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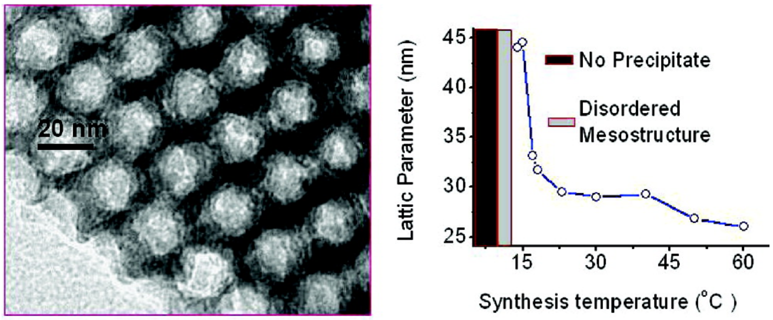

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Low-Temperature Strategy to Synthesize Highly Ordered Mesoporous Silicas with Very Large Pores

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Ordered mesoporous materials have attracted much attention because of their emerging applications in catalysis, adsorption, sensors, and biotechnologies.[1−4] The successful control over the composition[4,5] and pore structure[3] of mesoporous materials is the key factor for their functionalities. Ordered mesoporous materials with very large pores are in urgent demand for applications in the encapsulation and separation of proteins where biomolecules with large molecular weights are involved. Moreover, our recent results revealed that their ordered large mesopores are promising for developing a highly efficient device for proteolysis reactions. Current synthesis strategies to meet this challenge often include the careful choice of templates, the addition of swelling agents such as 1,3,5-trimethylbenzene (TMB), and the utilization of high-temperature processing.[6] For example, adding a certain amount of TMB during the synthesis of SBA-15 may increase the pore size to 12 nm. It has been found that further increasing the TMB amount might expand SBA-15 pore size up to 30 nm.[7] However, the domain size for hexagonal regularity is quite small, and a phase transformation to mesostructured cellular foam (MCF) has occurred.[8] On the other hand, both EO and PO moieties in poly(ethylene oxide)−poly(propylene oxide) (EO−PO)-type block copolymer templates are more hydrophobic at higher temperatures. It is probable, therefore, that increasing the synthetic temperature or using a postsynthesis hydrothermal treatment may enlarge the pore size of ordered mesoporous materials in a certain range. However, all these strategies failed to obtain ordered mesoporous materials with pore sizes larger than 12 nm.[9]

Here, we demonstrated a novel low-temperature pathway to synthesize highly ordered face-centered cubic (*fcc*) mesoporous silica structure with hitherto the largest pore sizes (up to 27 nm) and unit cells (up to 44 nm) (denoted LP-FDU-12). Meanwhile, the entrance dimension can be adjusted between <4 and 16.7 nm.

The synthesis of LP-FDU-12 is similar to our previous report[3] by using a block copolymer and an organic solvent as the template with the addition of inorganic salts; however, the synthesis temperature (*T*) was as low as 15 °C and was controlled to vary only ±0.1 °C (see Supporting Information [SI]). As-made products were incubated by a high-temperature hydrothermal treatment at *Y* °C. Final samples were denoted as S-*T*-*Y*.

LP-FDU-12 materials synthesized at low temperatures were first examined by X-ray diffraction (XRD) and further confirmed by the small-angle X-ray scattering (SAXS) method. The XRD pattern of S-17-100 shows six well-resolved diffraction peaks (SI). A typical SAXS pattern of sample S-17-100 (Figure 1a) also exhibits six peaks, which can be exactly indexed to the 111, 220, 311, 331, 333, and 442 reflections of a *fcc* structure (*Fm*3*m*). The cell parameter is calculated to be 34.6 nm (33.0 nm from XRD). We have examined the synthesis of FDU-12 in a broad temperature range (10−60 °C). The unit-cell parameter does not change very much in the range of 23−60 °C (29.5−26.0 nm), but swells sharply from 29.5 to 44.5 nm when the synthetic temperature, *T*, decreases to 15 °C (Figure 1b). Disordered mesostructured products were obtained at *T* < 14 °C, and no solid precipitate was observed when *T* was lower than 10 °C.

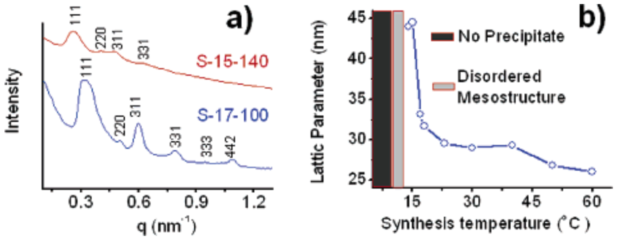

Figure 1. (a) SAXS traces of mesoporous silica LP-FDU-12 sample (S-17-100 and S-15-140). (b) Dependence of lattice parameter of mesoporous silica FDU-12 on synthesis temperature.

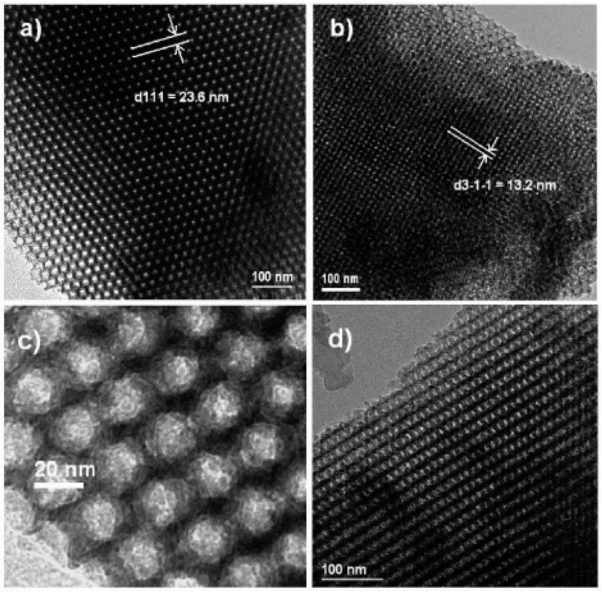

Figure 2. TEM images of mesoporous silica FDU-12 (S-15-140) viewed from (a) [110] and (b) [233] directions, (c) with large-magnification. (d) TEM image of FDU-12 (S-16-100) viewed from [112] direction.

The excellent *fcc* mesostructure of LP-FDU-12 is further confirmed by the transmission electron microscopy (TEM) technique. Parts a and b of Figure 2 are the TEM images of S-15-140 with an exceptionally large cell unit (44 nm) taken along the [110] and [233] directions, respectively. The *d*(1-11) and *d*(3-1-1) values calculated from TEM images are 23.6 and 13.2 nm, respectively, in good agreement with the values (25.2 and 13.2 nm) derived from

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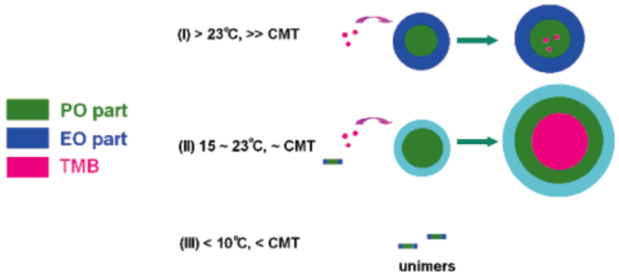
Scheme 1. Model Illustrating the Behavior of TMB Penetration into Block Copolymers at Different Synthesis Temperatures[a]



[a] Deep blue and pale blue represent the association number as relatively larger and smaller; the aggregation of EO in micelles is assumed to be tight and loose in processes I and II, respectively.

SAXS and XRD results. In Figure 2c, although the diameter of the white disks is not simply correlated to the pore size, the edge of the particle might be very thin, and the image contrast is dominated by mass contrast. In this case, the pore size can be estimated to be larger than 20 nm, in accordance with the N_2 sorption measurements (see below). To our knowledge, this is the largest pore size among all reported ordered mesoporous materials. Figure 2d shows the TEM image taken along [112] direction of mesoporous silica S-16-100. Its cell unit is estimated to be 36.7 nm, in agreement with the XRD result (37.5 nm, SI).

Nitrogen sorption measurements were conducted to determine the cavity and entrance size of FDU-12 materials (SI). The dependence of the cavity size on T is similar to that of the lattice parameter. The cavity size varies slightly (14.1−12.7 nm) in the T range of 23−60 °C. However, decreasing the synthetic temperature from 23 to 15 °C leads to a dramatic increase of the cavity size from 14.1 to 22.3 nm (SI). In addition, as we previously reported,[3] the entrance size can be enlarged by a high-temperature hydrothermal treatment. By comparing the sorption isotherms of S-15-100 with S-15-140, it is obvious that the type of hysteresis loop changes from H2 to H1 with a shift of desorption branch to higher relative pressure, indicating an expansion of the entrance size from <4 nm to 16.7 nm (SI). The BET surface area and pore volume of LP-FDU-12 samples varies from 271 to 677 m^2/g and 0.60−0.94 cm^3/g, respectively.

The successful synthesis of highly ordered mesoporous materials with very large pore is indebted primarily to our low-temperature synthesis strategy. It is generally accepted that preformation of micelles is crucial to produce mesoporous silica from a dilute solution, and the cooperative assembly of composite micelles leads to ordered mesostructures.[10] Furthermore, TMB as the swelling agent may profoundly penetrate into and swell the core of micelles formed by $EO_{20}PO_{70}EO_{20}$ (P123) copolymers with short hydrophilic segments, leading to a large extent of pore size expansion (>300%), although the structure is not ordered for very large pore materials.[8] However, for block copolymer $EO_{106}PO_{70}EO_{106}$ (F127) used in the synthesis, the large moiety of hydrophilic block may hinder the penetration of apolar TMB into the micelle cores (Scheme 1, process I). This probably explains the small extent of pore size and cell parameter enlargement of FDU-12 materials synthesized at a relatively high T range (23−60 °C). On the other hand, the correlation between critical micelle concentration (CMC) or critical micelle temperature (CMT) of block copolymers and the resulting mesostructures has been studied so far.[10,11] When the synthesis temperature is lower than CMT, block polymers exist mainly in the form of unimers in an aqueous solution, and thus no cooperative self-assembly occurs (Scheme 1, process III). In our experiments, no mesoporous product was yielded at $T < 10$ °C; Therefore, it is assumed to be close to CMT in this system. When synthetic temperature is increased above CMT, a unimer-to-micelle transition occurs.[12,13] The micelle−unimer equilibrium is influenced by two processes: a fast process associated with the dynamic exchange of molecules between micelles and unimers and a slow process associated with the adjustment of the micelles to a new association number.[14] It is also important to note that the association number of micelles increases remarkably as the temperature increases from 10 to 20 °C and then tends to plateau. However, the radii of micelles change less distinctly and are not very temperature dependent.[14−16] This phenomenon explains quite well what we observed. At a relatively lower-temperature region (Scheme 1, process II), the smaller association number and less tight aggregation of the micelles lead to a weaker hindrance of the hydrophilic EO moiety on the penetration of TMB molecules. This can, in turn, cause a higher content TMB swelling and a subsequent pore size expansion.

Another significant feature of current synthesis strategy is that the mesostructures remain highly ordered even when the pore sizes and cell parameters have been greatly enlarged, in great contrast to the MCF-type materials.[7] We attribute it to the presence of inorganic salts in the synthesis system, which may enhance the interaction of silicate species with nonionic block copolymers, and hence result in highly ordered products.[10]

In general, a low-temperature strategy has been developed to synthesize highly ordered mesoporous materials with exceptionally large pore sizes (up to 27 nm). Cubic mesoporous carbon (*fcc*) with very large cell parameters (44.5 nm) have also been obtained by using LP-FDU-12 as templates.[17] More importantly, since the micelle at a low synthesis temperature range may possess different properties such as more flexible shapes than at relative high temperature, preliminary results in this laboratory have shown that this low-temperature strategy may be useful to synthesize mesoporous materials with new structures and morphologies.

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Supporting Information Available: Synthesis details, XRD, N_2 sorption isotherms of LP-FDU-12 and additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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