

# Micrometer-Sized Mesoporous Silica Spheres Grown under Static Conditions

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Mesoporous silica spheres ranging from 2 to 6  $\mu\text{m}$  in size were synthesized under static acidic conditions by mixed cationic–nonionic surfactant templating. The mesoporous structure of the calcined silica microspheres was characterized by X-ray diffraction (XRD) and nitrogen sorption, whereas the morphology and size of the microspheres were revealed by scanning electron microscopy (SEM). It was shown that stirring is unfavorable for the formation of silica spheres in the present synthesis. The growth of the micrometer-sized mesoporous silica spheres was examined by transmission electron microscopy (TEM), and an undirectional aggregation process was proposed for the formation of these spheres.

## Introduction

The discovery of the M41S family of mesoporous silicas<sup>1,2</sup> has stimulated wide interest in the surfactant-templated synthesis of mesoporous materials because of their potential applications as versatile catalysts, catalyst supports, separation media, and hosts for clusters and nanowires. Mesoporous silica molecular sieves have been prepared by ionic<sup>1–4</sup> and neutral<sup>5,6</sup> surfactant templating pathways; however, the obtained mesoporous silicas normally yield irregular agglomerates consisting of a wide particle size distribution.<sup>7</sup> Because the control of the particle morphology and size of mesoporous silicas could open up new possibilities for the application of mesoporous silicas as a packing material in chromatography or as an easy-to-handle form for catalytic purposes, some recent efforts have been devoted to the synthesis of mesoporous silica spheres of defined size. For example, millimeter-sized mesoporous silica spheres ranging from 0.1 to 2 mm in size<sup>8</sup> and submicrometer-sized mesoporous silica spheres ranging from 0.4 to 1.1  $\mu\text{m}$  in size<sup>9</sup> have been synthesized under stirred basic conditions by modified cationic surfactant templating routes. However, further efforts are required toward the synthesis of micrometer-sized mesoporous silica spheres, which could be directly used in high-performance liquid chromatography (HPLC) and related separation techniques.<sup>9</sup> It is noteworthy that

mesoporous silica spheres with diameters of 1–100  $\mu\text{m}$  have been synthesized under stirred acidic conditions by emulsion templating; however, the obtained microspheres are in fact hollow after the organic phase has been removed and are readily crushed.<sup>10</sup>

Recently, mesoporous silica that produces a remarkable array of shapes and surface patterns has been synthesized under quiescent acidic conditions, which favor curved morphologies including toroidal, disklike, spiral, and spheroidal shapes.<sup>11</sup> This result led us to explore the possibility of the synthesis of mesoporous silica spheres under static acidic conditions. On the other hand, mixed surfactants have been used as mixed micellar templates for the synthesis of mesoporous silicas with modified properties recently; examples include the mixed cationic surfactant templating route to mesoporous silicas with tunable mesophase configurations<sup>12</sup> or mesopore sizes.<sup>13</sup> It is well-known that cationic surfactants can interact with nonionic surfactants to form mixed surfactant micellar aggregates in aqueous solution.<sup>14</sup> Therefore, it could be expected that the mesoporous silica synthesized in the presence of mixed cationic–nonionic surfactant micellar templates would possibly exhibit modified morphology. This report describes the first synthesis of mesoporous silica spheres ranging from 2 to 6  $\mu\text{m}$  in size under static acidic conditions by mixed cationic–nonionic surfactant templating. The typical product was characterized by X-ray diffraction (XRD), nitrogen sorption, and scanning electron microscopy (SEM). The growth of the micrometer-sized mesoporous silica spheres was examined by transmission electron microscopy (TEM), and an undirectional aggregation process was proposed for the formation of these spheres.

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(4) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schuth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

(5) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

(6) Bagshaw, S. A.; Prouzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.

(7) Tanev, P. T.; Pinnavaia, T. J. *Chem. Mater.* **1996**, *8*, 2068.

(8) Huo, Q.; Feng, J.; Schuth, F.; Stucky, G. D. *Chem. Mater.* **1997**, *9*, 14.

(9) Grun, M.; Lauer, I.; Unger, K. K. *Adv. Mater.* **1997**, *9*, 254.

(10) Schacht, S.; Huo, Q.; Voigt-Martin, I. G.; Stucky, G. D.; Schuth, F. *Science* **1996**, *273*, 768.

(11) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692.

(12) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(13) Khushalani, D.; Kuperman, A.; Coombs, N.; Ozin, G. A. *Chem. Mater.* **1996**, *8*, 2188.

(14) Holland, P. M.; Rubingh, D. N. *Surfactant Sci. Ser.* **1991**, *37*, 141.

## Experimental Section

**Synthesis.** The mesoporous silica spheres were synthesized by the hydrolysis of tetraethyl orthosilicate (TEOS) at ambient temperature in an aqueous acidic solution using cetyltrimethylammonium bromide (CTAB) and decaethylene glycol mono-hexadecyl ether ( $C_{16}EO_{10}$ ) as mixed surfactant templates. In a typical synthesis, 0.35 g of CTAB and 0.33 g of  $C_{16}EO_{10}$  were dissolved in 20 mL of 4 M HCl aqueous solution. To this solution, 1.79 g of TEOS was added at room temperature with stirring. After the complete addition of TEOS, the mixture was allowed to age for 16 h either without stirring or with additional stirring for a certain period of time. The stirring was conducted using an electromagnetic stirrer with a stirring speed of ca. 400 rpm. Then the white precipitate was recovered by filtration, washed with water, and dried at 80 °C. Finally, the product was calcined in air at 600 °C for 4 h (heating rate, 2 °C/min) to remove the surfactants.

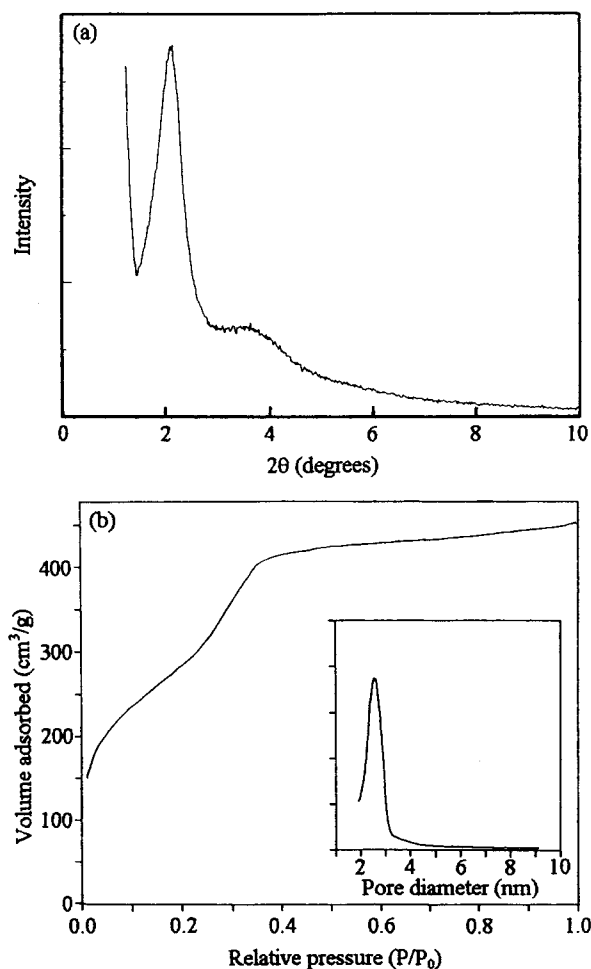
**Characterization.** The XRD pattern was obtained with a Rigaku Dmax-2000 diffractometer using Cu K $\alpha$  radiation. The nitrogen adsorption-desorption isotherm was measured at 77 K on a Micromeritics ASAP 2400. SEM micrographs were recorded with an AMARY 1910FE microscope operated at 5 kV, and TEM micrographs were taken on a JEOL 200CX microscope operated at 200 kV. Samples for TEM observation were prepared at different intervals of aging time by sonication of the precipitate in ethanol and suspension on Formvar-covered copper grids.

## Results and Discussion

The XRD pattern of the calcined mesoporous silica grown under static conditions shows an intense peak at a  $d$  spacing of 4.1 nm along with a broad shoulder (Figure 1a). This pattern is characteristic of a mesophase with a pore system lacking long-range order, which is reminiscent of the disordered mesoporous silicas prepared by nonionic surfactant templating<sup>6</sup> and made with cationic surfactant in the presence of organic salts.<sup>15</sup> The nitrogen adsorption-desorption isotherm of the product and the corresponding BJH (Barrett-Joyner-Halenda) pore size distribution curve from the adsorption branch are presented in Figure 1b. A well-defined step occurs in the adsorption curve at a relative pressure  $P/P_0$  of ca. 0.3, which is indicative of the filling of framework-confined mesopores.<sup>7</sup> The BET (Brunauer-Emmett-Teller) surface area is 1042 m<sup>2</sup>/g, and the single-point total pore volume at a relative pressure of 0.983 is 0.70 cm<sup>3</sup>/g, which gives an average pore diameter of 2.7 nm, a value in good agreement with the BJH value of 2.6 nm.

Figure 2 shows representative SEM micrographs of the calcined mesoporous silica grown under static conditions. It can be seen that the product consists almost entirely of spherical particles, although some agglomeration is evident. The sizes of these silica spheres range from 2 to 6  $\mu$ m with an average size of ca. 4  $\mu$ m. It is noteworthy that the exterior surfaces of these spheres are very smooth, which is in contrast to the faceted and corrugated surfaces exhibited by the mesoporous silica bodies synthesized under static acidic conditions by cationic surfactant templating.<sup>11</sup>

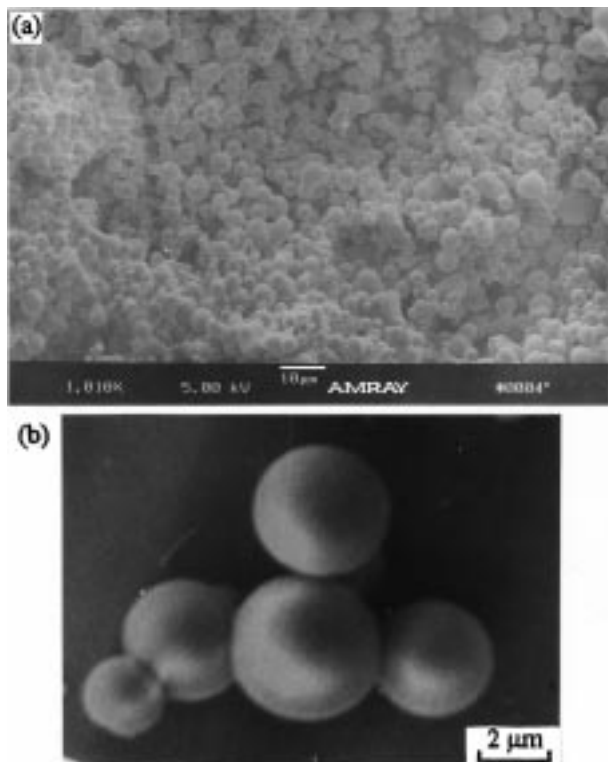
To examine the effect of stirring on the morphology of the product, two samples stirred for different periods of time after mixing were prepared. As shown in Figure 3a, the sample stirred for 0.5 h comprises two dominant



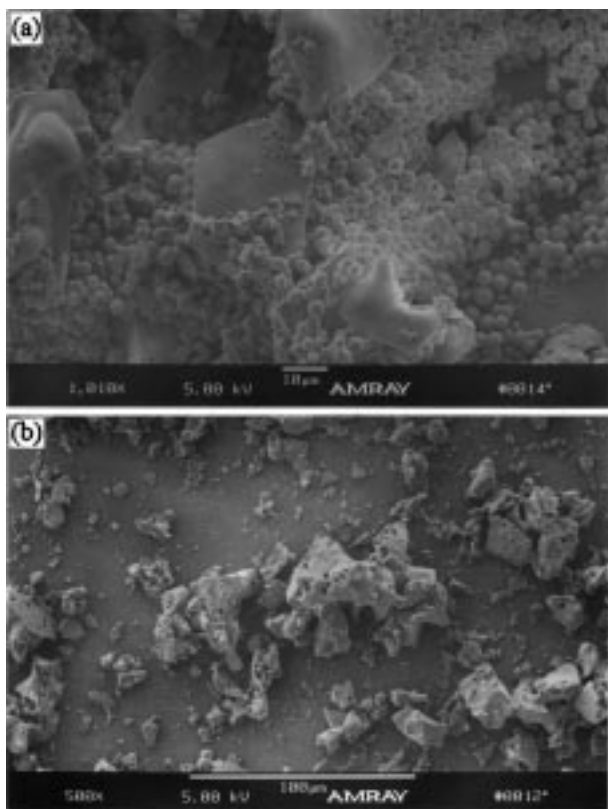
**Figure 1.** (a) XRD pattern and (b) nitrogen adsorption-desorption isotherm of calcined mesoporous silica grown under static conditions. Inset of panel b: the corresponding BJH pore size distribution curve.

morphologies. One of these has the form of micrometer-sized spheres, and the other exhibits the morphology of much larger, irregular monoliths. For the sample stirred for 16 h, only irregular monoliths can be observed (Figure 3b). This result suggests that stirring is unfavorable for the formation of silica spheres, whereas a quiescent synthesis condition favors spherical morphology.

Some insight into the formation mechanism of the mesoporous spheres has been obtained by examining TEM micrographs of the samples obtained at different stages of the sphere formation. As shown in Figure 4a, the sample aged under static conditions for 5 h exhibits nearly spherical particles of several micrometers, which show a spongy and fluffy structure, indicating their formation by aggregation of subunits, i.e., primary particles. A large number of tiny particles that lie around the micrometer-sized particles are apparently aggregating. The micrograph with a higher magnification shown in Figure 4b confirms that the exterior surfaces of these micrometer-sized particles are formed by aggregation of subunits about 0.1  $\mu$ m in size. Figure 4c presents a micrograph with an even higher magnification, which shows that the subunits have rough surfaces and contain a large number of nanometer-sized pores, indicating that under acidic conditions cationic silica solution species bind to the mixed CTAB- $C_{16}EO_{10}$



**Figure 2.** SEM micrographs of calcined mesoporous silica grown under static conditions.



**Figure 3.** SEM micrographs of calcined mesoporous silica stirred for (a) 0.5 and (b) 16 h.

micelles by counterion-mediated electrostatic binding and/or hydrogen bonding and subsequently aggregate into a mesostructure. After 16 h of aging, the micrometer-sized spongy and fluffy particles finally grow and reconstruct into much denser, perfectly spherical par-

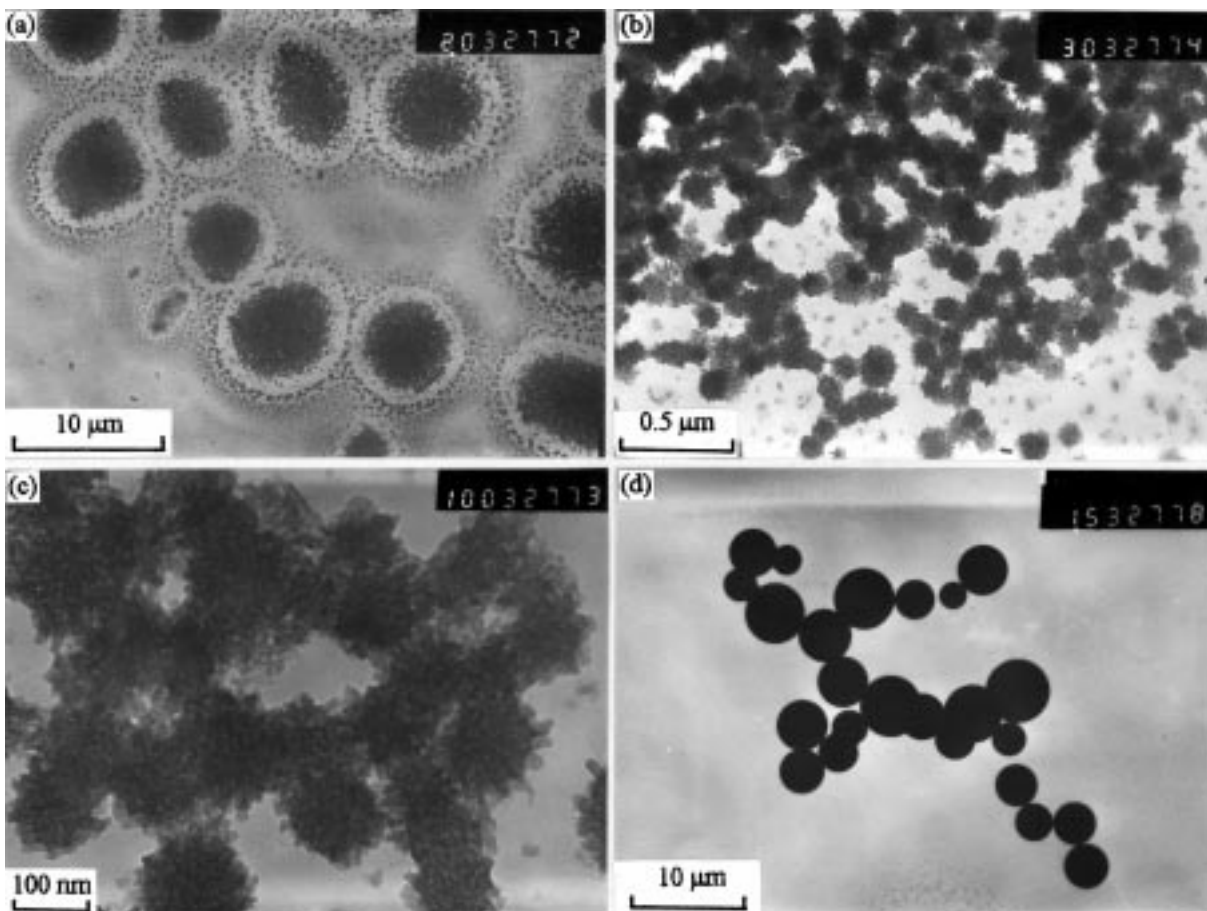
ticles ranging from 2 to 6  $\mu\text{m}$  in size (Figure 4d). The sizes of these spheres are essentially unchanged on further aging. This result demonstrates that the final mesoporous spheres result from the growth in the mother solution rather than the drying and calcination process.

According to the TEM observations, we speculatively propose that the mesoporous spheres could be formed by an unidirectional aggregation process that has been established for the formation of some monodisperse, equiaxial (spherical) inorganic particles.<sup>16</sup> First, TEOS hydrolyzes in the presence of mixed cationic–nonionic micellar templates to produce mesoporous primary particles (subunits) about 0.1  $\mu\text{m}$  in size. Then, these primary particles aggregate unidirectionally to form micrometer-sized, nearly spherical, spongy and fluffy particles, which finally reconstruct into much denser spheres with smooth surfaces through internal cementation<sup>16</sup> on aging. Such an unidirectional aggregation process could be favored under static conditions where the deposition of soluble silica species on solid silica surfaces, which could result in large monoliths, is relatively slow and aggregation between silica particles may act as a major growth mechanism. Moreover, continuous stirring may lead to unexpected coagulation between silica particles and possible damage to the preformed particle morphology.

To substantiate the proposed formation mechanism, we have examined the effects of the nonionic/cationic surfactant ratios in the mixed surfactant templates. Our preliminary results show that under similar static acidic conditions a variety of mesoporous silica bodies with faceted or corrugated surfaces together with irregularly shaped monolithic aggregates are obtained by single cationic surfactant templating. On the other hand, mesoporous silica spheres can be produced under similar static acidic conditions by single nonionic surfactant templating; however, there is relatively severe agglomeration, and the presence of very large aggregates of spherical particles is evident. When mixed cationic–nonionic surfactant templates are used, the products contain spherical particles, and the proportion of spherical particles in the products increases with increasing nonionic/cationic surfactant ratios until the product consists almost entirely of spherical particles. With further increases in the nonionic/cationic surfactant ratio, the agglomeration of the spherical particles seems to become more severe. These results indicate that the presence of nonionic surfactant plays an important role in the mixed cationic–nonionic surfactant templating route to the mesoporous silica spheres.

It has been revealed that mesoporous silicas templated by cationic surfactants ( $S^+$ ) under strongly acidic conditions are produced by a counterion ( $X^-$ )-mediated  $S^+X^-I^+$  pathway where positively charged silica precursors ( $I^+$ ) are assembled at the interface of rodlike micelles through triple-ion electronic interactions, resulting in a hexagonal mesostructure.<sup>3,4</sup> In contrast, mesoporous silicas templated by nonionic poly(ethylene oxide) (PEO)-based surfactants ( $N^0$ ) under neutral conditions are synthesized by a neutral  $N^0I^0$  templating pathway where neutral silica precursors ( $I^0$ ) are as-

(16) Ocana, M.; Rodriguez-Clemente, R.; Serna, C. J. *Adv. Mater.* **1995**, *7*, 212.



**Figure 4.** TEM micrographs of mesoporous silica aged under static conditions for (a–c) 5 and (d) 16 h.

sembled at the interface of flexible wormlike micelles by hydrogen bonding, resulting in a disordered mesostructure.<sup>6</sup> Accordingly, the mesoporous silica templated by nonionic surfactant under the present acidic conditions, which also shows a disordered mesostructure, could be produced by a  $N^0I^+$  templating pathway that is mainly based on hydrogen bonding and self-assembly between  $N^0$  and  $I^+$  at the interface of wormlike micelles. Thus it may be reasonable to assume that the mesoporous silica synthesized by mixed cationic–nonionic surfactant templating under acidic conditions forms by a complex templating pathway that involves both  $S^+X^-I^+$  and  $N^0I^+$  assemblies at the interface of wormlike mixed micelles, resulting in a disordered mesostructure. It is worth noting that the mesoporous silica synthesized under static acidic conditions by cationic surfactant templating, which often exhibits faceted or corrugated surface patterns, has been suggested to form by directional accretion of surfactant–silicate micelles on a hexagonal cylindrical surfactant–silicate embryo.<sup>11</sup> When nonionic surfactant is employed in combination with cationic surfactant for the synthesis of mesoporous silica as in the present case, a disordered mesostructure rather than the ordered, hexagonal mesostructure is formed, which could contribute to an unidirectional aggregation process rather than the directional growth process. With small and increasing nonionic/cationic surfactant ratios, the mixed micelles become less hexagonal-like and more wormlike, which could lead to a more disordered mesostructure, resulting in an increase in the proportion of spherical particles. When the nonionic/cationic surfactant ratio is large enough, spheri-

cal particles with smooth surfaces will become the dominant morphology. Since the adsorption of cationic surfactant on the spherical particles may play a role in preventing the spherical particles from aggregating due to electrostatic repulsion, the agglomeration of spherical particles will become more severe with further increases in the nonionic/cationic surfactant ratio. It may be inferred that the mixed cationic–nonionic surfactant templating route provides a suitable approach to mesoporous silica spheres with little agglomeration.

In summary, the present work demonstrates that micrometer-sized mesoporous silica spheres can be synthesized under static acidic conditions by mixed cationic–nonionic surfactant templating. An unidirectional aggregation process has been proposed for the sphere formation according to the TEM observations of the sphere growth. The formation of these mesoporous spheres presents another example of the selective processing of mesoporous silica into a macroscale form<sup>17</sup> and provides further evidence that supramolecular templating is able to create inorganic materials organized over several size scales.<sup>18</sup>

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(17) Huo, Q.; Zhao, D.; Feng, J.; Weston, K.; Buratto, S. K.; Stucky, G. D.; Schacht, S.; Schuth, F. *Adv. Mater.* **1997**, *9*, 974.

(18) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313.