Polymorphism of Silica Mesostructures Templated by Poly(Ethylene Oxide)-*b*-Poly(Butylene Oxide) Diblock Copolymer

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A family of silica mesostructures including highly ordered 2-dimensional (2D) hexagonal (H_1) and lamellar (L_α) symmetries have been prepared by using poly(ethylene oxide)-poly(butylene oxide) diblock copolymer as a structure-directing agent under acidic synthesis condition.

The synthesis of inorganic-organic composites and mesoporous materials with structures and functions over different length scales has ramifications in diverse areas, such as large-molecule catalysis, biomolecule separations, miniaturization of electronic devices, chromatographic supports, and the formation of semiconductor nanostructures.[1-5] Zhao et al.[6,7] have prepared a series of mesoporous silica structures (SBA) including hexagonal (H_1), lamellar (L_α) and cubic (I_1) phases using poly (ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) PEO-PPO-PEO triblock copolymer as the templates. However, the attempt to synthesize mesoporous silica materials by using PEO-PPO diblock copolymers as the templates was unsuccessful,[6,7] because of the minor difference of hydrophilicity/hydrophobicity between PEO and PPO chains. Here we report the synthesis of 2D hexagonal (H_1) and lamellar (L_α) silica mesostructures under acid-based condition by using poly(ethylene oxide)-*b*-poly(butylene oxide) (PEO-PBO) diblock copolymer as a template, which has a more hydrophobic segment PBO. After the copolymer is removed, highly ordered 2D hexagonal mesoporous silica with uniform large pore size of 6.0 nm and high surface area of 900 m²/g has been obtained.

The silica mesostructures were synthesized by using diblock copolymer $EO_{16}BO_{10}$ (BL50-1500, Dow Company) under acidic condition over a wide range of composition. In a typical preparation in aqueous solution, 0.4 g BL50-1500 was dissolved in 30 g (2M) HCl and then 3 g tetraethyl orthosilicate (TEOS) was added. The solution was stirred for 24 h and kept at 100 °C for another 24 h. The solid products were recovered, washed, dried at room temperature.

Powder XRD pattern (Figure 1a) of as-made mesoporous silica shows three reflection peaks at 2θ values between 0.5 and 2.5°, which can be indexed to (100), (110), (200) diffractions of hexagonal (p6mm) symmetry with a cell parameter of 10.1 nm (d_{100}= 8.75 nm). After calcination at 500 °C for 6 h in air, these peaks are retained and a better-resolved XRD pattern is obtained with a little shrinking of the cell parameter to 9.26 nm (d_{100}=8.02 nm), as expected.[8] The results indicate that the mesoporous materials have a even better long-range ordered 2D hexagonal mesostructure. When the concentration of the block copolymer increases from 0.67 wt% to 2.67 wt%, the cell parameters of the as-made materials remain almost unchanged. However, those of the calcined products decrease from 10.2 nm
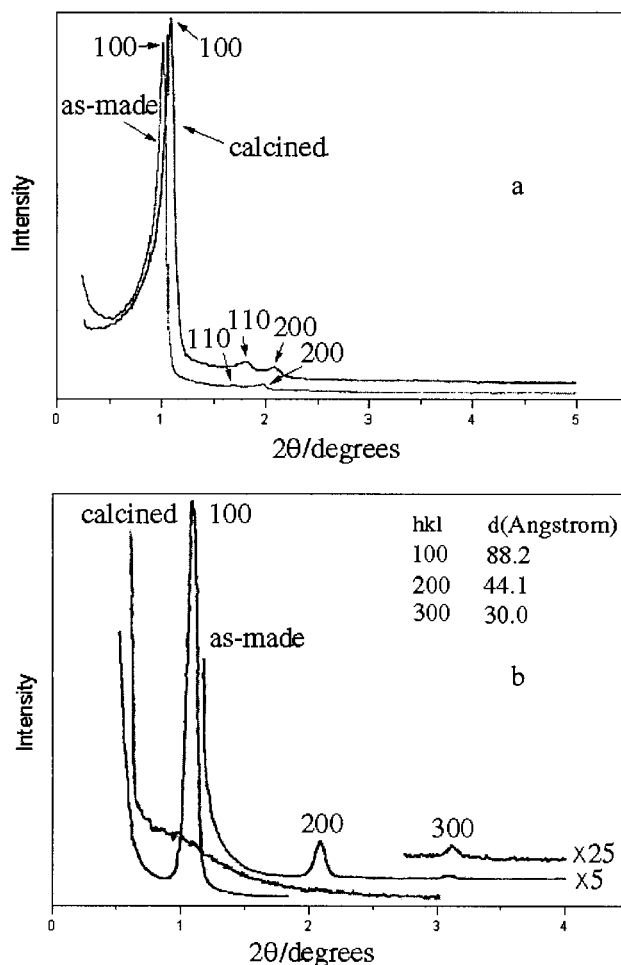

Figure 1. Powder XRD patterns of (a) hexagonal and (b) lamellar silica mesostructures prepared by using $EO_{16}BO_{10}$ diblock copolymer as the template. XRD patterns were recorded with a Rigaku D/Max-II A diffractometer using Ni-filtered Cu-K$_\alpha$ radiation with λ= 0.154178 nm.

to 9.5 nm.

TEM measurements further confirm the conclusion. As shown in Figure 2a, b, a large area of homogeneous ordered hexagonal mesostructure and highly ordered long mesochannels can be observed. SEM image (Figure 2c) shows that calcined hexagonal mesoporous silica has a sphere morphology with a relative uniform diameter of 3μm, suggesting that the materials are of great value in direct use as chromatography supports for separation of large molecules.

N_2 adsorption-desorption isotherm (Figure 3) of calcined hexagonal mesoporous silica is a clear type IV curve with a
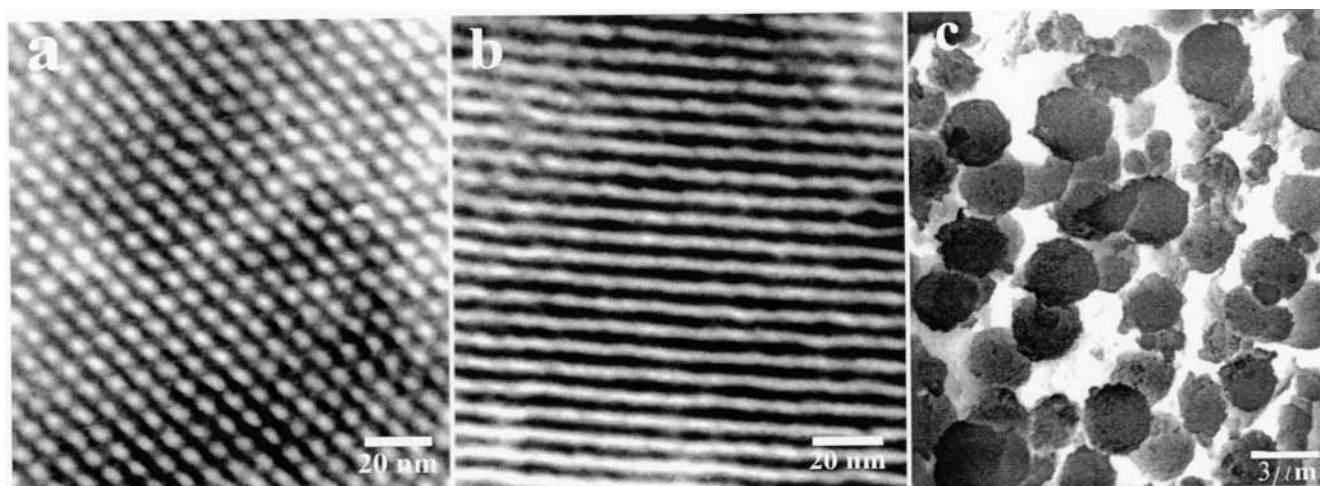
Figure 2. (a), (b) TEM images and (c) SEM image of calcined hexagonal mesoporous silica templated by $EO_{16}BO_{10}$ diblock copolymer. TEM images recorded along different zone axes (a) [100], (b) [110].
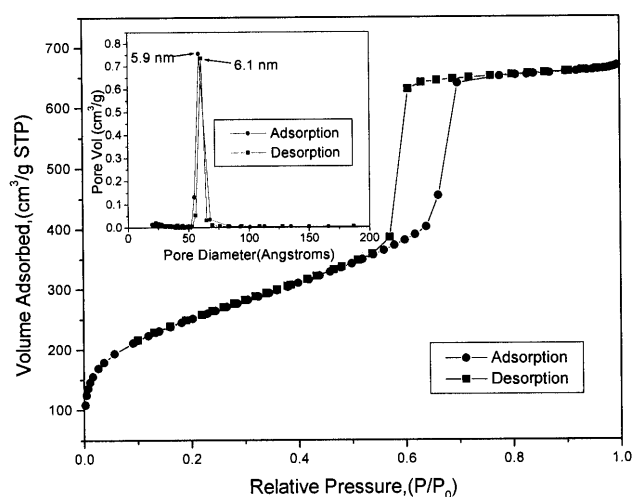

Figure 3. Nitrogen adsorption-desorption isotherm plots and pore size distribution curves from both the adsorption and desorption branch of hexagonal mesoporous silica prepared with $EO_{16}BO_{10}$ diblock copolymer.

type H_1 hysteresis loop. The pore size distribution curves calculated from BdB model[9] (Figure 3) are quite narrow at the mean value of ~ 6.0 nm, indicating that the material has a quite uniform pore size. The pore diameter calculated from the adsorption branch is 5.9 nm, which is quite consistent with 6.1 nm calculated from the desorption branch using a cylinder model. The calcined sample has a BET surface area of 902 m^2/g, and a pore volume of 1.03 cm^3/g.

Thermogravimetric and differential thermal analysis of as-made hexagonal silica mesostructures show three loss steps with a total weight loss of 45 wt%. The exothermic weight loss at 185 °C and 245 °C (totally 43.2 wt%) can be assigned to the desorption and decomposition of the diblock copolymer, suggesting that after calcined at 245 °C, most of the copolymer species can be removed from the channels.

When the concentration of the diblock copolymer is higher than 16 wt%, lamellar silica mesostructure can be formed. XRD pattern (Figure 1b) of as-made products shows three well-resolved diffraction peaks with d spacing of 8.82, 4.41, and 3.01 nm, respectively, which can be indexed as the (100), (200), (300) reflections of a lamellar mesostructure. While after calcination at 500 °C, all the peaks disappear because of the collapse of the lamellar structure when the diblock copolymer species are removed, as expected.[10] Higher concentration of block copolymer increase the cell parameter of the lamellar silica mesostructure.

References
1 T. Lee, N. Yao, and I. A. Aksay, *Langmuir*, **13**, 3886 (1997).
2 S. Mann and G. A. Ozin, *Nature*, **382**, 313 (1996).
3 P. Yang and C. M. Lieber, *Science*, **382**, 313 (1996).
4 C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, **115**, 8706 (1993).
5 J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, **7**, 607 (1995).
6 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science*, **279**, 548 (1998).
7 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024 (1998).
8 Q. Huo, D. I. Margolese, and G. D. Stucky, *Chem. Mater.*, **8**, 1147 (1996).
9 W. Luckens, Jr., P. Schmidt-Winkel, D. Zhao, J. Feng, and G. D. Stucky, *Langmuir*, **15**, 5403 (1999).
10 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).