

Research Article

# Study and Synthesis of Titanium Nanotube Arrays at High Temperature by Electrochemical Method

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## Abstract

*Titanium nanotube arrays were synthesized in ethylene glycol as base material. The effects of anodization at voltage and time, as well as chemical composition and pH of the electrolyte bath were studied. Using Ethylene glycol 99.5 % with 0.5% NH<sub>4</sub>F solution and deionized water 10%wt, resulted in nanotube length up to 430 nm after 1.5 hr anodization time at 65V voltage. Then it is dried in the process of heat treatment at 450°C in muffle furnace for 1-hours annealing. Finally UV- test and SEM to be used to characterize the Titanium nano tubes.*

**Keywords:** Titanium Nanotube Arrays, Electrochemical Method etc.

## 1. Introduction

In the most recent decade, low-dimensional nano auxiliary materials have pulled in expanding investigative and innovative consideration because of their physical properties and their potential applications (Fujishima and Honda, 1972). Dimensionality has a pivotal part in deciding the properties and execution of nano materials. Subsequently, the control of size and state of nano materials is of extraordinary significance. Rather than size control, control of the state of nano basic materials is more troublesome and testing. The tubes, pieces or wires in the nano scale locale have novel properties. The revelation of carbon nano tubes by Iijima (1991) with their different fascinating properties has spurred the mission for the combination of nano tubular structures of different substances and concoction mixes, for example, V<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and MoO<sub>3</sub>. Among these materials, titanium dioxide (titania) has pulled in incredible enthusiasm since the disclosure of its photograph affectability by Fujishima and Honda (1972) and because of its solid photograph oxidizing potential, high substance dependability, non-lethality and minimal effort (Guozhong, 2004). Titania nanotubes have enhanced properties contrasted with whatever other type of titania for applications in water and air refinement photograph catalysis, detecting, water photograph electrolysis for hydrogen era, photovoltaics, photograph electrochemical sun oriented cells, gadgets, optics, tissue building and sub-atomic filtration. The boundless innovative utilization

of titania is impeded by its wide band-crevice (3 eV for anatase stage and 3.2 eV for rutile stage), which requires bright (UV) illumination for photograph synergist initiation. Since UV range represents just a little portion (8%) of the sun powered range contrasted with noticeable light (45%), any movement in the light absorbance of titania from the UV towards unmistakable range district will enhance the photograph synergist and photograph electrochemical utility of the material. Titania band hole can be limited by doping with diverse nonmetal particles, for example, N, C and S and distinctive metal particles, for example, Fe, Mo, Ru, Os and V (Shen et al., 2006; Wu et al., 2005; Yuan and Su, 2004). This study goes for examination of the impact of diverse anodization parameters on titaniananotubes morphology created in fluid ethylene glycol as base delectrolytes.

### 1.1 Overview

The goal of this thesis is to study the synthesis of titanium nanotubes using electrochemical anodization techniques, create hybrid materials by the addition of other nano particulate composites, and furthermore approach some solar energy harvesting applications of these new materials. The important electrochemical parameters controlling the growth of the nanotubes have been extensively studied and optimized. Also, appropriate post-fabrication processing conditions such as heat treatment conditions have been optimized for the production of crystalline anatine titanium nanotubes offers a literature survey on the development of fabrication methods for titanium nanotubes.

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A mechanistic explanation of the synthesis process much faster and with radically different results than the anodization in fluoride ions containing electrolytes is also presented. It describes the challenges encountered when titanium nanotube powders for crystallization purposes, and how related parameters have been adjusted for optimal results. It presents our results on photovoltaic properties of titania nanotubes and modified titanium nanotubes. A custom experimental setup, easy to adapt for both photovoltaic and photocatalytic measurements has been developed and subsequently used for these studies. Finally, it provides a summary of the results and describes future outlook.

## 2. Experimental setup and methods

The trials were done in a two terminal electrochemical cell where the two anodes were set 4 cm separated. Titanium foil, over which titania nanotubes were developed, was utilized as anode while platinum foil was the counter cathode. An immediate current power supply (Bio-Rad Laboratories, model 400, Irvine, CA) was utilized as a wellspring of consistent potential. The DC power supply was furnished with an information securing framework and a cutting edge calculation and interface for continuous observing of electrical current and voltage amid the trials. An ultrasonic shower was utilized for degreasing of titanium foil and last cleaning of manufactured nanotubes.

The ultrasonic waves were additionally utilized for unsettling of the electrolyte amid the anodization procedure to enhance the nature of nanotubes by blending at minuscule level. The pH of the electrolyte was measured utilizing an Orion 5-star in addition to Benchtop multimeter (Thermo electron Corp., Waltham, MA). All examinations were done at room temperature around 25 °C. The morphology of titania nanotube clusters was contemplated utilizing Hitachi S 4500 field outflow SEM. The cross sectional pictures were tackled mechanically twisted specimens where titania nanotube layers were freed from the supporting Ti foil. All tests were done under a smoke hood. Titanium foils (0.89 mm thick, 99.7% purity, Alfa Aesar, Ward Hill, MA) cut into 1.4 cm distance across plates. The Ti circle was mounted in a Teflon holder so that stand out face of it was presented to the electrolyte. Glycerol (A. R., 99.5%, Caledon Laboratory Ltd., Georgetown, ON), ethylene glycol 99.5 % with water lingering ~ 0.4%. (Caledon Laboratory Ltd., Georgetown, ON), NH<sub>4</sub>F, NH<sub>4</sub>NO<sub>3</sub>, urea (All three chemicals were A.R. 98 %, J. T. Bread cook bought from Mallinckrodt Baker Inc., Phillipsburg, NJ) and deionized water were utilized as a part of the investigations with no further treatment.

Titanium foil circles were degreased by sonication in methanol then after by washing with deionized water. At that point, they were synthetically cleaned in nitric and hydrofluoric acids arrangement (5.6M and 3.3 M, separately) for 10 sec.

### 2.1 Electrochemical anodization

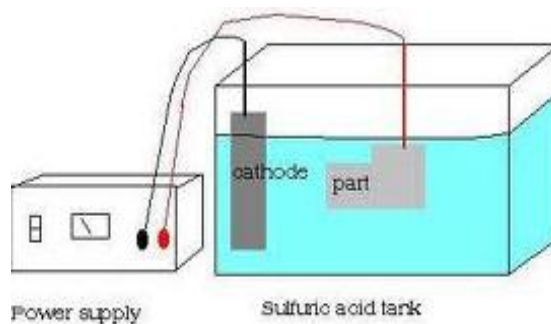


Figure 2.1 Anodizing Experimental setup model diagram-1

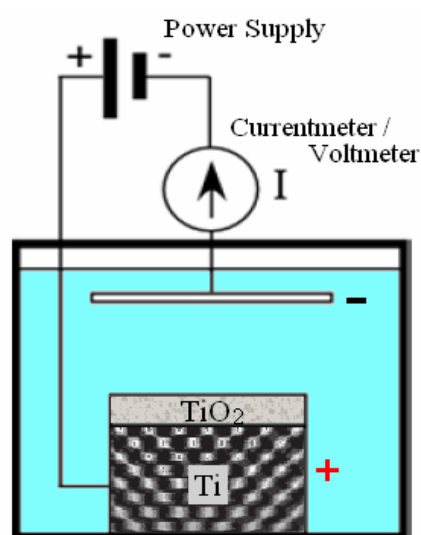


Figure 2.2 Anodizing Experimental setup model diagram-2

Titanium dioxide nanotubes are synthesized by anodized method. In this study, the growth of nanotubes is anodized on Ti foils (purity of 99.6%, thickness of 0.4 mm) by constant current at 15 mA in the ethylene glycol solution containing 0.3 wt.% NH<sub>4</sub>F and 2 vol.% deionized water kept at 25°C. The anodized TiO<sub>2</sub> nanotubes are annealed in oxygen at 350°C for 60 min. platinum plate as a counter electrode. Structural Analysis shows - the XRD (x-ray diffraction) of nanotubes with different growth rates Morphological Analysis. HRTEM (high-resolution transmission electron microscopy) reveals information about the particle size and shape.

### 2.2 Nanotubes arrays synthesized by anodization

Early works on anodic titanium nano porous and nanotubular structures were conducted during late 1990's and early 2000's by several research groups, mainly those of E. Darque-Ceretti of the Ecole des Mines de Paris, P. Schmuki of Friedrich-Alexander University in Erlangen Germany and that of C. Grimes at Pennsylvania State University. Zwilling & Darque-

Ceretti used chromic acid combined with a small amount of hydrofluoric acid in their 1997 and 1999 trials. These were the first reports of the formation of a nano porous structure in titanium. It was clear that the nano porous structure observed only formed when sufficient HF was added to the electrolyte mixture, As pure chromic acid was leading to the formation of a thin but stable oxide layer with no apparent pore structure. In 2001 the Grimes group discovered that titania nanotubes could be grown by using an electrolyte consisting primarily of HF acid (0.5wt %) together with higher anodization voltages.

This finding revived interest in the anodization of titanium. Grimes and co-workers initially focused primarily on promising sensor applications but soon also realized the potential of these arrays in photo catalytic applications. The group of P. Schmuki, using a mixture of sulfuric acid and a small amount of HF (0.15wt%) , reported the synthesis 'tube-like structures' in 2003. Tubes up to 500 nm long were produced by this method in about 30-60 minutes of anodization.

### 2.3 Titania nanotubes synthesis

As presented in the previous chapter, until recently it was believed that fluoride ions are critical and maybe impossible to replace as catalyst for the synthesis of titanium nanotubes arrays by anodization, due to their unique property of reacting with titanium oxide forming the  $TiF_6^{2-}$  complex which was furthermore dissolved into the solution. As a consequence, all anodic nanotubes arrays reported before 2007 were produced in fluoride ions containing electrolytes.

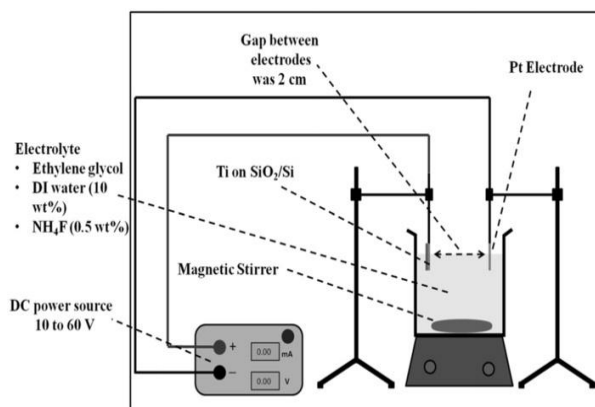
Assuming the possibility that chloride ions could have similar catalytic properties, thus constituting (at least) a less hazardous alternative to the highly toxic hydrofluoric acid, several trials have been performed in our laboratory in the summer of 2006 involving solutions of various acids (organic or inorganic) in combination with chlorine salts as the anodization electrolyte. While those trials resulted in the expected formation of a thin oxide layer on the surface of the original titanium foil, followed in some cases by the quick formation of corrosion pits in various "weak" spots on the sample surface, or on its edges.

However, closer inspection of those corrosion pits revealed the presence of titanium nanotubes bundles with lengths up to 50-60 microns and a cross section of the order of square microns. The successful synthesis of high aspect ratio titanium nanotubes in chloride ions containing electrolytes has been thus for the first time reported by our lab, and systematic studies have been employed for further optimization of the process.

### 2.4 Anodization setup

All the samples synthesized in our lab throughout this work were produced by a two-electrode DC anodization process in a beaker containing the desired electrolyte, with the initial titanium foil acting as the

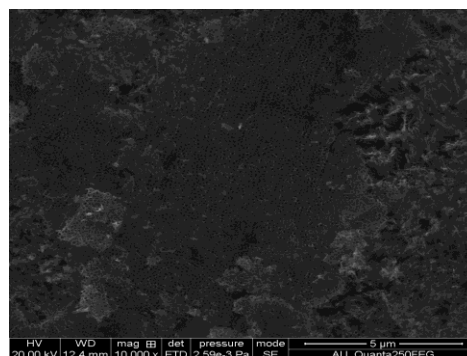
working anode, and a platinum mesh as the cathode. The electrodes were separated by a distance of 4 cm. The two-electrode configuration was preferred to the standard three-electrode configuration for simplicity and cost effectiveness reasons, as the results were proven to be similar. The constant voltage was provided by a computer-assisted Agilent 6811B power supply (Agilent Technologies, Santa Clara, CA), which was also employed for ensuring and recording the external current with the aid of a Lab VIEW program.



**Figure 2.3** Anodizing Experimental setup model diagram-3

## 3. Results and Discussion

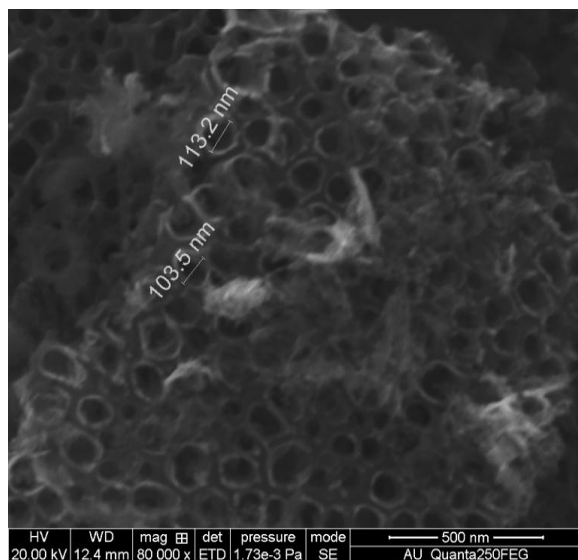
As presented before, a first success in the synthesis of titania nanotubes by anodization at 12-20 V DC in chloride ion containing electrolytes was obtained through the use of various acid solutions (oxalic acid 0.5M, formic acid 0.5M, sulphuric acid 0.05M) in combination with chlorine salts ( $NH_4Cl$ ,  $KCl$ ) in concentrations varying from 0.3 to 0.6M. KOH or NOAH was also added sometimes in order to control solution's pH, and successful results were obtained for pH values in the 1.3 – 3.2 range. Micron size 32 bundles of nanotubes averaging around 25 nm in diameter and with a wall thickness round 5 nm were spotted both on select attack areas on the sample and also forming a precipitate on the bottom of the beaker as they were released into the solution.



**Figure 3.1** Scanning electron microscopy image of titania nanotubes (side view) fabricated by anodizing titanium foil

By comparison, such lengths (and corresponding aspect ratios) are attained in fluorides only after tens of hours of anodization. This motivated us to further continue our study in order to optimize the anodization parameters for better, more uniform sample coverage with formation sites, ideally leading to the formation of ordered nanotubes arrays while keeping the advantages of using chlorine instead of fluorine. The nanotubes obtained by anodization are amorphous, and further employment in solar energy harvesting devices requires crystallization, routinely acquired by annealing. Titania nanotubes powders synthesized by anodization of titanium foils in solutions fluoride ions (resulting in long range ordered arrays with hexagonal orientation detached from the titanium substrate as free standing films), or chloride (short range ordered bundles formed as a precipitate in the solution and subsequently dried for nanotubes powders) were used.

While annealing temperatures lower than 300°C are insufficient for crystallization to occur, for temperatures higher than 400°C the nanotubes morphology is affected. While they are keeping the original ordering, the individual tubes are changing into one dimensional nano particulate structures. This leaves a small window for annealing condition which would result in crystallization of the powders to the phase, while keeping the nano tube structure intact. Annealing time may also play an important role, as solid diffusion may occur after crystallization, possibly changing the structure at the nano scale.

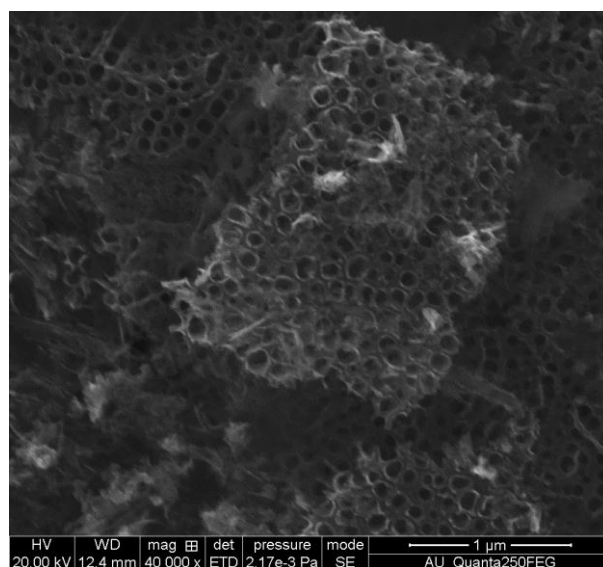


**Figure 3.2** SEM views of titania nanotubes powders synthesized by anodization

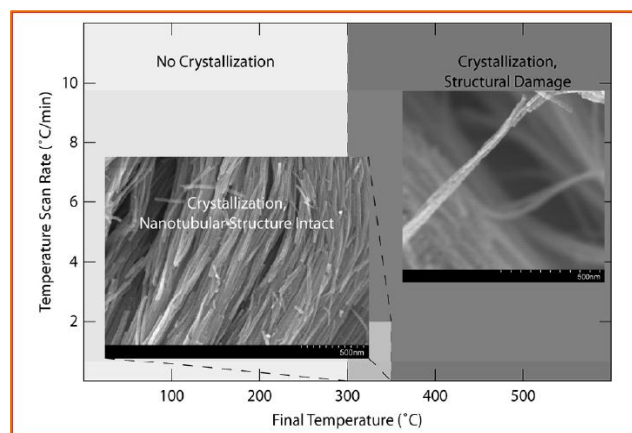
Differential scanning calorimeter studies revealed for all samples heated to a final temperature higher than 350° that the phase transition occurs between 270°C and 320°C, while for temperatures lower than 260°C no phase transition was observed. Subsequent trials at temperatures between 270°C and 300°C with a scan rate of 1-2°C/min still produced (sometimes partially)

crystalline structure as TEM this study results show that there is a narrow window in the annealing temperature and temperature scanning ranges where crystallization happens without damaging the tubes structure. Temperatures above 300°C are necessary for full crystallization, while scanning rate values above 2-5°C/min, coupled with temperatures above 350°C damage the nano tube structure of the material, breaking it into quasi spherical particles.

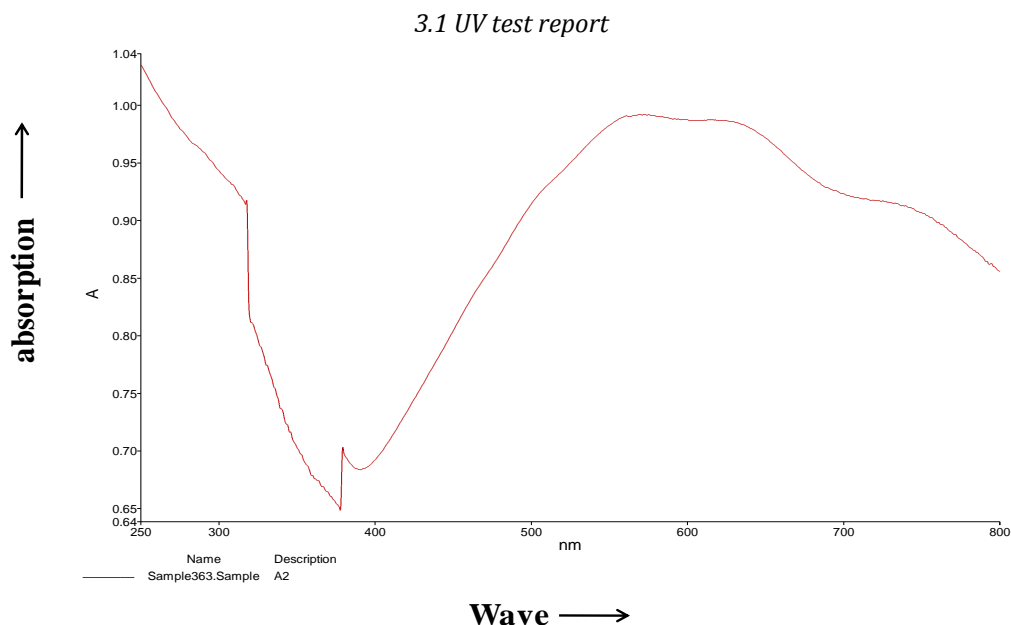
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**Figure 3.3** SEM views of titania nanotubes powders synthesized by anodization



**Figure 3.4** Identification of annealing outcome for various parameters in the Temperature Scan / Final Temperature space



**Figure 3.5** Identification of UV test report in the wave /absorption

## Conclusion

Throughout this study we investigated the synthesis of titania nano tubes using electrochemical anodization techniques, created hybrid materials by the addition of other nano particulate composites, and furthermore approach some solar energy harvesting applications of these new materials. Our study on titania nanotubes arrays by anodization of titanium sheets has led to the discovery of electrochemical fabrication of titania nanotubes by using chloride ions in place of fluorine ions. The advantages of this methods are a much faster synthesis (minutes with respect to tens of hours), and lower toxicity of the substances used.

A systematic study of the synthesis conditions from journals revealed clues to the mechanism of the new process, while also providing us with tools for optimization. Double anodization or usage of non-aqueous electrolytes improved the synthesis process; yielding superior nanotubes with respect to individual morphology, long range ordering and sample coverage. A further investigation of the annealing parameters allowed us to create crystalline nanotubes, suitable for solar energy harvesting applications. Such applications included dye sensitized and CdTe sensitized solar cells, photo electrochemical water splitting, and controlled gold attachment to the nanotubes for improved photo catalytic devices (such as photo-assisted CO oxidations).

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