Synthesis of Mesoporous Silica Single Crystal SBA-16 by Fluorinated Surfactants with Short Carbon Chains

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Single crystals of mesoporous silica SBA-16 with the shape of rhombododecahedron consisting of 12 flat crystal faces can be obtained by the addition of fluorinated surfactants with short carbon chains.

Mesoporous materials, especially mesoporous silica, have been intensively researched in the past two decades, in which attentions have been mainly focused on the composition, structure, and morphology.[1,2] Morphology of mesoporous silica plays an important role in their applications to separation, photoelectronic and catalytic area, etc.[2] Therefore, synthesis of mesoporous silica with well-controlled morphology has been widely investigated, and some successful examples have been reported.[2–5] Recently, Mou et al.[6] have prepared faceted single crystals of mesoporous silica SBA-16 from a ternary surfactant system and proposed that the addition of ionic surfactants results in the decrease in surface tension and formation of single crystals.

It is well known that fluorinated surfactants can effectively decrease the surface tension of the system. Moreover, fluorinated surfactants have attracted much attention of the researchers to the use as templates in the synthesis of mesoporous materials because of their ultrahigh stability and special physicochemical properties, which would exhibit superiority in the preparation of mesoporous materials.[7] However, most investigations focused on the structure and pore size of mesoporous materials prepared by fluorinated surfactants,[7–11] and the morphology is seldom concerned. Herein, we show that perfect single crystals of mesoporous silica SBA-16 can be obtained by adding of fluorinated surfactants.

In a typical synthesis, 1.0 g of cationic fluorinated surfactant FC-4911 ($CF_3(CF_2)_3SO_2NH(CH_2)_3N^+(CH_3)_3I^-$) (or 0.4 g of anionic fluorinated surfactant FC-480 ($CF_3(CF_2)_3SO_3K$)) and 0.3 g of F127 ($EO_{106}PO_{70}EO_{106}$) (or 0.6 g in the case of FC-480) were dissolved in 40 g of dilute HCl solution (pH 1.7), followed by the addition of 2.2 g of tetraethyl orthosilicate under stirring, and then the mixture was kept under static condition at room temperature for one day. The mixture was treated by two methods: (1) crystallization under static condition at room temperature for further 1–5 days; (2) crystallization at 100 °C for another day after being transferred into autoclaves. The products were collected by filtration, dried in air, and calcined at 600 °C for 5 h to remove the surfactants. The products crystallized at room temperature were denoted by $\text{SBA-16}_{\text{rt}(n)}$, where n is the total days for crystallization ($n = 2$–6), while the product crystallized at 100 °C was denoted by $\text{SBA-16}_{100(\text{C})}$ or $\text{SBA-16}_{100(\text{A})}$, where C stands for the cationic fluorinated surfactant, and A stands for the anionic fluorinated surfactant.

SEM images of the samples prepared under different conditions are given in Figure 1. Obviously, single crystals can be obtained by using FC-4911, even for crystallization at room temperature for a relatively short time (2 days) (Figure 1a). After crystallization for longer time (4 days) or at high temperature, the products are mainly composed of relatively large single crystals (3–5 μm) with the shape of rhombododecahedron, consisting of 12 flat crystal faces, which can be indexed to the (110) planes (Figures 1b and 1c).[5,6] These crystals have four three fold axes and three four fold axes and exhibit cubic symmetry belonging to the $Im\bar{3}m$ group (Figure 1d).[5,6] Similar crystals can also be obtained with anionic fluorinated surfactant FC-480 instead of cationic fluorinated surfactant FC-4911 (Figures 1e and 1f).

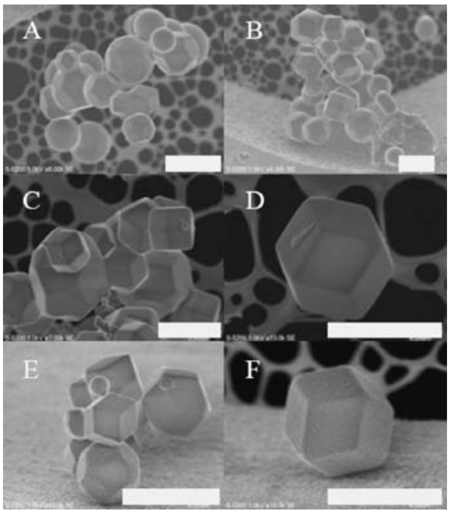

Figure 1. SEM images of (A) $\text{SBA-16}_{\text{rt}(2)}$, (B) $\text{SBA-16}_{\text{rt}(4)}$, (C) $\text{SBA-16}_{100(\text{C})}$, (D) $\text{SBA-16}_{100(\text{C})}$, (E) $\text{SBA-16}_{100(\text{A})}$, and (F) $\text{SBA-16}_{100(\text{A})}$. The scale bar is 5 μm.

TEM images and small angle X-ray diffraction patterns confirm the structure of the products. TEM images provide the direct evidence for the structure of the single crystal mesoporous silica. It is reasonable that the TEM image along [110] incidence can be easily observed since 12 faces of the crystals are all (110) planes (Figure 2). After grinding, other incidences of the samples such as [100], [111], and [211] can also be observed. XRD patterns for the samples prepared by cationic and anionic surfactants both clearly show three well-resolved peaks in the region of 0.8–2° indexed to the (110), (200), and (211) reflections (Figure 3a), which can be associated with the body-centered cubic space group ($Im\bar{3}m$).[12]

Figure 3b demonstrates the N_2-adsorption isotherms for the samples prepared by cationic and anionic fluorinated surfactants. The isotherms have a broad hysteresis loop, similar to those of SBA-16 materials,[5,6,12] characteristic of materials with uniform, cage-like mesopores with an entrance much narrower than the

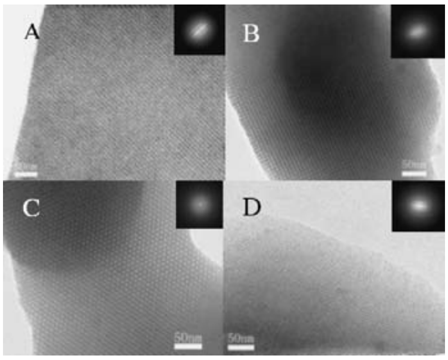

Figure 2. TEM images of (A) [110], (B) [100], (C) [111], and (D) [211] incidence of SBA-16_{100}. Inserts are ED patterns of these images.

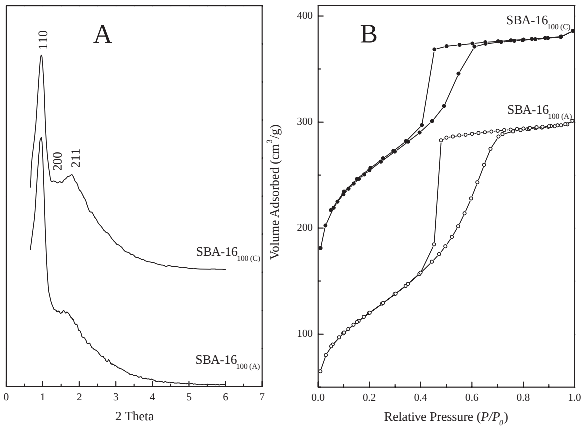

Figure 3. (A) XRD patterns and (B) N_2-adsorption isotherms of SBA-16_{100} samples.

diameter of the cage itself. BET surface area and pore volume are 508 m^2/g and 0.37 cm^3/g for the sample prepared by FC-4911, and 436 m^2/g and 0.47 cm^3/g for the sample synthesized by FC-480, which are similar to the previous report for SBA-16 crystals.[5,6]

Further investigation reveals that neither FC-4911 nor FC-480 can template the ordered mesoporous silica without F127; conventional SBA-16 samples without definite morphology were formed without fluorinated surfactants under similar conditions. These results suggest that copolymer surfactant F127 templates the mesostructure while fluorinated surfactants are essential for the formation of the well-faceted crystals. It should be noted that not all the fluorinated surfactants have such a function. For example, the use of FC-4 ($C_3F_7O(CFCF_3CF_2O)_2CFCF_3CONH(CH_2)_3N^+(C_2H_5)_2CH_3I^-$), which has been used in previous reports,[7–9] results in nanoparticles (100–300 nm) with different mesoporous structures ($Fm\bar{3}m$ or $Im\bar{3}m$) when mixed with F127 in the presence or absence of trimethylbenzene.[9] FC-911 ($CF_3(CF_2)_7SO_2NH(CH_2)_3N^+(CH_3)_3I^-$) and FC-80 ($CF_3(CF_2)_7SO_3K$) with the same functional group as FC-4911 and FC-480, respectively, but a longer carbon chain, cannot either afford single crystals under the same conditions. Thus, unique structure and properties of FC-4911 and FC-480 should be responsible for the formation of single crystals. Generally, it is believed that fluorinated surfactants would be enriched on the particle periphery when they are mixed with hydrocarbon surfactant because of their strong hydrophobicity and special surface activity.[9] However, the fluorocarbon parts of FC-4911 and FC-480 are too short to ensure that they pack around the particle, but the existence of fluorocarbon parts indeed results in the decrease in the interface surface intension.[13] Such a decrease would lead to the formation of single crystals. This mechanism is supported by the previous reports about the single crystal SBA-16.[5,6] Zhao et al.[5] and Mou et al.[6] have reported that the addition of inorganic salts (K_2SO_4) or ionic surfactants (C_8MTAB/SDS) results in the decrease in surface tension and formation of single crystal SBA-16. Preparation of large single crystals is the new function of fluorinated surfactants with a short carbon chain, compared with the previous findings for synthesis of mesoprous materials with nanosize or hierarchically structure.[9]

In summary, large mesoporous silica single crystals of an $Im3m$ structure and in rhombododecahedron shape have been prepared in the presence of a mixture of a nonionic surfactant and fluorinated surfactants with short carbon-chains.

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References

1 A. Corma, *Chem. Rev.* **1997**, *97*, 2373.
2 H. P. Lin, C. Y. Mou, *Acc. Chem. Res.* **2002**, *35*, 927.
3 J. M. Kim, R. Ryoo, *Chem. Commun.* **1998**, 259.
4 S. Che, S. Lim, M. Kaneda, H. Yoshitake, O. Terasaki, T. Tatsumi, *J. Am. Chem. Soc.* **2002**, *124*, 13962.
5 C. Z. Yu, B. Z. Tian, J. Fan, G. D. Stucky, D. Y. Zhao, *J. Am. Chem. Soc.* **2002**, *124*, 4556.
6 B.-C. Chen, M.-C. Chao, H.-P. Lin, C.-Y. Mou, *Microporous Mesoporous Mater.* **2005**, *81*, 241.
7 F.-S. Xiao, *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 94.
8 Y. Han, D. Li, L. Zhao, J. Song, X. Yang, N. Li, Y. Di, C. Li, S. Wu, X. Xu, X. Meng, K. Lin, F.-S. Xiao, *Angew. Chem., Int. Ed.* **2003**, *42*, 3633; X. Meng, Y. Di, L. Zhao, D. Jiang, S. Li, F.-S. Xiao, *Chem. Mater.* **2004**, *16*, 5518.
9 Y. Han, J. Y. Ying, *Angew. Chem., Int. Ed.* **2005**, *44*, 288; S. Areva, C. Boissière, D. Grosso, T. Asakawa, C. Sanchez, M. Lindén, *Chem. Commun.* **2004**, 1630.
10 B. Tan, A. Dozier, H. J. Lehmler, B. L. Knutson, S. E. Rankin, *Langmuir* **2004**, *20*, 6981; B. Tan, H. J. Lehmler, S. M. Vyas, B. L. Knutson, S. E. Rankin, *Chem. Mater.* **2005**, *17*, 916.
11 J. L. Blin, P. Lesieur, M. J. Stébé, *Langmuir* **2004**, *20*, 491; J. L. Blin, M. J. Stébé, *J. Phys. Chem. B* **2004**, *108*, 11399; J. L. Blin, C. Gerardin, C. Carteret, L. Rodehuser, C. Selve, M. J. Stébé, *Chem. Mater.* **2005**, *17*, 1479.
12 Y. Sakamoto, M. Kaneda, O. Terasaki, D. Y. Zhao, J. M. Kim, G. Stucky, H. J. Shin, R. Ryoo, *Nature* **2000**, *408*, 449; D. Li, Y. Han, J. Song, L. Zhao, X. Xu, Y. Di, F.-S. Xiao, *Chem. Eur. J.* **2004**, *10*, 5911.
13 K. Wang, G. Karlsson, M. Almgren, T. Asakawa, *J. Phys. Chem. B* **1999**, *103*, 9237.