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Preparation of porous materials with controlled pore size and porosity

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Abstract

Well-defined porous ceramics with controllable pore size and porosity were fabricated via a hetero-coagulation of template/ceramic particle colloidal processing. Monodispersed polymer spheres were used as template and ceramic nanoparticles as inorganic building blocks to create porous structures. The preparation of well-dispersed suspensions of polymers and ceramics is essential for the fabrication of uniformly porous materials. Core–shell composites of polymer/ceramic could be obtained by mixing the oppositely charged two suspensions via electrostatic attraction following by filtration and calcination to produce macroporous ceramic materials. SEM images and pore size distribution results revealed that various materials, such as Al_2O_3, TiO_2 and ZrO_2, with ordered and uniform macropores have been obtained by this simple procedure. The pore size could be controlled readily by varying the polymer size and the porosity could be manipulated by modifying the volume ratio of polymer/ceramic particles.

Keywords: Al_2O_3; Microstructure; Porosity; TiO_2; ZrO_2

1. Introduction

Porous materials are of significant interest due to their wide applications in catalysis, separation, lightweight structural materials, biomaterials and so on.[1,2] Various processing techniques have been utilized to fabricate porous ceramic materials. Replamineform process has been utilized to fabricate porous ceramic and biomaterials to duplicate the macroporous microstructures of the foams that have interconnected pores.[3–5] Using foam-producing materials that evolves gases during calcination might be an alternative to prepare porous materials.[6,7] Some agents have also been introduced that can decompose or react to form pore structures after sintering.[8] Partial sintering is another technique to obtain porous ceramic structures.[9] To date, ceramic materials, such as Al_2O_3, SiC, TiO_2 and hydroxyapatite with porous structures, have been successfully fabricated. Unfortunately, most of these processes only form structures with randomly arranged irregular pores with a wide variety of sizes and have limited flexibility to control pore volumes and porosity distribution in the final structure.

In this study, we propose a novel approach to prepare porous materials with controlled pore size and porosity via a hetero-coagulation method. Our strategy is based on the templating-assisted approach of core–shell composite.[10] Monodispersed polymer spheres are used as templates and ceramic particles act as target materials. By particle surface modification, well-dispersed suspensions of polymer and ceramic particles with highly opposite charge could be obtained at the same pH condition, which is very important for preparing uniform core–shell composites. Upon mixing the two suspensions, core–shell structures are formed via electrostatic attraction. The flocculated particles are subsequently closely packed by vacuum filtration. The polymers are finally removed by calcination, resulting in the porous structures. A schematic procedure for preparing well-defined porous materials is shown in Fig. 1. Compared with common methods used to prepare porous ceramics, our strategy has several advantages: the formation of core–shell structure via flocculation of the suspension makes it easy to filtrate the suspension and the pores distributes uniformly; the pore size can be controlled by varying the polymer size and calcination temperature;

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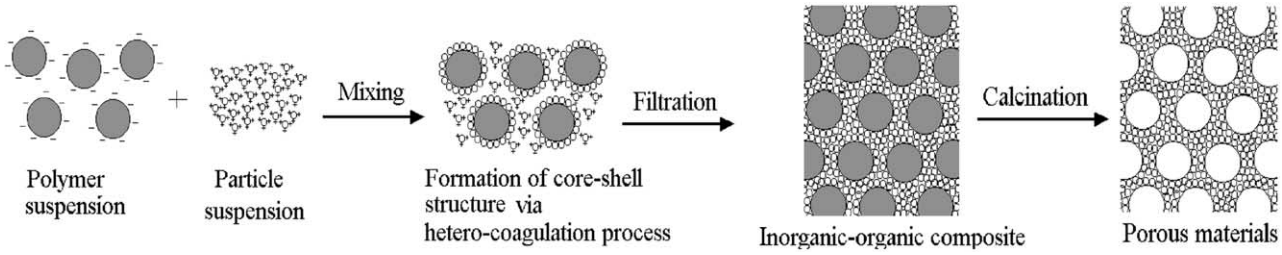

Fig. 1. Schematic procedure for fabrication of macroporous materials via core–shell flocculation of polymer spheres and inorganic particles.

the porosity of the materials can be manipulated readily by changing the volume ratio of polymer/ceramic particles.

2. Experimental

2.1. Materials

In the experiments, the spherical polymer (polymethyl methacrylate, PMMA) with an average diameter of 350 nm (P350), 800 nm (P800), 1300 nm (P1300) (Soken Chemical and Engineering Co., Japan) were used as template materials; γ-Al_2O_3 powder with an average particle size of 34 nm (NanoTek), α-Al_2O_3 with an average particle diameter of 150 nm (Taimei Chemicals, TM-DAR), TiO_2 (NanoTek) and ZrO_2 (3 mol% Yttria tetragonal zirconia polycrystals) powders (Tosoh Co. Ltd.) with an average particle size of 30 and 70 nm respectively were used as the inorganic building blocks. Polyethylenimine (PEI) with an average molecular weight of 10 000 was utilized to modify the surface properties of ceramic particles.

2.2. Preparation processing

In a typical synthetic procedure for the preparation of α-Al_2O_3 porous material, 5 wt.% of the positively charged α-Al_2O_3 powder was dispersed in distilled water at pH 8 with 1 wt.% PEI addition, 2 wt.% of the negatively charged P800 suspension was prepared at the same pH. 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 P800 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 mixture was then vacuum filtrated to pack the flocculated particles together, which can be finished in a very short time. After drying, the polymer spheres were removed by calcination at 500 °C for 4 h in air and further heat-treatment was continually conducted for 2 h at 1100 °C at a heating rate of 1 °C/min to enhance the mechanical strength of the ceramic framework. Porous γ-Al_2O_3 and TiO_2 were prepared according to a similar procedure by using P350 as template and heating at 850 °C; porous ZrO_2 was fabricated by mixing ZrO_2/P1300 suspensions and calcined at 1100 °C.

2.3. Characterization

Zeta potential of powders was characterized by a laser electrophoresis analyzer (LEZA-600, Otsuka Electronics Co.). The density and porosity of calcined samples were measured using the Archimedes' method with distilled water as the immersion medium. A JSM 5400 scanning electron microscope (SEM) was used to observe the microstructure and morphology of the porous materials. Mercury porosimetry measurements were carried out on a Micromeritics Poresizer (Shimatsu Autopore 9520) for characterizing the pore size distribution.

3. Results and discussion

The structure of the macroporous materials is highly dependent on the properties of the starting materials and suspension conditions, such as zeta potential, particle size and volume ratio of the ceramic/polymer. In order to fabricate the core–shell composite with uniform structures via our strategy, a key point is to prepare well-dispersed suspensions of both the template and the nanoparticle in the same pH range, otherwise, uniform core–shell structures should be difficult to obtain due to the pre-agglomeration of one suspension.

Fig. 2 shows the zeta potential (ζ) of α-Al_2O_3 and P800 versus pH measured by a laser-doppler electrophoresis analyzer. P800 is negatively charged in the measured pH range of 3–12. A relatively high ζ value can be obtained between pH 6 and 10, indicating that the P800 suspension is well-dispersed in this pH range. On the other hand, the α-Al_2O_3 with a highly positive surface charge ($\zeta \geqslant 30$ mV) can be obtained only below pH 5. For the purpose of preparing two well-dispersed suspensions under the same pH, PEI was used as the cationic dispersant to modify and enhance the positive charge potential of α-Al_2O_3 surfaces.[11] The isoelectric point (iep) of α-Al_2O_3 shifted from pH 7.5 to pH 11

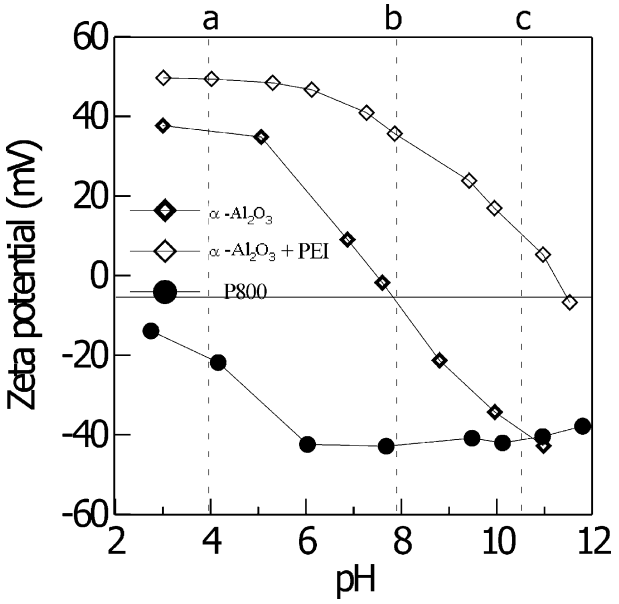

Fig. 2. Zeta potentials of P800 and α-Al_2O_3 in the presence/absence of PEI in aqueous suspensions.

with PEI addition, and a highly positive ζ value of over 30 mV in the pH range of 3–8.5 can be obtained. Taking into account the ζ-potential results of both the polymer and alumina powder, pH 8 was chosen to prepare the α-Al_2O_3 and the P800 suspensions.

Fig. 3 shows the SEM images of porous α-Al_2O_3 prepared by P800 template. The pores are distributed uniformly throughout the whole sample, three-dimentional porous structures can be seen through the pore windows of next layer. The pore size is around 700 nm. Compared with the size of original polymer, the shrinkage of the pore size is about 13%. The alumina particle size is about 210 nm, slight sintering of the porous framework makes the sample mechanically stable. The wall thickness, density and porosity of materials depend on the volume ratio of the ceramic/polymer particles. Porous alumina with a 75.5% porosity could be obtained when the volume ratio of Al_2O_3/P800 was 0.42, which is very close to the ideal voids of close packed spheres (Fig. 3a), strongly suggesting the well-defined pore structure and uniform pore distribution in this material. An excess content of oxide particles produced macroporous materials with a thick wall, low porosity and poor pore regularity (Fig. 3b), whereas too low an amount of the oxide particles produced macroporous materials with a partially broken wall framework since the oxide particles might not be sufficient to cover the total surface of the template.

Fig. 4 shows several typical macoporous ceramic materials prepared with different sizes of the polymer template via the similar synthetic procedure. γ-Al_2O_3 with periodic ordered spherical pore structure could be obtained by using nano-γ-Al_2O_3 particles and P350 spheres, which had an average pore size of about 280 nm (Fig. 4a), further supporting the feasibility of our approach to prepare porous materials with defined pore structure. Fig. 4(b) shows the porous TiO_2 obtained using P350 template. Due to the rapid grain growth and phase transformation from anatase toward rutile of TiO_2 particles, the pore lost its spherical shape and became irregular, but still distributed uniformly. The mean pore size was about 250 nm. Porous ZrO_2 with a pore size of about 1 μm was prepared using P1300 template, as shown in Fig. 4(c). The spherical pores were maintained and the particle size of ZrO_2 framework was about 180 nm. Fig. 4(d) shows the fracture morphology of this porous material, closely packed and uniformly distributed spherical pores could also be clearly observed. The mercury porosimetry measurement indicated that the pore size distribution of the macroporous materials was very narrow.

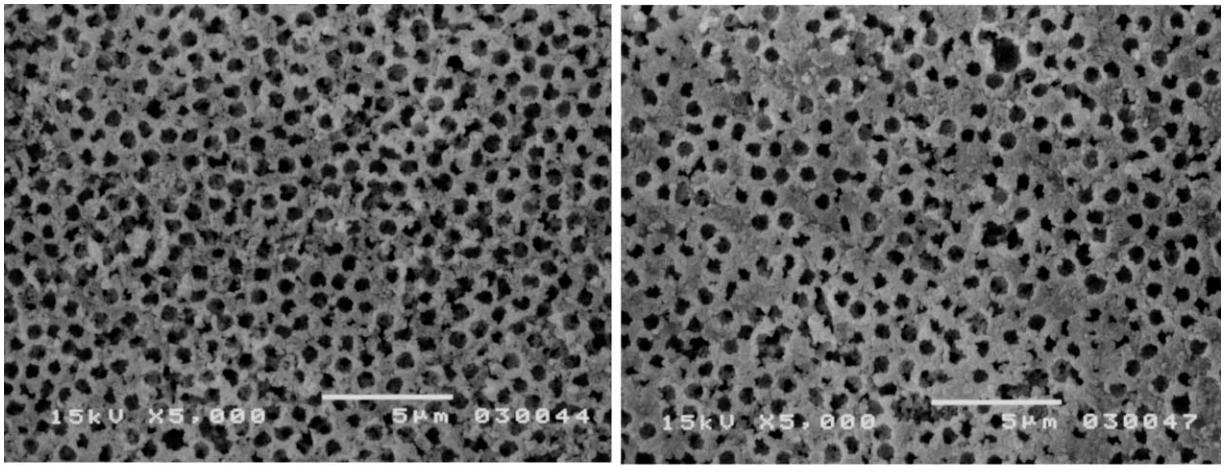

Fig. 3. Porous α-Al_2O_3 prepared with different volume ratio of α-Al_2O_3/P800: (a) 0.42:1, (b) 0.63:1.

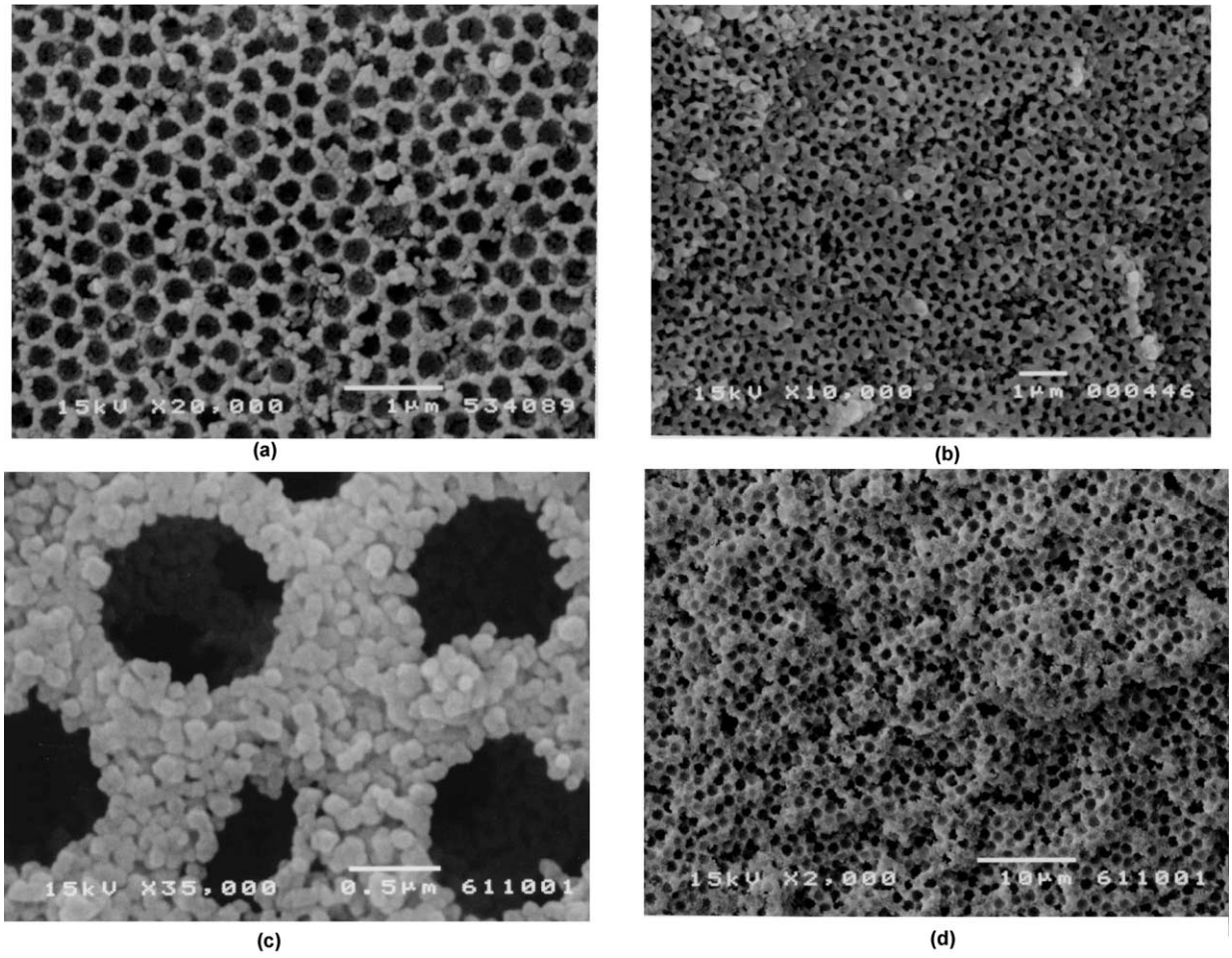

Fig. 4. Macroporous materials prepared with different size of polymer by the same method: (a) γ-Al_2O_3, (b) TiO_2, (c) 3Y-TZP and (d) fracture surface of (c).

4. Conclusions

Porous ceramic materials with well-defined pore size and porosity were fabricated through a hetero-coagulation template processing. The modification of the oppositely charged polymer and ceramic suspensions is the key for fabrication of such closely packed structures with high porosity. Our experiment results have shown that this strategy might be developed into a general pathway to prepare various porous inorganic materials with well-defined pore structure.

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