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ZnO Spin-Coating of TiO₂ Photo-Electrodes to Enhance the Efficiency of Associated Dye-Sensitized Solar Cells

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ABSTRACT

Dye-sensitized solar cells (DSSCs) with ZnO spin-coated TiO₂ photo-electrodes are compared to DSSC with a bare TiO₂ photo-electrode. It is demonstrated that the deposited ZnO of controlled amount, by varying the precursor concentration in the coating sol, can indeed enhance the performance of the DSSC. The measured power conversion efficiency shows a maximum around the precursor concentration 0.1 M and falls down sharply to 0% beyond this point. The results are interpreted on the basis of two competing factors: At ZnO concentrations less than 0.1 M, the formation of an energy barrier increases the photocurrent by reducing the rate of interfacial back-recombination. At ZnO concentrations greater than 0.1 M, the screening of the TiO₂ film by thicker ZnO layers decreases the photocurrent through the reduction of TiO₂ dye-adsorption efficiency.

Keywords: TiO₂ Photo-Electrodes; ZnO Sol-Gel Spin-Coating; Dye-Sensitized Solar Cells; Power Conversion Efficiency

1. Introduction

The ZnO sol-gel spin-coating method is a combination of two techniques applied to produce thin nanostructured ZnO films: The sol-gel technique consists of the preparation, under defined conditions, of a ZnO solution from the mixture of a ZnO precursor [Zn(CH₃COO)₂·2H₂O: zinc acetate dehydrate] and a solvent (2-methoxyethanol) with the addition of a stabilizing substance (ethanolamine). The clear transparent colloidal solution thus obtained, containing suspended ZnO nanoparticles, is deposited on the surface of a substrate by the spin-coating technique [1-4]. Nanostructured ZnO films prepared by this method have been used as photo-electrodes in DSSC fabrication [5,6], but low efficiencies were recorded compared to TiO₂-based DSSCs. However, the deposition of a ZnO layer on the surface of a nanoporous TiO₂ film to improve the DSSC photovoltaic properties is an active issue in the context related to surface treatment of TiO₂ photo-electrodes by thin metal oxide films [7-11]. Kao *et al.* [12] employed the sol-gel spin-coating method to prepare TiO₂ and ZnO spin-coated TiO₂ electrodes for DSSCs. Multilayer coating was applied to TiO₂ to reach the required thickness and a monolayer of ZnO was applied to spin-coat the TiO₂ film. All the photovoltaic parameters were increased upon ZnO spin-coating, resulting in the promotion of the power conversion efficiency η from 2.5% to 3.25%. In this paper, we use the sol-gel technique to prepare ZnO solutions of 5 different precursor concentrations (0.1, 0.2, 0.3 and 0.4 M). An amount of 5 drops from each solution is used to deposit a ZnO layer on the TiO₂ photo-electrode surface by spin-coating. The measured efficiency of the associated DSSC shows a variation with the ZnO precursor concentration, exhibiting a maximum at 0.1 M, beyond which it shows a sharp decrease to 0%. It is explained that this optimal amount of the deposited ZnO forms the thinnest layer that can create the required energy barrier to reduce the rate of back-recombination of electrons to dye molecules and electrolyte species, enhancing the photocurrent without affecting the dye-adsorption efficiency of the TiO₂ film.

2. Experiment

Titanium dioxide (TiO₂) was coated on F-doped SnO₂ (FTO) glass using the classical screen printing technique. The TiO₂ film was then dried and sintered at 450°C for 1 hour to obtain the bare TiO₂ photo-electrode to be used in this work for the preparation of the DSSCs. The sol-gel spin-coating method is employed to deposit thin layers of ZnO on the surface of TiO₂ photo-electrodes. The precursor (Zn(CH₃COO)₂·2H₂O) is mixed with the solvent (2-methoxyethanol) and the stabilizer (mono-

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ethanolamine) is added drop wise until satisfying a molar ratio of 1 with the precursor. The solution is heated at 60°C under continuous magnetic stirring for one hour. The prepared solution containing suspended ZnO nano-particles is then kept firmly enclosed in a clean flask before spin-coating. The spin-coater (SPIN-150, SPS) is adjusted to run at a speed of 3000 rpm for 30 s to produce reasonable thin films. The ZnO amount is monitored by the number of ZnO sol drops injected through the needle of a "smart" dispenser by carefully advancing the plunger into the barrel. The ZnO-coated TiO₂ photo-electrode is annealed at 400 K for one hour. Ruthenium-based dye ($C_{26}H_{20}O_{10}N_6S_2Ru$) known as N_3 (Solaronix) is used to sensitize the bare and ZnO-coated TiO₂ photo-electrodes by immersing in 3×10^{-4} M ethanolic solution for 24 hours. Pt-coated FTO-glass (Solaronix) is assembled as the counter-electrode against the dye-loaded photo-electrode using two paper clips. The electrolyte solution (Solaronix) containing Iodide/Triodide Redox couple is injected through a capillary channel originally drilled across the counter-electrode. The I-V characteristics of the DSSCs are measured using a solar simulator (So-lar-Light) and an electrometer (Keithley 2400). The latter is computer-controlled to acquire and plot the I-V data, while AM1.5-filtered light from the 300 W-Xenon lamp of the solar simulator shines the DSSC at a power density $P_i = 100$ mW/cm² . The transmittance and absorbance spectra of the different films are measured in the visible range by means of a UV/VIS/NIR spectrophotometer (Jasco V-570).

3. Results and Discussions

Before studying the ZnO as a spin-coating layer to improve the performance of TiO₂ DSCs, it is worth presenting first some optical characteristics of this ZnO layer, with the aim to identify the coating material prior to its application. The transmittance spectra of five ZnO films with different ZnO precursor concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M) are shown in **Figure 1(a)** together with the transmittance spectrum of the TiO₂ film for comparison. The ZnO layers were deposited by the sol-gel spin-coating technique on FTO-glass substrates using 5 sol drops for each layer, while the Solaronix TiO₂ film was screen-printed on FTO-glass substrate. The transmission wavelength threshold of the ZnO (~300 nm) is lower than that of the TiO₂ (~350 nm), suggesting a wider energy gap for the ZnO, which can be the physical reason for the observed higher ZnO transmittance.

In **Figure 1(b)**, we present the plots $(\alpha h\nu)^2$ versus $h\nu$ for the curves of **Figure 1(a)**, with $h\nu = hc/\lambda$ the photon energy ($c = 3 \times 10^8$ m/s is the light velocity, $h = 6.66 \times 10^{-34}$ Js is the Plank constant and λ is the light wavelength) and α the optical absorption coefficient determined by the approximate relation $T = \exp(-\alpha \cdot d)$ which
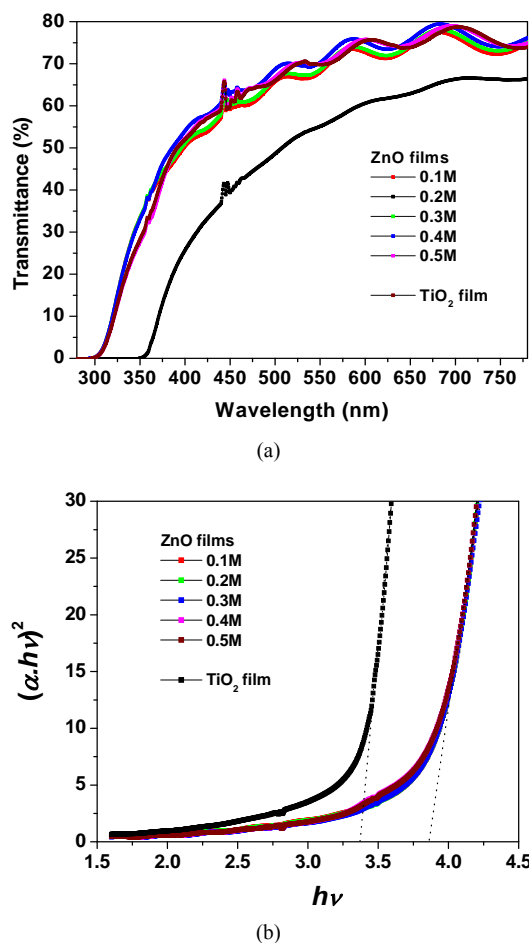

(a)

(b)

Figure 1. (a) Transmittance spectra for five ZnO films spin-coated on FTO-glass at different ZnO precursor concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M). (b) $(\alpha \cdot h\nu)^2$ versus $h\nu$ curves plotted from the transmittance spectra of Figure 1 (a).

ignores the film reflectance (d is the film thickness). The plots of **Figure 1(b)** are based on the assumption of direct electron transitions in ZnO and TiO₂ semiconductors where the relation $\alpha h\nu \sim (h\nu - E_g)^{1/2}$ holds. The parameter E_g called "optical gap" can be experimentally determined by extrapolating the line portion of the plot $(\alpha h\nu)^2$ versus $h\nu$ to zero absorption coefficient. Thus, average optical gap values of 3.8 eV and 3.4 eV for the ZnO and TiO₂ films are respectively determined from the curves of **Figure 1(b)**.

Figure 2 shows the I-V characteristics of DSSCs with ZnO spin-coated TiO₂ photo-electrodes at five different precursor concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M). The I-V characteristic of a DSSC with bare TiO₂ photo-electrode is included for comparison. In **Table 1**, we present the PV parameters extracted from the I-V curves of **Figure 2**. At the smallest precursor concentration 0.1 M, there is a clear enhancement of the short circuit photo-current J_{SC} from 5.73 to 7.48 mA/cm², while small shifts

Table 1. DSSC PV-parameters at different ZnO precursor concentrations.

ZnO precursor concentration	DSSC PV-parameters		
	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)
0 M	5.73	0.576	62.6
0.1 M	7.48	0.611	58.7
0.2 M	2.74	0.602	64.4
0.3 M	0.184	0.239	25.6
0.4 M	0.174	0.209	25.1
0.5 M	0.095	0.173	25.2
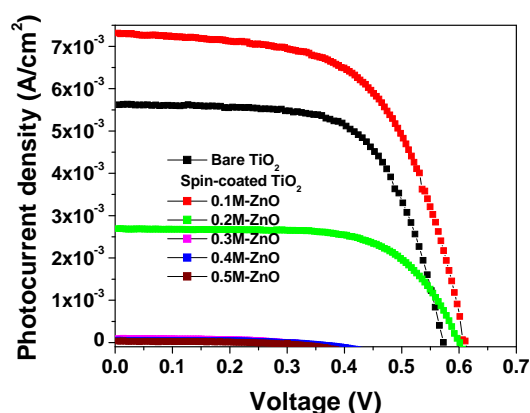
Figure 2. I-V characteristics of DSSCs with ZnO spin-coated TiO$_2$ photo-electrodes at 5 different precursor concentrations. The I-V characteristic of the DSSC with uncoated TiO$_2$ photo-electrode is included for comparison.

upward from 0.58 to 0.61 V and downward from 62% to 59% for the open circuit voltage V_{OC} and the fill factor FF are respectively observed. Further increase of the ZnO precursor concentration, to 0.2 M, causes J_{SC} to decrease remarkably to 2.74 mA/cm^2, whereas small shifts to 0.6 V and to 64.4% for V_{OC} and FF are again respectively observed. Beyond 0.2 M, the PV-parameters decrease drastically and almost no photovoltaic effect is detected ($J_{SC} \sim 0.2 - 0.1$ mA/cm^2, $V_{OC} \sim 0.2$ V and FF $\sim$ 25%).

The resulting power conversion efficiency $\left[\eta = \left(FF \cdot J_{SC} \cdot V_{OC} \right) / P_i \right]$ is plotted in **Figure 3** as a function of the ZnO precursor concentration. An optimum $\eta \sim 2.7\%$ is observed at the smallest concentration 0.1 M followed by a sharp decrease to 0%. While the small upward shift of V_{OC} can be explained by a small shift of the Fermi-level upon ZnO coating, it is clear from **Table 1** and **Figure 3** that the variation of η is mainly due to the variation of J_{SC}. It is known in the literature that the deposition of a metal oxide layer, with a higher conduction band energy minimum than that of TiO$_2$, on the surface of a TiO$_2$ photo-electrode creates an energy barrier that can inhibit the injected electrons from the dye molecules to recombine back with the electrolyte species
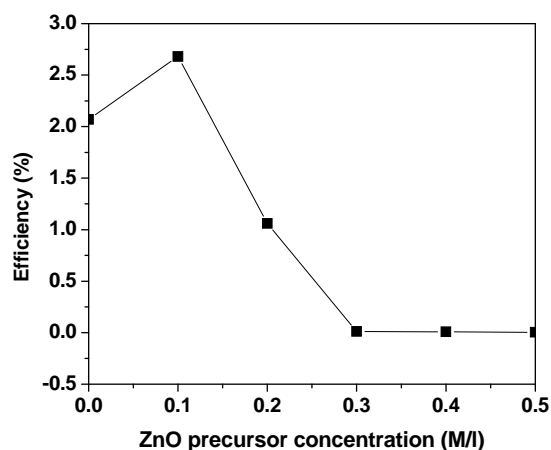
Figure 3. Variation of η with the ZnO precursor concentration.

[12,13]. This recombination inhibition is the direct cause of the photocurrent enhancement occurring at ZnO precursor concentrations around 0.1 M. However, there must be an optimal amount of ZnO in the deposited layer above which the illuminated TiO$_2$ surface is partially obscured by the ZnO layer. The original dye-adsorption efficiency of the TiO$_2$ film decreases when the coating ZnO of much lower dye-adsorption efficiency [14] screens the TiO$_2$ surface. The light harvest rate and the electron injection rate will consequently decrease and this will be reflected by the decrease of J_{SC} and η (**Figure 3**).

Figure 4 shows the absorbance spectra of dye-loaded ZnO-coated TiO$_2$ films at five different ZnO precursor concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M), plotted together with the spectrum of the dye-loaded uncoated TiO$_2$ film. The spectrum of the bare TiO$_2$ film is also plotted in **Figure 4** for comparison. We can first compare the spectrum of the dye-loaded TiO$_2$ with that of the bare TiO$_2$: It is noticeable that the spectrum of the bare TiO$_2$ film (black line) is much lower than the spectrum of the film with loaded dye (black curve), which means that the dye molecules form the main light absorber in the visible range. Since ZnO is more transparent in the visible range than TiO$_2$, one would expect that the dye molecules will still form the main absorber in the presence of the ZnO layer and that the spectra of the dye-loaded ZnO-coated TiO$_2$ films will be similar to that of the dye-loaded uncoated TiO$_2$ film. In contrast, ZnO coating of the TiO$_2$ film using only 0.1 M-ZnO sol results in a much higher spectrum (red curve) than that of the uncoated TiO$_2$ film. In fact, the chemical instability of ZnO against acidic dye molecules results in partial dissociation of Zn^{2+} ions from ZnO particles during the dye-loading process [5,15]. The Zn^{2+}-dye aggregates thus formed on the TiO$_2$ film must be the cause of the observed high excess absorption. This light loss by the Zn^{2+}-dye absorption does not affect the
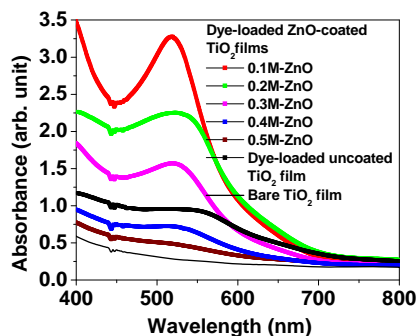
Figure 4. Absorbance spectra for dye-loaded ZnO-coated TiO$_2$ films at five different precursor concentrations. The absorbance spectra for the dye-loaded uncoated TiO$_2$ film and the bare TiO$_2$ film are also presented for comparison.

photocurrent because the 0.1 M-ZnO layer is very thin and the low surface density of the deposited ZnO particles on the TiO$_2$ film will not affect the dye-adsorption efficiency of the TiO$_2$. Yet, the necessary energy barrier to minimize the rate of electron back-recombination is established. The photocurrent density J_{SC} and the cell efficiency η of the associated DSSC will then be enhanced, as detailed above (**Figures 2** and **3**). With increasing the concentration of the ZnO precursor to 0.2 M, the deposited ZnO particles will partially screen the dye molecules from being efficiently adsorbed by the TiO$_2$ material. The effective dye-covered TiO$_2$ area reduces and the electron light harvest efficiency reduces as a consequence. The ZnO sol amount of 5 drops must then be sufficiently high, so that an increase of the ZnO concentration to 0.2 M will cause considerable reduction of the TiO$_2$ dye adsorption efficiency. Thereby, J_{SC} shifts well below that of the bare TiO$_2$ case (**Figure 2**) and η reduces to about 1%. Further increase of the ZnO concentration to 0.3, 0.4 and 0.5 M will vanishingly reduce the dye adsorption efficiency of the TiO$_2$, resulting in absorbance spectra lower than that of the uncoated TiO$_2$ film (bleue curve for 0.4 M ZnO and brown curve for 0.5 M ZnO).

4. Conclusion

The role of ZnO, as spin-coated on TiO$_2$ phto-electrodes, to enhance the power conversion efficiency of the corresponding DSSC is studied. The I-V characteristics of ZnO-coated TiO$_2$ DSSCs with 5 different ZnO precursor concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M) are compared to that of a bare TiO$_2$ DSSC. The results show maximum power conversion efficiency at 0.1 M with enhancement of about 35%. A sharp decrease of η to 0% with increasing ZnO concentration follows this maximum. The efficiency enhancement upon ZnO coating is due to the formation of an energy barrier which limits the rate of electron back-recombination without affecting the dye adsorption efficiency of the TiO$_2$ film. The decrease

of the efficiency with increasing ZnO concentration is attributed to the reduction of the dye-adsorption efficiency of the TiO$_2$ film due to screening by thicker ZnO layers.

5. Acknowledgements

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