A facile route to accelerate the formation of TiO$_2$ nanotube arrays

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Abstract. Highly ordered TiO$_2$ nanotube arrays fabricated by electrochemical anodization of titanium have attracted significant attention due to their splendid promising applications. One of the factors 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 this paper, we reported for the first time a facile and effective route to accelerate the formation of TiO$_2$ nanotube arrays by proper proportional addition of sodium carbonate(Na$_2$CO$_3$) into the anodization electrolyte. In our experiments, we adopted the 0.3 wt% NH$_4$F + EG (ethylene glycol) + 3.0 vol% H$_2$O electrolyte and we added Na$_2$CO$_3$ with the proportion n(NH$_4$F) : n(Na$_2$CO$_3$) = 1:1, 2:1, 3:1, 4:1 and 5:1. The field-emission scanning electron microscope (FESEM) characterization results suggested the Na$_2$CO$_3$ additives accelerated the growth rate of the TiO$_2$ nanotubes with the quickest growth rate 1100 nm/min when n(NH$_4$F) : n(Na$_2$CO$_3$) = 2:1. Finally, we investigated the mechanism of the Na$_2$CO$_3$ additives accelerating the growth rate of the TiO$_2$ nanotubes. It was believed that the hydrolyzation of the Na$_2$CO$_3$ additives in the electrolytes accelerated the formation of the TiO$_2$ nanotubes and at the same time restrained the chemical dissolution of the formed TiO$_2$ nanotubes.

1. Introduction

Nanostructured TiO$_2$ is one of the most widely studied materials due to its unique and excellent properties in optics, electronics, photochemistry and biology, as well as its

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applications in photovoltaic cells, photocatalysis, and sensors [1-4]. Among the various forms of nanostructural titania, TiO$_2$ nanotube had attracted increasing interest because of its highly ordered structure and the convenient controlling of the tube size. And since 2001[5], highly ordered TiO$_2$ nanotube arrays fabricated by electrochemical anodization of pure titanium foil had became the research focus due to their promising application in areas ranging from photocatalysis for hydrogen generation [6], photovoltaics [7, 8], gas sensing [9] to drug delivering [10, 11]. To the best of our knowledge, during the electrochemical synthesis of TiO$_2$ nanotube arrays, the reaction time of anodization generally lasts 6-12 hours, as in our previous work [12-14], and even longer when synthesizing thicker nanotubular layers [15, 16]. To explain 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 [17, 18]. Hence, in the present work we demonstrate how TiO$_2$ nanotube arrays can be achieved by rapid anodization with the growth rate up to 1100 nm per minute. And this outbreaking style formation of nanotubes is actualized by dominating the H$^+$ concentration at the pore tip and bottom with a certain amount of sodium carbonate (Na$_2$CO$_3$) additives into the anodization electrolyte.

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 minutes, then chemical polished and pre-oxidized in 0.1 M NH$_4$F aqueous solution for 5 minutes. Finally, the pre-treated Ti were rinsed in ethanol and dried in oven. Titanium samples were anodized using the equipment consisting of a two-electrode configuration with a piece of highly pure graphite (50 × 30 × 5 mm) as cathode. All the experiments were carried out at room temperature about 295K. Electrolytes were 0.3M NH$_4$F + x M Na$_2$CO$_3$ + 3.0 vol % H$_2$O in ethylene glycol and all the chemicals are AR grade. We controlled the value x with the proportion n(NH$_4$F) : n(Na$_2$CO$_3$) = 1:1, 2:1, 3:1, 4:1 and 5:1. The anodization treatment processed under constant direct current potential 80V, which was achieved by a ramp from open-circuit potential to 80V with a sweep rate of 0.5V/s. The anodization time period adopted in this experiment was 60 minutes.

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, Cu K$_\alpha$) 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 ×20000 a), ×80000 a’) magnifications and cross-sectional characteristic. From the FESEM images, it is evident that the self-organized highly ordered nanotube arrays consist of uniform pore arrays with pore 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 (Fig.1 b)-f) and Fig. 2). It can be clearly seen from Fig. 2 that the thickness of the as-prepared TiO$_2$ nanotube layers changed gradually with the addition of
Na₂CO₃ into the anodization electrolytes and the maximum thickness was achieved when the Na₂CO₃ additives concentration was 0.15 M \( (n(\text{NH}_4\text{F}) : n(\text{Na}_2\text{CO}_3) = 2:1) \). The average growth rate of the whole rapid anodization process was 1100 nm per minute, much quicker than that in our previous work [12-14]. Finally, we annealed the TiO₂ nanotube arrays at 300°C for 2h and the XRD patterns shown us anatase phase only (Fig. 3).

Fig. 1 The top FESEM view images of TiO₂ nanotubes with ×20000 a), ×80000 a’), and cross-sectional view of nanotubes arrays with gradually changed nanotube layers thickness produced in series of anodization electrolytes for 60 min time periods. The electrolytes and the thickness of the nanotube layers are b) 1:1, 38.7μm; c) 2:1, 66.1μm; d) 3:1, 51.1μm; e) 4:1, 37.8μm; f) 5:1, 25.2μm.

Fig. 2 Thickness of TiO₂ nanotube arrays in series of anodization electrolytes for 60 min
In previous work the length of TiO$_2$ nanotubes has been recognized as the equilibrium 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 [1, 17, 18], shown as Eq. (1) and (2):

$$\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1)$$

$$\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \quad (2)$$

From the TiO$_2$ electrochemical formation [Eq. (1)] and chemical dissolution [Eq. (2)] process, we discerned that the H$^+$ played an egregious role. We hypothesized Eq. (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 which would accelerate the formation of the oxide layer locating at the tip of TiO$_2$ nanotube. Contemporarily, the H$^+$ concentration reduction would promote the equilibrium of Eq. (2) to move backward, restraining the chemical dissolution of formed TiO$_2$ in the electrolyte. Hence, timely removal of the H$^+$ generated during the anodization process would expedite the fabrication of TiO$_2$ nanotube arrays.

Fig. 3 XRD pattern of the TiO$_2$ nanotube arrays annealed at 300°C for 2h.

Fig. 4 Schematic representation of the acceleration mechanism
During the anodization in the electrolyte, a great deal of bubbles could be observed at the graphite cathode. And at the same time a few bubbles with little smaller diameters appeared at the Ti foil anode. We convinced this phenomenon consistent with the Eq. (3), shown as,

$$\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2 \uparrow$$ (3)

When the anodization was conducted in the electrolyte containing Na$_2$CO$_3$, 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$_2$CO$_3$ and almost no bubbles could be observed anywhere. Fig. 4 showed the mechanisms of the Na$_2$CO$_3$ 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 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, in this paper we report a facile route to accelerate the formation of the TiO$_2$ nanotube arrays by proper proportional addition of Na$_2$CO$_3$ into the anodization electrolyte. And the maximum growth rate achieved in our experiment was 1100nm/min. Finally, the accelerating mechanisms were discussed and it was believed that the hydrolyzation of the Na$_2$CO$_3$ additives in the electrolytes accelerated the formation of the TiO$_2$ nanotubes.

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