Study of TiO$_2$ nano-tubes using electrochemical anodization method for applications in dye-sensitized solar cells

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Abstract. TiO$_2$ nano-tubes are getting strong attraction in many fields due to their unique properties. They are important in biomedical application, Dye sensitized solar cells, sensor and photocatalysis applications, etc. Our prime interest is to grow these tubes for dye-sensitized solar cells with high conversion efficiency and low production cost. In this research, we have synthesized TiO$_2$ nanotubes by anodizing 25 μm thick titanium foil at 40V using two-step anodization method. The electrolyte used is the ethylene glycol with varying concentration of NH$_4$F and fixed concentration of deionized water. Effect of different concentrations of the electrolyte on tube crystal structure has been studied. It is observed that crystallinity increases with increased concentration of fluoride ions. It is found that two-step anodization method results in more crystalline and open structures. Scanning electron microscopy is utilized to study the surface morphology and tubes growth, whereas observation of the crystal structure of nano-tubes is made by X-ray diffraction.

1. Introduction
Titanium oxide (TiO$_2$) is a famous and versatile oxide being used for many applications such as biosensors, gas sensors, as a photo-catalyst, in biomedical application, for photo degradation and photovoltaic devices [1-3]. Over the last few years, many researchers have focused their research on the processing and production of nanostructured titanium oxide such as nanopowders, nanowires, nanorods, nano-tubes utilizing different methods, e.g., anodization, sol-gel, vapour deposition, hydrothermal, etc., [4-7]. TiO$_2$ has three different crystalline forms as rutile, anatase and brookite. Anatase is more active phase for photovoltaic applications having better electronic and surface chemistry properties as compare to other forms, however, it is rare in abundance.

Our main concern is to grow titania nano-tubes for Dye Sensitized Solar Cells (DSSCs). DSSCs are based on nano-crystalline semiconductor oxide layer on conducting surface, dye sensitizer and electrolyte [8]. The first DSSC was reported by Miecheal Gratzel and O’ Regan in 1991 [9]. It was made by nanocrystalline titania layer produced by nano particles. Since, electrons, passing through the TiO$_2$ nanocrystalline film produced by nanoparticles, trap at grain boundaries and irregular pores structure result in low electron diffusion. One-dimensional nano-structures of TiO$_2$, e.g., nanorods,
nano-tubes, nanowires provide efficient charge transport. Among these one dimensional structure, nano-tubes based on TiO$_2$ proves to be very effective to reduce the possibility of charge recombination in DSSCs. Zwilling [10] and Gong [11] were the early reporters of TiO$_2$ tubes in aggressive electrolytes by anodization method. Later on many researchers synthesize these tubes with same method but different electrolytes [6-7, 12-14]. Now a days, ethylene glycol and glycerol with the addition of ammonium fluoride are frequently used to fabricate smooth and open ended tubes.

For the fabrications of TiO$_2$ nano-tubes, we have preferred anodization method as it is a relatively low cost process and easily controllable. By this method two types of oxides can be grown one is barrier type by using solutions of sulfuric, phosphoric and acetic acid, second is nanoporous and nanotubular type oxide utilizing chlorine base solutions, aqueous and organic solutions containing fluoride ions. This method allows the variation of different parameters, e.g., voltage, electrolyte concentration, temperature, etc., and accordingly to control the tubes morphology and structure. We have fabricated nano-tubes using double anodization method. It is observed that crystallinity of tubes increases with two step anodization. It is found that annealing is the important step to convert amorphous TiO$_2$ into crystalline anatase form desired for DSSCs.

2. Experimental steps
A 25 μm thick Ti foil was anodized for at 50 V at room temperature. The electrolyte used is ethylene glycol containing 0.5 wt % Ammonium fluoride (NH$_4$F) and 3 wt % deionized water. Before anodization, samples were cleaned by sonicating in different solvents such as ethanol, acetone and deionized water. For double anodization experiments, oxides produced by first anodization were removed by sonicating in deionized water. The second step anodization was performed in same electrolyte for same experimental conditions. For characterization of samples Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were utilized.

3. Results and discussions
Valve metals such as Ta, W, Ti, etc., can produce their oxides in oxygen containing environment. These naturally produced and ultrathin oxides remain present on their surface and affect experimental growth of anodically produced oxides. Therefore it is necessary to clean the surface before anodization. Sonicating in ethanol and acetone and finally deionized water removed dust and debris from the surface. Anodization experiments were performed at 40 V keeping temperature, time and electrolyte concentration as constant. These experiments were usually performed at room temperature for one to two hours. Figure 1 shows surface of TiO$_2$ nano-tubes prepared after first anodization at 40 V at room temperature. The surface of tubes is not very clear instead debris are present. Tubes seem to entangled in the form of branches and groups, also most of the tubes are closed from their ends.

To get the regular pattern, we have utilized the two step anodization method as people usually do with aluminium oxide. It is clear from the Figure 2 that after removal of TiO$_2$ produced by first anodization, surface of TiO$_2$ has regular hexagonal pattern.
Figure 1. Top surface of TiO$_2$ nano-tubes after single anodization at 40 V in ethylene glycol containing 0.5 wt% NH$_4$F and 3 wt% deionized water at room temperature.

Figure 2. Ti foil surface showing hexagonal pattern after removal of TiO$_2$ tubes produced by anodization at 40 V.

Figure 3. Top surface of TiO$_2$ nano-tubes after two step anodization at 40 V in ethylene glycol containing 0.5wt% NH$_4$F and 3 wt% deionized water at room temperature.

Figure 4. Cross-section of TiO2 tubes fabricated by two step anodization experiment at 40 V.

Upon second anodization with same experimental conditions regular ordered pattern is formed as presented in Figure 3. Still at some part of surface, tubes are covered. It is expected that doing such experiment at higher voltages results in open ended surface. Cross-sectional images in Figure 4 show that tubes are very smooth. The SEM image b in the same Figure is taken by breaking the produced...
oxide intentionally. The different steps in Figure shows that inner surface of tube grows in conical shape.

It is found that oxide produced is very fragile, amorphous and brittle and, therefore, during sample handling, some tubes get broken. The surface of oxide produced by single anodization is rough and have irregular pore pattern with foreign particles or debris present on it. Most of the tubes are closed at the ends. Special etching processes by mechanical and chemical treatments to remove these debris are required for clean and open ended surfaces. The resulting samples get reduced in thickness after such etching processes. However utilizing the two step anodization method, such steps could be avoided.

It is observed in our experiments that oxides got peeled off or rolled during drying and annealing processes. After first anodization, TiO₂ broke into pieces after being detached from the substrate. However, after second anodization, oxide is detached in the form of thin (few micrometer) layer with area equal to the substrate. It is expected that it can be used as free standing membrane in energy applications. However, more work is required to understand such thin sheets structure, stability, their mechanical and optical properties.

**Figure 5.** XRD plot of TiO₂ nano-tubes after annealing at 550 ºC, as anodized (a), after first anodization (b), after second anodization (c)

**Figure 6.** XRD plot of TiO₂ nano-tubes after two step anodization and annealing at 550 ºC for different concentrations of NH₄F (C₁= 0.3wt %, C₂= 0.4 wt%, C₃ = 0.5 wt%, C₄ = 0.6wt%)

XRD plots (taken at 5º grazing angle) of Figure 5 show that as anodized sample is amorphous. Whereas after annealing at 550 ºC, anatase polymorph’s small peak (101) is obtained for the samples singly anodized at room temperature in ethylene glycol electrolyte. The crystallinity of tubes increases for doubly anodized samples. It may be possible that the increase in crystallinity after second anodization is due to the ordering nature of the oxide. The peaks of Ti are present as a substrate effect.

Figure 6 shows the effect of increased concentration of NH₄F. It is observed that crystallinity of tubes increases with increasing the concentration of F⁻ ions.

**4. Conclusion**

In this paper we have presented a study of TiO₂ nano-tubes by performing anodization experiment at 40 V. Templates are prepared by two step anodization experiments. It is observed that after second anodization tubes with open pores and very regular pattern could be obtained. Such results could be enhanced at higher voltages. The two step anodization experiments have improved the crystallinity of tubes. Crystallinity also increases with increase in concentration of NH₄F. This is due to the increased concentration of fluoride ions. It is expected that such nanostructured templates, when used as
photoanode in DSSCs, would result in efficiency greater than the found values with nano-tubes so far.

5. References
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