

## Development and Morphology of Titanium Nanotubes Anode for New Generation Solar Cell by Electrochemical Anodizing Method

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This work investigated the effects of parameters of the anodization process on the geometrical features of the Titanium nanotubes anode. The topography of Titanium nanotube diameter and length had been affected without usage of magnetic stirrer by applying at three different DC voltage. In this study, we had synthesized Titanium nanotube arrays by electrochemical anodization of Ti foil by direct current (D.C.). Ethylene glycol and ammonium fluoride electrolyte was used to study the development of nanotubes above atmospheric temperature with varying D.C voltages. Then the Ti foil was annealed to form anatase for one hour in a muffle furnace. High Resolution Scanning electron microscopy, UV-vis spectroscopy and X-ray diffraction were used to characterize the Ti thin film nanotubes anode. HRSEM revealed the topography of the titanium nanotubes anode. At 60 V to 30 V, the mean tube diameter was 57.34 nm. At 50 V to 25 V, the mean tube diameter was 97.64 nm. At 40 V to 20 V, the mean tube diameter was 122.45 nm.

**Keywords:** Nanotube anode, Titanium nanotubes, HRSEM, TNT arrays.

### Introduction

The last decade had seen comprehensive research on self-aligned Titanium nanotube arrays. Well-aligned, vertically oriented Titanium nanotube arrays were synthesized by the anodization method. Titanium dioxide is the most attractive semiconductor having the unique property to withstand nontoxic, photo-corrosion and low cost. Unfortunately, it is having a wide bandgap (for anatase 3.2 eV and rutile 3.0 eV). Titanium nanotube arrays have outstanding properties such as charge transport and carrier lifetime property useful in a wide range of applications in many areas, such as dye sensitized solar cells<sup>1-3</sup>, sensors<sup>4-6</sup>, generation of hydrogen by photoelectrolysis method<sup>7-9</sup> and supercapacitors<sup>10</sup>. Furthermore, Titanium nanotube arrays have been used in other areas, such as in biomedical field related applications including for molecular filtration, biosensors, drug delivery system and tissue engineering technology<sup>11-13</sup>. The literatures have a number of investigating reports on the synthesis of Titanium nanotube arrays. Gong *et al.* had examined the well-aligned Titanium nanotube arrays of up to a 500 nm tube length by the electrochemical oxidation process of titanium foil in

an aqueous electrolyte of HF<sup>14</sup>. In the second generation synthesis, Cai *et al.*<sup>15</sup> changed the pH values of both NaF and KF aqueous electrolytes to minimize the chemical decomposition of the oxide and increased the length of Titanium nanotube arrays to several microns. The growth rate of nanotube was approximately 0.25 mm/h. Allam *et al.* investigated a fourth generation of nanotube arrays by a Titanium anodization method with the help of non-fluorine bearing chemicals, particularly HCl<sup>16,17</sup> and the combination of HCl with H<sub>2</sub>O<sub>2</sub><sup>18</sup>. The properties of Titanium nanotube arrays depended on their geometrical dimensions such as tube length, tube wall thickness, tube wall roughness, tube diameter and space between the nanotubes. The geometrical dimensions of the Titanium nanotube arrays growth have been restricted by a number of anodization parameters including the anodization voltage, composition of electrolyte and electrolyte properties such as conductivity, viscosity as well as the anodization temperature and time. This work looked into the electrochemical anodization method with organic electrolyte such as ethylene glycol in combination with NH<sub>4</sub>F. The X-ray diffraction method has been utilized to study the crystal structure of the fabricated anodic thin film.

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### Materials and Methods

Grade-2, 99.6% purity Ti foil was purchased from Ti TEK UK LTD, Birmingham, UK. Ti foil of size (10×10×0.45mm) has been serially rinsed in acetone, ethanol and deionized (DI) water. The electrochemical anodization process has been conducted in a two-electrode arrangement with titanium thin foil as anode electrode and stainless steel foil as the cathode electrode. A power supply was used for DC voltage to operate the anodization process. The distance between the anode and cathode was kept at about 2.5 cm. Three different samples were anodized in a combination of 0.77 wt %  $\text{NH}_4\text{F}$  and 7 vol.% deionized water in ethylene glycol as electrolyte.

The Titanium nanotube arrays have been developed by applying three anodization voltages with a 1.5 hours of anodization process time, above room temperature and without stirrer operation in same electrolyte composition in the Lab. In scenario 1, the first type of nanotube arrays was grown using anodization voltage of 40V for 45 minutes and after 15 minutes break, 20V was supplied for another 45 minutes without stirrer. Anodization temperature was maintained between 35°C to 37°C and the amorphous Titanium nanotube arrays were annealed at 500°C for 1 hour in a muffle furnace at the heating rate of 10°C /4 minutes. In scenario 2, the second type of nanotube arrays was grown using anodization voltage of 50V for 45 minutes and then voltage was reduced at the rate of 1V per second up to 25V and then the same 25V was supplied for another 45 minutes without stirrer. Anodization temperature was maintained between 35° C to 36° C and the amorphous Titanium nanotube arrays were annealed at 470°C for 1 hour in a muffle furnace at the heating rate of 10°C /4minutes. In scenario 3, the third type of nanotube arrays was grown using anodization voltage of 60V for 45 minutes and then voltage was reduced at the rate of 1V per second up to 30V and then the same 30V was supplied for another 45 minutes without stirrer. Anodization temperature was maintained between 27° C to 41°C. The as-prepared amorphous Titanium nanotube arrays were annealed at 470°C for 1 hour in a muffle furnace at the heating rate of 10°C /4minutes.

### Characterization

The morphology of the anodized samples was analyzed by high resolution scanning electron microscopy (HRSEM, AU Quanta250FEG). Titanium nanotubes structural characterization was done by

X-ray diffraction (XRD, Flat stage PW 3050/60) using  $\text{Cu K}\alpha$  radiation, at 40 kV and current of 30 mA. The scan range was 10.0167° to 79.9767°, 5 minutes with a scanning rate 12.7°/Sec. UV-vis spectroscopy (Erkin Elmer Lambda 750, USA) showed the maximum absorbance edge at 610 nm wavelengths. The back of the samples was scratched badly with a diamond cutter and bent mechanically, for the cross sectional images of nanotube arrays. A small piece of Titanium oxide thin film was prepared for the cross sectional HRSEM images of nanotube arrays.

### Results and Discussion

Different anodizing parameters led to different morphology Titanium nanotube arrays. Fluorine-containing electrolytes were the most efficient electrolytes for the anodic formation of Titanium nanotube arrays. Titanium nanotube arrays have been fabricated by the self-formation of  $\text{TiO}_2$  as a result of the fragile balance of the electrochemical oxidation of Ti to  $\text{TiO}_2$ , the anodization potential stimulated suspension of  $\text{TiO}_2$ , and the chemical suspension of  $\text{TiO}_2$  by fluorine ions in the electrochemical anodization method.

#### High Resolution Scanning Microscope (HRSEM)

This study examined the effects of both the organic electrolyte and the anodization potential for the formation of  $\text{TiO}_2$  nanotube arrays. Figure 1-(A) shows HRSEM images of the surface topology of Titanium nanotube arrays obtained by anodizing a Ti foil under three different DC voltages of 40V-20V, 50V-25V and 60V-30V for 1.5 hours. The nanotube diameter and length were changed with the applied different DC voltages. The HRSEM result shows the nanotube arrays with diameter value. The mean inner diameter of the first type of nanotube was 122.4 nm at 40V-20V condition for 1.5 hours. The mean inner diameter of the second type of nanotube was 97.64 nm at 50V-25V condition for 1.5 hours. The mean inner diameter of the third type of nanotube was 57.34 nm at 60V-30V condition for 1.5 hours. The well structured nanotubes with its mean diameters were obtained. Nanotubes grown at 40V-20V for 1.5 hours had a larger mean diameter, than nanotubes grown at 50V-25V for 1.5 hours and 60V-30V for 1.5 hours. A mixture of 0.77 wt %  $\text{NH}_4\text{F}$  and 7 vol.% deionized water in ethylene glycol was used as electrolyte for fabrication of nanotubes. Figure 1-(A) shows lower and a higher magnification HRSEM image of

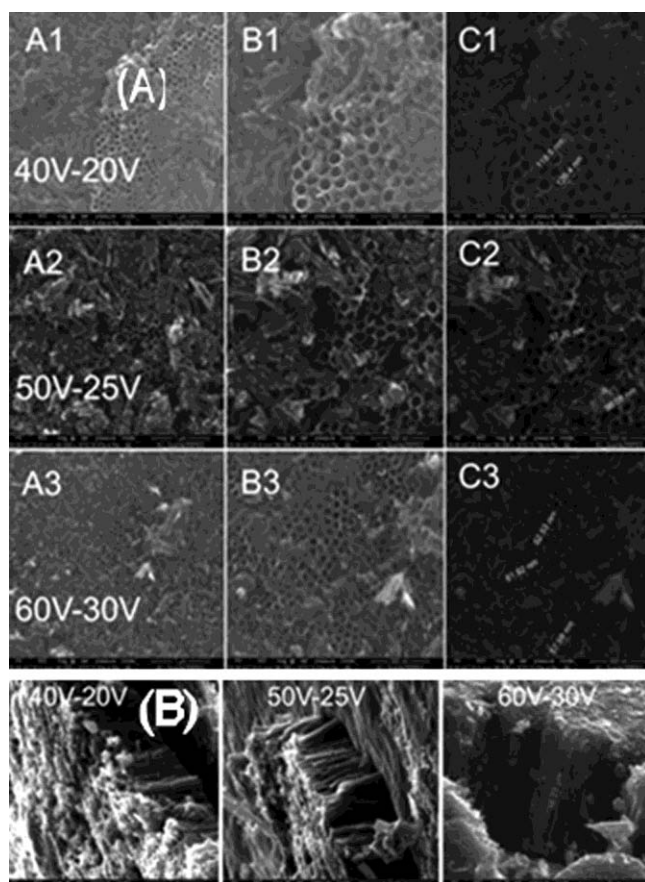
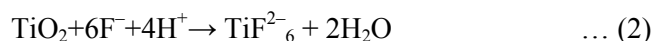
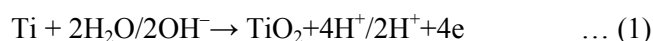


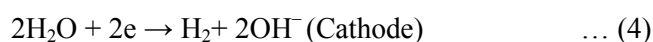
Fig. 1 — (A) HRSEM images of the surface topology of TiO<sub>2</sub> nanotube arrays at three different DC voltages (B) HRSEM images of the cross-sectional view of TiO<sub>2</sub> nanotube arrays at three different DC voltages

Titanium nanotube arrays. Figure 1-(B) shows a cross sectional morphologies of the nanotube arrays obtained at three different voltages with the same electrolyte composition. The length of the first type nanotube arrays at 40V-20V condition had 1.948μm. The length of the second type nanotube arrays at 50V-25V condition had 4.470μm. The length of the third type nanotube arrays at 60V-30V condition had 16.23μm. The diameter and length of the resulting nanotubes depended on not only the electrolyte composition and applied anodization voltage, but also the usage of magnetic stirrer in the anodization method. The HRSEM result revealed that the diameter and length of the nanotube arrays, the growth rate of tubes has been affected, due to non usage of magnetic stirrer. From this study, it is found that magnetic stirrer played important role in the growth of nanotube arrays. The magnetic stirrer helped to mix the ammonium fluoride in the DI water and ethylene glycol solution perfectly. Yasuda and

Schmuki<sup>19</sup>, studied the ion diffusion in the electrolyte with the growth of nanotube arrays in the thin film foil. In the case of Titanium nanotube arrays grown in organic electrolyte, the influence of DC voltage, magnetic stirrer would also be considered into account. Two kinds of diffusion processes are examined, namely the H<sup>+</sup> ion diffusion toward the cathode and F<sup>-</sup> ion diffusion toward the anode electrode. The following chemical reactions take place at the anode<sup>19-21</sup>, in the growth of Titanium nanotube arrays. The chemical reaction process of forming TiO<sub>2</sub> nanotube arrays was expressed by first equation. The second equation revealed TiO<sub>2</sub> dissolution by chemical formation.



Chemical reaction one was responsible for field-assisted oxidation process, while chemical reaction two helped in field-assisted dissolution. Nanotube growth had taken place, due to adjustment between these two chemical reactions. The fluorine ion is essentially a very important factor in the growth rate of nanotube arrays, in the absence of which only a thin titanium oxide layer was grown through chemical reaction one<sup>20-22</sup>. Without magnetic stirrer in the anodization method, mobility of ions and its reaction have been affected drastically and It leads to affect greatly the growth rate of nanotube arrays as per this study. The magnetic stirrer contributed to mix the NH<sub>4</sub>F in the DI water and ethylene glycol solution perfectly. The magnetic stirrer ultimately improved the mobility of fluoride ions in the electrolyte. Hence, the performance of chemical reaction in the electrolyte and the growth rate of nanotube arrays has been increased. In the present organic electrolyte required hydrogen ions originating mainly from field-assisted oxidation through chemical reaction to the growth of nanotube arrays. Emission of gas had been noticed from both titanium thin film foil and stainless steel thin film, foil surfaces in the first tens seconds after initiating the anodization method. This suggested the existence of the following chemical reactions under DC power supply condition. Lidong Sun *et al.* explained the chemical reactions of the following equations<sup>23</sup> during the anodization process.



We had considered a potential drop in the electrolyte, ionic flux at the front side of Titanium foil consisted of two parts which were ion diffusion under concentration gradient and ion migration under electric fields. In contrast, only ion diffusion existed at the front side of Titanium foil, as follows:

$$J_f = -pD \frac{\partial c}{\partial x} + ucE \quad \dots (5)$$

where  $J_f$  is the ionic flux at the front side of Titanium foil,  $p$  is the porosity of the nanotube arrays surface,  $D$  is the diffusion coefficient,  $c$  is the concentration,  $\frac{\partial c}{\partial x}$  is the concentration gradient,  $u$  is the ion mobility, and  $E$  is the strength of electric field in the organic electrolyte. In this anodization process theoretically, mass transport in the electrolyte solution happened by diffusion, convection, or migration. In this study, all the experiments had been carried out under above ambient temperature for 1.5 hours only, without stirring.

#### Visible light absorbance Test

Figure 2 shows the UV-vis spectroscopy of the nanotube arrays after annealing process. The visible light absorbance of  $\text{TiO}_2$  nanotube arrays on titanium foil have been recorded in the range of 300-800 nm. The first type of nanotube arrays fabricated at 40V-20V condition has exhibited maximum absorbance edge at wavelengths around 300nm to 610 nm. The second type of nanotube arrays fabricated at 50V-25V condition has exhibited maximum absorbance edge at wavelengths around 300 nm

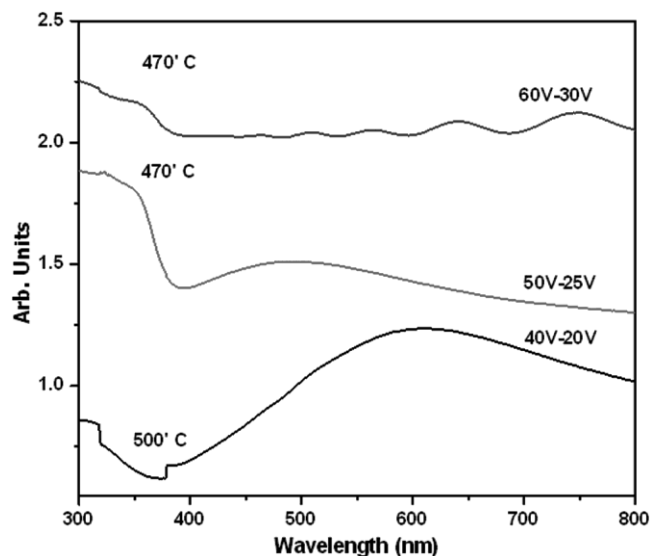


Fig. 2 — The UV pattern of the  $\text{TiO}_2$  nanotube arrays fabricated at 40V to 20 V, 50V to 25V, and 60V to 30V for 1.5 h and heat treated at 500°C, 470°C and 470°C for 1 h respectively.

to 500 nm. The third type of nanotube arrays fabricated at 60V-30V condition has exhibited maximum absorbance edge at wavelengths around 300 nm to 750 nm. From this UV-vis spectroscopy study of the nanotube arrays revealed that the third type of nanotube arrays fabricated at 60V-30V had maximum absorbance ability.

$$E_g = h \times (v/\lambda) \quad \dots (6)$$

$E_g$  is the band gap of Titanium nanotube arrays,  $h$  is the Plank constant,  $v$  is the speed of light and  $\lambda$  is the cut off wavelength of radiation generated by UV-vis spectroscopy.

#### XRD analysis

The X-ray diffraction analysis had been performed for crystal phase identification. After annealing, diffraction peaks of  $\text{TiO}_2$  were clearly investigated which could be referred to anatase. The first type nanotubes fabricated at 40V-20V condition showed a presence of anatase  $\text{TiO}_2$  with  $2\theta$  peaks at 24.9°, 37.5°, 38°, 39.8°, 52.6° and 70.3°. The second type nanotubes fabricated at 50V-25V condition showed a presence of anatase  $\text{TiO}_2$  with  $2\theta$  peaks at 38°, 39.8°, 52.7° and 70.3°. The third type nanotube arrays fabricated at 60V-30V condition showed a presence of anatase  $\text{TiO}_2$  with  $2\theta$  peaks at 38°, 39.8°, 52.6° and 70.3°. The average size of particles can be calculated from the XRD pattern of samples using Schere's equation. Figure 3 shows the X-ray diffraction analysis of annealed at different temperatures of

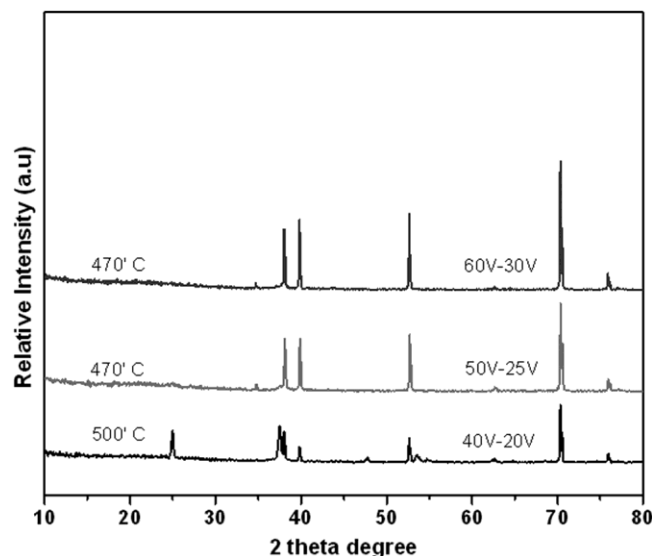


Fig. 3 — The XRD pattern of the  $\text{TiO}_2$  nanotube arrays fabricated at 40V to 20 V, 50V to 25V, and 60V to 30V for 1.5 h and heat treated at 500°C, 470°C and 470°C for 1 h respectively.

Titanium nanotube arrays. XRD patterns recorded at room temperature of the Titanium nanotube arrays, after annealing for 1 hour.

### Conclusion

The Titanium nanotube arrays have been synthesized successfully by anodizing method. This study examined the effect of without usage of magnetic stirrer in the anodization process. Surface and cross sectional morphologies of the Titanium nanotube arrays obtained at three different voltages with same electrolyte composition. The diameter and length of the resulting nanotubes depended on not only the electrolyte composition and applied anodization voltages, but also magnetic stirrer RPM in the anodization process. The HRSEM result revealed that the diameter and length of the nanotube arrays growth has been affected greatly, due to without usage of magnetic stirrer. From this study, We concluded that the magnetic stirrer played important role in the growth rate of nanotube arrays. From this UV-vis spectroscopy study of the nanotube arrays revealed that the third type of nanotube arrays fabricated at 60V-30V condition had the maximum absorbance ability then other two types.

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