



STUDY OF THE EFFECT OF NH_4F CONCENTRATION ON THE STRUCTURE OF ELECTROCHEMICALLY PREPARED TiO_2 NANOTUBES

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Abstract

In this study Titania nanotube arrays were prepared at room temperature ($\sim 25^\circ\text{C}$) via electrochemical anodization process of pure titanium foil in glycerol base electrolyte, different concentrations of ammonium fluoride salt (0.5 and 1.5wt.%) were added to the electrolyte as a tube enhancing agent. When anodizing Ti in 0.5 wt. % NH_4F , nanotubes are formed with 54 ± 10 nm tube diameter, 20 ± 3 nm wall thickness and $1.76 \mu\text{m}$ tube length. When anodizing Ti in 1.5 wt. % NH_4F , nanotubes are formed with 69 ± 10 nm tube diameter, 29 ± 3 nm wall thickness and $2.71 \mu\text{m}$ tube length. The morphology and structure of the Titania films were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM).

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Keywords: TiO_2 nanotubes; electrochemical anodization; morphology.

دراسة تأثير تركيز NH_4F على تركيب الانابيب النانوية لـ (TiO_2) المحضرة الكهروكيميائياً

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الخلاصة

في هذه الدراسة صفوف التيتانيا نانوتيوب حضرت في درجة حرارة الغرفة 25°C بطريقة الانودة الكهروكيميائية لصفائح التيتانيوم النقي في محلول كهربائي اساسه جليسيرول (glycerol)، تراكيز مختلفة من ملح فلوريد الامونيوم 0.5 and 1.5wt.% اضيفت الى المحلول كعامل محسن للانبوب. عندما يؤكسد التيتانيوم في 0.5 wt.% NH_4F ، كان قطر الانابيب النانوية المشكلة 54 ± 10 nm، سمك الجدار $3 \pm$ nm و $20 \mu\text{m}$ طول الانبوب. عندما يؤكسد التيتانيوم في 1.5 wt.% NH_4F ، كان قطر الانابيب النانوية المشكلة 69 ± 10 nm، سمك الجدار 3 ± 29 nm و $2.71 \mu\text{m}$ طول الانبوب. تمت دراسة مورفولوجية وتركيب افلام التيتانيا بواسطة المجهر الالكتروني الماسح، مجهر القوة الذرية و حيود الاشعة السينية.

INTRODUCTION

Nanomaterials have attracted increasing attention over the past few decades because of

their excellent properties and wide applications as compared to their bulk counterparts. One-dimensional nanostructures such as nanotubes, nanorods, nanofibers, nanoribbons and nanowires, are expected to play important roles in the fabrication of functional nanodevices [1]. Recently, special interest has been focused on (TiO₂) nanostructures, which have many potential applications in gas sensors [2] and biocompatible [3], photovoltaic [4], and photocatalytic materials [5]. Fabrication of (TiO₂) nanotube arrays via anodic oxidation was first reported in 2001 by Grimes et. al. [6] using titanium foil in a fluoride-based electrolyte.

This work is aimed to overcome the ability to control the structure and properties of the nanostructural (TiO₂) by variation the fluoride ions concentration.

EXPERIMENTAL

Pure titanium foil (99.7% purity, 0.25mm in thickness) purchased from Sigma Aldrich and cut into the desired size (20×20 mm). A direct current power supply (Agilent E3612A) was used as the voltage source for the anodization. The anodization process was carried out in a homemade Teflon cell with two electrode configuration; Titanium foil as the working electrode and 0.1 mm thick. Platinum foil (10×5 mm) as the counter electrode under constant potential at room temperature (~25°C). The titanium sheets were sonicated in acetone and ethanol each for 15 minutes, followed by rinsing with de-ionized (DI) water to remove the impurities and then drying in (N₂) gas. The anodization set-up is shown in Figure-1. The anodization was carried out at 15 Vdc, the cell electrolyte was glycerol solution containing different amount of ammonium fluoride (0.5, 1.5wt.%) at 2hours. The prepared samples were rinsed immediately with (DI) water for several minutes and dried with high pressure (N₂) gas. For the structural and morphological characterization of the anodized samples, top views were recorded by scanning electron microscopy (SEM) using a Hitachi FE- SEM model S-4160, Japan and (AFM) study carried out by (AA3000, Angstrom Advanced Inc. USA). Samples were prepared by annealing at 530°C temperatures in ambient atmosphere for 3h. The crystallographic structures of the samples were determined using Philips pw 1050 X-ray diffractometer of 1.54 Å from Cu-k α

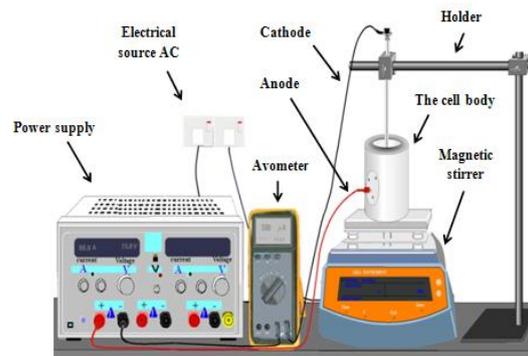
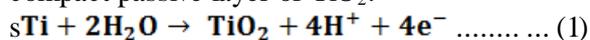


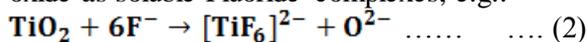
Figure-1: Apparatus set-up of titanium anodization experiment.

RESULTS AND DISCUSSIONS

The growth of Titania nanotubes is, in simplest approach, governed by a competition between two reactions. The first one is anodization, which leads to formation of compact passive layer of TiO₂:



The second one is a chemical dissolution of the oxide as soluble Fluoride complexes, e.g.:



The reaction (1) describes the oxide growth on an anodized metal surface, in a fluoride free electrolyte (for example NH₄F). Oxidized metal species react with O²⁻ ions from H₂O to form an oxide layer. The oxide growth is governed by ion transport through the growing oxide. As the system is under a constant applied potential, the field within the oxide is progressively reduced by the increasing oxide thickness, the process is self-limiting. The current density converges to limit value close to zero.

Situation becomes less simple in the presence of fluoride ions. This is mainly caused by two effects of the fluoride ions: (i) the ability to form water-soluble (TiF₆²⁻) complexes according to reaction (2), and (ii) the small ionic radius that makes them suitable to penetrate through the growing TiO₂ lattice and thus competing with O²⁻ transport. The complex formation ability leads to a continuous chemical dissolution of formed TiO₂. The current response of system under applied potential. There are three stages of process: At the first stage, growth of compact titanium dioxide occurs. The current response of the system is similar with that of the system without fluorides Figure-2. The second stage represents an initial stage of the nanotubes formation. The fluoride ions interact with titanium dioxide and selective dissolution on the high-energy places begins Figure-3. The increasing current is a consequence of competition between oxidation (electrochemical

process) and chemical dissolution of the oxide layer. At the third stage, the equilibrium between oxidation and dissolution is reached. The current flow is constant and nanostructured surface begins to form Figure-4.

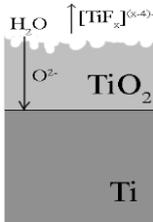


Figure-2: Second stage of nanotubes growth-nucleation (based on [7]).

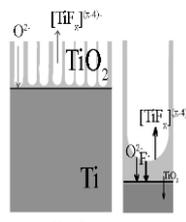


Figure-3:Regular TiO2 nanotubes growth (based on [7]).

It is important to compare the electrochemical data recorded during anodization in these electrolytes since the nanotube growth was achieved over comparably wider (F⁻) concentration range. Figure-4 shows curves current transients recorded during Titania growth in 0.5 and 1.5wt.% NH₄F concentrations at 2 hours and 15V. The magnitude of the current is clearly affected by fluorides in the electrolyte – in the same trend as for the thickness.

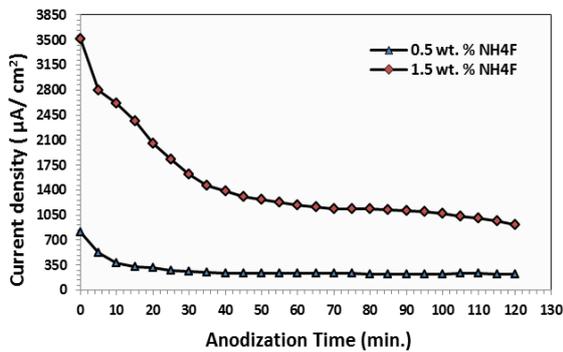


Figure-4: The current transient recorded during anodization during 2 hours at 15V in the glycerol + 0.5Wt. %NH₄F and glycerol + 1.5Wt. %NH₄F.

This relation is shown with decreasing(F⁻) concentration, the dissolution rate of TiO₂ becomes slower, therefore the anodizing current is smaller and the tubes are shorter.

Figures-5 and 6 (a and b) show the SEM images of TiO₂ nanotubes prepared by anodization treatment under 15V for 2hr in different NH₄F concentration in glycerol electrolyte. When the NH₄F concentration is 0.5 wt. %, self-organized TiO₂ nanotubes are obtained. However, when the concentration increases to 1.5 wt. % or above, only

nanoporous structure are formed. From the results, it can be seen that the formation of nanotubes is very sensitive to the concentration of NH₄F. The argument is similar to that using aqueous electrolyte. When anodizing Ti in 0.5 wt. % NH₄F, nanotubes are formed with 54 ± 10 nm tube diameter, 20 ± 3 nm wall thickness and (1.76 ± 0.5 × 10³) nm tube length. When anodizing Ti in 1.5 wt. % NH₄F, nanotubes are formed with 69 ± 10 nm tube diameter, 29 ± 3 nm wall thickness and (2.71 ± 0.5 × 10³) nm tube length.

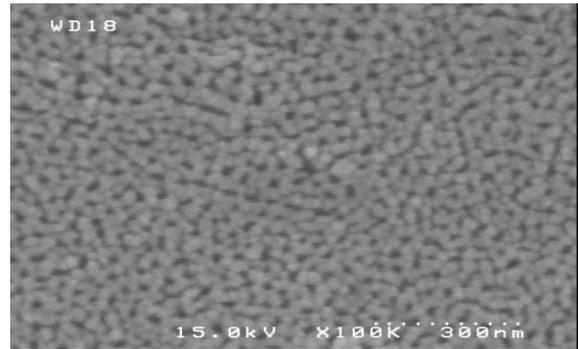


Figure-5:SEM images of Ti anodized in 0.5 wt.% NH₄F in glycerol electrolyte at 15V for 2 h.

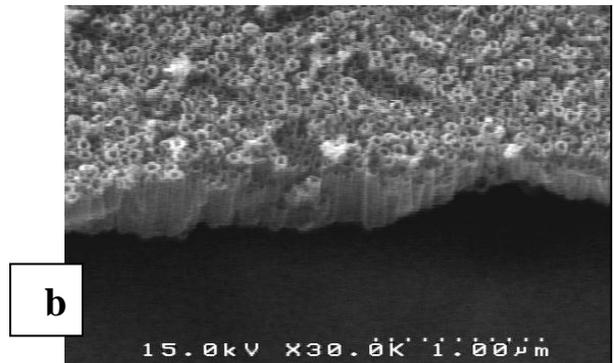
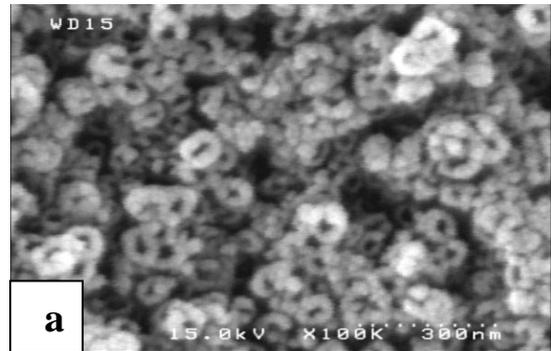


Figure-6: SEM images of Ti anodized in 1.5 wt. % NH₄F in glycerol electrolyte at 15V for 2 hr., (a) the top and (b) the cross-sectional.

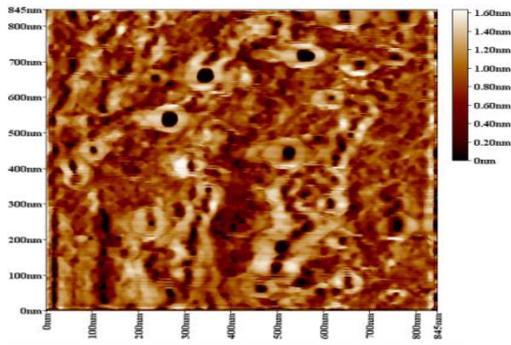
Figures-7 (a and b) and 8 (a and b) show the results (AFM). Various electrolytes determine the diameter of etching pores and the degree of ordering. The images show the differences of

Titania morphology of Titania obtained with 0.5wt.% and 1.5wt.% NH₄F. We conclude that concentration of fluoride has a significant effect on the surface of the sample because the increase of concentration (F) increases the surface etching and the generation of more pores. According to the result, Titania etching by a low concentration of Fluoride generated smaller pores.

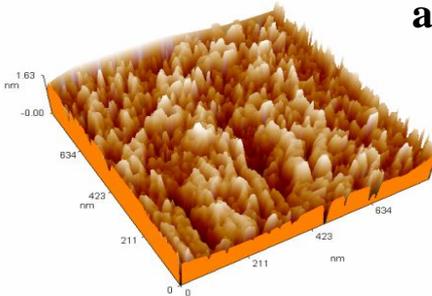
The terms of diameter of the pores has been shown that when increasing the concentration of Fluoride increased diameter of the pores. Increase average roughness (RF) with increasing concentration of fluoride as in the (Table-1) and the surface is more uniform.

(Table-1) The average Roughness and Pores diameter of TiO₂ nanotubes under different proportion of NH₄F

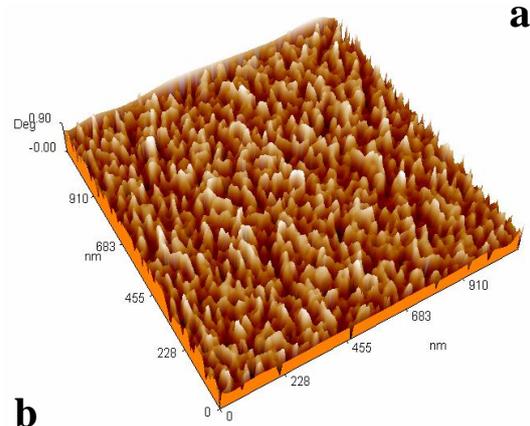
Sample ID	Concentration of NH ₄ F wt.% in glycerol	Pores diameter (nm)	Average Roughness (nm)
1	0.5	15.5	0.25
2	1.5	22	0.16



a



b



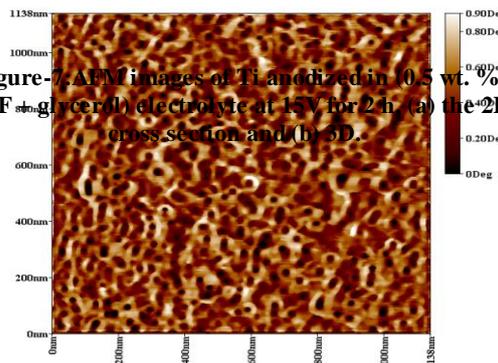
a

Figure-8:AFM images of Ti anodized in (1.5 wt. % NH₄F + glycerol) electrolyte at 15V for 2 hr, (a) The 2D, cross section, (b) 3D.

TiO₂ layers were studied by X-ray diffraction (XRD) techniques. It is a noncontact and nondestructive technique used to identify the crystalline phases present in materials and to measure the structural properties of these phases.

We took a sample under conditions (0.5wt.% NH₄F + 99.5wt % glycerol) electrolyte at 15V for 2hr and we had a measurement of (XRD). Figure-9 shows the XRD measurement result of TiO₂ nanotubes formed before and after annealing. Before annealing, it can be seen that the Titania is a poly-crystalline nature, where three strong peaks are recognized. In this diffraction pattern, the peaks at 2θ =38.4°, 2θ =40.2° and 2θ = 70.6° are corresponding to the diffraction from Anatase TiO₂ (112), Brookite TiO₂ (022) and Anatase TiO₂ (220) planes which are related to the formation of TiO₂ nanotube

Figure-7:AFM images of Ti anodized in (0.5 wt. % NH₄F + glycerol) electrolyte at 15V for 2 h, (a) the 2D, cross section and (b) 3D.



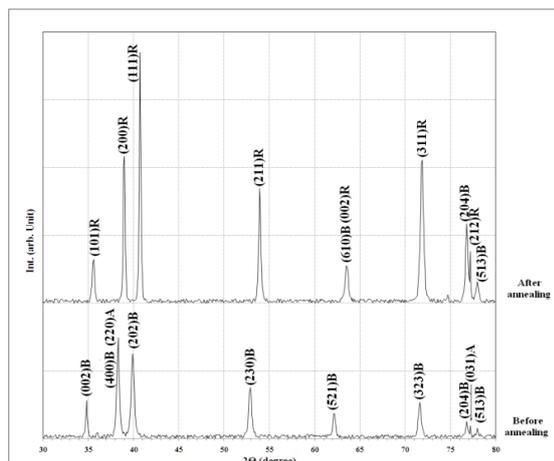


Figure-9: XRD pattern of Titania before and after annealing at temperatures 530 °C for 3hr on Ti foil substrate.

After annealing at temperatures 530°C for 3hr on Ti foil substrate, It can be seen that after annealing the intensity of the A (220) appears with peak located at $2\theta=70.4^\circ$ increases

CONCLOSIONS

In this work, highly ordered TiO₂ nanotube arrays with length of a few of micrometer and rough tube wall were fabricated using electrochemical anodization of Ti foil. We controlled ammonium florid concentration in electrolyte. Main functional for Fluoride ions in the process of anodizing is the etching and pores formed to the tubes that grows on a regular basis, also increasing of Fluoride concentration affects increase the diameter of the pores, the wall thickness and tube length, but this increase is not large compared to other factors. All the TiO₂ nanotube layers synthesized in this work have an unstable structure (Anatase and Brookite) phases. This unstable structure can be converted to a crystalline structure more stable (Rutile) phase by annealing.

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