On seeding of the second layer in growth of double-layered TiO$_2$ nanotube arrays

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ABSTRACT

Double-layered architecture is capable of growing high-aspect-ratio TiO$_2$ nanotubes of small diameter to increase dye loading ability for dye-sensitized solar cells. The tube growth of the second layer is significantly affected by initial seeding sites. However, the seeding mechanism of the bottom nanotubes is still ambiguous. In this work, the seeding sites of the bottom nanotubes are tailored to be at upper tube bottoms, intertube gaps or random position on an interlayer by varying interim treatments. The results reveal that new tubes form preferentially at the location where the oxide layer is etched faster to a critical thickness for pore nucleation. In the presence of an interlayer (e.g., >10 nm), random seeding is induced. A model is thus created to interpret the relevant seeding behaviors. The mechanistic study is useful in tailoring the configuration of double-layered structure for growing high-aspect-ratio nanotubes.

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1. Introduction

Vertically-oriented TiO$_2$ nanotube arrays prepared by electrochemical anodization have been investigated extensively since reported [1]. The intriguing features of vertical alignment, high surface area, controllable geometry and facile fabrication enable versatile applications in photocatalysis [2], photocleavage of water [3], dye-sensitized solar cells (DSSCs) [4–6], and so on. In DSSCs based on anodic nanotubes, one of the major problems is the low dye loading ability which results in a low photocurrent and power conversion efficiency [7]. In our previous work [8], two-step anodization was used to grow high-aspect-ratio nanotubes of small diameter (~35 nm) in an attempt to increase the dye loading ability. However, the presence of an interface hinders the growth of bottom tubes by slowing down mass transport. It is expected that much longer tubes can be obtained in the absence of the interfacial blocking, where the lower tubes penetrate through the bottoms of the upper tube arrays. This provides a direct ion supply for the lower tube growth. Therefore, tailoring the interfacial structure of the double-layered nanotubes is essential in growing high-aspect-ratio tubes of small diameter.

To date, double-layered TiO$_2$ nanotubes can be fabricated with a two-step anodization by changing electrolyte [9–11], adjusting applied voltage [8,11–15], or varying bath temperature [16]. In particular, adjusting voltage is relatively easy and straightforward.

Two major structures have been reported so far with this method: branched and stacked structures. In branched nanotubes, one single large tube diverges into several small tubes, as obtained by stepping down voltage, e.g., from 120 V to 40 V [15], from one particular voltage to another one locating at a special region [13], or by a factor of $\frac{1}{\sqrt{n}}$ in the range of 85 V to 28 V [14]. In stacked structure, new tubes grow from the intertube gaps to form a second layer underneath, as attained by decreasing voltage from 20 V to 10 V at a rate of 0.1 V/s or repeated anodization at 20 V after interrupting the power supply for 1 min [12]. Obviously, the newly formed nanotubes can seed either from the tube bottoms of the first layer (branched structure) or from the intertube gaps (stacked structure) under similar conditions, i.e., stepping down voltage from high to low in the same electrolyte. It also seems that branched structures can be formed easily under high voltage (e.g., above 20 V) [13–15] while stacked structures are usually under low voltage (e.g., below 20 V) [8,12]. On the other hand, the high-aspect-ratio nanotubes of small diameter can only be achieved under low voltage, e.g., 15 V in our previous work [8]. This has raised another challenging issue: how to produce branched structure under a low voltage?

In this work, we alter the interim treatment conditions under a low voltage scheme (i.e., from 30 V to 15 V) to induce seeding of the second layer nanotubes at intertube gaps, tube bottoms, or random positions in search for the rules that govern the choice of the "seeding sites". The interim treatments include annealing or drying after the first anodization, interrupting power supply between two anodizations, decreasing the voltage abruptly or gradually at the end of the first anodization. The seeding mechanism of new tubes under the existing layer is investigated and interpreted. This

work provides a useful insight into the nanotube growth in double-layered structure.

2. Experimental

Prior to anodization, titanium foils (0.25 mm, 99.5% purity, Alfa Aesar) were degreased ultrasonically in acetone, ethanol and deionized (DI) water for 20 min each and dried by air stream. The electrolyte solution was ethylene glycol (extra pure, Merck) containing 0.3 wt.% ammonium fluoride (98+ %, Reagent, Sigma–Aldrich) and 2 vol.% DI water. All the anodizations were carried out at room temperature (~20 °C) in a two-electrode configuration with a titanium foil as the working electrode (back side unprotected [17]) and platinum gauze as the counter electrode. The distance between the two electrodes was 22 mm.

Double-layered TiO$_2$ nanotubes were prepared with a two-step anodization under the same voltage sequence, i.e., at 30 V in the 1st step and subsequently at 15 V in the 2nd step. Before the second anodization, five different interim treatments were applied separately: Scenario 1, annealing the first layer nanotubes at 450 °C for 3 h; Scenario 2, drying the first layer nanotubes in air for 24 h; Scenario 3, interrupting power supply for 5 min; Scenario 4, deceasing voltage abruptly from 30 V to 15 V; Scenario 5, reducing voltage gradually from 30 V to 15 V at a rate of 1.5 V/min. In all these scenarios, the first anodization was kept for 1 h to maintain the same thickness of the first layer. Double-layered nanotubes with a thicker first layer (i.e., at 30 V for 2 h or 3 h) were also fabricated for comparison purpose. The as-formed double-layered nanotubes were rinsed with DI water and dried in air.

Surface and cross-sectional morphologies of the nanotubes were characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-7600F). Phase composition was examined by glancing angle X-ray diffraction (GAXRD; PANalytical Empyrean, Cu Kα radiation). Chemical composition of the oxide was determined by X-ray photoelectron spectroscopy (XPS, KRATOS, AXIS ULTRA) using a monochromated Al Kα (1486.7 eV) X-ray source at a power of 150 W (15 kV × 10 mA). The binding energy of C 1s peak at 285.0 eV was used as the reference for all the spectra. A digital multimeter (Agilent, 34401A, 6½ Digit) was used to record the current transients.

3. Results and discussion

3.1. Seeding sites of the second layer

Different interim treatments result in different seeding sites of the second layer nanotubes, as detailed below from Scenario 1 to 5.

In Scenario 1, nanotubes of the first layer were annealed at 450 °C for 3 h prior to the second anodization. The as-grown double-layered structure is presented in Fig. 1(a). The larger tubes on the top belong to the first layer while the smaller tubes at the down-left and top-right corners are from the second layer. In between, a compact interlayer is present, originating from the thermal annealing. This interlayer is around 25 nm, as shown in Fig. 1(b). Fig. 1(c) displays the tube bottoms of the first layer and also the compact interlayer. Obviously, the tube bottoms are closed. Some remnant tube tops from the second layer are discernible from the interlayer surface. These demonstrate that small tubes of the second layer initiate randomly beneath the compact interlayer without any preferential seeding sites. Fig. 1(d) shows the relevant XRD patterns of the nanotubes at different stages. Annealing the first layer at 450 °C for 3 h transforms the nanotubes from amorphous
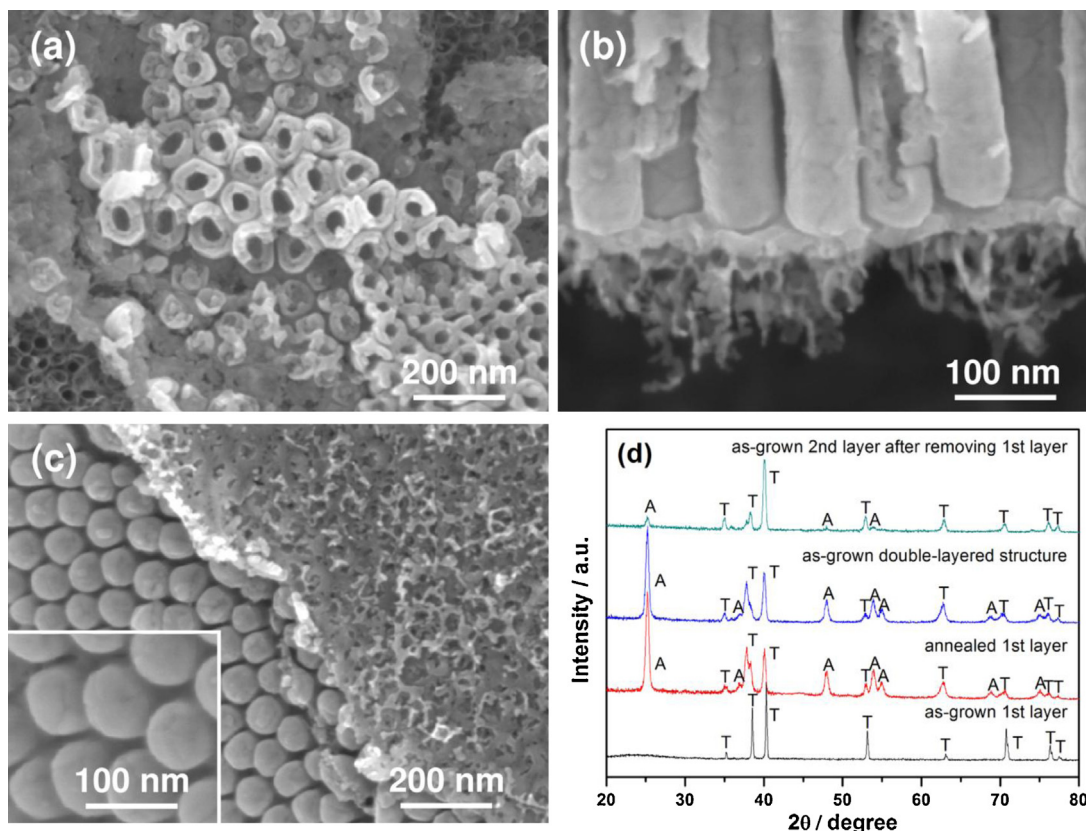

Fig. 1. FESEM images of double-layered TiO$_2$ nanotubes grown under Scenario 1 (anodized at 30 V for 1 h, annealed at 450 °C for 3 h, and then anodized at 15 V for 1 h): (a) top view; (b) interfacial region; (c) bottom view of the first layer and the compact interlayer. Inset is local magnification. (d) XRD patterns of the relevant nanotubes. A: anatase; T: titanium.