 M) HCl:4.4 g of TEOS.

Micrometer-sized hard sphere mesoporous SBA-15 was synthesized by using a cationic surfactant, cetyltrimethylammonium bromide (CTAB) (Aldrich), as a cosurfactant according to above procedure with a typical composition of 2.0 g of P123:0.2 g of CTAB:45.0 g of (2 M) HCl:15.0 g of H_2O:5.8 g of TEOS.

Gyroid- and discoidlike morphology mesoporous SBA-15 were synthesized by prehydrolyzing TEOS in

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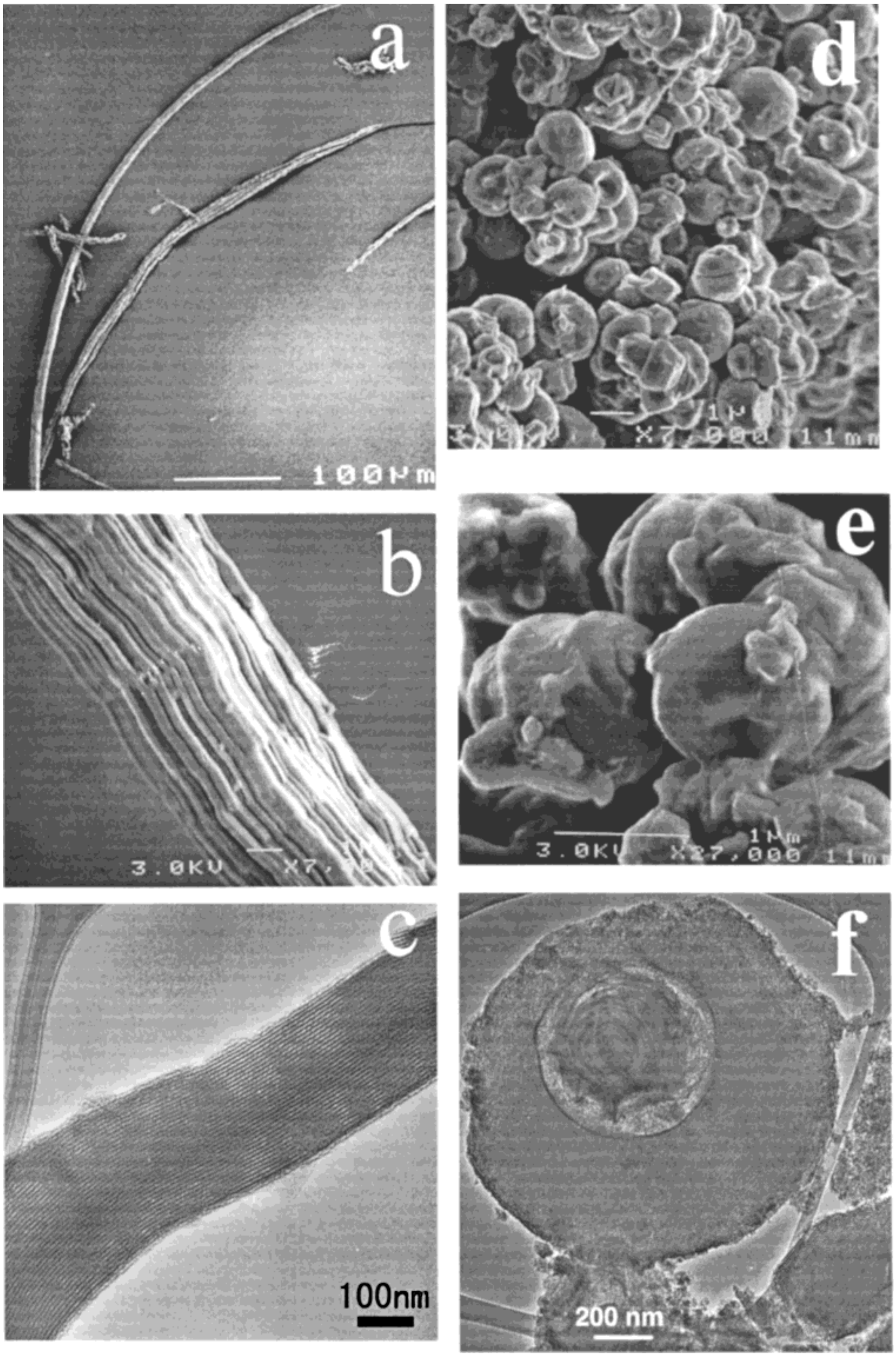

Figure 1. Scanning electron micrographs (a), (b), (d), and (e) and transmission electron micrographs (c) and (f). (a) and (b) As-synthesized mesoporous silica SBA-15 prepared by using TMOS as the silica source. (c) SBA-15 from part a calcined at 500 °C for 6 h in air. (d) and (e) As-synthesized mesoporous SBA-15 prepared by using DMF as a cosolvents. (f) SBA-15 from part d calcined at 500 °C for 6 h in air. SEM images were obtained on a JEOL 6300-F microscope and a Hitachi S-520 microscope. TEM were taken on a Philips EM430 electron microscope operating at 200 kV. For TEM measurements, the sample was prepared by dispersing the powder products as a slurry in acetone and subsequently deposited and dried on a honey carbon film on a Cu grid.

ethanol (EtOH) solution by an acid-catalyzed process to obtain an oligomeric silica sol, [13,23] which was added to a solution of P123 triblock copolymer and inorganic salts in water and ethanol. The final composition of the mixture was 1.0 TEOS:0.03 P123:1.0 $MgSO_4$ or Na_2SO_4: 65 H_2O:0.005 HCl:40 EtOH (mol ratio). The solid products were obtained after being dried at room temperature and washed with water to remove residual inorganic salts. The calcination was carried out in an oven at 500 °C for 6 h in air to remove the block copolymer species.

Figure 1 shows several representative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images for mesoporous silica SBA-15. The morphology of mesoporous SBA-15 can be controlled by the silica source and the hydrolysis products associ-

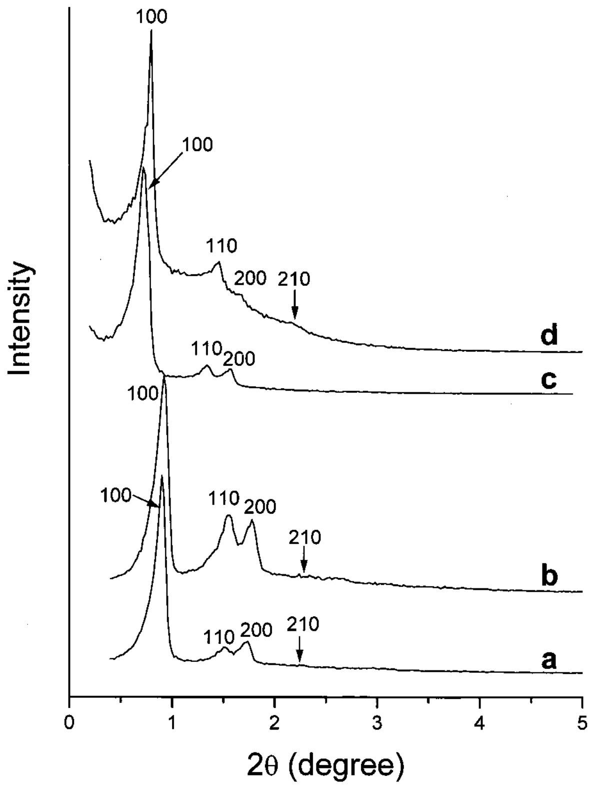

Figure 2. Powder X-ray diffraction patterns of (a) as-synthesized and (b) calcined fiberlike mesoporous silica SBA-15 prepared using TMOS as a silica source and (c) as-synthesized and (d) calcined doughnutlike mesoporous silica SBA-15 prepared by using DMF as a cosolvent. XRD patterns were acquired on a Rigaku D/Max-IIA PADX diffractometer using Cu Kα radiation.

ated with the silica source. TMOS yields fiberlike mesoporous silica SBA-15 in the presence of the amphiphilic triblock copolymer P123 (Figure 1a,b). The yield for fiberlike solid product is as high as 95% (no less than that calculated from silica). Fiberlike mesoporous SBA-15 can have a long aspect of as much as several hundred micrometers with a relatively uniform diameter of $\sim$10 μm that is made up of a bundle of wires of diameter $\sim$300 nm, as shown in Figure 1a,b. X-ray diffraction (XRD) patterns of as-made fiberlike mesoporous SBA-15 (Figure 2a) show four diffraction peaks that can be indexed to (100), (110), (200), and (210) reflections with cell parameter a = 11.8 nm. The observation is in agreement with that of our previous reports, [5,6] indicating that as-made fiberlike mesoporous SBA-15 has a well-ordered two-dimensional (2D) mesostructure (p6mm). After calcination at 500 °C in air, the four diffraction peaks can be observed with a small contraction in d spacing (a = 11.0 nm), and increased intensities of these peaks (Figure 2b), indicating that highly ordered mesoporous structures of fiberlike SBA-15 are stable. As shown in parts a and b of Figure 2, the intensities of the (110) and (200) reflections are increased upon calcination compared to that of the (100) reflection. SEM images show that after carefully being calcined, the fiberlike morphology for mesoporous SBA-15 is retained, indicating that the macroscopic structure of fiberlike SBA-15 is thermally stable. TEM images (Figure 1c) further confirm this conclusion and show that the parallel orientation of channels for fiberlike SBA-15 is preferably along the long axis.

When a longer alkyl chain orthosilicate such as TEOS is used as the silica source, ropelike mesoporous SBA-15 (Figure 3a) can be formed under similar acidic synthesis condition with a yield of $\sim$98%.[5,6] The diameter size ($\sim$1 μm) of the rope is relatively uniform, and the rope can be aggregated into a wheatlike macroscopic structure (10 × 80 μm^2).[5,6]

The morphology of mesoporous SBA-15 can also be controlled by the cosolvent. When DMF as a cosolvent is added into the synthesis solution, doughnutlike SBA-15 particles can be obtained with a yield of $\sim$94% (Figure 1d,e). The diameter of the doughnutlike particles is relatively uniform, about 1 μm. TEM images of doughnutlike SBA-15 (Figure 1f) show that it consists of a highly ordered 2D hexagonal mesostructure with circle channels. XRD measurements further confirm that doughnutlike SBA-15 has an ordered hexagonal mesostructure (p6mm).[5,6] As shown in Figure 2c, the XRD pattern of as-made SBA-15 with cosolvent DMF consists of three diffraction peaks at a 2θ range of 0.5$-$2°, which correspond to (100), (110), and (200) reflections.[5,6] The (210) diffraction is too broad to be observed. The d spacing (12.5 nm) for the (100) reflection is substantially larger than that without DMF.[5,6] After calcination at 500 °C in air, the diffraction intensities increase due to the further cross-linking of silicates, the d spacing (11.0 nm) of the (100) reflection decreases due to contraction (about 11%), and an additional diffraction peak corresponding to the (210) reflection is observed (Figure 2d). It is interesting that both morphological curvature and the d (100) spacing of as-made and calcined mesoporous silica SBA-15 increase with the amount of cosolvent DMF.[5,6] As shown in Figure 3b, when a smaller amount of DMF is added into the synthesis solution, egg-sausage-like mesoporous silica SBA-15 can be formed. The egg-sausage-like SBA-15 particles have a relatively uniform size ($\sim$1 μm) with a diameter of $\sim$700 nm and tend to aggregate into a wheatlike macroscopic structure ($\sim$100 × 8 μm^2 in size). In addition, when ethanol and tetrahydrofuran (THF) are used as the cosolvents, the longer egg-sausage-like or ropelike SBA-15 particles can be obtained (Figure 3c). In general, more highly polar cosolvents introduce more curvature for a given reaction mixture. Cosolvents can function as swelling agents (such as 1,3,5-trimethylbenzene), and form microemulsions,[5,6] resulting in the formation of large pores. Nitrogen adsorption and desorption measurements also reveal that the mesopore size of the calcined SBA-15 synthesized by using DMF as the cosolvent increases with the amount of DMF added (see below).

The morphology of mesoporous SBA-15 can also be controlled by the addition of highly concentrated or charged inorganic electrolytes such as $MgSO_4$ and Na_2SO_4 through a multiphase assembly process.[23] For example, when prehydrolyzed TEOS in EtOH solution is added into a copolymer surfactant solution containing the inorganic salt Na_2SO_4, gyroidlike SBA-15 particles are formed after drying and washing (Figure 3d). The yield ($\sim$100%, calculated from silica) is much higher. In addition, discoid morphological mesoporous silica SBA-15 crystals are formed in the presence of the inorganic salt $MgSO_4$ (Figure 3e). Highly ordered hexagonal 2D (p6mm) mesostructures of gyroid- and

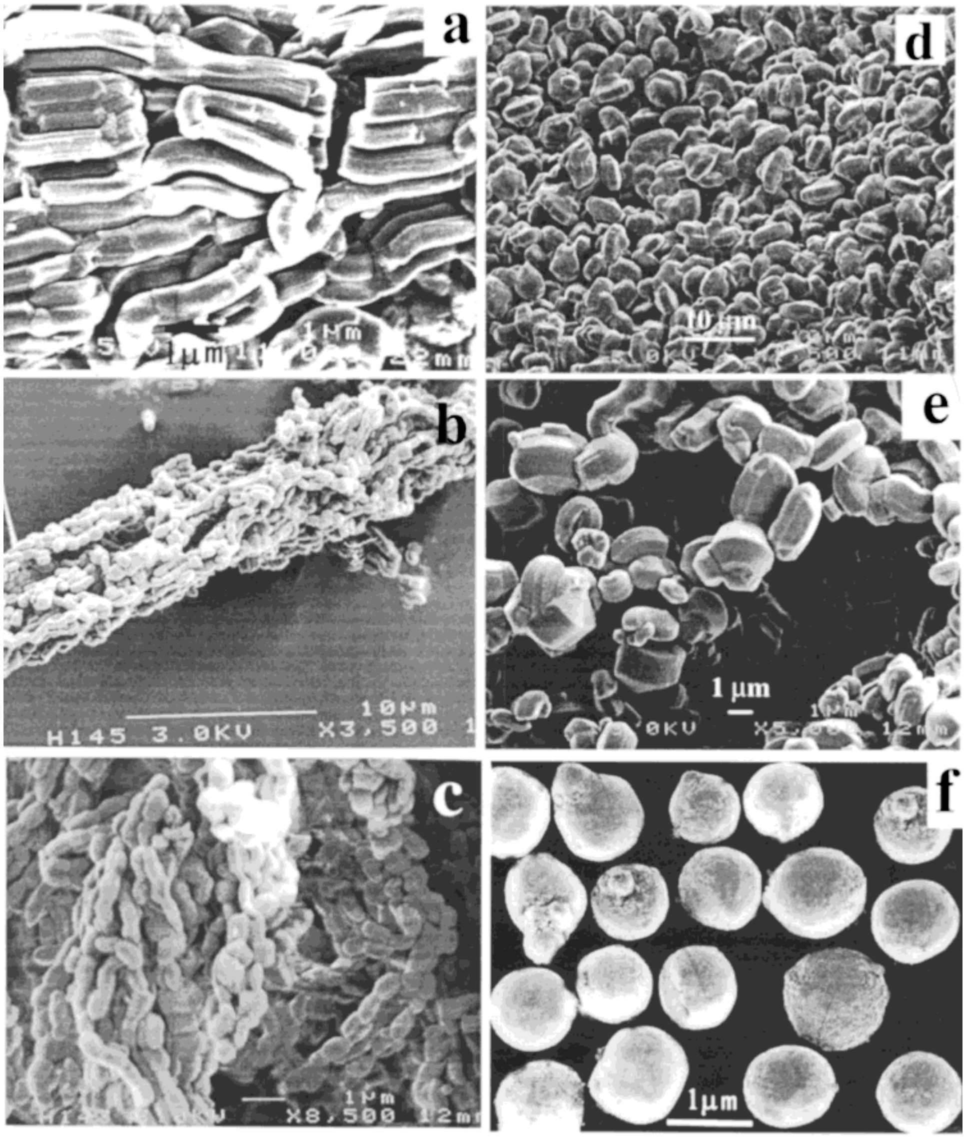

Figure 3. SEM images: (a) as-synthesized SBA-15 prepared by using TEOS as a silica source; (b) and (c) as-synthesized SBA-15 prepared by using small amounts of DMF (part b) and THF (part c) as the cosolvents; (d) and (e) as-synthesized SBA-15 prepared by using P123 block copolymer in Na_2SO_4 (part d) and $MgSO_4$ (part e) solution; and (f) hard sphere SBA-15 prepared by using CTAB as a cosurfactant.

discoidlike morphological SBA-15 are also confirmed by XRD and TEM measurements. Both as-made and calcined SBA-15 show three well-resolved diffraction peaks in the 2θ range of 0.5−3 °, which is similar to what we previously reported.[23] TEM images of these mesoporous SBA-15 materials show many circle mesoporous channels similar to those of the doughnutlike SBA-15 (Figure 1f).[14,15] However, when low-charge inorganic salts such as NaCl, LiCl are used, 3D continuous meso−macroporous silica membranes can be formed.[23] We have previously demonstrated that this process is the result of a multiphase assembly.[23] The macroscopic structures with gyroid- and discoidlike morphologies are formed around aqueous inorganic salt solution droplets, which macroscopically phase separate from the assembling inorganic oxide-block copolymer mesophase during evaporation of the ethanol.[23]

Hard sphere mesoporous SBA-15 can be synthesized by using the cationic surfactant CTAB as a cosurfactant under acidic condition. The yield for SBA-15 spheres can reach 90%. As shown in Figure 3f, the diameters ($\sim$1 μm) of the spheres are quite uniform and increase with the concentration of CTAB. XRD measurements of the mesoporous silica spheres show a small broad diffraction peak at a 2θ scattering of $\sim$0.8° with a *d* spacing of 11.0 nm; if indexed as hexagonal to the (100) reflection, two additional peaks can be indexed as (110) and (200) reflections in p6mm. The (100) diffraction peak of the hard sphere SBA-15 becomes broader as the amount of cosurfactant is increased in the synthesis.[5,6]

Representative nitrogen adsorption/desorption isotherms and the corresponding pore size distribution (analyzed by using the Broekhoff and de Boer model[24]) are shown in Figure 4. Fiberlike mesoporous silica SBA-15 prepared by using TMOS yields an isotherm (type IV) with H_1-type hysteresis that is typical of mesoporous materials with 1D cylindrical channels (Figure 4a).[5,6] A narrow pore size distribution with a mean value of 80 Å is found for both the adsorption and desorption processes. This material has a Brunauer−Emmett−Teller (BET) surface area of 710 m^2/g and a pore volume

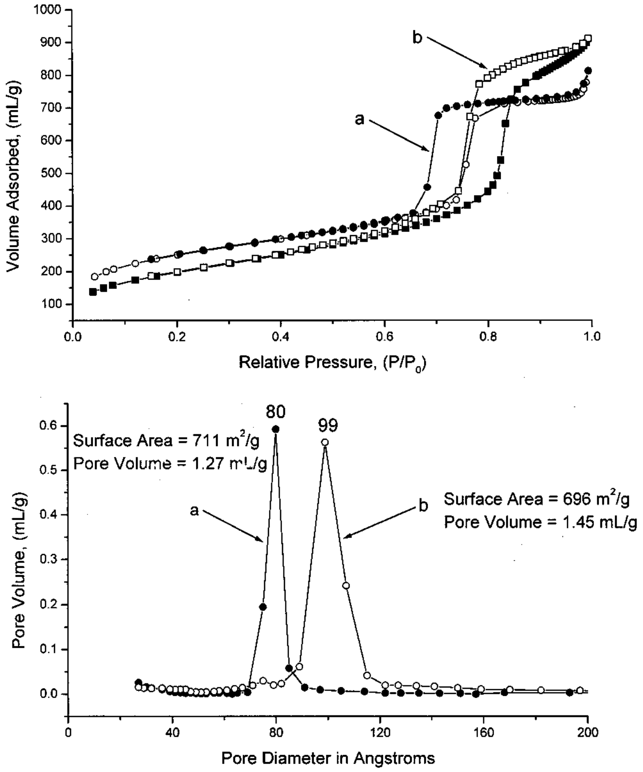

Figure 4. Nitrogen adsorption−desorption isotherm plots (top) and pore size distribution curves (bottom) for (a) calcined fiberlike mesoporous silica SBA-15 prepared using TMOS as a silica source and (b) calcined doughnutlike mesoporous silica SBA-15 prepared by using DMF as a cosolvent. The isotherms were measured using a Micromeritics ASAP 2010 system. The data were calculated by using the BdB (Broekhoff and de Boer) model. The pore size distribution curve was obtained from an analysis of the adsorption branch of the isotherm. The sample was pretreated at 200 °C overnight on a vacuum line.

of 1.3 mL/g, which is similar to that we previously reported,[5,6] confirming that the pore size and BET surface area for mesoporous SBA-15 are not dependent on the silica source but on the nature of the amphiphilic block copolymer species and its associated cosolvent. Mesoporous SBA-15 prepared with DMF cosolvent, such as the doughnutlike morphology SBA-15, also yields a type IV isotherm with H_1-type hysteresis, for a typical 1D hexagonal cylindrical channel mesoporous material (Figure 4b).[5,6] The mesopore size associated with the doughnutlike morphology is 99 Å, and the pore volume is 1.45 mL/g. Compared to values obtained under similar reaction conditions for mesoporous SBA-15 without cosolvent,[5,6] it appears that the cosolvent functions as a swelling agent.

The shape of mesoporous silica SBA-15 powder is controlled by several complex factors including (1) the condensation rate of silica species, (2) shape of surfactant micelles, (3) the concentration of inorganic salts, and (4) stirring rate.[21,22,27–29] In particular, it is evident that the macroscopic mesoporous SBA-15 morphology is crucially dependent on the local curvature energy that is present at the interface of the inorganic silica and amphiphilic block copolymer species. Michalet and Bensimon[25] recently assigned the equilibrium shapes of phospholipid vesicles in solution to various topological genus by accounting for the minimization of the elastic energy of a homogeneously curved surface.[25] We have previously also observed curved surface morphologies in MCM-41 resulting from disinclination and dislocation.[26] When TMOS is used as the silica source, the condensation rate of silicate species is fast, which results in a high local curved energy, so that energy penalty for cylindrical channel bending is also high and results in the formation of fiberlike SBA-15 macroscopic structure with straight channels. Slower condensation rates (such as that for TEOS) yield a more curved ropelike SBA-15 morphology. Polar cosolvent such as DMF can interact with amphiphilic block copolymer species, resulting in lower local curvature energy and formation of a more curved macroscopic structure, the doughnutlike morphology for SBA-15. Addition of cosurfactant and concentrated strong inorganic salts can lower the local curvature energy and facilitate the formation of curved morphologies for SBA-15 such as sphere-, gyroid-, and discoidlike.

In summary, highly ordered hexagonal mesoporous silica SBA-15 with tunable morphologies such as fiber-, rope-, doughnut-, sphere-, gyroid-, and discoidlike have been synthesized through the cosolvent, cosurfactant, and inorganic electrolyte approaches. Fiberlike SBA-15 prepared by using TMOS as the silica source under acidic synthesis condition can be long as several hundred micrometers with a relatively uniform diameter size ($\sim$1 μm) and shows highly ordered mesostructure with straight channels parallel to the long axis. Doughnutlike SBA-15 prepared by using DMF cosolvent shows highly ordered circle mesochannels, a large mesopore size of 9.9 nm and high pore volume of 1.45 mL/g. Highly ordered mesoporous silica spheres with uniform diameters of $\sim$1 μm can be synthesized by using cationic surfactant CTAB as the cosurfactant. The morphology of mesoporous SBA-15 is strongly dependent on the surface curvature energy at the interface of inorganic silica and organic block copolymer species.

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