Preparation of Closed Macroporous Al_2O_3 Membranes with a Three-dimensionally Ordered Structure

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3D-ordered closed macroporous Al_2O_3 was prepared by the codeposition method using PMMA as the template and Al_2O_3 colloidal particles as the building block. The ordered closed structure of the macroporous Al_2O_3 was affected by the pH value of the dispersions, the volume ratio of the PMMA and Al_2O_3 particles, and the feature of the template's surface charge.

Three-dimensionally ordered macroporous (3DOM) materials have attracted much attention in recent years because of their potential in a variety of applications. Basically, 3DOM materials exhibit two typical structures with 3D-ordered open or closed macropores. In the former, the macropores in the material are interconnected by small windows while the macropores are disconnected with adjacent ones in the latter. Currently, most of studies are focusing on the ordered open macroporous materials. Various oxides[1–5] and metals[6,7] as well as polymers[8,9] with the ordered open macroporous structure have been successfully synthesized using template-assisted methods.

In contrast, research on the template-assisted synthesis to prepare the 3D-ordered closed macroporous materials has been less reported. This is because most of methods to prepare the 3D-ordered materials need assemble the template first, which makes the materials interconnect and hard to prepare the closed structure. Rhodes et al. utilized the layer-by-layer assembly of zeolite nanoparticles and polystyrene (PS) beads to make a core–shell structure that in turn used as a template to prepare the ordered closed porous materials by centrifugation.[10] Dong et al. prepared mechanically stable 3D-ordered closed macroporous zeolite monoliths using hydrothermal treatment of pre-seeded mesoporous silica templates.[11] Wang and Caruso prepared enzyme-modified zeolite membranes with interconnected and closed macroporous structures and compared the enzyme activities of these two membranes.[12] However, the structural control of the closed macroporous materials was less mentioned.

In present work, 3D-ordered closed macroporous Al_2O_3 membranes have been prepared by the codeposition method using Al_2O_3 colloidal particles as the building block and poly(methyl methacrylate) (PMMA) as the template. The key factors of synthesis such as material surface charge, the pH value of the mixed dispersions, and the volume ratio of the template and Al_2O_3 colloidal particles were investigated. Al_2O_3 material was chosen as the model material in the study because porous Al_2O_3 materials have been extensively used as catalysts and separation materials in many applications due to their excellent thermal stability and low cost. Given the unique structure of high porosity but low porous connection, the 3D-orderedclosed macroporous Al_2O_3 materials are expected to find new applications such as for low dielectric insulators and the ceramic membrane with this unique structure for separation.

In the codeposition process, the PMMA particles were dispersed into the deionized water. Both the PMMA and Al_2O_3 colloidal (50 nm) dispersions were stabilized at pH 4. The next step involved mixing these two dispersions in a glass vial with a desired ratio and then drying at 70 °C. Calcination process was carried out in a muffle oven by increasing the temperature from room temperature to 500 °C at the rate of 1 °C/min and heating at 500 °C for 120 min.

The SEM images of the ordered macroporous Al_2O_3 membranes prepared using negatively charged PMMA (680 nm) and positively charged Al_2O_3 particles at pH 4 are shown in Figure 1. For the membrane made of PMMA/Al_2O_3 particles in the volume ratio of 70/30, it can be seen from the top surface image of the membrane (Figure 1a) that the hollowed Al_2O_3 sphere array is ordered close-packed without pores on the surface after the calcinations. And the diameter of the spheres is about 795 nm, corresponding to a linear increase of ca. 17% with respect to the initial size of the PMMA. The center-to-center distance of the adjacent-hollow spheres is around 743 nm which is larger than the PMMA size of 680 nm but less than hollow sphere size. That indicated that the shells of the adjacent Al_2O_3 spheres were merged, but the adjacent PMMA did not contact each other in the codeposition process. So the removal of the PMMA by calcination led to the formation of closed macroporous Al_2O_3 membranes with an ordered structure. The cross-sectional image (Figure 1b) also shows that there were almost

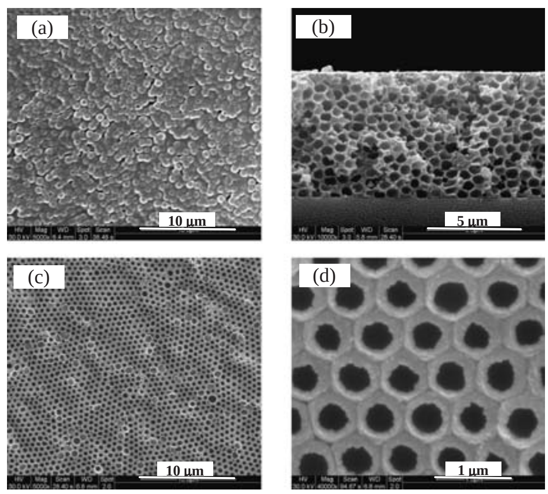

Figure 1. SEM images of 3D-ordered closed macroporous Al_2O_3 membranes prepared in different volume ratio of PMMA/Al_2O_3. (a) Top surface image with PMMA/Al_2O_3 of 70/30. (b) Cross-sectional image with PMMA/Al_2O_3 of 70/30. (c) Top surface image with PMMA/Al_2O_3 of 90/10. (d) Top surface image with a higher magnification of (c).

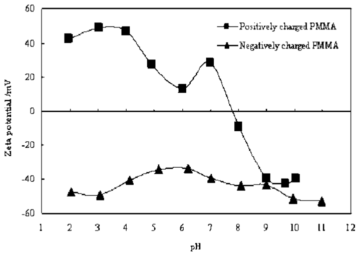

Figure 2. Zeta potentials of the negatively and positively charged PMMA.

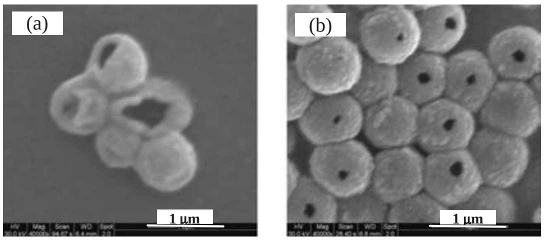

Figure 3. SEM images of Al_2O_3 hollow sphere samples after calcination at different pH. (a) pH 1. (b) pH 4.

no small windows to connect the hollows of adjacent spheres inside the membrane. Figures 1c and 1d show the top surface of the Al_2O_3 membrane prepared in the PMMA/Al_2O_3 volume ratio of 90/10 in different magnifications. Surprisingly, the image of the top surface of the membrane was quite different. Nearly half hollow spheres of Al_2O_3 with an average particle size of 714 nm were displayed in an ordered manner. It indicated that the precoated Al_2O_3 layer on the PMMA spheres was too thin to maintain the spherical shape after the removal of PMMA. But there were no small windows to connect the hollows of the spheres, thus the ordered closed macroporous structure was still attained.

Figure 2 shows the zeta potentials of two types of PMMA with negative charge and positive charge. It can be seen that the negatively charged PMMA spheres exhibited a relatively high zeta potential of around −30 to −65 mV in the measured pH range of 2 to 11, while the zeta potential for the positively charged PMMA was around +20 to +50 mV in the pH range of 2 to 7. It indicated that both types of PMMA spheres could be well dispersed in water under the condition of pH 2 to 7 because of the mutual electrostatic repulsion between the particles. As shown in Figure 3a, which presents the SEM image of the Al_2O_3 core–shell particles prepared at pH 1 after calcination, the hollow microspheres were not round and smooth. This probably happened because the charge density on the Al_2O_3 particles was rather high at pH 1 and this highly repulsive force between Al_2O_3 particles inhibited the formation of a smooth and compact Al_2O_3 coating.[13] The best result can be obtained when the pH value was adjusted to 4. As shown in Figure 3b, The Al_2O_3 hollow particles after calcination presented uniform spherical shapes. It demonstrated that pH 4 was most suitable for Al_2O_3 to deposit onto the negatively charged PMMA spheres.

Figure 4 shows the SEM image of macroporous Al_2O_3 membranes that were made using positively charged PMMA spheres with an average diameter of 318 nm as the template, and the volume ratio of PMMA/Al_2O_3 particles was 85/15. The average size of the top surface pores was 250 nm in diameter, corresponding to a linear shrinkage of ca. 20% with respect to the initial size of PMMA. It can be seen that the void spaces were interconnected in three dimensions through small windows whose diameters were typically about 145 nm. Compared with the image shown in Figure 1d where the boundary of each half hollow sphere could be clearly observed, there was no similar boundary occurring in Figure 4. It suggested that there was no Al_2O_3 hollow spheres produced after calcination. Instead, the adjacent PMMA spheres contacted each other during the codeposition process, which made the macropores to be connected each other after the removal of PMMA spheres.

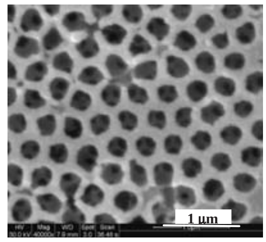

Figure 4. SEM image of ordered open macroporous Al_2O_3 membrane prepared at PMMA/Al_2O_3 of 85/15.

In summary, the 3D-orderedclosed macroporous Al_2O_3 was prepared by the codeposition method using PMMA as the template and Al_2O_3 colloidal particles as the building block. The ordered closed structure of the macroporous Al_2O_3 was affected by the pH value of the dispersions, the volume ratio of the PMMA and Al_2O_3 particles, and the feature of the template's surface charge. The negatively charged PMMA and positively charged Al_2O_3 particles can form the 3D-ordered closed macroporous structure in a suitable pH value, but both positively charged PMMA and Al_2O_3 can be used to prepare the 3D-ordered open macroporous membranes.

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