Preparation of Three-dimensionally ordered Macroporous SiO_2 Membranes with Controllable Pore Size

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Three-dimensionally ordered macroporous SiO_2 membranes are prepared by the codeposition method using SiO_2 colloidal particles as building blocks and polymethyl methacrylate as the templates. The pore size of ordered macroporous SiO_2 membranes can be controlled by changing the volume ratio of templates to SiO_2.

The materials with three-dimensionally ordered macroporous (3DOM) structures are useful in a wide range of applications: for instance, as photonic bandgaps and optical stop-bands[1] owing to their spatially periodic structures, as supports for sensors and catalysis,[2] as building blocks in tissue engineering,[3] and so on. Three-dimensionally ordered macroporous oxides (oxides of Si, Ti, Al, Zr, Co, and Fe),[4–8] metals (Au and Ag)[9,10] as well as polymers[11,12] have been successfully synthesized. For synthesis of ordered macroporous materials, ordered arrays of colloids or emulsions have been employed as templates. This templating method typically consists of two processes. First, the interstitial voids of the templates are filled with various kinds of materials which formed a solid framework around the templates. Second, the templates are removed either by heat treatment or solvent extraction to form the three-dimensionally ordered arrays. Sol–gel method[4] is the most popular route to prepare 3DOM materials, but the drawback of this method is that there is severe shrinkage and defect when the templates are removed. Subramanian et al. employed monodispersed polystyrene (PS) particles as templates and mixed the PS dispersion with the ceramic colloidal dispersions directly at first. On evaporating the water slowly, the templates assembled themselves in an ordered lattice and the ceramic particles packed into the voids between the templates particles at the same time. Subsequent removal of the PS by calcinations led to an ordered macroporous ceramic materials.[13,14] The use of this codeposition with nanoparticles as building blocks can reduce the shrinkage significantly and get well-ordered sample with bigger dimensions. Tang et al. prepared 3DOM ceramic materials first using the heterocoagulation method that is based on the oppositely charged materials.[5] Xia et al. prepared 3DOM organic membranes using PS with different particle sizes as templates.[11] Since the dimension of the pores depends on the diameters of the templates, the pores sizes of three-dimensionally ordered macroporous materials are typically controlled by using the templates with various sizes. But relatively a few studies have been conducted to control the dimension of the pores when the size of the templates was invariable. Zhao and Zhou prepared the 3D macroporous SiO_2 materials and controlled the size of the surface pores by infiltrating the precursors with different times.[15] Kanungo and Collinson fabricated the two-dimensionally ordered macroporous SiO_2 materials of varying size and depth on an electrode surface by changing the mole ratio of PS to silica sol.[16] In this paper, three-dimensionally ordered macroporous SiO_2 membranes are prepared by the codeposition method using SiO_2 colloidal particles as building blocks and polymethyl methacrylate (PMMA) as the templates. Furthermore, we demonstrate the size of the pores can easily be controlled by changing the volume ratio of PMMA/SiO_2 in starting materials and we show the three-dimensionally ordered macroporous structure can be maintained in a range of the volume ratios.

In our synthetic procedure, the PMMA particles with an average diameter of 610 nm was dispersed into the deionized water, then the dispersion was ultrasonically treated for 15 min to disperse the powders, and further stirring was carried out for another 30 min. The next step involved mixing the PMMA dispersion with the silica dispersion (NYACOL 2040, Eka Chemicals) at 40 wt % solids in a glass vial and then dried in an oven at 70 °C. The dispersions were stabilized at pH 10. At this pH value, the zeta potential of the silica particle is -65 mV and the PMMA is -50 mV. So the mutual electrostatic repulsion between the particles provides effective stability against coagulation. On evaporating the water slowly, the PMMA assembled themselves in an ordered lattice and the SiO_2 particles packed into the voids between the PMMA particles at the same time. After drying, calcination process was carried out in a conventional muffle oven by increasing the temperature from room temperature to 500 °C at 1 °C/min and heating at 500 °C for 120 min.

Figure 1 shows the SEM images of macroporous SiO_2 membranes that are synthesized by the codeposition method using PMMA spheres with an average diameter of 610 nm as the templates, and the volume ratio of PMMA/SiO_2 particles in the starting materials is 70/30. The surface of the membranes is smooth, and the porous structure exhibits long-range ordering as shown from a low-magnification SEM image (Figure 1a). Figure 1b shows a closeup view of the top surface. The pores are ordered with the silica particles forming the framework. The samples undergo shrinkage during calcinations. The size of the top surface pores is 528 ± 22 nm in diameter and corresponds to a linear shrinkage of ca. 13.5% with respect to the initial size of PMMA. The void spaces are interconnected in three dimensions through small windows whose diameters are typically about 145 nm. The SEM image of Figure 1c is taken from a section inside the membrane and Figure 1d shows both the top surface and the fracture surface. The ordered porous structure of the top and fracture surfaces are similar as seen in the SEM images. But the pore size of this fracture surface is ca. 600 nm and corresponds to linear shrinkage less than 5% which is different from the top surface.

Figure 2 shows the top view images of ordered macroporous SiO_2 membranes made with different volume ratio of PMMA/

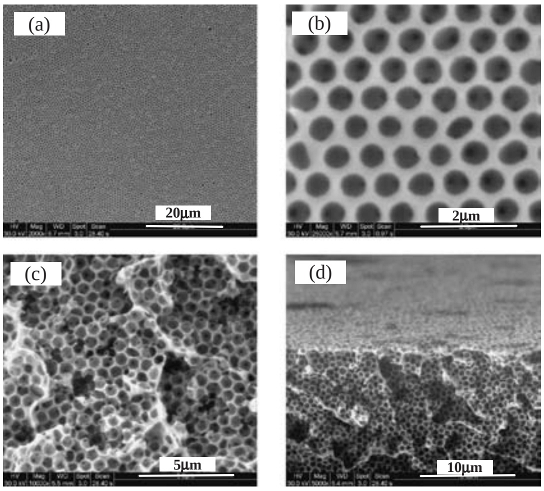

Figure 1. SEM images of ordered macroporous SiO_2 membranes made with PMMA and silica suspension. (a) Top surface with ordered regions extending over 60 μm. (b) Top surface with higher magnification image. (c) Fracture view image. (d) Top and fracture view image.

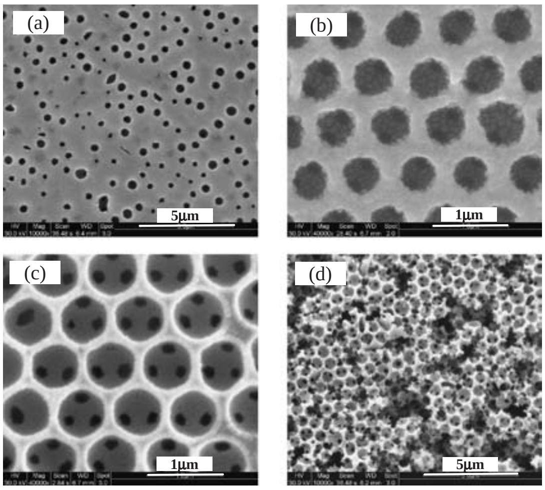

Figure 2. SEM images of ordered macroporous SiO_2 membranes made with different volume ratio of PMMA/SiO_2. (a) 35:65. (b) 65:35. (c) 90:10. (d) 98:2.

SiO_2. When the volume ratio of PMMA/SiO_2 is from 65/35 to 90/10, it is seen that the surface morphology of the membranes are similar and remain ordered. The difference between these membranes is the pore size on the top surface. The diameter of the pores is 600 nm which is close to that of the PMMA particles with the volume ratio of 90/10 (Figure 2c). With this ratio, the linear shrinkages of the top and fracture surface are almost the same. It is apparent that the PMMA are embedded in the silica after the deposition, and only the top 1/2 of the surface is exposed, so the diameter of the pore on the top surface is near to the PMMA size after the calcinations. The slight linear shrinkage is caused by the grain growth of the SiO_2 particles. When the volume ratio reduces and reaches to 65/35, more SiO_2 particles will pack in the surface voids and the PMMA spheres are embedded deeper in the SiO_2 framework after the deposition, so the diameter of the pores reduced in succession after removal of the PMMA (Figure 2b). In this range of the volume ratios, the average pore size can be changed controllably from 600 to 500 nm and the materials have uniform and ordered pores, but the center-to-center distance is invariable. The volume ratio of less than 65/35 gives rise to poor pore regularity, because an excess content of SiO_2 breaks the stability of mixed dispersions and covers more surface of the PMMA after the deposition. The ordered structure of the fracture surface also can be maintained in this volume ratio from 65/35 to 90/10. Figure 2a shows that parts of the pores are covered by the SiO_2, and the open pores in the surface are not ordered. Whereas the volume ratio of more than 90/10 makes the macroporous structure partially broken since the SiO_2 particles are insufficient to fill the void spaces among the PMMA particles (Figure 2d). So the pore size and the linear shrinkage of the top surface are determined by the volume ratio of PMMA/SiO_2 and can be controlled easily.

In summary, we have prepared the three-dimensionally ordered macroporous SiO_2 membranes by the codeposition method using SiO_2 colloidal particles as building blocks and polymethyl methacrylate as the templates. The macroporous structure can maintain three-dimensionally ordered with the volume ratio of PMMA/SiO_2 from 65/35 to 90/10. In this range, the pore size of the materials can be easily controlled by changing the volume ratio and beyond this range the structure of the materials is disordered or broken. These three-dimensionally ordered macroporous membranes with controllable pore size have potential uses as catalyst supports and macromolecular separations.

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