

Three-Dimensional Ordered Macroporous Structures With Mesoporous Silica Walls

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Three-dimensional (3D) cubic ordered macroporous (140 nm) and binary macroporous (140, 80 nm) silica structures with ordered mesoporous (7.7 nm) walls have been synthesized by using cubic closed-packing colloidal crystals as templates. The colloidal crystals can be made from equal-sized or binary-sized latex spheres by the simple methods of self-sedimentation on the film or pressing into a pellet.

Utilizing templates is a common method to prepare porous materials.¹⁻¹¹ Many kinds of supermolecular aggregates of surfactant molecules or amphiphilic block copolymers have been employed to create mesoporous materials.^{1,2} By a cooperative assembly process between organic templates and inorganic species, resulting products are directed into highly-ordered mesostructures.¹ Mesopores size can be adjusted by using the surfactant aggregates with different length.¹ But obtained mesopores were limited to 30 nm or less in size.¹ In order to achieve macropores with sizes extended to a few hundreds nanometers, colloidal crystals assembled from monodisperse colloid-sized particles were used as templates.³⁻¹¹ Under the effect of gravity and centrifugal force, the latex spheres are closely packed into highly-ordered 3D structures.⁵⁻⁸ Face-centered cubic (fcc) crystals of nanospheres in the structure have been illustrated by computer simulations and experiments.^{3,4} Since the 3D periodic structure of macroporous materials presents interesting technological applications on photonics, electronics, sorption and separation processes, many kinds of materials have been synthesized by the colloidal crystallization templating technique.⁵⁻¹⁰ They included macroporous carbon,⁵ photonic crystals of titania, zirconia,^{6,7} macroporous phosphates, hybrid composites⁸ and macroporous polymers with tunable pore sizes.⁹

In this paper we report syntheses of 3D cubic (fcc) ordered macroporous and binary macroporous (AB₁₃) silica structures with ordered mesostructured framework. Ordered macroporous structures are templated by using fcc closed-packing crystals of uniform diameter-sized latex or mixture of binary-sized latex spheres. Two simple methods can be used to create polystyrene (PS) sphere template crystals: one is self-sedimentation on the narrow pore size (100 nm) membrane, another is pressing the dried PS powder to a pellet. Silica precursor is filled into the voids between spheres and condensed in air. Amphiphilic block copolymers in precursor lead to the ordered mesostructures² by a cooperating assembly with silica species.

The colloidal suspensions containing monodisperse PS latex spheres 210 nm in diameter were loaded on a smooth porous (100 nm) membrane. Self-sedimentation of spheres completed within 24 h under the effect of gravity and capillary forces. After the colloidal crystals were dried in air for 24 h, silica precursor was permeated into the voids of latex spheres by adding drop-

wisely on membrane. The silica precursor was prepared with composites of 2.08 g tetraethyl orthosilicate: 15 g ethanol: 0.4 g (0.1 M) HCl: 0.5 g H₂O: 0.9 g amphiphilic triblock copolymer [poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer (Aldrich, M_w = 5800, EO₂₀PO₇₀EO₂₀, P123)] according to a previous report.² Resulted colloid crystals were dried for 8 h in a vacuum desiccator. Dual 3D macroporous silica structure was prepared as above by using two diameter-sized PS spheres (210 and 130 nm) with a 1:13 sphere ratio. PS and surfactant were removed by calcination at 450 °C for 4 h. Another simple method was used to create a colloidal crystal templates: the dried PS particles ca. 170 nm in diameter was compressed to a pellet (~1 cm) at a pressure of 1x10⁴ kPa. The resulting pellet was dipped into silica solution precursor and the weight ratio of PS pellet with silica was kept at 1:1. SEM images were performed on a Hitachi S450 microscope. TEM photographs were obtained with a Philips EM 430 microscope operated at 200 kV.

Woodcock and Mignez et al. have proved that the structure packed by monodisperse nanospheres is 3D ordered fcc arrangement.^{3,4} Latex spheres dispersed in colloidal suspension can be sedimentated and closely packed on the smooth membrane by gravity. Perfectly ordered structures of the resulting crystals show bright colors such as green. SEM photographs of ordered closely packed PS crystal templates are shown in Figure 1. In

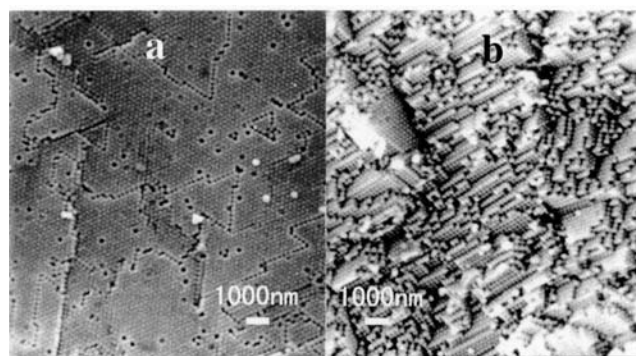


Figure 1. SEM images of a, PS colloid crystal (diameter ~210 nm) on (111) plane; b, cross-section of PS nanosphere colloid crystals.

general, ordered domain range is usually larger than a few hundreds micrometers. Hexagonal packing corresponding to the (111) plane of a fcc closed-packing structure can be observed on the facet of the PS crystals (Figure 1a); however, (100) and (110) planes can be observed in a cleaved edge's photograph. (Figure 1b). It suggests that almost entirely opal crystals have a fcc structure. Pressing the dried PS nanosphere powder into a pellet can also result in the closed packing of PS spheres on basis of SEM results; however, the ordered domain is limited to several

micrometers. Binary-sized (210 and 130 nm) PS nanospheres (sphere ratio 1:13) can also be used to create the opal template crystal by self-sedimentation. When the diameter ratio of the two PS spheres is 0.62 (sphere ratio is 13:1) or 0.58 (sphere ratio is 2:1), the AB₁₃ and the AB₂ superlattice structures can be obtained.¹²

The silica precursor creating mesostructure can be filled into the voids in the opals by capillary forces and form the continuous inorganic frameworks. After evaporation of ethanol, the condensation of silicate occurred and mesostructure of silica is formed.² XRD pattern of as-made product shows a very weak peak at *d*-spacing of 10.2 nm.

The well ordered macroporous material can be formed from PS nanosphere by sedimentation after calcination at 450 °C in air. SEM images (Figure 2a) show that macrostructure is 3D ordered fcc structures. The size of macropores is about 140 nm, shrank about 33% contrast with diameter of latex spheres (210 nm in diameter) after calcination. Thickness of the walls between adjacent pores is 80 nm in average, based on SEM images. The macropore size can be tunable by simply using different diameter-sized PS spheres. On the other hand, macroporous silica templated by a dried PS pellet shows partly ordered at the domain of several micrometers.

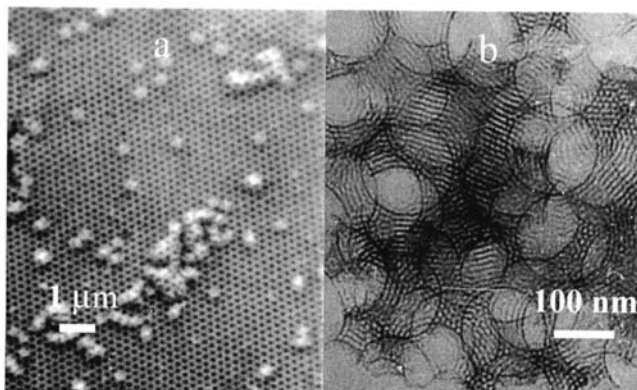


Figure 2. a, SEM b, TEM photographs of calcined macro-mesoporous silica prepared by combining latex sphere templating and the cooperative assembly of silicate species and triblock copolymer P123.

The mesostructure of silica wall is revealed by XRD and TEM images. XRD pattern of calcined macro-mesoporous silica shows a relative weak reflection peak at *d* value of 9.2 nm corresponding (100) diffraction. The diffractions for (110), (200) are too broad to observe. The result can be explained that it has no long range ordering due to the limit of the wall thickness with only 80 nm. This can be further confirmed by TEM image (Figure 2b). Both ordered macroporous and mesoporous silica can be observed (Figure 2b), images recorded along the [110] and [100] zone axes of calcined product show ordered and channel mesostructures. In some regions, the wall thickness is so thin that only one hexagonal mesostructure cell can be observed. The 1D mesochannel is formed around the PS nanosphere. The Dual macroporous silica with mesostructured framework can be synthesized by using binary-sized (210 and 130 nm) PS sphere opal as the template. After calcination, the macroporous silica show binary macroporous structures with pore size (140, 80 nm) similar to AB₁₃ structure.¹²

Figure 3 shows N₂ adsorption-desorption isotherm curves of calcined macro-mesoporous silica measured at 77 K. A steep increasing occurs at a relative pressure $0.60 < p/p_0 < 0.82$, which is due to the filling of mesoporous walls by capillary condensation. The BET surface area of the calcined sample is 915 m²/g. Figure 3 (inset) shows the pore size distribution calculated by BdB method. It is evident that mesoporous silica wall has a narrow pore size distribution with the mean size of about 7.7 nm, which is in agreement with the value from TEM images. The total pore volume at relative pressure of 0.973 is 1.02 cm³/g.

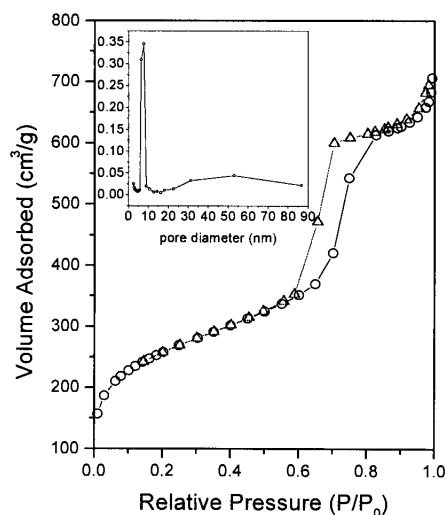


Figure 3. Nitrogen adsorption/desorption isotherm curves and pore size distribution plot for calcined macro-mesoporous silica.

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