Highly ordered three-dimensional large-pore periodic mesoporous organosilica with \textit{Im}3\textit{m} symmetry

Wanping Guo, Il Kim and Chang-Sik Ha*  
Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

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Highly ordered three-dimensional \textit{Im}3\textit{m}-type periodic mesoporous organosilica with a cavity size of 9.8 nm has been synthesized under strongly acidic media in the presence of inorganic salts using triblock copolymer F127 as the template and 1,2-bis(trimethoxysilyl)ethane as the organically bridged silica source.

In recent years, surfactant-templated synthesis strategies have been successfully applied to the preparation of a variety of mesoporous materials.\textsuperscript{1} One of the most exciting new developments was the discovery of a novel class of organic–inorganic hybrid materials called periodic mesoporous organosilicas (PMOs) through surfactant-templated condensation of organosilanes with two organically bridged trialkoxysilyl groups.\textsuperscript{2–4} To date, PMO materials have been prepared with various bridged organic groups including methane,\textsuperscript{5} ethane,\textsuperscript{2–3} ethylene,\textsuperscript{2,4} benzene,\textsuperscript{4,6} thiophene,\textsuperscript{4} biphenylene,\textsuperscript{7} etc. In addition, successful syntheses of PMOs have been achieved under a wide range of pHs from highly basic to strongly acidic conditions using cationic,\textsuperscript{2–7} anionic,\textsuperscript{8} neutral,\textsuperscript{9} and nonionic oligomeric\textsuperscript{10} surfactants. Furthermore, several recent reports\textsuperscript{11–13} have demonstrated the preparation of two-dimensional hexagonal PMOs with well-ordered large pores using triblock copolymer P123 (EO\textsubscript{20}PO\textsubscript{80}EO\textsubscript{20}) as the template. Especially, the salt-assisted synthesis route\textsuperscript{13} was a paradigm in the preparation of highly ordered large-pore hexagonal PMOs. At present, three-dimensional (3D) mesoporous materials are of particular interest for applications such as catalysis, separation and chemical sensing. An attempt to synthesize 3D large-pore PMOs using triblock copolymer B50-6600 (EO\textsubscript{39}BO\textsubscript{47}EO\textsubscript{39}) under low-acidic conditions led to the formation of PMOs with large cage-like pores in limited long-range order and undetermined structural assignment.\textsuperscript{14} Up to now, the synthesis of 3D large-pore PMOs with long-range structural order has not been realized. In this communication, we present the first synthesis of highly ordered large-pore PMO with 3D cubic \textit{Im}3\textit{m} mesostructure.

Pluronic F127 (EO\textsubscript{106}PO\textsubscript{70}EO\textsubscript{106}) was employed to prepare cubic PMO material (designated PMO-SBA-16), as in the preparation of silica-based SBA-16 mesoporous material.\textsuperscript{15} [1,2-Bis(trimethoxysilyl)ethane] (BTME) was chosen as the organically bridged silica source only because of its commercial availability. In a typical synthesis of PMO-SBA-16, 0.9 g of F127 (Sigma) and 8.07 g of K$_2$SO$_4$ (Aldrich) were dissolved in 40 g of 2.0 M HCl solution (Wako, Japan) with stirring at 40 °C for 24 h. The mixture was then aged at 80 °C and (211) reflections of the body-centered 3D cubic space group (\textit{Im}3\textit{m}) similar to that reported for the silica-based mesoporous counterpart SBA-16.\textsuperscript{15} The unit cell parameter of the cubic lattice is as large as 18.1 nm. This is the first large-pore PMO material that exhibits such a highly ordered 3D mesostructure. By contrast, the SAXS pattern [Fig. 1, trace (b)] of the solvent-extracted control sample F127 blank prepared in the absence of K$_2$SO$_4$ reveals the formation of amorphous gel.

The SAXS pattern of the solvent-extracted PMO-SBA-16 [Fig. 1, trace (a)] shows three well-resolved peaks at very small scattering angles, with interplanar \textit{d} spacings of 12.8, 9.03, and 7.38 nm. These three peaks can be indexable as (110), (200), and (211) reflections of the body-centered 3D cubic space group (\textit{Im}3\textit{m}), similar to that reported for the silica-based mesoporous counterpart SBA-16.\textsuperscript{15} The \textit{d} spacings were determined by X-ray diffraction data measured at 298 K with Co K\textsubscript{α} radiation. In addition, successful syntheses of PMOs have been achieved under a wide range of pHs from highly basic to strongly acidic conditions using cationic,\textsuperscript{2–7} anionic,\textsuperscript{8} neutral,\textsuperscript{9} and nonionic oligomeric surfactants. Furthermore, several recent reports\textsuperscript{11–13} have demonstrated the preparation of two-dimensional hexagonal PMOs with well-ordered large pores using triblock copolymer P123 (EO\textsubscript{20}PO\textsubscript{80}EO\textsubscript{20}) as the template. Especially, the salt-assisted synthesis route\textsuperscript{13} was a paradigm in the preparation of highly ordered large-pore hexagonal PMOs. At present, three-dimensional (3D) mesoporous materials are of particular interest for applications such as catalysis, separation and chemical sensing. An attempt to synthesize 3D large-pore PMOs using triblock copolymer B50-6600 (EO\textsubscript{39}BO\textsubscript{47}EO\textsubscript{39}) under low-acidic conditions led to the formation of PMOs with large cage-like pores in limited long-range order and undetermined structural assignment.\textsuperscript{14} Up to now, the synthesis of 3D large-pore PMOs with long-range structural order has not been realized. In this communication, we present the first synthesis of highly ordered large-pore PMO with 3D cubic \textit{Im}3\textit{m} mesostructure.

Fig. 1 Small-angle X-ray scattering (SAXS) patterns of solvent-extracted samples: (a) PMO-SBA-16 and (b) F127 blank. SAXS measurements were carried out using 4C2 beam lines with Co K\textsubscript{α} synchrotron radiation (\textit{λ} = 0.1608 nm) at 2.5 GeV and 140 mA in the Pohang Accelerator Laboratory, POSTECH, Korea.

The nitrogen adsorption–desorption isotherm and the corresponding pore size distribution calculated by the BdB (Broekhoff and de Boer) method\textsuperscript{16} for the solvent-extracted PMO-SBA-16 is shown in Fig. 2. The isotherm was obtained using a Quantachrome Autosorb-1 apparatus at liquid nitrogen temperature.

Fig. 2 Nitrogen adsorption–desorption isotherm for solvent-extracted PMO-SBA-16. The inset shows the pore size distribution calculated by the BdB method. The isotherm was obtained using a Quantachromie Autosorb-1 apparatus at liquid nitrogen temperature.
extracted PMO-SBA-16 sample. The isotherm is of type IV with an H-type hysteresis loop at high relative pressure characteristic of large cage structures. The pore size analysis by the BJEB method with a spherical model gives a cavity size of 9.8 nm determined from the adsorption branch of the isotherm and the pore entrance size is estimated to be smaller than or equal to 5.5 nm from the desorption branch of the isotherm. The solvent-extracted PMO-SBA-16 has a BET surface area of 989 m$^2$ g$^{-1}$ and a pore volume of 0.65 cm$^3$ g$^{-1}$. The combination of SAXS and nitrogen adsorption data provides strong evidence of the high quality of PMO-SBA-16 material. The structural order of the PMO material is analogous to that observed in silica-based SBA-16 counterpart.

As shown in the SAXS experiments, inorganic salts were indispensable in the synthesis of PMO-SBA-16. Only an amorphous gel was obtained in the absence of inorganic salts. The well-ordered PMO-SBA-16 could be prepared in the presence of Na$_2$SO$_4$ instead of K$_2$SO$_4$. But the use of NaCl or KCl resulted in the deterioration of the long-range order of PMO-SBA-16. It could be suggested that the addition of inorganic salts, especially highly charged salts, should increase the self-assembly interaction between the headgroups of triblock copolymer surfactant and the organosilane species, which led to the formation of highly ordered 3D large-pore PMO materials.

In summary, we have demonstrated for the first time that 3D cubic Imcm-type PMO with well-ordered large pores was synthesized using triblock copolymer F127 as the template under strongly acidic media in the presence of inorganic salts. It should be noted that the salt-assisted synthesis strategy could be extended to the preparation of other types of highly ordered large-pore PMO materials using other kinds of triblock copolymers as the templates.

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Notes and references