On seeding of the second layer in growth of double-layered TiO₂ nanotube arrays

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ABSTRACT

Double-layered architecture is capable of growing high-aspect-ratio TiO₂ 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 TiO₂ 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 TiO₂ 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 1 2 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 TiO₂ 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 TiO₂ 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.](image-url)
into anatase. The phase components keep unchanged after growing the double-layered structure. To examine the phase of the interlayer, the nanotubes of the first layer were removed intentionally (see Figure S1 of the Supporting Information). Fig. 1(d) reveals that the interlayer is of anatase structure, considering the amorphous nature of the as-grown tubes. The anatase interlayer originates from thermal oxidation of the titanium substrate beneath the upper nanotubes upon annealing [18]. No preferential seeding sites exist in the presence of thermal annealing, due to the formation of a thick anatase interlayer underneath the upper tubes.

In Scenario 2, prior to the second anodization, nanotubes of the first layer were dried in air for 24 h. The double-layered structure is shown in Fig. 2(a), with larger tubes stacking on top of the smaller ones. There exists a thin interlayer (≈10 nm) consisting of annular cells, as displayed in Fig. 2(b). Small tubes grow beneath the interlayer. Fig. 2(c) reveals that tube bottoms of the first layer are closed. The interlayer is thus developed from the pits left by the closed bottoms, as illustrated in Fig. 2(d). Each annular cell in the interlayer corresponds to one tube bottom of the first layer. Small holes form randomly on the interlayer which features a lotus-root-shaped structure. The small holes penetrate the interlayer and subsequently deepen into the substrate to form lower tubes, leaving a porous appearance of the interlayer. This discloses that the second layer tubes also seed randomly on a thin interlayer.

In Scenario 3, power supply was interrupted for 5 min between two anodizations. The stacked double-layered nanotubes are shown in Fig. 3(a). Similarly, small tubes grow underneath the larger ones. At the interface, small channels are formed on the upper tube walls, which are the remnant of lower tube tops, as revealed in the inset in Fig. 3(a). Fig. 3(b) displays the tube bottoms of the first layer, where the tube tops of the second layer initiate from intertube gaps and organize surrounding each tube bottom, as illustrated by dashed circles. This indicates that new tubes of the second layer seed from the intertube gaps of the first layer, in line with the previous report [12]. Additionally, a very thin interlayer exists beneath the tube bottoms of the first layer, as highlighted by the arrow in Fig. 3(c). Since the lower tubes of small diameter at intertube gaps can hardly occupy the total area of the titanium substrate, new tubes subsequently form to fill up the vacancy under each tube bottom, as depicted by the circles in Fig. 3(d). These circled regions match well with those shown in Fig. 3(b). Hence, nanotubes of the second layer seed preferentially at the intertube gaps in the presence of a very thin interlayer.

In Scenario 4, applied potential was reduced abruptly from 30 V to 15 V. The seeding sites are also from the intertube gaps, as shown in Fig. 4(a). The structure is similar to that in Scenario 3, while no obvious interlayer is observed under the current condition, as displayed in Fig. 4(b). The absence of the interlayer may explain why the two layers tend to separate under the same mechanical force when preparing FESEM samples, in contrast to Scenario 3. Besides, the seeding is not as uniform as that in Scenario 3, since some of the intertube gaps are untouched and the new tubes are not well-organized surrounding the tube bottoms. This suggests that subsequent tube formation is possible to fill up the vacancies under the untouched regions after seeding. The seeding sites also locate preferentially at the intertube gaps in the absence of a clear interlayer.

In Scenario 5, applied potential was gradually reduced from 30 V to 15 V at a rate of 1.5 V/min. Branched double-layered TiO2 nanotubes are achieved, as presented in Fig. 5(a). New tubes of the second layer penetrate through tube bottoms of the first layer. Fig. 5(b) shows one trunk tube diverging into two or three smaller
tubes. This is distinct from the above Scenarios where tube bottoms of the upper layer are closed. It is noteworthy that new tubes can also form at the intertube gaps while cease eventually due to spatial limitation by neighboring branched tubes, as indicated by the arrows in Fig. 5(a). Consequently, seeding of the second layer takes place by penetrating through the upper tube bottoms when decreasing the voltage gradually.

The above results reveal that the interfacial region between two nanotube layers is affected by interim treatments significantly. The interlayer plays an essential role in seeding of the second layer nanotubes. As the interlayer attenuates and disappears eventually, seeding evolves from random sites to intertube gaps, and finally to upper tube bottoms. The branched structure is thus realized under a low voltage (i.e., 15 V) in Scenario 5, which is preferred for growing long nanotubes of small diameter, owing to a direct ion pathway for lower tube growth.

3.2. Seeding mechanism of the second layer

To look into the seeding mechanism of the second layer, the growth process of titania nanotubes with conventional one-step anodization is briefed below. Growth of anodic nanotubes is mainly governed by the following two processes [19–21]: field-assisted oxidation of titanium metal at TiO₂/Ti interface and field-assisted dissolution of titanium oxide at TiO₂/electrolyte interface, as
illustrated in Fig. 6. The relevant chemical reactions during the processes are as follows [17,20,22]:

\[
\text{Ti} + 2\text{H}_2\text{O}/2\text{OH}^- \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e} \tag{1}
\]

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \tag{2}
\]

Formation of TiO₂ nanotubes mainly goes through three stages, as shown in the inset of Fig. 7(a). At the first stage (Stage I), a compact titanium oxide layer is formed by field-assisted oxidation via Reaction (1), resulting in an abrupt decrease of current. Subsequently (Stage II), the compact layer is etched by field-assisted dissolution through Reaction (2) to form soluble TiF₆²⁻ complex, giving rise to small pores. At the pore bottoms, electric field is concentrated due to thinner oxide. The field-assisted oxidation and dissolution accelerate each other at the bottoms [23], thus the current increases to a local maximum where the pore density becomes saturated. After the competitive selection process of the initial pores, steady growth of nanotubes is established (Stage III). Thereafter, the current drops gradually as the pores deepen. At the steady state, the oxidation and dissolution processes reach equilibrium and thereby the barrier layer (see Fig. 6) thickness at tube bottoms keeps constant. The thickness is closely related to the applied potential. In general, the larger the potential is, the thicker the barrier layer will be [23,24]. Accordingly, in this study the barrier layer grown at 30 V is much thicker than that at 15 V, yielding a larger critical thickness to maintain steady-state tube growth at 30 V.

When decreasing voltage from 30 V to 15 V suddenly (Scenarios 1–4), the electric field is nearly halved as it is determined by the potential drop across the barrier layer [21,25]. As a result, the field-assisted oxidation is slowed down or even may be terminated, since the electric field (at 15 V) is too weak to drive the ions passing through the thick barrier layer (formed at 30 V). In this case, nanotubes cannot grow further until the barrier layer thickness is reduced to the critical value by field-assisted dissolution process to enable ion transport at 15 V. Therefore, seeding of new tubes occurs at the sites where the oxide layer is dissolved faster to the critical thickness maintaining steady-state tube growth at 15 V. There are two different active locations suffering the dissolution: tube bottoms (Location A) and intertube gaps (Location B), as illustrated in Fig. 6. These two locations compete with each other and new pores form preferentially at the one where the oxide layer is etched faster to the critical thickness.

The current transients provide more insights into tube seeding during the second anodization, as presented in Fig. 7(b). Compared with one-step anodization at 15 V, the current density for two-step anodizations is much smaller since ions have to diffuse in the upper tubes and transport through the barrier layer. During this period, chemical dissolution at the active location A and B competes with each other for preferential pore nucleation, as will be discussed in detail below.

In addition, the as-formed anodic film is fluoride-containing titanium oxide, as evidenced in Fig. 8 which is in good agreement with our previous study [26]. The presence of the fluoride also plays an essential role in seeding of the second layer. The content of the incorporated fluorine is ~5 wt.% and can be removed upon thermal annealing [24,27]. Since the migration speed of F⁻ ions is twice the O²⁻ ions in the growing oxide under an electric field, fluoride is accumulated at the TiO₂/Ti interface to form a thin fluoride-rich layer [24,28], as illustrated in Fig. 6. The formation of intertube gaps is proposed to originate from chemical dissolution of the fluoride-rich layer between tubes [28,29]. Therefore, the oxide layer between intertube gaps (Location B) has a smaller thickness and higher fluoride concentration, in comparison to that at tube bottoms (Location A) [28,30].

For clarification, five interim treatments, i.e., annealing or drying the nanotubes, interrupting the power supply, reducing the voltage abruptly or gradually, are denoted as $T_A$, $T_D$, $T_I$, $T_{AR}$, and $T_{GR}$ below, respectively.
Fig. 7. Current transients during growth of double-layered TiO₂ nanotubes in a two-step anodization with different interim treatments: (a) first anodization at 30 V for 1 h and (b) second anodization at 15 V for 1 h in which a single-step anodization at 15 V is also shown for comparison. The inset is the current transient in the first 600 s at 30 V, which is divided into three stages.

\( T_A \) converts the nanotubes from amorphous to anatase (see Fig. 1(d)) and meanwhile produces a crystallized compact oxide layer underneath (see Fig. 1(b)). The crystallized titanium oxide has a good conductivity and small resistance in comparison to amorphous oxide [31]. This gives rise to a relatively high current density compared to the other interim treatments, as shown in Fig. 7(b). The crystallized compact interlayer is difficult to be dissolved. Hence, the chemical etching rates at tube bottoms (Location A) and intertube gaps (Location B) are both extremely slow. In this case, no preferential seeding sites are present. As a result, new tubes seed under the thick crystalline interlayer randomly, equivalent to a regrowth process, as illustrated in Schematic 1 of Table 1.

\( T_D \) facilitates the oxidation process of the second anodization by providing additional oxygen, especially at the intertube gaps. The as-grown oxide is enriched in Ti cations and deficient in oxygen anions, forming TiO\(_{2-x}\) oxide which has many oxygen vacancies.

Fig. 8. XPS spectra of the initial titanium oxide layer after anodization at 30 V for 1 min only: survey scan (a) and core levels of Ti2p (b); O1s (c); F1s (d).
Table 1
Interfacial structures and seeding sites of the second layer nanotubes under different interim treatments.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Schematics</th>
<th>Interfacial structures</th>
<th>Seeding sites</th>
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<tr>
<td>Scenario 1</td>
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<tr>
<td>Annealing the first layer</td>
<td>Thick interlayer</td>
<td>Random</td>
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<tr>
<td>Scenario 2</td>
<td></td>
<td>Thin interlayer</td>
<td>Random</td>
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<tr>
<td>Drying the first layer</td>
<td></td>
<td>Very thin interlayer</td>
<td>Intertube gaps</td>
</tr>
<tr>
<td>Scenario 3</td>
<td></td>
<td>No interlayer but interface</td>
<td>Intertube gaps</td>
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<tr>
<td>Interrupting power supply</td>
<td></td>
<td>Branched structure</td>
<td>Upper tube bottoms</td>
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<td>Scenario 4</td>
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<td>Reducing voltage abruptly</td>
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<td>Scenario 5</td>
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<td>Reducing voltage gradually</td>
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When drying the first layer in air, oxygen molecules are adsorbed on the surface of TiO$_{2-x}$ oxide and partially fill the oxygen vacancies [32–34]. The adsorbed oxygen promotes the initial oxidation of titanium by providing direct oxygen source rather than decomposing H$_2$O in the electrolyte, as evident from the highest current density at the very beginning of the second anodization in Fig. 7(b). As the original oxide layer at intertube gaps is much thinner than that at tube bottoms (see Fig. 6), a relatively thicker oxide is produced underneath the Location B upon the second anodization, as displayed in Fig. 2(b, d). In this case, a thin interlayer with a lotus-root-shaped structure is developed under tube bottoms (see Fig. 2(b, d)). Consequently, new tubes seed randomly underneath the thin interlayer, which is still a regrowth process, as presented in Schematic 2 of Table 1.
$T_1$ gradually attenuates the ion concentration gradient that established at 30 V. During the interruption of 5 min, the first layer nanotubes suffer from chemical attacking by $F^-$ and $H^+$ ions produced at 30 V, leading to thinning of the oxide [35]. Hence, at the moment 15 V is applied, current density is high and then abruptly decreases to a local-minimal value, as displayed in Fig. 7(b). This produces a very thin interlayer as revealed in Fig. 3(c). Even so, the oxide layer is still much thinner at Location B, as illustrated in Fig. 6. As a consequence, seeding of the new pores occurs preferentially at intertube gaps (see Fig. 3), in line with the previous report in which multi-layered zirconium titanate nanotubes were prepared by repeated anodization with 1 min interrupting intervals in between [12,23]. The double-layered structure is presented in Schematic 3 of Table 1.

$T_{\text{AR}}$ alters the ion concentration gradient when abruptly reducing the voltage from 30 V to 15 V [15]. At the initial stage, the oxidation is almost ceased under the low electric filed, and hence no obvious interlayer is formed. The seeding of tubes in the second anodization is similar to that under $T_1$, as illustrated in Schematic 4 of Table 1. New tubes preferentially seed at intertube gaps and subsequently beneath the tube bottom. The barrier layer at tube bottom (Location A) is too thick to be etched to the critical thickness during the pore nucleation, leading to the closed-ended tubes.

$T_{\text{GR}}$ gradually reduces the potential at a very slow rate (i.e., 1.5 V/min) so that ion concentration keeps almost unchanged during the early stage. Therefore, the chemical dissolution rate at tube bottoms (Location A) is approximately as high as that in the first anodization. The barrier layer at tube bottoms is thus thinned faster to a critical thickness, in view of the larger ionic flux as compared to the intertube gaps (Location B). New tubes grow steadily at tube bottoms to form branched structure, as shown in Schematic 5 of Table 1. Notably, with a thicker first layer, a much smaller decreasing rate is required to keep a relatively higher chemical dissolution rate at tube bottom rather than intertube gaps, as proved in Fig. 9. With a thicker first layer grown at 30 V for 2 h, reduction rate of 1.5 V/min leads to the seeding at both intertube gaps and tube bottoms, as shown in Fig. 9(a, b). A smaller reduction rate, i.e., 1.5 V/min from 30 V to 22.5 V and then 0.5 V/min from 22.5 V to 15 V, results in a preferential seeding at tube bottom, as presented in Fig. 9(c, d). In additional, for $T_1$ (interrupting power supply) and $T_{\text{AR}}$ (abrupt voltage reduction), new tubes still preferentially seed at the intertube gaps (see Figures S2 and S3 in the Supporting Information) even under a thicker first layer.

Therefore, seeding of new tubes originates from the sites where oxide layer is dissolved faster to a critical thickness. This depends on dissolution ability of the existing oxide layer, the interlayer thickness, electric field, ion concentration profile, etc. In a two-step anodization by stepping down voltage, the intrinsic factor affecting the structure of double-layered nanotubes is the chemical dissolution rate at the respective electrochemical active locations.

4. Conclusions

In growth of double-layered TiO$_2$ nanotube arrays, seeding sites of the second layer are tailored to initiate from intertube gaps, tube bottoms, and random positions of the upper tubes by controlling interim treatments. The mechanistic study reveals that the seeding takes place preferentially at the location where the oxide layer is etched quickly to a critical barrier layer thickness for pore formation in the second anodization. Gradual reduction of anodizing voltage results in fast etching of the oxide at tube bottoms, giving rise to a branched structure. In contrast, abrupt decrease of the voltage or interruption of the anodization results in fast etching at intertube gaps, therefore producing a stacked structure. Annealing
or drying after the first anodization produces a thick crystalline or thin amorphous interlayer respectively, leading to random seeding underneath the interlayer. The branched feature is a preferred double-layered structure capable of producing high-aspect-ratio TiO₂ nanotubes of small diameters, which is currently under investigation in our group.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2013.06.047.

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