Supporting Information

Free–Standing Periodic Mesoporous Organosilica Film with a Crystal–Like Wall Structure

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Experimental Section

Synthesis of benzene-bridged PMO film

The synthesis of free–standing and benzene–bridged periodic mesoporous organosilica (benzene–PMO) films in the reactant solution is achieved using the following reactant molar ratios and synthesis procedure: 1.0 BTEB : 0.57 C_{18}TABr : 2.36 NaOH : 353 H_2O, where C_{18}TABr is the cationic surfactant $CH_3(CH_2)_{17}N(CH_3)_3Br$ and BTEB is the orgsanosilica source reagent $(C_2H_5O)_3SiC_6H_4Si(O\ C_2H_5)_3$. Typically, we synthesized the benzene–PMO film in a 50 ml polyethylene (PE) bottle (diameter, 4.5 cm) with 1/353 scale of the reactant molar ratios. The surfactant solution is mixed with BTSB and stirred at 40 ^oC for 12 h and heated to 95 ^oC. The film–forming process works well under static conditions at 95 ^oC over a reaction time of from 2 h to 24 h. The benzene–PMO film, with thickness from 1.6 μm to 3.5 μm and width of about 2.5 cm, has been grown at the liquid–reaction bottle interface (Figure S1). The benzene–PMO films were rinsed with distilled water, and dried at 80 ^oC for 12 h in air. The benzene–PMO films can be transferred from the solution onto a substrate such as a glass slide *etc*. by the 'pull up' technique. The films are optically semitransparent. The surfactant in the films was removed by a solvent–extraction process with 150 ml of EtOH including 3 ml of 35wt% HCl at 60 ^oC for 12 h and dried at 80 ^oC for 12 h. During the surfactant–extraction with the adopted method in this work, some of the films were broken into pieces with several millimeter sizes. Transparency of the film pieces was almost similar to that of the film of large size. Transparency of the benzene–PMO films with thickness from 1.6 μm to 3.5 μm was similar to the naked eyes, as shown in the photographs of Figure S2.

During reaction for the formation of the benzene–PMO film, the bulk product benzene–PMO precipitated on the bottom of the PE bottle. With reaction condition at 95

^{o}C for 24 h, the yields of the benzene–PMO film and the bulk product benzene–PMO were 1.7 mol% and 98.3 mo%, respectively.

Characterization

The powder X–ray diffraction (XRD) patterns were obtained by a Rigaku Miniflex diffractometer (40 kV, 30 mA) using Cu K_{α} radiation of wavelength 1.541 Å. The adsorption and desorption isotherms of nitrogen at –196 ^{o}C were measured using a Micromeritics ASAP2010 instrument. All samples were outgassed at 150 ^{o}C for 12 h under vacuum ($p < 5 \times 10^{-6}$ Torr) in the degas port of the adsorption analyzer. The pore size distribution curve was obtained from an analysis of the desorption branch by using Barrett–Joyner–Halenda (BJH) method. Field emission scanning electron microscopy (FE–SEM) images were obtained using a Philips XL30 S FEG (Netherland) with an acceleration voltage of 15 kV. The samples were coated with osmium using an OPC 80T plasma coater prior to imaging. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM–2010 microscope operating at 200 kV, for the epoxy–embedded and microtomed sections cut orthogonally to the film surface. ^{29}Si and ^{13}C cross polarization (CP) MAS NMR spectra were obtained on a Bruker DSX400 spectrometer at room temperature with a 4 mm zirconia rotor spinning at 6 kHz (Resonance frequencies of 79.5 MHz and 100.6 MHz for ^{29}Si and ^{13}C CP MAS NMR, respectively; 90° pulse width of 5 μs, contact time 2 ms, recycle delay 3 s for both ^{29}Si and ^{13}C CP MAS NMR). The fluorescence spectra were obtained with HITACHI Instrument F–4500 Fluorescence spectrometer equipped with a xenon lamp.

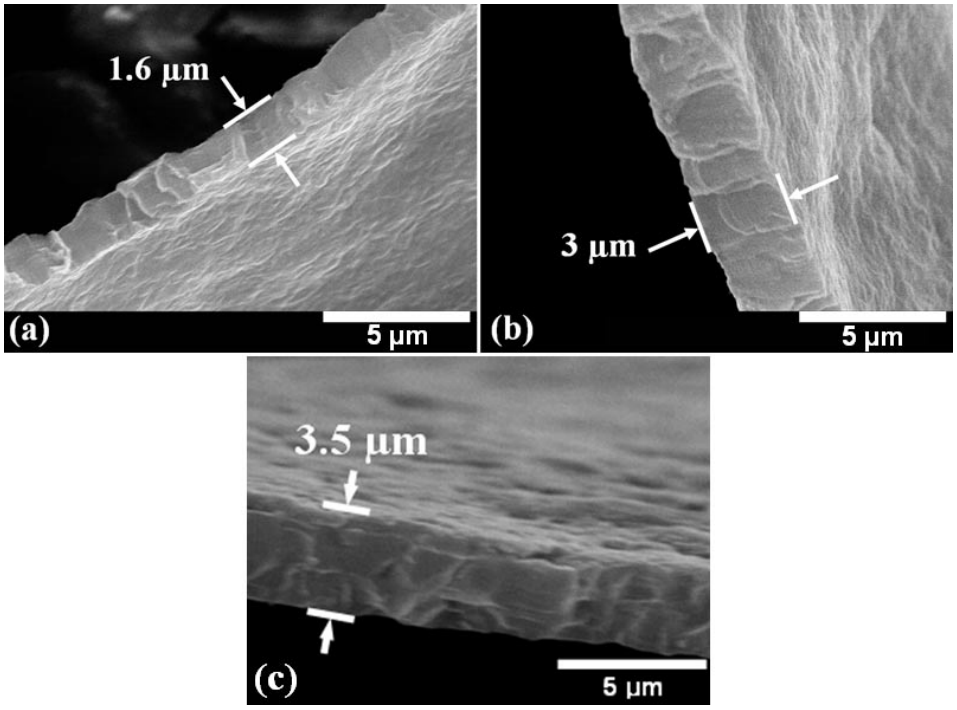

Figure S1. SEM images of the magnified edge part of the as–synthesized benzene–PMO films grown at the liquid–polyethylene bottle interface at 95 ^{o}C for (a) 2 h, (b) 6 h, and 24 h.

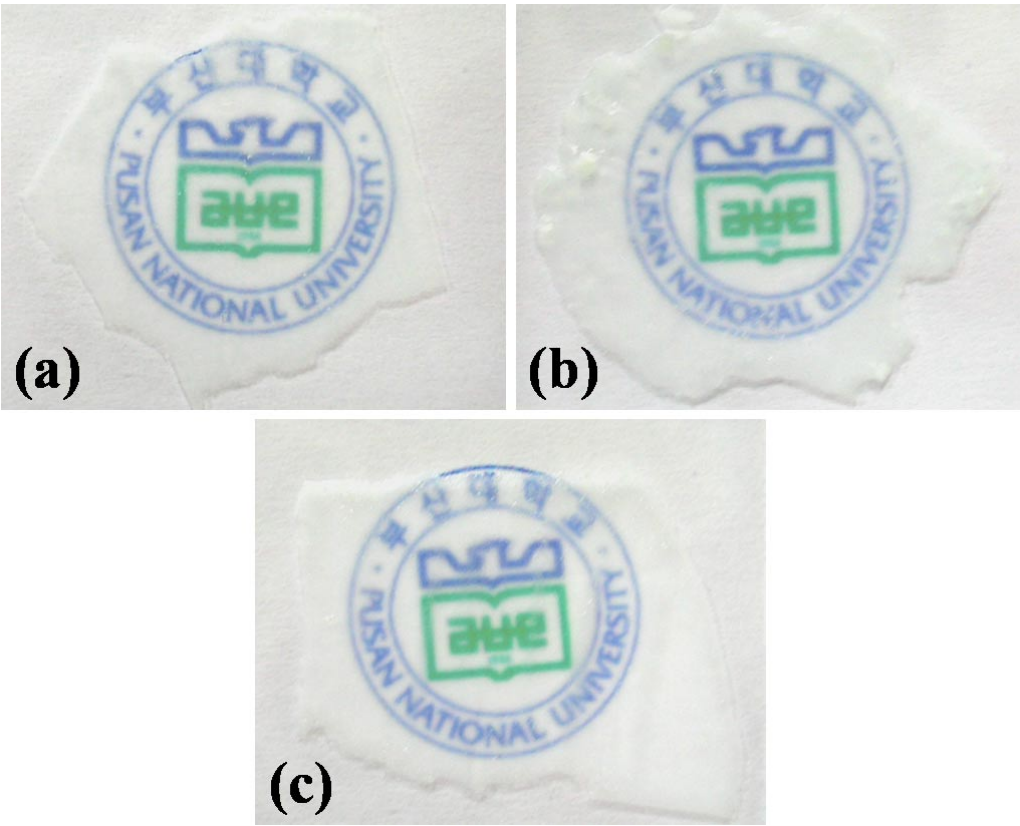

Figure S2. Photographs of the semitransparent as–synthesized benzene–PMO films grown at the liquid–polyethylene bottle interface at 95 ^{o}C for (a) 2 h, (b) 6 h and 24 h.

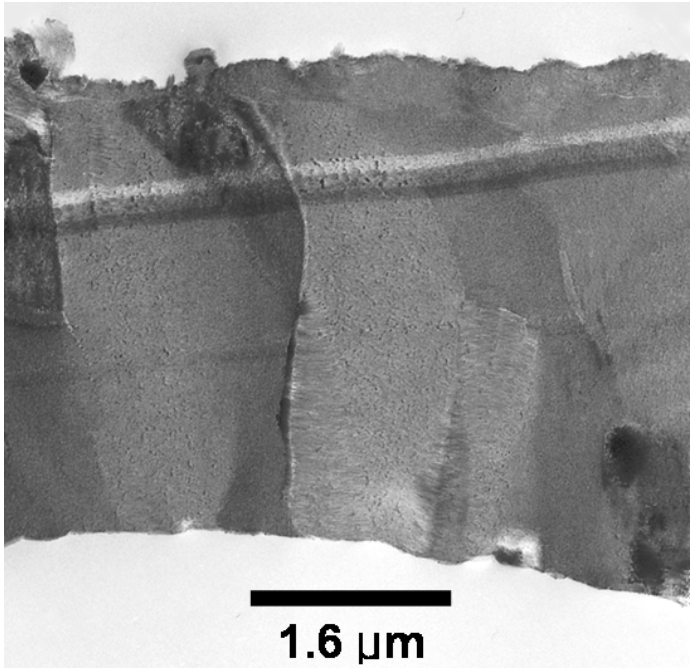

Figure S3. Low magnified TEM image of an as–synthesized benzene–PMO film cut orthogonally to the film surface.

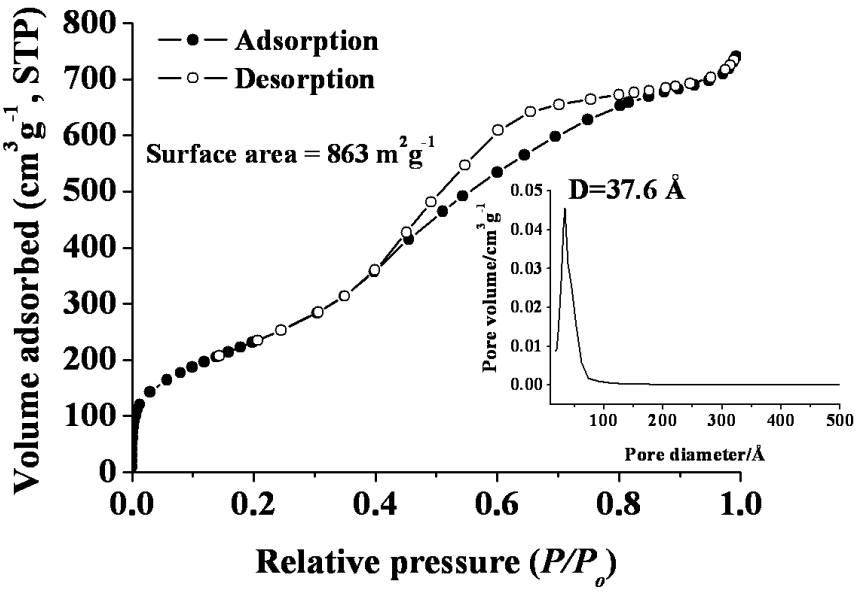

Figure S4. Nitrogen adsorption–desorption isotherms for surfactant–extracted benzene–PMO film. Inset shows the pore size distribution obtained using desorption branch by BJH method.

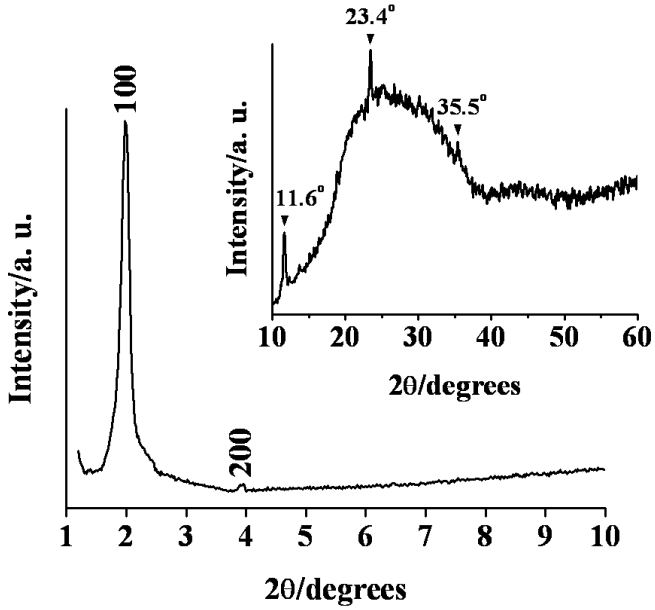

Figure S5. XRD pattern of an as–synthesized benzene–PMO film after removed excess surfactant. Inset shows XRD pattern in the range of 2θ = 10–60°.

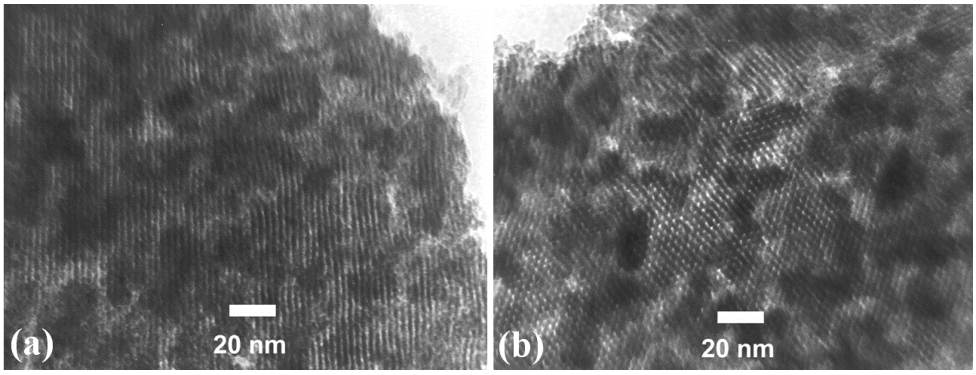

Figure S6. TEM images of the benzene–PMO film calcined at 400 ^{o}C for 2 h in N_2, showing (a) a highly ordered periodic structure consistent with a hexagonal close–packed arrangement of channels running parallel to the surface of the benzene–PMO film, and (b) hexagonal basal plane well–ordered hexagonal array.

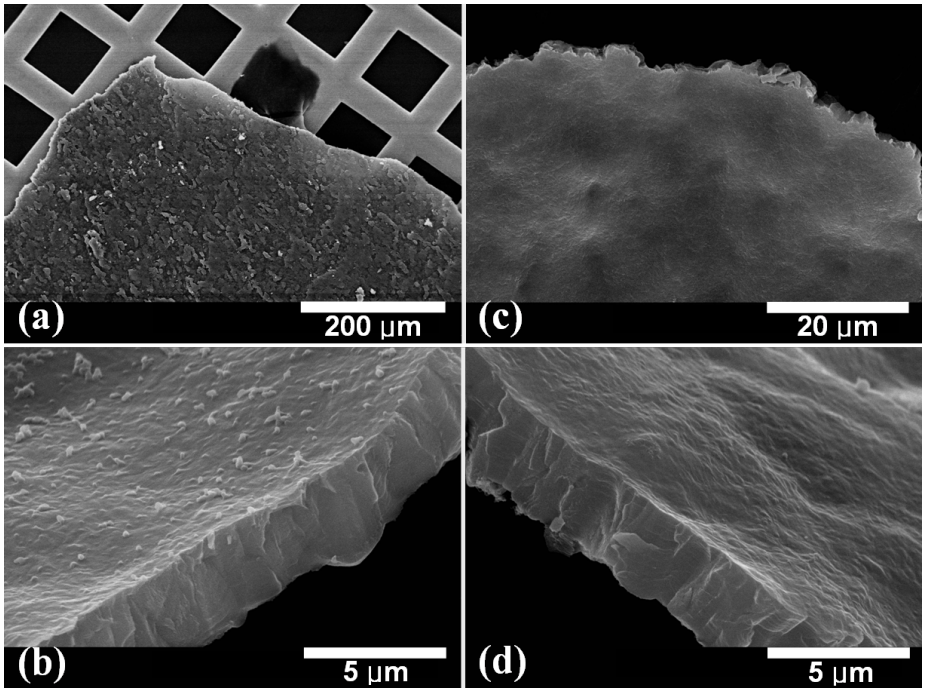

Figure S7. SEM images of the as–synthesized benzene–PMO films grown at (a and b) the liquid–polypropylene bottle interface and (c and d) the liquid–Teflon bottle interface: (a and c) low magnification and (b and d) highly magnified edge of the films.

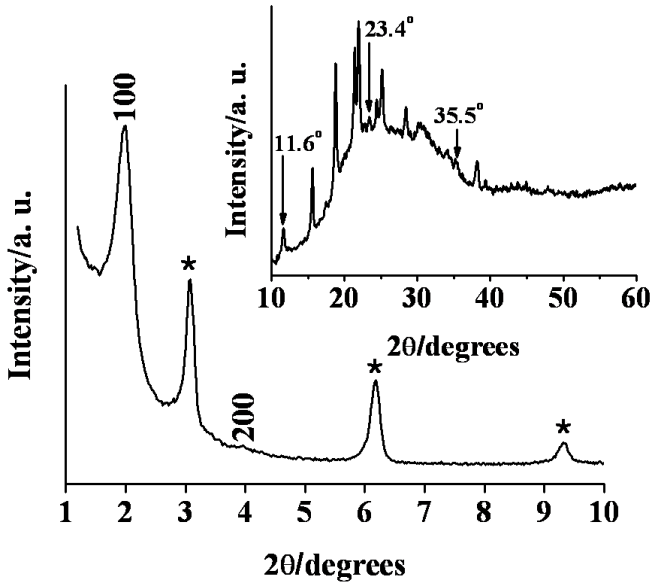

Figure S8. XRD pattern of an as–synthesized benzene–PMO film grown at the liquid–polypropylene bottle interface. Inset shows XRD pattern in the range of 2θ = 10–60°.

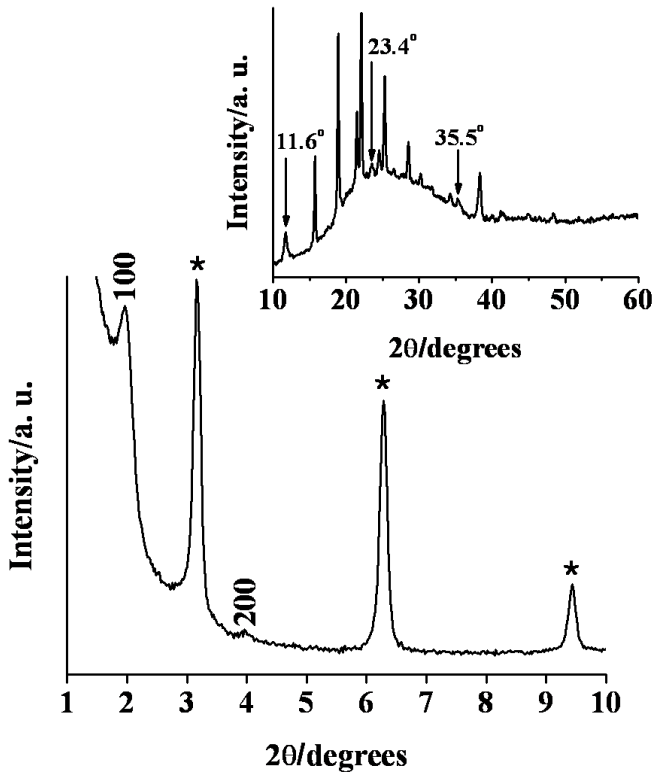

Figure S9. XRD pattern of an as–synthesized benzene–PMO film grown at the liquid–Teflon bottle interface. Inset shows XRD pattern in the range of $2\theta = 10–60^{o}$.

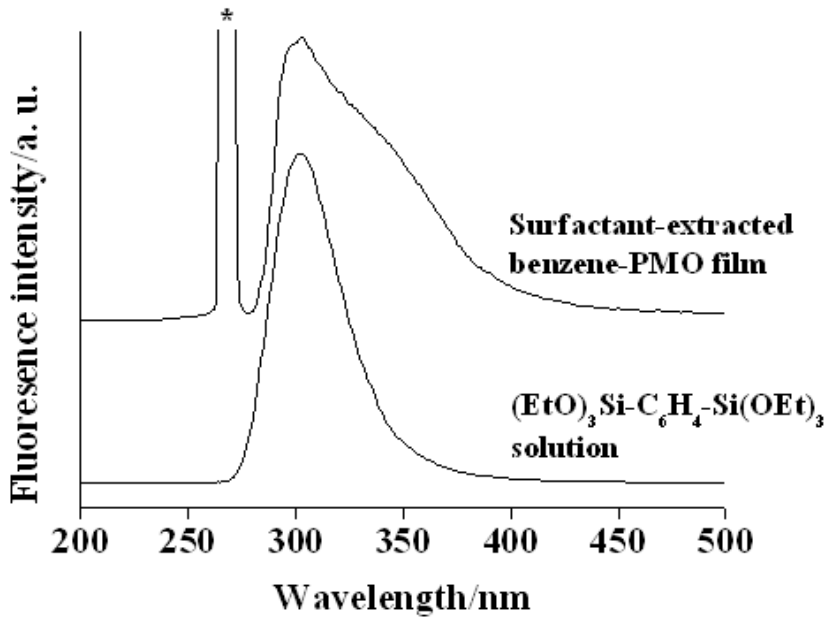

Figure S10. Fluoresence spectra of mesoporous benzene–PMO film and the BTEB monomer solution. Spectra were collected with excitation at 269 nm. (*) refer to scatter of light from the illuminant.