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# Crystalline Phase and Photocatalysis Activity of Electrochemically Anodized Titania Nanotubes

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## Abstract

Titania (TiO<sub>2</sub>) nanotubes were developed by electrochemical anodization method. The crystalline phase of TiO<sub>2</sub> nanotubes annealed at different temperatures was identified by X-ray diffraction. Anatase phase TiO<sub>2</sub> started revealing at 300 °C and pronounced at 500 °C indicating the better crystallinity of TiO<sub>2</sub> nanotubes. Photocatalysis activity of TiO<sub>2</sub> nanotubes in methylene blue solution was also examined under UV light irradiation. High temperature annealed TiO<sub>2</sub> nanotubes improved the photodegradation of methylene blue in aqueous solution.

**Keywords:** Titania nanotubes, Electrochemical anodization, Anatase phase, Photocatalysis activity

## Introduction

Titania (TiO<sub>2</sub>) is an extremely versatile semiconducting material, suitable for a variety of technological applications. TiO<sub>2</sub> exist in three distinct crystalline polymorphous: rutile, anatase, and brookite. Rutile is the most common natural form of titania, the most studied and well known of the three polymorphs. Anatase, which is rare in comparison to rutile, is also of great interest, particularly for its key role in the injection and transport of electrons in photovoltaic devices. Brookite is the rarest form of the mineral, and is not easily obtained synthetically.

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In the past decade, considerable attention has been focused on using nanocrystalline TiO<sub>2</sub> as a photocatalyst for the degradation of organic pollutants. The photocatalyst titanium dioxide is a wide bandgap semiconductor, corresponding to radiation in the near UV range. An electron-hole pair formation occurs within the conduction and valence bands of TiO<sub>2</sub> after the absorption UV radiation [A. Fujishima]. Highly order TiO<sub>2</sub> nanotube arrays have been regarded as potential superior photocatalyst due to their valuable high surface area structure. The one dimensional nanostructures with tubular symmetries possessed low recombination of light-induced electron-hole pairs and high photocurrent conversion efficiency [J. M. Macak]. Quan et al., and Wang et al. indicated that titanium dioxide (TiO<sub>2</sub>) nanotube attached to the parent titanium substrate improved the transport of the photo-induced electrons from photoanode to cathode and enhanced the photocatalytic activity of TiO<sub>2</sub> nanotube arrays.

Of the fabrication techniques of TiO<sub>2</sub> nanotubes, the electrochemical anodization is deemed popular due to its ease of process and good controllability on structural properties. The control parameters during anodization include the electrolyte concentration, pH, anodization voltage and time. Previous report showed that the fluoride concentration of 0.5 wt % in electrolyte and anodization voltage of 50 V provide a well-defined TiO<sub>2</sub> nanotubes with uniform morphology. This work involves the examination of the crystalline phase and photocatalysis activity of TiO<sub>2</sub> nanotubes developed by electrochemical anodization.

### **Experimental Details**

Titanium sheet (99.7% purity) with a thickness of 0.2 mm was taken for the anodization. Small pieces of Ti-sheet of size 25 mm x 20 mm were ultrasonically cleaned separately in acetone and ethanol for 10 minutes each and then rinsed in distilled water and finally dried by air blow. The volume ratio of ethylene glycol (EG) to distilled water (DW) was fixed at 9:1 and the ammonium fluoride (NH<sub>4</sub>F) content was 0.5 wt%. The electrolyte solution was

stirred for 30 min with magnetic stirrer before anodization. Anodization was performed at room temperature in a standard two-electrode electrochemical cell with Ti foil as the working electrode and platinum rod (diameter: 1mm; purity: 99.9%) as the counter electrode connected to a dc power supply. The applied voltage between the titanium sample and the platinum cathode (they are 2 cm apart) was 50 V and the anodization time was 1 hour. The anodized samples were rinsed with distilled water and dried in air. Anodized samples were annealed at 300 °C, 400 °C and 500 °C in a digital muffle furnace (DMF 05) for 3 hr.

The surface morphology and size of TiO<sub>2</sub> nanotubes array were investigated by Scanning Electron Microscopy (SEM ZEISS EVO 60). The crystal phases of the annealed nanotubes were studied by using X-ray diffractometer (Bruker D8 Advance). Photodegradation studies were performed by dipping anodized sample in 50 ml of 0.0006 g methylene blue (MB) in a beaker glass. Electrolyte solution was prepared at pH 1. The pH of the electrolyte solutions were measured by the pH meter (KEDIDA pH CT6021A). The sample was left in a dark environment for 30 min to achieve adsorption/desorption equilibrium. It was photo-irradiated at room temperature using 24 W UV light and then 3 ml solution was withdrawn every 30 min from the beaker glass to monitor the degradation of methylene blue after irradiation. The concentration of the degraded methylene blue was determined using UV-visible spectrometer (GENESYS 10S) [S. Sreekantan].

## **Results and discussion**

The scanning electron microscopy (SEM) image of TiO<sub>2</sub> nanotube arrays developed in the electrolyte solutions of NH<sub>4</sub>F concentrations 0.5 Wt % and anodization voltage of 50 V is shown in (Fig. 1 a). It is clearly seen that the TiO<sub>2</sub> nanotube arrays were well-defined and uniform morphology over large area. To carefully examine the diameter of TiO<sub>2</sub> nanotubes, the size distribution histogram was generated (Fig. 1 c). It is found that average inner

diameter of TiO<sub>2</sub> nanotube arrays spans from 70-160 nm with the highest frequency of nanotube size is 90-110 nm. Moreover, the length of TiO<sub>2</sub> nanotube arrays was also determined by scanning the cross-sectional view of TiO<sub>2</sub> nanotubes (Fig.1 b). From the SEM cross-sectional images of TiO<sub>2</sub> nanotubes, the length of the nanotubes is around 2 μm.

To get insight into the growth process during anodization, the anodization current behavior was recorded for the sample being studied. Fig. 1 d depicts the plots of current density against anodization time during the anodization of 1 hr. At the very beginning of the anodization, the current density was 25.28 mA/cm<sup>2</sup>. During the first anodization time period 5min, the current density sharply decreased due to the formation of oxide compact layer on the electrolyte/titanium interface. The current density then slightly increased indicating the breakdown of compact layer. Finally the current density got steady which implies that the nanoporous structure was gradually evolved.

We studied the effect of annealing temperature on the formation of crystalline phases of TiO<sub>2</sub> nanotubes by X-ray diffraction (XRD). Fig. 2 shows the XRD patterns of TiO<sub>2</sub> nanotubes annealed at 300 – 500 °C. The major diffraction peaks in obtained patterns were examined with standard diffraction data of pure Ti and anatase phase TiO<sub>2</sub>. As anodized TiO<sub>2</sub> exhibited the peaks corresponding to pure Ti (the data is not shown here). As seen in fig 2, TiO<sub>2</sub> nanotubes annealed at 300 °C started generating the diffraction peaks at 25.28°, 48.05° and 53.89° which correspond to anatase phase TiO<sub>2</sub>. At higher annealing temperatures (400 °C and 500 °C), the peaks were more intensified suggesting an improved crystallinity of TiO<sub>2</sub> nanotubes. The pure Ti peaks still existed in the obtained XRD patterns of annealed TiO<sub>2</sub> nanotubes because of the pure Ti base on which TiO<sub>2</sub> nanotubes were formed.

The photocatalytic properties of the TiO<sub>2</sub> nanotube arrays were evaluated by the degradation of methylene blue (MO) solution under UV light irradiation for 3 hr. Here we used TiO<sub>2</sub>

nanotubes as photocatalyst. The optical absorbance values of MB solution at the time (0 sec and t sec) during the photodegradation reaction correspond to the initial concentration of MB ( $C_0$ ) and the concentration of MB ( $C$ ) at the time t. The blank test was also carried out by irradiating MB solution without  $\text{TiO}_2$  nanotubes for checking the direct photolysis of MB. Fig. 3 shows the plots of  $C/C_0$  against degradation time (min) for MB solutions with  $\text{TiO}_2$  nanotubes annealed at  $400^\circ\text{C}$  and  $500^\circ\text{C}$ . This plots actually reflect the degradation rate or degradation efficiency of MB. It is seen in the plots that the  $\text{TiO}_2$  nanotubes annealed at higher temperature ( $500^\circ\text{C}$ ) facilitated a higher degradation rate for MB. The MB degradation efficiency was determined using the equation:  $\eta = (1 - C/C_0) \times 100\%$  [Z. Hu]. The MB degradation efficiency was found to be 55.35 % and 87 % for  $\text{TiO}_2$  nanotubes annealed at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  respectively.

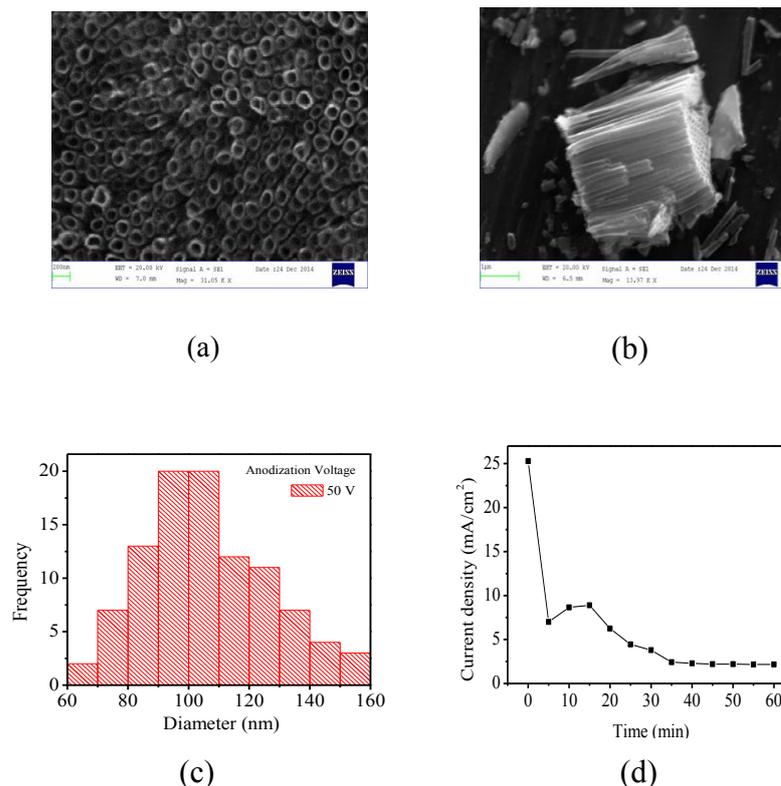


Fig. 1 SEM images of  $\text{TiO}_2$  nanotube arrays (a) Top view, (b) Cross- sectional view, (c) Size distribution histogram and (d) plot of current density against anodization time recorded during the growth of  $\text{TiO}_2$  nanotubes.

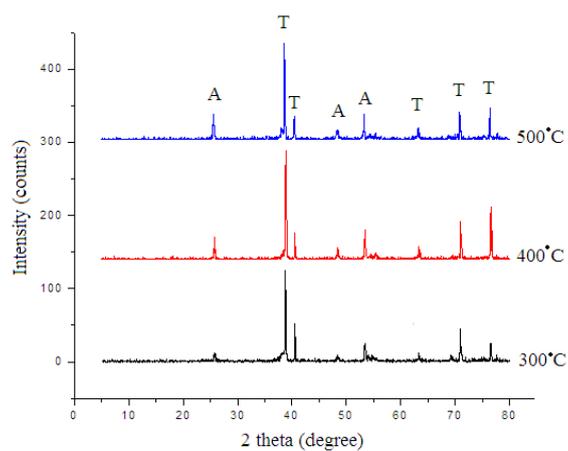


Fig. 2 XRD patterns of TiO<sub>2</sub> nanotube samples annealed at 300°C, 400°C and 500°C (“A” and “T” stand for - Anatase phase and pure Titanium respectively).

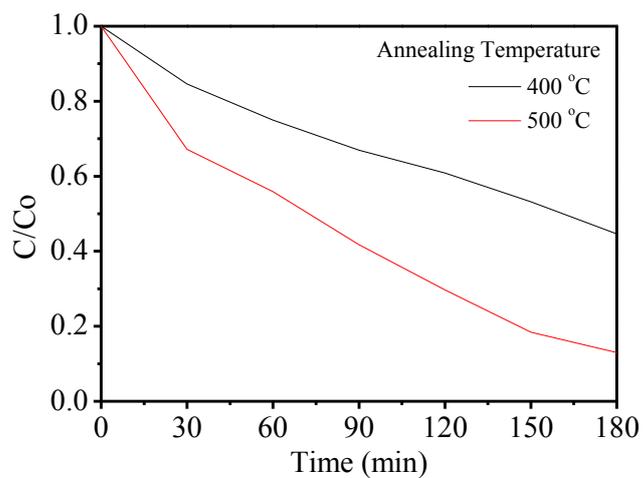


Fig. 3 Photodegradation of methylene blue (MB) solution using the photocatalyst (TiO<sub>2</sub> nanotubes annealed at 400 °C and 500 °C)

## Summary and Conclusion

Crystalline phase and photocatalysis properties of titania (TiO<sub>2</sub>) nanotubes developed by electrochemical anodization were investigated. TiO<sub>2</sub> nanotubes have the inner diameter of 70-160 nm and the length of 2 μm. A pronounced anatase phase TiO<sub>2</sub> was revealed by the TiO<sub>2</sub> nanotubes annealed at 500 °C indicating the better crystallinity of TiO<sub>2</sub> nanotubes. Monitoring the photodegradation of methylene blue (MB) using the photocatalyst TiO<sub>2</sub> nanotubes indicates that a higher photodegradation efficiency of 87 % was achieved with TiO<sub>2</sub> nanotubes annealed at higher temperature 500 °C.

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