Synthesis of Large-Pore Periodic Mesoporous Organosilica (PMO) with Bicontinuous Cubic Structure of *Ia*–*3d* Symmetry

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(Received September 24, 2004; CL-041114)

Ordered three-dimensional (3-D) bicontinuous cubic *Ia*–3*d*-type periodic mesoporous organosilica (PMO) with large pore size (>6 nm) has been synthesized by using triblock copolymer P123 as a template and 1,2-bis(triethoxysilyl)ethane as an organically bridged silica source.

Periodic mesoporous organosilicas (PMOs), a new class of organic–inorganic hybrid materials through surfactant-templated condensation of bifunctional organo-bridged silsesquioxanes, have been receiving much attention because of their versatile applications in catalysis, sorption, nanoscience and so on.[1–4] To date, PMO materials with various organic spacers have been prepared by using a number of new synthesis strategies under a wide range of pH values from highly basic to strongly acidic conditions mainly with cationic[1–4] or nonionic oligomeric[5] surfactants as the templates. Furthermore, large-pore PMOs with 2-D hexagonal (space group *p*6*mm*) structure have recently been reported by using triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) as a template from the viewpoint of the immobilization and encapsulation of large molecules.[6] It is generally accepted that 3-D mesoporous materials with linked pore systems exhibit more advantages in mass diffusion and transportation compared with mesoporous materials with 1-D channels. However, the preparation of 3-D PMOs is somehow difficult and resulted 3-D PMOs are usually limited in pore sizes and structure order. Until now, only few papers[7] have demonstrated the synthesis of ordered cubic large-pore PMOs with cage-like structure (space group *Im*–3*m*).

The *Ia*–3*d* cubic mesostructure (typical of MCM-48)[8] has recently attracted the most attention because of its unique interpenetrating bicontinuous networks of channels, which are very useful for applications requiring easy molecular accessibility and fast molecular transport. Several methods[8] have been developed to synthesize ordered *Ia*–3*d* cubic mesoporous silica materials. Up to now, however, there was no any reports on the synthesis of PMOs with 3-D bicontinuous cubic (*Ia*–3*d*) structure either by using cationic surfactants or block copolymers as the structure-directing agents. In this communication, we report the first synthesis of ordered large pore PMOs with bicontinuous cubic structure of *Ia*–3*d* symmetry utilizing solvothermal post-treatment method templated by triblock copolymers.

Large-pore *Ia*–3*d* cubic PMO materials (designated PMO-L-*Ia*3*d*) were synthesized by using 1,2-bis(triethoxysilyl)ethane (BTSE) as an organically bridged silica source and triblock copolymer Pluronic P123 as a structure-directing agent. In a typical synthesis, 0.9 g of P123 (Aldrich) was dissolved in 10 g of ethanol, then 0.1 g of 2 M HCl, 0.8 g of H_2O, and 1.77 g of BTSE (Aldrich) were added and the mixture was further stirred for 2 h at room temperature. The molar ratio of BTSE:P123 = 1:0.03. The solution was dried in air for 6 h. The resulting membrane was collected and solvothermally post-treated in *n*-hexane at 70 °C for 3 d, and a solid white product was obtained. The surfactant was removed from the as-made materials by the solvent-extracted method.[1a,6]

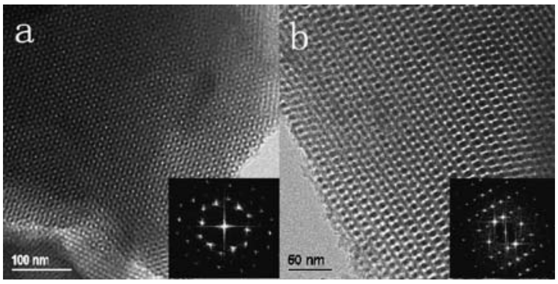

Figure 1. TEM images and Fourier diffractogram patterns of solvent-extracted PMO-L-*Ia*3*d* along (a) [111] and (b) [311].

Transmission electron microscopy (TEM) images and corresponding Fourier diffractograms of solvent-extracted PMO-L-*Ia*3*d* samples shown in Figure 1 provide a direct visualization of the PMO pore structure. The images exhibit typical [111] and [311] projection planes of the cubic *Ia*–3*d* mesophase, clearly indicating that the products have large domains of well-ordered 3-D bicontinuous mesostructure analogous to MCM-48 and FDU-5 or KIT-6.[8] The cell parameter *a* calculated from these TEM images is 24.3 nm. To the best of our knowledge, this is the first report of a large-pore PMO material that exhibits such a highly ordered 3-D bicontinuous cubic mesostructure.

Small angle X-ray diffraction (XRD) patterns (Figure 2A) further confirm the cubic (*Ia*–3*d*) mesostructure for PMO-L-*Ia*3*d*. Both as-synthesized and solvent-extracted samples show two diffraction peaks in the range of $2\theta = 0.85–1.02$ with a *d*-spacing ratio of 0.863, implying the indexation of (211) and (220) diffraction peaks for bicontinuous cubic space group *Ia*–3*d*. Another broad diffraction peak in the range of $2\theta = 1.3–2.0$ may be attributed to the overlapping of (321), (400), (420), and (332) diffraction peaks of the *Ia*–3*d* space group. The cell parameter, *a*, of solvent-extracted sample is calculated to be 24.6 nm, in good agreement with the value estimated from TEM images. The half band widths of the XRD paterns for both samples are narrow (less than 0.5 degree), suggesting that the PMO-L-*Ia*3*d* products have a ordered bicontinuous cubic *Ia*–3*d*-type mesostructure.

N_2 adsorption–desorption isotherms (Figure 2B) for the solvent-extracted PMO-L-*Ia*3*d* exhibit a typical type IV curve with a clear H_1 hysteresis loop and a well-defined step at 0.5–0.7 relative pressure (P/P_0) region, suggesting that the sample has or-

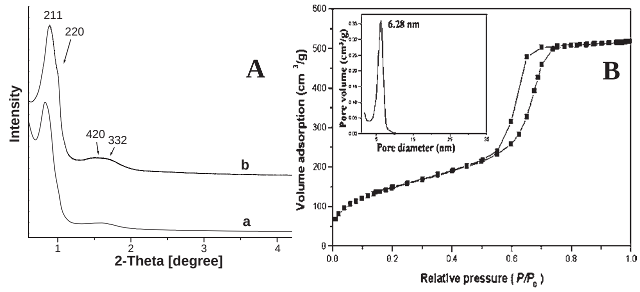

Figure 2. **A**: XRD patterns of (a) as-made and (b) solvent-extracted PMO-L-*Ia*3*d*; **B**: Nitrogen adsorption-desorption isotherm plots and pore size distribution curve (inset) for solvent-extracted PMO-L-*Ia*3*d*.

dered large 3-D pores without the windows or necks. The solvent-extracted PMO-L-*Ia*3*d* has a narrow pore size distribution (Figure 2B inset) with a mean value of 6.28 nm (calculated by BJH model), a BET surface area of 605 m^2g^{-1}, and a pore volume of 0.78 cm^3g^{-1}.

It is important to demonstrate that the Si–C bonds are maintained in the solvent-extracted organosilicas. ^{29}Si MAS NMR spectrum of the solvent-extracted PMO-L-*Ia*3*d* (Figure 3a) shows a broad ^{29}Si resonance at -56.6 ppm and a shoulder at -64.2 ppm, corresponding to T^2 [RSi(OSi)$_2$OH] and T^3 [RSi(OSi)$_3$] resonances, respectively. The absence of signals due to Q^n [$Si(OSi)_n(OH)_{4-n}$] species between -90 and -120 ppm, confirms that no cleavage of the carbon–silicon bond has been occurred during the hydrolysis and polymerization.

The incorporation of ethane groups inside the mesopore framework was further confirmed by ^{13}C CP MAS NMR spectrum of the solvent-extracted PMO-L-*Ia*3*d* (Figure 3b). A strong signal at 5.2 ppm is observed, which can be assigned to carbons sandwiched by Si ($Si–CH_2CH_2–Si$). The two weak bands at 15.6 and 57.6 ppm were attributed to carbons of surface ethoxy groups ($Si–OCH_2CH_3$), which were formed during the treatment with the HCl/EtOH solution for removal of the surfactants from the as-synthesized PMO-L-*Ia*3*d* materials.[1b] Nearly no carbon signals due to P123 copolymer were observed in the ^{13}C CP MAS NMR, suggesting almost complete removal of the block copolymer surfactant from the extracted sample.[1b,6a]

Unlike the traditional approach to the synthesis of similar material FDU-5 silica, the synthesis condition of PMO-L-*Ia*3*d* is much more stricted. When the molar ratio of BTSE:P123 was increased from 1:0.03, 1:0.025 to 1:0.02, the mesostructure transformed from a cubic structure to a poor hexagonal structure, further to worm-like disordered structure. Furthermore, the well-ordered PMO-L-*Ia*3*d* can only be synthesized in the presence of hexane *via* the facile solvothermal post-treatment method in our experiments, the use of benzene or toluene resulted in the deterioration of the long-range order of products. In addition, hydrothermal post-treatment instead of solvothermal post-treatment was found not efficient to synthesize PMO-L-*Ia*3*d*. According to the XRD and TEM measurements, the PMO materias prepared without solvothermal post-treatment exhibits 2-D hexagonal mesostructure (*p*6*mm*) and no bicontinuous cubic *Ia*–3*d*-type mesostructure, indicating that the solvothermal post-treatment plays an important role in the formation of PMO-L-*Ia*3*d*. It could be suggested that the solvothermal post-treatment, especially using long-chain alkanes, paves the successful synthesis of ordered bicontinuous cubic large pore PMO materials, and can be extended to prepare PMOs of different compositions with *Ia*–3*d*-type mesostructure using other kinds of triblock copolymers as the templates.

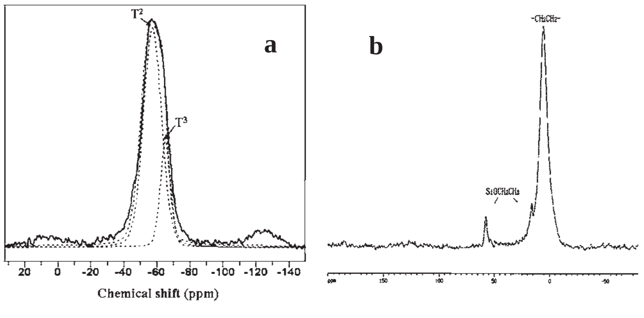

Figure 3. ^{29}Si MAS (a) and ^{13}C CP-MAS (b) NMR spectrums of solvent-extracted PMO-L-*Ia*3*d*.

In conclusion, ordered cubic *Ia*–3*d*-type mesoporous organosilicas (PMO) have been synthesized, for the first time, utilizing triblock copolymer as the template. The resulting PMO materials have a large pore sizs of 6.28 nm, a high surface area of 605 m^2g^{-1}, and a pore volume of 0.78 cm^3g^{-1}, and is being investigated for the promising applications in immobilization and encapsulation of large molecules.

This work was supported by NSF of China (Grant No. 2033030, 20101002, and 20173012), Shanghai Sci & Tech Committee (0212nm043, 03DJ14004, 02ZA14005), State Key Basic Research Program of PRC (2002AA321010, 001CB510202).

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