

**Aligned Titania Nanotube Array Thin Films: Growth Kinetics,  
Branched Structures, and Photovoltaic Characterization**

by

Gorun Butail

A Thesis Submitted to the Graduate  
Faculty of Rensselaer Polytechnic Institute  
in Partial Fulfillment of the  
Requirements for the degree of  
DOCTOR OF PHILOSOPHY  
Major Subject: Materials Engineering

Approved by the  
Examining Committee:

---

Prof. G. Ramanath, Thesis Adviser

---

Prof. D. J. Duquette, Member

---

Prof. L. Huang, Member

---

Prof. I. Bhat, Member

Rensselaer Polytechnic Institute  
Troy, New York

April 2011  
(For Graduation August 2011)

## ABSTRACT

Titanium dioxide or titania is an attractive raw materials in many applications such as energy generation, storage and delivery, gas sensing, and water purification. Titania due to its excellent photocatalytic activity, stability, and non-toxic nature helps in the efficient realization of number of applications. There is a great deal of interest to synthesize titania nanostructures by inexpensive methods to reap the photocatalytic activity over large surface areas for enhanced application. Recent developments have lead to huge effort that has been put into titania nanomaterials, which has resulted in a rich knowledge for their synthesis, properties and applications.

We study and investigate in detail the physical, chemical, electronic, and thermodynamic properties of titania and understand the applications of titania from the point of view of its properties. We emphasize and explore the synthesis of titania nanotubes promising greater surface area and enhanced mass and charge transport. We report the kinetics of titania nanotube length evolution during anodization of titanium films. Our results show that the nanotube length increase is thermally activated, and governed by a voltage-dependent activation energy  $0.6 \text{ eV} \leq E^{eff} \leq 1.1 \text{ eV}$  expressed by  $E^{eff} = E_0 - \alpha V_{anod}$  where  $\alpha$  is a constant and  $E_0 = 1.6 \text{ eV}$  is a voltage-independent term. The proximity of  $E_0$  to that of oxygen diffusion in titania suggests that oxygen transport across the titania walls at the pore bottoms is the rate-limiting step. These results provide insights into the mechanism of titania nanotube formation and a framework for their rational synthesis.

We further demonstrate synthesis of branched titania nanotube formation during potentiostatic anodization of titanium films or foils in a single electrochemical bath by stepping down the anodization voltage  $V_{anod}$  below a threshold value. The linear dependence on the titanium nanotube diameter with  $V_{anod}$  and the lack of nanotube formation for  $V_{anod} < 20 \text{ V}$  constrains homogeneous branching to occur only  $V_2 \leq \frac{V_1}{\sqrt{2}} - V_0$ , where  $V_1$  and  $V_2$  are the initial and final anodization voltages and  $V_0$  is a voltage offset dependent on the anodization bath chemistry. Our technique circumvents the constraints of multi-bath and multi-temperature methods for branching, and provides

a versatile means for creating hierarchically sized and/or interconnected titania nanotubes for applications.

Pore microstructure and photovoltaic characteristics of dye-sensitized solar cells fabricated from branched titania nanotube arrays are compared with those from unbranched ones. Branched titania nanotubes result in increased efficiency and short circuit density without any discernible increases in dark current, than in devices with unbranched tubes due to increased internal surface area measured by adsorption isotherms. Enhanced photovoltaic and photocatalytic activities in branched titania nanotubes could be attractive for use in photovoltaics, water purification and energy storage applications.