Preparation of Three-dimensionally Ordered Macroporous Oxides by Combining Templating Method with Sol–Gel Technique

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Three-dimensionally ordered macroporous (3DOM) inorganic oxides, SiO_2 and TiO_2, have been synthesized by combining template-assisted colloidal method with sol–gel technique. Close-packed PS beads were first prepared as template by using gravitational sedimentation, followed by infiltration with corresponding sol precursors rather than corresponding alkoxides, and then templates were removed by calcination. The morphology and crystalloid structure of samples were investigated by SEM and XRD, respectively. The results indicate that the structures of samples are well-inverse replicas of PS template and the method is also applicable to the preparation of other oxides.

Over the last few years, three-dimensionally ordered macroporous (3DOM) materials have been studied widely due to their potential applications in adsorptive separations, photonic crystals, catalysis, etc.[1,2] Among various processing techniques for macropore, it is believed that the colloidal-crystal-templating approach is a simple and efficient path to fabricate 3DOM materials. This method is based on the use of a template made of regular and periodical nanobead structure, then appropriate precursors are infiltrated in the nanostructure voids to form inverse structure after removing the template.

Highly ordered macroporous SiO_2 which is a commom support and TiO_2 which may form high-quality photonic crystal for its higher refractive index (>2.5) have been prepared by using poly(methyl methacrylate) (PMMA) or polystyrene (PS) beads as organic template and mixtures of corresponding alkoxides and ethanol as precursors, such as tetraethyl orthosilicate (TEOS), titanium tetraisopropoxide (TTIP), tetrabutyl titanate [$Ti(BuO)_4$], etc.[3–8] The templates were immersed in a mixed solution of alkoxide and ethanol, and then reacted with the water in the air which existed in the interstices of the templates to hydrolyze to form precipitation for completing the infiltration. However, it must be noted that the content of water in the interstices of templates is relatively less and the distribution is uneven. Under these circumstances, hydrolysis occurred incompletely and the degree of hydrolysis was various in different area. These factors would lead to inadequate filling and some organic compounds would be remaining as residues simultaneously. The residues can be acted as cave formers to cause the collapse and destruction of the porous structure in the process of calcination. In this paper, sols of SiO_2 and TiO_2 were first prepared from corresponding alkoxides, TEOS and $Ti(BuO)_4$, respectively, and then the systems of sol used as direct precursors were infiltrated in the interstices of PS templates to complete the filling by gelation in situ. Finally, PS templates were removed by calcinations. It will favor of sufficient filling and the control of the hydrolysis reaction by using sols as precursors because sols are not required to hydrolyze in the interstices of templates and the distribution of sols can be more uniform. And that, the gelation rate can be adjusted easily through changing the compound ratio of sols.

Monodisperse PS beads of 300 nm average diameter were prepared by emulsifier-free-polymerization (EFP), as reported elsewhere,[9] and then were self-assembly to colloidal crystal templates by the method of gravitational sedimentation. Sol of SiO_2 from TEOS, ethanol, hydrochloric acid (HCl), and water was prepared with a volume ratio of $V(\text{TEOS}):V(\text{EtOH}):V(\text{HCl}):V(H_2O) = 1:1:0.25:0.2$, and sol of TiO_2 were prepared with a volume ratio of $V[Ti(OBu)_4]: V(\text{EtOH}):V(\text{HCl}):V(H_2O) = 1:1:0.2:0.4$. PS templates were dipped in the corresponding sols for 8 h, then the excess sol precursors were removed by vacuum filtration. The infiltered templates were dried to form gel in situ at 70 °C for 2 h. This infiltration procedure was repeated several times. The coated PS templates with gel of SiO_2 were removed by calcinations under air flowing at 300 °C for 4 h, followed by calcination at 600 °C for 5 h, while the coated PS templates with gel of TiO_2 were calcined at 300 °C for 4 h, followed by calcination at 500 °C for 5 h at identical heating rate of 2 °C/min.

Figure 1 revealed that the PS beads displayed a highly ordered hexagonal close-packed arrangement and uniform size of beads over a large area, although the beads arrays contained some small stacking faults, point defects, and line defects. Multicolors can be seen from different angles for the sake of Bragg diffraction, which also testified the ordered structure of PS templates. In addition, an metastable square-packed arrangement of PS beads was also observed in small parts of the structures. This phenomenon is considered to be a very slow transforming process from metastable crystalline array to stable array spontaneously. The precursors were infiltrated into the interstices of templates mainly by capillarity action and then formed gel in situ. If alkoxides were used as direct precursors, the process of hydrolysis and gelation could not be adjusted during infiltration, but sols realized the control by adding HCl as acid catalyst. Simultaneously, the ethanol in the sol precursors can make the sols wet the PS templates more easily. From the TG-DTA curves of PS template, it can be found that the

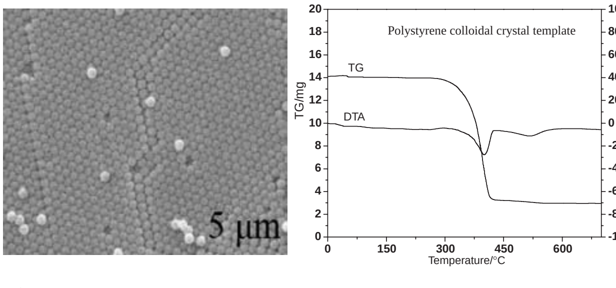

Figure 1. The SEM image of PS colloidal crystal template and TG-DTA curves of PS template.

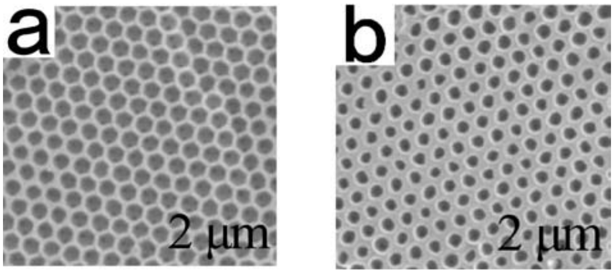

Figure 2. The SEM images of SiO_2 (a) and TiO_2 (b) with hexagonal array.

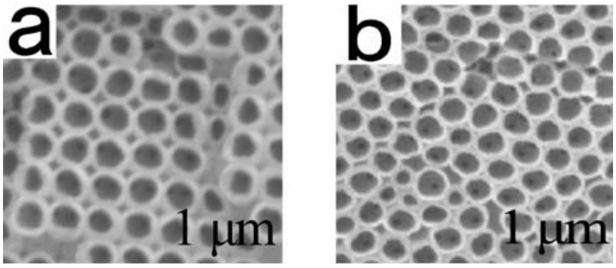

Figure 3. The SEM images of SiO_2 (a) and TiO_2 (b) with square array.

maximum weight loss appears in the temperature range 300–430 °C, which shows the combustion of PS. In order to avoid the adverse effects probably from intensively and fast combustion of PS, hybrids of coated templates were calcined at 300 °C for 4 h to make PS decompose slowly.

As shown in Figures 2 and 3, the resulted samples of macroporous SiO_2 and TiO_2 displayed well-ordered structures. Figure 2a shows a highly ordered three-dimensional structure of macroporous SiO_2 with a pore of appropriately 260 nm and the shrinkage is about 13%. The resulted samples of macroporous TiO_2 had a similar structure of SiO_2, as seen in Figure 2b and the pore with an average diameter of appropriately 220 nm and there was some shrinkage about 26%. Compared with 3DOM SiO_2 and TiO_2 obtained from direct alkoxides precursors,[4,6,8] the resulted samples in this paper had smaller shrinkages. These results indicated that the structure of pore wall had more compactness and mechanical intensity. Consequently, it would favor of sufficient infiltration by using sols as precursors. In addition, it was worth noting that an unique square arrangement of macropores was also observed in some parts of the structures, as shown in Figure 3. The interesting phenomena is consistent with some parts of PS templates. Compared with hexagonal close-packed arrays, square arrangement has more infiltrated spaces for its higher voidage, but the infiltration of precursors has a tendency to surface templating rather than volume templating to result in the lower infiltration in the same filling conditions.[10] On the other hand, TiO_2 sol had a higher viscosity than SiO_2 sol, so it was more difficult to ensure sufficient and symmetrical filling in some area of the PS templates. So, big distortion and the cleavage of pore walls of some local area in the structure were caused by the process of calcination and the orderliness of porous structure decreased. It has been confirmed by the structure dipicted in Figure 3b. Very few reports have mentioned the formation of macroporous structures with the square porous architecture to date.[4,11–13] It was considered that complete filling did not seem to be necessary[14] and this special structure might be beneficial to possible applications in the fields of catalysis and separation, etc.[4,15]

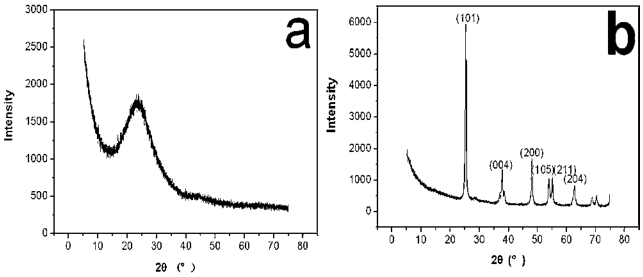

Figure 4. The XRD patterns of SiO_2 (a) and TiO_2 (b).

X-ray diffraction was used to reveal the crystalline form of the two kinds of macroporous materials. From Figure 4a, there were no sharp peaks which could characterize crystalline phase, which indicated the formation of an amorphous SiO_2. The XRD pattern of resulted macroporous TiO_2 were observed in Figure 4b. The sharp peaks were found to be very close to (101), (004), (200), (105), (211), and (204), indicating that the crystalline phase of TiO_2 was anatase form.

From the above discussion, it can be concluded that 3DOM materials can be synthesized effectively by combining sol–gel technique and colloidal-crystal-templated method. The resulted 3DOM SiO_2 or TiO_2 can be referred to as the inverse replicas of PS colloidal crystal template. The size of resulted macropores shrunk to some degree inevitably due to the common shrinkage of PS templates and gels during calcinations. This method is also expected to be applicable to the preparation of other materials which can be obtained by using sol–gel technique.

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