Fabrication of Ordered Macroporous Structures Based on Hetero-Coagulation Process Using Nanoparticle as Building Blocks

Fengqiu Tang, Hiroshi Fudouzi, Tetsuo Uchikoshi, Toru Awane, and Yoshio Sakka*
National Institute for Materials Science, 1-2-1, Sengen, Tsukuba, Ibaraki 305-0047

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A simple method based on hetero-coagulation process for the preparation of well-defined ordered macroporous inorganic materials from nanoparticles and spherical polymer templates is reported.

The synthesis of macroporous materials with a highly defined pore distribution have attracted much attention due to their potential applications as separation and absorbent media, catalytic supports, insulators, biomaterials, lightweight structural materials and photonic crystals.[1–6] These materials are created typically by colloidal crystals such as silica beads or polymer latexes, which are often the best templates used to prepare macroporous materials.[4–10] The template is first infiltrated with various materials, such as ceramic precursors, metals and polymers and subsequently removed by calcination or solvent extraction to create macroporous materials. To date, inorganic materials[11,12] such as silica, titania, zirconia, and some organic materials[6,7,13] with well-defined submicron-sized macropores have been successfully synthesized. However, it has proved difficult to fully infiltrate the liquid precursors into the voids by capillary action, as a result, the frameworks of porous materials have been mechanically fragile, easily cracked and difficult to prepare large-sized bulk materials. Moreover, one drawback of this method is that the quality of the porous structure is highly dependent on the quality of the template crystal itself.

The fabrication of highly ordered macroporous materials using particles instead of liquid precursors is of particular interest since many oxide and semiconductor materials are now easily available as nanoparticles with lower cost, which might be advantageous for some applications. Recently, some studies have focused on the fabrication of macroporous thin films on a glass or silicon substrates using nanoparticles as building blocks upon water evaporation by means of capillary forces,[14–16] but it was very time-consuming for solvent evaporation and difficult to prepare thick deposits of this kind of structures.

Here we demonstrate a straightforward way to prepare large-sized macroporous materials based on the hetero-coagulation process of oppositely charged core and shell materials in a suspension. First, by appropriate surface charge modification, both template spherical polymers and inorganic nanoparticles are dispersed in aqueous media with opposite surface charges separately. In a second step, the two suspensions are well mixed to form core-shell composites via electrostatic attraction. The hetero-coagulated mixture is then filtered to form an ordered structure of inorganic-organic composites. Finally, the polymer template is removed to produce an ordered 3D macroporous metal oxide after calcination.

In our experiments, the spherical polymer PMMA with an average diameter of 350 nm (P350) was used as the template material; γ-Al_2O_3 powder with an average particle size of 34 nm was used as the inorganic building blocks. The structures of the macroporous materials are highly dependent on the properties of the starting materials and suspensions, such as zeta potential, particle size and volume ratio of the two powders. In order to fabricate the core-shell composite with uniform structures via our strategy, the key point is to prepare well-dispersed suspensions of both the template and the nanoparticle materials in a same pH range. Figure 1 shows the zeta potential (ζ) of γ-Al_2O_3 and P350 versus pH measured by a laser-doppler electrophoresis analyzer. P350 is negatively charged in the measured pH range of 3–12. A relatively high ζ value can be obtained between pH 7 and 11, indicating that the P350 suspension is well-dispersed in this pH range. On the other hand, the γ-Al_2O_3 with a highly positive surface charge ($\zeta \geq 30$ mV) can be obtained below pH 8. Hence, well-dispersed suspensions of both the γ-Al_2O_3 and the P350 can be obtained in the pH range of 7–8 as shown by the dotted line in figure.

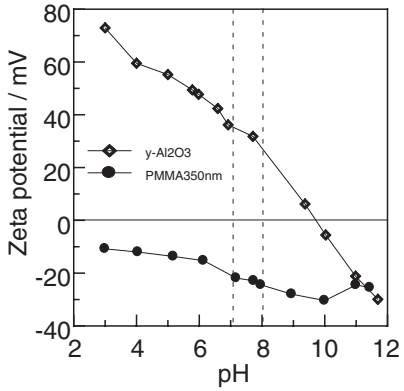
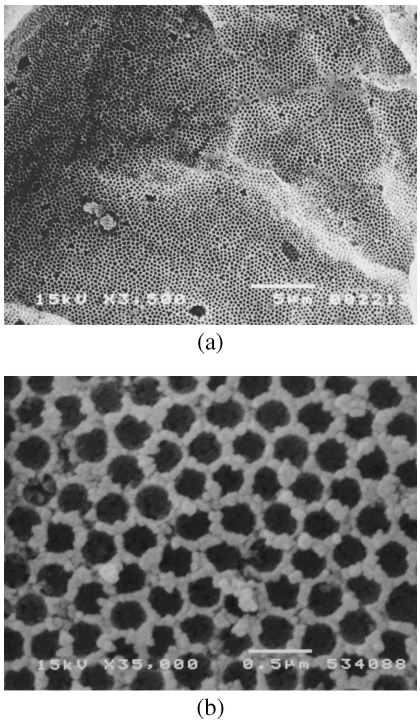


Figure 1. Zeta potentials of γ-Al_2O_3 and polymer P350 in aqueous suspensions.

In a typical synthetic procedure, 1.5 g of the γ-Al_2O_3 powder was dispersed in 40 ml of distilled water at pH 7. Thirty ml of aqueous suspension containing 1 g of P350 was also adjusted to pH 7. The suspensions were ultrasonicated for 10 min and then stirred for 1 h to ensure their good dispersal. Afterwards, the Al_2O_3 suspension was slowly added to the P350 suspension under stirring so that the smaller Al_2O_3 particles can uniformly adhere to the polymer surface to form the core-shell structure via electrostatic attraction. The resulting flocculated mixture was then vacuum filtrated to produce the close packed deposits of the core-shell structure, which can be finished in several tens of minutes. After drying, the polymer spheres were removed by calcination at 500 °C for 4 h in air, then further heat-treatment was continually conducted for 2 h at 850 °C at a heating rate of 1 °C/min to enhance the mechanical strength of materials.

Scanning electron microscope (SEM) images of the ordered porous structures are shown in Figure 2. Regular pores formed in a large area can be observed from Figure 2a. The well-ordered spherical macropores and polycrystalline alumina frames created interconnected three-dimensional porous structures. The higher magnification image clearly reveals that the skeleton of the materials consists of nano-sized alumina particles (Figure 2b). The average pore diameter is approximately 270–290 nm, these pore sizes were smaller than that of the original template PMMA spheres, corresponding to a contraction of about 18% due to the removal of the polymer and inorganic framework grain growth during calcination, this shrinkage is much smaller than the materials prepared from ceramic precursors (about 30% shrinkage) even though calcined at 550 °C.[8–11] The average γ-Al_2O_3 particle size is about 60 nm, which is enlarged upon calcination compared with that of the starting materials. The slightly grain growth of the γ-Al_2O_3 particles enhance the mechanical strength of the framework and can still keep the macropores spherical even though being calcined at 850 °C. Note that the appropriate calcination temperature is very important for the purpose of fabricating large-sized samples with high strength and keeping the pores spherical. In this experiment, macroporous materials with a diameter over 3 cm and a thickness of 8 mm (depending on the amount of original materials) can be easily obtained; moreover, the slightly sintered framework is quite robust and easy to manipulate. This clearly indicates the feasibility of our simple procedure.

The volume ratio of PMMA to Al_2O_3 also plays an important role in the fabrication of these kinds of ordered materials. The density of the porous materials decreased with decreasing volume ratio of the γ-Al_2O_3/P350 whereas the porosity of materials increased accordingly. The macroporous material with a 74.04% porosity at the volume ratio of 0.432:1 can be obtained, which is very close to the ideal voids of close packed spheres, suggesting the well-defined porous structure in the material. Too low an amount of the oxide particles produced macroporous materials with a partially broken wall since the oxide particles might not be sufficient to cover the total surface of the template, whereas an excess content of oxide particles produced macroporous materials with a thick wall, low porosity and poor pore regularity.



(a)

(b)

Figure 2. SEM images of macroporous γ-Al_2O_3 prepared with a volume ratio of Al_2O_3/P350 = 0.432:1. (a) low magnification image of natural surface ($60 \times 60\,\mu m^2$ region). (b) high magnification image showing the framework of macropores.

In summary, we have demonstrated a simple yet effective approach to prepare well-defined macroporous materials through the self-assembly and flocculation of oxide powders and templates in aqueous suspensions. The modification of oppositely charged suspensions is the key for the fabrication of such macroporous materials. Modifying the volume ratio of the shell/core can readily control the porosity and framework thickness. Large robust ordered macroporous materials could be obtained in a short time. Our recent investigation has shown that the strategy could also be extended to the fabrication of other inorganic macroporous materials, such as TiO_2, SiO_2, ZrO_2, etc. Hence, it can be expected that this approach may be developed into a general and economical pathway for preparing large-sized ordered macroporous inorganic materials, which may find potential applications in advanced catalysis, separation and optical field.

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