Growth and Performance of TiO_2 Nanotubes on Anatase Blocking Layer in Dye-Sensitized Solar Cells

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***Abstract*-The growth of nanostructured TiO_2 on indium tin oxide (ITO) coated glass substrate has been reported. A thin film of TiO_2 nanoparticles has been first layered down by dip coating and annealed followed by growth of anatase TiO_2 nanotubes with a remnant blocking layer by solvothermal process. The novelty of the task lies in the formation of blocking layer beneath the nanotubes to be employed as photoanode in front side illuminated dye-sensitized solar cell. The morphology and microstructure of the nanotubes have been characterized by x-ray diffraction and electron microscopy, Raman spectroscopy, UV-visible spectra. Dye-sensitized solar cell has been assembled using this nanotube film as photoelectrode. The performance of the cell has been analyzed on the basis of incident photon to current conversion efficiency (IPCE) spectra and current-density, voltage (*JV*) characteristics. The observed efficiency value is 7.28%.**

Keywords- Blocking Layer; Pinning; Fermi Level; Extinction Length

I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been extensively researched since their discovery because of optimum performance to cost ratio [1-4]. A typical DSSC consists of a metal oxide semiconductor film (generally TiO_2) covered by a monolayer of dye molecules, redox couple electrolyte and a counter electrode. To get the enhanced performance of DSSC, photoelectrode materials with diverse morphologies such as ordered mesostructures, nanoparticles, nanowires, nanotubes and nanorods have been intensively inquired [5-7]. Till now, it has been well established that large surface area for increased dye loading is not the only criteria for raising efficiency of DSSCs, on the other hand, tailored microstructures also enhance light harvesting and the rate of electron transport [8-11]. In the light of these requirements, researchers have paid attention to the development of bi-functional photoanode materials which constitute of a thin film of nanocrystalline particles to increase dye adsorption and a mesoporous structure to trap the incident light within the photoelectrode [12-14].

Wang et al. [15] have described the ZnO nanowire covered TiO_2 nanoparticles as photoanode and acquired an efficiency of 2.18%. Liu and Aydil [16] have synthesized TiO_2nanorods and concluded that this structure could be grown only on fluorine coated tin oxide (FTO) coated substrates. Thus, a lot of research has been executed to design dye-sensitized solar cells based on such structures but all methods are very lengthy and complicated [17-19].

Herein we report a two-step construction to develop TiO_2 nanotubes (TNT) on the surface of nanocrystalline TiO_2 anatase film along with the theoretical study of interface studies of TNTs and dye. To the best knowledge of the authors, this paper is the first of its kind presenting a simple and novel technique to fabricate blocking layer along with TNTs based front illuminated DSSC. Blocking layer prevents the electrolyte from permeating to transparent conducting oxide (TCO) layer thereby reducing recombination. The composition and crystallinity of the grown structures were determined by x-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). The nanotube arrays have also been examined by optical absorption spectra.

II. THEORETICAL

The interfacial kinetics of 2D nanotubes with dye molecules favorable for their use in dye-sensitized solar cells have been studied theoretically. In the nanometric metal oxide thin films, a high density of trap states leads to pinning of Fermi level. It has been expected that unpinning of Fermi level can take place in nano regime.

In the presented model, Poisson's equation in cylindrical co-ordinates has been solved for 2D nanotubes that are given as follows:

$$\frac{\partial^2 V}{\partial z^2}+\frac{1}{z}\frac{\partial V}{\partial z}=-\frac{en}{\varepsilon} \tag{1}$$

Here V is electrostatic potential and *n* is density of charge carriers for $r_0<z<r$, where r_0 is the inner radius of nanotube and r is outer radius.

The boundary conditions for nanotube system in dye-sensitized solar cell are:

$$V\big|_{Z\geq r}=0 \tag{2}$$

$$\left.\frac{\partial V}{\partial z}\right|_{Z\geq r}=0 \tag{3}$$

Using the boundary conditions in Eq. (1), the obtained solution for potential is:

$$V=-\frac{en}{4\varepsilon}\left\{\left(r^2-z^2\right)-2r^2\log\frac{z}{r}\right\} \tag{4}$$

Here $r\text{-}r_0\approx 0$.

The solution of Eq. (4) is shown in Fig. 1.

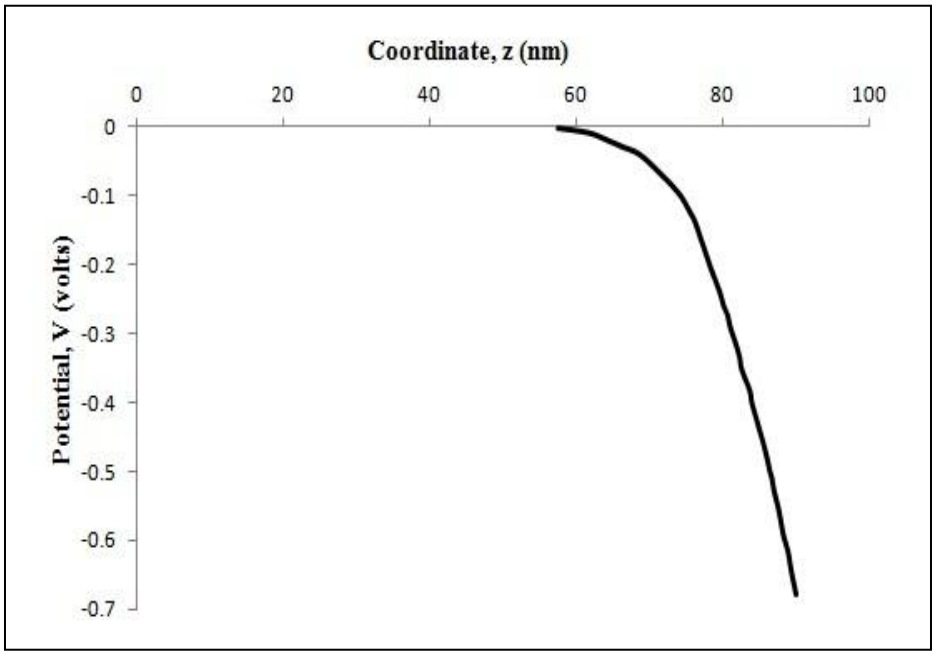


Fig. 1 Potential versus coordinate z for the parametric values $n=1x10^{18}cm^{-3}$, $\varepsilon=10^{-10}$ Fm^{-1} and r=90 nm

Potential extinction length has been found to be r=57.5nm.

For $r\text{-}r_0\neq 0$, the modified Poisson's equation is:

$$\frac{\partial^2 V}{\partial z^2}+\frac{1}{z}\frac{\partial V}{\partial z}=-\frac{en}{\varepsilon}+\frac{en}{\varepsilon}\exp\left(\frac{eV}{k_B T}\right) \tag{5}$$

Here k_B is Boltzmann constant. This equation differs from Eq. (1) in the sense that Eq. (4) takes the advantage of an extra exponential term introduced due to mobile charges. This makes the solution of the equation non-analytical. Second term on right hand side can be ignored for its small value and it becomes the same as Eq. (1). Now, boundary conditions change as given below.

Boundary conditions in this case are:

$$V\big|_{z=r} = v_m \tag{6}$$

$$\left.\frac{\partial V}{\partial z}\right|_{z=0} = 0 \tag{7}$$

These boundary conditions provide the solution for Eq. (5) given as:

$$V = -\frac{en}{4\varepsilon}\left(r^2 - z^2\right) - v_m \tag{8}$$

The solution of this equation is plotted in Fig. 2.

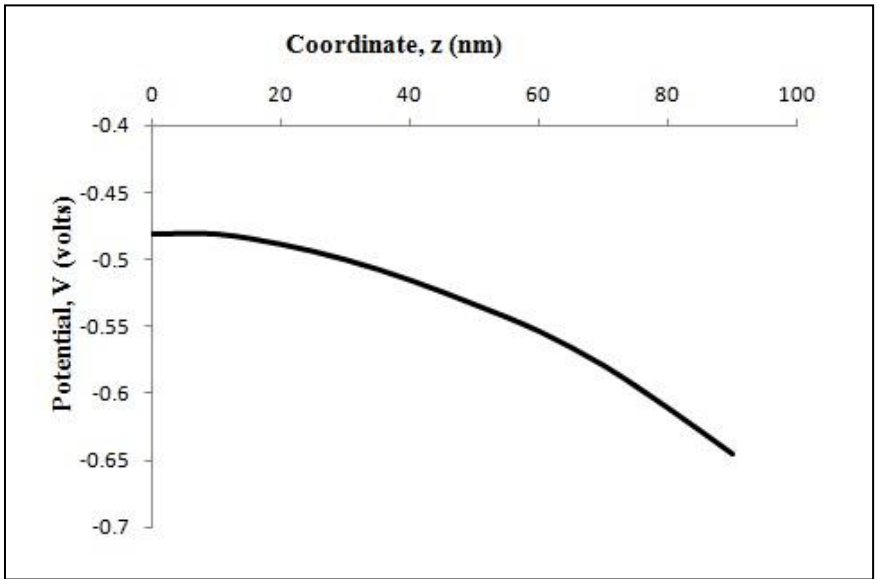


Fig. 2 Potential versus coordinate z for mobile electrons

This potential shape is helpful to calculate the density of adsorbed dye molecules by using Gauss theorem:

$$\left.\frac{\partial V}{\partial z}\right|_{z=r} = \frac{eN_d}{\varepsilon} \tag{9}$$

Here N_d is the density of trap states.

By substituting Eq. (8) into Eq. (9), it can be easily shown that N_d declines with the radius r decreases consequently unpinning of Fermi level takes place as *r* approaches nanometric scale.

Thus, instead of approximately same conductivity of metal oxide nanocrystals and nanotubes, nanotubular structures offers a major advantage for its use in dye-sensitized solar cell as photoanode. Lesser density of trap states means a lower recombination pathway for the transport of electrons. Less recombination definitely leads to an enhanced output from a dye-sensitized solar cell based on nanotubes.

III. EXPERIMENTAL SECTION

Titanium tetra isopropoxide (TTIP) has been used as precursor and 20 mL of it has been mixed with 120mL of 0.1M HNO_3 under vigorous stirring for half an hour followed by stirring at 80 ℃ for 10 hours. The flask containing this solution has been kept in microwave at 180 ℃ for 5 minutes.

The sol has been stirred until it reached at room temperature before coating and then deposited on indium tin oxide (ITO) coated glass plates using dip coater (MTI Corporation) at a dipping rate of 5cm/min and dried at 125 ℃ for 1 hour followed by calcination at 250 ℃. This procedure provides a thin layer of TiO_2 nanoparticles. Finally, this anatase film has been kept immersed in 0.1M HCl and 0.1M NH_4OH for 6 hours and afterwards treated with 5M NaOH for 10 hours. Further, the film has been heated at 200 ℃.

To assemble dye-sensitized solar cells, the synthesized films have been plunged in N719 dye solution overnight. 0.5M lithium iodide (LiI), 0.05M iodine (I_2) in acetonitrile solution is used as electrolyte.

Nanocrystalline and nanotube structures have been confirmed by x-ray diffraction (XRD) analysis. Investigations of surface properties have been made with the help of scanning electron microscopy (SEM). Solar cell characterizations have been executed by using Keithley unit (2400 source meter). A Newport AM1.5 solar simulator (91160 A) equipped with xenon arc lamp has been employed as source meter. Light intensity of the source meter has been calibrated to 100 $mWcm^{-2}$.

IV. RESULTS AND DISCUSSIONS

XRD spectrum of TiO_2 nanotubes has been shown in Fig. 3. The diffraction peaks at 101, 103, 004, 112, 200, 105, 211correspond to anatase phase of TiO_2nanotube film. Thus, Fig. 3 confirms polycrystalline anatase structure of TiO_2 nanotubes.

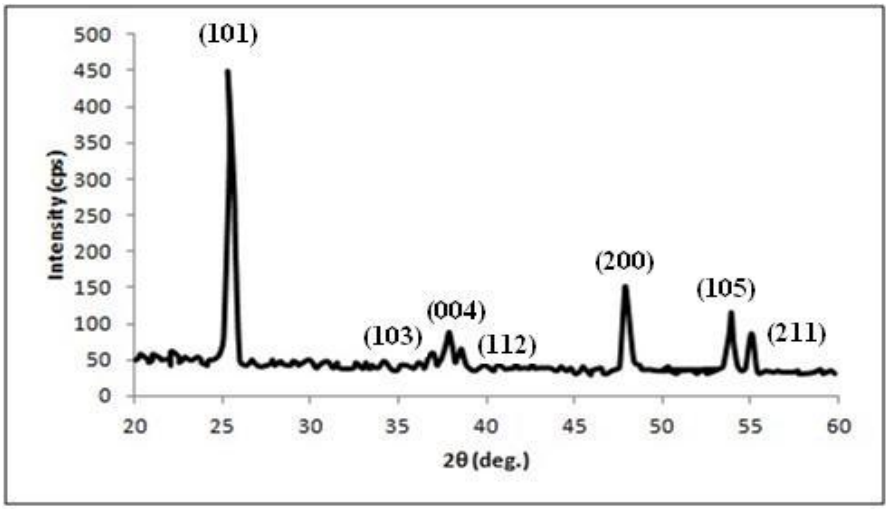


Fig. 3 XRD plot for TiO_2 nanotube structures

Fig. 4 shows surface SEM images of grown TNTs (TiO_2 nanotubes). The rough and porous structures are clearly visible in the images. As illustrated in these images, one can clearly recognize the morphology of the radially grown TNT structure of the fabricated film. This would surely lead to more dye loading thereby increasing the photocurrent. The average diameter of the TNT's was found to be approximately 90nm.

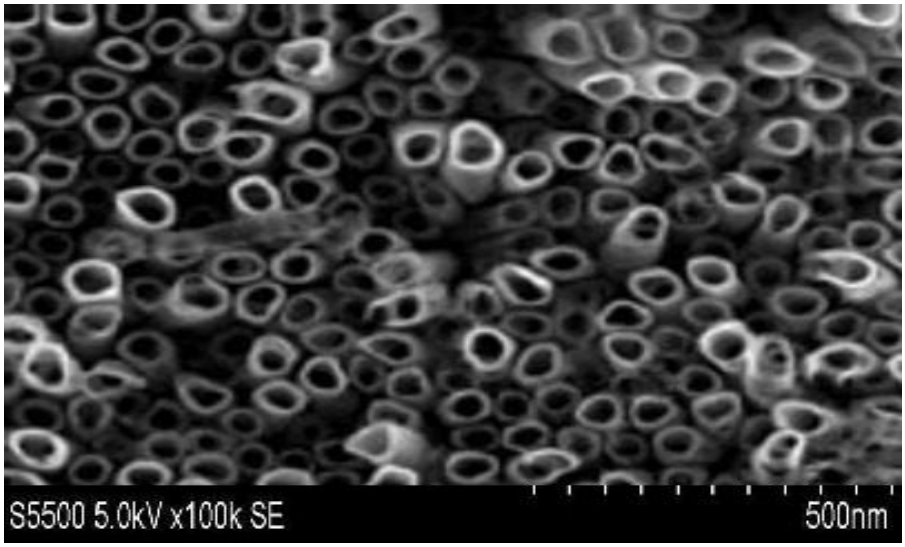


Fig. 4 SEM image for TiO_2 nanotubes (500nm)

Fig. 5 represents transmission electron microscopic image of the formed film and confirms the formation of nanotube structure. The image is obtained through HT7700 HITACHI based microscope. TEM image clearly show that straight and dense nanorods have been constructed along over TiO2 film acting as blocking layer.

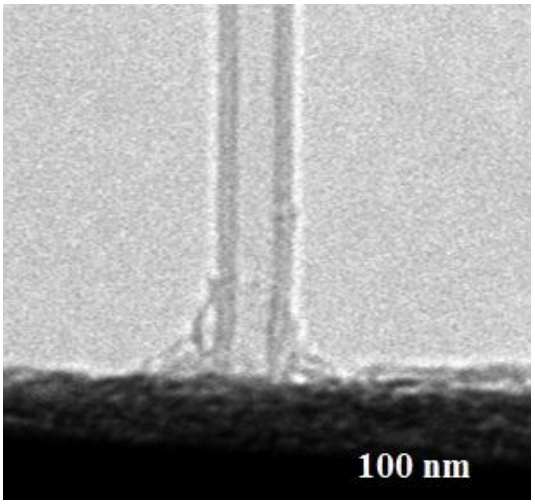


Fig. 5 Transmission electron microscopic (TEM) image (100nm)

Fig. 6 shows UV-vis absorption spectra for TiO_2 nanotubes. The spectral lines display only one characteristic absorption band corresponding to intrinsic transition from valence band to conduction band. The absorbance was observed below 370nm for TiO_2 nanotubes indicating a blue shift of absorption maximum when compared with bulk TiO_2 phase [20].

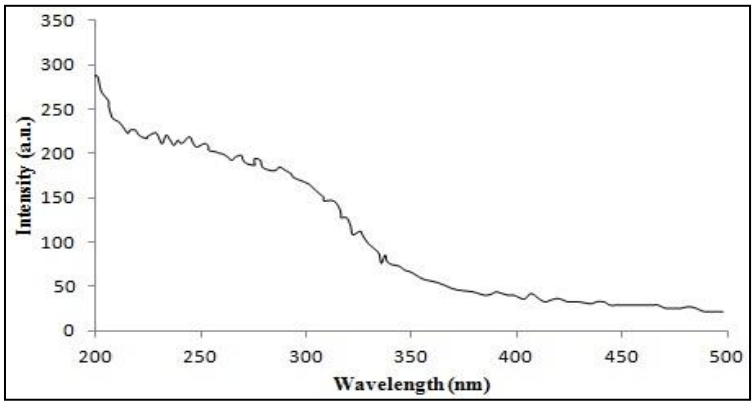


Fig. 6 UV-VIS spectra of TiO_2 nanotubes

X-ray diffraction results are very well supported by vibration mode symmetries indicated by Raman spectra (Fig. 7). Raman peaks found at 156.2, 408.3, 529.1 and 649.2cm^{-1} correspond with the anatase phase of TiO_2 [21, 22]. Shift of Raman spectra and broadening of peaks up to a significant extent were not observed as compared with bulk TiO_2.

Fig. 8 unveils the conductivity measurements for the grown nanotube arrays and shows that the conductivity of the grown films increases with increase in temperature. This increase is slight initially followed by a rapid rise. As conductivity value is governed by two factors: mobility and concentration; rise in temperature lowers down mobility of charge carriers and increases the concentration of electrons in the conduction band. Initially there is a gradual increase in conductivity because of these two counteracting parameters and a further increase in temperature leads to dominance of population increment by exponential factor over depression in the mobility value thereby causing sharp increases in conduction.

Fig. 9 (a) shows the current-density, voltage (*JV*) characteristics for nanotube based DSSC. The observed value for open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}) were found to be 0.734V and 14.23$mAcm^{-2}$ respectively corresponding to an efficiency of 7.28%. The results are very well verified by incident photon to current conversion efficiency (IPCE) spectra shown in Fig. 9 (b).

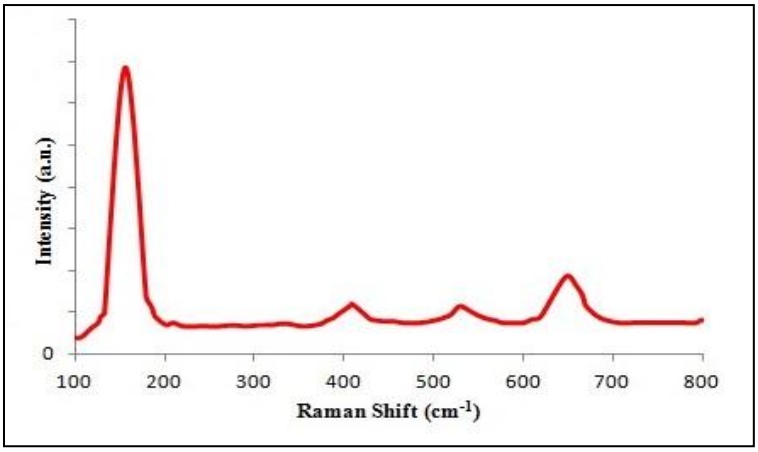


Fig. 7 Raman Spectra for anatase TiO2 nanotubes

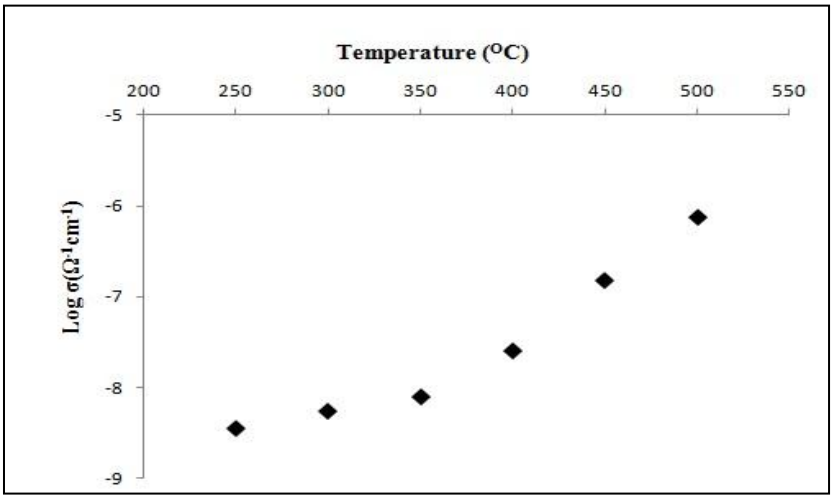
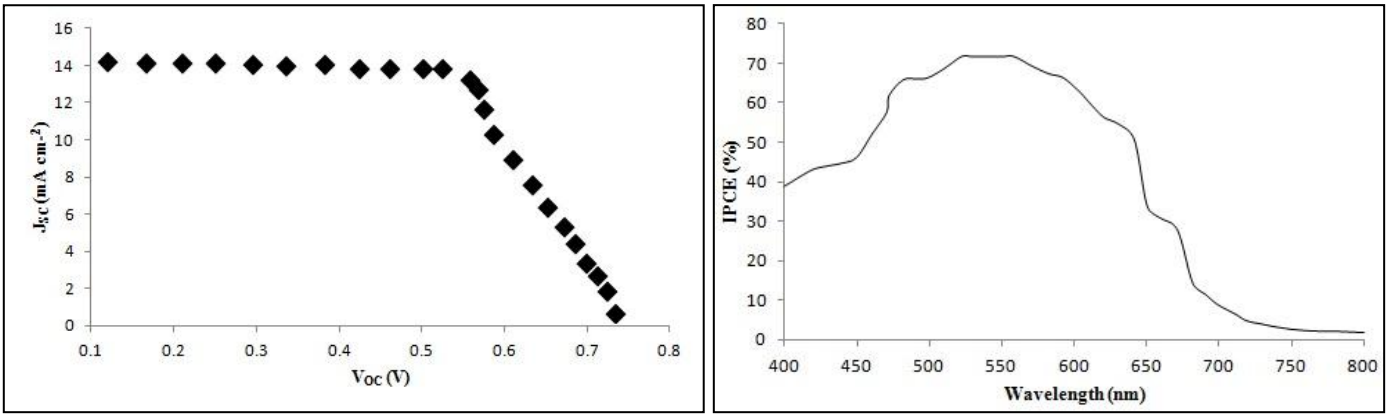


Fig. 8 Conductivity variation with temperature



(a) (b)

Fig. 9 (a) JV characteristics (b) IPCE spectra for anatase TiO2 nanotube DSSC

V. CONCLUSIONS

TiO_2 nanotubes have been synthesized successfully on the TiO_2 blocking layer by a very simple solvothermal technique. XRD and Raman measurements confirm the occurrence of polycrystalline anatase phase of the nanotubes. Due to this porous structure along with higher surface area, TNT based dye-sensitized solar cells exhibit more efficiency (η=7.28%) than planar TiO_2 based

DSSC. Simultaneously TNT-based DSSC displayed higher value of IPCE. It is expected that this method can also be used to tailor the diameter of the nanotubes to achieve better results with dye-sensitized solar cells.

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