Fabrication of ordered macroporous rutile titania at low temperature

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Macroporous rutile titania has been prepared by centrifugation sedimentation and evaporation approaches with $TiCl_4$ as the precursor and polystyrene (PS) spheres as the template. The nanocrystalline rutile titania particles were first synthesized at room temperature, then used to fill the voids between the PS spheres. The macroporous material was obtained after calcination at 450 °C. This is the first report of ordered macroporous rutile titania being obtained by calcination at such a low temperature. XRD results reveal that the titania nanoparticles of the as-synthesized and macroporous materials after calcination are rutile crystalline. SEM images show that the PS spheres and macroporous rutile form three-dimensionally ordered close-packed structures.

Three-dimensional (3D) ordered macroporous materials are an attractive research area because of their extensive applications in separation processes, adsorption, catalysis, battery materials, thermal insulators, low-dielectric constant materials, microelectronics and photonic crystals.[1,2] Many macroporous materials have been prepared in the past several years, including metals and metal alloys,[3–5] inorganic oxides,[6–9] metal chalcogenides,[10–12] polymers,[13,14] and salts.[15,16] Information transmitted by light, instead of electrons, is one of the great dreams of the telecommunications industry, because light has several advantages over electrons. In order to realize this dream, researchers have to prepare a basic component, the material in which the photons of light will behave in the same way as electrons do in semiconductors. Materials with such features are known as photonic crystal materials,[17,18] a concept first proposed by Yablonovitch[19] and John[20] in 1987. Scientists have made great efforts to prepare 3D photonic crystals with a band gap around 1.55 μm, which is the wavelength now used in optical fiber communication. In recent years, several methods have been developed to prepare photonic crystals, such as lithography, electrochemical deposition, chemical vapor deposition (CVD), and self-assembly.[10,21–25] The first photonic crystals with a photonic bandgap (PBG) in the microwave and centimeter regions were reported by the groups of Soukoulis[26] and Yablonovitch,[27] respectively. Recently, Noda and co-workers[28,29] have prepared 3D photonic crystals with wavelengths in infrared regions between 1 and 10 μm. In order to obtain a complete PBG, one should prepare macroporous materials with high refractive index (>2.8), such as titania, SnO_2, GaAs, CdSe, and SeS_2.[10–12]

Of the three crystalline phases of titania—anatase, rutile, and brookite—rutile is the most appropriate candidate for preparing photonic crystals because of its high refractive index (2.9), thermal stability and low absorptivity in the visible regions. Recently, macroporous anatase titania has been extensively researched.[7,9,30–36] However, the fabrication of rutile macroporous material is very difficult, due to its calcination at high temperatures (>800 °C). Pine and co-workers[33,34] prepared macroporous anatase TiO_2 by colloidal self-assembly. However, they have not obtained rutile macroporous materials, even when calcinated at 800 °C, and the porous structure was destroyed above 1000 °C. They believed that the most appropriate approach would be to employ nanocrystalline rutile particles directly to produce ordered macroporous rutile, even though they subsequently used emulsion templates to obtain macroporous rutile by calcination at 1000 °C.[37]

In the present work, the macroporous materials were synthesized using $TiCl_4$ as the precursor and polystyrene (PS) latex spheres as the template. Fig. 1 shows a typical SEM image of the PS spheres template. The diameter of the PS spheres is ~450 nm. The image shows that the PS spheres form a close-packed structure with 3D order over several tens of micrometers and a narrow size distribution.

Rutile TiO_2 nanoparticles were first prepared by the hydrolysis of $TiCl_4$ under acidic conditions at room temperature. In contrast to the conventional approach, which uses calcination at high temperature to prepare the rutile TiO_2, the present method has great advantages as nanocrystalline rutile is successfully prepared at room temperature. We can obtain different sizes of the nanocrystalline rutile TiO_2 particles by changing the concentration of $TiCl_4$, pH value, temperature, aging time, and stirring speed. Powder X-ray diffraction of as-synthesized TiO_2 is shown in Fig. 2(a). All the peak positions of the as-synthesized sample are in excellent agreement with those of authentic rutile TiO_2 (JCPDS card, no. 21-

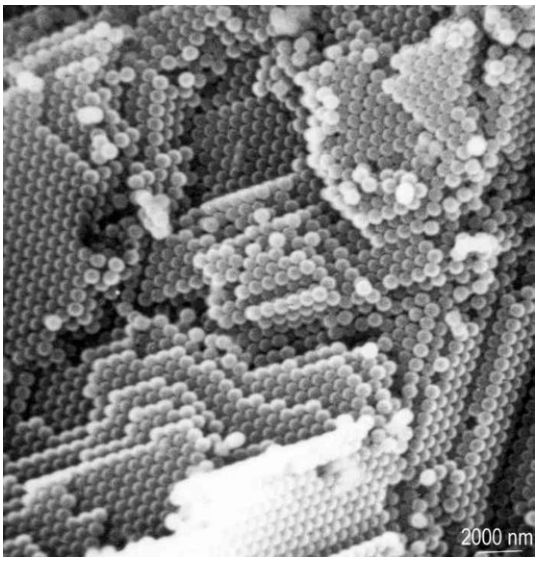

Fig. 1 Typical scanning electron micrograph (SEM) image of a polystyrene sphere template (~450 nm in diameter) for preparing macroporous rutile titania.

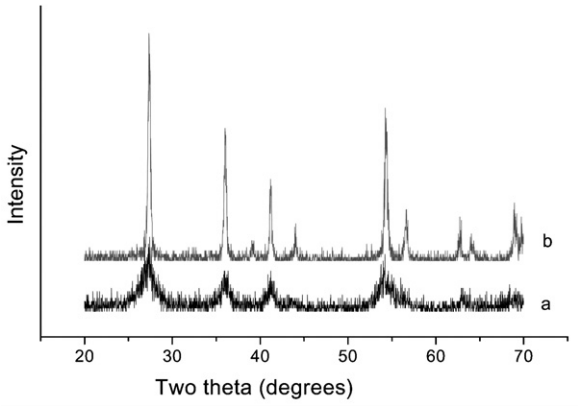

Fig. 2 Powder X-ray diffraction patterns of rutile titania in the form of (a) as-synthesized nanoparticles and (b) macroporous material calcinated at 450 °C.

1276), indicating that only the rutile phase is present. Fig. 2(b) shows the XRD spectrum of the macroporous sample after calcination at 450 °C. The increase in the diffraction intensity indicates an improvement in the degree of crystallinity after thermal treatment. The size of the rutile particles was estimated from the XRD data with the Scherrer formula to be about 5 nm for the as-synthesized sample and ~30 nm for the calcinated one.

In this work, two different methods were used to prepare the macroporous materials. One is the centrifugation sedimentation method. As the sedimentation rate is not the same for the slurry of rutile TiO_2 nanoparticles and the PS templates, ordered macroporous materials are very difficult to obtain by centrifuging directly a mixture of PS spheres and a slurry of nanocrystalline rutile. So the ordered PS spheres were first obtained by centrifugation (sedimented PS) and dried at room temperature. The rutile slurry was placed on top of the sedimented PS spheres powder and the mixture was centrifuged again; then the precipitate was then calcinated to remove the PS templates. Fig. 3 shows the scanning electron micrographs (Hitachi S-520) of rutile samples made by this method. Fig. 3(a) and (b) show different magnifications of the sample after calcination at 450 °C. These images reveal empty air spheres ordered over a range of tens of micrometers with the walls interconnected by rutile nanocrystalline. These images also show that the pore size of the air sphere samples of rutile titania is ~250 nm. There is a shrinkage of ~44% relative to the diameter of the original PS spheres template (~450 nm). The advantage of the centrifugation method is that a close-packed macroporous structure can be easily obtained in shorter times and with better order in comparison to the evaporation method (see below). The better ordered structure obtained by using the former method can be seen from the SEM images (see Fig. 3 and 4) of the macroporous material prepared by the two different methods.

The solvent evaporation method we used is analogous to that of Pine and co-workers.[33,34] They prepared macroporous anatase titania material with an anatase TiO_2 sol and PS spheres. In our experiment, measured amounts of PS suspension and rutile titania suspension were mixed and dried in an oven at 60 °C. The polystyrene beads arranged themselves into

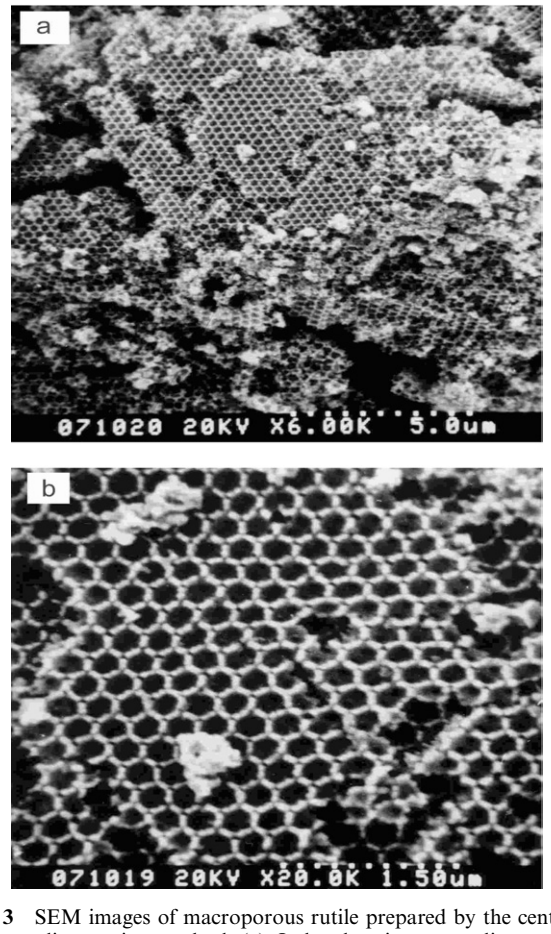

Fig. 3 SEM images of macroporous rutile prepared by the centrifugation sedimentation method. (a) Ordered regions extending over 10 μm. (b) Higher magnification image showing ordered and interconnected pores. The pore size is ~250 nm.

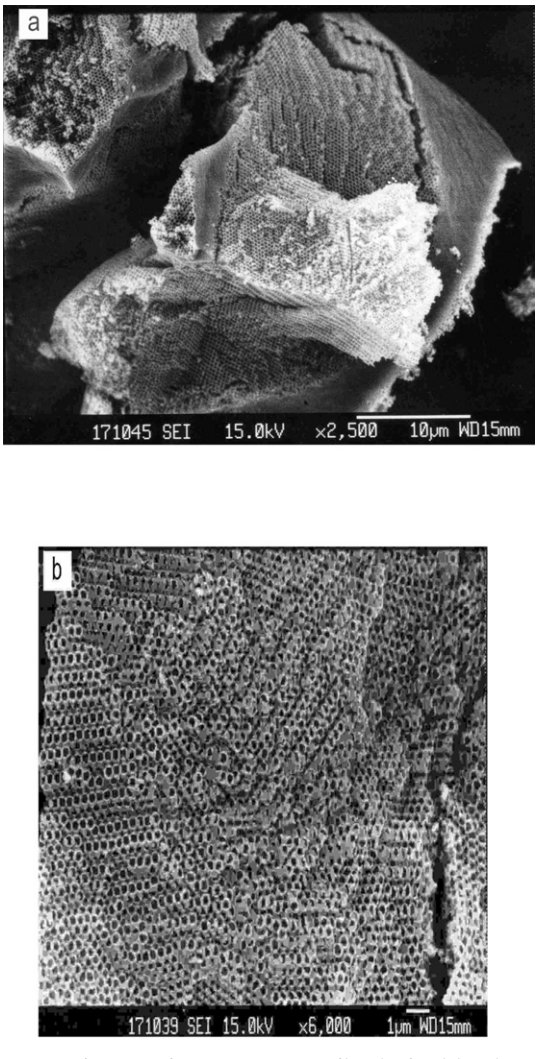

Fig. 4 SEM images of macroporous rutile obtained by the solvent evaporation method. (a) SEM image of three-dimensionally ordered material over several tens of micrometers. (b) Higher magnification SEM image.

an ordered structure; the water was slowly evaporated and the rutile nanoparticles filled the voids of the polystyrene beads to cement the network structure. Fig. 4 shows the SEM images (JSM-6330F) of macroporous rutile prepared by the solvent evaporation method. From the lower- and higher-magnification images, it can be seen that the macroporous structure is ordered over tens of micrometers and that the network is interconnected. From these images and those in Fig. 3, it is easily seen that the macroporous structures obtained using the two methods exhibit some differences. The rutile macroporous materials prepared by the solvent evaporation method show some distortion in the porous structure. The most likely reason is that some nanoparticles have covered the surface of the PS latex spheres during the water evaporation process.

During the traditional preparation of macroporous rutile by the sol-gel method, high temperatures ($>800\,^{\circ}C$) are essential to transform amphorous TiO_2 into anatase and then rutile. Grain growth often takes place during calcination, such that the porous structure is destroyed. In contrast to the high temperature calcination method, the procedures reported here are simple, inexpensive and effective. The method in which the crystalline nanoparticles are synthesized at room temperature and then embedded into the voids left by the latex sphere is very promising for the preparation of long-range 3D ordered macroporous materials and photonic crystals. The approach demonstrated in this work can be extended to produce other desired macroporous materials.

In summary, rutile titania nanoparticles were prepared at room temperature and ordered macroporous rutile material was also obtained by the centrifugation sedimentation and the solvent evaporation methods, from nanocrystalline rutile suspension and PS latex spheres. In these novel approaches, it should be easy to obtain other desired crystalline macroporous materials by avoiding the high temperature calcination step and hence retaining the ordered porous structure. These ordered macroporous rutile materials are expected to exhibit excellent properties for separation, catalysis and photonic crystals. Further investigations are under way in our laboratory.

Experimental

The rutile nanoparticles were prepared by the hydrolysis of $TiCl_4$. $TiCl_4$ (20 ml) was added slowly to ice-water (200 ml) containing HCl (1.5 ml, 37 wt %), the solution was stirred for 1 h and then aged for several days at room temperature to give a precipitate. A rutile suspension colloid was obtained after the precipitate was diluted with deionized water. Monodisperse polystyrene spheres were synthesized using potassium persulfate as the initiator as described previously.[9] The PS suspension was prepared from 73 g of styrene, 720 ml of deionized water, and 0.6 g of potassium persulfate. The PS suspension was dialyzed in deionized water over a week, packed into ordered colloidal crystals by centrifugation (1000 rpm, 24 h) and dried at room temperature.

Macroporous rutile materials were obtained by two different methods. The first is centrifugation sedimentation: the PS powder (0.3 g) was wet with absolute ethanol, then the rutile suspension ($\sim$0.12 g in 3 ml of H_2O) was added. The mixture was sedimentated by centrifugation (1000 rpm, 24 h). The excess solution was removed and the precipitate was then dried at 60 °C. The other method is solvent evaporation:[33] samples were made by mixing measured amounts of the PS suspension (10 ml from the aforementioned PS suspension) and rutile suspension (0.4 g in 10 ml H_2O) in a beaker, and then slowly drying them in an oven at 60 °C for 7 days. The macroporous materials were then obtained by calcination of both of the above dried samples in air at 450 °C for 7 h (heating rate: 3 °C per min).

The powder X-ray diffraction patterns were determined by a D/Max-IIIA diffractometer with Cu Kα1 radiation ($\lambda = 1.54056$ Å) at a scanning rate of $0.02^{\circ}\ s^{-1}$ for 2θ ranging from 20 to 70°. The porous structure was analyzed by SEM, which was performed on Hitachi S-520 or JSM-6330F field emission microscopes.

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