

Two-step templating route to macroporous or hollow sphere oxides

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Anatase TiO₂, hexagonal Nd₂O₃, amorphous SiO₂ and Al₂O₃ with macroporous or hollow sphere structures have been fabricated by employing periodically macroporous active carbon as a template; the final morphology of the oxides can be controlled by the number of infiltration steps and the addition of solvent to the precursor.

Ordered porous materials currently attract considerable interest due to their wide range of applications as catalytic supports,¹ thermal and acoustic insulators² and optical devices.³ According to their pore size, porous materials can be classified into three types: microporous, mesoporous and macroporous. Microporous and mesoporous materials are generally templated by organic amine molecules, surfactants and block copolymer assemblies. For three-dimensionally (3D) well-ordered macroporous materials, the recently developed colloidal crystal template method is a simple and effective route to fabricate these materials. Under gravity⁴ or electrophoretic deposition,⁵ monodisperse colloidal spheres, such as silica, polystyrene (PS) and poly(methyl methacrylate) (PMMA) can self-assemble into ordered 3D arrays denoted as artificial opals. These ordered arrays offer a 3D scaffold in which a variety of precursors can be infiltrated. Subsequent solidification of the precursor and removal of the template, either by chemically selective etching or by calcination leads to 3D periodic macroporous materials known as inverse opals. The pore size of these materials can be routinely tailored by using different sizes of colloidal spheres. As a result, a great number of methods, such as sol-gel,^{6–8} electrochemical deposition,^{9–11} chemical vapor deposition¹² and solvothermal syntheses¹³ have been applied to infiltrate materials into the templates, resulting in diverse well-ordered macroporous materials such as ceramics,^{14–16} sulfides,^{13,17} metals¹⁸ and polymers.^{19,20}

Based on these techniques, we have successfully fabricated 3D ordered macroporous active carbon with BET surface areas as large as 408 m² g⁻¹.²¹ This large surface area, in combination with the periodic macroporous structure endows the active carbon with many promising applications in separation and adsorption. Moreover, the periodic pores of this material can also serve as cavities to accommodate diverse guest molecules. Here, we demonstrate one of applications of this macroporous active carbon in the fabrication of macroporous or hollow sphere oxides. Materials with hollow spheres have found many applications in chemistry, biotechnology and material science.²² Fabrication of hollow spheres with homogenous shells will open up possibilities for various new application fields, such as controlled release capsules, artificial cells for drug delivery, light-weight fillers, shape-selective adsorbents

and catalysts. Traditionally, hollow spheres are fabricated by coating the template with a thin shell of the desired materials and subsequently removing the template.^{23–25} The difficulties of this method often arise from the control over the fabrication process,²³ as well as homogeneity and thickness of the coating.²⁵ In our approach, using well-ordered carbon as the template, the morphology of the sample can be controlled leading to uniform and homogenous shells for the hollow spheres.

Nearly monodisperse SiO₂ spheres were synthesized by hydrolyzing chemical grade tetraethyl orthosilicate (TEOS)²⁶ and assembling into SiO₂ opal by a vertical deposition technique.⁴ The macroporous active carbon used as template in the second templating process was fabricated according to the method previously reported.²¹ The rare earth oxide Nd₂O₃, absolute ethanol, glacial acetic acid, EDTA, concentrated HCl and 28% ammonia were purchased from Aldrich and were used directly without further purification. The precursor for TiO₂ was prepared by diluting chemical grade titanium butoxide in absolute ethanol with a volume ratio of Ti(OC₄H₉)₄: C₂H₅OH = 1:1. The precursor for SiO₂ was obtained by mixing 1.12 ml TEOS, 9.5 ml absolute ethanol, 0.2 ml 0.1 M HCl and 0.25 ml H₂O. The precursor for Nd₂O₃ was prepared by dissolving 1 mmol Nd₂O₃ in heated glacial acetic acid. Then 1 mmol EDTA was added to chelate Nd³⁺. The pH value of the solution was adjusted at 7 with diluted NH₃·H₂O. The final volume of this precursor was condensed to about 5 ml by gelling the solution at 70 °C. For Al₂O₃, 10% AlCl₃ aqueous solution as a precursor was employed.

The hollow spheres or macroporous oxides were obtained by templating the specific precursor with macroporous carbon. Typically, centimeter-scale, well-ordered macroporous carbon was soaked in the precursor for 3–5 min. After immersing the macroporous carbon into the above precursor the precursor completely infiltrates the pores in a few minutes under capillary action. The excess precursor on the surface of the macroporous active carbon was then removed by suction using filter paper. After exposure to moisture in the air, due to the hydrolysis of the precursor, a shell of TiO₂ or SiO₂ is formed and coated on the inner surface of the macroporous active carbon. In the case of Al₂O₃ and Nd₂O₃, after evaporation of excess solvent, a shell of compound is also formed on the inner surface of the pores of the carbon template. After solidification, the composite of precursor and the carbon template was calcinated at 600 °C (720 °C for Nd₂O₃) for 5 h. Elemental analyses (C, 0.8% for the TiO₂ sample) indicates, after this thermal treatment, that most of the carbon was burnt off, leaving behind the macroporous or hollow sphere structure of the oxide.

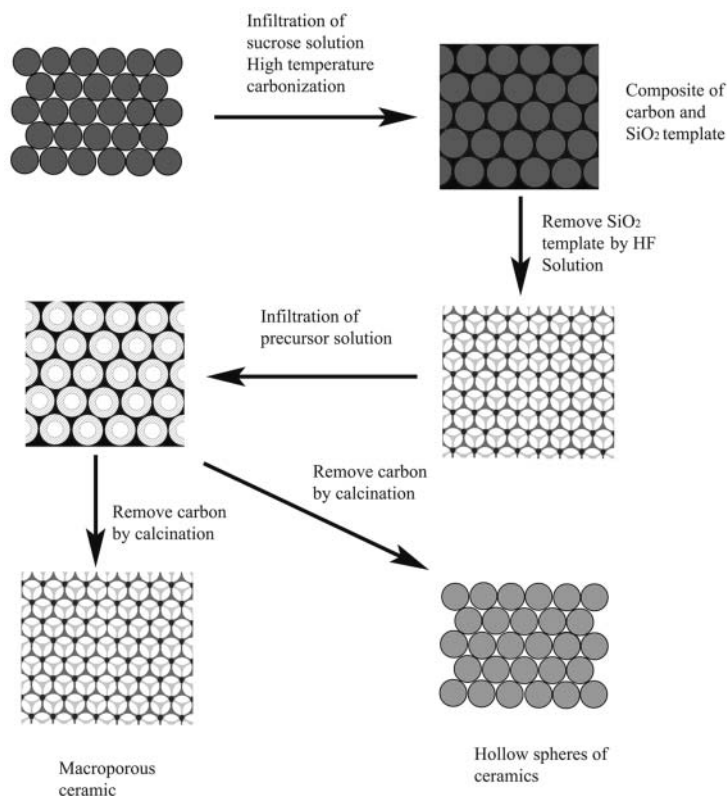


Fig. 1 Schematic procedure for the two-step templating method.

Two-step templating methods have been applied to the fabrication of well-defined colloidal metal spheres,²⁷ as well as polymers²⁸ and silica.²⁹ Fig. 1 illustrates the schematic procedure of the two-step templating method. The key feature of this procedure is that the final solids result from template-directed methods. From the initial SiO₂ opal (Fig. 2A) to the final macroporous or hollow sphere structure of the oxide, there are clearly two templating process. In the first templating process, SiO₂ opal was used as a template to fabricate the macroporous active carbon, as shown in Fig. 2B. In the second templating procedure, the well-ordered macroporous carbon was used as the template and infiltrated by other precursors leading to fabrication of the oxides. Jiang *et al.*²⁸ have used macroporous PS and PMMA films as templates. However, the hydrophobic surface of the polymer films may reduce the variety of the products fabricated by this two-step templating method. Macroporous carbon has the obvious advantages over such macroporous polymer templates with the hydrophilic surface of carbon allowing relatively concentrated solutions of precursors to completely infiltrate the whole template thus leading to more precursor inside the template after excess solvent is evaporated. This aids in eliminating defects and

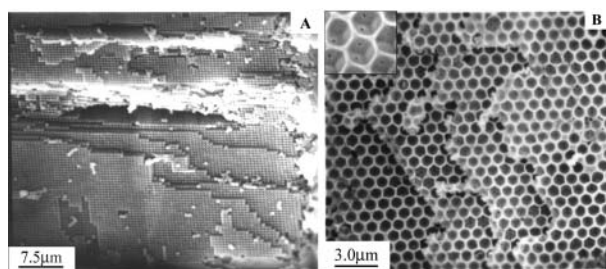


Fig. 2 (A) SEM images of SiO₂ opal, which was assembled by the vertical deposition technique.⁴ (B) 3D periodic macroporous carbon fabricated by the colloidal crystal template method.²¹ Small windows can be clearly observed in the upper inset of higher magnification ($\times 20000$).

vacancies, therefore producing strong walls in the final product so preventing collapse. Fig. 2B shows a scanning electron micrograph (SEM) image of the macroporous active carbon used as the template in the second templating process. The necks between the initial SiO₂ spheres, which were formed during thermal sintering at 820 °C,³⁰ can be clearly seen as small windows in each pore (see higher magnification images of the upper inset). These small windows play important roles in the fabrication of the template. First, they provide the necessary channels to allow the precursor solution to flow through the whole carbon template and form a shell of oxide on the inner surface of each pore. In addition, these windows also serve as the controlling feature for overlap between the hollow spheres. This feature provides the possibility to tailor the width of the photonic stop band.³¹ Fig. 3A shows an SEM image of macroporous TiO₂ fabricated by double infiltration of the TiO₂ precursor into the macroporous carbon template. The long-range ordered pore arrays extend this framework in three dimensions, indicating that the ordered macroporous active carbon is well replicated. The cross-sectional images of Fig. 3B and C (SiO₂ hollow spheres) indicate the precursor had completely infiltrated the inside of the template. The broken spheres present in Fig. 3B and C show that they are hollow and the shell is uniform. Powder X-ray diffraction (XRD) patterns (see Fig. 4A) show the wall of the broken TiO₂ spheres to consist of anatase. An interesting phenomenon is that when the number of infiltrations is increased from two to six, the morphology of TiO₂ sample shifts from macroporous to hollow sphere (see Fig. 3A and B). We believe this morphology shift is related to the change of the shell thickness. When the shell thickness increases, their greater strength can support hollow sphere structures. It should be noted that efforts to increase shell thickness of TiO₂ simply by successive infiltration, however, were not successful. Multiple infiltration and subsequent hydrolysis of the precursor eventually blocks the windows, which prevents the precursor from filling the internal pores of the carbon template. By heating the composite of carbon and precursor at 400 °C in vacuum, these blocked

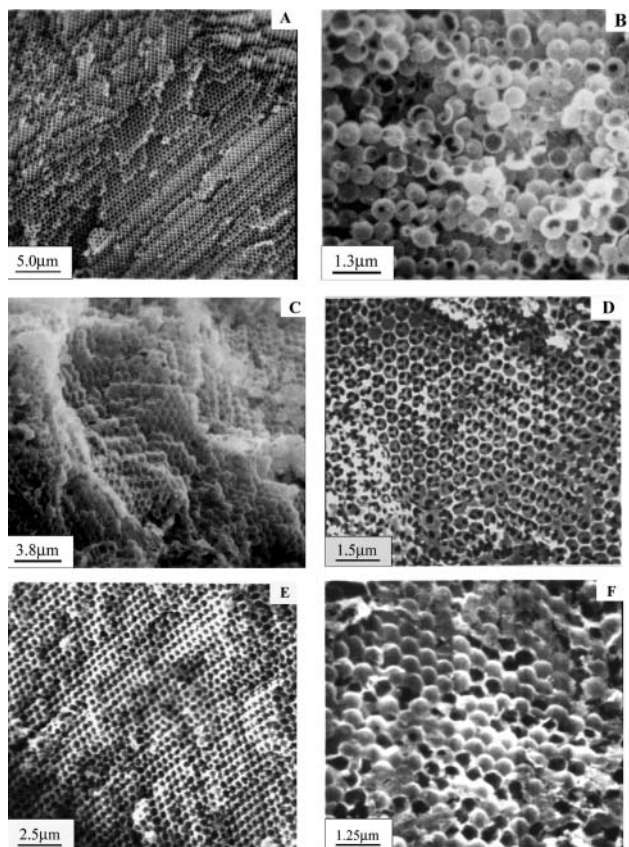


Fig. 3 (A) Macroporous TiO_2 fabricated by infiltration ($2\times$) of the precursor into macroporous carbon. (B) Hollow spheres after TiO_2 infiltration ($6\times$). (C) Cross-sectional images of SiO_2 hollow spheres. These close-packed spheres are well-ordered in three dimensions. (D) Macroporous Al_2O_3 fabricated by templating ($1\times$) AlCl_3 aqueous solution into macroporous carbon. (E) Macroporous Nd_2O_3 prepared by infiltrating ($1\times$) chelated Nd^{3+} . (F) Addition of a small amount of ethanol to the precursor changes the morphology of Nd_2O_3 from macroporous to that of hollow spheres.

windows, due to shrinkage, can be reopened. The onset of blockage is dependent upon the size of the windows of the carbon template, as well as the concentration of the precursor. In our method, for TiO_2 this maximum number of infiltration steps is four. Six infiltration steps of the precursor in Fig. 3B consisted of four infiltrations, vacuum heat treatment, the two further infiltrations. The precursor of SiO_2 was infiltrated twice with the carbon and hollow spheres rather than macroporous SiO_2 was obtained. Differences in the morphology for TiO_2 and SiO_2 after two infiltrations may be related to the interaction between the carbon and precursor, the concentration of the solution of the precursor and their different hydrolysis rates.

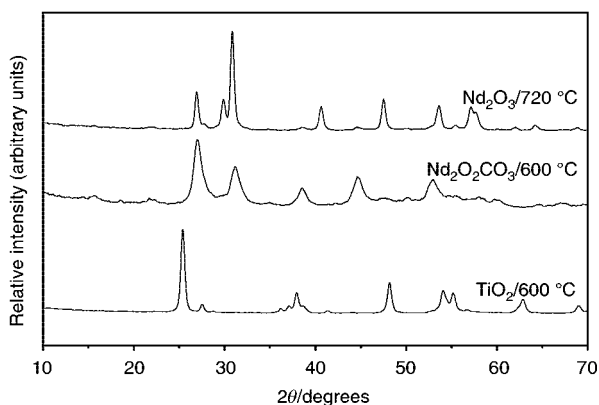


Fig. 4 Powder X-ray diffraction patterns of anatase TiO_2 (A), hexagonal $\text{Nd}_2\text{O}_2\text{CO}_3$ (B) and hexagonal Nd_2O_3 (C).

In addition, to investigate the reproducibility of the fabrication process, we also used aqueous AlCl_3 solution and aqueous chelated Nd^{3+} to infiltrate the macroporous carbon. Owing to the hydrophilic surface of carbon, these precursors are also retained in the inner surface of the macroporous carbon. Besides the removal of carbon, calcination also facilitates the formation of Nd_2O_3 and amorphous Al_2O_3 . XRD patterns show that hexagonal $\text{Nd}_2\text{O}_2\text{CO}_3$ present at 600°C is converted to hexagonal Nd_2O_3 at 720°C (Fig. 4B and C). SEM images of Al_2O_3 and Nd_2O_3 (Fig. 3D and E) are very similar to those fabricated by using colloidal polystyrene spheres as the template.³² The pores clearly have retained the long-range order of the carbon template and exhibit an ordered hexagonal close packing structure. The next lower layer is clearly seen, and the void spaces are interconnected by windows. However, the size of these windows in Fig. 3D seems to be larger than that of the carbon template itself, see the inset image of Fig. 2B. We believe the enlarged windows are related to the precursor and infiltration times. A dilute precursor and the fewer infiltration steps lead to lower loading of precursor, therefore the inner surface of these windows was not completely coated or only coated by a thin shell of the precursor. With a temperature increase, this thin shell shrank and left a portion of the inner surface of these windows not coated by the precursor. After removal of carbon, these windows seem to be larger than those of the carbon template itself. Another interesting phenomenon is that when a little ethanol was added to the precursor of Nd_2O_3 , the final morphology changed from macroporous to hollow spheres. Although a detailed mechanism is still unavailable, we believe the addition of ethanol may modify the interaction between the carbon template and the precursor and thereby change the final morphology.

In conclusion, we have fabricated macroporous or hollow spheres of TiO_2 , SiO_2 , Al_2O_3 and Nd_2O_3 by templating the respective precursor solution with the well-ordered macroporous carbon. The final morphology of the sample depended on the number of infiltration steps of the precursor, as well as the solvent. The outer diameter of the hollow spheres depended on the pore size of macroporous carbon, and thereby on the diameter of initial SiO_2 template in the first templating step. In addition, different shells can also be fabricated by successively infiltrating different precursor solutions into the carbon template. In principle, this method can be applied, in general, to sol-gel systems to fabricate macroporous or hollow sphere materials provided the solution is not viscous enough to block the windows and the precursor can completely wet the inner surface of the pores of the carbon template.

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