Dye-Sensitized Solar Cells with Zinc Oxide Nanostructured Films Made with Amine Oligomers as Organic Templates and Gel Electrolytes

Andigoni Apostolopoulou, Dimitris Karageorgopoulos, Andreas Rapsomanikis, and Elias Stathatos

Abstract—The demand for energy led to clean, renewable and cheap energy sources, while solar energy is the most abundant. Dye sensitized solar cells (DSSCs) are proposed as low cost alternatives to the conventional photovoltaics. These cells have been widely examined due to their low cost and high conversion efficiency. Several mesoporous metal oxides have been examined, where ZnO nanostructures have been taken much attention last years.

At the present work, we examine the use of nanostructured ZnO films as photoanodes in DSSCs. The simplicity of the ZnO films synthesis is demonstrated while solar cells are constructed and tested. In particular, we demonstrate a simple method combining Zn(NO$_3$)$_2$ as zinc precursor with different organic templates. Besides, the structural properties of the ZnO films are examined with porosimetry, microscopy methods and X-Ray diffractograms. Their electrical behavior is examined in terms of current-voltage characteristic curves under simulated solar light while electrochemical impedance spectroscopy is also used for measuring charge transfer across the ZnO-electrolyte interface and free electron lifetimes. We finally obtained an overall efficiency of 0.6% for DSSCs based on ZnO films and a commercial dye as sensitizer. It seems that ZnO films constitute promising nanostructures for DSSCs that can be further improved.

Index Terms—Dye-sensitized solar cells, photoanodes, thin films, zinc oxide.

I. INTRODUCTION

DSSCs have attracted much attention due to their low cost manufacturing, fabrication on flexible substrate and simple construction [1], [2]. Despite these advantages, the maximum certified efficiency for DSSCs is much lower compared to silicon based solar cells. Much research has been focused to enhance the performance of DSSCs with different anode materials such as TiO$_2$, ZnO, SnO$_2$, Nb$_2$O$_5$ etc. while TiO$_2$ is dominated most of times [3]-[8]. Recently, ZnO, with similar band gap to that of TiO$_2$, appears to be an alternative material for the fabrication of high efficiency DSSCs. It possesses high environmental stability and high electron mobility, providing a direct conduction pathway for rapid collection of electrons at the substrate of the photoanode [9]-[11]. ZnO is also a wide band gap semiconductor with energy band structure and physical properties similar with TiO$_2$. However, it has higher electron mobility (155 cm$^2$ v$^{-1}$ s$^{-1}$ versus to 10$^3$ cm$^2$ v$^{-1}$ s$^{-1}$ of TiO$_2$) favorable for electron transport, it is easily crystallized and anisotropically grow in a variety of morphologies such as nanowires, nanotubes, nanobelts, and nanoflowers [12]-[15]. Due to their aforementioned unique properties they have been proposed as alternative photoelectrodes in DSSCs in order to achieve better performance. In this work we report the synthesis and characterization of different ZnO photoanodes for dye sensitized solar cells. The simplicity of depositing ZnO films applied as photoanodes has been presented, while their electrical properties were studied, as solar cells with a ruthenium complex dye (N719) as sensitizer. In particular, the structural properties of the films with different organic materials as templates were examined in terms of their porosity using BET method and FE-SEM microscopy. More porous films were prepared when organic template with higher molecular weight was used. According to FE-SEM images, particles with average diameter of 30-60nm were prepared depending on the template. Furthermore, a better performance of DSSCs and improved electrical characteristics were obtained in the case of more porous films. This study attempts to take advantage of the proposed synthetic route of ZnO to prepare photoanodes for DSSCs but also for other applications that require nanocrystalline films of transition metal oxides.

II. EXPERIMENTAL

A. Materials

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$-6H$_2$O), poly (propylene glycol) bis (2-aminopropyl) ether (APPG) with different chain lengths M$_r \approx 230, 400, 2000$ were used to make different precursor sols. Lithium iodide (LiI), iodine (I$_2$), 1-methyl-3-propyl imidazolium iodide (MPII), guanidine thiocyanate (Gu-SCN), acetic acid (AcOH), 4-tert-butyl pyridine (TBP), 3-isocyanatopropyl triethoxy silane (ICS) were purchased from Sigma-Aldrich and used as received. Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$) and all solvents were also purchased from Aldrich and used as received. cis-disoiothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxyilato) ruthenium(II) bis(tetrahydroammonium), N719 was purchased from Solaronix S.A, Switzerland. SnO$_2$: F transparent conductive electrodes (FTO, TEC$^\text{TM}$ A8) 8

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Ohm/square were purchased from Pilkington NSG Group.

B. Preparation of ZnO Photoanodes Sensitized with N-719

ZnO nanocrystalline films were prepared by the sol-gel method. A small proportion of Zn(NO$_3$)$_2$ was added in n-propanol at 80°C followed by the addition of APPG with different molecular weights under stirring to modify surface morphology. Three different solutions were prepared by varying APPG molecular weight. Solution 1 consisted of 0.357g Zn(NO$_3$)$_2$, 6ml n-propanol and 0.218g APPG230. Solution 2 was consisted of 0.357g Zn(NO$_3$)$_2$, 6ml n-propanol and 0.252g APPG400 and solution 3 0.950g Zn(NO$_3$)$_2$, 6ml n-propanol and 0.8g APPG2000 (Fig. 1). FTO glasses were dipped into each solution and a thin film was deposited before calcination at 500°C for 15min. This step was repeated several times in order to achieve optimal film thickness. After cooling down at room temperature, ZnO films attached strongly to the FTO were immersed in a 5×10$^{-4}$M (50:50 ethanol: acetonitrile) N719 solution for 24h. Dye coated ZnO photoelectrodes were rinsed with acetonitrile to remove non-attached dye molecules and dried at 50°C before use.

Fig. 1. Preparation of ZnO solutions.

C. Preparation of Gel Electrolyte and Fabrication of Quasi Solid State Dye Sensitized Solar Cells

A gel electrolyte with an organic-inorganic hybrid material was prepared according to a procedure described in previous publications [16], [17]. Briefly, poly(propylene glycol) bis (2-aminopropyl ether) $M_r$=230 and 3-isocyanatopropyl triethoxysilane (ICS) with molar ratio ICS/diamine=2, react in a vessel (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part. The gel electrolyte was synthesized by the following procedure: 0.7g of the functionalized alkoxide precursor (PPG230-ICS) were dissolved in 1.6g of sulfolane and 0.8g of methoxypropionitrile under stirring. Then, 0.6ml of glacial acetic acid (AcOH) were added to accelerate gelation followed by 0.3M 1-methyl-3-propylimidazolium iodide, 0.1M LiI and 0.05M I$_2$ in a final molar ratio AcOH:LiI:MPIII:I$_2$ = 2.5:0.1:0.3:0.05. To complete the electrolyte solution, 0.204g of tert-butyl pyridine and 0.036g of guanidine thiocyanate were added to the above mixture. The still liquid electrolyte was placed on the top of the ZnO electrodes and a platinized FTO counter electrode was pushed by hand on the top to complete the cell. The electrolyte was finally gelled after several hours. The platinized FTO glass was made by casting a few drops of a H$_2$PtCl$_6$ solution (5mg/ml of ethanol) and calcination at 450°C for 15min. The active area of the as prepared cells was 2cm$^2$.

D. Characterization of Quasi-Solid State Dye Sensitized Solar Cells

The samples were illuminated with Xe light source using a Solar Light Co. solar simulator (model 165S-300) equipped with AM 0 and AM 1.5 direct Air Mass filters to simulate solar radiation at the surface of the earth. The light intensity was 100mW/cm$^2$. J-V curves were recorded by connecting the cells to a Keithley Source Meter 2601A. A black mask 0.264cm$^2$ was used in the measurements. For each case, we made three devices which were tested under the same conditions in order to avoid any misleading estimation of efficiency. The structural properties of the films were evaluated with field emission scanning electron microscopy (FE-SEM). Electrochemical impedance spectroscopy (EIS) was also used for the interface characterization of individual components of the cells.

III. RESULTS AND DISCUSSION

The structural properties of the films were initially studied by images of the three nanostructured photoanodes using FE-SEM (Fig. 2). The smaller the size of nanoparticles, the more porous film is generated which results in higher specific surface area and therefore a greater amount of dye is adsorbed.

Fig. 2. SEM top view from ZnO photoanodes 1, 2, and 3 made of APPG230, APPG400, APPG2000 as templates respectively. 4. Cross-section image for sample 3.

In the first case the large size of nanoparticles (58.3nm diameter) results in poor dye adsorption, while in the third case, where nanoparticles exhibit the smallest size (32.4nm), the amount of dye adsorption is greater. The cross-section image from the most efficient photoanode was found to be 10μm.

The structural properties of the ZnO films were also characterized with porosimetry method. The total pore volume ($V_p$), ranged from 0.045 to 0.106cm$^3$/g for the three samples. The BET specific surface area ($S$), the total pore volume ($V_p$), the mean pore diameter $D_{por}$ and the total porosity ($\phi$) were calculated for all samples and they are presented in Table I.
TABLE I: BRUNAUER–EMMETT–TELLER (BET) MEASUREMENTS

<table>
<thead>
<tr>
<th>Cell</th>
<th>( V_p ) (cm(^3)/g)</th>
<th>( S ) (m(^2)/g)</th>
<th>( \phi ) (%)</th>
<th>( D_{\text{por}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.045</td>
<td>13.04</td>
<td>20</td>
<td>12.7</td>
</tr>
<tr>
<td>2</td>
<td>0.098</td>
<td>22.47</td>
<td>35</td>
<td>15.2</td>
</tr>
<tr>
<td>3</td>
<td>0.106</td>
<td>26.44</td>
<td>37</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Nitrogen adsorption-desorption isotherms are shown in Fig. 3.

The sample 3 seems to exhibit higher pore volume compared to the other two photoanodes and thus growth of the specific area. The behavior of the pore volume affects the porosity, which defines the quantity of dye adsorption. X-ray diffraction patterns were used to identify the synthesized zinc oxide nanoparticles. The polycrystalline X-ray diffraction for the third sample is presented in Fig. 4. All the typical diffraction peaks are referred to wurtzite ZnO phase.

ZnO were successfully used as photoanodes in DSSCs. The current density–voltage (J–V) characteristic curves of quasi solid-state dye sensitized solar cells based on ZnO are presented below in Fig. 5.

The quasi solid-state DSSCs constructed with a combination of Zn(NO\(_3\))\(_2\) and APPG2000 exhibits improved performance, with an increase in current density compared with the other oligomers (Table II). This means that faster electron transport and by extension lower recombination rate occurs in the third case.

TABLE II: ELECTRICAL CHARACTERISTICS OF DSSCs EMPLOYING DIFFERENT ZINC OXIDE PHOTOANODES

<table>
<thead>
<tr>
<th>Cell</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( V_{oc} ) (V)</th>
<th>( P_{max} ) (mW)</th>
<th>( FF )</th>
<th>( \eta % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.392</td>
<td>0.607</td>
<td>0.036</td>
<td>0.50</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>0.430</td>
<td>0.551</td>
<td>0.037</td>
<td>0.52</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>2.080</td>
<td>0.574</td>
<td>0.166</td>
<td>0.47</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The effect on the electron transport at the interfaces in the DSSCs under simulated solar light can be investigated with electrochemical impedance spectroscopy (EIS). Fig. 6(a) shows the Nyquist plot while Fig. 6(b) the Bode plot obtained from cells with ZnO photoanodes. The charge transfer resistance at the counter electrode \( (R_{pt}) \) is represented as a semicircle in the impedance spectra and a peak in the Bode phase angle plot.

The resistance element related to the response in the intermediate frequency represents the charge transport at the ZnO/dye/electrolyte interface \( (R_{tr}) \) and shows diode like behavior. The semicircle at the low frequency is attributed to the diffusion in the electrolyte \( (R_{dif}) \).

From the fitted parameters for the three cells the equivalent circuits were \( R(RC)(RC)(RC) \) for cell 1 (Fig. 6(c)) and \( R(RC)(RC) \) for the 2 and 3 cells. \( J_{sc} \) values appeared at Table
nanostructures with improved porosity and smaller particle size, future research will be focused on the fabrication of advanced ZnO nanostructures with improved porosity and smaller particle size, which will offer an enhancement in the DSSCs’ efficiency.

TABLE III: ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FITTED PARAMETERS FOR DSSCS EMPLOYING DIFFERENT ZINC OXIDE PHOTOOANODES

<table>
<thead>
<tr>
<th>Cell</th>
<th>$R_\text{s}$ (Ω)</th>
<th>$R_\text{p}$ (Ω)</th>
<th>$C_\text{p}(10^{-6})$ (F)</th>
<th>$R_\text{ct}$ (Ω)</th>
<th>$C_\text{dt}(10^{-6})$ (F)</th>
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<tr>
<td>1</td>
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<td>26.6</td>
<td>0.382</td>
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<td>0.0540</td>
</tr>
<tr>
<td>2</td>
<td>19.9</td>
<td>34.2</td>
<td>0.252</td>
<td>267</td>
<td>0.0776</td>
</tr>
<tr>
<td>3</td>
<td>15.5</td>
<td>20.8</td>
<td>0.320</td>
<td>43.2</td>
<td>0.3540</td>
</tr>
</tbody>
</table>

TABLE IV: ELECTRON LIFETIME OF CORRESPONDING CELLS

<table>
<thead>
<tr>
<th>Cell</th>
<th>$f$ (Hz)</th>
<th>$\tau$ (msec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.29</td>
<td>7.85</td>
</tr>
<tr>
<td>2</td>
<td>20.29</td>
<td>7.85</td>
</tr>
<tr>
<td>3</td>
<td>16.02</td>
<td>9.94</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

Three different ZnO photoanodes were prepared and tested under 1 sun illumination. The incorporation of the highest molecular weight oligomer APPG2000, improves dye adsorption, and this found to be the most critical parameter related to the conversion efficiency. Dye sensitized solar cells employing gel electrolyte and ZnO photoanode showed an overall efficiency of 0.6% which was found that it was strongly affected by the nanostructure of ZnO films. Future research will be focused on the fabrication of advanced ZnO nanostructures with improved porosity and smaller particle size, which will offer an enhancement in the DSSCs’ efficiency.

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