STUDY OF DYE-SENSITIZED SOLAR CELLS WITH TiO₂
NANOPARTICLES/NANOFIBERS COMPOSITE ELECTRODE USING
PHOTOVOLTIC AND EIS MEASUREMENTS

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ABSTRACT

Increment of the efficiency of dye-sensitized solar cells (DSSC) by an innovative type of photoanode consisting of a composite mixture of conventional P-25 titanium dioxide (P25-TiO₂) nanoparticles and electrospun TiO₂ nanofibers (EL TiO2 NF) with optimized weight ratio is obtained. This novel composite photoanode harvests sunlight more strongly compared to a DSSC made with conventional photoanode which consists only P25-TiO₂. Thus the efficiency of DSSCs made with this novel composite photoanode is significantly higher than the DSSC made with conventional P25-TiO₂ photo anode. The TiO₂ nanofibers were prepared by the electrospinning technique and the composite photoanode was prepared by using different weight ratios of TiO₂ nanofibers in the TiO₂ nanoparticle mixture. These cells were characterized by UV-Vis spectroscopy, J-V characteristics, EIS analysis and dark I-V measurements.

While the overall efficiency of the DSSC comprising with novel photoanode with nanofibres showed 7.01% under the illumination of 1000 W m⁻², the DSSCs with conventional P-25-TiO₂ photoanodes showed 5.11% under the same conditions. Therefore, 37.18% enhancement in the overall efficiency is achieved by employing this novel photoanode in the DSSCs. The high efficiency of the solar cell appears to be due to the increased short-circuit photocurrent density by enhanced light harvesting caused by the increased light absorption due to scattering within the composite TiO₂ Nano-structure with nanofibres.

Keywords: Dye-sensitized solar cells, performance, nanoparticles, nanofibers, electrospinning, UV-VIS spectroscopy, photocurrent, light harvesting, electrolyte.

1. INTRODUCTION

The solar cell which converts sunlight into directly into electricity is a rapidly growing energy technology which is gaining great popularity because of the low cost in fabrication and minimized transition losses by fixing them near the end user. In terms of higher efficiency and easy fabrication, the dye-sensitized solar cell (DSSC) is one of the most promising replacement to the currently available high cost silicon solar cells. The third generation, low manufacturing cost and simple structure Dye-sensitized solar cells have been widely investigated by B. O’Regan and M. Gratzel in 1991 [1-10]. This simple structure and low cost technology have further stimulated great research interest to improve the efficiency of dye-sensitized solar cells [11].

Typical lab scale DSSC consists of a transparent mesoporous semiconducting photoanode usually TiO₂, made up on a glass substrate coated with a thin film of Fluorine doped SnO₂ layer, a charge transfer dye covalently bonded to the surface of the oxide layer to enhance light harvesting, an electrolyte containing redox mediator (I⁻ / I³⁻) in a solvent effecting dye-regenerating and a cathode made of a plate coated with a catalyst (typically, platinum) to enable electron circulation
through an external circuit. Fig.1 shows the schematic diagram of a DSSC. When exposed to sunlight, the dye sensitizer gets excited from which an electron is injected into the conduction band of the TiO$_2$. These produced electrons diffuse to the anode and are transferred to the external load before being collected by the electrolyte at cathode surface to complete the cycle. At the other side of the DSSC, counter electrode collects the electrons coming through the external load and transferred them to tri-iodide to yield iodide according to \( I_3^- + 2e^- \rightarrow 3I^- \). When iodide (\( I^- \)) diffuses to dye sensitized porous TiO$_2$ electrode, it reduces the oxidized dyes (\( S^+ \)) following \( 2S^+ + 3I^- \rightarrow 2S + I_3^- \). Thin layer of platinum on the counter electrode plays a major roll in this process [12-13].

![Schematic diagram of a Dye-sensitized solar cell.](image)

To enhance the efficiency of the DSSC, numerous tasks need to be addressed. One of the tasks is, their slow electron transport rate. One-dimensional (1D) nanostructures including TiO$_2$ nanowires, nanorods, nanotubes, and their composites with TiO$_2$ nanoparticle (TiO$_2$-NPs) have been studied to improve the electron mobility and the transport rate [14-19]. However, the attachment of dye molecules to these 1D nanostructures is often inefficient. Another task is the enhancement of light harvesting by the photoanode [20]. In order to get this done in-cooperation of additional scattering layers made of large TiO$_2$ particles, nanorods, and/or nanofibers have been coated onto photoanodes having two layered structures [21].

In this study we report an employment of composite photoanode prepared with TiO$_2$-NPs and electrospun TiO$_2$ nano fibres (TiO$_2$-NFs) as an alternative to the conventional photoanode in DSSCs. This type of composite photoanode harvests sunlight more strongly compared to a conventional photoanode which consists only TiO2-NPs made from commercially available P-25 TiO$_2$ . The excellent sunlight harvesting has been found to be very effective according to Mie scattering theory [22]. The incooperation of TiO$_2$ NF in this photoanode scatters more light inside the photanode and therefore overall light absorption inside the cell is high. Therefore, the rate of generating electron by dye excitement is high which helps to enhance the overall efficiency of the device [23].

2. EXPERIMENTAL

2.1 Materials

Poly (vinyl acetate) (PVA, (C$_4$H$_6$O$_2$)$_n$), Titanium isopropanoxide (TIP, C$_{12}$H$_{26}$O$_4$Ti) was purchased from Fluka Chemie, Switzerland. Acetic acid, N,N-dimethylformamide (DMF), P-25
TiO$_2$ NPs (NPs) was from Degussa, AEROXIDE TiO$_2$ P-90 was from Evonic Industries AG, Germany, ruthenium- (II) bis(tetrabutylammonium) (N-719), and an iodide-based redox electrolyte, FTO glass (Solaronix sheet glass 8 Ω/sq, Switzerland).

2.2 Preparation of TiO$_2$ Nanofiber

A mixture containing of 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 6 hours. The final solution was injected using a syringe. The needle was connected to the positive terminal of a power supply. The flow rate of the solution was adjusted to $2 \text{ml/h}$, controlled by a syringe pump. A voltage of 15 kV was applied between the needle tip and the grounded drum collector, which was grounded and used to collect the NFs at room temperature, and the distance between the nozzle and collector was 6.5 cm. The TiO$_2$ NFs were deposited on to pre-cleaned glass plates which were attached to the drum collector by an aluminium foil. The drum was adjusted to rotate with a rotational speed of 650 rpm. Next, the electrosynspun NFs were calcined at 450 °C for 45 min. The prepared TiO$_2$ NFs were etched by glass plate to obtain porous TiO$_2$ NFs.

2.3 Preparation of TiO$_2$ compact layer

0.25g of AEROXIDE TiO$_2$ P-90 powder (EVONIC) was ground for 10 minutes with 1ml of 0.1M HNO$_3$ till it forms a creamy paste. Appropriate amounts of the paste were deposited by spin coating method on a pre-cleaned Fluorine-doped conducting Tin Oxide (FTO) glass (Solaronix sheet glass 8 Ω/sq). FTO/CL plates were sintered at 450 °C for 45 min and slowly cooled down to room temperature.

2.4 Assembly of DSSC

In the current study, TiO$_2$ NFs were synthesized using electrospinning method and incorporated into TiO$_2$ photoanode by the weight ratio of 0%,1%,2%,5%,10%,15%,20% and 25%. In order to do this several nanocrystalline TiO$_2$ photoanodes were prepared by using the following procedure. 0.2475g, 0.245g, 0.2375g, 0.225g, 0.2125g, 0.200g, and 0.1875g of TiO$_2$ powder (Degussa P-25) were mixed with corresponding weights, 0.0025g, 0.005g, 0.0125g, 0.025g, 0.05g and 0.0625g of electrospun TiO$_2$ NF powder respectively and mixtures was ground well for 30 min with 1 ml of 0.1M HNO$_3$, one drop (about 0.02 g) of Triton X-100 and about 0.05g of PEG until the mixture forms a creamy paste. Appropriate amounts of the paste were doctor bladed on a Fluorine-doped conducting Tin Oxide (FTO) glasses with compact layer, keeping the active cell area of 0.25 cm$^2$. In order to compare the effects of TiO$_2$ NFs in the TiO$_2$ films, pristine TiO$_2$ films were also prepared without adding TiO$_2$ NFs. FTO/CL/ TiO$_2$ plates were sintered at 450 °C for 45 min and slowly cooled down to room temperature. They were subsequently dipped in an ethanolic dye (0.3 mM) solution containing Ruthenium Dye N-719 [Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-bicarboxylato) ruthenium(II)] for 24h.

2.5 Preparation of the electrolyte

The electrolyte solution for the DSSCs was prepared by adding 0.738 g of tetrpropyl ammonium iodide (Pr$_3$NI) and 0.060 g of I$_2$ to a pre-cleaned 10 ml volumetric flask containing 3.6 ml of molten (MP 40 °C) ethylene carbonate (EC) and 1.0 ml of acetonitrile. The solution mixture was stirred overnight.
2.6 Optical absorption measurement

Optical absorption spectra of the TiO$_2$ NP and TiO$_2$ NFs powder samples were taken by Shimadzu 2450 UV-Vis spectrophotometer in the wavelength range from 400 nm to 800 nm.

2.7 Fabrication of solar cell and I-V characterization

DSSCs were fabricated by sandwiching the electrolyte solution containing ($I^-/I_3^-$) redox couple in the configuration [FTO/TiO$_2$NP/dye/electrolyte/Pt] and [FTO/TiO$_2$NP+NF/dye/electrolyte/Pt]. The photocurrent-voltage (I-V) characteristics of the cells were measured under the illumination of 1000 Wm$^{-2}$ (AM 1.5) simulated sunlight using a computer-controlled setup coupled to a Keithley 2000 multi-meter and a potentiostat/galvanostat HA-301. A Xenon 500 W lamp was used with AM 1.5 filter to obtain the simulated sunlight with above intensity. When preparing these DSSCs, it was ensured to have the same TiO$_2$ film thickness and the same amount of dye loading.

2.8 EIS measurements

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

2.9 Dark I-V measurements

Dark I-V measurements were performed for the two different types of DSSCs using Autolab PGSTAT 128 N in order to see the effect of TiO$_2$ NFs incorporated TiO$_2$ NPs on the reverse breakdown voltage of the DSSCs.

3. RESULTS AND DISCUSSIONS

3.1 Surface morphologies of photoanodes

Fig.1 shows the scanning electron micrographs (SEM) of different photoanodes namely (a) surface of TiO$_2$ NFs (Mag 50000) electrospun before sintering (b) surface of sintered NFs, (c) the surface of photoanode of control cell (pristine TiO$_2$),(d) the innovative type of 5% TiO$_2$ NF 95% TiO$_2$ NP composite photoanode,(e) enlarge surface view of TiO$_2$ NFs (Mag 100000) photoanode and (f) cross section of compact layer. As can be seen from Fig 1 (a) and (b) electrospun nanofibres converts in to elongated beets like structure (rice grain type) after sintering. The surface view of the conventional photanode and the composite photanode are not very distinguishable. One of the reasons might be due to the small amount of TiO$_2$-NF incooretated in to the photoanode. However, it can be seen that the surface of the composite photoanode is slightly denser than the conventional photoanode prepared with TiO$_2$-NP due to the incooperation of TiO$_2$-NF. In order to estimate the average diameter of the nanofibres and the thickness of the photoanode, corsooo sectional view of photoanode is obtained togetehre with the enlarge picture of the nanofibres as

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depicted in Fig 1 (e) and (f). The average diameter of the TiO₂-NF before sintering is around 115 nm. The overall thickness of the composite photoanode is approximately 17.9 µm thick with 1.34 µm thick compact layer.

![Fig.1. Scanning electron micrographs (SEM) of different photoanodes namely (a) surface of TiO₂ NFs (Mag 50000) electrospun before sintering (b) surface of sintered NFs, (c) the surface of photoanode of control cell (pristine TiO₂),(d) the innovative type of 5% TiO₂ NF 95% TiO₂ NP composite photoanode,(e) Surface of the TiO₂ NFs (Mag 100000) and (f) cross section of compact layer.](image)

3.2 Photoelectric conversion efficiency

Fig.2 (left) shows the efficiency variation of the DSSC comprising with different amounts of TiO₂-NF in the photoanode. It can be clearly seen that, when the amount of nano fibre increase in the photoanode, the efficiency increase up to 5% of nanofibres and then decrease with higher amounts. Fig.2 (right) shows the I-V curves of the DSSCs fabricated with conventional photoanode (TiO₂ P-25) tothre with the 5% amount of NF in the photoanode.
Table 1. shows the photovoltaic parameters extracted from the I-V curves of the different DSSCs fabricated with various amounts of nanofibres in the photoanode. As it is illustarde in the fig 1 and the table the short-circuit photocurrent density ($I_{SC}$), and the efficiency values of the DSSC comprising with 5% NF with 95% NP shows the highest values.

![Image of Table 1](image)

According to the values given in the table 1, the efficiency for DSSCs made with pristine TiO$_2$ and 5% TiO$_2$ + NF 95% TiO$_2$ NP are 5.11%, 7.01 %, respectively, showing clearly the enhancement in the efficiency due to the incorporation of nanofibres in the photoanode. The photocurrent density enhancement evidently takes place due to the improved light harvesting by the TiO$_2$ NF containing TiO$_2$ photoanode in the DSSCs by Mie Scattering. The overall solar cell efficiency has shown a dramatic increase by 37.18 % for the solar cells with 5% NF 95% NP. However, it should be noted that the $V_{OC}$ values of the DSSCs have decreased relative to the control DSSC. This might be due to the negative shifting of Fermi level in the composite TiO$_2$ photoanode due to the incorporation of nanofibres.

### 3.3 EIS analysis

Electrochemical impedance spectroscopy (EIS) measurement performed to understand the charge transfer inside the DSSCs. The Nyquist plots of the electrochemical impedance spectra of DSSCs with TiO$_2$, TiO$_2$ NPs and TiO$_2$ NFs in the frequency range of $1 \times 10^{-2} - 1 \times 10^6$ Hz shown in Fig.3 (left) and the equivalent circuit used to estimate the interfacial resistances is shown in the right. Resistance $R_s$, the starting point, $R_{1_{CT}}$ first semicircle and $R_{2_{CT}}$ second semicircle are the resistance of TiO$_2$/FTO glass, interface of the counter electrode/electrolyte and interface of the TiO$_2$/dye/electrolyte, respectively $R_s$ and $R_{1_{CT}}$ and $R_{2_{CT}}$ in all cases were similar due to the same preparation procedure. $R_{2_{CT}}$ corresponds to charge recombination.

The resistance values estimated from the Nyquist plots are tabulated in table 2. As can be seen from table 2, $R_s$, $R_{1_{CT}}$, and $R_{2_{CT}}$ values of the 5% NF DSSC is significantly lower than the corresponding quantities of the control DSSC. This could be due to the enhancement of the surface contacts between TiO$_2$-NP due to the incorporation of nanofibres.
The Nyquist plots of the electrochemical impedance spectra of DSSCs with TiO\textsubscript{2}, TiO\textsubscript{2} NPs and TiO\textsubscript{2} NFs (left) and the equivalent circuit used to estimate the interfacial resistance in DSSCs (right).

Table 2: Series resistance ($R_s$), charge-transfer resistance of the Pt/electrolyte ($R_{1CT}$), charge-transfer resistances of the TiO\textsubscript{2}/electrolyte ($R_{2CT}$) of DSSCs with TiO\textsubscript{2}, TiO\textsubscript{2} NFs

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA/cm\textsuperscript{2})</th>
<th>$V_{OC}$ (mV)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{1CT}$ (Ω)</th>
<th>$R_{2CT}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0% NF 100% NP</td>
<td>10.080</td>
<td>776.8</td>
<td>334.0</td>
<td>321</td>
</tr>
<tr>
<td>D</td>
<td>5% NF 95% NP</td>
<td>13.528</td>
<td>748.7</td>
<td>13.6</td>
<td>24.5</td>
</tr>
</tbody>
</table>

3.4 The UV-Vis optical absorption spectra

The UV-Vis optical absorption spectra of the two DSSCs are shown in Fig. 4. Titanium dioxide is optically transparent at wavelengths above 400 nm. It is well known that a higher level of dye absorption is needed to increase the efficiency of DSSCs. By immersed the N719 ruthenium based dye they absorb light at visible region. The absorption of 5% NF 95% NP cell is greater than pristine TiO\textsubscript{2} (control cell) at wavelength of 536 nm. Fig.4 reveal the light-scattering signatures of the nanofiber samples, providing evidence of the best light harvesting. The Mie scattering theory was successfully improved to describe the light scattering properties of electrospun nanofibers.

Fig. 3. The Nyquist plots of the electrochemical impedance spectra of DSSCs with TiO\textsubscript{2}, TiO\textsubscript{2} NPs and TiO\textsubscript{2} NFs (left) and the equivalent circuit used to estimate the interfacial resistance in DSSCs (right).

Fig. 4. Absorbance spectra of different photoanodes TiO\textsubscript{2} and TiO\textsubscript{2} NF with N719 Dye.

3.5 Phase analysis-electron life time

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The electron lifetime is one of the parameter that affects the efficiency of DSSC. Fig.5 shows the frequency peaks of the charge-transfer process at the photoanode/electrolyte interface of the DSSCs. The typical low-frequency peak $f_{\text{max}}$ is located at 18.42 Hz for the 5% NF 95% NP cell, at 26.00 Hz for control cell. The electron lifetime ($\tau_r$) in the DSSCs can be determined from the value of $f_{\text{max}}$ from Eqn (1). [24]

$$\tau_r = \frac{1}{2\pi f_{\text{max}}} \quad \text{(1)}$$

Table 3 shows the relationship between $V_{\text{OC}}$, $I_{\text{SC}}$, and $\tau_r$ for the two types of DSSCs.

Table 3: Electron life time from phase plot.

<table>
<thead>
<tr>
<th>Device</th>
<th>$I_{\text{SC}}$ (mA/cm$^2$)</th>
<th>$V_{\text{OC}}$ (mV)</th>
<th>$\eta$ (%)</th>
<th>$f_{\text{max}}$ (Hz)</th>
<th>$\tau_r$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control cell</td>
<td>10.080</td>
<td>776.8</td>
<td>5.11</td>
<td>26.00</td>
<td>6.12</td>
</tr>
<tr>
<td>5% NF 95% NP</td>
<td>13.528</td>
<td>748.7</td>
<td>7.01</td>
<td>18.42</td>
<td>8.64</td>
</tr>
</tbody>
</table>

According to the table 3 the electron life time $\tau_r$ is highest for the 5% NF 95% NP and the $V_{\text{OC}}$ of this cell is lowest. $\tau_r$ value of control cell is significantly lower, and its $V_{\text{OC}}$ value is higher compared to the 5% NF 95% NP cell. This clearly explains why the 5% NF 95% NP offers the highest efficiency.

![Graph showing variation of phase angle vs frequency for two DSSCs with different photanodes.](image)

Fig.5. Variation of Phase angle vs frequency of two DSSCs with different photanodes in the frequency range of $1 \times 10^{-2}$ and $1 \times 10^6$ Hz.

4. CONCLUSION
This project reveals that the fabrication of composite made of electrospun TiO$_2$ NFs and TiO$_2$ NPs is an innovative type of photoanode that significantly enhanced the harvesting of light according to Mie scattering theory. The excellent light scattering behavior of these TiO$_2$ NFs was investigated using absorptions UV-vis spectroscopy. Under the same fabrication conditions and film thickness, the DSSC made using the composite with 5% NFs and 95% NPs by weight demonstrated 37.18% higher device efficiency than that made using pristine TiO$_2$ NPs.

5. REFERENCES