

Influence of anodization parameters on topographic and morphological properties of TiO₂ nanotube arrays: A reconstruction from SEM measurements

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Received: 15 September 2016, Revised: 25 October 2016 and Accepted: 20 November 2016

DOI: 10.5185/amlett.2017.7109

www.vbripress.com/aml

Abstract

In this work, we fabricated samples of titanium dioxide nanotube arrays via electrochemical anodization by using titanium foils as anode and cathode. A solution of water, ethyleneglycol, and ammonium fluoride (NH₄F) at room temperature was used for the samples synthesis process. Different times and anodizing voltages were used during reaction. From X-ray diffraction (XRD) and micro-diffraction (μ XRD) measurements, rutile and anatase phases were identified as function of deposition parameters. The Ti₃O₅ phase was observed by deconvolution of Debye-Scherrer rings of the microdiffraction spectra. Annealing processes were performed for all samples in the range between 273 and 723 K, without changes in the material's morphological properties, while the crystalline structure was affected. Nanotube diameters varying between 30 and 42 nm were observed from SEM micrographs, when NH₄F concentration was changed from 0.25 to 0.50 wt%. An alternating anodizing voltage generates the formation of nanotubes evenly spaced on the surface with nodes in bamboo-type form, while a smooth form for nanotubes was observed with constant applied voltage. From stereoscopic 3D micrographs, a reconstruction of the topographic surface of the TiO₂ nanotubes was conducted. A correlation between synthesis parameters and morphological properties is presented. Copyright © 2017 VBRI Press.

Keywords: Titania, TiO₂, bamboo-type, nanotubes, microdiffraction.

Introduction

Titanium dioxide (TiO₂) is among the most-studied compounds in materials science due to its chemical stability, which places it as an oxide with various applications in different areas, like photocatalysis [1], dye-sensitized solar cells [2], and biomedical devices [3], among others. Regarding the synthesis of TiO₂ nanotubes, different methods have been implemented, including the assisted-template method [4], hydrothermal treatment [5], chemical bath deposition method (CBD) [6], RF sputtering [7], and oxidation by electrochemical anodization [8, 9], etc. Interest in researching TiO₂ nanotubes fabricated through electrochemical anodization has increased progressively due to the study of synthesis parameters to produce nanotubes with ordered alignment and a pure TiO₂ phase at room temperature [3]. This work presents a study of synthesis parameters to fabricate TiO₂ nanotubes, using the electrochemical anodization method, as well as their morphological and structural characterization. The μ XRD measurements provided information on the presence of local phases and polymorphous TiO₂. In addition, a correlation between morphological and structural characterization is shown.

Experimental

Synthesis parameters

Titanium dioxide nanotubes were prepared via chemical anodization method from titanium (Ti) foils measuring 8 cm² and 50 μ m thick. The Ti foils were used with 99.97% pure cathode and anode. Ethyleneglycol solution, deionized water, and ammonium fluoride (NH₄F) at a concentration between 0.15 and 0.50 %wt was used as mixture in the solution. The applied voltage profile involved two types: first, a squared wave starting with 80 V for 1 min, alternating to 20 V for 5 min for a 2-h period; in the second stage, nanotube preparation started with constant voltage values of 20, 40, and 80 V for 45 min. All samples were fabricated at room temperature. Annealing processes were carried out between 373 and 723 K at atmospheric pressure, after synthesis.

Characterizations

Characterization of samples took place through XRD and μ XRD with X-ray diffractometer (Empyrium from PANalytical), equipped with Co-K α : 1.7890 Å, potential difference of 40 KV, current at 40 mA with PIXcel 3D

2x2 detector. The software used to compare the samples was the X'Pert High-Score Plus through Rietveld refinement in the range of $10^\circ \leq 2\theta \leq 140^\circ$ with angular steps of 0.0001° . Morphological characterization of the samples employed scanning electron microscopy (SEM), using a VEGA3 SB microscope containing a tungsten filament and applying an acceleration voltage of 4.89 KV under high vacuum conditions ($\sim 10^{-6}$ mbar); the microscope also contains an Xflash 410M detector for stereoscopic micrographs.

Results and discussion

The XRD pattern at room temperature presented (**Fig. 1a**) shows the phases found for the samples in which the NH_4F concentration varied in the solution. Given that the H_2O and NH_4F concentration in the solution affects the formation of TiO_2 phases, a structural analysis of the samples was performed by varying NH_4F : 0.15, 0.25, 0.35, and 0.5 wt%; H_2O concentration of 2 wt% with constant and alternating voltage were used.

As observed, the Brookite phase is present when NH_4F concentration was 0.15 and 0.25 wt%, while Anatase (PDF 01-073-1764) and Rutile (PDF 01-088-1174) phases appear for 0.35 and 0.5 wt% NH_4F concentrations (**Fig. 1a**). Other polymorphous phases were identified in the nanotubes as TiO_2 with orthorhombic characteristic (PDF 01-082-1137) in their structure.

Samples with constant voltage (**Fig. 1b**) present decreased amorphous halo and higher peak intensity, compared to the XRD pattern of the samples with alternating voltage. This can be associated to the continuum competition between oxide formation and Ti^{4+} solvent during synthesis process favored by constant voltage. Increased applied voltage during the anodizing process revealed the presence of the Anatase and Rutile phases.

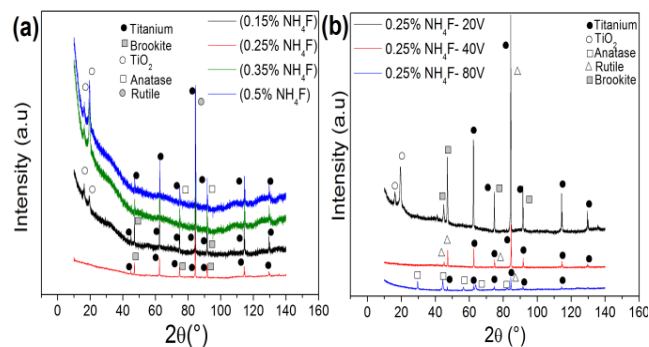


Fig. 1. XRD patterns of TiO_2 nanotubes: (a) varying NH_4F in the solution, and (b) 0.25 wt% NH_4F sample with constant voltage.

Nanotubes TiO_2 fabricated by electrochemical anodization have an amorphous crystallographic structure, that after annealing processes realized at atmosphere of oxygen, the walls of the nanotubes become crystalline phases like brookite, rutile and Anatase depending on the thermal process; however the rutile phase is more thermodynamically stable [8, 10].

Additionally, annealing processes were conducted for the sample with 0.25 wt% NH_4F concentration. The XRD and μXRD measurements are presented (**Fig. 2**).

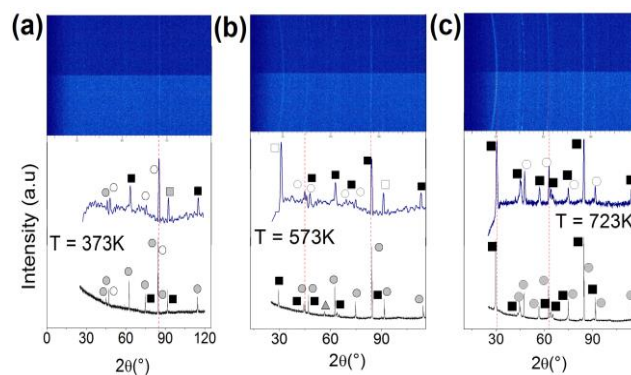


Fig. 2. XRD patterns of TiO_2 nanotube samples with 0.25 wt% concentration of NH_4F (bottom), μXRD obtained from the deconvolution of the Debye rings (middle), and Debye rings (upper): (a) $T = 373\text{ K}$, (b) $T = 573\text{ K}$, and (c) $T = 723\text{ K}$. (●) Titanium, (○) Rutile, (■) Anatase, (□) TiO_2 , (■) Ti_6O , (▲) Ti_3O_5 .

From μXRD the Rutile phase was observed in the sample with 0.25 wt% NH_4F concentration when temperature varied between 373 and 723 K (**Fig. 2**); this can be attributed to Rutile being a segregated phase in the nanotubes and its identification is only located in some regions of the sample. The Ti_3O_5 is a metastable phase associated to Ti and O recombination in the solution [11].

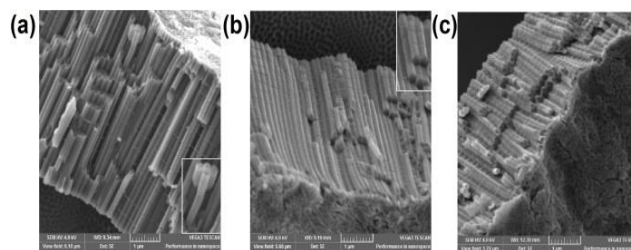


Fig. 3. SEM micrograph of the TiO_2 nanotubes, varying annealing temperature in the sample (2 wt% H_2O and 0.25 wt% NH_4F): (a) 293 K, (b) 373 K, and (c) 723 K.

SEM micrographs of the TiO_2 nanotubes after the annealing process are presented for $T=293\text{ K}$, 373 K, and 723 K (**Fig. 3**). Note that sample surface is characterized for homogeneous formation of nanotubes with a hexagonal structure of thick walls. Temperature changes did not alter surface morphology, while the crystalline structure was modified (**Fig. 2**). The inner diameter of the nanotubes was $34.34 \pm 1.95\text{ nm}$ and their length was $5.96 \pm 0.43\text{ }\mu\text{m}$.

On the other hand, SEM micrographs for the same sample; in this case, at 80 V for 45 min are presented (**Fig. 4**). Nanotubes fabricated with constant voltage present a cylindrical morphology of thin walls and without nodes, confirming that bamboo-type structures are a consequence of the alternate voltage applied between electrodes (**Fig. 4b**). Samples fabricated with constant voltage have been reported using Pt and Ti like electrodes, respectively [12, 13]. A dependency of the pores size and smooth surface have a direct correlation with low constant voltages (20V - 40V) [10, 13]; while that when the voltage is alternant during the reaction, there is a possibility of to obtain changes in the superficial morphology of the nanotubes and their applications [14].

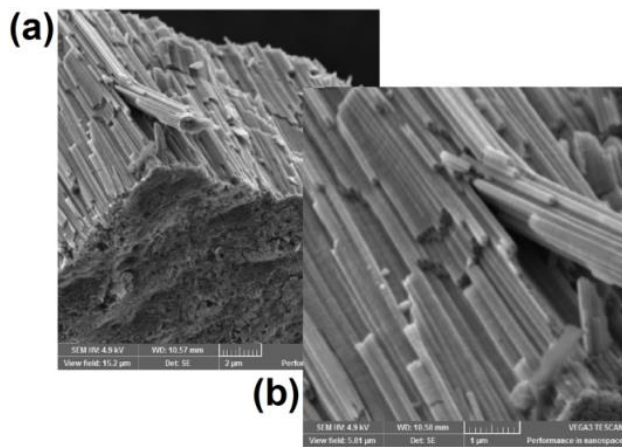


Fig. 4. SEM micrograph of the TiO₂ nanotubes, varying annealing temperature with a 0.25 wt% concentration of NH₄F, 80 V and 723 K. **b)** presents a magnification of the upper part of the nanotubes.

From micrographs it was possible to obtain, that the internal diameter of the nanotubes was 29.56 ± 1.93 nm and their length was 2.97 ± 0.19 μ m (**Fig. 4**). The decreased values, compared to those obtained, can be associated to the relaxation times because of alternating voltage changes [15]. Stereoscopic images of the TiO₂ nanotubes were obtained from of the sample with 0.25 wt% NH₄F and 2 wt% H₂O parameters and alternating voltage (**Fig. 5**).

The stereoscopic image of the nanotubes, where the dark parts are associated to regions with greater depth is showed (**Fig. 5b**). This image shows the inhomogeneity of the nanotube surface associated to imperfections on the Ti foil surface. Also, presents the nanotube reconstruction, showing further evidence of topography and surface inhomogeneity (**Fig. 5c**); an inner diameter of 34.34 ± 1.95 nm was obtained.

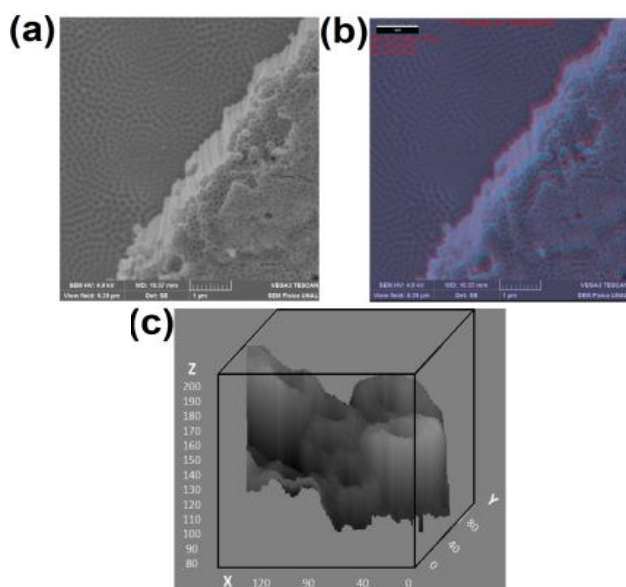


Fig. 5. TiO₂ nanotubes from the sample with 0.25 wt% NH₄F concentration: **a)** SEM micrograph, **b)** Stereoscopic image, and **c)** nanotube reconstruction (nm).

With constant voltage, note that the decreased diameter may be associated to the oxide layer on the surface

becoming self-limiting, *i.e.*, when no competition is generated between O₂ and soluble [TiF₆]²⁻, which limits the attack on the oxide compact layer and reduces nanotube dimension, compared to when alternating voltage was applied [15, 16]. Inner diameter and length of titania nanotubes were obtained from SEM measurements and compared with others reports that using the same synthesis method (**Table 1**). It was observed that in our case, both constant and alternant voltages have a strong dependence with the porous size and length of nanotube.

Table 1. Dimensions for TiO₂ nanotubes reported for electrochemical anodization method.

Constant Voltage (V)	Length (μ m)	Inner diameter (nm)	Reference
10 -28	-	40 - 120	[17]
20 - 50	3.5	54 - 96	[18]
20	0.32 - 1.2	98	[19]
50 -57	0.1	34 - 58	[20]
10 - 100	0.78 - 5	38 - 70	[21]
60	5	100	[22]
30	4	100	[23]
60	46	120	[24]

Conclusion

This work fabricated TiO₂ nanotubes via anodization process and by changing applied voltage. Synthesis parameters affected inner diameter and length. As noted, annealing processes do not affect nanotube morphology, whilst the crystalline structure revealed changes in the phases. The SEM micrographs evidence a correlation between synthesis parameters and TiO₂ nanotube morphology.

Acknowledgements

This work was supported by Universidad Nacional de Colombia – DIB, Project Code Quipú No. 201010020493.

Author's contributions

All authors contributed equally to the work. Authors have no competing financial interests.

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