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Nonionic Block Copolymer Synthesis of Large-Pore Cubic Mesoporous Single Crystals by Use of Inorganic Salts

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Mesoporous materials synthesized by the cooperative assembly of surfactants and associated species[1] possess little short-range order on the atomic length scale but obvious order on the mesoscopic scale. Unlike microporous materials that usually show well-defined crystal morphology corresponding to their order at atomic level, it is unusual to synthesize mesoporous materials with crystal shapes, especially with uniform morphology in a batch synthesis. Kim and Ryoo[2] have reported the synthesis of MCM-48 crystals (*Ia*3*d*) with a truncated rhombic dodecahedral shape. Guan[3] and Sayari et al.[4] have reported the synthesis of hybrid cubic mesoporous crystals (*Pm*3*n*) with well-defined decaoctahedron shape. Recently, Che et al. have reported the synthesis of SBA-1 (*Pm*3*n*)[5] with crystal morphologies of a large number of facets. However, because the crystals are too small, the structure could not be solved by single-crystal X-ray diffraction studies. Moreover, it should be noted that in all these reports, ionic surfactants have been used, and the pore sizes of these materials are smaller than 4 nm. Until now, there has been no successful report of the synthesis of mesoporous single crystals using nonionic block copolymers as templates. This is believed to be related to the specific interaction of surfactant headgroups and inorganic species in solution. The Coulombic interactions of ionic surfactants, either under acidic conditions ($S^+X^-I^+$) or basic conditions (S^+I^-),[6] are much stronger than hydrogen-bonding interactions of nonionic block copolymer under acidic conditions (S^0H^+)(X^-I^0).[7]

Here, we report the first synthesis of cubic mesoporous silica single crystals using a commercial nonionic block copolymer as a template under acidic conditions. This is achieved by using inorganic salts to increase the interaction between silicate species and nonionic block copolymers. These single crystals possess exclusively uniform rhombdodecahedron shapes (~1 μm) with ~100% crystal yield and uniform large pores (up to 7.4 nm). By resolving the mesopore array of each crystal face with transmission electron micrographs (TEM), we have further confirmed that these crystals are perfect single crystals with a body-centered cubic space group (*Im*3*m*).

In a typical synthesis of mesoporous silica single crystals, 2 g of triblock copolymer F108[8] and 5.24 g of K_2SO_4 were dissolved in 60 g of 2 mol/L HCl at 38 °C. To this solution, 4.2 g of tetraethyl orthosilicate (TEOS) was added under stirring for 15 min, and then the reaction was continued under static conditions for 24 h at 38 °C. The final reactant molar composition was 0.007 F108/1.5 K_2SO_4/6 HCl/166 H_2O/1 TEOS. The solid products were collected by filtration, washed with water, and dried at room temperature in air. The resulting powders were calcined at 400 °C for 4 h to remove the templates.

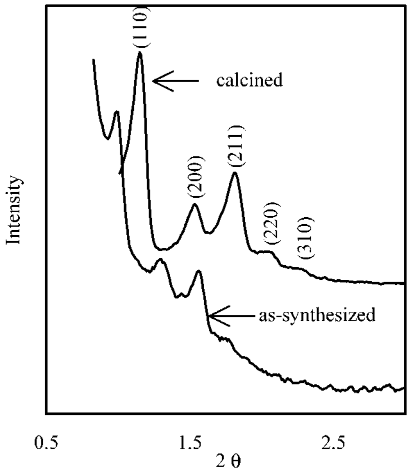

Figure 1. XRD patterns of as-synthesized and calcined mesoporous single crystals synthesized with F108 and 0.5 mol/L K_2SO_4 at 38 °C

Powder X-ray diffraction (XRD) patterns of as-synthesized and calcined mesoporous silica materials synthesized by F108 and K_2SO_4 at 38 °C are shown in Figure 1. The as-synthesized powders show four well-resolved XRD patterns in the region of $2\theta = 0.9-1.8°$, which are indexed to the 110, 200, 211, and 220 diffraction peaks of a body-centered cubic space group (*Im*3*m*). After calcination, the intensity of these peaks is much stronger, and an additional peak at high angle is observed, which can be indexed to the 310 diffraction of the cubic *Im*3*m* mesostructure. The cell parameters, *a*, are 13.7 and 11.6 nm for as-synthesized and calcined samples, respectively.

Scanning electron microscope (SEM) images reveal that as-synthesized samples made with F108 and K_2SO_4 at 38 °C are composed of ~100% single-crystal particles uniform in morphology (~1 μm in size, Figure 2a). All of these particles have the shape of a rhombdodecahedron, consisting of 12 well-defined crystal faces (Figure 2b). These 12 faces can be indexed to {110} planes (Figure 2c). The crystal has four three-fold axes and three four-fold axes and exhibits cubic symmetry which belongs to *m*3*m* point group class. On the basis of (1) XRD analysis and comparison of the relative intensity of these observed peaks with that reported in liquid crystal studies,[9] (2) comparison of the large headgroup ratio of F108 with that of F127, where the latter leads to SBA-16 with the *Im*3*m* structure,[7,10] and (3) TEM studies (see discussion below), we propose that the single crystals prepared with F108 have *Im*3*m* symmetry.

TEM images further confirm that these mesoporous silica crystals are perfect single crystals (Figure 3). The shape of the single crystal can be easily seen in TEM, and it is noteworthy that for thin sections

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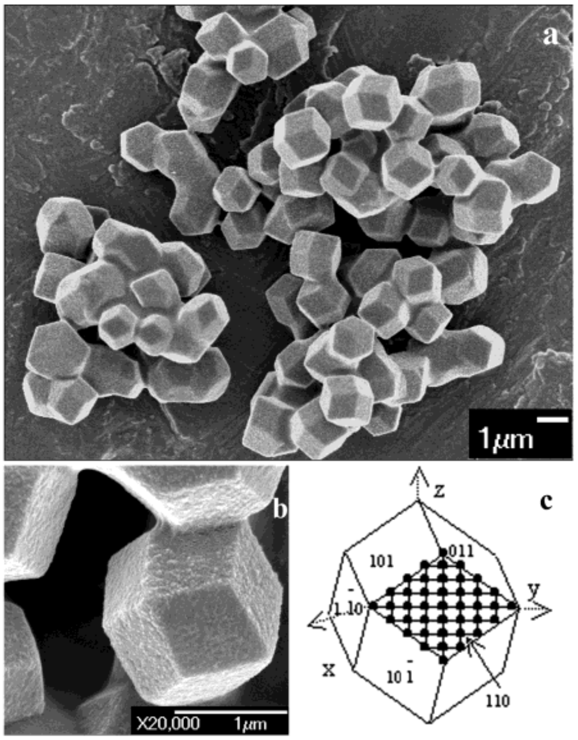

Figure 2. SEM images of mesoporous single crystal synthesized with F108 at 38 °C with 0.5 mol/L K_2SO_4: (a) at low magnification, (b) at high magnification, (c) index of a rhombdodecahedron model, the mesopore array in {110} plane is demonstrated.

of each crystal face, the TEM image along only the [110] direction is observed. This is in accordance with the crystal structure and morphology, since the {110} face has the lowest surface energy during crystal growth, and the 12 faces are equivalent in space. Moreover, at each crystal face, the diagonal of the rectangular repeating unit is parallel to the crystal edge, thus the lattice array in each crystal face can be easily solved (Figure 2c), in accordance with an ideal crystal model with *Im*3*m* symmetry. The unit cell is propagated throughout the faceted particles without twinning or apparent dislocations and fault planes, unambiguously confirming that the particles are perfect single crystals. It is notable that in previous studies, TEM images of large domain order and SEM are main criteria for mesoporous single crystals. In this paper, TEM is directly used to confirm the symmetry in view of the entire single crystal.

Calcined cubic mesoporous single crystals yield a type IV N_2 adsorption−desorption isotherm (Supporting Information). The calcined crystals have a pore volume of 0.67 cm^3/g, a BET surface area of 670 m^2/g, and a mean pore size value of 7.4 nm (BdB model).[11]

Inorganic salts play an important role in the synthesis of mesoporous single crystals.[12,13] For the same reactant components but without salt, only amorphous gel was obtained. A decrease of concentration of K_2SO_4 from 0.5 to 0.25 mol/L resulted in no precipitates from solution. Instead of K_2SO_4, Na_2SO_4 can also be used to form the single crystals. However, using the anion Cl^- instead of SO_4^{2-} gave rise to mixed morphologies, suggesting that highly charged salts favor the formation of the single crystals. Increasing the temperature (>45 °C) or TEOS/F108 ratio (>1.5/0.007) produced some spherical particles, mostly due to fast condensation of silica species under such conditions.

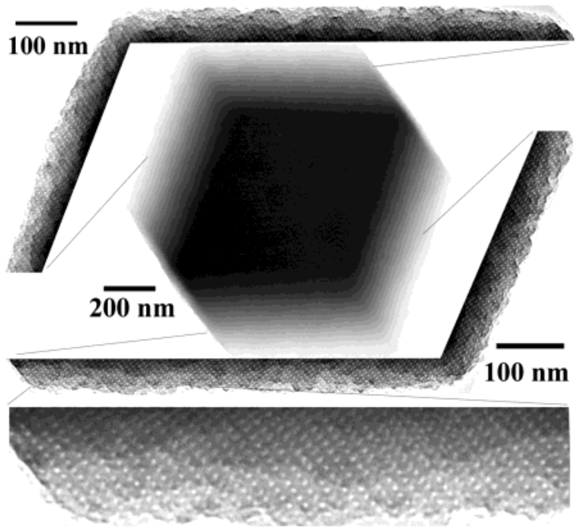

Figure 3. TEM images of mesoporous single crystal synthesized with F108 at 38 °C with 0.5 mol/L K_2SO_4.

For block copolymer surfactants with large CMC values, the use of inorganic salts facilitates the formation of highly ordered mesostructure.[14] Current results further suggest that the addition of inorganic salts, especially highly charged salts such as K_2SO_4, can increase the interaction of silicate species with hydrophilic headgroups of nonionic block copolymers. The strong interaction can result in long-range ordered domain of silica−surfactant mesostructure and favor the formation of mesoporous single crystals.

In summary, large-pore (7.4 nm) mesoporous silica single crystals with ∼100% rhombdodecahedron shapes have been synthesized by nonionic block copolymer surfactants and inorganic salts. Uniform single crystals with large mesopores may have potential use in electrooptic devices and as templates for the generation of 3D carbon, metal, and other nano-objects.

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Supporting Information Available: N_2 analysis data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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