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Investigation of surface morphologies of TiO_2 nanotube arrays by anodization in ethylene glycol electrolytes

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This work describes the morphological-controlled growth of the TiO_2 nanotube arrays by anodization of Ti foils in the ethylene glycol electrolytes containing 0.5 wt % NH_4F and amount of water under a constant anodization voltage. FESEM was used to investigate the structure and morphology of the TiO_2 nanotube arrays. It was found that the morphology is much different obtained in different electrolytes component by manipulating electrochemical conditions. The results of characterization indicate that the morphology with a bundled “nanograss” or nanowires appearance at the tube top depends on anodization voltage, electrolyte component and electrolyte viscosity. In addition, the formation details for these morphological features and the transformation relations among them were studied. In the present work, we demonstrate a simple approach how to prevent this effect.

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1. Introduction

Titanium dioxide (TiO_2) is known to be one of the best catalysts due to their unique structure, remarkable properties and wide-range potential applications in photocatalysis[1-2], photoelectrocatalytis[3], photovoltaic cell[4], water splitting[5], degradation of organic pollutants biocompatible materials[6-7]. In recent years, a increasing attention has been given to fabricate highly ordered TiO_2 nanotube arrays, because it is expected that an remarkably enhanced photocatalytic activity can be achieved in comparison with other existence forms of TiO_2, which is closely related to the higher specific surface area and superior physical activity of TiO_2 nanotube arrays[8-9].

It is well-known that TiO_2 has several advantages as described above, it has two critical limitations: its relatively low efficiency of light utilization due to its wide band gap (3.0~3.2 eV) and its poor charge-transfer properties[10]. To overcome this problem, considerable efforts have been taken to narrow the band gap. Such as doping with different types of transition metal cations[11], surface modification with noble metal[12], as well as doping with nonmetal anions[13], external dye sensitization[14] and coupling with a narrow band gap semiconductor[15] have been explored in an effort to increase the visible light absorption or suppress the recombination of photo-generated carries. Therefore, the surface morphologies of TiO_2 nanotube arrays were played a great role for modification of TiO_2 nanotube arrays and its effect on photocatalytic properties.

In this paper, we introduce a process modification providing means for the fabrication of without any surface debris on the TiO_2 nanotube arrays. The formation details for these morphological features and the transformation relations among them were studied. It was found that the morphologies of the surface debris can be tailored accurately by controlling the anodization voltage, water content in organic solution and electrolytes pH. We expect that altering the surface of the nanotube arrays can be used to modify their physical and chemical properties.

2. Experimental

2.1 Preparation of TiO_2 nanotube arrays

The chemicals were of analytical grade and used without further purification. All the solutions were prepared with distilled water. The titanium foils (0.5 mm thick, 99.6% purity, from Tianjin Gerui, China) with a size of 10 mm×20 mm were used as starting materials. Prior to any electrochemical treatment, the titanium foil was mechanically polished with different abrasive papers and cleaned in an ultrasonic bath containing cold distilled water for 15min, then chemically etched in strong acidic mixture solution of HF and HNO_3 ($HF:HNO_3:H_2O$ = 1:4:5 in volume) for 30 s to form a fresh smooth surface. The last step of pretreatment was rinsing the solution with acetone, absolute alcohol and distilled water in turn. The substrate was then dried in air at room temperature. Anodization was performed in a two-electrode configuration with one titanium foil as the working electrode and the other foil with the same area as the counter electrode under constant potential at room temperature. The interval between working electrode and counter electrode was about 3 cm. TiO_2 nonotube arrays were formed in an electrolyte comprised of 0.5wt % NH_4F

and 1~5 wt % H_2O in ethylene glycol at constant potential supplied by a DC power (YJ32-1, Shanghai). The pH of the electrolyte was adjusted at 4.5 by a small amount of phosphoric acid during the entire process. Somewhat electrolyte without the addition of phosphoric acid has a pH of around 6.5. The as-prepared electrodes immersed into absolute alcohol bath during overnight and ultrasonically cleaned in absolute alcohol for 30 s to remove any surface debris, then dried in air naturally. Finally, to crystallize the TiO_2 nonotube arrays, obtained in amorphous form by anodization growth, the sample has been placed in a tubular furnace for 2 h at 450 ℃ with a slope of 2 ℃/min in air, so to be transformed into the anatase phase, which shows a higher photo-electrochemical properties.

2.2. Morphology characterization

A field emission scanning electron microscope (FESEM; Hitachi, S–4800) is used to analyse the morphology of TiO_2 nonotube arrays.

3. Results and discussion

3.1 Structure of anodized Ti as a function of pH

The different pH levels of the electrolyte lead to different surface morphologies of TiO2 nanotube arrays. Fig. 1 shows SEM images of TiO2 nanotube arrays obtained from 0.5 wt % NH4F and 5 wt % DI water ethylene glycol electrolyte for 3 h at 30 V with various pH levels. As observed from Fig. 1a, the TiO2 nanotube arrays show an inside diameter of about 100 nm and a wall thickness of around 10 nm. The nanotubues were ordered and vertically oriented. At neutral of ethylene glycol electrolyte, from Fig. 1b, a mixed structure of inhomogeneous and cracked nanotubes could be clearly observed, and the surface was partially covered by the Ti-hydroxide precipitates[16]. The top surface has a uniformly distributed sponge-like nanostructure which can be called “nanograss”[17]. These cracks may be the result of surface stress induced during the formation of the oxide films. The growth of TiO2 nanotube arrays depended remarkably on local electric field and solution diffusion rate and took place preferentially at some locations on the Ti substrate[18]. The anodization formation mechanism of the TiO2 nanotube arrays can be represented as follow[19].

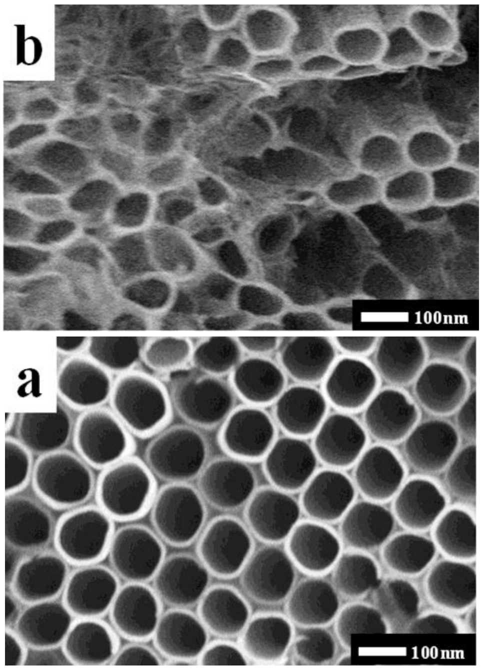

Fig. 1 FESEM images of TiO_2 nanotube arrays obtained from various pH levels: (a) electrolyte with pH~4.5; (b) electrolyte with neutral

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

$$Ti^{4+} + 4H_2O \rightarrow Ti(OH)_4 \downarrow + 4H^+ \qquad （2）$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \qquad （3）$$

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

Based on this equation, it is apparent that metal Ti is dissolved concurrent with the electrolysis of water and the release of O_2 and local pH decrease corresponding to the electrochemical anodization. Ti is dissolved and ejected from nanotubes to outside and accumulated at the top of nanotubes, where Ti-hydroxide precipitate is formed via the instantaneous hydrolysis reaction. This leads to the generation and the accumulation of Ti-hydroxide precipitate at the top of nanotubes as shown in Fig. 2. At the same time, the dissolution of TiO_2 in the presence of fluoride and high acidic environment also occurs corresponding to the chemical dissolution, which is the key in controlling the surface morphology.

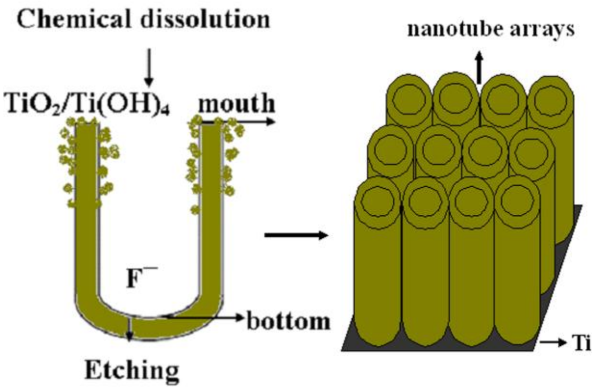

Fig. 2 Schematic representation of relevant processes in Ti-hydroxide precipitate dissolution

3.2. Impact of anodization voltage

The anodization voltage is one of the most important parameters pertaining to the surface morphology of TiO_2 nanotube arrays[20]. Fig. 3 gives the SEM image of the surface structure obtained with anodization voltages of 60 V in the ethylene glycol and 5wt% DI water mixed solution containing 0.5wt% NH_4F for 3 h.

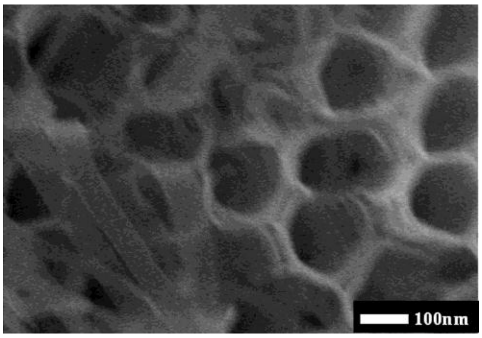

Fig. 3 Surface morphology of the titanium foil anodized in electrolyte with pH 4.5 at 60 V

It is evident that this TiO_2 nanotube arrays is the highly ordered with cylindrical features, an ordered porous structure of approximately 120 nm in diameter and 15 nm in wall thickness was formed. Compared with the Fig. 1a, the top surface of the freestanding TiO_2 nanotube arrays appears nanowires was revealed at 60 V of anodization voltage. At low anodization voltages, the electrochemical anodization speed was very slow and the nanotubes had small pore sizes and length. However, the chemical dissolution was larger than electrochemical etching so that no nanowires layer was formed on the top of nanotubes. Upon further increase the anodization voltage up to 60 V, the electrochemical etching increased as indicated from with the increase of the nanotubes length and the pore size, while the electrochemical etching exceeded chemical dissolution. Consequently, the obtained TiO_2 nanowire–nanotube has an interconnected complex structure. It is believed that the chemical etching process directed by the electric field can vertically split off TiO_2 nanotube arrays into large numbers of nanowires at the nanotubes mouth[21].

3.3 Effect of water content

The water is essential for the formation of anodization TiO_2 nanotube arrays, whose microstructure depends on water content when anodization at 60 V in ethylene glycol electrolyte containing 0.5wt% NH_4F and without the addition of phosphoric acid for 3 h. As it can be seen, the surface morphologies of the TiO_2 nanotube arrays formed with the two different sample surfaces.

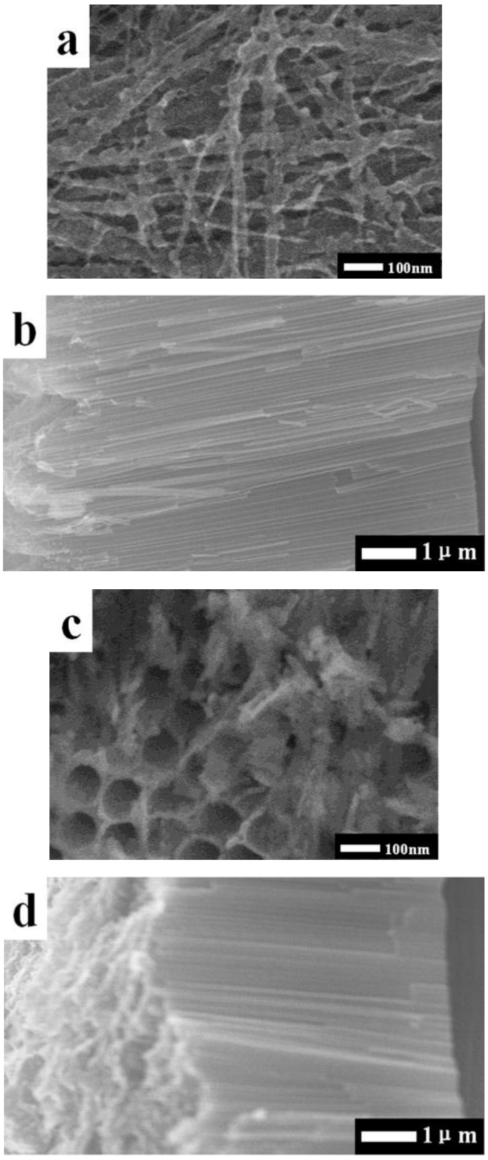

Fig.4 Effect of water content in electrolyte on surface morphologies of TiO_2 nanotube arrays:
(a) 1 wt% (b) 5 wt%

Fig.4a presents the film grown in electrolyte with 1 wt% water. As is observed, the obtained TiO_2 nanowire-nanotube electrode has an interconnected composite structure. The top surface of the freestanding TiO_2 nanotube arrays is covered with a layer of TiO_2 nanowires. Herein, the surface thin layer is composited of dense TiO_2 nanowires with an average width of 20~30 nm, which is also the same as a film thickness of approximately 200 nm. At 5 wt% water content, the surface thin layer is composed of dense TiO_2 nanowires with a film thickness of approximately 100 nm, which is much thinner than above nanowires. It is also observed from Fig. 4b and 4d that the underlaying layer is the highly ordered TiO_2 nanotube arrays with the pore size of about 120~130 nm and wall thickness of 20 nm. TiO_2 nanotube arrays are one-dimensional, compact (nanotubes were well attached to each other) and vertically oriented (straight). Such a nanocomposite structure film is composited of the compact packing nanowires and the highly ordered nanotubes with length of 8.0 μm and 6.5 μm, respectively.

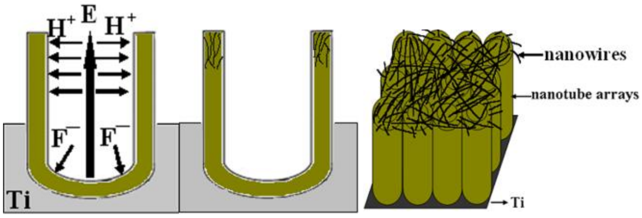

Fig. 5. Schematic diagram of the mechanism of the formation of TiO_2 nanowire-nanotube electrodes: a) growth of nanotubes ; b) splitting of the nanotubes by electric-field-directed chemical etching ;c) formation of nanowires by further splitting. E: the direction of electric field.

The schematic diagram of Fig. 5 indicates the suggested composition of the TiO_2 nanowire-nanotube electrode. It has been reported that the chemical etching process directed by the electric field can vertically split off TiO_2 nanotubes into large numbers of nanostrips at the pore mouth. It means that a high electric field is necessarily required for the formation of anodization TiO_2 nanowires. According to Misra et al., a small amount of water is essential for the formation of anodization TiO_2 nanotube arrays [22]. In the case of less water content, the electrolysis of water mainly takes place at the pore bottom of nanotubes due to its maximum electric field, leading to a local low pH value. This condition provides the favorable environment for the growth of nanotubes at the tip by fluorine ions. The viscous ethylene glycol solution allows a localization of this low pH condition at the pore bottom, thereby restricting the chemical dissolution of nanotubes at the pore mouth. In addition, if a high potential is employed, the hydrogen ions generated on the surface of nanotubes are consequentially driven to the cathode by the electric field, leading to the creation of an interface tension stress of nanotubes in the viscous electrolyte. Chemical dissolution of TiO_2 nanotube arrays may occur along with this stress, thereafter a longitudinal flow of ions in the channel of nanotubes caused by a high electric field is responsible for vertically splitting off nanotubes in the viscous electrolyte and producing the nanowires. Since water electrolysis in ethylene glycol medium is an inefficient reaction, the chemical etching process is suppressed and the longitudinal splitting reaction of nanotubes is also restrained at the pore mouth. Accordingly, this leads to the formation of TiO_2 nanowires on the entire TiO_2 nanotube arrays. Herein, the water content determines the chemical etching rate during spitting off nanotubes.

4. Conclusions

In summary, this paper reports on the structural and morphological features of self-aligned titanium oxide nanotube arrays grown by electrochemical anodization in ethylene glycol electrolytes comprising aqueous acidic media or organic neutral media, the controlled water content and at several anodization voltages ranging between 30 and 60 V. The results showed that the water content determines the chemical etching rate during spitting off nanotubes. An electric field-directed longitudinal splitting reaction of nanotubes is occurred under a high anodization voltage and a viscous medium condition. Ti-hydroxide precipitate on the top of nanotubes occurs corresponding to the chemical dissolution at high acidic environment. It was found that debris and tubes bundling can be avoided by adjusting the reaction conditions during anodization to balance electrochemical etching and chemical dissolution. We expect that altering the surface of TiO_2 nanotube arrays can be used to modify their physical and chemical properties.

Acknowledgments

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