

Study of Titanium Dioxide Nanotube Array for the Application in Dye-Sensitized Solar Cells

Swati Bhardwaj, Tushar Rana, Pinaki Laha, Anjan Barman, and Subhayan Biswas

Abstract—Highly ordered, self-organized TiO₂ nanotube arrays (TNA) have been successfully prepared by anodization of titanium foil in ethylene glycol electrolyte containing 0.01% ammonium fluoride (NH₄F). The effect of variation of applied anodization voltage ranging from 50V to 57 V on the morphology of the TNA has been studied using field emission scanning electron microscope. The increase in applied voltage enhances average pore size from 34nm to 58nm and reduces wall thickness. Diffuse reflectance spectroscopy has been used to evaluate the amount of dye absorption on the surface of various TNA which reveals direct correlation between the dye absorption and the morphology of the sample.

Index Terms—Titanium dioxide, Dye-sensitized solar cell, anodization

I. INTRODUCTION

In the recent years, vertically oriented, highly ordered titanium dioxide (TiO₂) nanotube array, prepared by anodization of titanium, and has attracted huge attention [1]-[5]. Highly ordered vertically oriented nanotube architecture of high surface to volume ratio exhibit unique properties. Nanotube offers a larger interfacial area due to their external and internal surfaces, which make them suitable for applications in dye-sensitized solar cells [6]. It also provides excellent electron pathways for charge transfer between interfaces. TiO₂ nanostructures can be synthesized by various methods like sol gel transcription using organogelator template [6]-[7], seeded growth mechanism [8], hydrothermal techniques [9]. Among these processes, the electrochemical anodization of titanium in fluorinated electrolytes is a simple method to synthesize porous highly vertically ordered structures with high aspect ratios. The process of self organization of nanotube is a complex mechanism [10]-[13] and requires extensive study. The properties of self-organized TNA can be tailored using various anodization conditions and post deposition treatment. In the present work, anodization condition is varied to observe change in the morphology of TNA and the corresponding dye absorption on TNA surface. Various anodization voltages ranging from 50-57V has been applied to prepare TNA samples.

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II. MATERIALS AND METHOD

Titanium sheet (99.9% purity, Sigma Aldrich) with a thickness of 0.25mm was taken for the anodization. Small pieces of Ti- sheet of size 1 × 1 cm were cleaned by sonicating separately in acetone, methanol, and finally with de-ionized water (DI), for 10 min each. Electrochemical anodization of titanium was carried using a two-electrode configuration with Ti as working electrode and Pt as counter electrode. The distance between the two electrodes kept at about 12cm. Anodization was performed in room temperature under constant-voltage conditions using a source meter (Model-2400 Keithley Instruments, Inc) and the current response of the sample was monitored in real time. All experiments were performed at room temperature with different constant anodization voltages ranging from 50 to 57V for 30min time duration. Ethylene glycol, ammonium fluoride and DI-water were used as electrolyte in the electrochemical anodic reaction. The electrolyte was stirred continuously during the anodization process. The anodized samples were washed with ethanol, ultra-sonicated for 10 min to remove the debris from the surface. Anodized samples were annealed at 450^oC for 1 hour in air. The absorbance of Ru-based N719 dye on TNA was obtained by diffuse reflectance UV-vis spectroscopy (DRS) using integrated sphere (ISR 240A) attached with UV-vis spectrophotometer (Shimatdzu-2450) The morphology of different TNA was studied by field emission scanning electron microscope (Quanta FEG250).

III. RESULTS AND DISCUSSIONS

The Fig. 1 represents the anodization current vs. time for the TNA, deposited with 50V and 57V. Initially, with the increase of voltage, anodization current increases rapidly and reaches maximum point with in 150sec. After that an abrupt decrease of current is observed which is due to the formation of an oxide barrier layer that induces a voltage drop between the working electrode, Ti layer, and electrolyte. In this region, electronic conduction decreases and ionic conduction through the TiO₂ increases. This stage is followed by a steady state, when anodization current reaches a saturation value. At this stage dissolution and oxidation of titanium reaches a kind of equilibrium which leads to maximization of formation of nanotube. The anodization current depends upon different phenomena that take place during anodization process [14]. Higher anodization voltage enhances both field assisted movement of fluorine ion towards TiO₂ layer at the electrolyte/oxide interface and ejection of Ti₄⁺, which in turn induces more dissolution of TiO₂. The Fig. 1 indicates that increase of

anodization voltage enhances anodization current in the entire deposition period. It is important to note that the samples, deposited at 55V and 57V, show comparatively high anodization current even when it reaches steady state conditions.

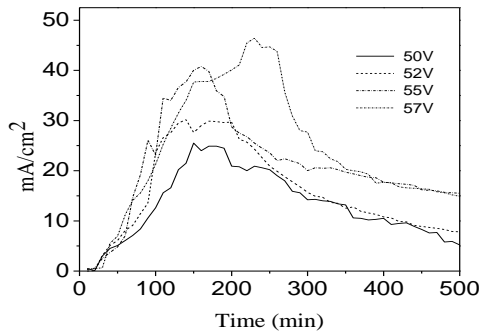


Fig. 1. Anodization current vs. time of TiO₂ nanotubes, deposited at various anodization voltages.

Fig. 2 shows a comparison of XRD patterns of nanotubes samples after their formation and after annealing at 450°C in air. The X-ray diffraction measurement reveals that although as-deposited film shows amorphous nature but annealed film shows the anatase peaks (101), (211) and (216).

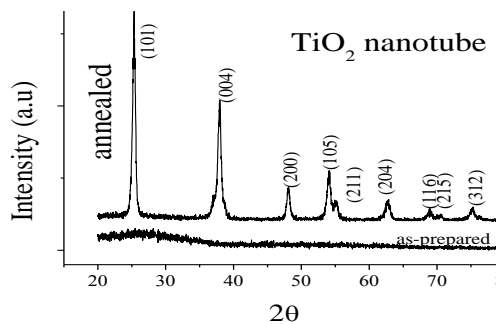


Fig. 2. X-ray diffraction of TiO₂ nanotube array: as-prepared and annealed

The field emission electron microscopy (FESEM) images of the nanotubes deposited at different potentials from 50V to 57V are shown in Fig. 3. Gradual change has been observed in the diameter of the pore and wall-thickness of TiO₂ nanotube as anodization voltage is increased from 50V to 57V. For TNA, prepared with 57V, etching of top layer leads to very low wall thickness. The distribution of pore-diameter is shown in Fig. 4, which reveal definite increase of pore diameter. The average pore diameter of the TiO₂ nanotube prepared at 50, 52, 55 and 57V is 34±4, 44±3, 53±5 and 58±4nm respectively. Fig. 5 is an indicative figure, which shows highly ordered vertically arranged TiO₂ nanotube prepared at 52V. Fig. 6 presents UV-vis diffuse reflectance spectra of TiO₂ nanotube prepared at different anodization voltages. The entire sample show typical variation of diffuse reflectance of TiO₂ nanotube array [15]. The reflectance of TiO₂ nanotube array prepared on Ti metal, increases with increase of anodization voltage. This is due to the voltages. The possible reason behind the variation of variation of thickness of TNA, prepared at different thickness with anodization voltage is that increase of anodization voltage enhances anodization current substantially, as shown in Fig. 1. This high current enhances temperature of the electrolyte which in turn reduces the

deposition rate and thickness [16].

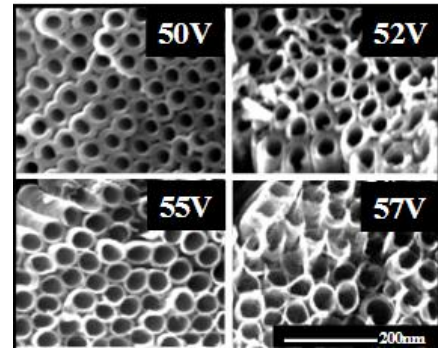


Fig. 3. FESEM images of top view of TiO₂ nanotube array, deposited at anodization voltage 50V, 52V, 55V and 57V.

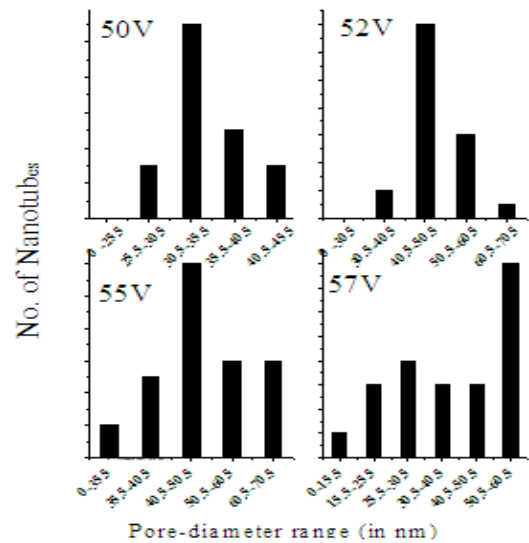


Fig. 4. Pore size (nm) distribution of TiO₂ nanotube array, deposited at anodization voltage 50V, 52V, 55V and 57V.

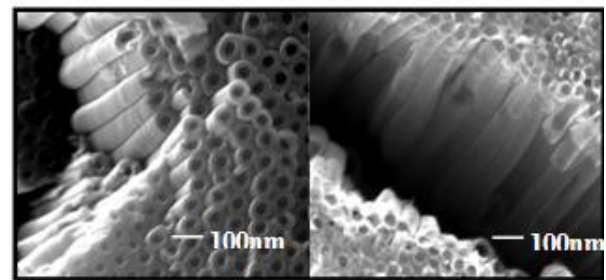


Fig. 5. Side view of TiO₂ nanotube array prepared with 52V anodization voltage.

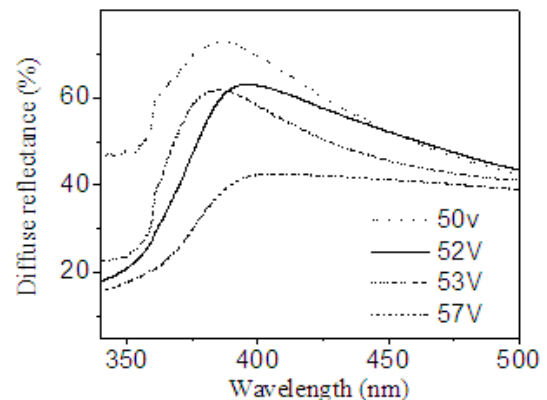


Fig. 6. Diffuse reflection spectra of TiO₂ nanotube array, prepared at different anodization voltages.

The measured reflectance was converted directly to

absorbance ($\log(1/R)$) where R represents relative diffuse reflectance. Since the purpose of the reflectance measurements was not to determine the N719 concentration but to measure the absorbance of the N719 adsorbed on TNA, the Kubelka-Munk function, was not used [17]. Fig. 7 presents variation of absorbance of TiO₂ nanotube array, prepared at 50 and 57V (with and without dye), with wavelength. It has been observed that in the visible light range, dye-sensitized TNA, deposited at 50V exhibits much lesser enhancement of absorbance, in compare to the sample, deposited with 57V. It is due to the fact that increase of pore diameter and decrease of wall thickness of TNA, deposited at higher anodization voltage, provide more surface area for dye-absorption.

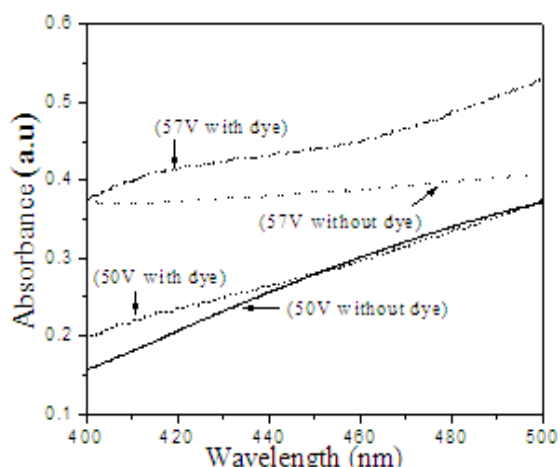


Fig. 7. Absorption spectra of TiO₂ nanotube array with and without dye, prepared at 50 and 57V.

IV. CONCLUSION

In conclusion, vertically ordered TiO₂ nanotubes array have been successfully prepared by anodization technique with varying anodization voltages ranging from 50V to 57V to study the variation of dye absorption. The study reveals that increase of anodization voltage induces systematic changes in the morphology of TNA. This gradual morphological change is very useful for fine tuning properties that are appropriate for various applications. The effect of increase of applied anodization voltage has been reflected in the real time measurement of anodization current. In this present investigation, FESEM measurement confirms that increase of anodization voltage enhances diameter of the TiO₂ nanotubes and reduces wall thickness which provide higher surface area for dye-absorption. The absorbance, measured by diffuse reflectance spectroscopy, shows maximum values for N719 sensitized TNA, prepared at 57V.

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