

Formation and photoelectrochemical properties of TiO₂ nanotube arrays in fluorinated organic electrolyte

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ABSTRACT

Titanium oxide (TiO₂) nanotubes (TNTs) have been successfully formed by anodisation of pure Titanium (Ti) foil in an electrolyte consisting of 85 % glycerol with varying amount of NH₄F. Organic electrolyte was used to produce longer nanotubes with higher energy conversion efficiencies during photoelectrochemical. The effect of NH₄F and time for TNTs formation during anodisation was studied. The optimised amount of NH₄F was 0.7 g and anodisation time required for a complete dissolution was more than 15 min. This condition will produce adequate surface etching and inwards growth to occur. The comparison of photocurrent density between irregular and well organised TNTs was investigated. Photocurrent density enhancement was also observed. TNTs photocurrent density was 60% higher as compared to nanoporous TiO₂. The photoelectrochemical response of the TNTs photoelectrode was studied by using 1 M KOH solution under Xe lamp illumination.

Keywords: Anodisation; glycerol; TiO₂ nanotubes.

INTRODUCTION

TiO₂ nanotubes (TNTs) structures are desirable due to their large surface area and high compatibility for photocatalysis applications, photoelectrochemical (PEC) water splitting and biomedical coatings or drug release systems. TNTs can be produced by anodisation [1, 2]. The structural characteristic of the nanotubes can be controlled by various parameters, such as types of electrolyte, applied voltage as well as time. The length of the nanotubes can be controlled by using viscous electrolyte [3, 4]. Ethylene glycol (EG) for instance, was used as the electrolyte and had produced TNTs of length up to 130 μm [5] and 220 μm with a length-to-outer diameter aspect ratio of ≈1400 [6]. Organic electrolytes such as glycerol and EG have higher dielectric constants and are more viscous as compared to aqueous electrolyte. The low current density was found in the viscous electrolyte [7]. This facilitates the diffusion of reactants at the pore tip or reaction products away from the tip, resulting in longer nanotube length with larger pore size. Besides, the incorporation of organic species from organic electrolyte into the oxide film during anodisation allows the growth of nanotube arrays under a wide range of applied potential. In here 85% glycerol was used as the electrolyte and morphologies of TNTs formed in

this solution were investigated. The addition of water seemed to enhance the dissolution of fluoride rich layer which helps in nanotubes formation with a larger diameter at low voltage. Nonetheless the properties of TNTs, such as unidirectional pathways for photoexcited charge carriers, suppressed electron recombination, high reaction site and enhanced light scattering make the the most promising candidate for solar harvesting applications. PEC has attracted great interest as it can convert solar energy into clean and renewable energy. PEC performance is highly determined by the structural morphology of nanotube arrays. Hence the high efficiency of TNTs as photoanode in PEC cell requires suitable architectures that could minimise electron loss and maximise photon absorption. Thus in here the nanotubular structures of TiO₂ formed in fluoride/glycerol were investigated in terms of their PEC characteristic. In the present work, commercially available glycerol was used without any acid addition . Organic electrolyte was used to produce longer and wide tubes. As the electrolyte pH was rather high, the surface etching can only be done by adding NH₄F into the electrolyte and/or by prolonging the anodisation time. Thus the effect of NH₄F loadings was also studied.

METHODS AND MATERIALS

Experimental Procedure

Titanium foils (99.96 % pure, 10 x 30 mm and 0.13 mm thick) from Strem Chemical, in the USA were used in this experiment. Prior to anodisation, the foils were degreased by using ultrasonic bath in ethanol for 15 min and rinsed with de-ionised water (DI) followed by drying in an air stream. The anodisation was performed at room temperature by using two-electrode electrochemical cell with Ti foil as the anode and Platinum rod as cathode (Figure 1) [8]. The distance between these electrodes was about 3 cm. The electrodes were connected to a DC power supply. The anodisation electrolyte used was 100 ml of glycerol (85 %, Merck) for each anodisation process. The effects of NH₄F and time on the morphology of the anodic oxide were investigated. Anodisation time ranged from 1 min to 720 min and three different amounts of NH₄F ranging from 0.5 to 1g were studied. The anodisation was conducted at constant voltage of 20V. After anodisation was completed, the samples were cleaned by using DI water and subjected to morphological and structural characterisations. The morphologies were observed by field emission scanning electron microscope (FESEM), Zeiss Supra 35. The cross section images were obtained by observing mechanically fractured samples under the FESEM, utilising a 45° tilted sample holder. High-resolution transmission electron microscope (HRTEM), JEOL, JEM-2100F at an acceleration voltage of 200 kV was used to view the nanotubes formed. X-ray diffraction (XRD) analysis (Bruker D8) was done on the samples. The electrochemical properties of the samples were characterized using a three-electrode PEC cell with TNTs as the working photoelectrode, a Platinum rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A 1M KOH solution was used as the electrolyte. All of the three electrodes were connected to a potentiostat (μAutolab III), and the current and voltage were measured. A 150 W xenon lamp (Zolix LSP-X150) with an intensity of 800 W/m² was used to produce a largely continuous and uniform spectrum. Light (100%) was transmitted by a quartz glass as the xenon lamp shone on the TNTs (photoanode). The xenon lamp was switched on after the three electrodes were connected to the potentiostat. A linear sweep potential (LSP) was swept from -1.0 V to 1.0 V at a scan rate of 5 mV/s, and the corresponding photocurrent was measured.

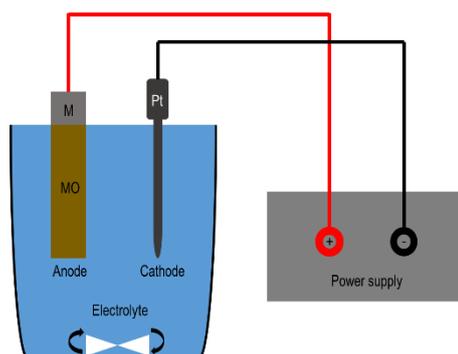


Figure 1. Experimental set up for anodisation.

RESULTS AND DISCUSSION

The effect of anodisation time in glycerol on the morphology of the TNTs is discussed. FESEM of the TNTs after anodisation at different times are shown in Figure 2. The surface morphologies of Ti foils after 1, 15, 30, 60, 360 and 720 min is shown in Figure 2(a-f). The inset are the cross sectional morphologies of the TNTs. In Figure 2(a), after 1 min of anodisation, the anodised Ti is seen to comprise of random porous structure with thickness of <10 nm. From the surface of this oxide, small pits with average diameters of 15 nm can be seen. During anodisation, Ti surface was oxidised to form a TiO_2 layer and followed by the dissolution of TiO_2 (field assisted oxidation and dissolution). Since the anodisation time was too short, dissolution can only form pits on the oxide surface. In Figure 2(b), even though the nanotubes were formed on the Ti foil, the tube surface appeared to be closed. This is due to the non-ordered initiation layers that originate from the dissolution and chemical etching in the electrolytes [9]. Initiation layers are formed in the first stage of tube growth and a longer time exposure to the anodisation electrolyte can remove the layer through a slow chemical etching that occurs when TiO_2 is exposed to a fluoride electrolyte. However better surface etching can be seen for sample anodised at 30 min, as seen in Figure 2(c), indicating that surface etching to reveal the opening of the nanotubes is time dependent. It was also evident from the FESEM images that the inward growth, which led to nanotube formation, was independent from the surface etching. For the inward growth, chemical dissolution at the pore bottom was the main process. During anodisation, H^+ is produced by oxidation of Ti. As oxidation front is at the electrolyte/barrier layer interface, this region would become acidic as more H^+ is produced as oxidation continues. This phenomenon is termed as local acidification process (increase of H^+ due to oxidation). Increasing H^+ concentration would increase the chemical dissolution rate, thus will increase the inward growth rate. Local acidification is therefore an important factor in the formation of TNTs. As the electrolyte has a pH of ~6, the surface etching rate is slower. A balance between the surface etching rate, and inward growth rate, is required for the formation of nanotubes with an open top.

In the study case, the surface etching was time dependent, whereby adequate etching can only be achieved after longer than 15 min of anodisation. Obviously, longer anodisation time will influence the length of TNT arrays. In Figure 2(d) sample prepared at 60 min has a length of 700 nm. After 360 min of anodisation, as shown in Figure 2(e), the length is 2 μm . A 3 μm long TNT array is seen after anodisation for 720 min (Figure 2(f)). For all samples, the outer diameter remains constant at ~80 nm, indicating that the diameter is not time dependent. Another obvious observation from these FESEM images is that the nanotubes formed have a serrated wall. This is because during the

intertubular gap separation, the dissolution of fluoride rich layer at the cell boundaries between the tubes causes the formation of intertubular gap separation [10]. The ripples at the tube wall are the consequences of access of electrolyte between nanotubes, due to chemical dissolution of fluoride-rich boundary layer [11]. Hence, it enables the transient formation of film around the external tube wall. One way to induce faster surface etching is by the use of more NH₄F in the electrolyte whilst maintaining the pH of the electrolyte at ~ 6.

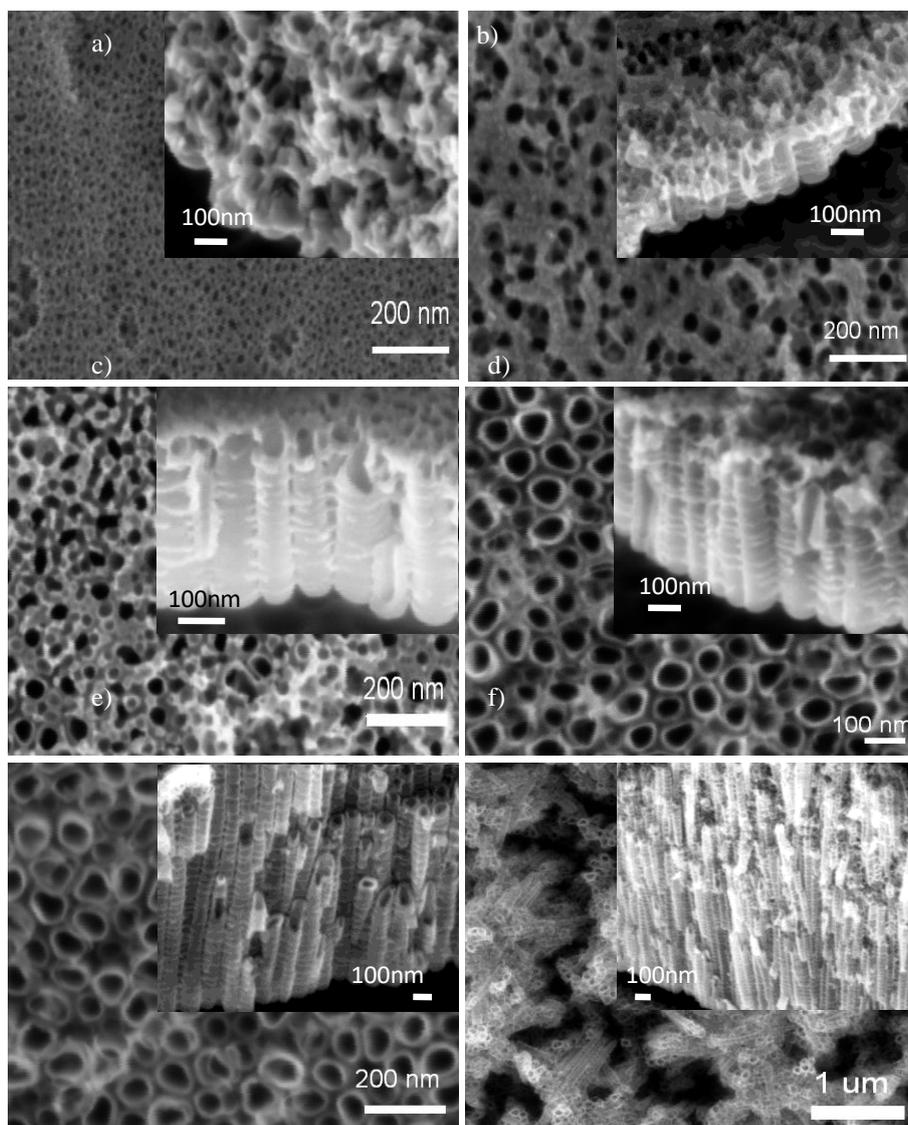
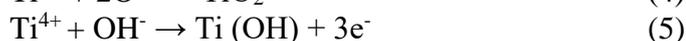


Figure 2. FESEM images of anodised Ti at different anodisation times: (a) 1 min, (b) 15 min and (c) 30 min (d) 60 min (e) 360 min and (f) 720 min. All samples were anodised at 20 V in 100 ml of 85 % glycerol with 0.7 g NH₄F

During the process of Ti anodisation, the majority of oxidising ions are from dissociation of water and field assisted dissolution of oxide [10]. At the electrolyte|oxide interface, three processes can occur: (Equation (1)), (Equation (2)) and (Equation (3)):



H^+ produced from Equation (1) and Equation (2) processes will move towards the cathode and ions (O^{2-} and OH^-) will accumulate at the anode. Some of these ions may migrate through the oxide layer to form a thicker anodic layer. The ions would react with metal ions (Ti^{4+}) that are ejected from the metal oxide interface under application of electric field and migrate towards the oxide electrolyte interface. By these processes, TiO_2 and $Ti(OH)$ will form at the oxide metal interface Equation (4) and Equation (5):



This process occurs when pits are formed randomly on the surface of the anodic oxide (the initial TiO_2) by electric field dissolution. The applied electric field results in the rupturing of the oxide due to the polarisation of the Ti-O bonds. Pits are pore nucleation centres and will grow due to chemical dissolution. Pits eventually will transform into stable pores. When a relatively strong acidic fluoride containing electrolyte is used for anodic process, chemical dissolution as shown in Equation (6) will occur. This reaction leads to the formation of larger pores.



Pits enlargement by F^- in the solution is due to chemical dissolution process, producing fluoro-complexes. The FESEM image in Figure 2(b) shows the enlargement of the pits to ~50 nm after 15 min of anodisation. From the cross sectional view, it could be seen that underneath this region, a self-aligned nanotubular structure has developed. Pore separation process is responsible in the formation of nanotubes. This process will differentiate between self-organized nanoporous structure like Al_2O_3 with nanotubular structure of TiO_2 . Two reasons are proposed for the separation of pores: (i) the formation of voids from dehydration of $Ti(OH)$ and (ii) the dissolution of boundaries between the oxide walls due to high fluoride content (fluoride rich layer form surround the nanotubes wall). The inward migration of F^- ions is much faster than O^{2-} thus they reside mostly at the outer shell of the pore boundaries. The inner shell is comprised of mostly TiO_2 . The removal of this outer layer will produce the nanotubes.

Figures 3(a) and 3(b) show the surface and cross sectional morphologies of anodised Ti using a lower (0.5 g) and higher (1.0 g) loadings of NH_4F respectively. As seen in these images, regardless of the amount of F^- in the bath, the TNTs arrays have formed as seen from the cross sectional images (Figure 3 (a-ii and b-ii)), suggesting that the inward growth is not affected as much by the amount of NH_4F . However as stated, with more NH_4F in the solution, the surface etching is much faster forming nanotubes with an open top, as seen in Figure 3(b-i) for the sample prepared using 1.0 g NH_4F . Meanwhile, for a sample made in the bath with 0.5 g NH_4F (Figure 3 (a-i)), the surface etching is incomplete. A typical HRTEM image of the nanotubes wall formed at 20 V is shown in Figure 4. Lattice fringes of the nanotube shown in Figure 4 indicates 0.35 nm and 0.27 nm d-spacing, corresponding to anatase (101) and rutile (110), respectively. The crystallite size from HRTEM is estimated to be <5 nm for this sample.

Figure 5 shows the comparison of the photocurrent density versus applied potential curves for two as anodized TiO_2 photoanodes with different morphologies under Xe lamp irradiation (~1000Mw/m²). The observed dark current (without illumination) for both samples was found to be negligible. As seen in Figure 5, at 0.4 V, the photocurrent

density of a TNT arrays (~ 700 nm length and ~ 80 nm diameter) was more than 60% greater than the value of nanoporous TiO_2 .

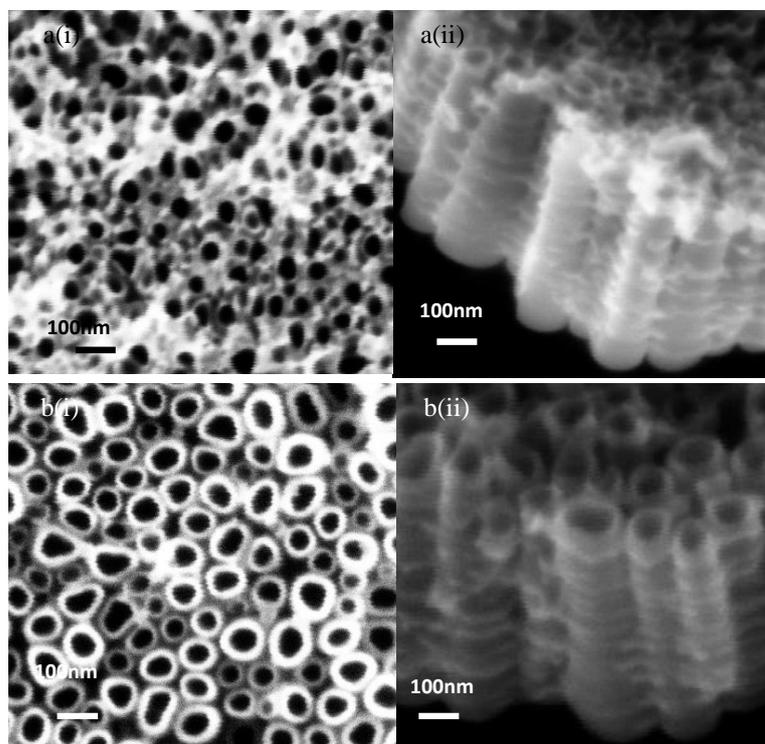


Figure 3. FESEM images of anodised Ti in bath with different loadings of NH_4F : (a) 0.5 g and (b) 1.0 g (i- surface morphologies and ii – cross section morphologies). All samples were anodised at 20V in 100 ml of 85 % glycerol for 60 min.

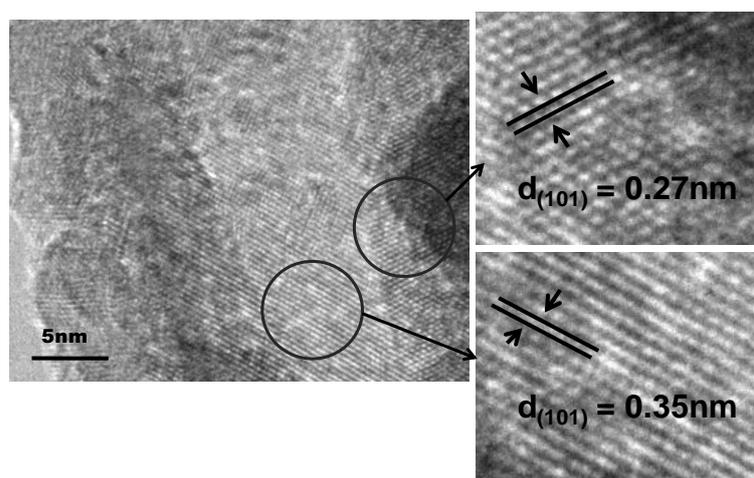


Figure 4. HRTEM image of the nanotube wall made at 20V. Arrows are pointing to higher magnification images to show the lattice fringes from anatase and rutile TiO_2 .

It is shown that by using nanotubes structures TiO_2 photoanode can harvest solar light more effectively than photoanode with irregular structure under same illumination. For tube-shaped n-type TiO_2 semiconductor, majority of the photoinduced charge carriers (e^-/h^+) are generated at both sides of the tube walls and the entire tube sidewalls, which

consist of space charge layers. Theoretically, the space charge layer is necessarily close to the tube wall to generate the photocurrent under illumination [12]. Thus, steep increase in the photocurrent with applied potential is indicated by TNTs compares to nanoporous structure. Similar result is produced when TiO₂ nanotube arrays (average inner pore diameter of 110.5 nm, length of ~7.5 μm) fabricated at room temperature in Ethylene glycol containing 5 wt% NH₄F and 5 wt% H₂O₂ exhibits the highest photocurrent density at 1mA/cm² [13]. The highly ordered TiO₂ nanotube arrays without morphological disorder, bundling, and microcrack problems can significantly enhance the transport properties and reduce the recombination of charge carriers (e⁻/h⁺), which extends the residence time of electrons [14]. Hence, the effective transfer of photoinduced electrons to the counter electrode (Pt) with an external bias, has greatly reduced the recombination of charge carriers (e⁻/h⁺) at the thin walls of the nanotubes.

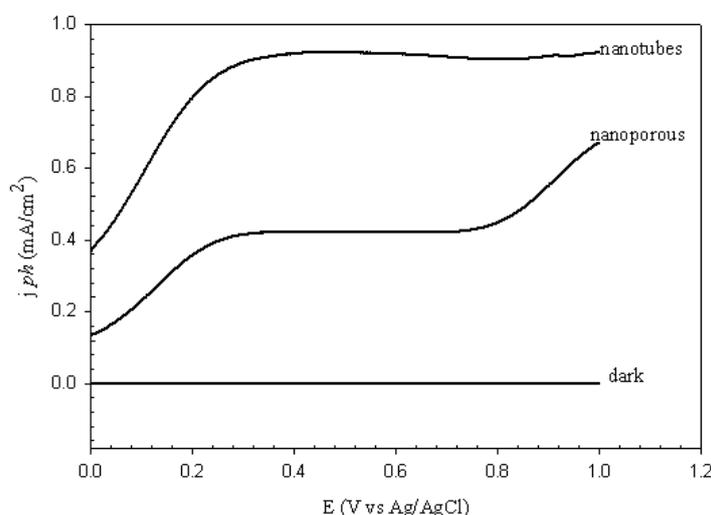


Figure 5. Variation of photocurrent density vs measured potential for the TiO₂ photoanodes in 1M KOH electrolyte.

CONCLUSIONS

The formation of TNTs in 85% glycerol solution is dependent on the amount of NH₄F in the bath and time of anodisation. For TNTs arrays with clear, open top and considerable length the process must be done in 0.7g NH₄F per 100 ml solution for more than 15 min in order for adequate surface etching and inwards growth to occur. The deepening process which leads to the TNTs formation at the metal oxide interface inside the TNTs is independent of the surface etching and will proceed as the time of anodisation was increased. The TNTs photoanode can harvest solar light effectively compared to nanoporous photoanode where high surface area exists and unidirectional electron migration between the tubes. However the efficiencies of the TNTs photoanode can be improved by adding dopant and decoration to the TNTs so that more effective charge carrier separation can be produced.

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