An Easy Route for the Synthesis of Ordered Three-Dimensional Large-Pore Mesoporous Organosilicas with *Im*-3*m* Symmetry

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Ordered three-dimensional (3-D) *Im*-3*m*-type mesoporous organosilicas with large-pore sizes (>6 nm) have been prepared by an easy solvent evaporation method by using bridged silsesquioxane 1,2-bis(triethoxysilyl)ethane precursor and triblock copolymers as the structure-directing agents.

The utilization of supramolecular assemblies of surfactants as structure-directing species has been widely explored to synthesize a variety of mesostructured materials.[1–3] One of the most exciting developments was the discovery of a new class of organic–inorganic hybrid materials called periodic mesoporous organosilicas (PMOs), which containing bridging organic groups integrated within a well-ordered mesoporous silica-based framework through surfactant-templated condensation of bifunctional organo-bridged silsesquioxanes.[4–6] Extensive researches have been conducted toward extending the variety of bridging organics and the versatile applications of these PMOs in catalysis, sorption, nanoscience and so on.[7–11] Furthermore, several groups have recently reported the synthesis of 2-D hexagonal PMOs with well-ordered large pores by using triblock copolymer as a template for the immobilization and encapsulation of large molecules.[12–14] 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. To date, the only exception is the synthesis of periodic cubic large PMO with the aid of concentrated inorganic salts in aqueous solution reported by Guo et al.[15]

Solvent evaporation method, which always adopt the well-known evaporation-induced self-assembly (EISA) process, has been proved to be one of the simplest and easiest methods for the preparation of highly ordered large-pore 3-D cubic mesoporous silica and non-siliceous materials with morphologies of films, membranes, fibers, and monoliths which offer a large scope of potential applications such as sensors, separation, supports for heterogeneous catalysis and optoelectric devices.[16–19] Up to now, however, the synthesis of 3-D caged large-pore PMOs with long-range structural order by solvent evaporation method has not been realized. Herein, we report for the first time, the synthesis of ordered large-pore PMOs with 3-D cubic *Im*-3*m* mesostructure through this rapid solvent evaporation approach, and further demonstrate the ability to fabricate materials in various forms such as films, monolith, and fibers.

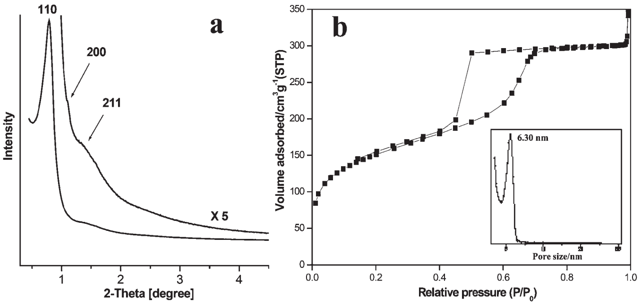

Figure 1. XRD patterns (a) and nitrogen adsorption/desorption isotherm curves (b) with BJH pore size distribution plot (inset) for surfactant-free PMO material prepared by the solvent evaporation method.

Ordered large caged cubic PMO materials were synthesized by using 1,2-bis(triethoxysilyl)ethane (BTSE) as an organically bridged silica source and triblock copolymer F108 (EO_{132}-$PO_{50}EO_{132}$) as a structure-directing agent. In a typical synthesis, 0.7–0.9 g of F108 (BASF) 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 mother liquors were transferred to petri dishes and underwent solvent evaporation for 8 h at 40 °C. The surfactant was removed from the as-made materials by the solvent-extraction method.[4,13] Nearly no carbon signals and adsorption bands due to F108 copolymer were observed in the ^{13}C CP MAS NMR and FT-IR spectra, suggesting almost complete removal of the surfactant from the extracted sample.

Small angle X-ray diffraction (XRD) patterns of the surfactant-free PMO material prepared by solvent evaporation are shown in Figure 1a. The sample shows several poor-resolved diffraction peaks, and combined with the results from transmission electron microscopy (TEM) (see below), these reflection peaks can be indexed to (110), (200), and (211) diffractions for cubic space group (*Im*-3*m*), similar to that reported for the silica-based mesoporous SBA-16.[2,3] The cell parameter, *a*, of surfactant-free sample is calculated to be 15.8 nm. To the best of our knowledge, this is the first report for synthesis of large-pore PMO materials with ordered 3-D caged cubic mesostructure by solvent evaporation method.

N_2 adsorption/desorption isotherms (Figure 1b) for the surfactant-free PMO material exhibit a typical type IV curve with a large H_2 hysteresis loop and a well-defined step at 0.5–0.7 relative pressure (P/P_0) region, further confirming that the product has a large caged cubic mesostructure.[2,15] The surfactant-free PMO material has a narrow pore size distribution (Figure 1b inset) with a mean value of 6.3 nm (obtained from the adsorption

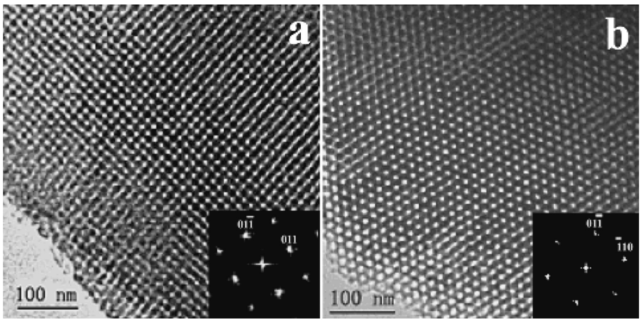

Figure 2. TEM images and Fourier diffractogram patterns of surfactant-free PMO materials prepared by the solvent evaporation method along (a) [100] and (b) [111].

branch based on the BJH model), a BET surface area of $580\,m^2g^{-1}$, and a pore volume of $0.46\,cm^3g^{-1}$.

TEM images and corresponding Fourier diffractograms of surfactant-free PMO sample shown in Figure 2 provide a direct visualization of the PMO pore structure. The images exhibit typical [100] and [111] projection planes of the cubic *Im*-3*m* mesostructure, clearly suggesting that the product has large domains of well-ordered caged-like mesostructure analogous to SBA-16.[2,3] The cell parameter, *a*, calculated from these TEM images is 15.6 nm, in good agreement with the value determined from the XRD data, and suggests that the PMO products have a large-pore *Im*-3*m*-type mesostructure.

It is important to demonstrate that the Si–C bonds are maintained in the surfactant-free organosilicas. ^{29}Si CP MAS NMR spectrum of the surfactant-free PMO material (Figure 3a) shows a broad ^{29}Si resonance at −55.7 ppm and a shoulder at −64.8 ppm, corresponding to T^2 [$RSi(OSi)_2OH$] 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 large caged cubic PMO can also be prepared easily by using other triblock copolymers, such as F127 ($EO_{106}PO_{70}EO_{106}$), F98 ($EO_{123}PO_{47}EO_{123}$), or B50-6600 ($EO_{39}BO_{47}EO_{39}$) as the templates via the solvent evaporation method (see Supplemental Information). Furthermore, the presence of acetone or tetrahydrofuran instead of ethanol can be efficiently to direct the formation of large caged cubic PMOs too. All the aforementioned results indicate that solvent evaporation route is an easy route to synthesize ordered large pore cubic PMO materials. In addition, using this method, cubic large pore PMO materials with different morphologies such as films (about 200-nm thick), monoliths and fibers (up to 5 cm in length, 120 nm in width) can be rapidly and easily prepared (Figures 3b–3d).

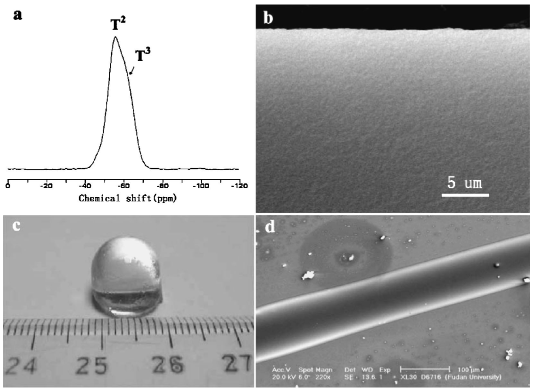

Figure 3. ^{29}Si CP MAS NMR spectrum (a) of PMO materials prepared by solvent evaporation method and SEM images of its different morphologies: (b) films, (c) monoliths, and (d) fibers.

As to the preparation of cubic large-pore PMOs, it is better to conduct the synthesis through this solvent evaporation method, concerning the fact that the interaction between the nonionic block copolymers and the inorganic species in aqueous condition is relatively weaker than that of ionic surfactants and charge density of organosilicate are lower than that of tetraethoxysilane (TEOS) in aqueous condition because of the organic moieties.[4] Solvent evaporation-induced self-assembly can enhance self-assembly capability of organosilicate with nonionic block copolymers and result in long range ordered domains for cubic large organosilica-surfactant mesostructure.

In summary, ordered cubic large-pore *Im*-3*m*-type mesoporous organosilicas have been successfully prepared by an easy solvent evaporation method by using triblock copolymers as the templates. The resulted PMO materials are expected to have promising applications in sorption, separation of large molecules and state-of-art micro-devices.

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