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Fabrication of double-walled TiO_2 nanotubes with bamboo morphology via one-step alternating voltage anodization

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ABSTRACT

Ordered arrays of TiO_2 nanotubes with double-walled structures and bamboo-like morphologies were prepared by a one-step titanium foil anodic oxidation using a solution of NH_4F and ethylene glycol as electrolyte. The as-prepared titania nanotubes exhibit double-wall morphology even prior to the heat treatment process. Field emission-scanning electron microscopy (FE-SEM), X-ray powder diffractometry (XRD) and Raman spectroscopy were used to investigate the structure and morphology of the obtained TiO_2 nanotubes. The current-versus-time curves were recorded to monitor the anodization process. Structural investigations of the obtained nanotubes revealed the presence of pure anatase phase TiO_2 after annealing at 500 °C, as confirmed by XRD and Raman spectroscopy measurements. By optimizing the electrochemical anodization conditions, TiO_2 nanotubes with tunable structures can be reproducibly prepared.

1. Introduction

Titanium dioxide with one-dimensional nanostructures such as TiO_2 nanotube have attracted great interest in recent years due to their wide applications in photocatalysis [1], sensing [2], solar energy conversion [3], and biomedicine [4]. Sol-gel [5,6], hydrothermal [7], anodic oxidation [8,9] sonoelectrochemistry [10] and microwave [11] synthetic approaches have been used to fabricate highly oriented TiO_2 nanotubular structures of which electrochemical anodization of titanium is one of the most commonly adapted route. With the goal to prepare TiO_2 nanotube arrays with a large surface area that is almost defect free and has perfect alignment, the Grimes and Schmuki groups have conducted comprehensive studies on Ti foil anodization [9,12]. In their published work, the effect of the electrochemical sweep rate, the electrolyte concentration, applied voltage, oxidation time, as well as other important factors on the nanotube structure was investigated in detail.

Recently, Albu and co-workers reported the formation of double-walled TiO_2 nanotubes in an ethylene glycol based electrolyte [13]. In addition, they also found out that nanotubes with bamboo-like morphologies could be obtained if the anodization process was carried out under alternating-voltage (AV) conditions [14]. The dye sensitized solar cells fabricated from these titania nanotubes were then shown to exhibit a significantly higher efficiency than those based on smooth-walled nanotubes due to substantial increase in dye loading achieved through the formed stratified rings [15]. These novel TiO_2 nanotube structures attracted tremendous interest among researchers and their investigations have provided a wider perspective in the synthesis of highly oriented TiO_2 nanotube arrays [9,16].

In this paper, we present a one-step electrochemical anodization approach that results in the formation of a novel structure that combines both the bamboo- and double-wall TiO_2 nanotube features. In our synthetic approach, the double-walled morphology is formed even prior to the annealing of the titania nanotubes. The morphologies and structures of the obtained TiO_2 nanotube arrays were characterized in detail by FE-SEM, XRD and Raman spectroscopy. Moreover, the effect of the variation of electrochemical parameters on the resulting structure of the TiO_2 nanotube arrays was investigated.

2. Experimental section

2.1. Preparation

Ordered arrays of double-walled TiO_2 nanotubes with bamboo-like morphologies were successfully prepared by anodic oxidation of Ti foil in an NH_4F/ethylene glycol electrolyte solution. The adapted synthetic approach was based on the method described by Albu et al. with some modifications [14]. First, titanium foils (99.7% purity, 0.25 mm thick, Sigma-Aldrich) were degreased prior to the electrochemical anodization experiments through a three-step sonication cleaning process using acetone, 2-propanol, and methanol as cleaning solvents. The Ti foils were subsequently dried in nitrogen gas. Anodizations were performed in an electrolyte medium of 0.25 wt.% NH_4F/ethylene glycol solution using a platinum gauze cathode operated at room temperature. In contrast to the anodization approach previously reported by Albu et al. [14], hydrogen peroxide (i.e. 0.12 M H_2O_2) was not added to the

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NH_4F/ethylene glycol electrolyte solution used in the experiment. Additionally, the electrolyte was used as prepared and no pre-anodization step ("electrolyte aging") was conducted. For the anodization experiments, a Keithley 2400 sourcemeter controlled by a programmable voltage source was used. The voltages used were 120 V/80 V (upper level) and 40 V/20 V (lower level); the holding time of the two voltages utilized during nanotube growth was varied. The geometry of the electrochemical cell is schematically shown in Fig. 1(a). For comparison, highly ordered TiO_2 nanotubes with smooth surfaces have also been prepared under constant applied voltage of 40 V in the same electrolyte. After anodic oxidation, the samples were rinsed with de-ionized water, and annealed at 500 °C for 2 h to obtain the anatase crystalline phase. The heating and cooling rates were set at 2 °C min^{-1}.

2.2. Characterization

The morphology of the annealed TiO_2 nanotube arrays was characterized using a field emission-scanning electron microscope (S4500 Hitachi). Moreover, X-ray diffraction (XRD) patterns were obtained for the nanotube samples using a Philips PW 3710 powder X-ray diffractometer. The crystalline nature of both as-prepared and annealed TiO_2 nanotube arrays was further investigated on a Thermo Nexus Raman spectrometer equipped with a diode laser (972 nm wavelength).

3. Results and discussion

Shown in Fig. 1(b) are the FE-SEM images of a nanotube array grown under constant-voltage conditions at 40 V in an electrolyte consisting of 0.25 wt.% NH_4F in ethylene glycol. After 6 h of anodization, an ordered array of smooth-walled TiO_2 nanotubes with diameters of 100 nm and average length of 10 μm was prepared. In comparison, nanotubes with bamboo-like morphologies were prepared electrochemically by using alternating voltage conditions during the anodization of Ti foil in the same electrolyte [Fig. 1(c)]. In contrast to the single-walled titania nanobamboo structures that were previously reported by Albu et al., the obtained amorphous titania nanotubes exhibit double-wall morphology [Fig. 2(a)]. Similar to what previous studies have shown, the double-walled structure can be further tuned by heat treatment [13]. Under the experimental conditions utilized in the synthesis, which involves slight variations in the reagents and reaction time, the nanotube layer has a thickness of approximately 20 μm after 16 hour anodization. The inner pore and total diameter of the double-walled nanotubes are 50 and 150 nm, respectively.

A schematic representation of the nanotubes with combined double-walled and bamboo-like structure and the corresponding SEM images of heat treated titania nanotubes are shown in Fig. 2(b) and (c)–(d), respectively. It was confirmed from SEM studies that the double-wall and bamboo-structure is evident before and after heat treatment, which indicates that the sintering process does not drastically change the overall morphology of the synthesized nanotubes (Fig. 2). The image at higher magnification clearly shows double-walled stratified structures. By close examination of the prepared nanotubes the average thickness of the outer shell was found to have an inner pore diameter of about 70 nm and an outer shell thickness of 30 nm. The distance between two neighboring rings is about 440 nm at the top area of the array structure [Fig. 2(c)] and 200 nm at the bottom portion [Fig. 2(d)]. Other parameters such as the diameter of the inner pore and the total diameter of the nanotube, including the outer shell thickness remain relatively constant throughout the entire nanotube length. The current density during the Ti foil anodization under AV conditions was recorded and is shown in Fig. 2(e). It was found that the average current density stabilized at 10 mA cm^{-2} during the first 1 hour period. However, the current density decreased and stabilized at 8 mA cm^{-2} after 15 h of AV anodization. The gradually decreasing anodic current density determined lower kinetics for the longitudinal tube growth, which well explained the gradual increase in bamboo ring spacing.

Shown in Fig. 2(f) is the XRD pattern of the annealed TiO_2 nanotube arrays on Ti foil. Since the as-prepared titania films are amorphous [17], it requires heat-treatment to crystallize the titania samples to the anatase phase. When the TiO_2 nanotubes are sintered at 500 °C, the anatase phase is obtained [18,19]. The peaks at $2\theta = 25.4°$, 38.3°, 48.1°, and 55.2° correspond to the different lattice planes in anatase titania, whereas all the other peaks could be related to the Ti metal substrate. Shown in Fig. 2(g) are the Raman spectra taken for the titania nanotube samples before and after annealing. The O–Ti–O network peaks in the 400–700 cm^{-1} range are characteristic of anatase structures [20]. Directly after anodization, the obtained TiO_2 nanotube structure was amorphous (red dashed curve in Fig. 2 (f)). After thermal annealing, the double-walled stratified TiO_2 nanotube arrays displayed Raman signals at 398 cm^{-1}, 516 cm^{-1} and 640 cm^{-1}, which can be attributed to the phonon modes of the anatase phase [21,22].

The effect of alternating voltage and the holding time on the microstructure of the double-walled stratified TiO_2 nanotube arrays

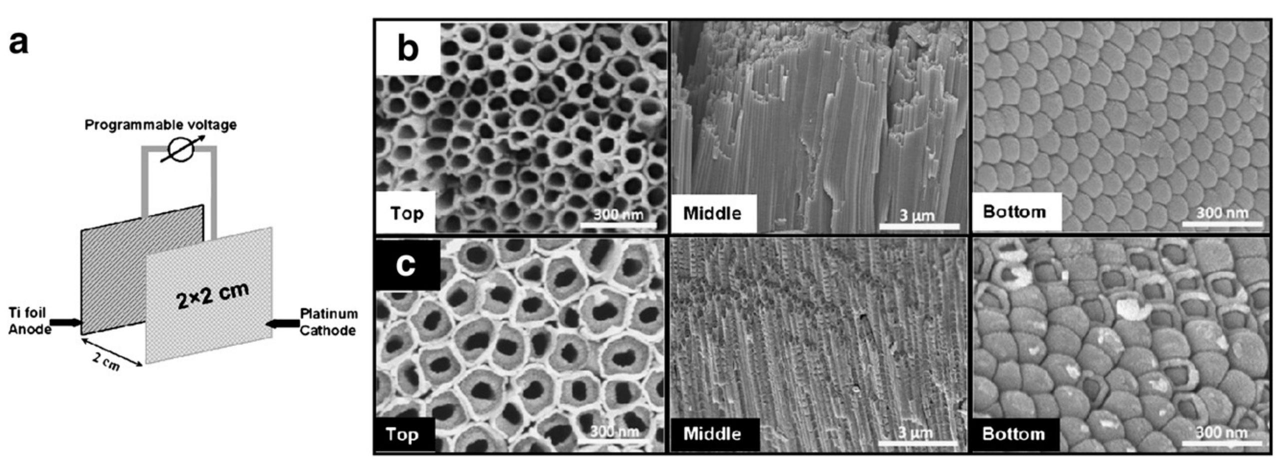

Fig. 1. (a) Schematic diagram of the electrochemical cell used in the anodization of the Ti metal foil. The distance between the anode and cathode is kept at 2 cm. The exposed surface area of the anode and cathode to the electrolyte is 2 cm^2 and 4 cm^2, respectively. SEM images of anodically grown nanotube arrays prepared under different conditions: (b) smooth-walled titania nanotubes, grown under constant-voltage conditions (40 V); (c) double-walled nanotubes with bamboo-like morphology, grown under alternating voltage conditions, with a sequence of 6 min at 40 V and 2 min at 120 V. The left most panels pertain to the top-views, the middle images show the side views, and the right most panels are bottom-views, respectively.

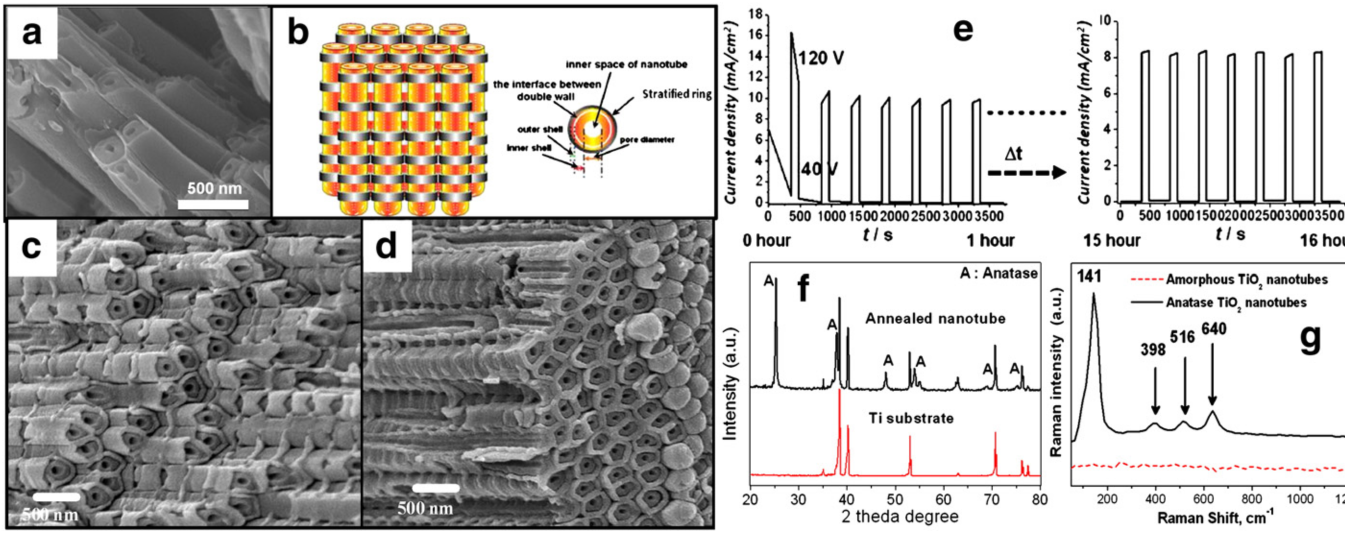

Fig. 2. (a) A close-up SEM image of the top-part of an amorphous titania nanotube sample showing double-walled structure prior to heat treatment. (b) A schematic representation of the double-walled nanotubes with bamboo-like morphology, showing the nanotube pore, and inner and outer shells with variable spacing, and corresponding higher magnification SEM images taken from the top part (c) and bottom part (d) of the nanotube arrays that have been sintered at 500 °C for 2 h. (e) Recorded current density during the anodization of Ti under AV condition. The left part shows the current versus time curves in the first hour; the right part between 15 and 16 h. (f) XRD patterns of the annealed titania nanotubes prepared on the surface of a Ti foil. (g) Raman spectra of amorphous (dashed curve) and anatase (solid curve) TiO_2 nanotube arrays. After annealing at 500 °C for 2 h, amorphous TiO_2 was transformed into the anatase phase.

were investigated. Fig. 3(a) shows the double-walled stratified TiO_2 nanotube arrays prepared under AV condition, with a sequence of 5 min at 20 V and 1 min at 80 V. One can see that the spacing between two neighboring rings is about 65 nm which is much less than that of tubes prepared under AV condition with a sequence of 6 min at 40 V and 2 min at 120 V shown in Fig. 2(c). On the other hand, when the AV conditions were kept at 40/120 V and the holding time changed to 12/2 min, the spacing of the structure increased noticeably. The distance between neighboring rings could reach 220 nm [Fig. 3(b)]. Based on the obtained results, one finds that the overall structure of the double-walled TiO_2 nanotube arrays with bamboo-like morphology can be controlled with the electrochemical parameters.

4. Conclusions

In summary, we have demonstrated that novel titania nanotubes with combined double-walled and bamboo-type structures can be prepared through a one-step anodization process. To the best of our knowledge, this is the first time to report this combined nanotubular titania structure. The obtained double-walled TiO_2 nanotubes have been characterized with SEM, XRD and Raman methods. Meanwhile, the corresponding current-versus-time curves were recorded to monitor the growth process. By optimizing the electrochemical conditions, tuning of the double-walled stratified structure such as spacing between bamboo rings, and the inner and outer diameter of the obtained nanotubes could be achieved. The amorphous structures have been transformed to anatase phase after the sintering process. With the presence of additional double-walled and bamboo-type structures compared to smooth nanotube arrays prepared under constant anodization, it is expected that these novel structures could have various application in the area of energy conversion research.

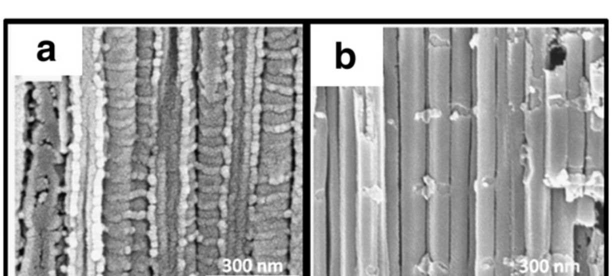

Fig. 3. SEM images of anodically grown nanotube layers under modified conditions. (a) Double-walled stratified nanotubes, grown under AV conditions, with a sequence of 5 min at 20 V and 1 min at 80 V for 6 h anodization; (b) with an AV sequence of 12 min at 40 V and 2 min at 120 V for 6 h anodization.

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