# PERFORMANCE ENHANCEMENT OF TIO<sub>2</sub> BASED DYE SENSITIZED SOLAR CELLS BY EMPLOYING TRIPLE LAYERED PHOTANODE CONSISTING WITH NANOFIBRES OF TIO<sub>2</sub>

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#### ABSTRACT

TiO<sub>2</sub> based Dye Sensitized Solar Cells (DSSCs) were fabricated with a triple layered structure of photoanode consisting with electrocpun nanofibres (NF) of TiO<sub>2</sub>. Characteristics of DSSCs comprising with this triple layered structure were compared with the performances of DSSCs fabricated with conventional nanoparticle (NP) TiO<sub>2</sub> photanodes under the identical conditions by using inexpensive Eosin-Y dye and electrolyte solution consisting of tetra propyl ammonium iodide and iodine dissolved in acetonitrile and ethylene carbonate. Dramatic enhancement in the efficiency of DSSC was obtained due to the in-cooperation of the nanofibre layer in to the structure of conventional photoanode. DSSCs fabricated with triple layered structure of NP/NF/NP showed 1.77% overall efficiency whilst the DSSC without the nanofibre layer having the same thickness showed 0.89% efficiency giving an increase of efficiency by ~ 98% under the irradiance of 1000 W m<sup>-2</sup> (AM 1.5). Photocurrent density and UV-Visible absorptions measurements revealed that the main cause for this improvement might be due to the enhanced light harvesting by scattering effect within the electro spun TiO<sub>2</sub> nanofiber layer.

#### **1. INTRODUCTION**

Solar energy is the most reliable and the most abundant energy resource in this globe. Hence it is considered as one of the alternative resources for fossil fuels. These cells were improved by generation wise where silicon based solar cells were the first generation of them. As the third generation of solar cells, Dye-Sensitized Solar Cells (DSSCs) with comparably high efficiency with silicon based solar cells were produced by O'Regan and Gratzel in 1991 where it stands as cost effective and ecofriendly devices [1-3]. The simple structure and low cost technology involved in these DSSCs created a great interest for further innovations. In DSSC, the conversion of visible light to electricity is achieved through the spectral sensitization of wide band gap semiconductors by using a sensitizing agent so called dye [4-5]. Commonly, TiO<sub>2</sub> is widely employed as the photoanode material in DSSC application due to its non-toxicity and chemical stability [5-6]. Ruthenium dye, N719 sensitized TiO<sub>2</sub> based DSSCs showed remarkable efficiencies and nearly 12 % was recorded in the recent past [4-8]. Since one of the key component of these DSSCs is the photoanode, numerous investigations have been carried out to optimize the structure, properties and shape of the particles together with different layers of photoanode material [9-13]. However, still there is a necessity to further improve the structure of photoanode towards the capturing and utilizing more sunlight effectively towards to efficiency enhancement of these DSSCs. Therefore, in this study we have attempted to modify the structure of photoanode by in cooperating nanofibres of  $TiO_2$  prepared by electrospun method. As a result of that, in this study we report the preliminary results obtained from DSSCs by incorporating nanofibre layer of  $TiO_2$ structure in between two nanoparticle structures (NP/NF/NP). Further, here we used inexpensive Eosin-Y dye to see this effect. Remarkable enhancement in the efficiency was achieved by in cooperating this nanofibre layer in the conventional structure of photoanode.

### **2. EXPERIMENTAL**

# 2.1Materials

FTO glass (Solaronix sheet glass 8  $\Omega$ /so, Switzerland), Titanium isopropoxide (TIP, C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti) was purchased from Fluka Chemie, Switzerland, Powder of P-25 TiO<sub>2</sub> NPs was purchased from Degussa. Titanium (iv) isopropoxide was purchased from Fluka and the other chemicals used, absolute ethanol, tertapropyl ammonium from Sigma Aldrich.

#### 2.2 Preparation of composite photoanode

Nano crystalline TiO<sub>2</sub> photoelectrodes were prepared using three layers. The first and the third layer of TiO<sub>2</sub> nanoparticles were prepared by "doctor blading" the TiO<sub>2</sub> paste prepared as follows on FTO glass. This paste was prepared by using a mixture of 0.25 g of TiO<sub>2</sub> powder (Degussa P-25), 1ml of 0.1 HNO<sub>3</sub>, 0.05g of PEG, 1drop of Triton-X 100. This mixture was ground for 45 min approximately and sintered them at 450 °C for 45 min and cooled down slowly to up to the room temperature. After preparing the first layer of TiO<sub>2</sub> layer of nanofibre layer of TiO<sub>2</sub> was introduced according to the method describe in next section and then again on top of the nanofibre layer another layer of nanoparticle was applied by "doctor blading " method and re -sintered the whole photoanode at 45° C for 45 minute. Finally photoanodes consists with triple layers were dipped in solution of 0.3 mM ethanolic solution of Eosin-Y Dye for 24 h . The effective area of the photoanode was kept as 0.25 cm<sup>2</sup>.

## 2.3 Preparation of TiO<sub>2</sub> Nanofiber

A mixture containing 1.5g polyvinyl acetate (PVA), 3g titanium (iv) isopropoxide (TIP) and 1.2g of Acetic acid as a catalyst for sol-gel reaction in 19ml of N, N-dimethylforamide (DMF) was subjected to magnetic stirring for 4 hours prior to electrospinning. This mixture was electro spun on the first  $TiO_2$  NP layer by a Nabond electro spinner with the parameters of 15 KV DC voltage between the spinneret and the drum collector, a distance of 6.5 cm between the syringe tip and the drum collector, polymer solution sucked in syringe's flow rate of 2 ml/h, drum collector's speed of 270 rpm and spinning time of 20 min.

#### 2.4 Preparation of Eosin-Y dye

0.0019 g of Eosin-Y dye powder with molar mass of 647.895 gmol<sup>-1</sup> was measured and dissolved in 10 ml of absolute ethanol. This solution was sonicated twice in ultra-sonic bath for 5 minutes.

### 2.5 Preparation of electrolyte

0.738 g of tetrapropylammonium iodide ( $Pr_4NI$ ) and 0.060 g of  $I_2$  to a pre-cleaned 10 ml volumetric flask containing 3.6 ml of molten (MP 40  $^{0}$ C) ethylene carbonate (EC) and 1.0 ml of acetonitrile. The solution mixture was stirred for 5 h.

## 2.6 Cell assembly and I-V characterization

In order to compare the effect of incooperation of nanofibre layers in the photoanode, DSSCs were fabricated and tested with conventional photanodes where no nanofibre was inserted and also with the nanofibre layer having the same overall thickness and the area of the  $TiO_2$  layer. Devices were fabricated by sandwiching the electrolyte solution in between the photoanode and

the platinum coated FTO substrate. DSSC configurations were FTO/NP/NF/NP/Pt-FTO and FTO/NP/Pt-FTO. Photovoltaic characteristics of DSSCs were measured by using a solar simulator which was coupled to a Keithly 2000 multimeter with potentiostat/galvanostat HA-301 under the illumination of 1000 Wm<sup>-2</sup> using a Xenon 500 lamp with an AM 1.5 filter.

#### 2.7 EIS measurements

Using the Metrohm Autolab Potentiostat/Galvanostat PGSTAT 128 N with a FRA 32 M Frequency Response Analyzer (FRA) Electrochemical Impedance Spectroscopy (EIS) measurement was performed on the DSSCs covering the frequency range of 1 MHz–0.01 Hz. These measurements were carried out under the illumination of 1000 Wm<sup>-2</sup> using the same solar simulator that was used for I–V measurements.

## 3. RESULTS AND DISCUSSIONS

#### 3.1 Photovoltaic performance

Fig. 1 shows the current voltage characteristics of the DSSCs fabricated with and without the nanofibre layer in the photoanode. As can be seen from the Fig. dramatic enhancement in the photoanode. Solar cell parameters namely the short-circuit photocurrent density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF) and the energy conversion efficiency ( $\eta$ ) of solar cells fabricated with and without the nanofibre incoopartion is tabulated in the table 1. When preparing these DSSCs, it was ensured to have the same TiO<sub>2</sub> film thickness, same amount of dye loading and soaking time.



Fig.1: Photocurrent-voltage curves for DSSCs fabricated with  $TiO_2NP/NF/NP$  composite photoanode and  $TiO_2NP/NP$  control photoanode.

Table 1: Photovoltaic parameters of Eosin-Y dye based DSSCs with TiO<sub>2</sub> NP/NF/NP composite photoanode and TiO<sub>2</sub> NP/NP control photoanode

Photoanode	$J_{SC}$ (mA cm <sup>-2</sup> )	V <sub>OC</sub> (mV)	FF (%)	η (%)
TiO <sub>2</sub> NP/NF/NP	3.98	662.2	67.0	1.765
TiO <sub>2</sub> NP/NP	2.14	643.5	64.6	0.890

It clearly shows that the composite anode comprising with nanofibre layer shows high short-circuit photocurrent density  $(J_{sc})$  and overall efficiency (n) compared to the device with no nanofibre layer. Both parameters show an enhancement by 85.9% and 98.3% respectively. This is because of the effect of NF which harvests more light due to the scattering effect.

## 3.2 The UV–Vis optical absorption spectra

In order to confirm the enhanced light haverstion and the scattering due to the insertion of NF layer in the photoanode, UV–Vis optical absorption spectrum measurements were perforemed on the photanodes with and without the dye adsorption and results are shown in Fig 2 and Fig. 3. As it is evedient from Fig 2 and Fig 3, photoanode consisting with NF layer , i.e.,  $TiO_2N/NF/NP$  absorbs more light in the wavelength range below 400 nm, than the photoanode with no NF layer in-cooperated. This must be due to the increased light harvesting as a result of the incooperation of NF layer in the photoanode. This observation is in agreement with the dramatic enhancement of the photocurrent as depicted in Fig 1. Moreover, according to the Fig. 3 , the light absorption of the photoanode with eosin Y dye shows an enhanced absorption of light at the wavelength at which eosin-Y absorbs in the visible range spectra of 514nm. All the absorption values were normalized with the mass of the photoanode from this comparison.



Fig.2. Normalized UV-VIS absorption spectra for TiO2 electrodes : TiO2 -NP/NP and TiO2- NP/NF/NP photoanodes.



Fig. 3. Normalized UV-VIS absorption spectra for  $TiO_2$  electrodes after dye absorption :  $TiO_2$  -NP/NP and  $TiO_2$ -NP/NF/NP photoanodes.

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### 3.2 EIS Measurements

Electrochemical impedance spectroscopy has been regarded as a powerful technique to characterize the carrier transport, electronic and ionic processes and recombination in DSSCs. Fig. 4 shows the impedance spectra of the device configuration FTO/TiO2 NP/NF/NP/Pt-FTO together with the equivalent circuit (insert) used to obtain the corresponding interfacial resistances of the device. The estimated fitting parameters where  $R_S$  gives the resistance of TiO<sub>2</sub>/FTO glass interface,  $R_1$  resistance of interface of the counter electrode/electrolyte,  $R_2$  the interface resistance of the TiO<sub>2</sub>/dye/electrolyte of TiO2NP/NF/NP from the impedance curves of both cells are tabulated in table 2.



Fig. 4: Impedance spectra of  $TiO_2NP/NF/NP$  photoanode and the equalent circuit used to estimate interfacial resistance of the device.

Table 2: Fitted impedance parameters of DSSCs for Eosin-Y with TiO2NP/NP/NP and TiO2NP/NP photoanodes

Photoanode	$R_s(\Omega)$	$R_1(\Omega)$	$R_2(\Omega)$
TiO <sub>2</sub> NP/NF/NP	36.0	11.7	39.7
TiO <sub>2</sub> NP/NP	74.2	41.5	98.3

As can be seen from the table 2 the photanode consists with NF layer shows remarkably low interfacial resistance values and this further confirms the suitability of the triple layerd photoanode in DSSCs.

#### 4. CONCLUSION

In this study we have fabricated and tested DSSCs with triple layered  $TiO_2NP/NF/NP$  composite photoanode sensitized with Eosin-Y synthetic dye and revealed that the overall efficiency of the device can be improved drastically by the in-cooperation of nanofibre layer in the conventional photanodes. The overall efficiency of DSSC can be enhanced approximately by 98%. This dramatic enhancement in the overall efficiency could be due to the remarkable enhancement in the light harvesting and internal scattering of the photoanode with NF layer as confirmed by the dramatic increment in the photocurrent density together with the increased light absorption. The overall interfacial resistance of the DSSC can be reduced by introducing this NF layer to the conventional photoanode structure as confirmed by the EIS measurements.

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