A new route to three-dimensionally well-ordered macroporous rare-earth oxides

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Ordered macroporous lanthanide oxides (Eu_2O_3, Nd_2O_3 and Sm_2O_3) have been fabricated using colloidal crystals of polystyrene (PS) spheres as a template in conjunction with the sol–gel method. Solidification of Ln^{3+}–EDTA chelates in the voids between the PS spheres and removal of the template by calcination yields three-dimensional ordered macroporous oxides. X-Ray diffraction reveals that the phases of Eu_2O_3, Nd_2O_3 and Sm_2O_3 are cubic, hexagonal and cubic, respectively, and scanning electron micrography shows that these oxides retain the structure of the initial template and exhibit 3D long-range ordered close packing of pores. The properties of these oxides are expected to allow them to find applications in areas including separation, catalysis and photonic crystals.

Template-directed syntheses have been broadly applied in materials science as they are expected to create porous materials with unique physical and chemical properties. Recently, three-dimensionally (3D) ordered macroporous materials have attracted extensive interest due to their unusual properties and potential applications in areas such as electrochemical sensors,[1] catalytic converters,[2] separation[3] and photonic crystals.[4–6] A typical procedure to prepare 3D macroporous materials by template-directed synthesis includes three steps, namely, the self-assembly of the template, deposition of the desired precursor inside the template and removal of the template, either by calcination or by chemical etching. By varying the way in which the precursors are introduced inside the template, various methods have been applied to the fabrication of 3D macroporous materials. These are sol–gel chemistry,[4,7–10] chemical vapor deposition,[5,11] nanoparticle infiltration,[12,13] electro-chemical methods,[6,14–17] chemical precipitation[18] and chemical conversion.[19–22] Although Yan *et al.*[18] recently presented a general method for the preparation of periodic macroporous transition metal oxides, so far, preparation of 3D macroporous rare-earth oxides has not been reported. Exploration of novel strategies for the synthesis of well-ordered macroporous rare-earth oxides is an interesting and challenging research project.

Rare-earth compounds, due to their dense energy levels, have been extensively used as light-emitting devices, hydrogen storage materials and catalytic and magnetic materials. In this communication, we present a novel sol–gel method for the preparation of well-ordered rare-earth oxides which involves chelation of Ln^{3+} with EDTA. The subsequent solidification of the precursor and removal of the template by calcination yields 3D periodic macroporous rare-earth oxides. Scanning electron micrographs (SEM) show that arrays of these oxides have long-range ordered periodic structures, which reflect the structure of the initial template.

Here, we use colloidal crystals of polystyrene (PS) spheres as the template. Fig. 1 shows a typical SEM image of the top view of our templates. Through convective self-assembly,[23–26] 726 nm PS spheres with a relative standard deviation of less than 4% are organized in a close-packed arrangement with long-range order both parallel and perpendicular to the glass dish. It was found that the concentration of the suspension of PS spheres and the evaporation rate of the solvent have significant effects on the formation of the template.[8,27] When the PS spheres were dispersed in absolute ethanol, we observed that the PS spheres were slightly swelled by the ethanol and the template displayed many cracks and was opaque. This indicates that the template lacks crystalline quality. High quality templates are easily identified by viewing in visible light. If the particle size of the PS spheres is of the order of visible wavelengths, the crystal reflection can be visually observed as a beautiful iridescence.

Fig. 2 shows typical SEM images of crystals of macroporous rare-earth oxides fabricated by using varying sizes of PS spheres colloidal crystals as templates. These oxides have clearly retained the three-dimensional crystalline order of the template and exhibit an ordered hexagonal pattern of pores in Eu_2O_3, Nd_2O_3 and Sm_2O_3. The next layer of pores below is visible in Fig. 2(E), as well as the holes that connect each air sphere to its nearest neighbors in the next layer. This image also shows that connecting pores appear to form around the points where the initial PS spheres once touched. Such a morphology has been observed for other porous materials fabricated with colloidal crystal templates.[4–11,19,20] Both the rare-earth oxides and the pores are interconnected, which constructs an open pore system in three dimensions. The SEM images show that the air sphere samples of these oxides have lattice parameters that are about 55–60% less than those of the original PS spheres. Differences in shrinkage can be attrib-

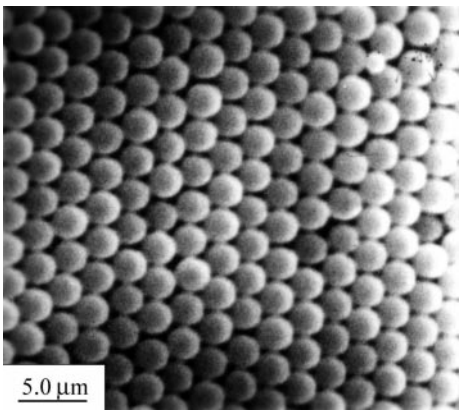

Fig. 1 Typical scanning electron micrograph (SEM) image of a polystyrene sphere template (726 nm with relative standard deviation less than 4%) for fabricating macroporous rare-earth oxides.

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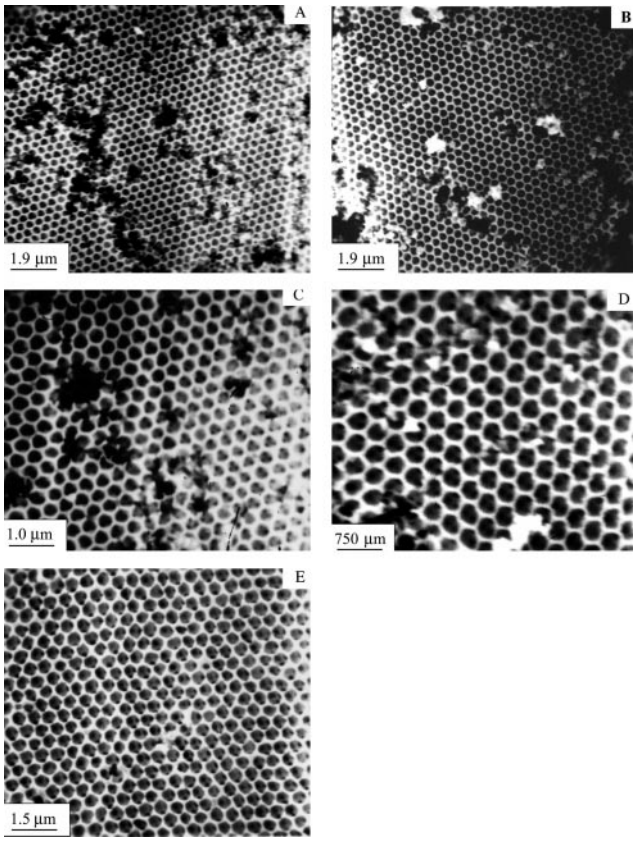

Fig. 2 Typical scanning electron micrograph (SEM) images of macroporous rare-earth oxides formed using 726 nm (A, B) and 833 nm (C, D, E) PS spheres as templates. (A) Top view of Eu_2O_3 with 310 nm diameter voids. The precursor was infiltrated into the template once. (B) Hexagonal Nd_2O_3 with 335 nm diameter voids showing the long-range order. The precursor was infiltrated into the template twice. (C), (D) Macroporous Sm_2O_3 fabricated by penetrating the precursor into the template in one and two cycles, respectively. (E) Macroporous Sm_2O_3 with the next layer visible through the pores. The precursor was infiltrated four times.

uted to different concentrations of precursor, synthetic conditions and individual crystallization kinetics. In addition, compared with previous reports, we also found that the shrinkage of our sample during calcination is much larger than others[4–11] prepared by sol–gel methods. We believe this phenomenon is associated with the decomposition of a great amount of chelating ligand. However, it should be noted that shrinkage is a common phenomenon in materials synthesized by template-directed methods, even when the template is removed by chemical etching.[6] Nevertheless, the long-range order and uniform pore structure of these oxides are not destroyed by this large shrinkage.

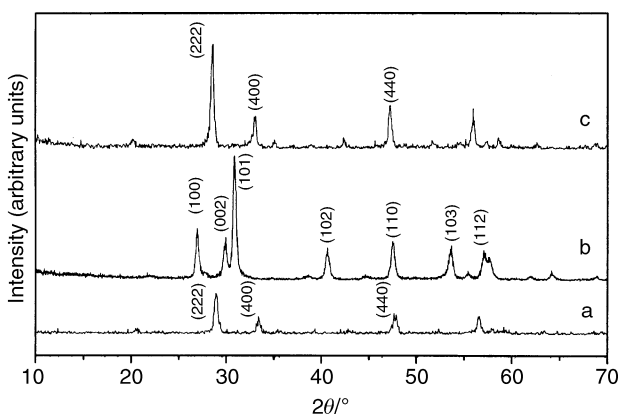

Fig. 3 X-Ray diffraction patterns of macroporous rare-earth oxides. (a) Cubic Eu_2O_3, (b) hexagonal Nd_2O_3, (c) cubic Sm_2O_3.

During the fabrication, we found that penetration times are very important to the final morphology of the samples. Fig. 2(A) and (B) show SEM images of Eu_2O_3 and Nd_2O_3 fabricated by using the same template. It can be clearly seen that the number of faults and vacancies decreases as the number of penetration cycles increases from one for Eu_2O_3 to two for Nd_2O_3. For the same sample of Sm_2O_3, this is also the case. When the number of penetration cycles increases from one [Fig. 2(C)], to two [Fig. 2(D)] to four [Fig. 2(E)], the number of faults and vacancies clearly decreases and well-ordered hexagonal arrangements are formed. These faults and vacancies are mainly produced by insufficient penetration of the precursor into the voids of the template. Multiple filling cycles allow complete infiltration of the voids; this process not only eliminates faults and deceases vacancies but also maximizes the precursor loading and thereby yields strong walls to avoid collapse of pores.

The TGA experiment reveals that EDTA and acetic groups are decomposed below 300 °C, the PS sphere template is burned and gasified at 350–430 °C and the inorganic compound is formed between 600–720 °C. The phases of the final inorganic oxides have been identified by powder X-ray diffraction and the patterns are shown in Fig. 3. The (222) reflection at about $2\theta = 29°$ and the (400) and (440) peaks correspond to the cubic phase of Eu_2O_3 (see spectrum a). In addition, the same three peaks are observed in spectrum c, which proves that the Sm_2O_3 is also the cubic phase. Calcination of the Nd sample at 640 °C gave a $Nd_2O_2CO_3$ phase due to incomplete calcination. Further calcination in air at 720 °C for another 2 h yields phase-pure hexagonal Nd_2O_3. Peaks typical of (101), (100) and (110) in spectrum b are clearly characteristic of the hexagonal phase of Nd_2O_3.

In summary, we present a new sol–gel method for the preparation of macroporous rare-earth oxides with long-range order and 3D periodic structure. Since the starting template can be made from spheres of variable size, the resulting macroporous rare-earth oxides have a tunable void volume. These materials may find applications in many fields, such as separation, catalysis and photonic crystals. Further investigations on the physical and chemical properties of each composite and to extend this method to other rare-earth oxides and to transition metal oxides are in progress.

Experimental

Nearly monodisperse PS spheres with an average diameter ranging from 300–1000 nm and relative standard deviation smaller than 4% (on the diameter) were obtained by emulsifier-free emulsion polymerization, using potassium persulfate as the initiator and sodium chloride to adjust the ionic strength to modify the size of the particles.[28] The colloidal crystals were assembled by the methods previously reported.[8,27] After repeated washing with dilute aqueous ethanol, PS spheres were dispersed in aqueous ethanol (1 : 1 v/v) in a flat bottom glass dish and spontaneously organized into the colloidal crystals by capillary forces. The precursor was prepared as follows: 1 mmol rare-earth oxide was dissolved in 15 ml glacial acetic acid with stirring and heating. Then, 10 ml aqueous EDTA with a concentration of 0.1 M was added to chelate the Ln^{3+} and the pH value of the solution was adjusted to 7 with dilute aqueous ammonia. The final volume of the solution was condensed to 5 ml by gelling at 70 °C. Before penetration, 2 ml methanol was added to increase the wetting between the precursor and template. After the voids of the template had been filled with precursor by capillary force, the template–precursor composite was dried in a vacuum desiccator for 24 h. The cycle of penetration and drying was repeated for several cycles to ensure that the voids of the template were sufficiently filled. The template was subsequently removed by calcining the composite at 600–720 °C for 5–7 h. The pore

structure of the materials was observed on a Hitachi X-650 scanning electron micrograph with an accelerating voltage of 25 kV. TGA experiments were performed on a Shimadzu TGA-50H analyzer with a heating rate of 10 °C min^{-1} in a N_2 atmosphere. The powder X-ray diffraction patterns were determined at a scanning rate of 0.06° s^{-1} for 2θ ranging from 10 to 70°, using a Y-4Q X-ray diffractometer with graphite monochromatized Cu-Kα radiation (λ = 1.541 78 Å).

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