

Effects of Electrolyte Natures on the Formation of Well-Ordered Titania Nanotubes Produced Via Anodisation

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Abstract: *The formation of well-ordered titania nanotubes is achieved by electrochemical anodisation under specific experimental conditions. In the present work, the formation of titania nanotubes on titanium substrates is investigated in two different electrolytes: Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$. The amount of fluoride was varied from 0.5 to 5 wt%. Scanning electron microscope (SEM), X-Ray diffraction (XRD), and Energy Dispersive X-ray (EDX) surface analyses were carried out to characterise the well-ordered titania nanotubes. The results show that the composition of electrolytes drastically influenced the final morphology of the titania nanotubes. Titania nanotubes with various diameters in the range of 20–100 nm and lengths of 0.3–0.7 μm were obtained by tailoring the electrochemical conditions during titanium anodisation. From the SEM images, it was evident that the well-ordered regular porous structure consists of pore arrays with a uniform pore diameter. It was also clear that pore mouths were opened on the top of the layer, while the tubes were closed by the presence of a layer of titania on the bottom of the structure. Here in, we discuss the influence of different electrolyte compositions on the structure of well-ordered titania nanotubes in detail. We furthermore show that the nanotubes consist of titania and that they remain unchanged when annealed.*

Keywords: titania nanotubes, anodisation, electrolyte composition, fluoride, annealing

Abstrak: *Nanotub titania tersusun teratur dihasilkan dengan menggunakan kaedah penganodan elektrokimia dalam suatu keadaan eksperimen tertentu. Dalam kajian ini, pembentukan nanotub titania di atas substrat titanium dalam dua jenis elektrolit; Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ telah diselidik. Kandungan florida diubah dari 0.5% ke 5% berat. Mikroskop elektron imbasan (SEM), teknik pebelauan sinar-X (XRD), dan penyerakan tenaga sinar-X (EDX) telah dijalankan untuk membuat perincian ke atas permukaan nanotub titania tersusun teratur. Keputusan menunjukkan komposisi elektrolit mempengaruhi morfologi nanotub titania yang dihasilkan. Nanotub titania dengan pelbagai diameter dalam julat 20–100 nm dan panjang dari 0.3–0.7 μm diperolehi dengan mengubahsuai keadaan elektrokimia semasa penganodan titanium. Berdasarkan imej SEM, maka terbukti dengan jelas struktur berliang tersusun teratur ini terdiri daripada liang yang mempunyai diameter yang seragam. Di dapati juga mulut liang struktur tiub tersebut terbuka pada lapisan atas manakala tertutup dengan lapisan titania pada bahagian bawah. Di sini, kami membincangkan kesan pelbagai jenis komposisi elektrolit terhadap pembentukan nanotub titania tersusun teratur dengan terperinci. Kami juga telah menunjukkan struktur nanotub titania tidak berubah apabila disepuhlandap.*

Katakunci: nanotub titania, penganodan, komposisi elektrolit, florida disepuhlandap.

1. INTRODUCTION

Over the years, titanium oxide, or titania, has been actively researched since it displays many unique properties that enable it to be utilised as an active component in renewable energy devices; specifically, photocatalysis, photoelectrolysis and photovoltaics.¹ Studies have indicated that, for these applications, well-arrayed titania nanotubes are of interest due to their one-dimensional (1D) nature, ease of handling and simple preparation. Not only can the band gap of the material be altered due to the quantum confinement effect, 1D nanoscale titania in nanotube form offers a larger surface area and, hence, higher photon absorption is expected.² Furthermore, titania nanotubes contain free spaces in their interior that can be filled with active materials such as chemical compounds, enzymes and noble metals, enabling them to be engineered to produce advanced materials of multi-functionality.³⁻⁶

To date, titania nanotubes have been produced by a variety of methods, including soft chemical,⁷ sol-gel⁸ and anodisation^{1,9} methods. Among all of these methods, anodisation of titanium allows the formation of highly ordered nanotube arrays demonstrating the most remarkable properties. Therefore, in this paper, a detailed study has been performed to evaluate the surface structure of the nanotubes as a function of different electrolytes. Based on the results, an appropriate electrolyte, allowing the formation of well-ordered titania nanotubes, can be understood.

2. EXPERIMENTAL

High purity titanium (T_i) foils (99.6% purity) of 0.2 mm thickness, purchased from STREM Chemicals, were used in this study. Prior to anodisation, the T_i foils were degreased by sonication in acetone for 15 min, followed by a deionised water rinse. They were then dried in a nitrogen stream. The anodisation was performed in a two-electrode configuration bath, with T_i foil as the anode and platinum (P_t) as the counter electrode. The surface area of the electrodes was 4 cm². The distance between the cathodic and anodic electrodes was 30 mm. A schematic representation of the anodisation setup is shown in Figure 1. The bath consisted of either 1 M $(NH_4)_2SO_4$ or 1 M Na_2SO_4 with different NH_4F concentrations (0.5, 1, 3, and 5 wt%). The pH of the solution was adjusted to 3 with H_2SO_4 and to 7 with $NaOH$. The anodisation was done potentiostatically with a constant potential of 20 V applied to the foil. During the experiment, the fluorinated electrolyte was stirred using a magnetic stirrer. Magnetic agitation of the electrolyte reduced the thickness of the double layer at the metal/electrolyte interface, and ensured uniform local current density and temperature over the T_i electrode surface.¹ The bath was kept at room temperature. The as-anodised T_i

foils were cleaned in distilled water and dried in a nitrogen stream. The structural and morphological conditions of the titania nanotubes were characterised using a field emission scanning electron microscope (FESEM SUPRA 35VP ZEISS) operating at working distances down to 1 mm and extended accelerating voltage ranges from 30 kV down to 100 V. The FESEM SUPRA 35VP ZEISS was capable of energy dispersive X-ray spectroscopy (EDX). In order to obtain the thickness of the nanotube layer, cross-sectional measurements were carried out on mechanically bent samples. Therefore, the actual length of tubes will be divided by $\cos 45^\circ$. Sidewall thickness was measured with a transmission electron microscope (Phillips 420T). Phase identification was carried out using an X-ray diffractometer (Philip PW 1729).

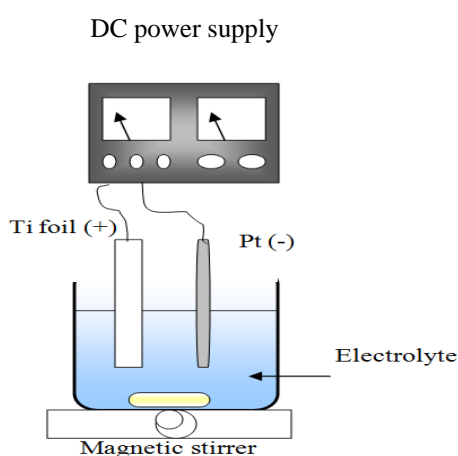


Figure 1: Schematic representation of the anodisation setup.

3. RESULTS AND DISCUSSION

3.1 Effects of Electrolyte Composition

Three different electrolytes, namely (a) NSNF, (b) NHSNHf, and (c) NSNHf were studied (Table 1). Comparison was made on the morphology of the titania nanotubes formed in 60 min of anodisation time.

Table 1: Electrolyte composition.

Electrolyte	SO ₄ ²⁻	F ⁻
NSNF	1 M Na ₂ SO ₄	0.5 wt% NaF
NHSNHF	1 M (NH ₄) ₂ SO ₄	0.5 wt% NH ₄ F
NSNHF	1 M Na ₂ SO ₄	0.5 wt% NH ₄ F

For the electrolyte NSNF, only a sponge-like porous nanostructure [Fig. (2a)] with a pore diameter of ~100 nm [insert in Fig. (2a)] was obtained. Unlike the microstructure in NSNF, formation of titania nanotubes [insert in Fig. (2b) and (2c)] was observed in NHSNHF and NSNHF. However, it can be clearly seen that the nanotubes were covered with a layer of precipitates [Fig. (2b) and (2c)]. The EDX analysis confirmed the precipitations were titanium oxide residuals [Spot A in Fig. (3a)] and the nanotubes were pure titanium dioxide [Spot B in Fig. (3b)]. We believe the precipitates hindered the continuous and uniformly distributed flux of ions. As a result, the nanotubes produced were non-uniform and not well organised.

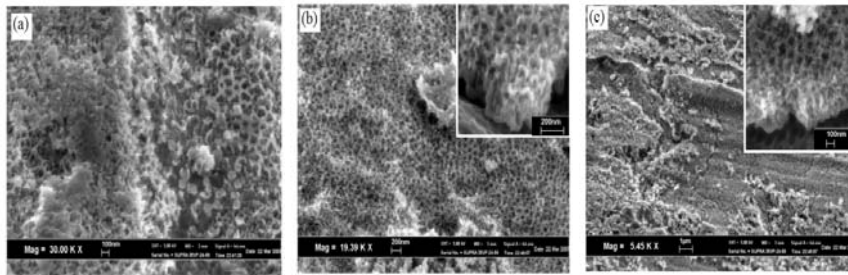


Figure 2: FESEM micrograph for various electrolytes (a) NSNF (b) NHSNHF and (c) NSNHF.

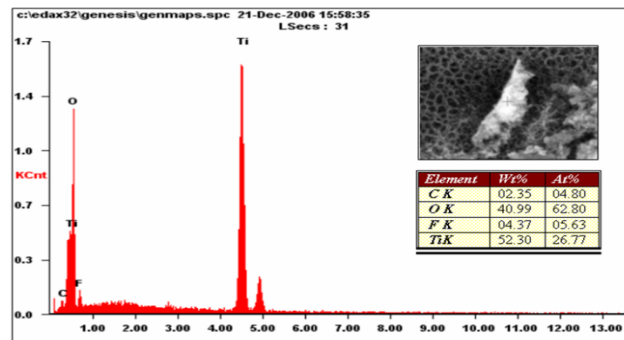


Figure 3: EDX spectra of oxide residual found on the surface.

3.2 Effects of Different Fluoride Ion (F⁻) Concentrations

The concentration of the fluoride ion added to the electrolyte was varied from 0.5 to 5 wt% to observe the changes in pore diameter and length of titania nanotubes. Table 2 and Figure 4 show the image of the foil anodised in (NH₄)₂SO₄ for 60 min.

Table 2: Pore diameter and length of titania nanotubes with different F⁻ concentrations in 1 M (NH₄)₂SO₄.

NH ₄ F (wt%)	Microstructure	Pore diameter (nm)	Length (nm)
0.5	Nanotubes	80–100	-
1.0	Nanotubes	90–130	-
3.0	Nanotubes	110–130	450–480
5.0	Nanotubes	60–90	300–340

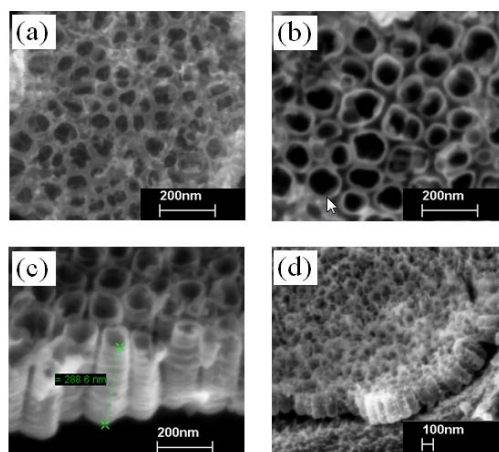


Figure 4: FESEM images of nanotubes produced in 1 M (NH₄)₂SO₄ with various NH₄F: (a) 0.5, (b) 1, (c) 3 and (d) 5 wt%.

The pore diameter of the nanotubes increased as the fluoride content in the (NH₄)₂SO₄ increased from 0.5 to 3 wt% [Table 2 and Fig. (4a), (4b) and (4c)]. However, for 5 wt% fluoride, the pore diameter was relatively small, and a very loose coverage of titania nanotubes formed on the substrate [Fig. (4d)]. As we know, the formation of titania nanotubes depends on the oxide growth rate and the dissolution rate. We believe that, with 0.5 wt% fluoride, the dissolution rate was very slow and thus resulted in small pore size. With increasing fluoride content, the dissolution rate increased and resulted in big pores. It is obvious that

the dissolution rate was extremely high with 5 wt% fluoride because the morphology is not uniform on the entire surface, and the Ti-substrate was practically etched away in certain spots.¹⁰

As for the nanotubes formed in 1 M Na₂SO₄ (Table 3 and Fig. 5), a similar trend was observed. Small nanotubes (20–30 nm) were formed with 1 wt% fluoride and with increasing fluoride content, the pore diameter increased in the range of 75–100 nm. In terms of length, the nanotubes produced in (NH₄)₂SO₄ were shorter by a factor of 2 as compared to nanotubes produced in Na₂SO₄. This might be related to different electrolytes having different current densities. According to Schmuki and co-workers,¹⁰ higher current density is achieved in the NH₄⁺ electrolyte as compared to Na⁺, thus the electrochemical etching rate was expected to be high in the NH₄⁺ electrolyte, resulting in pore widening and short nanotubes.

Table 3: Pore diameter and length of titania nanotubes with different F concentrations in 1 M Na₂SO₄.

NH ₄ F (wt%)	Microstructure	Pore diameter (nm)	Length (nm)
0.5	Nanotubes	50–80	-
1.0	Nanotubes	20–30	-
3.0	Nanotubes	75–100	670–730
5.0	Nanotubes	75–100	650–680

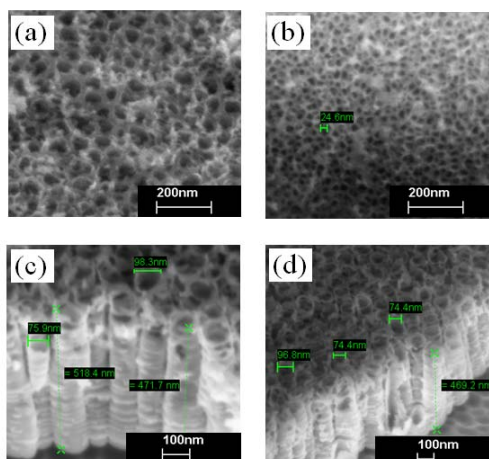


Figure 5: FESEM micrograph of nanotubes produced in 1 M Na₂SO₄ with various NH₄F: (a) 0.5, (b) 1, (c) 3 and (d) 5 wt%.

Figure 6 shows a FESEM micrograph of different regions of the foil anodised in 1M $(\text{NH}_4)_2\text{SO}_4$ containing 1.0 wt% NH_4F . From the SEM images, it was evident that the self-organised regular porous structure consists of pore arrays with a uniform pore diameter [Fig. (6a)]. It was also clear that pore mouths were open on the top [Fig. (6b)] of the layer, while the tubes were closed by the presence of a layer of titania on the bottom of the structure [Fig. (6c)].

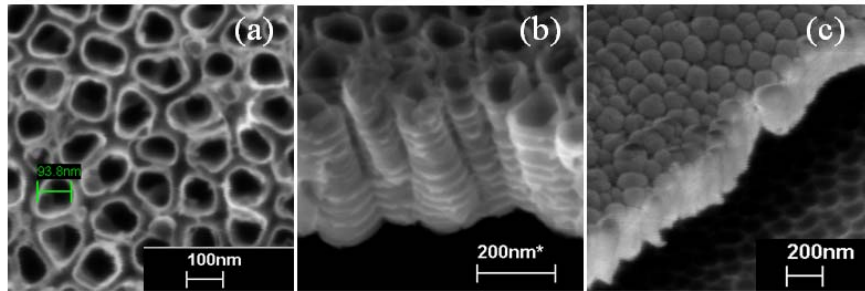


Figure 6: FESEM micrograph of (a) top view (b) cross-sectional and (c) bottom view of titania nanotubes.

3.3 Effects of Anodisation Time

Figure 7 gives the FESEM images of the foil anodised with different times (5, 30, 60, and 175 min).

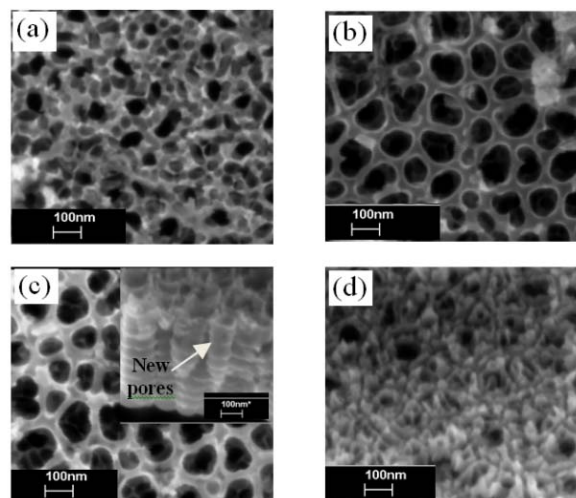


Figure 7: FESEM images of the foil anodised with different time: (a) 5 min, (b) 30 min, (c) 60 min and (d) 75 min.

Over the first 5 min, some titania nanotubes have already formed. Increasing the anodising time to 30 min resulted in uniform tubes with an average diameter of 100 nm. When the time increased further to 60 min, some overlapping nanotubes were observed. New pores inside existing pores were created [insert in Fig. (7c)]. The overlapping mechanism can be explained by the breakdown occurring inside the re-passivated pores [Fig. (8)].⁹ Finally, the tube structure collapsed with negligible thickness after 175 min, as an obvious dissolution of the T_i surface oxide took place.

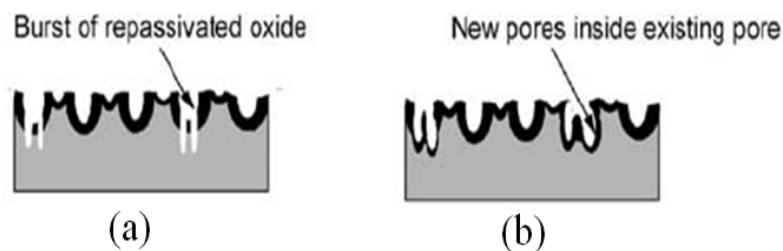


Figure 8: Schematic diagram of overlapping titania nanotubes phenomena: (a) burst of re-passivated oxide and (b) formation of new pores inside existing pores.⁶

3.4 Effect of Annealing

Comparisons were made for the sample that was anodised in 1 M Na_2SO_4 with 1.0 wt% NH_4F for 45 min to understand the effect of annealing on the formation of nanotubes. From the FESEM images, it was obvious that the morphology of the titania nanotubes, with and without annealing, remains unchanged [Fig. (9a) and (9b)]. However, the oxide layer after annealing was found to be 'lifted off' from the Ti-substrate [Fig. (9c)].

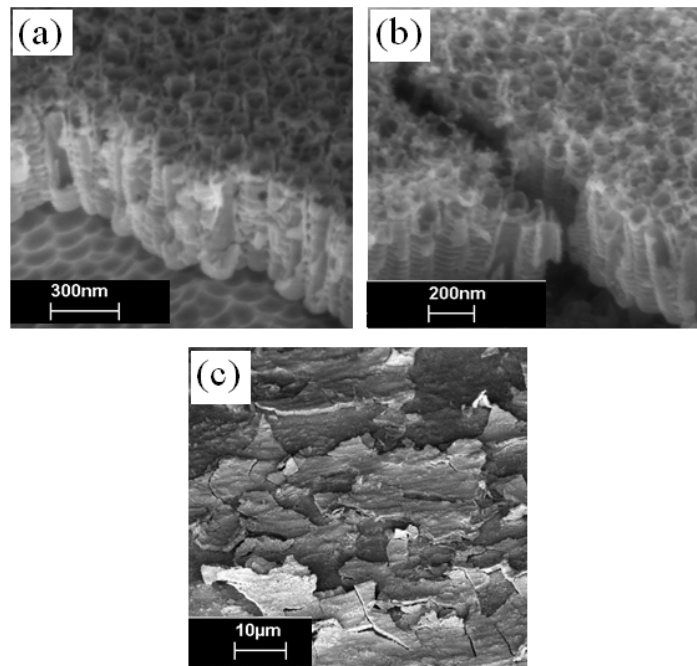


Figure 9: FESEM images of titania nanotubes: (a) before annealing (b) after annealing, and (c) FESEM image of low magnification showing the ‘lifted off’ oxide layer after annealing.

The induction of internal stresses that lead to warping and cracking may be explained by a rate of temperature change that was too great. The cracking of the oxide layer from the substrate was also due to the unsuitable cooling rate when the sample was cooled to room temperature.

Figures 10a and 10b show the XRD pattern of the sample anodised in 1 M Na_2SO_4 containing 1 wt% NH_4F before and after the annealing process at 600°C for 6 h, with heating and cooling rates of 5°C min^{-1} .

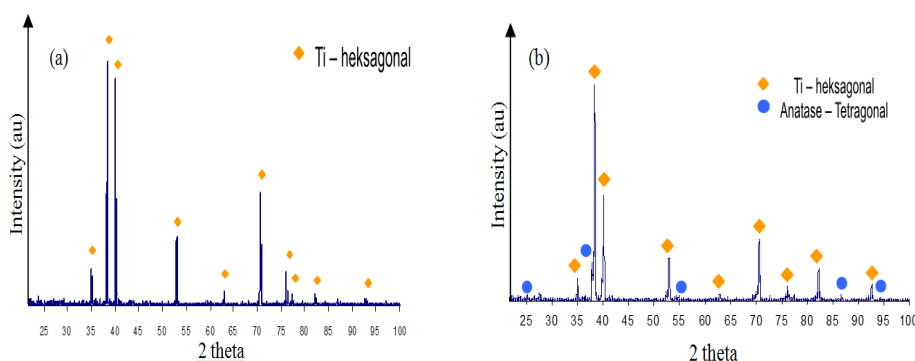


Figure 10: XRD pattern of (a) before annealing process and (b) after annealing process.

The XRD measurements of as-anodised samples without annealing revealed that the self-organised titania nanotubes had an amorphous structure, as only T_i -peaks were shown and it was originated from the foil. The XRD pattern of the sample after annealing showed anatase peaks and T_i -peaks. T_i -peaks were again present because the information from the substrate was revealed. The anatase phase was in tetragonal shape. The intensity of the anatase phase was relatively low as the thickness of the titania nanotubes was only a few hundred nanometres.

4. CONCLUSION

The results of this study demonstrated the possibility of obtaining TiO_2 nanotubes in 1M Na_2SO_4 and $(NH_4)_2SO_4$ solutions containing different NH_4F content. The diameter and length of the nanotubes vary with electrolyte composition, fluoride content and anodisation time. Smaller and longer tubes were obtained in $(NH_4)_2SO_4$ as compared to Na_2SO_4 . Control over the diameter was established by controlling fluoride content. However, the samples made with > 5 wt% NH_4F were independent of the amount of fluoride. Excess fluoride in the solution etches the tubes more vigorously, hence limiting the length of the nanotubes. The well-organised nanotube structure was obtained by anodisation of pure T_i for 60 min, but the structure collapsed when the time was increased to 175 min. The as-prepared nanotubes composed of an amorphous structure. Crystallisation of the nanotubes to anatase phase occurred at $600^\circ C$.

5. ACKNOWLEDGEMENTS

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