Preparation of Highly Ordered Well-defined Single Crystal Cubic Mesoporous Silica Templated by Gemini Surfactant

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Highly ordered well-defined single crystal cubic mesoporous silica SBA-1 has been synthesized under static acidic conditions at room temperature by using gemini surfactant as a structure-directing agent.

The utilization of self-assembled supramolecular arrays of organic amphiphiles as the structure-directing agents has been widely explored to synthesize mesostructured silica materials.[1–5] One of the advantages for mesoporous silicas is the ease of macroscopic morphological control; the rich diversity of morphologies in these materials may trigger new developments in catalysis, adsorption, nanotechnology, etc.[6] Many kinds of supramolecular templates have been employed to create mesoporous silicas with various morphologies, such as crystals, thin films, monoliths, spheres, fibers, hollow tubular shapes, etc.[7–19] Gemini surfactants have a high charge density and large head groups and have turned out to be suitable supramolecular templates for the construction of mesoporous materials especially for 3-dimensional (3D) hexagonal mesoporous silica SBA-2.[5] To our knowledge, however, the effort of these templates on the morphological control and the synthesis of cubic mesoporous silica SBA-1 by using such gemini surfactants have not been reported yet. On the other hand, it is not common to synthesize periodic mesoporous materials showing well-defined crystal morphology, in contrast to many microporous zeolites.

Using a series of gemini surfactants under different experimental conditions, we have finally prepared some novel mesoporous materials with various morphologies. Here we report a successful synthesis of cubic structured ($Pm\bar{3}n$) mesoporous silica SBA-1 with well-defined crystal morphology and uniform particle size at room temperature.

The SBA-1 single crystal was prepared in a biphasic reaction system at room temperature. Gemini surfactant [$C_{18}H_{37}N(CH_3)_2(CH_2)_3N(CH_3)_3$]$Br_2$ (designated as $C_{18\text{-}3\text{-}1}$) was employed as a template and tetrabutoxysilane (TBOS) as a silica source. In a typical preparation, 0.9 g of $C_{18\text{-}3\text{-}1}$ was dissolved in 140 g of water, then 15 g of HCl (4M) was added with stirring, resulting in a clear solution. To this solution, 1.1 g of TBOS was slowly added without stirring. The biphasic reaction mixture was allowed to stand for 2 to 6 days. The resultant white precipitates were filtered without washing then air-dried at room temperature. The organic structure-directing agent was removed by calcination at 550 °C for 6 h in air.

Scanning electron microscopy (SEM) images (Figure 1) reveal that the products are almost composed of single crystals with uniform size (about 5 μm in size) and the yield of crystal products is very high (>90%). In addition, the crystals have four three-fold axes and three four-fold axes and exhibit cubic symmetry which belongs to $m\bar{3}m$ point group. The SEM images also show that there are no detectable changes between the morphologies of as-synthesized (not shown) and calcined products, suggesting that the macroscopic structure of the products retains after calcination.

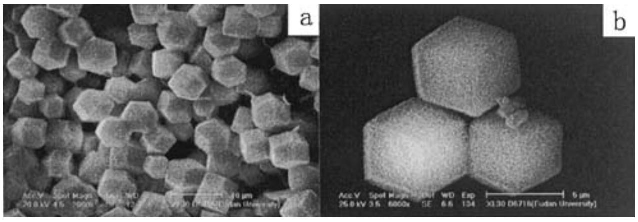

Figure 1. SEM images of calcined mesoporous silica SBA-1 prepared by using gemini surfactant $C_{18\text{-}3\text{-}1}$. (a) Low magnification, (b) enlarged. SEM micrographs were recorded with a Philips XL 30 microscope operated at 20 or 25 kV.

The powder X-ray diffraction (XRD) patterns of as-synthesized and calcined products are shown in Figure 2. All the samples show one broad peak around $2\theta = 20°$ (not shown), indicating that the wall of the sample is amorphous silica. The XRD pattern of as-synthesized sample with single crystal morphology shows four well-resolved diffraction peaks in the range of $2\theta = 1.5$–4.0. Combined with the results from SEM (the crystal is of $m\bar{3}m$ point group) and TEM (shown below), these peaks can be indexed to [200], [210], [211] and [321] diffractions of cubic ($Pm\bar{3}n$) symmetry with cell parameter $a = 9.8$ nm, similar to that for SBA-1 prepared by large headgroup cationic surfactant $C_{16}H_{33}N(C_2H_5)_3Br$. After calcination at 550 °C for 6 h in air, four well resolved diffraction peaks can be observed with a slight contraction in d spacing ($a = 8.9$ nm) and increased intensities result from the further cross-

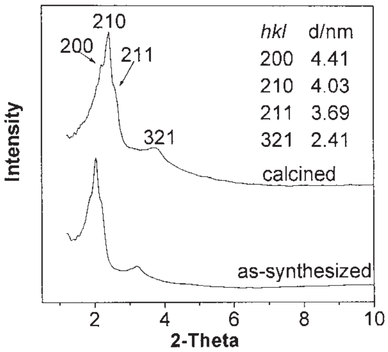

Figure 2. XRD patterns of as-synthesized and calcined mesoporous silica SBA-1 prepared by using gemini surfactant $C_{18\text{-}3\text{-}1}$. XRD patterns were carried out on a Rigaku D/Max-II A diffractometer using Cu Kα radiation.

linking of silicates. This observation is in agreement with that of previous report,[4] indicating that the single crystal product has a well-ordered cubic mesostructure ($Pm\bar{3}n$).

The transmission electron microscopy (TEM) images viewed along [100] and [210] directions (Figure 3) show that all areas for the calcined product have a well-ordered mesostructure with $Pm\bar{3}n$ space group symmetry, suggesting that the product is a high quality 3D cubic mesoporous silica material SBA-1. From the high dark contrast in the TEM images of this sample (Figure 3), the cell parameter is estimated to be 8.8 nm, in good agreement with the value determined from the XRD data.

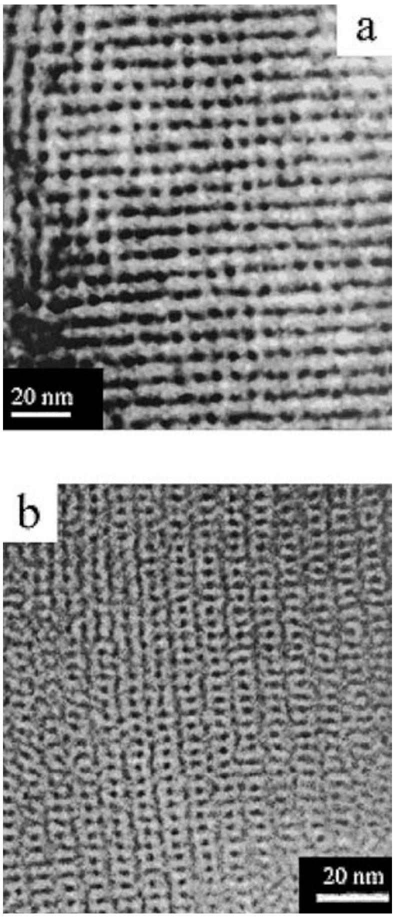

Figure 3. TEM images of calcined mesoporous silica SBA-1 prepared by using gemini Surfactant $C_{18\text{-}3\text{-}1}$: Along the direction (a), [100]; (b), [210]. TEM photographs were obtained with a Philips CM 200 FEG microscope operated at 200 kV.

The N_2 adsorption-desorption isotherms of calcined product (Figure 4) exhibit a typical adsorption curve of the type IV without hysteresis and a well-defined step at the relative pressure of 0.2 to 0.3, which is attributed to the mesoporous structure. Correspondingly, the BJH pore-size distribution for calcined product shows narrow uniform pore with a mean value of 2.2 nm. The calcined product has a BET surface area of 1050 $m^2 \cdot g^{-1}$ and a pore volume of 0.65 $cm^3 \cdot g^{-1}$.

We have found that the materials synthesized by employing stirring gave only the particles without any specific shape, indicating that quiescent treatment plays a key role in the formation of SBA-1 crystal. The synthesis temperature is another factor to influence the morphologies of the products. The cubic-shape SBA-1 products are favorable under room temperature in the reaction system. Lower temperature (0 °C) will lead to spherical morphologies similar to that reported by Che et al.[9,10,12] With increasing of the temperature (>40 °C), however, the yield of cubic-shape product is gradually diminished and the products become disordered mesostructure according to the SEM and XRD measurements.

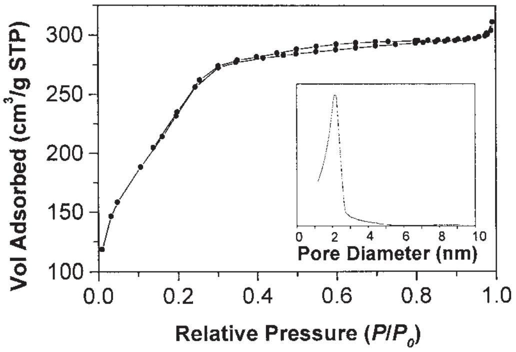

Figure 4. Nitrogen adsorption-desorption isotherm plots and BJH pore size distribution of calcined mesoporous silica SBA-1 prepared by using gemini surfactant $C_{18\text{-}3\text{-}1}$. The N_2 sorption isotherms were determined using Tristar 3000 analyzer at 77 K.

In summary, highly ordered, well-defined, single crystal mesoporous silica SBA-1 has been synthesized under static acidic conditions at room temperature with the gemini surfactant $C_{18\text{-}3\text{-}1}$ as the template. The well-defined cubic crystal morphology and the 3D-cubic structure for the resulting mesoporous silica are expected to be of great value in catalysis, chemical sensing and separation.

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