Influence of nanostructured TiO$_2$ film thickness on photoelectrode structure and performance of flexible Dye-Sensitized Solar Cells

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**Abstract**

A commercial Ti-Nanoxide was deposited on In-doped SnO$_2$ (ITO) polymer substrates by tape casting technique with different thicknesses (7, 14 and 36μm) to be used as photoelectrode in flexible dye-sensitized solar cells (DSSCs). Ruthenium dye was adsorbed on each TiO$_2$ film for 24 h. The resulting photoelectrodes were used to form flexible DSSCs in combination with electrolyte and counter electrode. The prepared films were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Photovoltaic parameters like short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and power conversion efficiency ($\eta$) were evaluated for fabricated cells. The cell formed with a TiO$_2$ film of 14μm thickness reached the best performance.

**Keywords:** Flexible Dye-sensitized Solar Cell; Nanostructured TiO$_2$; Thickness; Photoelectrode.

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1. Introduction

Dye-sensitized solar cells have attracted much attention for the last more than a decade since they were developed by Gratzel in 1980s [1-4] because of their low-cost, environment friendliness and high conversion efficiency of solar energy into...
electrical energy compared to silicon cells [5, 6]. A typical DSSC contains five components: 1) a transparent conducting oxide (TCO) substrate 2) a nanocrystalline network of a wide band gap semiconductor (usually TiO2), 3) a sensitizer, 4) an electrolyte, and 5) a counter electrode (CE). The total efficiency of the DSSC depends on the optimization and compatibility of each of these constituents [7, 8]. Using the very high surface area, which is provided by the nanocrystalline particles of TiO2, DSSC allowed for an adsorption of a sufficiently large number of dye molecules for efficient light harvesting [1-8]. Electron kinetics in the nanocrystalline TiO2 layer plays an important role in the operation of a dye solar cell. The electron injection from the excited dye to TiO2 takes place in femtoseconds while the time scale for the back electron transfer is several orders of magnitude slower, indicating the charge separation achieved on kinetic grounds. The dye regeneration process occurs in nanoseconds scale explaining the efficient operation of the dye solar cell since the oxidized dye should be reduced to its ground state as fast as possible. The injected electrons to TiO2 hop through the colloidal structure and finally arrive at the conducting glass collector [2], [9] and [10]. The adsorption of the dye to the nc-TiO2 surface usually takes place via special anchoring groups attached to the dye molecule. The high efficiency of the dye sensitized solar cell is accomplished by coating the internal surfaces of the porous TiO2 electrode with special dye molecules tuned to absorb the incoming photons [11] and [12]. Flexible DSSCs, based on the substrates of indium tin oxide (ITO) coated polyethylene terephthalate (PET), substituting for rigid glass substrates, are regarded as one possible breakthrough in the field of DSSCs regarding their commercialization, because flexible DSSCs have presented great advantages of low cost of production and wide application. Conductive plastic substrates, such as ITO/PET can be processed by a continuous process like roll-to-roll production for porous nanocrystalline film coating, therefore, greatly decreasing the production cost of the solar cells. In addition, it is light weight, having portable character [13]. In this work, our approach was consisting of a very simple procedure to deposit the TiO2 layer on the In-doped SnO2 (ITO) polymer substrates by a tape casting technique. The effect of TiO2 layer thickness on the photo-electrochemical performance was investigated.

2. Experimental

Polymer substrates (ITO, In2O3:SnO2 2.5 cm x 2.5 cm, Solaronix) were cleaned in an ultrasonic bath (Elmasonic E 60H) with acetone and ethanol (50:50 V/V %) at 60°C for 1 hour. TiO2 paste (Ti-Nanoxide D-I series, Solaronix) was deposited on ITO polymer having resistance of 20 Ω/cm2 by tape casting technique. The prepared photoelectrode was placed in the oven (Memert UFE 500) and sintered in 120°C for 24 hours.

The photoelectrode (TiO2 electrode) was immersed in dye (Ruthenium 535-bisTBA, Solaronix) solution for 24 hours. Dye solution was prepared by dissolving 20 mg of Ruthenium 535-bisTBA in 100 ml ethanol 99.9% (Merck). The
immersed TiO$_2$ electrode in dye was removed and rinsed with ethanol and dried at room temperature for 1 h. The graphite counter electrode was produced by spraying graphite 33 (Kontakt Chemie) on the glass substrate. The graphite counter electrode was then put in the oven at 150°C for 24 hours. The dye-covered nanocrystalline TiO$_2$ film and the counter electrodes were assembled into sealed sandwich-type cells applying one drop of electrolyte (MPN-100, solaronix) and sealing with Amosil 4 (solaronix)[14].

3. Results and Discussion

Fig. 1a, b, c shows cross-sectional SEM images (Philips XL30 model) of the TiO2-coated ITO polymer after the sintering process at 120°C. The different TiO$_2$ thicknesses (7, 14 and 36 μm) onto the ITO polymer are clearly observed in Fig. 1 a, b and c. Image of the top view of nanostructure TiO$_2$ film (14μm thickness) coated on Polymer substrate shows sponge-like structure of electrode after sintering process Fig. 1d. Further observation indicates that the morphology of samples is very rough and may be beneficial to enhancing the adsorption of dye due to its great surface roughness and high surface area.

Fig.1. SEM cross-sectional images of TiO$_2$ film coated on ITO polymer at high magnification (a), (b) and (c) with the estimation of TiO$_2$ thickness. Image (d) is Top view of SEM image of TiO$_2$ film.
The Surface morphology of the nanostructured TiO$_2$ films was studied using AFM microscopy (Dualscope C26, DME model). Three-dimensional AFM images of different TiO$_2$ thicknesses (7, 14 and 36 μm) onto the ITO polymer are clearly observed in Fig. 2 a, b and c. Spongy and Porous structure Films confirms the scanning electron microscope images. As can be seen in these images by increasing the thickness, roughness and surface area also increases. Roughness factor were obtained by means of AFM analysis is 42%, 48% and 73% for the 7, 14 and 36 microns thickness respectively. Therefore by increasing roughness can be concluded that the dye and light absorption will increase due to diffraction phenomena[15].

Fig. 2. AFM images of films of (a) 7μm, (b) 14μm and (c) 36μm TiO$_2$ thickness.

Fig. 3 shows the photocurrent-voltage curve for the DSSCs based on TiO$_2$ films with different thicknesses. The fill factor for DSSC was calculated from equation (1) where P$_{\text{max}}$ is the maximum electrical power obtained; I$_{\text{SC}}$ and V$_{\text{OC}}$ are the short-circuit current density and open-circuit voltage, respectively [16].

\[
\text{FF} = \frac{P_{\text{max}}}{I_{\text{SC}} \times V_{\text{OC}}} \tag{1}
\]

The conversion efficiency of the dye sensitized solar cell is obtained from equation (2). Where I is the intensity of incident light; A is the active area illuminated by halogen lamp.

\[
\eta = \frac{I_{\text{SC}} \times V_{\text{OC}} \times \text{FF}}{I \times A} \tag{2}
\]
The values of \( V_{OC} \), \( I_{SC} \), FF and cell efficiency (\( \eta \)) for the different DSSCs using various TiO\(_2\) thicknesses of active area 1cm\(^2\) illuminated by a halogen lamp with an incident light of 100 W/cm\(^2\) are shown in Table.1.

Table 1. Performance characteristics for the different DSSCs using various TiO\(_2\) thicknesses.

<table>
<thead>
<tr>
<th>TiO(_2) thickness (( \mu m ))</th>
<th>( V_{OC} ) (mV)</th>
<th>( I_{SC} ) (mA/cm(^2))</th>
<th>FF</th>
<th>( \eta ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>520</td>
<td>1.70</td>
<td>61</td>
<td>0.54</td>
</tr>
<tr>
<td>14</td>
<td>520</td>
<td>2.11</td>
<td>61</td>
<td>0.67</td>
</tr>
<tr>
<td>36</td>
<td>520</td>
<td>1.34</td>
<td>55</td>
<td>0.35</td>
</tr>
</tbody>
</table>

4. Conclusions

An investigation of the optimal TiO\(_2\) film thickness at the photo-anode of a flexible dye sensitized solar cell was carried out, without the use of pre- or post-layer in the photo-anode that may improve the performance, but also make more complicate the analysis of the effect played by the absorber layer. Three different thicknesses (7, 14 and 36 \( \mu m \)) of the TiO\(_2\) layer were prepared by using a tape casting technique and a thermal treatment. Compared to the various reports in the literature, we used an easy, fast and low cost preparation procedure. The photo-electrode with a thickness of 14 \( \mu m \) showed the best performance in terms of conversion efficiency (\( \eta \)), short circuit current density (\( I_{SC} \)), fill factor (FF) and the open-circuit photo-voltage (\( V_{OC} \)) was the largest for the electrode of 14 \( \mu m \).

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References