

Effect of TiO₂ blocking layer on TiO₂ nanorod arrays based dye sensitized solar cells

R Sivakumar and M Paulraj

Department of Physics, Faculty of Physical Sciences and Mathematics,
University of Concepcion, P.O. Box. 160-C, Concepcion, Chile

Email: paulrajm@gmail.com, sivakrk05@yahoo.com

Abstract. Highly ordered rutile titanium dioxide nanorod (TNR) arrays (1.2 to 6.2 μm thickness) were grown on TiO₂ blocking layer chemically deposited on fluorine doped tin oxide (FTO) substrate and were used as photo-electrodes to fabricate dye sensitized solar cells (DSSC's). Homogeneous layer of TiO₂ on FTO was achieved by using aqueous peroxo-titanium complex (PTC) solutions via chemical bath deposition. Structural and morphological properties of the prepared samples were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) measurements. TNR arrays (6.2 μm) with TiO₂ blocking layer showed higher energy conversion efficiency (1.46%) than that without TiO₂ blocking layer. The reason can be ascertained to the suppression of electron-hole recombination at the semiconductor/electrolyte interface by the effect of TiO₂ blocking layer.

1. Introduction

In DSSC's, the TiO₂ photo-electrode essentially collects and transports the photo-generated electrons [1, 2]. However, the electron transport in nanoparticle based device is suffered by trap limited diffusion process, a slow recombination step that results in low efficiency. Also the large grain boundaries of TiO₂ nanoparticles lead to fast recombination of the photo-generated electrons with I₃⁻ in the electrolyte prior to their collection at the electrode. Hence, to provide uninterrupted transport of photo-generated electrons in TiO₂, one dimensional (1D) nanostructure such as nanorods [3], nanowires [4], and nanotubes [5] etc. have been designed and demonstrated for their potential application in DSSC's. It has been proved that the electron transport in 1D nanostructure is expected to be several orders of magnitude faster than that of nanoparticle network [6, 7]. Several researchers fabricated thick 1D nanostructure arrays and achieved higher energy conversion efficiency [8, 9]. Another approach to improve the charge transport properties and collection efficiency is by introducing TiO₂ seed layer on the FTO layer prior to the growth of 1D nanostructure [10-15]. Recently, Qian et al. [16] and Yang et al. [17] derived TiO₂ blocking layers from peroxo-titanium solution and studied their effect on dye sensitized solar cells. Increase in photocurrent by the introduction of PTS overlayer was mainly attributed to the retardation of the back-transport reaction in the FTO/TiO₂ interfaces. In a systematic approach, hereby we made an endeavour to introduce TiO₂ blocking layer through per-oxo titanium method on TNR arrays based DSSCs.



2. Materials and methods

2.1. Materials

Fluorine doped tin oxide (FTO) glass plates (sheet resistance $7\Omega/\square$), Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$; $\geq 37.50\%$ Pt basis), Lithium Iodide (99.9% trace metals basis), Iodine ($\geq 99.99\%$ trace metals basis), 4-tert-Butyl pyridine (96%) were purchased from Sigma Aldrich. Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) (Ruthenizer 535-bisTBA), 1-methyl-3-propylimidazolium iodide and Surlyn polymer frame (Meltonix 1170-25) were purchased from Solaronix. Titanium (IV) chloride (TiCl_4) was purchased from Merck. All other chemicals used were of analytical grade, purchased from Merck and used without further purification.

2.2. Electrode preparation

2.2.1. Preparation of TiO_2 blocking layer on the FTO substrate. Titanium (IV) chloride was chosen as titanium resource for the preparation of stable transparent peroxo-titanium complex (PTC) solution. Briefly, 0.5 mL of TiCl_4 was dissolved in 50 mL of deionized water under the conditions of 0-3 °C and then 2 mL of H_2O_2 was added. The mixture turned to orange red with the addition of H_2O_2 and then to clear red after stirring for one hour at room temperature. Accordingly, TiCl_4 reacts with H_2O_2 to form stable PTC solution. Deposition of TiO_2 layer was carried out by vertical immersion of the FTO glass substrate in the PTC solution for 12 hour with constant stirring at room temperature (25 °C). After the deposition time, the substrate was withdrawn from PTC solution and rinsed with distilled water, dried and annealed at 450 °C for 30 minutes. On calcination, the deposited per-oxo titanium complex forms uniform layer of TiO_2 on FTO substrate and it is designated as FTO_{PTC} .

2.2.2. Fabrication of TNR arrays. TiO_2 nanorod arrays were grown on FTO_{PTC} substrate using Teflon-lined stainless steel autoclave (45 mL volume, Parr Instrument Co.) following the hydrothermal method [3]. Briefly, 0.30 mL of TiCl_4 was added to a mixture solution containing 5 mL of deionized water and 5 mL of hydrochloric acid (37 wt%) in a teflon container and was stirred for 5 minutes for homogenization. FTO_{PTC} glass plates were placed at an angle against the wall of the Teflon-liner with the conducting side facing downwards and the teflon liner was placed in a stainless steel autoclave to initiate the hydrothermal reaction. The reaction was carried out at 150 °C in an electric oven for 4, 8, 12, 20, 30 and 40 hours. For comparison TNR arrays were grown on bare FTO glass plates for 20 hours at 150 °C. After the set reaction period, the samples were taken out and rinsed extensively with deionized water and left to dry in ambient air. Finally, all the samples were annealed at 450 °C for 30 minutes.

2.3. Analytical measurements

X-ray diffraction patterns were recorded using a Bruker D4 Endeavor advance diffractometer with $\text{Cu K}\alpha$ radiation at a scanning rate of 2°/min. Morphology and microstructure analysis of the samples were performed using a JEOL JSM-6380LV scanning electron microscope (SEM). The samples under study were first sputtered with gold for 3 min. to obtain a layer of 150 Å thick using an Edwards S 150 Sputter Coater.

2.4. Fabrication of dye sensitized solar cells

TNR array electrodes were dipped in dye solution (3×10^{-4} M) in ethanol for 24 h. After the dye adsorption was complete, the electrode were withdrawn from the solution and dried under a stream of argon. The platinum counter electrode and the dye-coated TiO_2 electrode was then put together with a thin transparent film of Surlyn polymer frame (25 μm). The sandwiched electrodes were tightly held and then heated to 130 °C, so that the Surlyn frame would seal the two electrodes intact. A thin layer of electrolyte, consisting 0.6 M propyl methylimidazolium iodide (PMII), 0.05 M I_2 , 0.1 M LiI, and 0.5 M tert-butylpyridine in 1:1 acetonitrile/valeronitrile, was introduced into the inter-electrode space

from the counter electrode side through predrilled holes. The drilled holes were sealed with a microscope cover slide to avoid leakage of the electrolyte solution.

2.5. Photovoltaic Measurements

Solar simulator device (Model: CT80AAA, PET Photo Emission Tech., Inc., USA) incorporated with a 300 W xenon arc light source was used for measuring the photovoltaic properties. A 1 sun, AM 1.5G, light irradiance of 100 mW/cm^2 was achieved over the surface of the test cell. During each measurement, temperature of the platen which holds the cell was controlled at 25°C using a control system attached to the solar simulator. The power of simulated light was calibrated using a reference silicon photodiode ($20\text{ mm} \times 20\text{ mm}$) provided with the instrument. The test cell was placed at the same position as the calibration cell. Photocurrent-voltage plots for all cells were recorded using a Keithley 2400 digital source meter, from $+950$ to -300 mV , in steps of 10 mV .

3. Results and discussion

Figure 1 a and b shows the scanning electron microscopic images of bare FTO and FTO_{PTC} . A homogeneous layer of TiO_2 was observed for the TiO_2 blocking layer deposited over bare FTO (Fig. 1b). Small grains with dense structure and well surface coverage are observed for chemically deposited TiO_2 blocking layer. Accordingly, this blocking layer consisting of anatase TiO_2 nanocrystal formed upon high temperature treatment of per-oxo titanium complex [18]. Apparently, TNR arrays grown on FTO_{PTC} (Fig. 2a) and bare FTO (Fig. 2c) reveal uniform surface coverage and the shape of the nanorod is tetragonal with square top facets as expected for rutile TiO_2 structure. From cross sectional SEM images, the thickness of TNR arrays grown on FTO_{PTC} were found to be $1.2 \mu\text{m}$, $2.5 \mu\text{m}$, $4.2 \mu\text{m}$ and $6.2 \mu\text{m}$ for the hydrothermal duration set to 4, 8, 12 and 20 h respectively. For comparison, TNR arrays grown on bare FTO results in similar length, $6.1 \mu\text{m}$ (Fig. 2d). On prolonging the hydrothermal reaction to 30 and 40 h, no increase in nanorod length was observed in FTO_{PTC} and bare FTO.

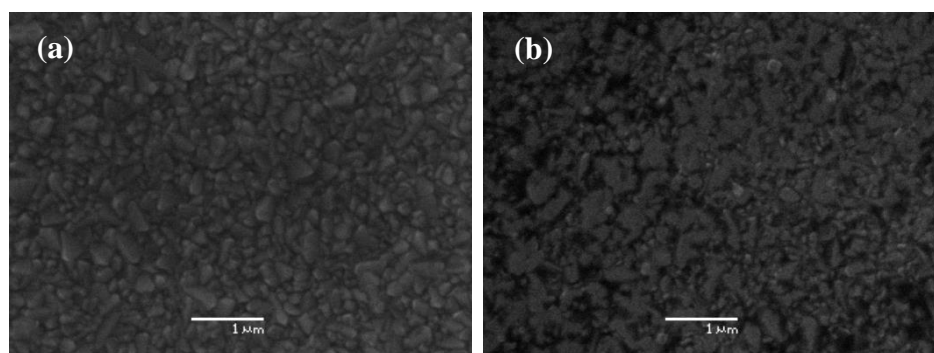


Figure 1. Scanning electron microscopic image of (a) Bare FTO and (b) FTO_{PTC} .

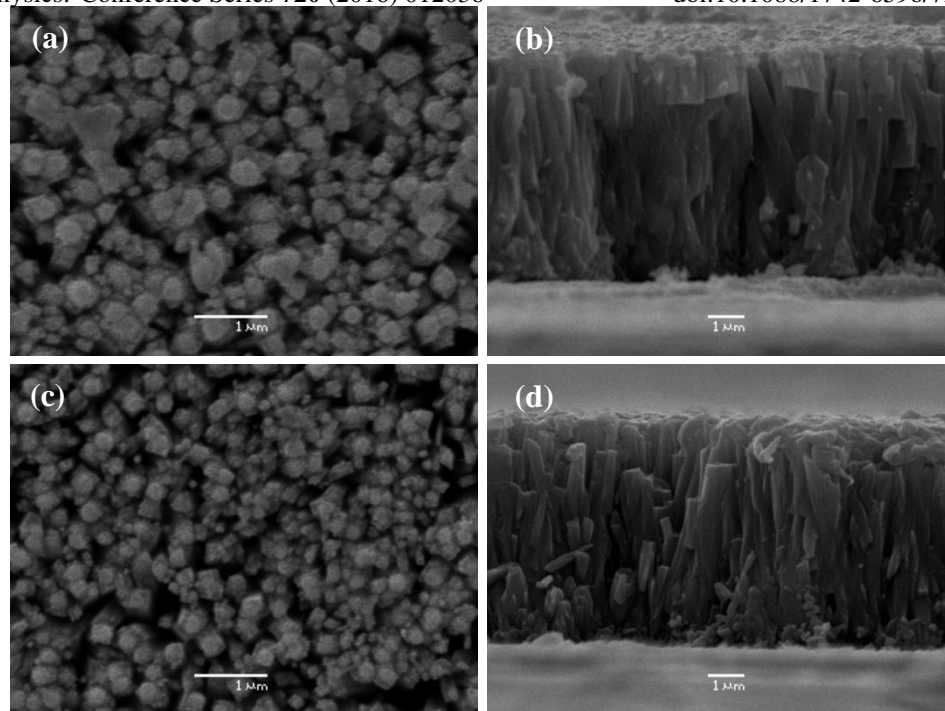


Figure 2. SEM images of TiO_2 nanorods grown on FTO_{PTC} and bare FTO. (a) and (c) are the top view of TNR arrays grown on FTO_{PTC} and FTO, respectively at 150 °C for 20 hr; (b) and (d) are the corresponding cross sectional view.

Figure 3 shows the X-ray diffraction patterns of bare FTO and FTO_{PTC} and TNR arrays grown on FTO_{PTC} and bare FTO. Diffraction peaks of bare FTO (Fig. 3a) correspond to tetragonal rutile phase of SnO_2 . The diffraction peaks of TiO_2 crystallites were not observed for TiO_2 blocking layer deposited FTO (Fig. 3b) due to the strong diffraction peaks of FTO. However, after the hydrothermal growth of TNR arrays on FTO_{PTC} and bare FTO, peaks corresponding to tetragonal TiO_2 with rutile phase were observed (Fig. 5c-g). The intensity of the peak (002) increases as the hydrothermal duration increases. Significantly, the enhancement of diffraction peak (002) is a clear indication of directed growth of TNR arrays perpendicular to the FTO substrate. Absence of diffraction peaks at (110), (111), and (211) is an evidence for uni-directional growth of TNR arrays with respect to the substrate surface.

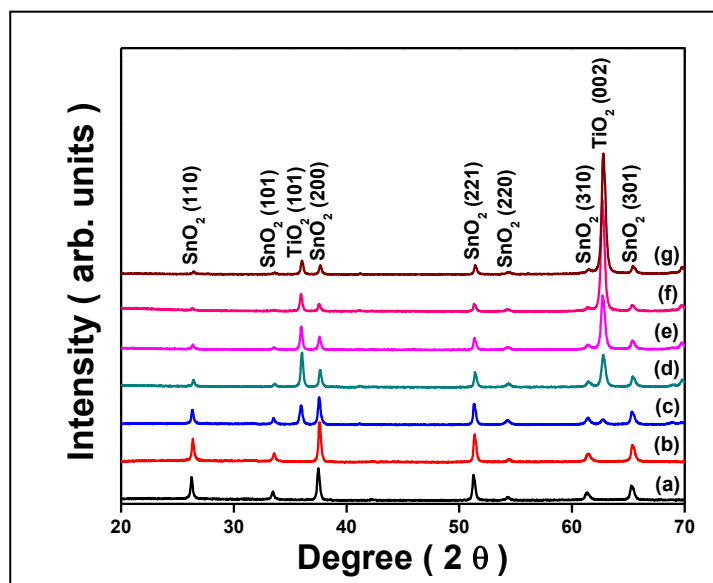


Figure 3. X-ray diffraction patterns of (a) bare FTO and (b) FTO_{PTC} ; (c), (d), (e) and (f) are diffraction patterns of TNR arrays grown on FTO_{PTC} for 4 h, 8 h, 12 h and 20 h at 150 °C respectively; (g) TNR arrays grown on bare FTO for 20 hr at 150 °C.

Figure 4 shows the photocurrent-voltage characteristics of DSSC fabricated using TNR array electrodes grown over FTO_{PTC} and bare FTO. The cell parameters such as, short circuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and the power conversion efficiency (η) are summarized in Table 1. It was observed that the efficiency increases as the thickness of the TNR arrays increases. DSSC assembled with 6.2 μm thick TNR arrays grown on FTO_{PTC} exhibits a photocurrent of 3.56 mA/cm^2 , open circuit voltage of 0.79 V and overall energy conversion efficiency of 1.46%. Whereas, TNR arrays (6.1 μm) grown on bare FTO showed marginally low efficiency (1.19%). It is noteworthy that the DSSCs assembled from TNR arrays with TiO_2 blocking layer show higher V_{OC} (0.79 V) than that without TiO_2 blocking layer (0.74 V). This indicates that TiO_2 blocking layer plays a vital part on the performance of rutile TiO_2 nanorod based DSSC's. This is because, TiO_2 blocking layer covering the vacant spaces unoccupied by TNR arrays on FTO are effective in blocking the direct contact of the redox electrolyte and FTO and diminishes the dark current that arises from reduction of I_3^- at the FTO/electrolyte interface. Also the increase in J_{SC} proves the lower recombination rate of the whole photo anode in the presence of TiO_2 blocking layer. We note that such a per-oxo titanium route presented here offers a significant advantage for the DSSCs.

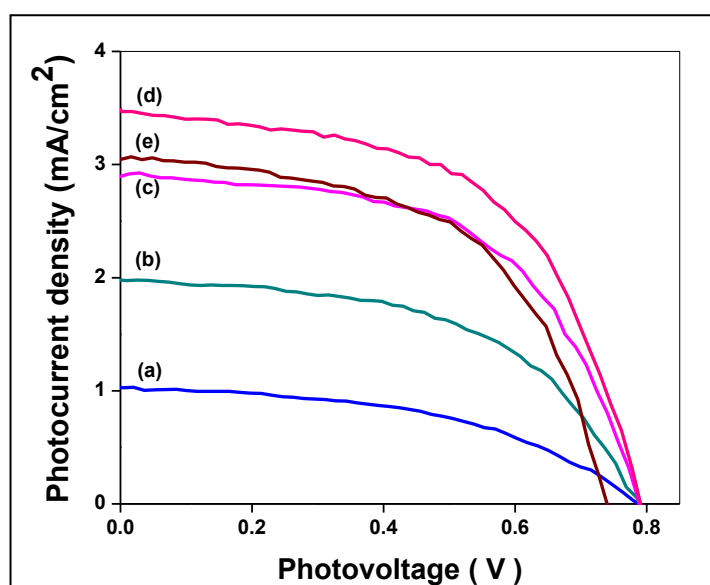


Figure 4. Photocurrent density (J) - voltage (V) characteristics of DSSC's assembled with TNR arrays (a) 1.2 μm , (b) 2.5 μm , (c) 4.2 μm and (d) 6.2 μm grown on FTO_{PTC} respectively, and (e) 6.1 μm on bare FTO.

Table 1. Photovoltaic performance parameter of DSSC's assembled with TNR arrays grown on FTO_{PTC} and bare FTO.

Photoelectrode	J _{sc} (mA)	V _{oc} (V)	FF	η (%)
TNR(1.2 μm)/FTO _{PTC}	1.02	0.786	0.47	0.38
TNR(2.5 μm)/FTO _{PTC}	1.98	0.787	0.49	0.76
TNR(4.2 μm)/FTO _{PTC}	2.92	0.789	0.52	1.20
TNR(6.2 μm)/FTO _{PTC}	3.56	0.791	0.52	1.46
TNR(6.1 μm)/FTO	3.04	0.739	0.53	1.19

4. Conclusions

TiO₂ nanorod arrays were grown on TiO₂ blocking layer chemically deposited on FTO substrate from per-oxo titanium complex solution. The peroxo-titanium route provides oxygen rich environment to enhance the Ti-O-Ti linkage which avoids the atomic incorporation of chlorine. DSSC assembled using TNR arrays (6 μm) in the presence of TiO₂ blocking layer produces 1.46% efficiency which is higher than that assembled in the absence of TiO₂ blocking layer (1.19 %). This enhancement was attributed to the effect of TiO₂ blocking layer on suppressing the dark current that arises from the direct contact of electrolyte with the FTO. These findings provide a new route to preparing highly pure TiO₂ nanocrystals on FTO and further extend their application into solid state DSSCs.

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