Fabrication of porous ceramics with controlled pore size by colloidal processing

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Abstract

Well-defined macroporous ceramics consisting of TiO$_2$ and ZrO$_2$ have been fabricated by two methods. One is via a template-assisted colloidal processing technique and the other is via a hetero-coagulation of template/ceramic particle colloidal processing. The former technique is as follows. Close-packed polymer spheres were first prepared as a template using centrifugation or gravitational sedimentation, followed by infiltration with alkoxide precursors. Then the removal of the template beads was achieved by calcination of the organic–inorganic hybrids at appropriate temperatures, yielding well-ordered macroporous ceramics. The latter technique is as follows. Core–shell composites of polymer/ceramic were obtained by mixing the oppositely charged two suspensions via electrostatic attraction following by filtration and calcination to produce macroporous ceramic materials. SEM images revealed that macroporous TiO$_2$ and ZrO$_2$ with ordered and uniform macropores have been obtained by both procedures.

Keywords: Titania; Zirconia; Macropore; Colloidal processing; Microstructure

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 employed to tailor different porous structures in ceramic materials. The use of pore formers or foaming agents that evolve gases during calcination is a common method [3,4]. Replamineform processes can duplicate the macroporous microstructures of the foams that have interconnected pores [5,6]. Partial sintering has also been used as an alternative approach to obtaining porous structures [7–9]. To date, a variety of materials that have porous structures have been successfully fabricated, such as Al$_2$O$_3$, SiC, TiO$_2$ and hydroxyapatite. However, these processes generally produce macroporous structures with a wide distribution of pore sizes.

Recently, a promising new method for the preparation of ordered macroporous solids was developed using close-packed arrays of monodisperse spheres (typically silica or polystyrene) as templates [10]. In this approach, the interstices of these colloidal crystals are infiltrated with a reaction solution of the material that will eventually comprise the replicate structure. The resulting inorganic–organic composites are then either calcined or chemically etched, yielding the macroporous replicate solid with periodic voids. A variety of macroporous materials have been prepared by this method [11,12]. However, modification of the synthetic parameters remains the main challenge for the template approach, since this ultimately influences the microstructures of the resulting macroporous structures [13].

On the other hand, we have proposed 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 [14–16]. 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.

In this study, we report two types of techniques for the fabrication of ordered macroporous ceramics of TiO$_2$ and ZrO$_2$. 

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One is via a template-assisted colloidal processing technique [13] and the other is via a hetero-coagulation of template/ceramic particle colloidal processing [14]. Modification of the synthetic conditions resulted in various ordered macroporous structures in ceramics.

2. Experimental

2.1. Materials

In the experiments, the spherical polymer (polymethyl methacrylate, PMMA) with an average diameter of 300 nm (P300) and 1300 nm (P1300) (Soken Chemical and Engineering Co., Japan) were used as template materials. Titanium tetraisopropoxide (TTIP) and zirconium butoxide of analytic purity were used as inorganic precursors. TiO2 (NanoTek) and ZrO2 (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. Procedure of a template-assisted colloidal processing technique

In a typical process, 0.5 g of P300 spheres were dispersed in 50 ml of pure water at pH 9 and were then ultrasonicated for 10 min [17,18], followed by stirring for 1 h to ensure complete dispersal. The resulting suspensions were then either centrifuged at 3000 rpm for 30 min or they underwent static gravitational sedimentation for about 1 month in order to obtain close-packed polymer colloidal crystals. After drying, the templates of the colloidal crystals were immersed in a mixed solution of alkoxide precursors and ethanol with a volume ratio of 1:1 to 1:2 in a glove box with an argon atmosphere. By diluting the alkoxide in ethanol, it was possible to adjust the viscosity and the hydrolysis/condensation rates of the alkoxide. The immersion procedure described above was repeated several times to ensure the complete infiltration of the voids of the template colloidal crystals with inorganic precursors. The resulting coated P300 spheres were dried in air and then the template was removed from the inorganic framework by calcination at 550 °C or higher for 4 h in air at a heating rate of 1 °C/min [15].

2.3. Procedure of a hetero-coagulation of template/ceramic particle colloidal processing

A schematic procedure for preparing well-defined porous materials is shown in Fig. 1 [14]. According to the hetero-coagulation strategy, both the suspensions of the template polymers and the nanosized coating particles should be electrostatically stabilized whereas the surface charges of these two particles should be opposite for the purpose of forming uniform core–shell structures. Because PMMA spheres used in this study are negatively charged, the PEI was selected to modify the surface of the TiO2 powder [19,20]. In a typical synthetic procedure, 1.2 g of the TiO2 was dispersed into 30 ml of deionized water with 0.075 g of 200 g dm−3 of PEI addition at pH 6, and 1 g of the P1300 was dispersed into 50 ml of deionized water at the same pH. The suspensions were ultrasonically treated for 10 min to disperse the powders [17,18], and further stirring was carried out for another 1 h to ensure saturated adsorption of PEI on the surface of the TiO2 particles. The modified TiO2 suspension was then dropped into the suspension of P1300. Immediately after the mixing, a flocculated phenomenon was observed in the mixture due to the electrostatic interaction of the oppositely charged TiO2 and polymers. The resulting mixture was subsequently vacuum filtered to pack the flocculated particles together. After drying at room temperature in air, the polymer spheres were removed by calcination at 500 °C for 4 h in air, and further heat-treatment was continually conducted at 850 °C for 2 h to enhance the mechanical strength. Porous ZrO2 was fabricated by mixing ZrO2/ P1300 suspensions and calcined at 1100 °C.

2.4. Characterization

Zeta potential of powders was characterized by a laser electrophoresis analyzer (LEZA-600, Otsuka Electronics Co.). The density and porosity of the calcined samples were measured by the Archimedes’ method with pure water as the immersion medium. Phase identification of the materials was achieved by using X-ray diffraction (Model JDX-3500, JEOL, Tokyo, Japan). A JSM 5400 scanning electron microscope (SEM) was used to observe the microstructure and morphology of the porous materials.
3. Results and discussion

3.1. Porous ceramics via a template-assisted colloidal processing technique

The microstructure of macroporous inorganic materials is highly dependent on the structure of the polymer crystal templates. Close-packed polymer spheres generally lead to well-ordered macroporous inorganic ceramics. In order to fabricate macroporous materials with uniform structures, a key requirement is to prepare well-packed polymer beads. Principally, this usually involves slow sedimentation of monodispersed polymer spheres, which results in hexagonal packed structures. In our experiments, we found that this form of sedimentation was time-consuming and that the precipitate was only partially closed-stacked. On the other hand, centrifugation of the polymer spheres led to the formation of an iridescent sediment on the bottom of the centrifuge tube, suggesting a well-ordered arrangement of the polymer spheres. The supernatant solution was decanted and the polymer spheres were air-dried before the infiltration process. Scanning electron microscope (SEM) images (Fig. 2) revealed that the centrifuged spheres were already ordered into close-packed domains, although the sphere arrays contained stacking faults, point defects, line defects and larger disordered regions. Previous result of silica showed that macroporous silica obtained using gravitational sedimentation showed relatively poorly-ordered structures but that macroporous silica prepared using centrifugation revealed uniformly-distributed macro-pores of up to several hundred micrometers in size throughout the whole sample [13]. Therefore, it is also shown that centrifugation is an effective route for the fabrication of macroporous materials. Therefore, we used the centrifugation method in the following preparations.

The resulting macroporous ceramics obtained by the infiltration of templates with inorganic precursors followed by calcination were firstly examined by X-ray diffraction (XRD). The XRD data revealed that the formation of the anatase phase of TiO$_2$ or a monoclinic structure of ZrO$_2$, indicating the formation of inorganic ceramic structures.

Fig. 3(a) depicts an ordered hexagonal arrangement of macroporous titania over a large area. From this image, we can find areas where hexagonal close-packed arrangements of pores and simple close-packed pores coexist (Fig. 3(b)). Due to the crystalline framework of anatase, some nanoparticles can be clearly observed in the walls. From the enlarged images of the trisection area (Fig. 3(c) and (d)), we can see that each pore was surrounded by about 10–14 small particles of titania with a size of about 60 nm, and that the wall thickness and the pores seem to be of equal size (about 130 nm) for both the hexagonal-packed pore structure and the simple close-packed arrangement.

In principle, the free energy is the lowest for a hexagonal closed-packed structure, whereas a square-packed arrangement of the spheres is only a metastable structure. However, infiltration with the concentrated alkoxide solution may result in this metastable arrangement of the templates, and could ultimately result in the formation of novel inorganic structures. It is worth noting that very few reports have mentioned the formation of macroporous structures with a square porous architecture to date. The formation of this structure may also be advantageous in terms of structural studies and could have possible applications in catalysis and separation. Others have also reported that control of the wall thickness and the size of the window openings between walls could be achieved by adjusting the dilution of the precursors with alcohols, which might modify the hydrolysis and gelation rates of the alkoxides [11,21,22].

Fig. 4(a) and (b) show another inorganic macroporous material consisting of ZrO$_2$. Again, a highly closed-packed fcc porous structure was obtained. The spherical pore size is about 200 nm and the wall thickness is about 80 nm, indicating that the shrinkage of the framework was appropriately 33% during the calcinations process resulting in zirconia particles that were about 30–40 nm in size. This macroporous structure almost remained intact even when heated at high temperatures as high as 850 °C, indicating the thermally-stable nature of ZrO$_2$ ceramics. On the contrary, the macroporous structure of TiO$_2$ was partially collapsed at this temperature.

3.2. Porous ceramics via a hetero-coagulation of template/ceramic particle colloidal processing

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 [15]. 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 nanoparticles in the same pH range with opposite surface charge.

Zeta potential of the TiO$_2$, PEI modified TiO$_2$ and P1300 are shown in Fig. 5. P1300 was negatively charged in the measured pH range of 3–12. A relatively high value of zeta potential could be obtained between pH 5 and 12, indicating that
the P1300 suspension is well-dispersed in this pH range. On the other hand, the isoelectric point (IEP) of the TiO\textsubscript{2} was located at pH 6.7, a highly positive surface charge could be obtained only below pH 5. For the purpose of preparation of TiO\textsubscript{2} suspension with a highly positive surface charge in a wider range, PEI was used to modify the surface charge of TiO\textsubscript{2}. The addition of PEI not only shifted the IEP to a higher pH value of 10.8, but also resulted in a good dispersion of the suspension. The zeta potential of the TiO\textsubscript{2} modified with PEI was much larger than that without PEI modification, moreover, the pH range with highly positive zeta potential turned wider, which makes the coating of polymer spheres much easier in a wide pH range, from pH 5 to pH 8, because the highly opposite-charged polymers and TiO\textsubscript{2} particles can be readily flocculated upon mixing due to the driving force of electrostatic interaction.

The microstructures of the calcined sample (Fig. 6) present the ordered porous structures. The pore size was uniform spherical with a pore diameter of ca. 1.0–1.2 \textmu m, being slightly smaller than the original PMMA spheres due to the calcination

![Fig. 3.](image1) ![Fig. 4.](image2)

Fig. 3. (a) Low magnification SEM image of macroporous TiO\textsubscript{2} materials with an ordered arrangement of the porous structure; (b) trisection area of hexagonal close-packed and simple close-packed porous TiO\textsubscript{2}; (c) and (d) SEM images of the TiO\textsubscript{2} materials showing a hexagonal close-packed arrangement of macropores and simple close-packed macropores, respectively.

Fig. 4. (a) Low-magnification and (b) high-magnification images of macroporous ZrO\textsubscript{2} materials calcined at 550 °C.

![Fig. 5.](image3)

Fig. 5. Zeta potential of TiO\textsubscript{2}, TiO\textsubscript{2} modified with PEI and P1300 particles.
contraction and grain growth of the TiO$_2$ nanoparticles upon heat treatment. The framework of the materials was relatively uniform with average thickness of ca. 200 nm, even though the TiO$_2$ particles with large size deviation was used as the starting materials, which is attribute to the slightly sintering of the nanoparticles. Note worthy that the slightly sintering is essential for the formation of porous materials with uniform framework and mechanical strength. It can be seen from the low magnification image (Fig. 6(b)) that the monodispersed spherical pores distribute uniformly throughout the whole sample, which proved the high porosity of the sample. The total porosity of the sample was determined to be ca. 69.6% while the open porosity was ca. 68.7%, suggesting that over 98% of the pores are opened pores, which may be advantageous for transportation of a certain kind of materials or use as catalyst.

Porous ZrO$_2$ with a pore size of about 1 $\mu$m was prepared using P1300 template, as shown in Fig. 7. The spherical pores were maintained and the particle size of ZrO$_2$ framework was about 180 nm. Fig. 7(b) 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 as is the case of alumina [15].

This approach has several advantages. First, the utilization of nano-ceramic particle is expected to result in less shrinkage than the molecular precursors. Second, the core–shell structure can proceed uniformly and rapidly due to the electrostatic adsorption of the two oppositely charged particles, as a result, the hetero-coagulation and filtration process is very time-saving. Finally, the large sample with enough mechanical strength can be obtained using this simple processing, which may be advantageous for manipulation of the samples. Consequently, this method may offer a general route and is expected to apply to many other materials nanoparticles.

4. Conclusions

In summary, macroporous materials of TiO$_2$ and ZrO$_2$ with well-defined pore architectures were fabricated through both a template-assisted strategy and a hetero-coagulation template processing. Through the former method, modification of the template arrangement resulted in novel structures with metastable square arrangements of the macropores. These macroporous materials with well-defined pore structures may find applications in areas such as photocatalysis and separation techniques. In the latter technique, the modification of the oppositely charged polymer and ceramic suspensions is the key for fabrication such kind of close-packed structures with high porosity. Our experimental results have shown that this strategy might be developed into a general pathway to prepare various porous inorganic materials with well-defined pore structure. Especially, the latter method has several merits such as time-saving, larger sample with enough mechanical strength, etc.

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