

Synthesis of Titania Nanotube Arrays by Anodization

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Titania nanotube arrays were synthesized in glycerol, ethylene glycol and carboxymethylcellulose as base materials. The effects of anodization voltage and time, as well as chemical composition and pH of the electrolyte bath were studied. Nanotube arrays with an inner diameter ranging from 16 to 91 nm, and wall thickness ranging from 7 to 29 nm were fabricated in a glycerol-water electrolyte. Water content of 5 wt% or higher was found to be essential for nanotubes fabrication in glycerol electrolyte. Using modified ethylene glycol (containing 2 wt % and 0.5 wt % NH_4F) instead of glycerol, resulted in nanotube length up to 430 nm after 1.5 hr anodization time. Nanotube arrays were also successfully fabricated in 2 wt % sodium carboxy methylcellulose aqueous electrolyte (CMC electrolyte). These nanotube arrays had an inner diameter of 42 nm similar to those fabricated in 2 wt % urea-ethylene glycol electrolyte but their length was 450 nm.

Introduction

In the last decade, low-dimensional nanostructural materials have attracted increasing scientific and technological attention due to their physical properties and their potential applications (Fujishima and Honda, 1972). Dimensionality has a crucial role in determining the properties and performance of nanomaterials. Therefore, the control of size and shape of nanomaterials is of great importance. In contrast to size control, control of the shape of nanostructural materials is more difficult and challenging. The tubes, flakes or wires in the nanoscale region possess novel properties. The discovery of carbon nanotubes by Iijima (1991) with their diverse interesting properties has motivated the quest for the synthesis of nanotubular structures of other substances and chemical compounds such as V_2O_5 , SiO_2 , TiO_2 , Fe_2O_3 , ZrO_2 and MoO_3 . Among these materials, titanium dioxide (titania) has attracted great interest since the discovery of its photosensitivity by Fujishima and Honda (1972) and due to its strong photo-oxidizing potential, high chemical stability, non-toxicity and low cost (Guozhong, 2004). Titania nanotubes have improved properties compared to any other form of titania for

applications in water and air purification photocatalysis, sensing, water photoelectrolysis for hydrogen generation, photovoltaics, photoelectrochemical solar cells, electronics, optics, tissue engineering and molecular filtration. The widespread technological use of titania is impaired by its wide band-gap (3 eV for anatase phase and 3.2 eV for rutile phase), which requires ultraviolet (UV) irradiation for photocatalytic activation. Because UV spectrum accounts for only a small fraction (8%) of the solar spectrum compared to visible light (45%), any shift in the light absorbance of titania from the UV towards visible spectrum region will improve the photocatalytic and photoelectrochemical utility of the material. Titania band gap can be narrowed by doping with different nonmetal ions such as N, C and S and different metal ions such as Fe, Mo, Ru, Os and V (Shen et al., 2006; Wu et al., 2005; Yuan and Su, 2004). This study aims at investigation of the effect of different anodization parameters on titania nanotubes morphology fabricated in aqueous glycerol, ethylene glycol and CMC based electrolytes.

Experimental setup and methods

The experiments were carried out in a two electrode electrochemical cell where the two electrodes were placed 4 cm apart (see Figure 1). Titanium foil, over which titania nanotubes were grown, was used as anode while platinum foil was the counter electrode. A direct current power supply (Bio-Rad Laboratories, model 400, Irvine, CA) was employed as a source of constant potential. The DC power supply was equipped with a data acquisition system and a state-of-the-art algorithm and interface for real time monitoring of electrical current and voltage during the experiments. An ultrasonic bath was used for degreasing of titanium foil and final cleaning of fabricated nanotubes. The ultrasonic waves were also used for agitation of the electrolyte during the anodization process to improve the quality of nanotubes by mixing at microscopic level. The pH of the electrolyte was measured using an Orion 5-star plus Benchtop multimeter (Thermoelectron Corp., Waltham, MA). All experiments were carried out at room temperature around 25 °C. The morphology of titania nanotube arrays was studied using Hitachi S 4500 field emission SEM. The cross sectional images were taken on mechanically bent samples where titania nanotube layers were liberated from the supporting Ti foil. All experiments were carried out under a fume hood.

Titanium foils (0.89 mm thick, 99.7% purity, Alfa Aesar, Ward Hill, MA) cut into 1.4 cm diameter discs. The Ti disc was mounted in a Teflon holder so that only one face of it was exposed to the electrolyte. Glycerol (A. R., 99.5%, Caledon Laboratory Ltd., Georgetown, ON), ethylene glycol 99.5 % with water residual ~ 0.4%. (Caledon Laboratory Ltd., Georgetown, ON), NH_4F , NH_4NO_3 , urea (All three chemicals were A. R. 98 %, J. T. Baker purchased from Mallinckrodt Baker Inc., Phillipsburg, NJ) and deionized water were used in the experiments without any further treatment. Titanium foil discs were degreased by sonication in methanol followed by rinsing with deionized water. Then, they were chemically polished in nitric and hydrofluoric acids solution (5.6 M and 3.3 M, respectively) for 10 sec.

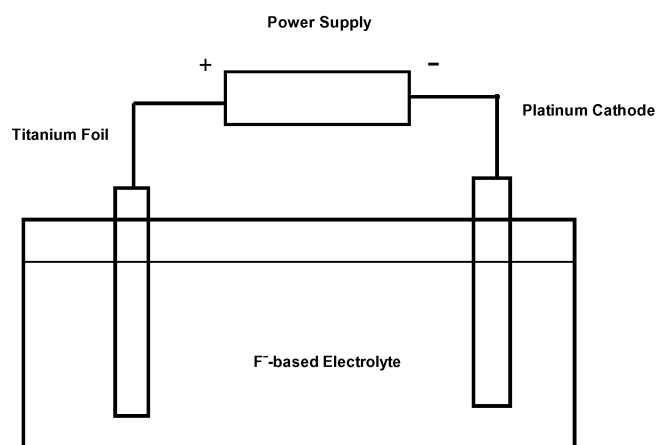
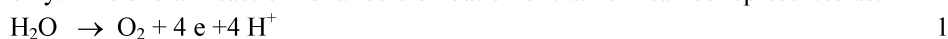


Figure 1. Schematic drawing of an electrochemical cell in which the Ti electrode is anodized.

Results and Discussion

Titania nanotubes were fabricated at different conditions and the effects of voltage, pH, water content and anodization time were investigated. In general in the absence of water in electrolytes, the anodization process will suffer from lack of H^+ ions and also high viscosity of the solution which leads to the formation of titanium dioxide layers only. The overall reaction for anodic oxidation of titanium can be represented as:



In the initial stages of the anodization process, field-assisted dissolution dominates chemical dissolution due to the relatively large electric field across the thin oxide layer (the resistance to the current is minimum). Small pits formed due to the localized dissolution of the oxide, represented by the following reaction, act as pore forming centres:



The pits convert into bigger pores and the pore density increases. Subsequently, the pores spread uniformly over the surface. The pore growth occurs due to the inward movement of the oxide layer at the pore bottom (barrier layer).

Several anodization experiments were conducted to study the effect of voltage on synthesis and nanoarchitecture at the following conditions: pH: 6, water content: 16 wt%, anodization time: 1.5 hr. Typical results are shown in Figure 2 and Table 1. Titania nanotube diameter increased with increasing voltage.

Table 2 shows the effect of different water contents at 20 volts, pH: 6 and anodization time 1.5 hr.

Acidity of electrolyte solution plays an important role in synthesis of titania nanotubes. Etching and corrosion processes are directly related to pH of the electrolytes containing fluoride ions. Interestingly, apart from the pH of electrolyte solution, the formation of anodization reaction products can induce local changes of pH in the vicinity of nanotubes which has more profound effect on anodization process compared to electrolyte acidity.

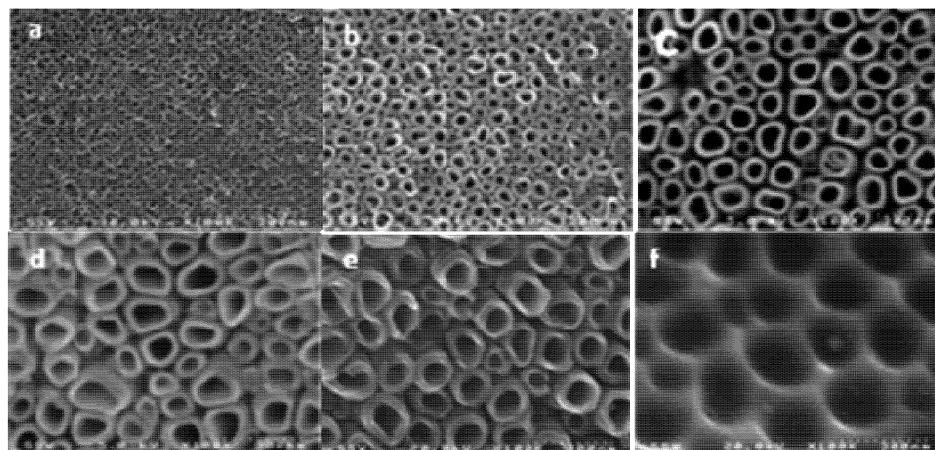


Figure 2. Scanning electron micrographs of the synthesized titania nano-tube arrays under various conditions

Table 1. Effect of water content on nanotube arrays formation and their nanoarchitecture (20 volts, pH: 6, 0.5 wt% NH_4F and 1.5 hr anodization time)

Water Content, wt%	0	2.0	5.0	16.0	30.0	50.0	70.0	90.0	99.5
Diameter, nm	n/a	n/a	38.0	64.0	76.0	72.0	48.0	43.0	40.0
Wall Thickness, nm	n/a	n/a	18.0	20.0	20.0	18.0	13.0	12.0	14.0
Length, nm	n/a	n/a	-	250.0	512.0	900.0	533.0	460.0	424.0

As mentioned earlier, viscosity of the electrolyte has a direct impact on diffusion of reactants and products to and from the titania nanotubes surface. It is necessary to control diffusion for synthesis of well organized titania nanotubes, however, there is a certain range out of which the viscosity has negative impact on synthesis and growth rate of titania nanotubes. The growth rate was low in glycerol-based ($\eta = 945$ cP at 25 °C) electrolytes and addition of water improved the growth rate due to the reduction in the viscosity of electrolyte solution. Ethylene glycol is less viscous ($\eta = 16$ cP at 25 °C)

compared to glycerol and results in lower diffusion resistance. Therefore, the growth rate would be higher in ethylene glycol electrolytes. Parameters that were previously studied in glycerol experiments were fixed at 20 volt, 1.5 hr, pH: 6 and water content was kept at only the residual amount (~ 0.4 wt %). Urea and NH_4NO_3 were added to study their effect on nanotubes morphology and as additional sources for nitrogen doping into the nanotubes. Results in Table 2 show that adding 1 wt% urea increased nanotube length from 286 nm to 397 nm (more than 27%) and adding 2 wt% urea increased the nanotube length to 430 nm (50 % increase). Adding 1-2 wt% urea increased the nanotube diameter from 30 nm to around 40 nm and thickness from 11 nm to 18 nm. Urea is likely to have an inhibitory effect on acid corrosion of metals in the presence of halide ions. Adding 1 wt% ammonium nitrate increased the nanotube length from 286 to 365 nm (21 % increase) while adding 2 wt% ammonium nitrate to the electrolyte increased the length to 320 nm. This increase in nanotubes length in the presence of ammonium nitrate was attributed to the increase of electrolyte conductivity by addition of this ionic compound.

Table 2. Anodization in Ethylene Glycol: Fabrication conditions and nanotubes dimensions

Experiment #	Urea %	NH_4NO_3 %	TNTAs * Length, nm	TNTAs Diameter, nm	Wall thickness, nm
1	0	0	286.0	30.0	11.0
2	0	1.0	365.0	28.0	11.0
3	0	2.0	320.0	33.0	9.0
4	1.0	0	397.0	40.0	18.0
5	2.0	0	430.0	43.0	16.0

- TNTA: titania nanotube array

Due to the high cost of glycerol and ethylene glycerol as viscous electrolytes for Ti anodization, preliminary investigation of nanotube arrays fabrication in sodium methyl carboxycellulose (CMC) aqueous solutions was conducted (see Table 3).

Table 3. Diameter, wall thickness and length of titania nanotube arrays synthesized in CMC aqueous electrolyte.

	CMC, wt %	Voltage, V	Length, nm	Diameter, nm	Wall thickness, nm
Expr. #1	2.0	20.0	450.0	42.0	13.0
Expr. #2	2.0	10.0	-	28.0	11.0

Conclusions

Highly ordered titania nanotube arrays were successfully fabricated in glycerol, ethylene glycol and CMC-based electrolytes. Our results showed that synthesis parameters play a crucial role in both nanotube arrays formation and tailoring of their nanoarchitecture. Nanotube arrays with an inside diameter ranging from 16 to 91 nm, and wall thickness ranging from 7 to 29 nm were fabricated in a glycerol-water electrolyte. Water content of at least 5 wt%, was found to be essential for nanotubes fabrication in glycerol electrolyte. Diameter and length were influenced by varying water content above 5 wt%. Maximum length of 900 nm was achieved at 50 wt% water content in glycerol. Nanotube length was found to be time dependent at high pH values and a pH value of 6 was favourable for fabrication of highly ordered, long and continuous nanotube arrays. Using modified ethylene glycol solution instead of glycerol resulted in nanotubes length up to 430 nm after 1.5 hr anodization time in ethylene glycol containing 2 wt % urea and 0.5 wt% NH₄F. Double-sided titania nanotube arrays layers with a total thickness of 9.5 μm were fabricated for the first time with a minor modification in the anodization cell. Nanotube arrays were successfully fabricated in 2 wt % sodium carboxy methylcellulose aqueous electrolyte.

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