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Crystal phase transition and properties of titanium oxide nanotube arrays prepared by anodization

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Abstract

Titanium oxide nanotube arrays were fabricated in mixed solutions of H_3PO_4 and HF. The diameters of the nanotube vary from 10 nm to more than 100 nm with the increase of applied voltages. The length of the nanotubes at first increases with the anodizing time and then reaches a maximum value due to a dynamic balance of titania formation and dissolution. Well-ordered nanotube arrays of titania with a length of up to 1.1 μm have been prepared via constant-voltage experiments. Stability of the nanotube structure and crystal phase transition were studied in different atmospheres. Experiments showed nanotube structures were stable up to 600 °C. Properties of titania nanotube arrays including photocatalytic degradation of methyl orange and their hydrophilic ability were also determined.

Keywords: Nanostructured materials; Oxide materials; Chemical synthesis; Nanofabrications

1. Introduction

Following the discovery of carbon nanotubes, one-dimensional inorganic nanomaterials (wires, rods and tubes) have attracted increasing research attention owing to their interesting properties and potential applications. Synthesis of nanomaterials has become on of the most active areas of research. Titanium dioxide is one of the most widely studied chemical substances because of its wide applications in catalytic, gas-sensing and corrosion-resistance materials [1–3]. Nanotubes of titania have been fabricated by many different methods such as hydrothermal treatment, template-assistant deposition, and electrospinning [4–7]. Anodic oxidation is also verified to be an effective method in fabrication of nanotube arrays of titania [8–11]. However, applications of these unique nanotube arrays are only beginning [12]. The studies on the crystallization and photocatalytic and hydrophilic properties of the nanotube arrays are very limited. We fabricated nanotube arrays of titania with length of up to 1.1 μm in H_3PO_4 and HF solution via simple constant-voltage experiments. Crystallization transformation of titania were studied in different atmospheres including air, vacuum, nitrogen and argon. Longer and well-crystallized nanotubes were prepared in our work. Moreover, anatase single crystal nanotubes were obtained under suitable annealing conditions. Properties of titania nanotubes arrays including photocatalytic degradation of methyl orange and hydrophilicity were determined for the first time.

2. Experimental

The high purity titanium foils (10 mm × 10 mm × 0.5 mm) used in this study were obtained from General Research Institute for Nonferrous Metals (Beijing, China). They were polished mechanically and washed in twice-distilled water and acetone by ultrasonic washing before use. Electrochemical experiments were carried out using a direct current voltage source (DH1722, Dahua Coop., Beijing, China). Titanium foils were used as anodic electrode while platinum (20 mm × 20 mm × 0.1 mm) was used as cathodic electrode. The distance between anodic and cathodic electrodes was 20 mm. Electrolytes in this process were 1 M H_3PO_4 and 0.5 wt% HF solution. All solutions were prepared from reagent grade chemicals and deionized water. Anodization experiments were carried out at room temperature. During the experiments, the solutions were stirred using a magnetic stirrer. In order to study the crystal phase transition, the nanotube samples were annealed at different temperatures from 300 °C to 700 °C in different atomospheres for 3 h with heating and cooling rates of 2 °C/min [13].

Raman spectra were obtained on a RM1000 Raman spectrometer (Renishaw PLC, UK). The microstructures were observed on field emission scanning electron microscopes (SEM, JSM-6301, JEOL Inc., Japan). The cross-section photographs were obtained by observing mechanically fractured samples. The specimens for transmission electron microscopes (TEM, JEOL-200CX) were prepared by scratching the nanotubes film into ethanol and observed on carbon-

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coated copper grid. Photocatalytic activities of the samples were measured by the decomposition of methyl orange. The samples of titania nanotube film were horizontally placed at the bottom of the testing cell containing 100 ml solution of 10 ppm methyl orange. The distance between the sample and the sterilamp was 7 cm. The UV light was provided by a 25 W UV lamp with radiation wavelength of 254 nm. Absorption spectra were measured by a UV–visible spectroscopy system (Thermo Spectronic, UK) with a wavelength range of 200–900 nm. Contact angle (CA) measurements were conducted with an OCA20 system at ambient temperature. The average CA value was obtained by measuring the same sample at different positions. Buffered solutions of different pH value were used to investigate the pH dependence of the hydrophilicity property.

3. Results and discussion

Fig. 1 shows the SEM images of titania nanotube arrays. Large area and uniform titania nanotubes were fabricated at 20 V in mixed solutions of 1 M H_3PO_4 and 0.5 wt% HF. The diameters of the nanotubes vary from 10 nm to more than 100 nm with increase of applied voltages. The length of the nanotubes increases from 250 nm at 30 min to 740 nm at 120 min. This is followed by a steady state with a length of 1.1 μm at 12 h.

Titanium dioxide minerals are found in three different crystallographic structures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Factors which influence the photocatalytic activity of titania include surface area, crystallinity, crystallite size and crystal structure. Typically, the photocatalytic activity of amorphous titania is negligible, and anatase shows higher photocatalytic activity than rutile [14]. It is generally accepted that anatase titania with high crystallinity and large specific surface area is desirable in photocatalytic reactions. In order to investigate the crystallization transformation, the nanotubes were annealed in air, vacuum, argon or nitrogen for 3 h, respectively, with heating and cooling rates of 2 °C/min. Results show that annealing atmosphere has little effect on titania crystallinity. In view of the costs and practical applications, further studies were conducted in air. X-ray diffraction patterns show that there is only anatase phase below 450 °C [13]. The rutile phase emerges near 480 °C. Above this temperature, the anatase phase transforms to rutile phase gradually. At 700 °C the titanium support becomes oxidized and transforms to crystalline titania. Raman spectra of anodized titanium annealed at 400 °C and 600 °C are given in Fig. 2. Transformation from anatase to rutile is obvious from 400 °C to 600 °C. Compared with that of the as-prepared nanotubes, the wall thickness of samples after annealing increases slightly. The nanotube structure was found to be stable after annealing for 3 h under 600 °C. However, at 700 °C, the nanotube structure was destroyed.

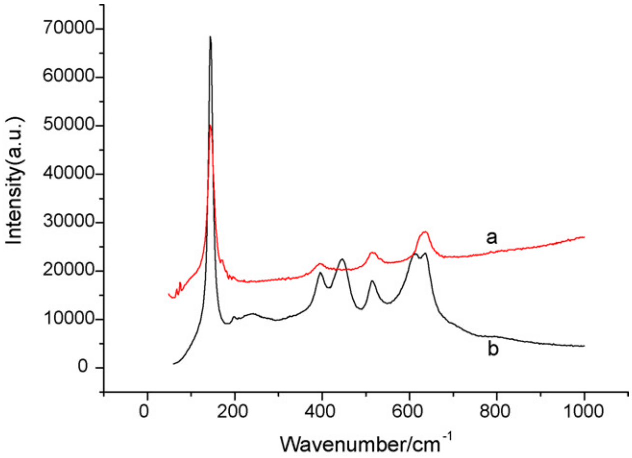

Fig. 2. Raman spectra of anodized titanium annealed at different temperatures. (a) 400 °C for 3 h and (b) 600 °C for 3 h.

Fig. 3 presents the TEM image and selected area diffraction pattern (SEAD) for the sample annealed at 450 °C. The diffraction spots demonstrated the single crystal nature of the nanotube and were indexed in accordance with anatase unit cell. Formation of single crystal can enhance material performance or improve industrial processing.

The photocatalytic activities of the titania nanotubes films were characterized by the degradation test of methyl orange. Titania films with the same surface area and the same thickness prepared by sol–gel method [15] were also studied at identical conditions to compare their photocatalytic effects with the titania nanotubes. The results are given in Fig. 4. As shown, the methyl orange have been effectively degraded by the films of titania nanotubes. Fig. 4c shows that the degradation of methyl orange still exists without titania films, which is probably due to homogeneous decomposition of methyl orange by UV irradiation. Meanwhile, it can also be seen that the photocatalytic activity of as-anodized nanotube films is higher than that of the films prepared by sol–gel method, which is because the nanotube films

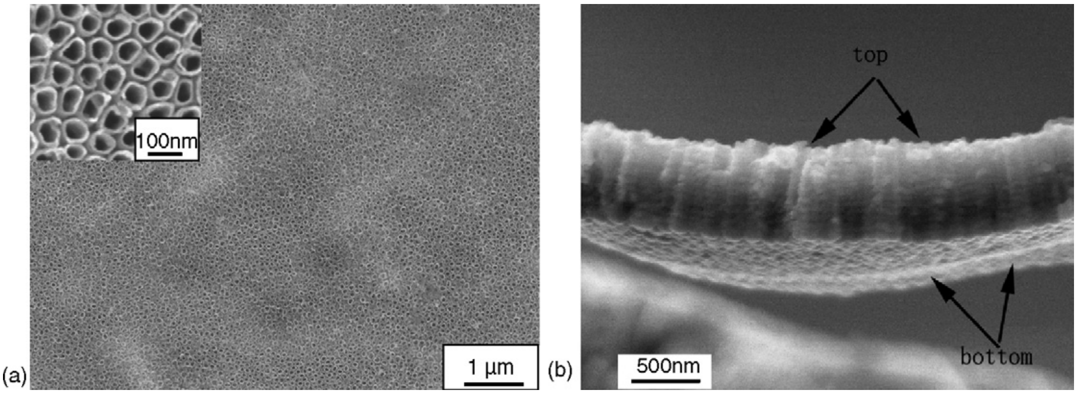

Fig. 1. SEM images of titania nanotube anodized in 1 M H_3PO_4 and 0.5 wt% HF at 20 V for 2 h. (a) Surface and (b) cross-section.

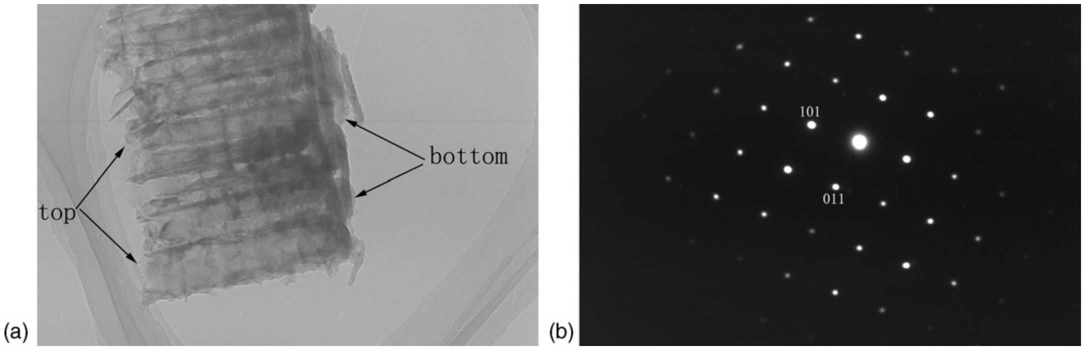

Fig. 3. TEM images and selected area diffraction pattern. (a) TEM images and (b) SEAD.

have larger specific surface area and result in a high quantum yield.

The wettability of materials is an important factor in numerous industrial and natural processes. Titania is a popular material, and its wettability is of significant practical interest. The contact angle is the simplest characteristic of the physical interaction between a liquid and a solid surface and is determined by the nature of the three contacting phases (solid, liquid and vapor). In our experiments, titania nanotube samples were subjected to two types of treatment: (a) thermal treatment at 450 °C and (b) irradiation with ultraviolet light. The original titanium metal and the as-anodized titania nanotube were also studied for comparison. The average contact angles at different pH value are given in Fig. 5. Compared with the original titanium metal, anodization decreases the average contact angle (Fig. 5b). It seems that the decrease of the contact angle is mainly due to the presence of porosities. The samples annealed at 450 °C for 3 h have smaller contact angle than the as-prepared film, which is due to the transformation of titania from amorphous to anatase structure (Fig. 5c). The decrease of the water contact angle after UV illumination is because ultraviolet light (254 nm) induces hydrophilicity on titania surfaces [16]. Hydrophilic activity is enhanced by UV radiation (Fig. 5d). The influence of UV light can be attributed to the well-known photocatalytic properties of TiO_2. Both the annealed nanotube films and the films after UV radiation show super-hydrophilic activities.

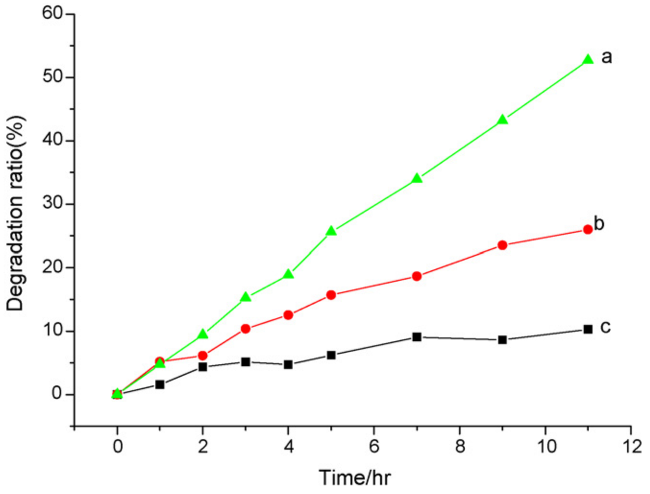

Fig. 4. Photocatalytic degradation of methyl orange. (a) Nanotubes, (b) films prepared by sol–gel method and (c) blank.

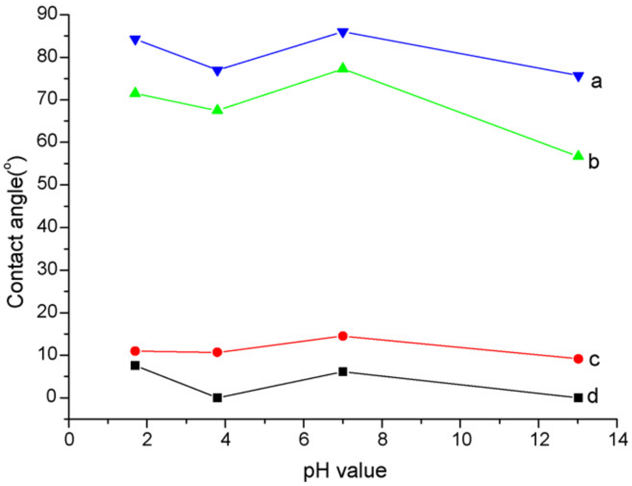

Fig. 5. Contact angle at diffrent pH value. (a) Titanium metal, (b) as-anodized nanotubes, (c) nanotube films annealed at 450 °C for 3 h and (d) nanotube films annealed at 450 °C and UV-irradiated for 3 h.

4. Conclusions

Large area and well-ordered titanium oxide nanotube arrays with diameters from 10 nm to 100 nm and length of up to 1.1 μm were formed in mixed solution of H_3PO_4 and HF. Stability of the nanotube structure and transition of crystal structure were studied in detail. Experiments show there is only anatase phase below the annealing temperature of 450 °C. The rutile phase emerges near 480 °C. The nanotube structure was stable up to 600 °C. Efficiency of the nanotube films for photocatalytic degradation are better than films prepared by sol–gel method due to larger specific surface area. The films of nanotube possess super-hydrophilic activities after thermal treatment below 450 °C and UV-irradiation.

Acknowledgments

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