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Fabrication and characterization of uniform TiO_2 nanotube arrays by sol–gel template method

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Abstract. **TiO_2 nanotubes have been synthesized by sol–gel template method using alumina membrane. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, UV absorption spectrum and X-ray diffraction techniques have been used to investigate the structure, morphology and optical properties of TiO_2 nanotubes. SEM image showed that TiO_2 nanotubes obtained were ordered and uniform. The diameter and length of the nanotubes were decided by the pore size and thickness of alumina template. Raman and XRD measurements confirmed the crystallinity and anatase phase of the TiO_2 nanotubes. The optical absorption measurement of TiO_2 nanotubes exhibits a blue shift with respect to that of the bulk TiO_2 owing to the quantum size effect.**

Keywords. **TiO_2 nanotubes; Raman spectra; template synthesis; alumina template.**

1. Introduction

Titanium dioxide (TiO_2) has been widely investigated as a key material for applications in photovoltaic cells, batteries, chemical sensing (Varghese *et al* 2003), optical emissions, photonic crystals, catalysis, photocatalysis (Livraghi *et al* 2005) and environmental purification (Homyara *et al* 2001). Anatase TiO_2 electrodes are used in solar cells, lithium batteries and electrochromic devices (Hagfeldt and Gratzel 1995; Kavan *et al* 2000; Gratzel 2001). Nanocrystalline form of anatase TiO_2 is a promising electrode material for Li-ion batteries, owing to its good Li-storage capacity, cycling-stability and safety against overcharging (Huang *et al* 1995). Non-toxicity, environmental compatibility and low price are other practical advantages of TiO_2. As a catalyst and/or catalyst support, it is employed in the processes of photo degradation of chlorine hydrocarbons. Recently, efforts have been directed to obtain nanostructured TiO_2-based materials with a large specific surface area. The energy band structure becomes discrete for titanium dioxide of nanometer scale, and its photophysical, photochemical, and surface properties are quite different from those of the bulk ones due to the quantum size effect. TiO_2-based nanotubes have attracted wide attention owing to their potential for application in highly efficient photocatalysis (Adachi *et al* 2000), lithium ion batteries (Zhou *et al* 2003), photovoltaic cells (Poulios *et al* 1998; Adachi *et al* 2002; Uchida *et al* 2002) and environmental applications (Quan *et al* 2005).

Many approaches such as template-assisted method (Sander *et al* 2004), electrochemical anodic oxidation of pure titanium sheet (Gong *et al* 2001; Macak *et al* 2005), and methods involving chemical treatment of fine titania particles (Kasuga *et al* 1998; Du *et al* 2001) have been reported to fabricate TiO_2 nanotubes. There are respective advantages and limitations in each of the above-mentioned methods. However, technical problems may arise from the difficulties in achieving uniform inner diameter of titanium oxide nanotubes. In addition, oriented nanostructures of the TiO_2 nanotubes are often more desirable for applications in photovoltaic cells, sensing, catalysis and photocatalysis. Template-synthesis method has been used to prepare nanotubes or fibrils of electronically conductive polymers (Martin *et al* 1993), metals (Martin 1996), semiconductors (Lakshmi *et al* 1997) and carbon nanotubes (Maiyalagan and Viswanathan 2005). This method entails synthesis of a desired material within the pores of an alumina membrane, which has cylindrical pores with monodisperse diameters. The tubule of the desired material is obtained within each pore. This template approach is proving to be a versatile method for synthesizing nanomaterials because the aspect ratio of the nanostructures prepared via this method can be controlled.

In this article, we report the sol–gel template synthesis of ordered TiO_2 nanotube of uniform diameter using alumina membrane as a template. The composition and crystallinity of these structures were determined by transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman spectroscopy and powder X-ray diffraction (XRD). The optical absorption spectra of these ordered TiO_2 nanotube arrays have also been investigated.

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2. Experimental

2.1 *Materials*

All the chemicals used were of analytical grade. Titanium isopropoxide (Aldrich), 2-propanol (Merck) and Degussa P-25 titanium dioxide (Germany) were used as received (BET surface area, 50 m^2/g and anatase : rutile ratio, 80 : 20). Anodisc alumina membranes with a pore size of 200 nm and thickness of 60 μm were purchased from Whatman (catalog no. 6809-6022; Maidstone, UK).

2.2 *Synthesis of TiO_2 nanotubes*

Titanium isopropoxide (5 ml) was added to 25 ml of 2-propanol (mole ratio $[Ti^{4+}]/[2\text{-propanol}] = 1 : 20$). The solution was stirred for 3 h at room temperature (298 K). The alumina template membrane was dipped into this solution for 2 min. After removal from the solution, vacuum was applied to the bottom of the membrane until the entire volume of the solution was pulled through the membrane. The membrane was then air-dried for 60 min at 303 K and then placed in a furnace (in air) with a temperature ramp of 2°C min^{-1} to 873 K for 2 h. The temperature was then decreased at a ramp rate of 2°C min^{-1} to room temperature (303 K). The ordered TiO_2 nanotube arrays were obtained by dissolving the alumina template in 3 M aqueous NaOH for several minutes. TiO_2 nanotubes thus formed were then washed several times with distilled water to remove the dissolved anodic alumina membrane and remaining NaOH solution.

2.3 *Characterization methods*

The scanning electron micrographs were obtained after the removal of alumina template using a JEOL JSM-840 model, working at 15 keV. For transmission electron microscopic studies, the nanotubes dispersed in ethanol were placed on the copper grid and the images were obtained using Phillips 420 model, operating at 120 keV. The UV-*vis* absorption spectra were obtained on a Cary 5E spectrophotometer. The X-ray diffraction patterns were obtained on a Philips PW 1820 diffractometer with CuK_α (1·54178 Å) radiation. Micro-Raman scattering experiments were performed on a Bruker FRA106 FT-Raman at room temperature in a quasi-backscattering geometry with parallel polarization incident light. The excitation source used was an Argon ion laser operating at 514·5 nm with an output power of 20 mW.

3. Results and discussion

The scanning electron microscopic (SEM) image of the TiO_2 nanotubes obtained after dissolving the 200 nm alumina template membranes is shown in figure 1a. It can be seen that an ordered array of nanotubes with uniform diameter and length is formed. The individual TiO_2 nanotubes were characterized by TEM after dissolving the alumina membrane template. The open end and the hollow nature of the TiO_2 nanotubes have also been confirmed by transmission electron microscopic (TEM) image as shown in figure 1b. The TEM image shows that the single

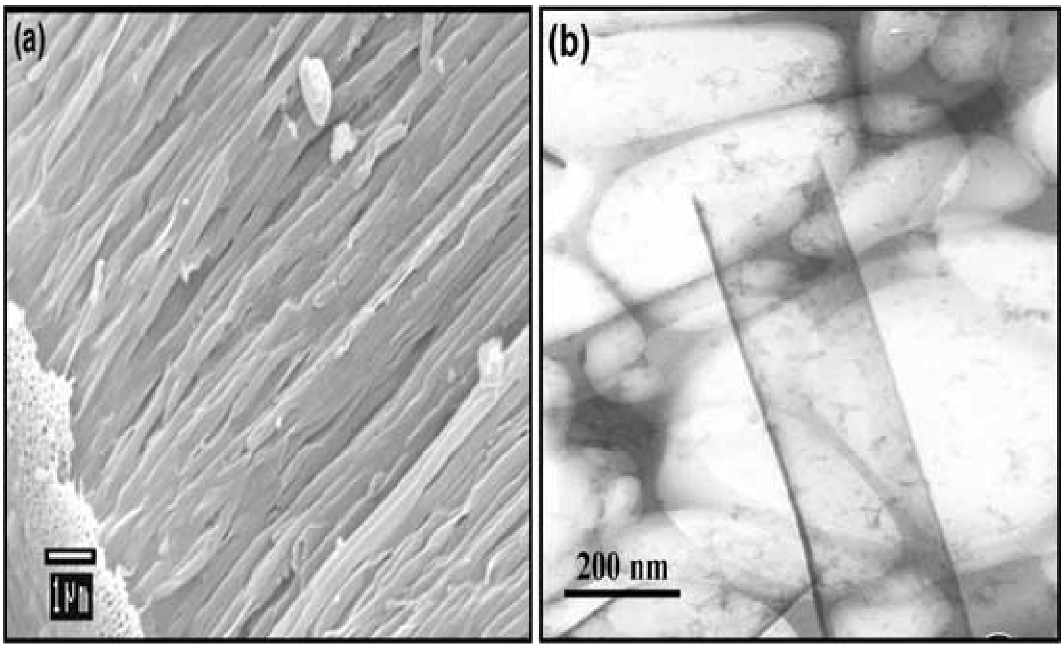

Figure 1. SEM image (**a**) and TEM image (**b**) of TiO_2 nanotubes obtained by sol–gel method calcined at 650°C for 2 h.

TiO_2 nanotube is straight and dense. The outer diameter of the nanotube is ca. 200 nm, retaining the size and near cylindrical shape of the pores of the aluminium oxide membrane. This indicates that the diameter of the nanotube synthesized is controlled by the pore size of aluminium oxide membrane. This result is in agreement with other reports on the sol–gel based template method (Lee *et al* 2004).

Figure 2 shows the UV-*vis* absorption spectrum of the anatase TiO_2 nanotube compared with that of the Degussa TiO_2. The spectral lines for both TiO_2 nanotubes and Degussa TiO_2 exhibit only one characteristic absorption band, which is assigned to the intrinsic transition from the valence band (VB) to the conduction band (CB). An absorbance below 370 nm was observed for the TiO_2 nanotubes, which is ascribed to bulk anatase TiO_2. Here the blue shift of absorption maximum with higher band energy of TiO_2 nanotubes compared with that of the bulk Degussa TiO_2 can be attributed to the quantum-size effect (Takagahara and Takeda 1992).

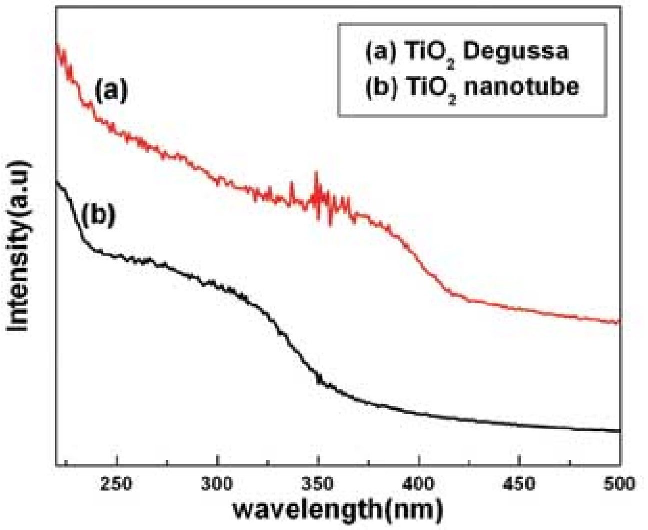

Figure 2. UV-*vis* absorption spectrum of (a) Degussa TiO_2 and (b) anatase TiO_2 nanotube.

The powder XRD was used to investigate the phase of TiO_2 nanotubes. The X-ray pattern of the TiO_2 nanotube arrays is shown in figure 3(b). The diffraction peaks of (101), (004), (200), (105) and (211) correspond to the anatase TiO_2 phase. The peak positions and their relative intensities are consistent with the standard powder diffraction pattern of anatase-TiO_2 and there is no preferred orientation. Figure 3 shows that the crystal phase of TiO_2 nanotubes is polycrystalline anatase structure whereas the Degussa P-25 contains a mixture of anatase and rutile phases. Further, no peaks for the amorphous alumina membrane were observed in the TiO_2 nanotubes.

The Raman spectra of fabricated anatase TiO_2 nanotubes and Degussa TiO_2 are shown in figure 4. The result of XRD analysis is supported by the Raman spectra of TiO_2 nanotubes as shown in figure 4(b). The vibration mode symmetries of the anatase are indicated. Raman peaks at 156·9, 206, 408·48, 529·54, 649·54 and 801 cm^{-1} were assigned to E_g, E_g, B_{1g}, A_{1g}, E_g and B_{1g}, respectively. The positions and intensities of the six Raman active modes correspond well with the anatase phase of TiO_2 (Bersani and Lottici 1998; Lei *et al* 2001). A weak overtone scattering (B_{1g}) at 801 cm^{-1} was observed in this study. Overtone can be found in both bulk Degussa TiO_2 and nanotube, but the intensity of overtone is very less in bulk Degussa TiO_2. This is due to the large intensity ratio of

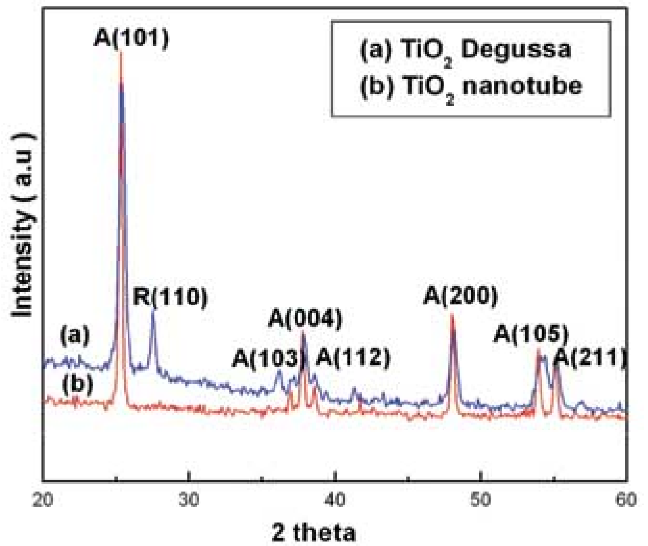

Figure 3. X-ray diffraction patterns of (a) Degussa TiO_2 as a reference and (b) TiO_2 nanotubes obtained by sol–gel method calcined at 650°C for 2 h anatase phase.

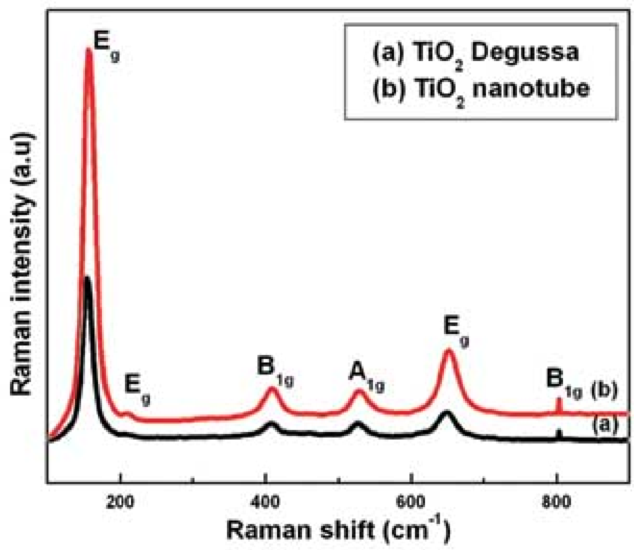

Figure 4. Raman spectrum of (a) Degussa TiO_2 and (b) fabricated anatase-TiO_2 nanotube (The vibration mode symmetries of the anatase are indicated).

fundamental peak to overtone one makes it difficult to be observed. While for nanotube, the decreasing ratio makes it easy to be observed. No significant broadening and shift of Raman spectra were found when one compared the obtained anatase-TiO_2 nanotube with that of the bulk Degussa TiO_2.

4. Conclusions

In summary, highly ordered TiO_2 nanotubes and nanofibrils have been synthesized by sol–gel chemical method within the pores of anodic alumina template membrane. The results of SEM and TEM show that the synthesized nanotubes have a uniform length, diameter and form a highly ordered array and the XRD measurements confirm the presence of polycrystalline anatase phase in the TiO_2 nanotubes. This method can be employed for obtaining large surface area TiO_2 for use in photocatalysis and as electrodes in solar cells.

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