



Growth mechanism and morphology control of double-layer and bamboo-type TiO₂ nanotube arrays by anodic oxidation

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ABSTRACT

We have synthesized multilayer and bamboo-type TiO₂ nanotube arrays via alternating-voltage anodization steps in hydrous ethylene glycol (EG) containing NH₄F and investigated their growth mechanisms using experimental and theoretical approaches. Current transients are recorded to study real-time morphological evolution of anodic TiO₂ films during anodization at high and low voltages (V_{high} , V_{low}). Current changes after each voltage ramp to V_{high} are observed along with sequential origination of pits, pores and tubes in a compact barrier layer at the base of oxide film. Two anodization steps at V_{high} separated by one step at V_{low} with equal holding time yield double-layer smooth-walled TiO₂ nanotubes. However, repetition of this sequence does not produce nanotubes of more layers, but makes lower-layer nanotubes longer and induces ridges on their walls to form bamboo-type tubes. Formation mechanisms of double-layer TiO₂ consisting of smooth-walled or bamboo-type nanotubes are explored. A proper holding time of low-voltage anodization is required for ridge formation, but ridge spacing is determined by high-voltage anodization time. The ridge spacing increases linearly with the high-voltage anodization time, and can be theoretically calculated for lower-layer bamboo-type nanotubes formed in EG electrolytes with 5 vol% H₂O. Less water (2 vol%) in electrolyte results in larger ridge spacing, while more water (10–15 vol%) not only reduces the ridge spacing, but also causes instability during growth of multilayer TiO₂ nanotube arrays and eventually leads to formation of a disordered porous TiO₂ structure.

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1. Introduction

Self-assembled TiO₂ nanotube arrays formed by anodic oxidation of Ti were firstly reported in 2001, and soon after they have drawn tremendous attention due to their well-ordered structure, large surface area and broad applications [1]. In the past decade, anodic TiO₂ nanotubes have been widely used in dye-sensitized solar cells (DSSCs) [2,3], photo catalysis [4,5], gas sensing [6–8], water splitting [9,10], biomedical materials [11,12], and lithium-ion batteries (LIBs) [13,14]. One advantage of these TiO₂ nanotubes is their easy fabrication via anodic oxidation. The length, diameter and wall features of tubes can be adjusted by tuning synthesis conditions, such as anodization voltage or current (constant [15–17] or alternating [18,19]), electrolyte composition and anodization time.

More recently, there have been some research efforts to further increase the surface area of anodic TiO₂ nanotubes, such as fabrication of multilayer TiO₂ nanotube arrays with extra porous interlayers [20,21] or bamboo-type TiO₂ nanotubes with ridges on outer tube walls by anodizing Ti under alternating-voltage (AV)

conditions [18,19]. These new TiO₂ nanostructures provide larger surface area due to extra interfaces or rough walls, while retaining the vertically ordered one-dimensional nanostructure. In addition, they enable more light scattering when used in DSSCs, and provide more flexibility for dimension tuning and morphology engineering. For example, our group synthesized and explored growth mechanism of double-layer and sandwich-structured smooth-walled TiO₂ nanotube arrays via modified AV anodization conditions [22]. Double-layer TiO₂ nanotube arrays can also be prepared by using stepping-voltage anodization [23], or by anodizing Ti in alternating aqueous and organic electrolytes [24,25]. Regarding bamboo-type TiO₂ nanotube arrays, Zhang et al. [26] achieved ordered bamboo-type TiO₂ nanotubes in electrolytes with different viscosity and water content. Li et al. [27,28] employed AV anodization to synthesize ordered TiO₂ nanotubes with bamboo-shaped upper section and smooth-walled lower section. Schmuki and co-workers [29] integrated bamboo-type TiO₂ nanotube arrays into DSSCs; the new DSSCs yielded a photo conversion efficiency 55% higher than that of DSSCs based on smooth-walled nanotubes with identical film thickness of 8 μm, due to larger surface area of bamboo-type nanotubes for more dye loading and enhanced light scattering for more photon absorption. In addition, Xie et al. [30] synthesized bamboo-type TiO₂ nanotubes with various ridge densities on tube walls, which

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found applications in DSSCs for up to 49% higher photo conversion efficiencies than smooth-walled nanotubes. Consequently, much attention is focused on the bamboo-type TiO₂ nanotube due to its unique advantages and potential applications in photo catalysts, LIBs and DSSCs [31].

To date, there are only a few papers about bamboo-type TiO₂ nanotube arrays as summarized above. Syntheses in these reports involve electrolytes containing hazardous HF, high voltage pairs (120 V/40 V), and slow TiO₂ nanotube growth rate (e.g., 12 nm/min and 37 nm/min) [18,29]. Though formation process of bamboo-type TiO₂ nanotubes is briefly outlined [18], there is no report about fundamental explorations of growth mechanism underlying the synthesis and no clear understanding of factors that control morphological features such as ridge spacing on bamboo-type nanotubes. Ridge spacing provides a simple way for measuring electrochemical growth rate of anodic TiO₂ nanotubes. It should be noted that the growth rate cannot be calculated directly from the final tube length divided by total anodic time, since the length of nanotubes is decided by both the growth process of their roots towards substrate and the dissolution process of their tops into electrolyte. However, ridge spacing on bamboo-type TiO₂ nanotubes is the intact outcome from the electrochemical growth length within a given time period, and thus it can be used to calculate the electrochemical growth rate. On the other hand, the ridge spacing can be calculated from the growth rate of TiO₂ nanotubes or electrochemical etching rate of Ti, which has been briefly mentioned in some early reports [32,33].

In the present work, we report facile synthesis of double-layer and bamboo-type TiO₂ nanotube arrays using non-toxic electrolytes (ethylene glycol containing NH₄F and H₂O) and relatively lower voltage pairs (60/10 V) with faster tube growth rate (60–70 nm/min). We synthesize and explore growth mechanism of double-layer TiO₂ nanostructures composed of smooth-walled nanotubes in the upper layer and bamboo-type nanotubes in the lower layer. For comparison purposes, single-layer smooth-walled TiO₂ nanotubes and double-layer smooth-walled TiO₂ nanotubes are fabricated as well. Current measurements are used to study the real-time growth process and morphological evolution of these anodic TiO₂ nanostructures. Formation mechanism of double-layer TiO₂ nanotubes with or without a bamboo-type layer is proposed based on ion diffusion-controlled process inside tubes and inter-tube cavities. Fundamental factors that affect the morphology of bamboo-type TiO₂ nanotubes are studied with both experimental approaches and theoretical calculations and by manipulating water content in electrolyte and adjusting high or low voltage anodization time. To the best of our knowledge, so far there is no report about the effect of water content and low-voltage anodization duration on ridge formation.

2. Experimental

Ti foils (99.5 wt%) (10 mm × 10 mm × 0.25 mm) in this study were purchased from Alfa Aesar. Prior to any electrochemical treatment, Ti foils were degreased and rinsed by sonicating in ethanol and deionized water. A two-electrode cell with a Pt mesh as the counter electrode was assembled for electrochemical anodization. Electrolytes were anhydrous ethylene glycol (EG) with 0.3 wt% NH₄F and 2–15 vol% H₂O. All the solutions were prepared from reagent grade chemicals and deionized water. The voltage was supplied by a DC power supply with digital display (Model 1623A, PK Precision). A Data Acquisition/Data Logger Switch Unit (Agilent 34970A) was employed to record real-time anodic current. To prepare multilayer TiO₂ nanotubes, the anodization process consists of several alternating high and low-voltage anodization steps, as shown in Fig. 1. The voltage is first increased from zero to V_{high} with

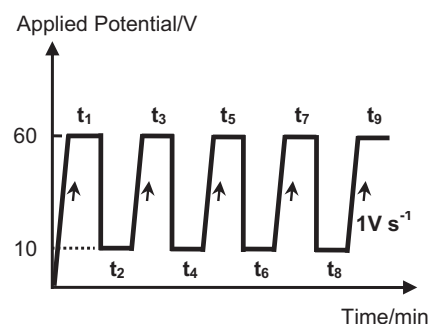


Fig. 1. Anodization sequence for the formation of double-layer and bamboo-type TiO₂ nanotube arrays.

a ramp rate of 1 V s⁻¹ and remains for a time t_1 , then drops to V_{low} and is kept at V_{low} for a time t_2 , followed by increasing to V_{high} with a rate of 1 V s⁻¹ and being kept at V_{high} for a time t_3 . Such voltage alteration is repeated for different TiO₂ nanotube structures. For comparison purpose, single-layer TiO₂ nanotubes were prepared by anodizing Ti sheets at 60 V for 20 min. All the experiments were carried out at room temperature. After anodization was completed, the samples were immediately rinsed in deionized water and dried in air. A FEI Quanta 3D FEG scanning electron microscope (SEM) was used to characterize the morphology of TiO₂ nanotube arrays formed on the front side of Ti foils.

3. Results and discussion

3.1. Morphology evolution of TiO₂ nanotube arrays

Table 1 summarizes various anodization conditions and morphological features of resultant TiO₂ nanotube arrays. It can be seen that the TiO₂ tubular structure evolves from single layer to double-layer structure of smooth nanotubes, and further to double-layer structure composed of smooth tubes above and bamboo-type tubes below, under constant voltage (CV) anodization and different alternating high and low-voltage anodization conditions. Clearly, number of anodizing steps and their holding time affects the quantity and spacing of bamboo ridges. The formation mechanism of these nanostructures and factors affecting their morphological features are discussed with both SEM observations and electrochemical analyses in the following sections.

Fig. 2 shows SEM images of TiO₂ nanotube arrays synthesized under CV or AV conditions in EG electrolytes containing 0.3 wt% NH₄F and 5 vol% H₂O. The direct anodization at 60 V leads to formation of single-layer TiO₂ nanotube arrays (CV-NT, Fig. 2a). The tubular structure is composed of hollow nanotubes (Fig. S1a) with a hemispherical closed bottom. These tubes have smooth walls with an average length of ~3.10 μm and their outer diameter is slightly increased from the top (120 nm) to bottom (152 nm).

Our previous results demonstrate that the 1:1 ratio of high-voltage anodization time (t_1) to low-voltage anodization time (t_2) is a critical parameter for synthesis of double-layer TiO₂ nanotube arrays by using three high/low-voltage anodization steps in EG electrolytes containing 0.3 wt% NH₄F and 5 vol% H₂O at room temperature [22]. This in-situ preparation of double-layer TiO₂ nanotubes is much more convenient than the two-step anodization method using alternating electrolytes with different compositions reported in literature [24,25]. Fig. 2b shows AV-NT1 composed of smooth-walled nanotubes in both the upper layer and lower layer. The upper layer reaches a thickness of ~1.6 μm where the nanotubes have an outer diameter of ~152 nm, and the lower layer is 1.7 μm thick and the outer tube diameter becomes a little larger (~172 nm). SEM image in Fig. S1b shows these upper-layer tubes

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