

# Optimizing the Growth Parameters of Highly Ordered TiO<sub>2</sub> Nanotubes during the Electrochemical Anodization

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**Abstract.** Dye-sensitized solar cells (DSSCs) are photo electrochemical cells that are produced using various semiconductor nanoparticles and dye solutions. Efficiency of these inexpensive solar cells is fairly low (less than 11 %) because of the slow ion diffusion, poor electron transport in electrodes, and high resistance at the electrode/electrolyte interface. In order to increase the efficiency of the DSSCs, larger diameter (550 nm) of TiO<sub>2</sub> nanotubes were produced using pure Ti foil through electrochemical anodization process. In terms of diameter, this is the largest diameter of TiO<sub>2</sub> nanotubes to date. This allows us to fill highly conductive C<sub>60</sub> and Indium Tin Oxide (ITO) nanoparticles into these tubes, increase the ion diffusion and electron transportation, and reduce the interfacial resistances. We believe that efficiency of DSSC can be considerably increased through this process.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) provides an inexpensive, cost effective and hence a promising green alternative to photovoltaic cells in the conversion of solar energy to electricity [1-5]. In this investigation, optimizing the parameters that control the structural and morphological characteristics of the nanotube arrays with the prime objective to shorten the tube's length and widen the diameter of the TiO<sub>2</sub> nanotubes arrays is reported. TiO<sub>2</sub> nanotubes provide the most direct pathways for electron transport and collection in DSSCs [1], and hence is the most important player in determining the efficiency of DSSCs [4]. By filling the shortened and widened TiO<sub>2</sub> nanotubes with C<sub>60</sub> and Indium Tin Oxide (ITO) nanoparticles, the surface area will be increased for electron absorption, hence improving the light harvesting and scattering (LHE) efficiency in DSSCs, more efficient electron carrier pathways will be created due to a reduction in grain boundary formation and defects. We hypothesized that the presence of conductive C<sub>60</sub> and indium tin oxide (ITO) nanoparticles increases the electron transport to the anode at the expense of electron recapture by the oxidized iodide ions hence greatly increasing two important factors: the electron injection

efficiency ( $\Phi_{INJ}$ ) of the excited dye into TiO<sub>2</sub> and the collection efficiency of the injected electrons ( $\Phi_{COL}$ ). This together with LHE controls the current conversion efficiency (IPCE) or the external quantum efficiency of DSSCs.

This paper outlines a simple and fast method of fabricating vertically oriented, uniform large diameter TiO<sub>2</sub> by optimizing the growth parameters that govern the morphological and structural characteristics of TiO<sub>2</sub> nanotubes by the process of electrochemical anodization in ethylene glycol solution. The composition of the etching or electrolytic solution, the solution pH, anodization voltage and time, the temperature of the solution, the water content of the solution, all play key roles in determining the morphology (length, pore size, diameter, and wall thickness) of the nanotubes formed through anodization. Our choice of electrolytic anodization is due to its simplicity, cost effectiveness and reproducibility and in the process; we have total control over the growth parameters.

## 2. Experiment Details and Discussion

The process of electrochemical anodization requires the application of a voltage across two parallel conductors (electrodes) immersed in an electrolytic solution. The two electrodes include a Titanium (Ti) foil (anode) and a Platinum (Pt) foil (cathode). The electrolyte is a mixture of ammonium fluoride (NH<sub>4</sub>F), ethylene glycol and nanopure de-ionized water. The formation of the nanotubes is controlled mainly by the competition between anodic oxide formation and chemical dissolution of the oxide as soluble fluoride complexes [4]. The Titanium foil undergoes oxidation ( $Ti \rightarrow Ti^{4+} + 4e^-$ ) upon application of a potential difference across the solution as well as reacts with water ( $Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$ ) to form TiO<sub>2</sub> and 4H<sup>+</sup> ions. NH<sub>4</sub>F provides F<sup>-</sup> ions that forms water soluble [TiF<sub>6</sub>]<sup>2-</sup> complex by reacting with Ti<sup>4+</sup> and TiO<sub>2</sub> formed by electrochemical oxidations at the

anode. It's important to note that  $\text{NH}_4\text{F}$  acts as a pore opening agent and thus controls the surface morphology of the nanotubes. At very low concentration of fluoride ions, a compact oxide is formed but no oxide is formed at high concentrations of fluoride ions as all the  $\text{Ti}^{4+}$  formed react with the abundant  $\text{F}^-$  to form the highly soluble  $[\text{TiF}_6]^{2-}$  complex. In this procedure, we employed 0.09M  $\text{NH}_4\text{F}$ .

The anodization voltage applied creates an electric field gradient, which drives the ions ( $\text{Ti}^{4+}$  and  $\text{O}^{2-}$ ) to their respective electrodes thus the oxide growth is controlled by field aided ion transport. As the  $\text{TiO}_2$  layer thickness increases, the anodization voltage drops corresponding hence the driving force for ionic migration decreases. This results in an exponential drop in the anodic current. During this process, the growth and chemical dissolution of the  $\text{TiO}_2$  layer formed occurs simultaneously. At steady state, the diameter and length of nanotube increases with an increase in the anodization voltage. It's worthwhile to note that the growth rate and hence the length and diameter is affected by the overall temperature. Growth rate increases with increase in temperatures but at low temperatures, smooth and well – ordered NT are formed. To optimize our diameter, an equilibrium temperature of 25°C was adopted after a series of trials.

Prior to the anodization process, the Ti foil (0.25 mm thick, 99.7 % purity, Sigma Aldrich, USA) and the counter Pt electrode were cleaned and digested using an ultrasonic bath in acetone, isopropyl alcohol and ethanol respectively for an hour followed by rinsing in deionized water. The anodization was carried out in an electrolyte of EG in 0.09M  $\text{NH}_4\text{F}$  at a constant voltage of 70V. The water concentration of the solution was varied from 1 to 90% by volume while for each experiment; the temperature was gradually increased from 20 °C to 45°C over the 12h anodization period. Field emission scanning electron microscope was used to characterize the morphological and structural characteristics of the samples.

### 3. Results, Significance and Conclusion

By varying the percent by volume of water, the temperature of the anodic solution at an optimal voltage, we successfully produced uniform diameter  $\text{TiO}_2$  NT arrays about 500 nm (Figure 1).

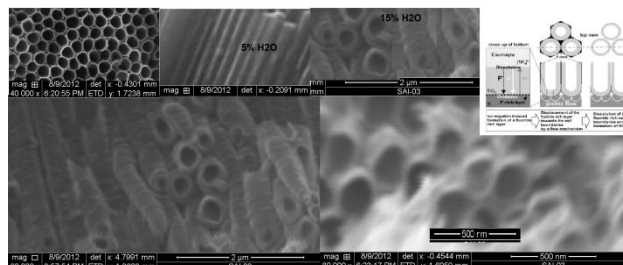


Figure 1: SEM images of  $\text{TiO}_2$  nanotube layers grown in a mixture of EG and deionized water containing 0.09 M  $\text{NH}_4\text{F}$  at 70V

By varying the percent by volume of water, the temperature of the anodic solution at an optimal voltage, we successfully produced uniform diameter  $\text{TiO}_2$  NT arrays about 500 nm. Bases on our experimental observation, the diameter increases as the water content increases but sidewall ripples are developed on the NT at high water concentrations. As temperature increases, the viscosity ( $\eta$ ) of the EG solution decrease thus increasing the corresponding diffusion coefficient ( $D$ ) of the  $\text{F}^-$  ions. This speed up the rate of chemical dissolution at the bottom becomes larger leading to U – shape NT according to Stokes Einstein relation. Further research will focus on refining our temperature variation as well as the pH of the anodic solution. This significant development will help further the studies of the parameters that govern the morphology of  $\text{TiO}_2$  NT.

### 4. Conclusions

Self – organized  $\text{TiO}_2$  nanotubes with a diameter of 500 nm were successfully produced by optimizing the growth parameters through electrochemical anodization. In comparison with current research, this work shows a significant improvement of the dimensions, morphology and structures of the nanotubes by simultaneously optimizing the parameters that growth the growth and development of  $\text{TiO}_2$ .

### References

- [1] P.K. Kahol and M. Mehring, *Conjugated Conducting Polymers*, Springer Series in Solid State Sciences, Vol. 102 (Editor: H.G. Kiess), Springer Verlag, Berlin, 1992.
- [2] D.A. Tallman and W. Horn, *Phys. Rev. B* 90, 13 (1997).
- [3] B. Wessling, in *Handbook of Nanostructured Materials and Nanotechnology* (Ed. H.S. Nalwa), Academic Press, Vol. 5, Chapter 10, p. 525, 1999.
- [4] R. Asmatulu, A. Karthikeyan, D.C. Bell, S. Ramanathan, and M. Aziz, "Synthesis and Variable Temperature Electrical Conductivity Studies of Highly Ordered  $\text{TiO}_2$  Nanotubes," *Journal of Materials Science*, 2009, Vol. 44, pp. 4613–4616.
- [5] R. Asmatulu, H. Haynes, M. Shinde, Y.H. Lin, Y.Y. Chen, and J.C. Ho, "Magnetic Characterizations of Sol-gel Produced Mn-Doped  $\text{ZnO}$ ," *Journal of Nanomaterials*, 2010, Article ID 715282, 3 pages.