

## Effect of fluoride content and cleaning agent on the formation of self organized TiO<sub>2</sub> nanotube arrays

Lai Chin Wei and Srimala Sreekantan

**Abstract**—Titania nanotube arrays were synthesized by anodizing Ti foil in ethylene glycol (EG) containing ammonium fluoride (NH<sub>4</sub>F). The role of fluoride ion and the different cleaning agents were investigated. The morphology was observed via Field Emission Scanning Electron Microscopy (FESEM). A self-organized TiO<sub>2</sub> nanotube with an average inner diameter of 110 nm and length of 9.5 μm was acquired by anodizing the foil at 60 V for 60 minutes. The presence of F<sup>-</sup> ions leads to chemical dissolution of Ti oxide layer. The chemical dissolution rate increased with increasing the fluoride content because more F<sup>-</sup> ion is available to attack the barrier layer. When the barrier layer gets thinner the oxidation rate will increase and thus formed the long tubes. Acetone and DI water were used as a cleaning agent. It was found that sample washed in acetone and ultrasonic for 1 minute, the precipitates like oxide layer formed onto surface of the nanotubes was successfully removed and revealed smooth and clean pores. Such clear opening enhanced the photocatalytic activity of methyl orange degradation because the diffusion of methyl orange takes place not only on the outer surface of TiO<sub>2</sub> nanotube but also on the inner walls.

**Keywords:** Titania nanotube, cleaning agent, photocatalytic activity

### 1. INTRODUCTION

TiO<sub>2</sub> has attracted great attention owing to their excellent characteristic such as great capacity for oxidation, wide band gap, non-toxicity, low cost and long term stability [1]. Due to its wide range of characteristics, TiO<sub>2</sub> photocatalyst is applied to the field of environmental clean-up including deodorization, antibacterial protection, anti-fouling protection, water treatment, emission gas treatment, dye-sensitized solar cells, hydrogen generation by water photoelectrolysis, gas sensors and so on [2, 3].

Studies have indicated that for such applications, well-arrayed TiO<sub>2</sub> nanotubes are of great importance due to their one-dimensional (1D) nature, ease of handling and simple preparation [1,2,3].

Several preparations of TiO<sub>2</sub> such as sol-gel method, hydrothermal method, anodization, metallorganic chemical vapor deposition (MOCVD) and templating have been reported [4-10]. However, there is growing interest on anodization method due to the vertically oriented and highly ordered TiO<sub>2</sub> nanotube arrays, which is its most remarkable property [11]. In earlier research work, most of TiO<sub>2</sub> nanotubes have been manufactured by anodization in aqueous HF-based electrolyte, but they grew only up to a length of about 500nm. This limited growth may be assumed to be due to the fast dissolution process of the TiO<sub>2</sub> nanotube layer rather than the formation of an oxide layer by the chemical oxidation process [12,13]. Understanding the formation of nanotube arrays structure of the anodized Ti surface is important in order to have controlled dimensions for specific applications. The main disadvantage of this anodization process is the precipitation or flaky structure placed at the top of the nanotube surface. This condition will reduce the efficiency of the photocatalytic activity. Recently, a large volume of literature regarding the formation of TiO<sub>2</sub> nanotubes in different organic electrolyte has been reported [14,15].

However, there still has been less work regarding the effect of fluoride in organic electrolyte on the growth of the nanotube. Furthermore, TiO<sub>2</sub> nanotube produced in organic solvent often results in the formation of nanotubes with “dirty” surface with precipitates like oxide on the surface. The “dirty” part of the surface seems to consist of conglomerates of partially dissolves tubes that still connected on top of the tubes. Therefore, in this work, attempts have been made to investigate the behavior of ordered TiO<sub>2</sub> nanotubes anodized in ethylene glycol (EG) containing different amount of ammonium fluoride and different type of cleaning agents after anodization process.

### 2. EXPERIMENTAL PROCEDURE

The high purity (99.6% purity with 0.1mm thickness) titanium (Ti) foils from STREM Chemicals was used in this study. Prior to anodization, Ti foils were degreased by sonicating in ethanol for 30 minutes. The foils were then rinsed in deionized water and dried in nitrogen stream. The anodization was performed in a two-electrode configuration bath with Ti foil as the anode and the platinum electrode as the counter electrode. The electrolyte used in this study is ethylene glycol with the

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addition of different wt% of  $\text{NH}_4\text{F}$ . The pH of the solution is about 6.5.

During the anodization process, the fluorinated electrolyte was agitated using a magnetic stirrer to homogenize the electrolyte. The magnetic agitation of the electrolyte reduces the thickness of the double layer at the metal/electrolyte interface, which ensures uniform local current density and temperature over the Ti electrode surface. The as-anodized Ti foils were cleaned using different cleaning agents and then dried in nitrogen stream. Then, these samples were annealed at 400 °C for 4 hours in argon atmosphere.

The morphological conditions of the  $\text{TiO}_2$  nanotubes were characterized using a field emission scanning electron microscope (FESEM) Zeiss SUPRA 35VP at working distances down to 1mm and extended accelerating voltage ranging from 30 kV down to 100 V. In order to obtain the thickness of the nanotube layer, cross-sectional measurements were carried out on mechanically bent samples. The actual length of the tubes were divided by  $\cos 45^\circ$ .

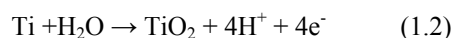
The photocatalytic degradation studies were performed by dipping 4.0  $\text{cm}^2$  of Ti foil in 100 ml of 30 ppm methyl orange in a custom-made photoreactor consisting of a quartz glass. Blank sample (without  $\text{TiO}_2$ ) was also prepared in order to eliminate the effect of the light towards the degradation of methyl orange. Both samples were left in the reactor for 30 minutes in dark environment to achieve the adsorption/desorption equilibrium. It was then photoirradiated at room temperature by using TUV 18W UV-C Germicidal light. 5 ml solution was withdrawn for every 1 hour from the both quartz tubes to monitor the degradation of methyl orange after irradiation. The concentration of the degraded methyl orange was determined by using UV spectrometer.

### 3. RESULTS AND DISCUSSION

The formation of the nanotube arrays in fluoride containing electrolyte is the result of three simultaneously occurring process: (1) field-assisted oxidation of Ti metal to form  $\text{TiO}_2$ , (2) field-assisted dissolution of Ti metal ions in the electrolyte and (3) chemical dissolution of Ti and  $\text{TiO}_2$  in the presence of hydrogen and fluoride ions [16]. In general, it appears that the electrochemical condition is an important factor for the formation of well-ordered nanotube arrays.

In this part of experiment, ethylene glycol electrolyte containing different amounts of  $\text{NH}_4\text{F}$  to grow  $\text{TiO}_2$  nanotube arrays by potentiostatic anodization of Ti foil at 60 V for 1 hour. The variations of surface morphology of  $\text{TiO}_2$  nanotubes for different amount of ammonium fluoride ( $\text{NH}_4\text{F}$ ) during the anodization process are exhibited in Fig. 1a–1d. By addition of 1.67wt%  $\text{NH}_4\text{F}$ , a thin  $\text{TiO}_2$  compact oxide layer forms on the surface of titanium (as marked in Fig. 1a). This indicates that low concentration of  $\text{F}^-$  ions (1.67wt%  $\text{NH}_4\text{F}$ ) cannot form the

pit on the oxide layer due to the inactively chemical dissolution reaction. This corresponds to passivation behavior of the foil and can be described by reaction below [17]:



Sample prepared in EG containing 3.33wt%  $\text{NH}_4\text{F}$  have surface morphology as seen in Figure 1b. The surface contained irregular features and no ordered nanoporous could be seen. The structure is formed probably due to the inadequate fluoride ion lead to incomplete chemical dissolution and oxidation at the interface between Ti and barrier layer. For 5wt%  $\text{NH}_4\text{F}$ , hollow like cylindrical oxide was observed indicates the amount of fluoride present in the EG sufficient to increase the chemical dissolution and thus drives further acidification to develop nanotube structure. Beyond the 6.67wt% of  $\text{NH}_4\text{F}$ , the length of the nanotubes becomes shorter (Figure 1d). This may be attributed to the excess electrochemical etching on the top of nanotubes during the chemical dissolution process. Therefore, the higher content of  $\text{F}^-$  faster the electrochemical etching of oxide layer [15]. This is further support by the pH of the electrolyte which showed more acidic condition with increasing the fluoride content [17,18].

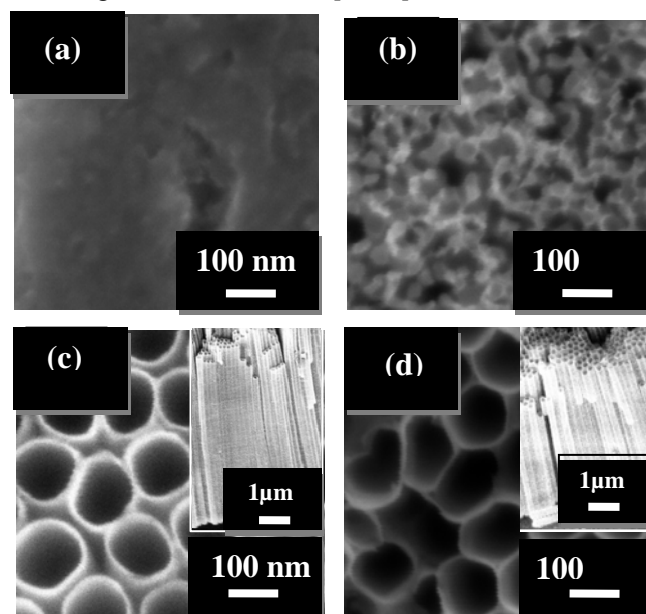


Figure 1. FESEM micrograph of the top view of the  $\text{TiO}_2$  nanotubes formed by anodization by addition different amount of  $\text{NH}_4\text{F}$  (a) 1.67wt%, (b) 3.33wt%, (c) 5wt% and (d) 6.67wt%. The insert is the cross-section showing the length of the tubes at different amount of  $\text{NH}_4\text{F}$ .

Table 1. Summary of the effect of  $\text{NH}_4\text{F}$  on the formation of  $\text{TiO}_2$  nanotubes

Amount of $\text{NH}_4\text{F}$ (wt%)	1.67	3.33	5	6.67
Amount of EG (wt%)	98.33	96.67	95	93.33
Microstructure	compact layer	Compact layer	Nano tubes	Nano tubes

	with pits			
Diameter (nm)	-	-	110	115
Length ( $\mu\text{m}$ )	-	-	9.5	6
Wall thickness (nm)	-	-	14.25	13.25
Aspect ratio	-	-	86.36	52.17

In order to study the effect of different cleaning agents after anodization process on the morphology of  $\text{TiO}_2$  nanotube arrays, Ti foil anodized at 60V in the mixture of electrolyte 95wt% EG and 5wt%  $\text{NH}_4\text{F}$  was selected. Cleaning method like DI water with ultrasonic, hot rinse of DI water at 90°C and acetone ultrasonic were investigated.

As seen from Figure 2,  $\text{TiO}_2$  nanotubes cleaned in acetone and subsequently ultrasonic for 1 minute showed clean surface. For the DI water with ultrasonic, the precipitate structure was found to remain on the surface. These results indicate that acetone assist to loosen the precipitate oxide layer on top of  $\text{TiO}_2$  nanotubes surface is better than DI water. On the other hand, the use of hot rinse DI water at 90°C caused the nanotubes adherence to become weak and eventually peeled off after few minutes in ultrasonic.

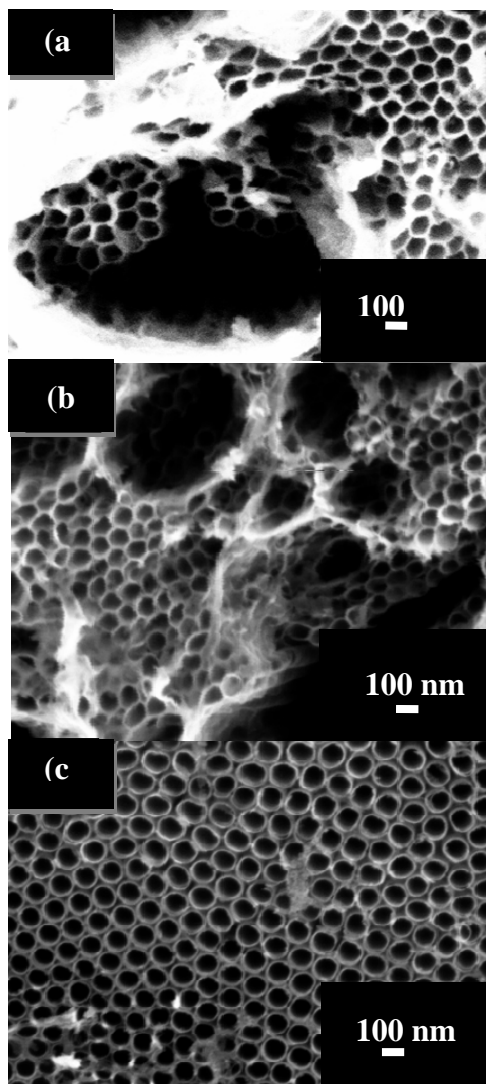


Figure 2. FESEM images of  $\text{TiO}_2$  nanotubes obtained with different cleaning method after anodization process. The cleaning method: (a) DI water in ultrasonic for 1 minutes, (b) Hot rinse in DI water for 1 minute and (c) Acetone in ultrasonic for 1 minute

The photocatalytic activity of the  $\text{TiO}_2$  nanotubes was evaluated by photodegradation of methyl orange aqueous solution after UV irradiation for 5 hours. In order to evaluate the effect of  $\text{TiO}_2$  nanotubes surface structure (smooth and flaky surface) on its photocatalytic activity, the degradation of methyl orange was carried out and the results are shown in Figure 3. It can be clearly observed that sample with covered with precipitated on the surface of  $\text{TiO}_2$  nanotubes showed poor degradation as compared to the sample with clean  $\text{TiO}_2$  nanotubes. It may be understood that when  $\text{TiO}_2$  nanotubes covered with precipitated, the methyl orange species do not easily penetrate inside the tubes and thus the effective surface area exposed to methyl orange degradation is reduced and resulting poor photocatalytic activity. In contrast, the sample cleaned with acetone in ultrasonic for 1 minute favor increasing the photocatalytic activity because more reactants are absorbed onto inner and outer surfaces of the tubes.

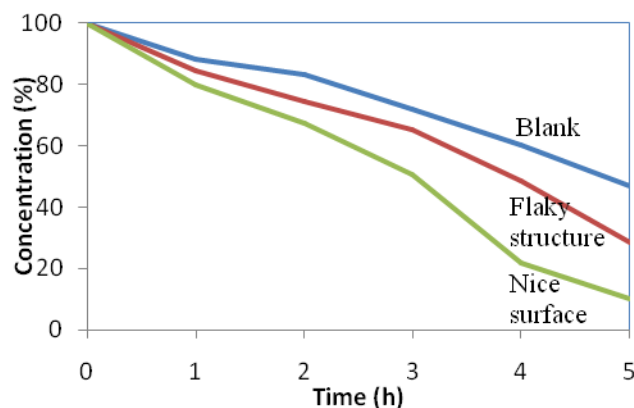


Figure 3. Plots of methyl orange concentration versus irradiation time for nice surface structure and flaky structure on the top surface of  $\text{TiO}_2$  nanotubes

#### 4. CONCLUSION

The effect of amount  $\text{NH}_4\text{F}$  and cleaning agents on the morphology of anodic oxide formed in fluorinated ethylene glycol electrolyte on titanium was investigated. A thin  $\text{TiO}_2$  compact oxide layer is formed in EG with 1.67wt%  $\text{NH}_4\text{F}$ . The optimum chemical dissolution of the  $\text{TiO}_2$  layer to form smooth  $\text{TiO}_2$  nanotubes is by addition of 5wt% of  $\text{NH}_4\text{F}$  in electrolyte. Beyond 5wt% of  $\text{NH}_4\text{F}$ , well aligned nanotube arrays was formed. However excess  $\text{F}^-$  ion will shorten the length of nanotubes again. The sample cleaned with acetone under ultrasonic for 1 minute is the best way to remove the flaky structure on the top surface of  $\text{TiO}_2$  nanotubes and thus resulted in better photocatalytic activity.

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