Cathodic Electrodeposition of Ordered Porous Titania Films by Polystyrene Colloidal Crystal Templating

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The fabrication of ordered porous titania films using polystyrene colloidal crystal templates by cathodic electrodeposition is reported. A new strategy using $Ti(SO_4)_2$ as Ti source for the potentiostatic electrodeposition of titania has been developed. An improved post-treatment of the electrodeposited samples was executed to obtain long-range ordered porous films.

Porous materials based on colloidal crystal templating possess uniform pore size and highly ordered pore arrangement, which have many potential applications in separations, sensors, catalysis, and photonic crystals.[1–4] Using three-dimensional colloidal crystal template various types of ordered porous materials have been synthesized, including oxides, chalcogenides, nonmetallic and metallic elements, and polymers.[5–9] Titania as an attractive material has been investigated in recent years for its applications in photocatalysis, dye-sensitized solar cells, and photonic crystals.[10–12] Preparation of three-dimensionally ordered porous titania is very attractive especially in photonic crystals. Kuai et al. obtained highly ordered macroporous titania films using silica colloidal crystals as templates through a dip-infiltrating sol–gel process.[13] King et al. recently reported the low-temperature fabrication of titania inverse shell opals using atomic layer deposition.[14] Electrodeposition as an effective and economical technique was also adopted to fabricate titania inverse opals. Kavan et al. prepared anatase inverse opals which exhibited the long-range ordering of pores by galvanostatic electrodeposition.[15]

Electrodeposition of titania was investigated by many researchers in recent years. Ti sources having been used included Ti powder, $TiCl_3$, $TiCl_4$, $(NH_4)_2[TiO(C_2O_4)_2]$, and $TiOSO_4$.[16–19] The potentiostatic electrodeposition is fast and produces layers of densely packed ultrasmall TiO_2 crystallites.[15] Furthermore, the bottom-up growth in the electrodeposition will provide a sufficient filling of the template. In this letter, we reported the template-directed electrodeposition of anatase TiO_2 in potentiostatic mode using $Ti(SO_4)_2$ as Ti source. In the electrodeposition the mixed ethanol–water solvent was employed to make the electrolyte wet the colloidal crystal template. After the electrodeposition, an improved post-treatment was utilized where the samples were dissolved in toluene before heat treating in order to obtain long-range ordered porous structure.

Monodisperse polystyrene (PS) spheres were prepared using an emulsifier-free polymerization technique according to the literature.[20] The prepared PS spheres were washed by repeated centrifugation and ultrasonic dispersion cycles, and then assembled into three-dimensionally ordered colloidal crystals on the indium tin oxide (ITO) coated glass substrates.[21] A three-electrode electrodeposition system was exploited to prepare TiO_2 porous films, with a saturated calomel electrode (SCE), platinum foil, and the PS–opal/ITO as the reference electrode, counter electrode, and working electrode, respectively. Cathodic electrodeposition was carried out at -1.8 V (vs SCE) in a mixed ethanol–water solution containing 0.02 M $Ti(SO_4)_2$, 0.1 M KNO_3, and 0.5 M H_2O_2, in which the volume ratio of the ethanol/water was 2:8. All the samples were electrodeposited for 30 min at room temperature. After electrodeposition the samples were soaked in toluene for 24 h to remove the PS templates. Subsequently, the samples were annealed in air at 450 °C in order to obtain crystalline TiO_2. The heating rates were 1 °C/min.

The as-deposited film is $TiO(OH)_2 \cdot xH_2O$ gel film, which is colorful after the PS template has been dissolved in toluene. It is amorphous from the X-ray diffraction measurement (not shown). Having been heat-treated at 450 °C, the film became the crystalline, anatase form. As shown in Figure 1, five well-resolved Raman peaks are observed which are located at 144, 195, and 395 cm^{-1} (O–Ti–O bending-type vibrations) and at 516 and 638 cm^{-1} (Ti–O bond stretching-type vibrations). These Raman peaks are corresponding to the characteristic peaks of anatase TiO_2. It was mentioned by other authors that the electrochemical deposition produced invariably anatase regardless of the precursor and solvent used for the preparation of TiO_2 films.[17] This is further demonstrated in our case.

The obtained PS colloidal crystal films have uniform color indicating the presence of long-range ordering in the structure. Figure 2 displays a field emission scanning electronic microscope (FE-SEM) image of a PS template. As seen from the image, the PS spheres are uniform in size and are closely packed. The average diameter of PS spheres is 330 nm as measured from the FE-SEM image.

Figure 3 shows the FE-SEM images of the electrodeposited porous TiO_2 film which was annealed at 450 °C. A clear three-dimensional pore structure is observed where the pores are

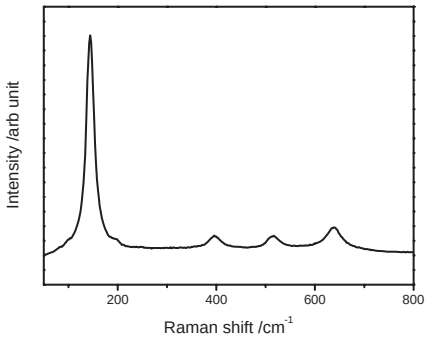

Figure 1. Raman spectrum of electrodeposited and annealed anatase TiO_2 porous film.

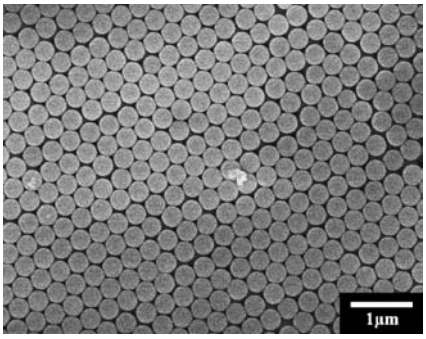

Figure 2. A typical FE-SEM image of a PS colloidal crystal template.

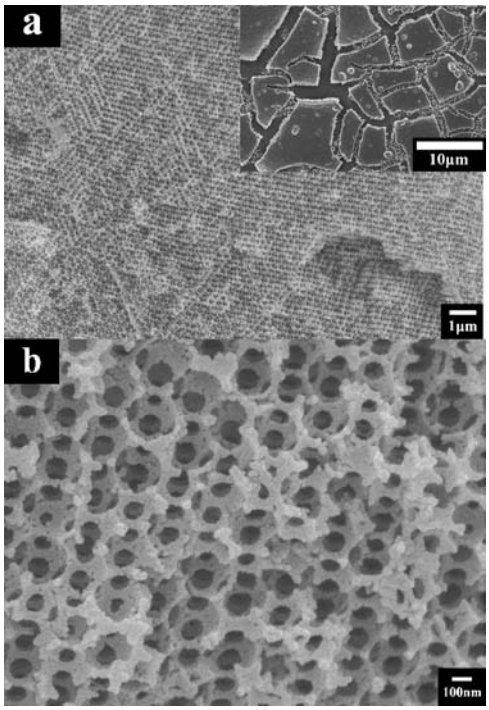

Figure 3. The electrodeposited porous TiO_2 film where the PS template was removed before heat treatment. (a) Low magnification FE-SEM image, (b) higher magnification FE-SEM image. Inset: the electrodeposited porous TiO_2 film which was directly sintered at 450 °C without removing the PS template in advance.

closely packed. This indicates that the void structure of the original PS template is precisely replicated. As measured from the FE-SEM image, the diameter of pores is ca. 260 nm which is ca. 20% smaller than the diameter of the parent latex spheres (330 nm). As a comparison, the as-deposited film was directly sintered at 450 °C without removing the PS template in advance. As shown in the inset of Figure 3a, the film contains big cracks and its top surface was coated by a solid layer.

In our experiments, ethanol was added to the electrolyte in order to make the electrolyte wet the PS template but itself did not participate in the electrochemical reaction. Dissolving $Ti(SO_4)_2$ in water must be careful, otherwise white precipitate will appear. When H_2O_2 is added to the solution, a clear orange-colored solution is obtained. According to the literature,[16,19] the reaction process should be described as following:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-, \quad (1)$$

$$Ti(SO_4)_2 + H_2O_2 \rightarrow Ti(O_2)SO_4 + H_2SO_4, \quad (2)$$

$$Ti(O_2)SO_4 + 2OH^- + (x+1)H_2O \rightarrow TiO(OH)_2 \cdot xH_2O + H_2O_2 + SO_4^{2-}. \quad (3)$$

The content of ethanol should not exceed a specific value or else white precipitate will form. The electrodeposited $TiO(OH)_2 \cdot xH_2O$ gel film was amorphous, and therefore the heat treatment was inevitable to obtain crystalline titania film. During heating PS spheres will soften and then be burned off. The $TiO(OH)_2 \cdot xH_2O$ gel will undergo the removal of absorbed water (xH_2O) and the decomposition of $TiO(OH)_2$ under heat treating.[16] All these processes are not favorable to the formation of ordered porous structure. Therefore, removing the PS template before heat treating reduced the damage for the ordering of porous TiO_2 films. As a result, a precise replica of the void structure was achieved when the PS template was removed before heat treating.

In summary, we have described a simple method to fabricate three-dimensionally ordered TiO_2 porous films. Cathodic electrodeposition of TiO_2 was executed on the PS colloidal crystal template. The use of mixed ethanol–water solvent made the electrolyte wet the PS template; thus the void space of the original template achieved a good filling resulting in the formation of a tough porous skeleton. Through modified post-treatment of the electrodeposited samples, long-range ordered TiO_2 porous films were obtained.

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