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Letter

Rapid anodic oxidation of highly ordered TiO_2 nanotube arrays

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ABSTRACT

Highly ordered TiO_2 nanotube arrays prepared by anodic oxidation have attracted increasing research interests due to their promising applications in many scientific areas. To the best of our knowledge, a factor limiting the application of TiO_2 nanotube arrays was their long sustaining reaction time by anodic oxidation, usually lasting 6–12 h and even longer when synthesizing thicker nanotubular layers. In the present paper, we reported for the first time a facile but effective approach to accelerate the anodic formation of TiO_2 nanotube arrays by proper addition of sodium carbonate (Na_2CO_3) into the anodization electrolyte. We adopted the 0.3 M NH_4F + 0.03 M Na_2CO_3 + EG (ethylene glycol) + 3.0 vol.% H_2O electrolyte and the average growth rate of the nanotubes achieved in our experiments could be accelerated to 1100 nm/min. The possible mechanism of the rapid electrochemical process was also presented.

1. Introduction

Well aligned titania (TiO_2) nanotubes fabricated by electrochemical anodization of pure titanium foil have attracted tremendous attention because of their promising applications in various areas, including photocatalysis for hydrogen generation [1–3], photovoltaics [4–6], gas sensing [7,8], drug delivering [9,10], lithium anode materials [11] and so on. During the past decades, this anodization method for fabricating TiO_2 nanotubes has undergone four stages of development [12–14]. In 2001, self-organized and highly uniform TiO_2 nanotubes were firstly synthesized by Gong et al. [15]. An aqueous dilute HF solution was adopted as electrolyte and the Ti substrate was kept anodizing for several minutes under constant voltage. However, as a result of the high rate chemical dissolution of the already formed TiO_2 in the HF acid based electrolyte, maximum nanotube length in this first synthesis generation was approximately 500 nm, which could not meet the requirement of practical applications. TiO_2 nanotubes with length up to 7 μm and high aspect ratio, called the second stage, were then successfully prepared by altering pH value of the anodization electrolyte, which severely influenced the chemical dissolution rate of the formed TiO_2 layer [16–18]. The third generation of the TiO_2 nanotubes was prepared by anodization using organic electrolyte which resulted in the ultra long nanotubes with length more than 100 μm and even up to 1000 μm [19]. The results showed that the organic electrolyte could well restrict the movement of fluoride ions. And the fourth synthesis stage was achieved by non-fluoride-based anodization electrolyte [20,21]. To the best of our knowledge, during these four synthesis stages of TiO_2 nanotube arrays, the reaction time of anodization generally lasts 6–12 h, as in our previous work [22–24], and even longer when synthesizing thicker nanotubular layers [19,25]. To understand the slow growth of nanotubes during the anodization, the chemical dissolution related to the acidification of the electrolyte ought to be firstly taken into account [14,26]. Hereon we investigated how TiO_2 nanotube arrays can be achieved by rapid anodization with the growth rate up to 1100 nm/min. And this fast style formation of nanotubes was actualized by dominating the H^+ concentration at the pore tip and bottom with a certain amount of sodium carbonate (Na_2CO_3) additives into the anodization electrolyte.

In previous work the length of TiO_2 nanotubes has been recognized as the equilibria of the electrochemical formation of TiO_2 at the pore tip and the chemical dissolution of the formed TiO_2 by fluorides at the mouth of the tubes (nanotube arrays surface) in the F^--containing electrolyte [13–16,22–26], shown as Eqs. (1) and (2):

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (1)$$

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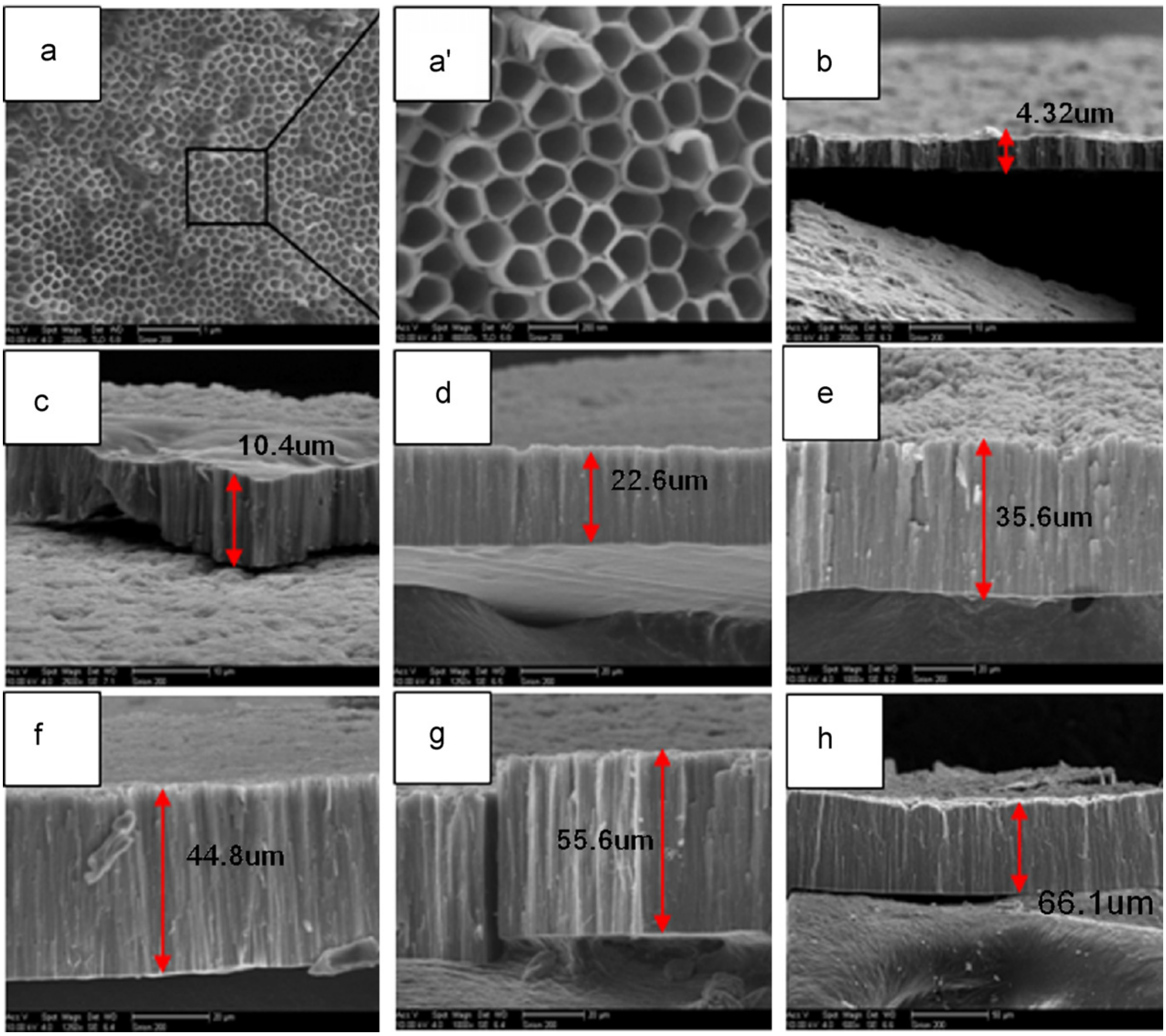

Fig. 1. The top FESEM view images of TiO_2 nanotubes with ×20,000 (a), ×80,000 (a′), and cross-sectional view of series of nanotube arrays with gradually changed nanotube layer thickness produced by series of anodization time periods. They are (b) 4.32 μm, 5 min; (c) 10.4 μm, 10 min; (d) 22.6 μm, 20 min; (e) 35.6 μm, 30 min; (f) 44.8 μm, 40 min; (g) 55.6 μm, 50 min; (h) 66.1 μm, 60 min.

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \qquad (2)$$

From the electrochemical formation of TiO_2 [Eq. (1)] and chemical dissolution [Eq. (2)] processes, we found that the H^+ played an important role. We hypothesized Eqs. (1) and (2) as separate dynamic chemical equilibrium during the anodization process. Whenever the H^+ concentration was lowered down by additive alkaline materials, the dynamic chemical balance of Eq. (1) would move forward and this would accelerate the formation of the oxide layer locating at the tip of TiO_2 nanotube. At the same time, the H^+ concentration reduction would make the equilibrium of Eq. (2) move backward, restraining the chemical dissolution of the already

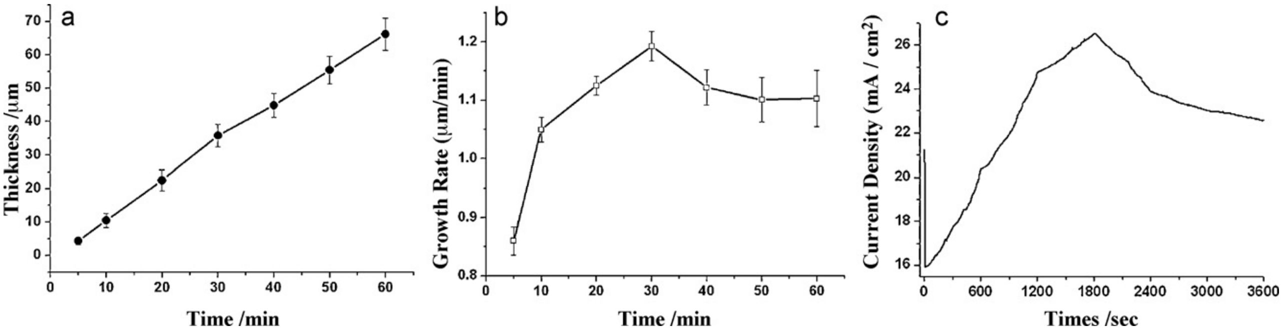

Fig. 2. (a) Thickness of the TiO_2 nanotube arrays with series of anodization times; (b) growth rate of the TiO_2 nanotubes; and (c) current density during the anodization process for 3600 s (60 min).

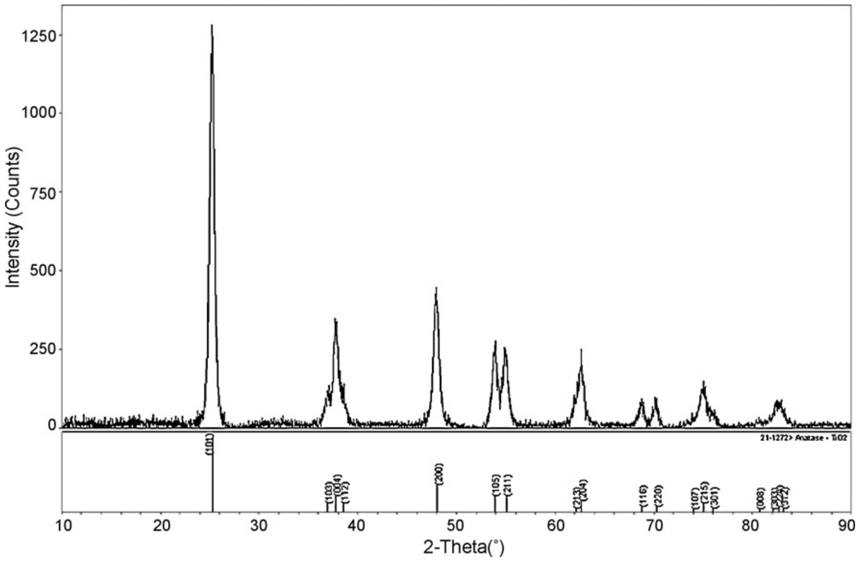

Fig. 3. XRD pattern of the TiO_2 nanotube arrays annealed at 400 °C for 2 h.

formed TiO_2 in the electrolyte. Hence, timely removal of the H^+ ions generated during the anodization process could hasten the growth of TiO_2 nanotube arrays.

2. Experimental details

In this experiment, Ti foils (0.1 mm thick foils with 99.6% purity) were firstly polished by various abrasive papers. After polishing, polished Ti substrates were degreased in acetone with ultrasonic treatment for 15 min, then chemical polished and pre-oxidized in 0.3 M NH_4F aqueous solution for 5 min. Finally, the pre-treated Ti were rinsed in ethanol and dried in oven. Titanium samples were anodized using the self-designed equipment consisting of a two-electrode configuration with a piece of highly pure graphite (50 mm × 30 mm × 5 mm) as cathode. All the experiments were carried out at room temperature about 295 K. Electrolytes were 0.3 M NH_4F + 0.03 M Na_2CO_3 + 3 vol% H_2O in ethylene glycol and all the chemicals are AR grade. The anodization process was carried on under constant direct current potential 80 V, which was achieved by a ramp from open-circuit potential to 80 V with a sweep rate of 0.5 V/s. Series of the anodization time were firstly 5, 10, 20, 30, 40, and 50 min and finally 60 min.

After the electrochemical treatment, the samples were rinsed in distilled water and dried in the oven. Samples were also annealed in order to obtain the crystalline phases of TiO_2. Field-emission scanning electron microscope (FESEM, FEI Sirion 200) was employed for the structural and morphological characterization of the TiO_2 nanotube arrays. The TiO_2 nanotube layers were taken off the titanium substrates by mechanical bending and then put directly on the electric adhesive tape in order to gain the thickness information from the cross-sectional FESEM characterization. X-ray diffraction analysis (XRD, Rigaku D/Max-2500VL/PC, CuKα) was performed for crystal phase identification.

3. Results and discussion

Fig. 1 shows the FESEM images of the as-prepared TiO_2 nanotubes with the top view ×20,000, ×80,000 magnifications and cross-sectional characteristics. From the FESEM images, it is evident that the self-organized highly ordered nanotube arrays consist of uniform pore arrays with pore inner diameter approximately 110 nm. Furthermore, only from the cross-sectional images of samples with series of anodization time can the thickness information of the porous arrays be obtained (shown in Fig. 2(a)). Then the average growth rate during the whole 60 min reaction process could be calculated (shown in Fig. 2(b)).

It can also be clearly seen from Fig. 2(b) that at the beginning of the anodization the growth rate of nanotubes was slow and then increased to the maximum value. The maximum growth rate 1186 nm/min occurred during the reaction time period from 30 to 40 min. Then the growth rate began to drop till the experiment ended. The average growth rate of the whole rapid anodization process was 1100 nm/min, much faster than that in our previous work [22–24]. We found the current density *vs* time curve of our anodization experiment was dissimilar to other curves during their anodic reactions [18,27]. However, the tendency of the current density consisted with the movement of the nanotube growth rate. Finally, we annealed the TiO_2 nanotube arrays at 400 °C for 2 h and the XRD patterns (Fig. 3) showed anatase phase only.

During the anodization in the electrolyte, as shown in Fig. 4(a), a great deal of bubbles could be observed at the graphite cathode. At the same time a few bubbles with little smaller diameter appeared at the Ti foil anode. This phenomenon was probably consistent with Eq. (3), shown as.

$$CO_3{}^{2-} + 2H^+ \rightarrow H_2O + CO_2\uparrow \tag{3}$$

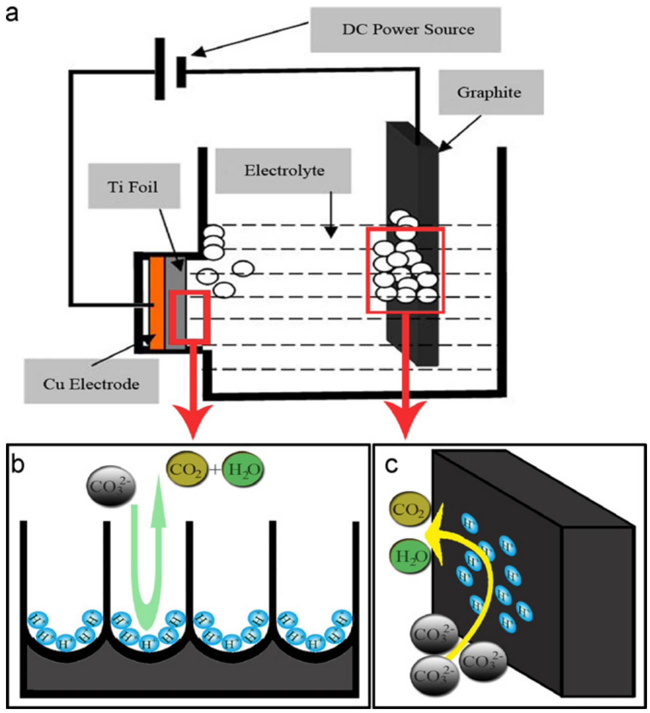

Fig. 4. (a) Experimental equipment of accelerated anodic oxidation of TiO_2 nanotube arrays. (b) and (c) Schematic representation of the acceleration mechanisms.

When the anodization was conducted in the electrolyte containing Na_2CO_3, the H^+ generated during the Ti oxidation at the oxide layer/Ti substrate would move quickly towards the graphite cathode under the assistance of the electric field. Hence, the chemical reaction between CO_3^{2-} and H^+ mainly occurred around the cathode (exhibiting as the bubbles) and only a small part of H^+ reacted with CO_3^{2-} in the vicinity of anode and elsewhere. The parallel experiment was taken in the electrolyte without Na_2CO_3 and almost no bubbles could be observed anywhere. Fig. 4(b) and (c) showed the mechanisms of the Na_2CO_3 addition accelerating the formation of TiO_2 nanotube arrays. Timely elimination of H^+ by the CO_3^{2-} (forming the gas CO_2) resulted in the drastic reduction of the H^+ concentration situated at the interface of oxide layer/Ti substrate[26] and would in turn accelerate the Ti substrate oxidation, causing the forward movement of the interface into the substrate. Therefore, TiO_2 nanotube arrays could grow with a straightforward rate.

4. Conclusions

In summary, the normal anodization method for the synthesis of TiO_2 nanotube arrays was exhausted with the local acidification at the pore tips during the entire reaction process as well as the high-speed of fluoride chemical dissolution of the formed TiO_2 nanotubes assisted by the H^+. These two factors resulted in the sluggish formation of TiO_2 nanotubes. We tackled these two obstacles by using the alkaline additive Na_2CO_3 into the NH_4F/ethylene glycol electrolyte and the experiment achievement proved our hypothesis. This phenomenon was mainly due to the opportune suppression of the local H^+ concentration fluctuation, resulted from the spontaneous ion reaction between the H^+ and CO_3^{2-}.

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