

## DYE SENSITIZED SOLAR CELL BASED ON HYDROTHERMALLY SYNTHESIZED TITANIA NANOTUBES

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### Abstract

Titania nanotubes were introduced into conventional Dye Sensitized Solar Cell (DSSC) as an electron conducting medium as they provide straight pathway to electron transport. Titania nanotubes were synthesized via hydrothermal treatment of commercially available TiO<sub>2</sub> powder and deposited onto the conducting substrate FTO (F doped SnO<sub>2</sub>) via electrophoretic deposition technique. Thin film of TiO<sub>2</sub> nanotubes was found to be nearly 10 nm diameter and ~200 nm long. Solar cell fabricated with TiO<sub>2</sub> nanotube and sensitized with N3 dye showed an open circuit voltage (Voc) of 0.75 V and short circuit current (Jsc) of 3.81 mA/cm<sup>2</sup> under AM 1.5 G irradiation. The cell performance further improved by treating the titania nanotubes electrode with TiCl<sub>4</sub>.

**Key words:** *Dye Sensitized Solar Cell, nanotube, hydrothermal, nanocrystalline*

### 1. Introduction

In 1991, Michael Gratzel introduced a new type of solar cell called DSSC which is a promising and best alternative concept to conventional silicon based solar cells with very low material cost making economically viable<sup>1</sup>. These devices consist of a wide band gap semiconductor covered by a monolayer of sensitizing dye, an electrolyte and a counter electrode. The semiconductor is directly supported by a transparent electrode on one side, while the dye is connected to the back electrode via a liquid electrolyte or a solid hole conducting material. The initial step of the photovoltaic process is a light induced electron injection from the dye into the semiconductor material. This process yields an oxidized dye and an energetic electron. Rapid regeneration of the dye by the electrolyte prevents back transfer of the electron or degradation of the photo-oxidized dye. Meanwhile, the energetic electron diffuses away from the dye, passing through the electrode and an external load, finally reaching the counter electrode where it regenerates the redox couple.

In conventional DSSC, despite of the high surface area, random nature of the titania nanocrystalline particle network results in electron to recombine as they move through the surface of the titania nanocrystalline network reducing cell performance<sup>2</sup>. In order to facilitate direct electron transfer within the electron conducting material, 1-D nanomaterials such as arrays of nanowires and nanotubes can be introduced instead of particle network as they provide short direct pathways. In DSSC, high electron collecting efficiency has been observed when 1-D nanostructure such as ZnO, TiO<sub>2</sub> were employed<sup>3</sup>. Compared to other nanostructured materials, TiO<sub>2</sub> has better performance giving higher open circuit voltages and fill factors leading to high efficiency. There are several methods available to synthesis titania nanotube such as ZnO template method<sup>4</sup>, anodization<sup>2</sup>, hydrothermal method<sup>5-7</sup>. Among these methods, hydrothermal is being used as it provides easy synthesizing method, cost effectiveness and possibility of bulk production. Though, anodization method provides well aligned array of nanotubes which results in better performance of the cell,

the fabrication cost is high compared to hydrothermal method. In this investigation titania nanotubes have been synthesized via hydrothermal treatment of commercially available titania powder.

### 2. Material and methods

Titania nanotubes were synthesized via hydrothermal treatment of titania nanoparticles: 2 g of TiO<sub>2</sub> powder (Degussa P 25) dispersed in 10 M NaOH (aq) solution by stirring for one hour followed by transferring into a Teflon lined autoclave. The autoclave was kept at 150<sup>0</sup>C for 48 hours. The resulted precipitate was washed with distilled water and 0.1 M HCl until pH reaches 8.5. TiO<sub>2</sub> nanotube working electrode was prepared by using this precipitate by electrophoretic deposition technique on a

FTO substrate (Sheet resistance 8 Ohm/cm<sup>2</sup>). The electrolyte for electrodeposition was prepared by ultra sonicating the precipitate for 60 minutes to make a nanotube suspension. The electrolyte was prepared by mixing nanotube suspension and methanol in 2:1 volume ratio. Pt was used as counter electrode and FTO substrate was kept as anode at optimized voltage of 40 V for 5 minutes in a two electrode system. After electrodeposition of TiO<sub>2</sub> nanotubes on FTO, the film was dried at 130 °C for 10 minutes followed by sintering at 450 °C for 30 minutes. The electrode was immersed into the dye solution containing 0.3 mM cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N3, Solaronix) for 12 hours. Finally, DSSC was assembled using TiO<sub>2</sub> nanotube working electrode and Pt counter electrode using iodine/triiodine redox couple as an electrolyte in between these two electrodes. Cell performance was measured under AM 1.5 G solar simulation using home made I-V analyzer based on Keithley 2000 multimeter and potentiostat POT1000M. Scanning Electron Microscopy (SEM) and UV-Visible analysis were used to study the surface morphology and absorption measurements respectively of the film prepared. The nanotube based electrode was treated with TiCl<sub>4</sub> in some cases. For this, two drops of 0.04 M TiCl<sub>4</sub> was dropped onto the surface of the TiO<sub>2</sub> nanotube coated electrode followed by washing in distilled water then again the film was sintered at 450 °C for 30 minutes.

### 3. Results and Discussion

The electrodeposition time was optimized using uv-visible absorption (transmittance) analysis. The titania nanotubes was deposited on to the FTO surface by varying deposition time from 1 to 10 minutes. With the increase in deposition time from 1 to 5 minutes, the film thickness increases. With further increase in deposition time even thicker film could be obtained however, these films tend to peel-off during sintering process. We noted formation of nearly uniform TiO<sub>2</sub> film in 5 minutes electrodeposition time.

The formation of fairly uniform TiO<sub>2</sub> nanotube films on FTO glass substrate with the optimum electrodeposition conditions was confirmed by the SEM analysis. Figure 1 shows the SEM image of the TiO<sub>2</sub> nanotubes synthesized via hydrothermal method which confirmed the formation of nearly 10 nm diameters and average length of 200 nm nanotubes.

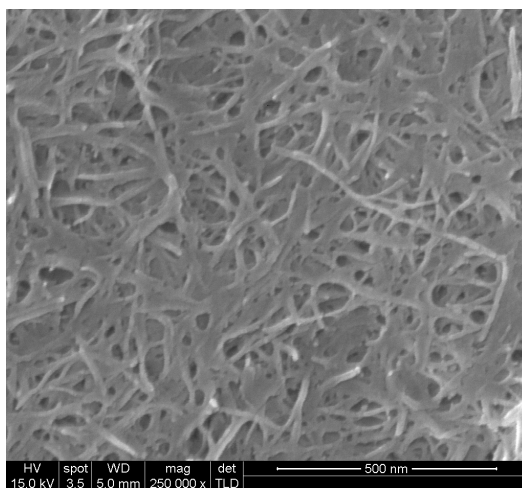


Figure 1: SEM image of the hydrothermally synthesized titania nanotubes

Also, it can be clearly seen in the SEM image, that there are few uncurled TiO<sub>2</sub> nano-structures which are similar to TiO<sub>2</sub> nanoribbon or nanobelt. In hydrothermal method, depending on the preparation conditions such as reaction temperature, reaction time, reactant concentration and the acidic/basicity of the reaction medium, defects could be formed. Changchun et.al reported formation of only titania nanoparticles with anatase and rutile phase following the same experimental conditions and procedure described above except the concentration of the NaOH (5 mol/L), indicating that at low basicity, formation of TiO<sub>2</sub> nanotube does not occur or if formed they are with defects<sup>7</sup>.

Figure 2 and Figure 3 show the I-V characterization of the solar cells fabricated with TiO<sub>2</sub> nanotube films that are treated with TiCl<sub>4</sub> and untreated films respectively and which were sensitized with Ru-dye and the results are summarized in Table 1.

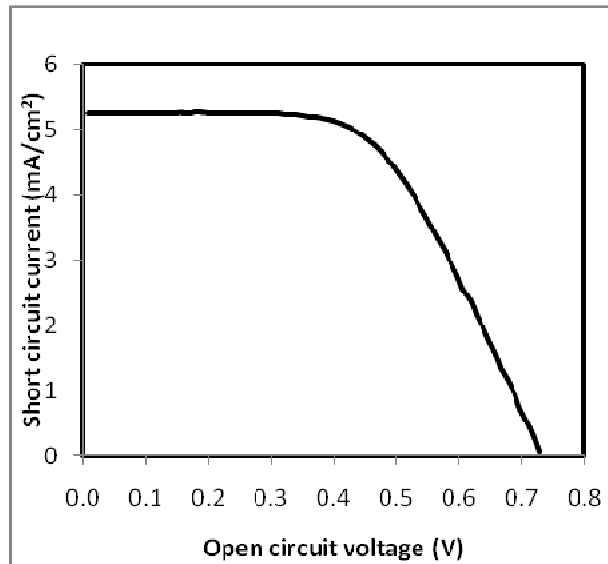


Figure 2: The I-V characterization of the  $\text{TiO}_2$  nanotube electrode after  $\text{TiCl}_4$  treatment sensitized with N3 dye under AM 1.5 G irradiation.

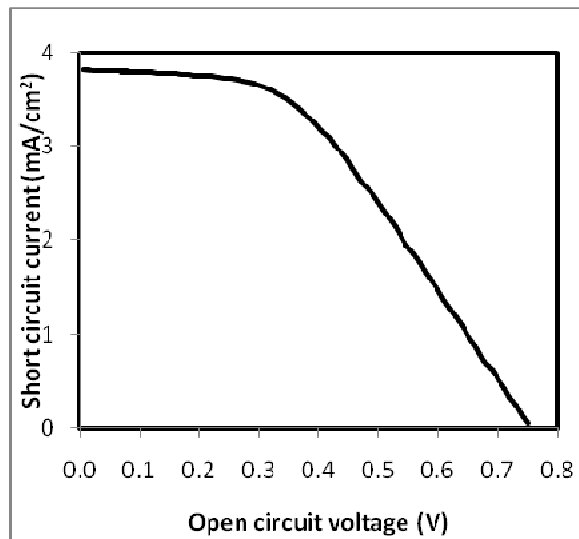


Figure 3: The I-V characterization of the  $\text{TiO}_2$  nanotube electrode before  $\text{TiCl}_4$  treatment sensitized with N3 dye under AM 1.5 G irradiation..

Table 1: DSSC parameters for  $\text{TiO}_2$  nanotube electrodes sensitized with N3 dye under AM 1.5 G irradiation.

	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	$V_{oc}$ (mV)	FF (%)	$\eta$ (%)
Bare $\text{TiO}_2$ nanotube electrode	3.81	750	45	1.28
$\text{TiO}_2$ nanotube electrode treated with $\text{TiCl}_4$	5.24	728	58	2.21

It is clearly seen that the  $\text{TiCl}_4$  treatment increases the overall solar cell performance compared to  $\text{TiCl}_4$  untreated films. It has been shown that the  $\text{TiCl}_4$  treatment of mesoporous  $\text{TiO}_2$  layer enhances the overall solar cell performance of DSSC due to increase in dye uptake and change in surface properties of mesoporous  $\text{TiO}_2$  layer.<sup>8,9</sup> Dye adsorption analysis and surface morphology study of pristine  $\text{TiO}_2$  nanotube and  $\text{TiCl}_4$  treated  $\text{TiO}_2$  nanotube revealed the same trend. Figure 4

shows the dye absorption spectra of  $\text{TiCl}_4$  treated and untreated  $\text{TiO}_2$  nanotube arrays. As shown in Figure 4, the optical absorption of Ru-TPA-NCS dye coated  $\text{TiCl}_4$  treated  $\text{TiO}_2$  nanotube electrode is higher than that of the bare  $\text{TiO}_2$  nanotube electrode indicating that enhanced dye uptake by  $\text{TiCl}_4$  treated  $\text{TiO}_2$  nanotubes which in turn resulted in higher  $J_{sc}$  than untreated  $\text{TiO}_2$  nanotube electrode. Furthermore, it has been reported that the  $\text{TiCl}_4$  treatment of  $\text{TiO}_2$  results in increased charge injection efficiency as a result of a positive shift in the flat-band potential of  $\text{TiO}_2$ .<sup>8, 9</sup> Also it has been suggested that the thin  $\text{TiO}_2$  layer formed on mesoporous particles may acts as a charge recombination barrier preventing electron access to the surface. Therefore, we believe that a combination of effects of enhanced dye adsorption, efficient charge injection and reduced charge recombination, resulted in higher solar cell efficiency in  $\text{TiCl}_4$  treated  $\text{TiO}_2$  nanotube.

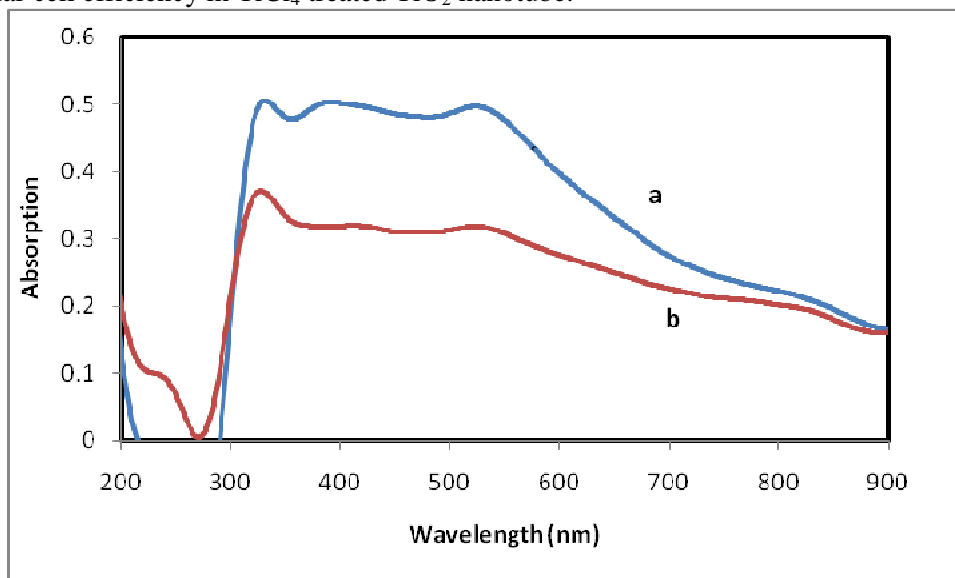


Figure 4: UV-Visible absorption spectroscopy of titania nanotubes deposited on FTO substrate sensitized with Ru dye (N3). a) Electrode treated with  $\text{TiCl}_4$ . b) Untreated

The solar cell performance reported in this investigation is low compared to that of reported values. We believe that this could be due to the defect present in our nanotubes such as nanoribbons and nanobelts. Furthermore, as shown in Figure 1, nanotubes were randomly oriented resulting in zig-zag movement of electrons in between nanotubes leading to enhance charge carrier recombination. Therefore increasing the orientation of nanotube would provide opportunity to improve the solar cell efficiency further and our research is been focused on this aspect.

#### 4. Conclusion

In this investigation  $\text{TiO}_2$  nanotubes were synthesized by hydrothermal method and fabricated in to Dye Sensitized Solar cell. Reaction conditions such as temperature and concentration are found to be very important in hydrothermal treatment for formation of titania nanotubes. Treatment of  $\text{TiCl}_4$  with  $\text{TiO}_2$  nanotubes increases the short circuit current and efficiency roughly 40 % and 72 % respectively. The performance of the cell largely depends on the ordered and vertical alignment of the nanotubes. Therefore, in order to improve the cell performance nanotubes should be deposited in a well ordered manner.

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