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## The role of anodizing potentials in making TiO<sub>2</sub> nanotubes in (ethylene glycol / NH<sub>4</sub>F /water) electrolyte

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### ABSTRACT

Titania (TiO<sub>2</sub>) nanotube is considered a very important material due to its promising applications in many fields ranging from energy harvesting to sensors and photocatalytic applications. TiO<sub>2</sub> nanotubes were grown electrochemically in Plexiglas cell, the Ti foils (99.96%) serves as anode and platinum foil as cathode while the electrolyte was ethylene glycol containing (0.5%) NH<sub>4</sub>F and (4%) de-ionized water at 20°C for one hour. The effect of anodizing voltages at the range 10 to 100V is studied by extensive current / voltage plots and microstructure examination using SEM, and AFM techniques. All potentials were led to highly ordered nanotubes but they have different micrographic parameters; tube length, tube diameter and tube wall thickness, a role these parameters with the values of anodizing potentials are investigated.

**Keywords:** TiO<sub>2</sub> nanotubes (TNTs), anodizing titanium oxide (ATO), highly ordered nanotubes

### INTRODUCTION

Nano-sized objects show a great variety of interesting properties and this is the main driving force of the research in the field of nanotechnology today. The anodization of some metals, (ex;Ti,Al), under suitable conditions, leads to the formation of ordered arrays of pores in an oxide matrix. This technique has implemented and is now able to tune pore diameter and period.

Highly ordered vertically oriented TiO<sub>2</sub> nanotube arrays outperform their colloidal counterpart for applications including sensors[1], water photoelectrolysis[2-3], Photocatalytic degradation of gas pollutants[4], dye-sensitized solar cells[5], and for super capacitors [6]. In addition to biomedical applications including biosensors, molecular filtration, drug delivery and tissue engineering[7]. Furthermore, initial investigations indicate that they also may be useful for energy storage devices such as Li-ion batteries, and super- capacitors [8]. The widespread technological use of titania is impaired by its wide band gap (3-3.2eV) which can be narrowed by different methodologies. The anodization method has attracted the most interest among the other fabrication methods due to its ability to produce integrative, vertically oriented highly ordered nanotube arrays with controllable dimensions [9]. This study aims at investigation of the effect of anodizing voltages on morphology, dimensions, and degree of order of the grown titania nanotubes.

### MATERIALS AND METHODS

Titanium (Ti) metal foils (99.7% purity of Alfa aesar), rectangular piece of 1.5\* 1.0 cm and 0.25 mm thick, were cut out of a sheet, then degreased by ultrasonic treatments in de-ionized water (DI>3μs.sec), and ethanol for 10 min. The Ti foils were then anodized in homemade Plexiglas cell using a two electrode configuration, with Ti foil as anode and a platinum electrode (99.9% Sigma-Aldrich) with thickness of 0.1 mm, served as a cathode, the separation

between the two electrodes was 2.0 cm, the electrolyte was 0.5 wt %  $\text{NH}_4\text{F}$  (98% Sigma-Aldrich) with 4ml (DI) in ethylene glycol (Anhydrous, 99.8%, Sigma Aldrich). Anodization was carried out at different voltages in the range between 10 to 100 v ,the temperature kept constant at 20°C by circulating cooled water through copper coil warped around the Plexiglas cell ,the anodizing duration was 1hour in all experiments. In each case the voltage was held constant using a DC voltage supply, during anodization period the current (mv throw  $1\Omega$  resistance) & voltage were recorded for time monitoring using two channels millivoltmeter XY recorder (siemense8800) as shown in schematic diagram in figure.1. The anodized samples were cleaned with distilled water to remove the occluded ions from the anodized solutions, and dried in a nitrogen gas then annealed at 500 C for 3hours. The produced anodized titanium oxide nanotubes (ATO) were examined for morphology and topography investigation by Scanning Electron Microscopy (Hitachi 4500) and Atomic Force Microscopy (AFM-AA3000 of Angstrom Advanced Inc.).

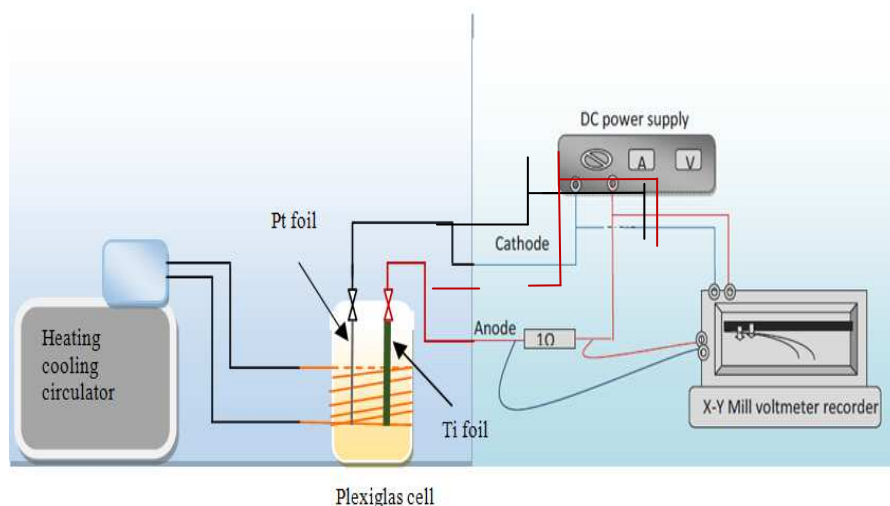


Figure 1. Setup of Titanium anodizing apparatus

## RESULTS AND DISCUSSION

### 3.1 Current –Voltage behaviors

The I-V behaviors during anodizing time was recorded , always and for all process potentials (10 to 100 v ) ,the current start to increases suddenly and reaches a maximum point at the first (3-5 min) ,then a fast decays of the current started until a steady reading was recorded which remained nearly constant for the rest time of the process, as shown in figure (4-1). Recently some workers published on the formation of metal oxides by anodization and analyze the formation thermodynamically and mechanistically[10].

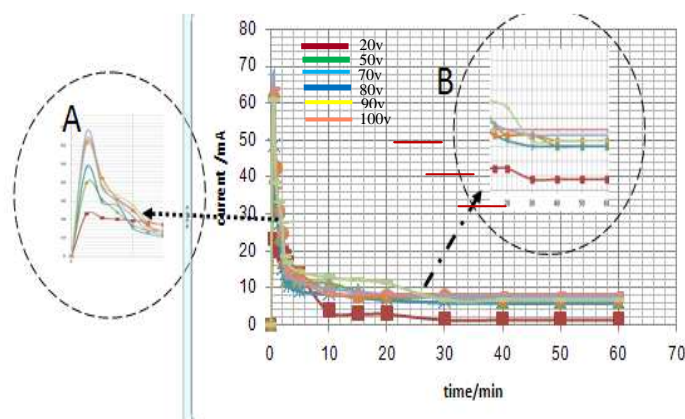


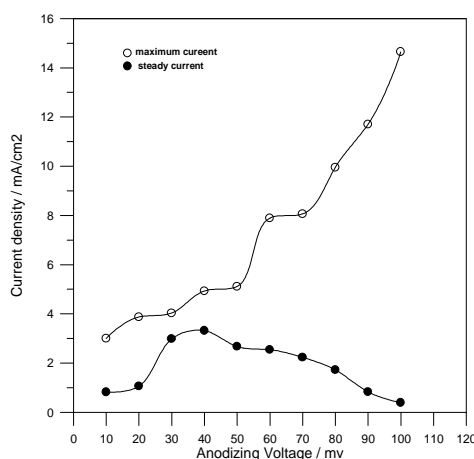
Figure 2. The variation of current against time at different anodizing voltages of Ti foil in 0.5 wt %  $\text{NH}_4\text{F}$  4ml (DI) in ethylene glycol for 1 hour at 20°C, section A represent maximum current, section B represent steady stat current

In spite of the similarity of the I-V behavior at all potentials ,but a differences in the values of maximum current density, the steady stat current density ,and the time of reaching them ,table 1 show all these parameters:

**Table 1** time of reaching maximum and steady currents of anodizing of Ti foils in (95.5wt% ethylene glycol, 4wt% H<sub>2</sub>O and 0.5wt %NH<sub>4</sub>F), at different anodizing potentials

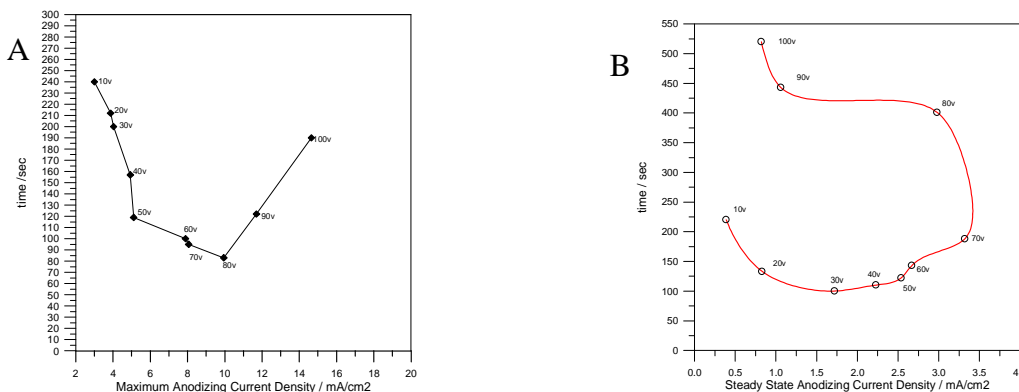
Anodizing Potentially/volt	Max/current density mA/cm <sup>2</sup>	Time second	Steady Current density mA/cm <sup>2</sup>	Time second
10	3.00	240	0.82	520
20	3.87	212	1.06	443
30	4.03	200	2.98	401
40	4.93	157	3.32	188
50	5.11	119	2.67	143
60	7.89	100	2.54	122
70	8.06	95	2.23	110
80	9.95	83	1.72	100
90	11.70	122	0.83	133
100	14.65	190	0.39	220

The data showed that the current was increased with increasing process potentials at the first 1-4min, this behavior is expected to occurs according to ohm's low ( $I=V/R$ ), this stage of anodizing process is responsible for making full coverage of TiO<sub>2</sub> on the Ti surface. The maximum current density always increased with increasing anodizing voltages, while the steady state current density increases with increasing potentials till reaching 40 v dc, then the current decreased with increasing voltage reaching minimum value at 100 v dc, figure (3).



**Figure 3.**The variation of maximum current and steady current against anodizing voltage of Ti foil in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C

The time required to reach maximum current showed mainly two manners : the first was that time was decreased with increasing potentials in the range of 10 to 80 v dc, while this time increased ongoing up to 100 v ,figure (3A), the time to reach the steady current shown in figure (3B).These behaviors may be attributed to the variation of the tubes properties (diameter, length, and wall thickness) of the new Ti-TiO<sub>2</sub> formed after reaching the maximum current step.



**Figure 4.**The variation of; A-maximum current ,and B-steady current against anodizing time of Ti foil in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C

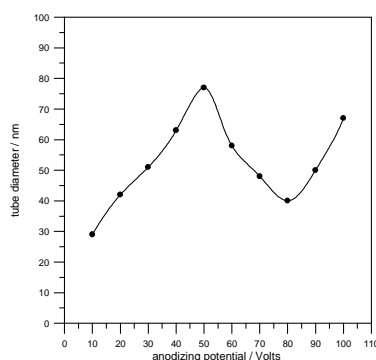
### 3.2. The morphologic Examination:

The prepared TNT's were subjected to extensive SEM and AFM examination ,an information about ;tube diameter ,tube length , tube wall thickness , and degree of the order of the TiO<sub>2</sub> arrays were obtained , the measurements conducted on SEM images using (Imager J) software, are tabulated in table (2).

**Table 2. Variation of TNT's parameters (length, diameter, and wall thickness) against anodizing voltages of Ti foil in 0.5 wt % NH<sub>4</sub>F and 4ml (DI) in ethylene glycol at 20°C**

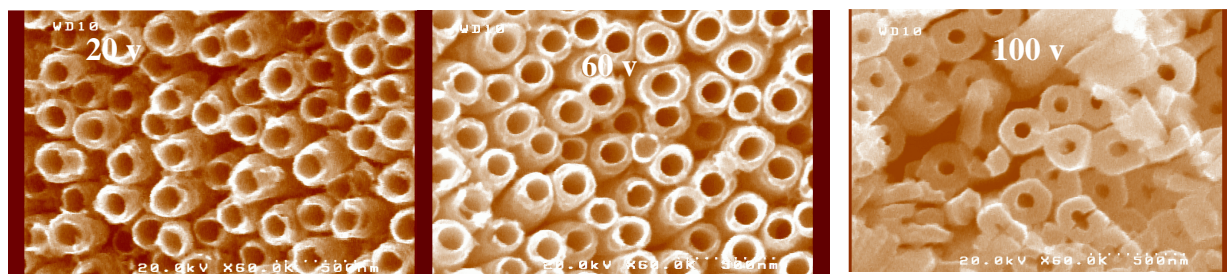
Anodizing potential V	Tube diameter nm	Tube length nm	Tube wall thickness nm	Cell Diameter nm	Degree of order
10	38	780	33	104	bad
20	54	845	29	112	v.good
30	62	1900	31	114	v.good
40	68	2200	22	112	good
50	80	3010	26	132	v.good
60	65	7000	30	125	good
70	58	8000	25	108	bad
80	48	8200	26	100	good
90	63	9500	39	141	v.good
100	70	5000	48	166	v.good

The variation of tube diameters with increasing the anodizing potentials showed three different manners ;the first was at the range 10 v to 50 v ,in which the diameter increases with increasing potentials and this agrees with the result in a similar work of others [11-13] ,so it was around 40 nm when the potential was 10 v , and increased up to higher potentials and became around 80 nm on reaching 50 v, the second behavior have seen at the range 60 to 80 v ,at which the diameter decreased with increasing potential , they were around 65 nm at 60 v,and became nearly 48 nm on reaching 80 v ,figure 6,the last variation way appeared at the potentials of 90 and 100 v , the diameter started to increases again with increasing voltage as shown in figure (5).



**Figure 5. Tube diameters against anodizing potentials. of prepared ATO in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C**

Images in figure (6) reflect the variation of tube diameters, and tubes wall thickness with anodizing potentials of 20, 60, and 100 v.



**Figure 6. SEM images top views of ATO prepared in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C and anodizing potentials of 20,60,and 100 v.**

The length is almost increases with increasing potentials this fact agree with many works of others [14-18], except that of 100 v which was shorter than 90 v, figure (7), this may attributed to the dominate of the rate of oxide dissolving step over the rate of oxide formation one, the maximum length that achieved was at 90 v, it was around 10 microns.

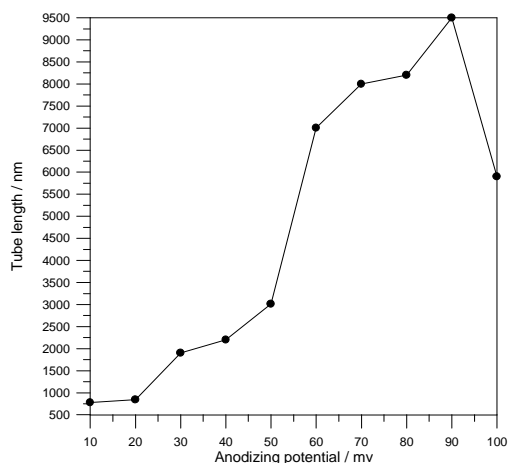


Figure 7. Tube length against anodizing potentials, of prepared ATO in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C

figure (8) show SEM images that revealed the tube length at different anodizing voltages(20,40,60,90,and100v);

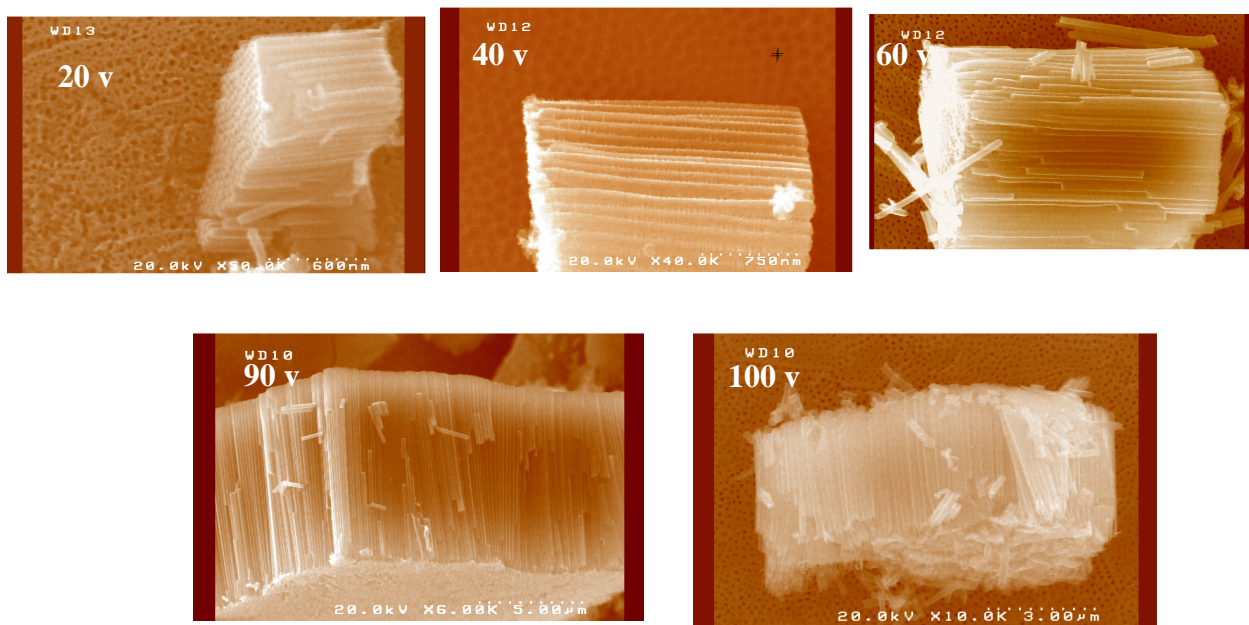


Figure 8. SEM images reflect the length of prepared ATO in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C at different anodization voltages

Somehow similar results achieved using AFM images, and highly accurate ATO cell dimensions measured , figure 9 show 2D and 3D views by AFM contact mode scan:

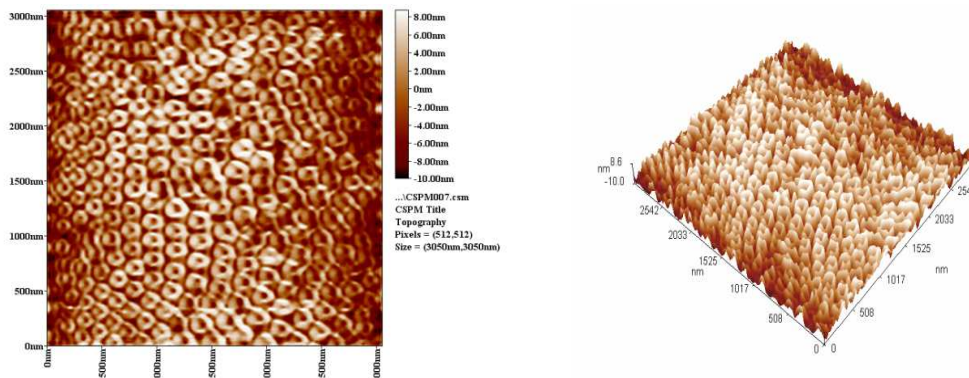


Figure 9. 2D and 3D AFM views of ATO produced in 0.5 wt % NH<sub>4</sub>F 4ml (DI) in ethylene glycol at 20°C and 60 v

The roughness report was deduced by Imger 4.2 software show that for the longest ATO arrays which formed using 90 v , the R average was equal to 1.54 nm and the RMS was 1.96 nm and the surface yield (peak-peak) was 14.2nm.

A footprint were established by AFM scans with three types of contact mode images includes; topography, deflection, and lateral force for the back of free stand ATO template prepared at 50 v and removed by double sided adhesives and mounted on microscopic glass slide, a novel pictures for a TNT honey combs structures were recorded at several magnifications starting from several thousand of microns going to single unit cell with, as shown in figures 10 (a, b, and c)

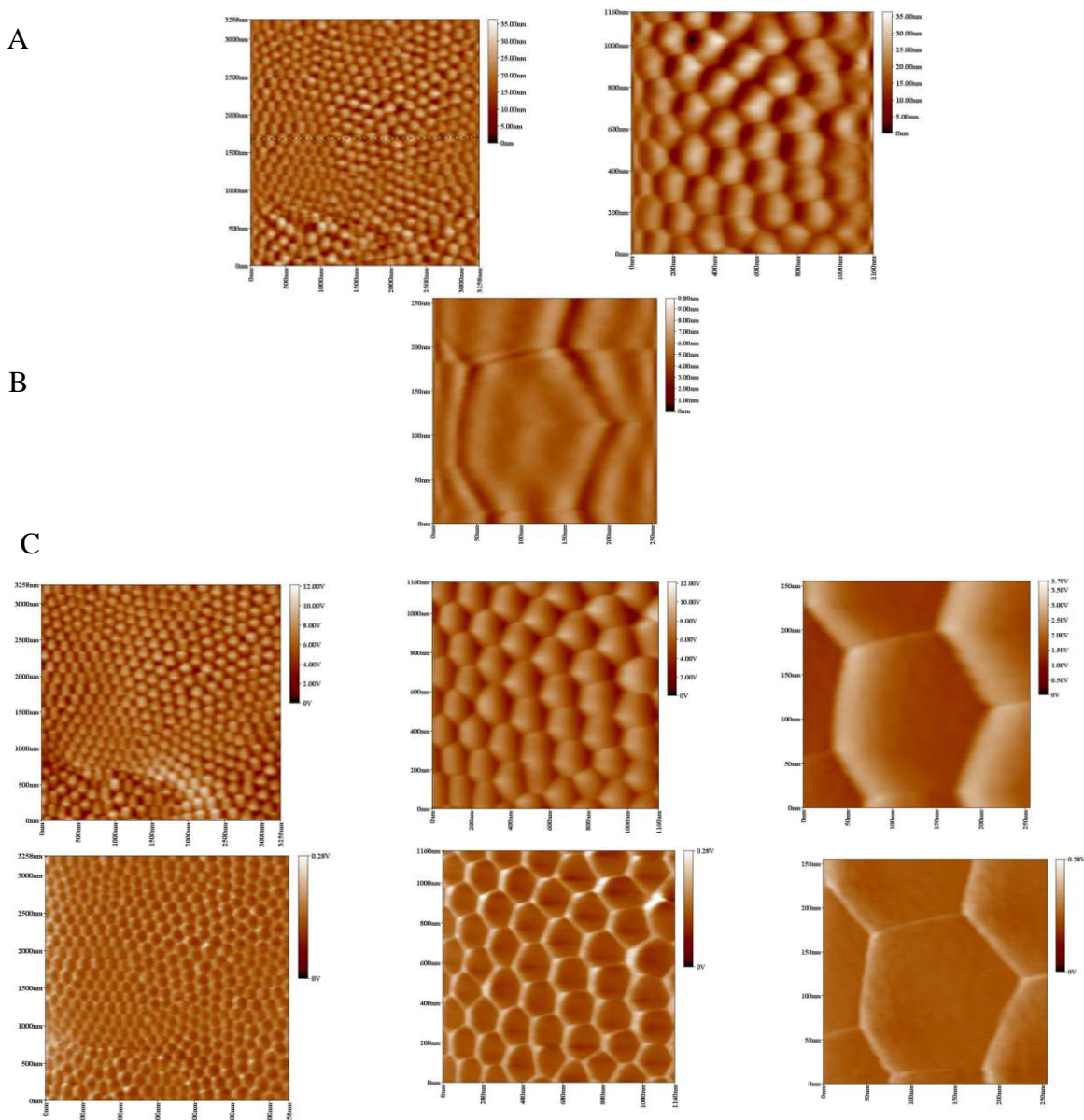


Figure 10. Different magnification AFM images of TNT prepared at anodizing potential of 50 V for 1 hr; A-topography, B-deflection, and C-lateral force

The deflection and lateral force images revealed more detailed surface structure than the topography images.

### CONCLUSION

Highly ordered titania nanotubes (TNTs) were prepared via anodizing in ethylene glycol containing (0.5%)  $\text{NH}_4\text{F}$  and (4%) de-ionized water at 20°C and different anodizing potential for one hour, the current / voltage profiles showed behaviors related to the microstructure of the produced template.

The morphologic properties of the TNTs are strongly affected by anodizing potentials in the range 10 to 100 v, the diameters ranged between 40 and 70 nm, maximum length of about 10 microns achieved at 90 v. Lateral force and deflection AFM images showed more detailed surface structures than AFM topographic images.

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