

Free-Standing Periodic Mesoporous Organosilica Film with a Crystal-like Wall Structure

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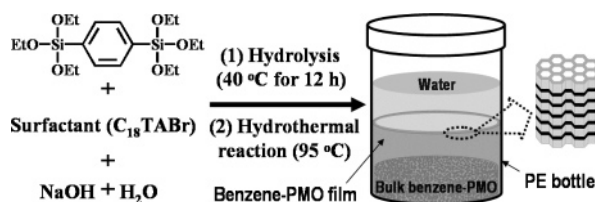
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Periodic mesoporous organosilica (PMO) materials are usually prepared via hydrolytic polycondensation of an alkoxy silane with bridging organic groups ($(R''O)_3Si-R'-Si(OR'')_3$ ($R'' = -CH_3$ or $-C_2H_5$, $R' =$ methane, ethane, ethylene, acetylene, ferrocene, thiophene, and benzene)^{1–5} or via a cyclic siliquoxane precursor $[(EtO)_2SiCH_2]_3$ ⁶ using surfactant-templated assembly. In general, PMO samples have amorphous pore walls, which could limit their utility. Recently, Inagaki and co-workers reported a pioneering work in the PMO field, where an ordered benzene–silica hybrid PMO of a type of powder with a crystal-like wall structure was synthesized.⁷ The benzene–silica hybrid PMO, where hydrophilic silicate layers and hydrophobic benzene layers are alternately arrayed alternately, has potential use in improved selectivity and activity of catalysis, separation, sensing, and enhanced opto-electrical efficiency of included molecules and clusters.^{5,7,8,10,11}

It is generally accepted that the morphology of PMO materials often controls their function and utility. The film type of PMO materials is very important for more diverse applications.^{5,6,9–12} Here, we report the synthesis of the free-standing and oriented mesoporous organosilica films with a crystal-like wall structure grown at the liquid–reaction bottle interface.

Scheme 1. Illustration for the Synthesis Process of the Free-Standing and Oriented Benzene–PMO Film with a Crystal-like Wall Structure



The synthesis of free-standing benzene-bridged periodic mesoporous organosilica (benzene–PMO) films is achieved with 1.0:0.57:2.36:353 BTEB/ $C_{18}TABr$ / $NaOH/H_2O$, where $C_{18}TABr$ is the cationic surfactant $CH_3(CH_2)_{17}N(CH_3)_3Br$ and BTEB is the organosilica source $(C_2H_5O)_3SiC_6H_4Si(OC_2H_5)_3$ (see Experimental Section in Supporting Information).¹² Films with a thickness of 1.6–3.5 μm and a width of ca. 2.5 cm have been grown at the liquid–polyethylene (PE) bottle interface, while the reactant solution is heated to 95 $^{\circ}C$ from 2 to 24 h under static conditions (Scheme 1 and Figure S1, Supporting Information). The films were optically semitransparent (see Figure S2, Supporting Information). A scanning electron microscopy (SEM) image of a benzene–PMO film that has been transferred onto a copper grid revealed that the film is continuous, as shown in Figure 1a. The film has a uniform thickness of ca. 3.5 μm from a magnified film edge, as shown in Figure 1b. During the hydrothermal reaction, the small particles adhered to the surface of the film, as shown in Figure 1c.

As-synthesized and free-standing benzene–PMO films were lifted onto transmission electron microscopy (TEM) grids and directly viewed. The TEM images of the films showed that the films have a highly ordered periodic structure with a hexagonal closed-packed arrangement of channels running parallel to the flat external surface of the film, as shown in Figure 1e. The periodicity of the hexagonal closed-packed arrangement of one-dimensional channels viewed orthogonally to the flat surface of the film was observed from the microtomed section cut orthogonally to the film surface, as shown in Figure 1d (see also Figure S3, Supporting Information). A highly magnified TEM image reveals many lattice fringes, stacked along the channel axes, with a uniform spacing of 7.6 \AA ⁷ on the pore walls over the whole region, as shown in Figure 1f. After extraction of surfactant, the pore diameter and surface area of the film obtained from an N_2 sorption isotherm were determined to be 37.6 \AA and 863 $m^2 g^{-1}$ (Figure S4, Supporting Information).

Figure 2a,b shows the X-ray powder diffraction (XRD) patterns for the as-synthesized and calcined free-standing films lifted onto a glass slide substrate. They both reveal (100) and (200) reflections, although the calcined free-standing film has a broad (200) reflection at $2\theta = 4.5^{\circ}$, consistent with the TEM observation that the channels run parallel to the flat external surface of the film. The as-synthesized benzene–PMO film (Figure 2a) has a d -spacing of 44.8 \AA from the (100) reflection. Star-signed peaks are

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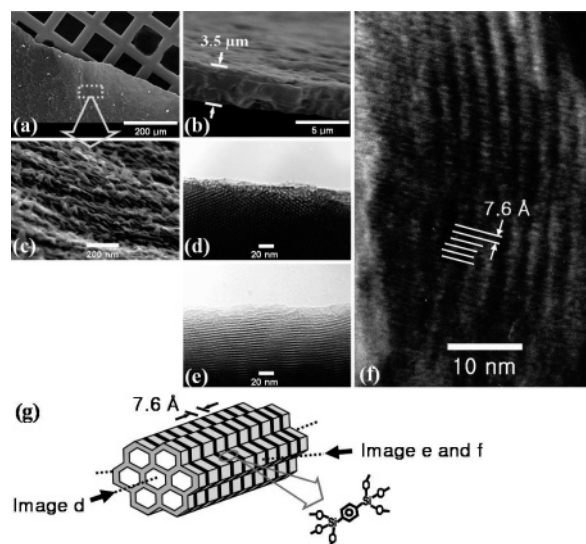


Figure 1. SEM images of (a) an as-synthesized and free-standing benzene-PMO film transferred from the solution onto a copper grid and the highly magnified (b) edge and (c) flat surface of the film. TEM images of as-synthesized benzene-PMO film obtained with the microtomed section cut orthogonally to the film surface, showing (d) highly ordered mesoporous channels consistent with a hexagonal close-packed arrangement, (e) hexagonal basal plane with a well-ordered hexagonal array, and (f) many lattice fringes with a spacing of 7.6 Å in the pore walls with [100] incidence perpendicular to the channels. (g) Schematic model of mesoporous benzene-PMO film derived from the results of the TEM images.

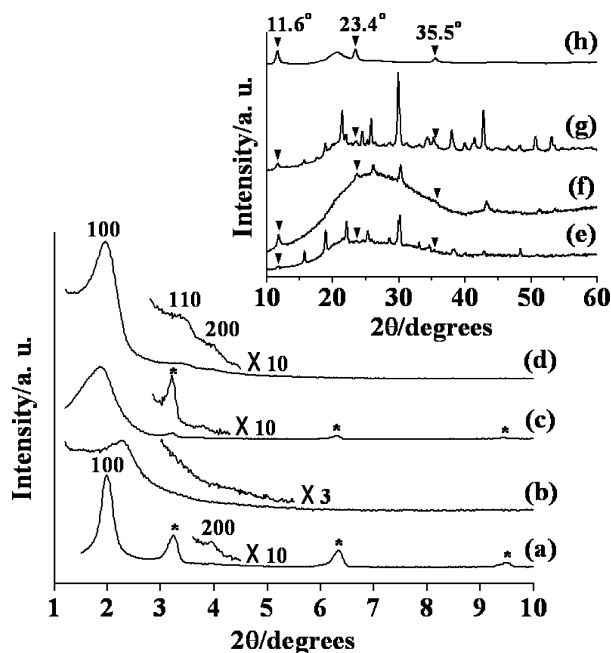


Figure 2. XRD patterns of (a) as-synthesized and free-standing benzene-PMO film, (b) benzene-PMO film calcined at 400 °C for 2 h in N₂, (c) as-synthesized and powdered benzene-PMO film, and (d) powdered and surfactant-extracted benzene-PMO film. Inset shows XRD patterns (e, f, g, and h) in the range of $2\theta = 10\text{--}60^\circ$ for samples a, b, c, and d, respectively.

due to extra surfactant. The extra surfactant can be removed by rinsing the film with hot water repeatedly (Figure S5, Supporting Information). The peaks due to extra surfactant almost disappeared with the retained mesostructure after calcinations at 400 °C for 2 h in N₂ (Figure 2b, Figure S6, Supporting Information). The absence of the (110) reflection for the film sample confirms that the channel axis is oriented parallel to the flat external surface of the film.¹² On calcination of the film (Figure 2b), the anticipated contraction

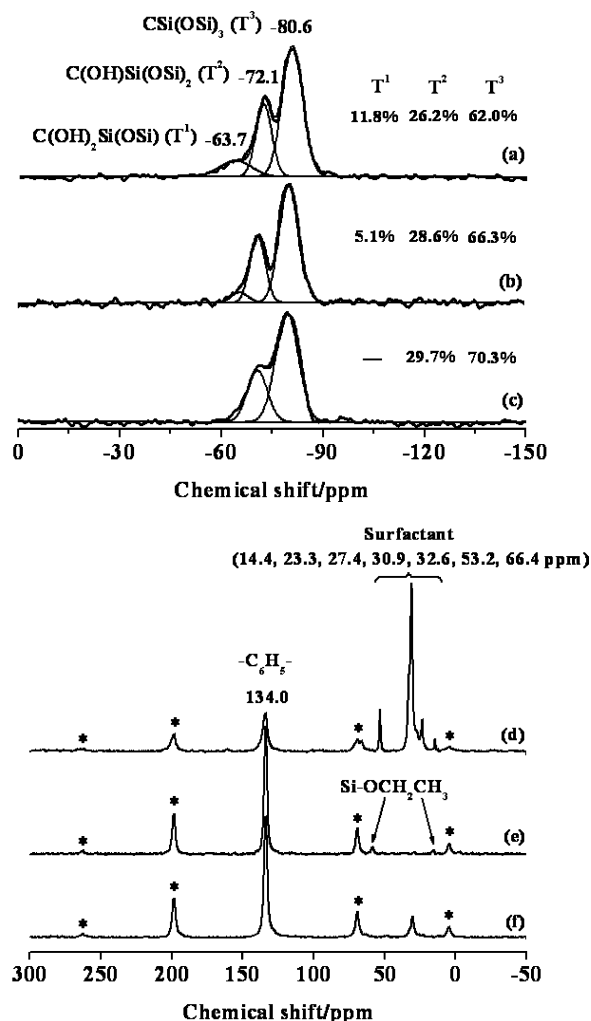


Figure 3. ²⁹Si MAS NMR spectra (a, b, and c) and ¹³C CP MAS NMR spectra (d, e, and f) of (a, d) as-synthesized, (b, e) surfactant-extracted, and (c, f) calcined benzene-PMO film. Asterisk (*) refers to side bands.

($\Delta d_{100} = 6.2 \text{ \AA}$) of the hexagonal *ab*-unit cell is observed as a result of the removal of the surfactant template from the channels and is concomitant with the condensation of silanol (SiOH) groups in the channel walls.¹² From ²⁹Si magic angle spinning (MAS) NMR measurements (Figure 3), the fraction of T³ for the calcined benzene-PMO film (70.3%) is higher than that of the as-synthesized benzene-PMO film (62.0%), which is consistent with the XRD results (i.e., the decreased *d* spacing after calcination). The XRD patterns at $2\theta = 10\text{--}60^\circ$ of as-synthesized and calcined benzene-PMO films display three peaks at $d = 11.6^\circ$, 23.4° , and 35.5° with the peaks due to extra surfactant, as shown in Figure 2e,f. These diffraction peaks can be explained by a periodic structure with a spacing of 7.6 Å.⁷ This XRD result cannot be expected from the wall of the benzene-bridged channel running parallel to the flat external surface of the film and the alternating arrangement of benzene layers and silicate layers along the direction of the channel (Figure 1g). However, the appearance of these diffraction peaks can be due to the small particles adhered to the surface of the film in a gradient, as shown in Figure 1c. The XRD pattern of the as-synthesized and powdered benzene-PMO film shows (100) and (200) reflections at $2\theta = 1.2\text{--}10^\circ$ (Figure 2c). The (110) reflection could not be observed because of overlap with the surfactant

peak at $2\theta = 3.2^\circ$. On the other hand, at high angles ($2\theta = 10\text{--}60^\circ$), three peaks due to molecular-scale periodicity of mesopore walls were observed at $2\theta = 11.6^\circ$, 23.4° , and 35.5° with the peaks due to extra surfactant.⁷ After extraction of surfactant with the sample in Figure 2c (Figure 2d,h), the XRD pattern showed the expected (100), (110), and (200) reflections in powder PMO material at $2\theta = 1.2\text{--}10^\circ$ with the three peaks to indicate molecular-scale periodicity in the pore walls.⁷

²⁹Si and ¹³C MAS NMR measurements clearly showed that the pore walls of the mesoporous benzene-PMO film are made of a covalently bonded network composed of $\text{O}_{1.5}\text{Si}-\text{C}_6\text{H}_4-\text{SiO}_{1.5}$ units and that no carbon-silicon bond cleavage of the BTEB molecule occurred during the synthesis (Figure 3).⁷ ²⁹Si MAS NMR spectrum of the as-synthesized benzene-PMO film (Figure 3a) shows three peaks at -63.7 , -72.1 , and -80.6 ppm, which can be assigned to $\text{T}^1 \text{C}(\text{OH})_2\text{Si}(\text{OSi})$, $\text{T}^2 \text{C}(\text{OH})\text{Si}(\text{OSi})_2$, and $\text{T}^3 \text{CSi}(\text{OSi})_3$.^{3,7} The ¹³C CP MAS NMR spectroscopy of the as-synthesized benzene-PMO film exhibits a peak at 134.0 ppm, which is attributed to carbons covalently linked to Si ($\text{Si}-\text{C}_6\text{H}_4-\text{Si}$; Figure 3d).^{3,7} Peaks due to surfactant carbon atoms were observed at 14.4, 23.3, 27.4, 30.9, 32.6, 53.2, and 66.4 ppm.¹² After surfactant extraction, the ²⁹Si MAS NMR spectrum shows three signals which are assigned to $\text{T}^1 \text{C}(\text{OH})_2\text{Si}(\text{OSi})$, $\text{T}^2 \text{C}(\text{OH})\text{Si}(\text{OSi})_2$, and $\text{T}^3 \text{CSi}(\text{OSi})_3$, as shown in Figure 3b. The fraction of T^1 (5.1%) decreased remarkably compared with that of the as-synthesized benzene-PMO film (11.8%); on the other hand, the fraction of T^2 and T^3 obtained from the fitted curves for the surfactant-extracted benzene-PMO film (28.6% and 66.3% for T^2 and T^3 , respectively) is higher than that of the as-synthesized benzene-PMO film (26.2% and 62.0 for T^2 and T^3 , respectively). The ¹³C CP MAS NMR spectrum shows a strong single resonance at 134.0 ppm, which is attributed to carbons covalently linked to Si ($\text{Si}-\text{C}_6\text{H}_4-\text{Si}$), as shown in Figure 3e. The two peaks at 15.6 and 58.5 ppm are attributed to carbons of surface ethoxy groups ($\text{Si}-\text{OCH}_2\text{CH}_3$), which are formed during the treatment with the HCl/EtOH solution for removal of the surfactant from the as-synthesized benzene-PMO film. It was confirmed by NMR experiments that the organic-inorganic moiety ($-\text{Si}-\text{C}_6\text{H}_4-\text{Si}-$) is the basic structural unit in the film. The benzene-PMO film was calcined at 400 °C in N_2 and investigated by ²⁹Si (Figure 3c) and ¹³C cross-polarization (CP) MAS NMR (Figure 3f) spectroscopy. The ²⁹Si MAS NMR spectrum of the calcined benzene-PMO film shows two peaks (T^2 and T^3), indicating that the Si-C bonds remained intact. The fractions of T^2 and T^3 obtained from the fitted curves for the calcined benzene-PMO film (29.7% and 70.3% for T^2 and T^3 , respectively) are higher than that of the as-synthesized and the surfactant-extracted benzene-PMO film. The result reveals that the calcined benzene-PMO film has high degree of condensa-

tion of silanol ($\text{Si}-\text{OH}$) groups in the channel wall at high temperature. The ¹³C CP MAS NMR spectrum of the calcined benzene-PMO film shows a strong single resonance at 134.0 ppm, which is attributed to carbons covalently linked to Si ($\text{Si}-\text{C}_6\text{H}_4-\text{Si}$), as shown in Figure 3f. In addition, a small peak at 30.2 ppm was observed because the surfactant was not completely removed.

With the results described above, the mechanism for the formation of the free-standing and benzene-bridged PMO film with a crystal-like wall structure can be explained. Benzene groups are somewhat hydrophobic. Therefore, co-assembled surfactant/benzene-bridged organosilica species may interact with the hydrophobic surface of the PE bottle when it is used as the reaction bottle to form a benzene-PMO film. When polypropylene and Teflon bottles were used as reaction bottles, free-standing benzene-PMO films were formed at the liquid-reaction bottle interface like the formation of the film by using the PE bottle (Figures S7-S9, Supporting Information). However, a free-standing benzene-PMO film was not formed by using a glass bottle with the more hydrophilic surface. Film growth is probably regulated by matching charge and geometry between micellar aggregates and benzene-bridged organosilica species. Finally, the free-standing and oriented benzene-bridged PMO film has been grown at the liquid-reaction bottle interface, while mesoporous channels were formed parallel to the flat external surface of the film.

Free-standing and benzene-bridged PMO films have a well-ordered hexagonal mesostructure and molecular-scale periodical pore walls, in which hydrophilic silicate layers and hydrophobic benzene layers are alternately arrayed. The benzene-bridged PMO films have potential use in improved selectivity and activity of catalysis, separation, sensing, and enhanced opto-electrical efficiency of included molecules and clusters. Moreover, fluorescence spectra indicate some interactions between benzene rings in the walls (Figure S10, Supporting Information). If closer stacking of benzene rings in the walls could be achieved, $\pi-\pi$ conjugation of the rings would render the porous framework conducting.⁷

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Supporting Information Available: Experimental section, magnified SEM images, N_2 adsorption-desorption isotherms, XRD patterns, TEM images and photographs of the as-synthesized films, TEM images of the calcined film, and fluorescence spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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