

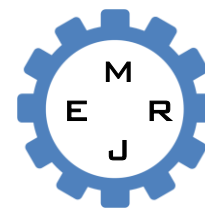


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SYNTHESIS OF TiO₂ NANOTUBE BY ELECTROCHEMICAL ANODIZATION OF Ti FOIL IN ROOM TEMPERATURE

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Abstract: Titania nanotubes (TNTs) were synthesized in the solution of 0.5 wt% NH₄F dissolved in 1 M (NH₄)₂SO₃ at room temperature. The effects of anodization time were studied. TNTs with an inner diameter ranging from 27 to 73 nm, and length of TNTs ranging from 0.5 to 0.95 μm were fabricated in fluoride containing electrolyte. It was observed that anodization time has proportional relationship to the inner diameter of as-grown TNTs. In contrast, anodization time had modest effect on the length of the as-grown TNTs.

Keywords: *Titania Nanotubes, Titanium dioxide, Anodization, Synthesis, Morphology.*

1. INTRODUCTION

The carbon nanotubes (CNTs), which were found by Iijima *et al.*, have great potential as materials with novel properties that are not found in conventional graphite or fullerene [1-3]. This discovery of CNTs has motivated the quest for the synthesis of nanotubular structures of other substances and chemical compounds such as V₂O₅, SiO₂, TiO₂, Fe₂O₃, ZrO₂ and MoO₃. Among all these transition-metal oxides, bulk TiO₂ is frequently used in paint, white pigments, and sun-blockers due to its especial characteristics such as non-toxic, environmentally friendly, and corrosion resistive material [4]. Titania nanotubes (TNTs) with high surface-to-volume ratios have recently been reported for improved properties compared to any other forms of titania in application such as photocatalysts in water and air purification, gas sensing, water photoelectrolysis for hydrogen generation, photovoltaic cells, optics, drug delivery, tissue engineering and molecular filtration [4,5], and rechargeable lithium batteries [6-8]. Therefore, particular attention has been paid to the fabrication of TNTs, or arrays of tubes, and many methods have been developed including chemical processing [9, 10], hydrothermal treatment of TiO₂ nanoparticles [11,12], microwave irradiation [13], deposition of sol-gel within templates [14,15], hydrolysis of TiF₄ under acidic conditions [16], sonication [17] of titania particles in aqueous NaOH solution [18], surfactant-assisted templating methods [19], and anodization of titanium foils [15, 20-23]. Among all these

fabrication methods, both anodization and hydrothermal treatment are more attractive due to their easy method to obtain nanotubes, feasibility of widespread applications, and cost effectiveness. However, over the past several years, preparation of TNTs by anodization process has caught the attention of the scientific community due to its one dimensional nature, ease of handling, and simple in preparation. Nevertheless, the main disadvantage of this method is that the as-synthesized nanotubes are amorphous and post heat treatment is required to crystallize them into anatase, rutile or brookite structure [24]. In addition, the annealing had an adverse effect on the stability of nanotubular structure [25]. However, at elevated temperature, high surface makes the nanotubes prone to solid-state sintering, which leads to grain growth, densification and eventually complete collapse of the nanotubular structure [26].

This paper investigates the oxidation of titanium foil at constant voltage in an electrolyte containing NH₄F and (NH₄)₂SO₃. Titanium foils anodized at different time periods possess well-ordered nanotubes with different size. The crystal changes of structures of TNTs from amorphous to anatase, rutile and brookite were investigated by calcination of fabricated nanotubes at 500 °C. The morphology and chemical nature of the as-prepared nanotubes were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX); crystallinity and phase information were obtained by X-ray diffraction (XRD).

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2. EXPERIMENTAL

Pure Ti foils (99.5%) with a thickness of 0.025 mm were used to prepare TiO₂ (Titania) nanotubes arrays. The titanium foil was first mechanically polished with different abrasive papers, rinsed in a bath of room temperature (20 ± 2 °C) deionized water for 10 minutes. Thereafter, the titanium foils were rinsed with acetone and ethanol in an ultrasonic bath for 10 minutes, respectively. Electrochemical anodization was carried out at room temperature in a homemade cell with two-electrode configuration, as shown in Fig. 1. A dc power supply was used to provide a constant potential of 15 V during the anodization process. Ti foils with an exposed area of about 2.0 cm² (considering both side of the Ti foil) acted as the anodes, and a Pt electrodes with an area of 2.0 cm² (considering both side of the Pt plate) was used as the cathode.

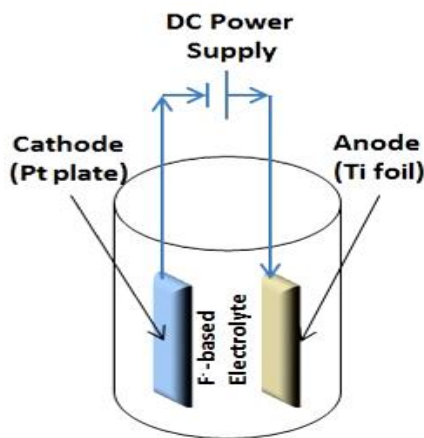


Fig. 1 Schematic representation of experimental setup for Ti anodization.

The distance between the anode and the cathode was maintained at 2.0 cm. Electrolyte was a solution of 0.5 wt% NH₄F (Sigma-Aldrich) dissolved in 1 M (NH₄)₂SO₃ (Sigma-Aldrich). Potential was increased from 0 volt to 15 volts gradually and then hold constant for 1, 2, 6, and 24 h. All anodization experiments were conducted at room temperature (20 ± 2 °C) with magnetic stirring, and fresh 100 ml electrolyte used each time. In the first few seconds of the anodization, the current observed to decrease drastically, and then they approached a stable value of 0.03 A. During the anodization experiment, the color of the titanium foil's surface normally changed from purple to blue, yellow, red and then finally light red. After anodization, samples were washed with deionized water for 10 minutes and cleaned by compressed air. Finally, samples were heated by 1 °C/minute rate in a furnace to 500 °C, and kept 1 hour at this temperature, and then cooled to room temperature before characterization.

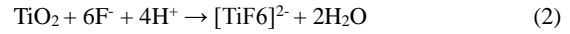
3. TiO₂ NANOTUBE FORMATION MECHANISMS

The formation mechanism of the TNTs can be explained as follows [27]. In aqueous acidic medium, titanium oxidizes to

form TiO₂.



The pit initiation on the oxide surface is a complex process. However, TiO₂ is stable thermodynamically at a pH range 2-12, a complexing ligand (F⁻) leads to substantial dissolution. The pH of the electrolyte is a deciding factor. The mechanism of pit formation due to F⁻ ions is given by as follows:



This complex formation leads to breakage in the passive oxide layer, with pit formation continuing until repassivation occurs [27, 28]. Nanotube formation goes through the diffusion of F⁻ ions and simultaneous effusion of the [TiF₆]²⁻ [17]. The pore growth occurs due to the inward movement of the oxide layer at the pore bottom.

4. RESULTS AND DISCUSSION

4.1 XRD Analysis

Figure 2 is the XRD patterns of TNT arrays after sintered in air at 500 °C. However, all the as-grown TNT arrays are amorphous before calcination as determined by XRD. The XRD peaks of anatase, rutile and brookite phase are unambiguously visible, indicating that phase transition from amorphous to anatase crystal. The strongest anatase phase appears corresponding to 25.356° (101), 25.281° (101), 25.301°, and 25.356° (101) for 1 h, 2 h, 6 h, and 24 h anodization time, respectively. In addition, the strongest rutile phase appears corresponding to 27.438° (110), 27.495° (110), 27.434° (110), and 27.438° (110) for 1 h, 2 h, 6 h, and 24 h anodization time, respectively. Furthermore, the strongest brookite phase appears corresponding to 25.34° (120) for all 1 h, 2 h, 6 h, and 24 h anodization time. However, the strongest titanium phase appears corresponding to 40.17° (101) for 1 h anodization, 40.41° (101) for 2 h, 6 h, 24 h anodization time, respectively.

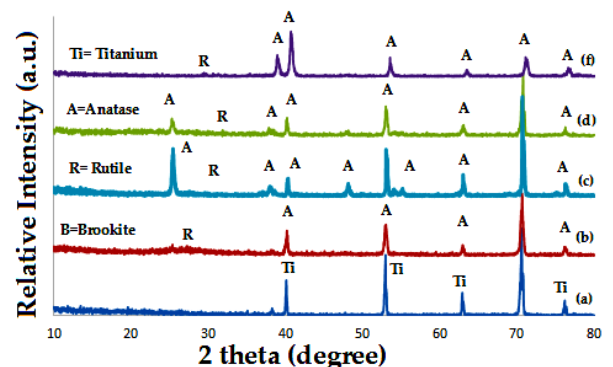


Fig. 2 XRD pattern of Ti and Titania with various anodization times.

4.2 Morphology of TiO₂ Nanotubes Arrays

Figure 3 shows the SEM top view and side view of the TiO₂ nanotube layers on Ti substrates after annealing at 500 °C. As can be seen from the images, nanotubes with different dimensions formed on the substrates. All samples exhibited a bamboo stalks texture with well-developed nanotubes. It is

believed that the nonuniform TNTs domain is due to nonuniformly distributed stresses among Ti atoms prior to anodization. It is reported that mechanical stresses exist in the TiO₂ of the as-received Ti foil due to the volume change accompanying the oxidation of Ti since the TiO₂ has high volume change compared to Ti metal [29]. In addition, the length of the nanotubes after 1, 2, and 6 h (Fig. 3(e)) anodization was observed to be 0.95 μm. However, the length of the nanotubes decreased and observed to be 0.50 μm after 24 h anodization.

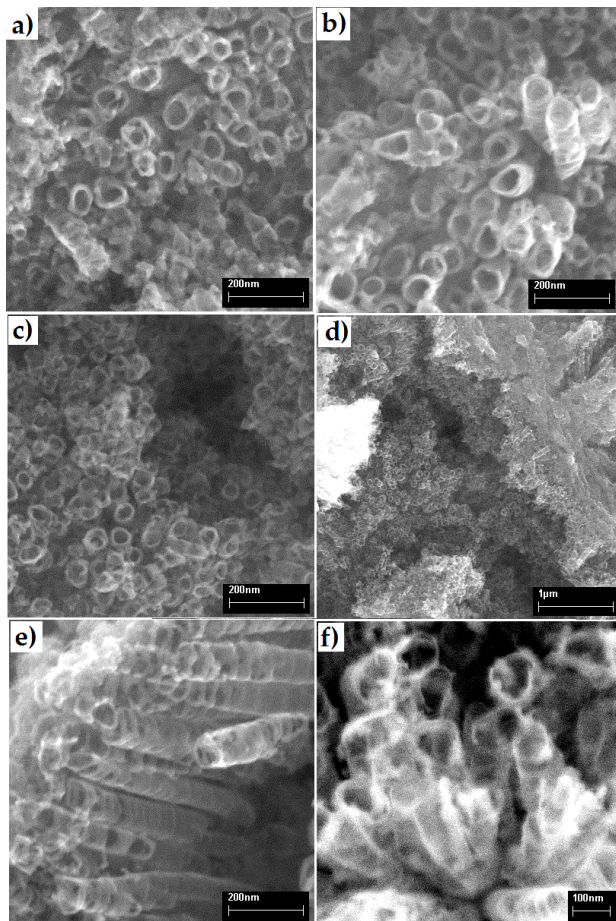


Fig. 3 SEM images of TiO₂ nanotubes arrays with different anodization times after calcination at 500 °C for 1 h in air: (a) 1 h, (b) 2 h, (c) 6 h, (d) 24 h, and length of the nanotubes after (e) 6 h and (f) 24 h anodization.

Figure 4 shows the frequency distribution of the inner tube diameter (D_i) of TNT. It should be noted that the nano-tube diameter size distribution graphs were generated from 100 individual measurements from SEM images of all four types of TNTs by Image J software. The mean inner diameter of TNT was 27.40 ± 19.23 nm (Fig. 4(a)), 34.93 ± 30.43 nm (Fig. 4(b)), 73.77 ± 167.4 (Fig. 4(c)), and 31.63 ± 25.31 nm (Fig. 4 (d)) after 1 h, 2 h, 6 h, and 24 h anodization, respectively. It was observed that the D_i increased with an increase in the anodization time in the range of 1 to 6 h. However, D_i decreased after 24 h anodization.

Figure 5 shows the selected area EDX spectra of bare Ti foil and various TNTs at different anodization time. The tubes are composed of Ti and oxygen (O) ignoring some undetectable

light elements and background signals. Strong $K\alpha$ and $K\beta$ signals from Ti were seen at 4.42 and 4.52 keV, respectively, for all three anodization times. However, $L\alpha$ peak from Ti and the $K\alpha$ peak from O are not accurately splitting. It is shown that $K\alpha$ O at 0.52 keV and $L\alpha$ Ti peak at 0.34 keV. In addition, a quantitative Ti/O ratio analysis has been performed and the Ti/O ratio estimated as 1:2. In contrast, the ratio of Ti/O can be checked from the ratio of heights of the O peak at 0.52 keV and Ti peak at 4.52 keV. However, there is no significance difference in the compositions of these as-grown nanotubes.

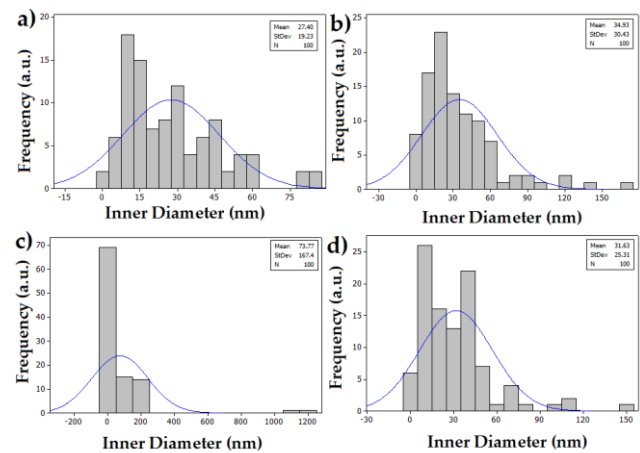


Fig. 4 Frequency distribution of TiO₂ nanotubes after (a) 1 h, (b) 2 h, (c) 6 h, and (d) 24 h anodization time.

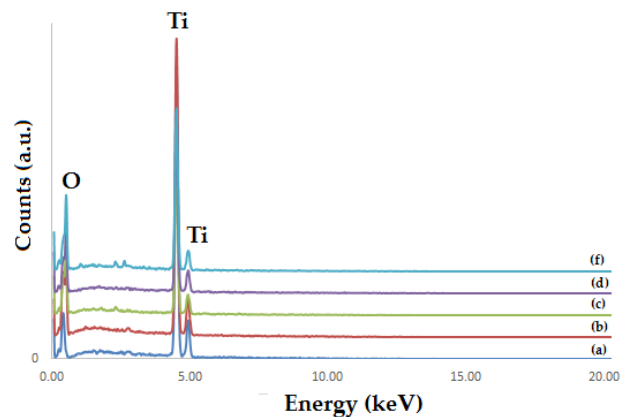


Fig. 5 Selected area EDX spectra: (a) bare Ti foil, after (b) 1 h, (c) 2 h, (d) 6 h, (e) 24 h anodized TNTs.

5. CONCLUSIONS

The present work describes the influence of anodization time on the morphology of nanotubes formed on titanium in small amounts of fluoride containing electrolyte. The morphological features of the nanotubes were related to a fluoride-induced dissolution of a porous structure and anodization time. It was found that the inner diameter of the as-grown TNTs were directly proportional to the anodizing time (up to 6 h). However, the inner diameter of TNTs was observed to be 31.63 ± 25.31 nm at 24 h anodization time which was smaller than the observed inner diameter of TNTs at anodizing time of 1 to 6 h.

6. ACKNOWLEDGMENT

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