

## Effect of fluoride and water content on the growth of TiO<sub>2</sub> nanotubes synthesized via ethylene glycol with voltage changes during anodizing process

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**Abstract.** In this work, titanium foils were anodized in ethylene glycol solutions containing different amounts of water and fluoride to determine their effects on the top morphology and crystalline structure of the formed titania nanostructures. Anodizing was performed for 2 h by using titanium foils as both anode and cathode applying a squared-pulse voltage profile composed of one step at 80 V for 3 min followed by another at 20 V for 5 min; constant voltage conditions were also used to study the nanostructure formation on the surface. We found the formation of nanostructured titania on the surface of the anodized foil when small amounts of water and fluoride are present in the anodizing solution. The top of these nanostructures is irregular when no water is added, but is expected to change with different amounts of water and fluoride in the ranges of 1 - 9 % and 0.05 - 0.5 %, respectively. Synthesis parameters also change nanotube morphology. The morphology and structure properties of the samples were studied by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Formation of TiO<sub>2</sub> nanotubes by anodization method are strongly correlated to conditions like fluoride concentration and applied voltages. Tube length varying between 2 and 7 µm, exhibiting different diameters and wall thicknesses were obtained. When an alternate voltage was applied, the wall of the nanotubes presented evenly spaced rings while nanotubes with smooth wall form were observed when constant voltage was applied. Reflection peaks corresponding to Brookite, Anatase, and Rutile of TiO<sub>2</sub> phases were observed from XRD measurements. A correlation between the effects of synthesis parameters on nanotube formation and morphological properties is presented. TiO<sub>2</sub> nanotubes prepared by electrochemical anodization have excellent performance in various applications such as photocatalysts, solar cells, gas sensors, and biomedical applications.

### 1. Introduction

The main achievements of technology based on foils or semiconductor thin films and oxide materials have contributed to the development of optical, microelectronic, and nanoscale devices. This has generated important interest in the study of optical, structural, mechanical, and electrical properties for



several applications [1]. One-dimensional nanostructures, like nanotubes, nanowires and nanorods began with the discovery and development of carbon nanotubes [2] and their high impact upon nanotechnology systems due to their molecular geometry and interesting properties such as high electron mobility, the effects of quantum confinement, and high specific surface area, among others [3-5].

Titania or titanium dioxide ( $\text{TiO}_2$ ), as part of oxide materials, is used in different applications including photocatalysis [6], dye sensitized solar cells (DSSC) [7], gas sensors [8], paints [9], biomedical devices [10], and the food industry [11]. Compared to other methods such as chemical vapor deposition (CVD) [12], sol-gel synthesis [13], hydrothermal [14] and magnetron sputtering deposition [15], the electro-chemical anodization method is regarded as one of the simplest techniques to obtain  $\text{TiO}_2$  nanotubes with large internal surface area without a concomitant decrease in geometric and structural order [16].

Anodization parameters play an important role on the titania nanotube formation with characteristics defined in their form, length, pore or tube diameter, thickness and pore-pore distance. Titanium dioxide nanotubes by electrochemical anodization method were reported using a titanium foil in acid electrolyte HF [17]. Other studies have reported that the crystalline structure of the titania nanotubes is characterized by a mix of anatase and rutile phases that changes with the annealing process [18].

This work presents a detailed study of the dependence of anodization parameters on  $\text{TiO}_2$  nanotubes by electrochemical anodization method, using ethylene glycol with voltage changes during the anodizing process. Structural and morphological properties were studied via X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was observed that tube length varying between 2 and 7  $\mu\text{m}$ , exhibited different diameters and wall thicknesses formations. When alternate voltage was applied, the outer wall of the nanotubes presented evenly spaced rings, while it was smooth when constant voltage was applied.

## 2. Experimental procedure

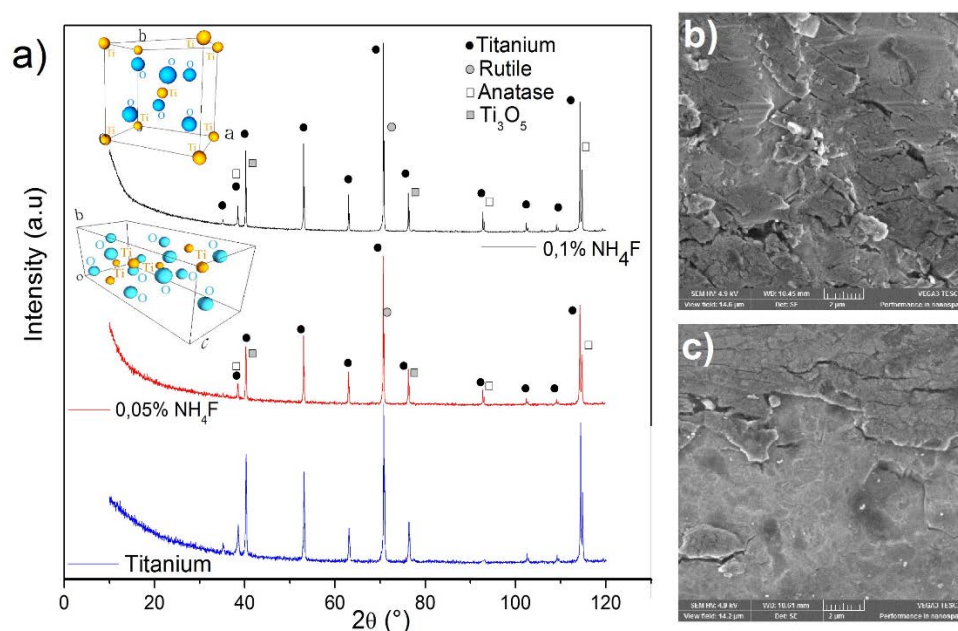
Prior to the anodization process, the Ti foils used in this study were cleaned with methanol at room temperature and air dried after that. The titanium foils used in this work were a 99.97% pure. The  $\text{TiO}_2$  nanotubes were prepared from Ti substrates 2 x 4 cm in size with 50  $\mu\text{m}$  thickness. An ethylene glycol solution, deionized water, and ammonium fluoride ( $\text{NH}_4\text{F}$ ) were used in the mixture. All samples were fabricated at 300 K.

During the first stage of fabrication,  $\text{NH}_4\text{F}$  was dissolved in deionized water and mixed in 126 ml of ethylene glycol while being stirred at 120 rpm until obtaining a clear and uniform solution; subsequently, two Ti foils that work as the anode and cathode with 2 cm separation from each other were introduced into the solution while being stirred. Nanotubes were obtained from a solution containing between 0.05 - 0.5 w% of  $\text{NH}_4\text{F}$  and 1 - 9% of  $\text{H}_2\text{O}$  in ethylene glycol for 2 h. The anodizing process was performed by applying a squared-pulse voltage profile composed of one step at 80 V for 3 min, followed by another one at 20 V for 5 min. Additionally, constant voltage conditions were also used to study the nanostructure formation on the surface.

The samples were characterized through XRD measurements by using an Empyrean diffractometer (PANalytical) equipped with a Co- $\text{K}\alpha$  source: 1.7890 Å, 40 kV and 40 mA with a Bragg-Brentano configuration and Pixel<sup>3D</sup> 2X2 detector. X'Pert High-Score Plus software was used to compare the samples through Rietveld refined in the range of  $10^\circ \leq 2\theta \leq 140^\circ$  with angular steps of  $0.0001^\circ$ . The morphological characterization of the samples, through SEM measurements, was performed by using a microscope (VEGA3 SB) with a tungsten filament, an accelerating voltage of 4.89 kV in low vacuum conditions ( $10^{-3}$  mbar), and a XFlash Detector 410M.

## 3. Results and discussion

Figure 1a shows XRD patterns of the  $\text{TiO}_2$  samples changing from 0.05 to 0.1% ammonium fluoride concentration and maintaining other parameters constant: 9%  $\text{H}_2\text{O}$ , 126 ml ethylene glycol,  $T = 300\text{K}$ , squared-pulse voltage profile 80 – 20 V. In this figure the XRD pattern corresponding to the samples after the annealing process to  $T = 723\text{K}$  during 1 h. It is well known that an amorphous nature in all samples is presented when the samples are prepared by anodization method and, subsequently, their crystal structure changes with a high temperature anneal around 700 K [19]. Higher temperature anneals improve crystallinity, showing a mix of anatase and rutile phases on nanotube walls. However, in this case 9% of  $\text{H}_2\text{O}$  into ethylene glycol solution,  $\text{TiO}_2$  nanotubes formation on surface weren't observed. (Figure 1b). Figure 1b and 1c show SEM images of the  $\text{TiO}_2$  samples with 0.1 and 0.05%  $\text{NH}_4\text{F}$  concentration. It can be seen that the surface, after annealing at 723 K, is characterized by a uniform morphology and the absence of nanostructures with nanotube shape or other structures.



**Figure 1.** a) XRD of the  $\text{TiO}_2$  obtained with 9% of  $\text{H}_2\text{O}$  in ethylene glycol solution changing ammonium fluoride concentration: 0.10 % (black line) and 0.05 % (red line), Ti foil pattern (blue line); SEM images with b) 0.10 % and c) 0.05 %  $\text{NH}_4\text{F}$ . Inset shows atomic positions obtained for anatase and rutile phases.

From Figure 1, it was observed that crystalline structures are characterized mostly by the presence of Ti and rutile phases in relation to the anatase phase in the compound. Peaks located at  $42.07^\circ$  and  $78.35^\circ$  (Figure 1a) were associated to the  $\text{Ti}_3\text{O}_5$  phase, possibly formed during the anodization process due to high water concentration in the ethylene glycol solution. The  $\text{Ti}_3\text{O}_5$  phase is a transition metal oxide with an octahedral formation, where Ti is the transition metal ion with 3d orbitals and known to undergo phase transitions of crystal structures, electron transport, or magnetic properties. This transition is of the first order accompanied by a rapid decrease of resistivity and a rapid increase of the c axis and magnetic susceptibility, caused by heating to a transition temperature of about 460 K on a sample containing considerable amounts of elements other than titanium and oxygen [20]. Rutile and anatase phases were identified from PDF files 01-088-1174 and 00-021-1272, respectively, and compared to peak positions obtained by XRD measurements (Figure 1); that is,  $70.87^\circ$  for the rutile phase and  $114.82^\circ$  for the anatase phase.

The inset in Figure 1a shows the crystal structure of the anatase and rutile phases simulated from the crystalline parameters (obtained from XRD) and reported in Tables 1 and Tables 2, respectively.

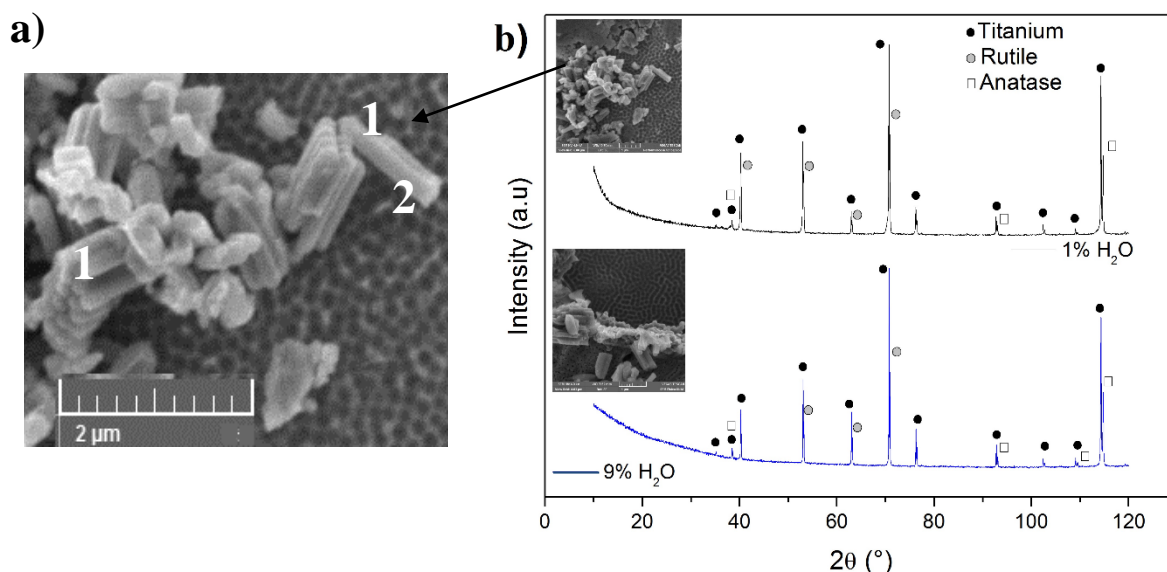
**Table 1.** Crystalline parameters of anatase phase.

| Crystalline parameters |             |              |                          |                    | Atomic Positions |      |       |   |
|------------------------|-------------|--------------|--------------------------|--------------------|------------------|------|-------|---|
| a (Å)                  | b (Å)       | c (Å)        | Space Group              | N° Space Group     | Element          | X    | Y     | Z |
| 3,77                   | 3,77        | 9,48         | I4 <sub>1</sub> /amd     | 141                | Ti               | 0,25 | 0,375 | 0 |
| $\alpha$ (°)           | $\beta$ (°) | $\gamma$ (°) | Volume (Å <sup>3</sup> ) | Crystalline System | O                | 0,25 | 0,167 | 0 |
| 90                     | 90          | 90           | 135,25                   | Tetragonal         |                  |      |       |   |

**Table 2.** Crystalline parameters of rutile phase.

| Crystalline parameters |             |              |                          |                    | Atomic Positions |        |        |   |
|------------------------|-------------|--------------|--------------------------|--------------------|------------------|--------|--------|---|
| a (Å)                  | b (Å)       | c (Å)        | Space Group              | N° Space Group     | Element          | X      | Y      | Z |
| 4,53                   | 4,53        | 2,92         | I4 <sub>2</sub> /amd     | 136                | Ti               | 0      | 0      | 0 |
| $\alpha$ (°)           | $\beta$ (°) | $\gamma$ (°) | Volume (Å <sup>3</sup> ) | Crystalline System | O                | 0,3039 | 0,3039 | 0 |
| 90                     | 90          | 90           | 56,94                    | Tetragonal         |                  |        |        |   |

Figure 2 shows X-ray spectra of the TiO<sub>2</sub> samples, changing H<sub>2</sub>O concentration in the ethylene glycol solution by 9% (blue line) and 1% (black line). The other parameters were maintained constant: ammonium fluoride concentration of 0.05%, squared-pulse voltage profile composed of one step at 80 V for 3min, followed by another one at 20 V for 5 min; anodization time of 2 h and environment temperature during the anodization process. Anatase and rutile phases were observed in all samples after annealing at T = 723 K.



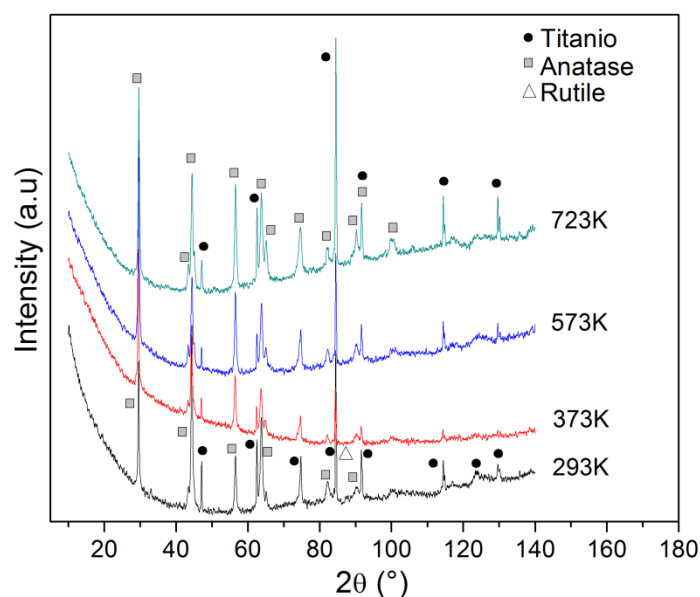
**Figure 2.** a) Magnification of SEM micrograph for the sample with 1% H<sub>2</sub>O (where 1- is tubes closed at the bottom and 2- is tubes open at the top.) and b) X-ray diffractogram of the TiO<sub>2</sub> obtained with 1% (black line) and 9% (blue line) H<sub>2</sub>O in ethylene glycol solution. In the inset, SEM images are showed for each one.

For main peak  $2\theta = 70, 69^\circ$  (see Figure 2) is possible to observe Ti and anatase phases contribution for all samples; while, Ti<sub>3</sub>O<sub>5</sub> phase was not observed due to low amount of oxygen in the solution. Other studies has been reported with a similar behavior [20].

On the other hand, the inset in Figure 2b shows SEM images for TiO<sub>2</sub> samples with 0.15 and 0.05% ammonium fluoride concentration, prepared at an alternate voltage of 80 – 20 V. Figure 2a was shows

the surface exhibits the tubes open on the top and closed at the bottom, nearly parallel and closed down. At the bottom on the surface of Ti foil, traces of the tubes were observed when they were detached from the solid TiO<sub>2</sub> layer.

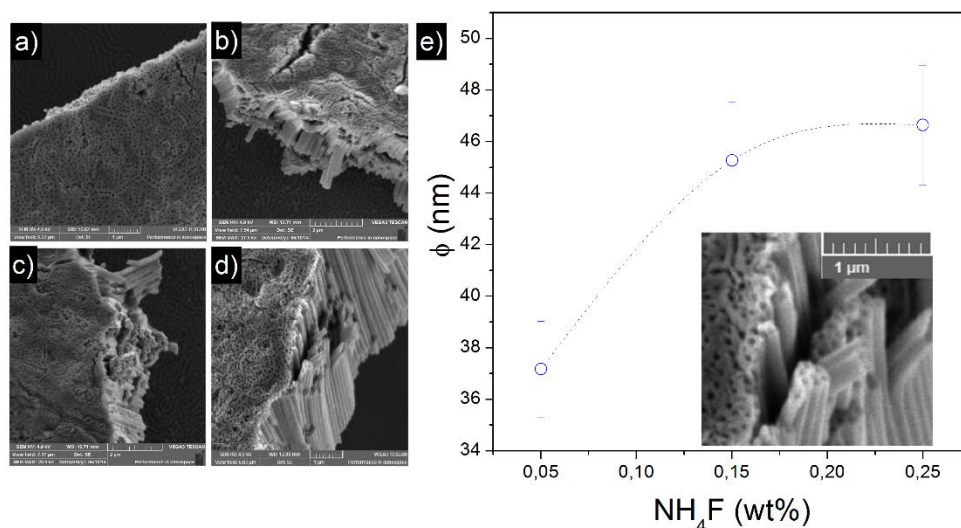
Figure 3 shows the XRD pattern of the TiO<sub>2</sub> sample when subjected to the annealing process varying temperature between 293 and 723 K. A sample was prepared by using NH<sub>4</sub>F concentration varying from 0.05% to 0.25% (2% H<sub>2</sub>O into solution) and constant voltage of 80V for 45 min. From the annealing process a decrease in the amorphous fraction of the material was observed, together with a change in the crystalline structure. An anatase phase was obtained from a TiO<sub>2</sub> sample with a high presence in the material at T = 723 K.



**Figure 3.** XRD pattern for the TiO<sub>2</sub> sample prepared with 2% H<sub>2</sub>O, 0.25% NH<sub>4</sub>F, and constant voltage 80 V.

Both, alternate and constant voltage conditions were used to study the topographic and morphological properties of nanotube formation on the surface; it has been reported that sidewall inhomogeneity is associated to current fluctuations [16], but studies on voltage change on nanotube formation have yet to be reported. It was observed that, when alternate voltage was used for nanotube preparation, these were small and thick-walled (Figure 2a); while, the application of a constant voltage allowed for nanotube formation with a length of  $2.97 \pm 0.19 \mu\text{m}$  with thin walls (Figure 4e).

Figure 4a-d) shows SEM micrographs of the TiO<sub>2</sub> sample subjected to annealing process and shown in Figure 3.



**Figure 4.** a-d) SEM micrographs of the TiO<sub>2</sub> sample varying annealing temperature 293, 373, 573, and 723 K; e) variation of inner diameter of titania nanotubes ( $\phi \pm 4.30$  nm).

In these images (Figure 4), surface morphology is not altered by annealing times, as observed in the crystal structure (Figure 3). The inner diameter size for nanotubes was obtained, varying between 37 and 46 nm when NH<sub>4</sub>F concentration varied from 0.05 to 0.25% (Figure 4e). This indicates that the size of the nanotube diameter is greatly dependent on anodization parameters and, in this case, on the NH<sub>4</sub>F concentration for a constant voltage. From SEM images, values close 2  $\mu$ m in length and 29.56 nm in thickness of barrier layer were obtained with the nanotube arrays grown vertically on the Ti foil.

#### 4. Conclusions

Titanium dioxide nanotube arrays were successfully obtained by electrochemical anodization method, varying both voltage and NH<sub>4</sub>F concentration from 0.05 to 0.25% and the amount of water into the ethylene glycol solution. From the XRD pattern, the peaks corresponding to anatase and rutile phases were identified for a temperature range between 293 and 723 K. Irregular nanostructures were observed in different amounts of water and fluoride solutions in the ranges of 1 to 9 % and 0.05 to 0.25 %, respectively. From SEM measurements, the diameter of the nanotubes was obtained varying between 37 and 46 nm when NH<sub>4</sub>F concentration varied from 0.05 to 0.25%. Values around  $2.98 \pm 0.19$   $\mu$ m length and  $29.56 \pm 1.93$  nm in diameter were obtained with constant voltage.

#### 5. Acknowledgments

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