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Increasing Dye-Sensitized Solar Cell Efficiency by ZnO Spin-Coating of the TiO₂ Electrode: Effect of ZnO Amount

Fahd Al-Juaid, Amar Merazga[*]

Physics Department, Faculty of Science, Taif University, Taif, Saudi Arabia
Email: [*]merazga_amar@yahoo.fr

ABSTRACT

This paper is concerned with the improvement of dye-sensitized solar cell (DSSC) efficiency upon ZnO-coating of the TiO₂ electrode. Sol-gel ZnO of controlled amount by varying the number of sol drops during spin-coating is shown to increase the DSSC efficiency. The highest efficiency is obtained at a single sol drop with enhancement of 40%, while beyond this amount the efficiency falls down sharply to zero. Based on measured optical absorption spectra of the different dye-loaded electrodes, it is concluded that this amount of ZnO sol corresponds to the thinnest layer that can create the energy barrier to minimize the electron recombination rate without seriously affecting the dye adsorption efficiency of the TiO₂ film.

Keywords: ZnO Spin-Coating; Dye-Sensitized Solar Cell; Efficiency

1. Introduction

DSSCs based on nanocrystalline TiO₂ have attracted extensive attention in academic research and industrial application, since O'Regan *et al*. reported their breakthrough discovery in 1991 [1]. They may offer an alternative to conventional semiconductor solar cells due to their low cost and relatively high efficiency.

Spin-coating is a simple deposition technique to produce desired nanostructured materials in the form of thin films. It is often applied in connection with the sol-gel method [2-5] and consists of a preparing solution by mixing the precursor of the desired material with a solvent and adding a stabilizing substance. The solution, kept under continuous magnetic stirring for a certain period of time at a certain temperature, should contain suspended particles of the material which are subsequently spin-coated and sintered onto a substrate.

Most applications of the sol-gel spin-coating method to ZnO are related to the study of film properties, while only a few are related to ZnO DSSCs [6,7]. However, the deposition of a ZnO layer by spin-coating on the surface of the nanoporous TiO₂ electrode of a DSSC is an active issue related to surface treatment of TiO₂ electrodes by

thin metal oxide films to improve the DSSC photovoltaic properties [8-13]. Kao *et al*. [13] used the sol-gel spin-coating technique to fabricate TiO₂ DSSCs and ZnO-modified TiO₂ DSSCs. They applied multilayer coating for the TiO₂ to reach the required thickness of a nanoporous film and a monolayer for the ZnO to coat the TiO₂ film. The photovoltaic parameters were all found to increase upon ZnO spin-coating, resulting in the increase of the DSSC efficiency from 2.5% to 3.25%.

In this paper, we examine the effect of varying the amount of ZnO, as expressed by the number of sol drops during coating, on the efficiency of the DSSC. The variation of measured efficiency with ZnO amount shows a remarkable increase by about 40% at the ZnO amount of a single drop followed by a sharp decrease to 0%. While the efficiency increase can be attributed to the energy barrier created by the ZnO layer, which reduces the rate of electron recombination back to dye molecules and electrolyte species [12-14], the decrease of efficiency with further increasing ZnO amount is attributed to the decrease of dye-adsorption efficiency of the TiO₂ film due to screening by larger amount of ZnO.

2. Experiment

A ZnO layer was deposited on the surface of TiO₂ elec-

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[*]Corresponding author.

trode (Solaronix) by the sol-gel spin-coating technique. Zinc Acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was used as a precursor at a concentration of 0.4 M in the solvent 2-methoxyethanol. Mono-ethanolamine was added drop wise as a stabilizer until satisfying a molar ratio of 1 with the precursor, while the solution was being heated at 60°C under continuous magnetic stirring. The prepared solution containing suspended ZnO nanoparticles is kept in a clean and firmly closed flask before spin-coating. The spin-coater (SPS Spin-150) is adjusted to run at a speed of 3000 rpm for 30s to produce reasonable thin films.

The deposited 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. In **Figure 1**, we plot the weight (mg) of released ZnO sol amount versus the contained number of drops.

Such a calibration of the sol dispenser clearly indicates that the drops are identical with a homogeneous material of about the same weight. It also indicates that the number of drops in the released sol content is proportional to its weight, and therefore the number of drops is reliable as a parameter to monitor the coating ZnO amount. The ZnO-coated TiO_2 electrodes are annealed at 450 K for one hour.

Ruthenium-based dye ($C_{26}H_{20}O_{10}N_6S_2Ru$) known as N3 (Solaronix) is used to sensitize the bare and ZnO-coated TiO_2 electrodes by immersing in 3×10^{-4} M ethanolic solution for 24 hours. Before immersing the electrode, half cm of the material was peeled off from one side to leave uncovered the FTO for electrical contact. Another FTO-glass substrate coated with platinum catalyst (Solaronix) is assembled as a counter-electrode against the ZnO-modified dye-loaded electrode by means of two paper clips. Iodide-based electrolyte (Solaronix Iodolyte R-100) containing Iodide/Triodide Redox couple with 100 mM tri-iodide concentration is injected through a capillary channel originally drilled across the counter-electrode. The illuminated area of 1 cm^2 through the FTO-glass substrate is determined using a mask from black tape.

The I-V characteristics of the DSSCs are measured using a photovoltaic system consisting of a solar simulator (Solar-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/cm^2. The absorbance spectra of the different films and dye solutions are measured by means of a UV/VIS/NIR spectrophotometer (Jasco V-570).

3. Results and Discussion

A TEM image of the prepared 0.4 M-ZnO colloidal solu-
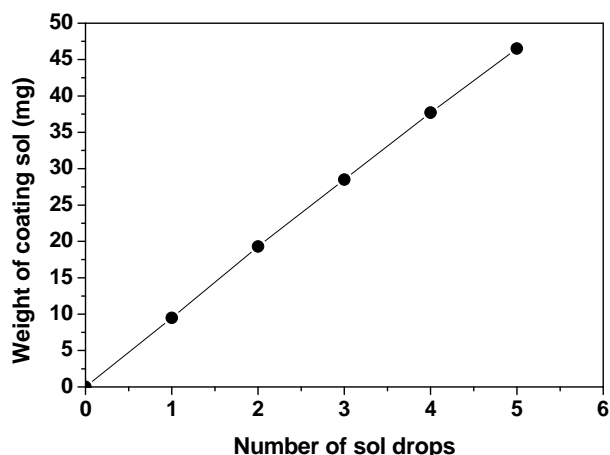
Figure 1. Calibration of the ZnO sol dispenser: Weight of coating ZnO sol against contained number of drops.

tion is shown in **Figure 2** to identify the nature and size of the coating ZnO particles prior to optical and photovoltaic characterization of the ZnO-coated electrodes and DSSCs. Well observed crystallites with average size of 100 nm are illustrated. Song *et al*. [15] have reported similar TEM-observed crystallites of ZnO prepared by the same sol-gel method as described above.

Figure 3 shows the I-V characteristics of DSSCs with ZnO-coated TiO_2 electrodes prepared at five different ZnO amounts (1 - 5 drops). The characteristic of the DSSC with uncoated TiO_2 electrode is also shown for comparison. In **Table 1**, we present the PV parameters extracted from the I-V curves of **Figure 3**. With a single drop of ZnO sol, there is a clear enhancement of the short circuit photocurrent J_{SC} from 5.73 mA/cm^2 to 7.01 mA/cm^2, while a small shift upward from 0.58 to 0.65V is observed for the open circuit voltage V_{OC} and a practically unchanged fill factor 62.5% is found at this level of ZnO amount. Further increase of the ZnO amount causes J_{SC} to fall drastically to zero. V_{OC} shows a small decrease to 0.54 V at the amount of 2 drops, whereas FF still remains unchanged. Beyond this range, both V_{OC} and FF decrease remarkably. The resulting conversion efficiency $\eta = [(FF \times J_{SC} \times V_{OC})/P_i]$ is presented in the last column of Table 1, where a maximum $\eta \sim 3\%$ is found at the ZnO amount of 1 drop followed by a sharp decrease.

It is known in the literature that the presence of a metal oxide layer deposited on the TiO_2 electrode with a lower electronic affinity (higher minimum energy level of the conduction band), such as for the ZnO case, creates an energy barrier that can prevent the injected electrons from the dye to recombine back to dye molecules or electrolyte species [12-14].

The dark I-V characteristics are usually measured and reported [12,13,16,17] to endorse such an interpretation related to reduction of the recombination rate under illumination due to coating the TiO_2 electrode with a suit-
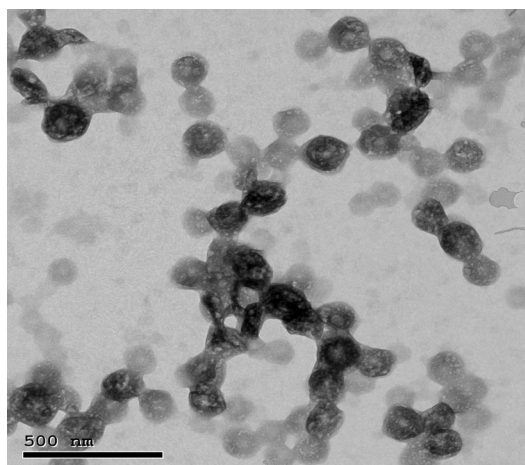
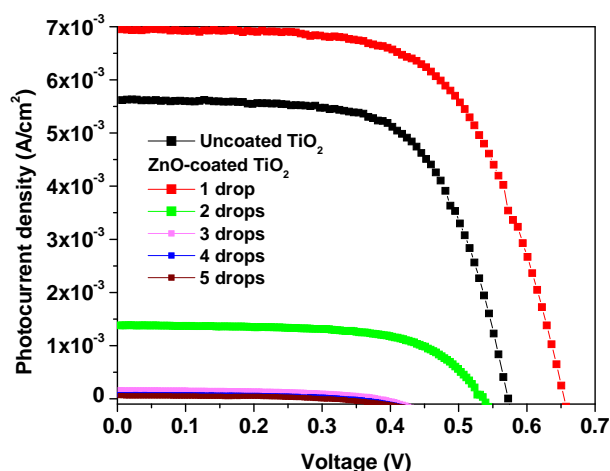**Figure 2. Suspended 0.4 M-ZnO particles as observed by TEM.**

Figure 3. I-V-characteristics of ZnO-coated TiO$_2$ DSSCs at different ZnO amounts (1 - 5 drops) and that of the DSSC with uncoated TiO$_2$ electrode.

Table 1. PV parameters for five DSSCs with ZnO-coated TiO$_2$ electrodes prepared at five different ZnO amounts (1 - 5 drops) and the DSSC with uncoated TiO$_2$ electrode.

ZnO amount: (Nº of sol drops)	PV parameters			
	J_{SC} (mA/cm^2)	V_{OC}(V)	FF (%)	η (%)
0	5.73	0.576	62.6	2.07
1	7.01	0.654	62.3	2.86
2	1.40	0.536	63.1	0.47
3	0.179	0.386	46.7	0.03
4	0.084	0.337	40.1	0.011
5	0.174	0.209	25.1	0.009

able metal oxide layer. **Figure 4** shows the dark I-V characteristics of the DSSCs for the five different amounts (1 - 5 drops) of ZnO, as compared to the dark I-V curve corresponding to the uncoated TiO$_2$ electrode. In the dark, the electron injection from the dye is totally absent and the current is limited to electron diffusion from the TiO$_2$

semiconductor to the electrolyte [18]. As we increase the ZnO amount, the current decreases and requires the assistance of a higher voltage to regain the value of the bare TiO$_2$ case. In other words, the electrons require higher voltages to overcome energy barriers created by larger amounts of spin-deposited ZnO.

The photocurrent and the DSSC efficiency show sharp decreases with increasing ZnO amount above 1 drop (**Table 1**). The reasonable cause of this must be a sharp decrease of the electron injection rate as a result of the decrease of dye-adsorption efficiency of the TiO$_2$ film. The factors at the origin of this decrease can be revealed by the measurement and comparison of the absorbance spectra of the different ZnO-coated TiO$_2$ films with loaded dye. In **Figure 5**, we present the absorbance spec-
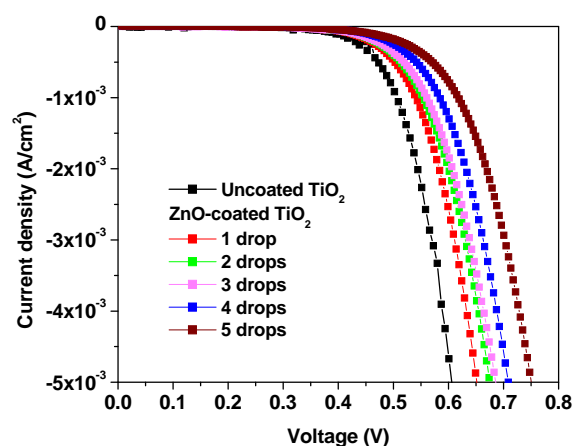

Figure 4. Dark I-V characteristics of the DSSCs with ZnO spin-coated TiO$_2$ electrodes for 5 different ZnO amounts (1 - 5 drops) as compared to that of the DSSC with uncoated TiO$_2$ electrode.
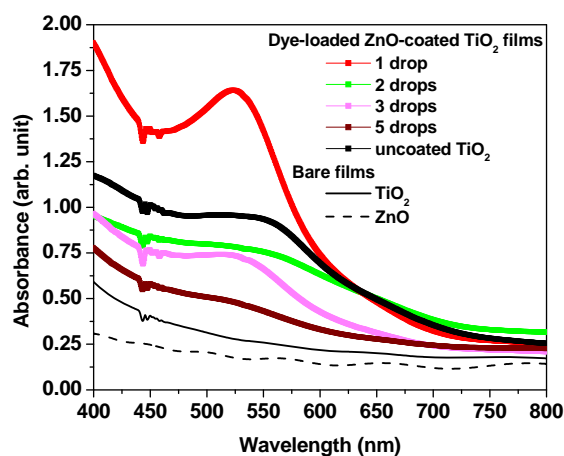

Figure 5. Absorbance spectra of 4 different dye-loaded TiO$_2$ films pre-coated by 0.4M-ZnO layers using 4 different ZnO amounts (1, 2, 3 and 5 drops), as compared to that of the dye-loaded uncoated TiO$_2$ film (curve with symbol ■). The spectra of bare TiO$_2$ (solid line) and ZnO (dashed line) films are also included.

tra of 4 different dye-loaded TiO₂ films pre-coated by ZnO using 4 different amounts (1, 2, 3 and 5 drops). The absorbance spectra of the dye-loaded uncoated TiO₂ and the bare TiO₂ and ZnO films with no loaded dye are also shown for comparison.

It is noticeable that the spectrum of the bare TiO₂ film (solid line) is much lower than that of the dye-loaded TiO₂ film (curve with symbol ■), which means that the dye molecules form the main light absorber in the visible range. **Figure 5** contains also the absorbance spectrum of the bare ZnO film (dashed line) as spin-coated on FTO-glass substrate, which is even lower than that of the bare TiO₂ film. Therefore, one would expect that the dye molecules will still form the main absorber in the presence of the coating ZnO layer and that the spectra of the dye-loaded ZnO-coated TiO₂ films will be similar to that of the dye-loaded uncoated TiO₂ film. In contrast, the coating of the TiO₂ film using a single sol drop results in a much higher spectrum (red curve) than that of the uncoated TiO₂ 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 [5,19]. The Zn^{2+}-dye aggregates thus formed on the TiO₂ film should, therefore, be responsible of the observed excess absorption in this case. This light loss by Zn^{2+}-dye absorption does not affect the photocurrent because the one-drop ZnO layer is so thin that the dye adsorption efficiency of the TiO₂ film is still high and not seriously affected by the ZnO coating. Yet, the required energy barrier to minimize the rate of electron recombination is established, causing the enhancement of photocurrent and DSSC efficiency as detailed above (**Figure 3** and **Table 1**). With increasing the amount of ZnO, this will partially screen the dye molecules from being efficiently adsorbed into the pores of the TiO₂ film. The effective dye-covered area reduces and the electron light harvest effi ciency reduces as a consequence. The ZnO precursor concentration of 0.4M used in this study is high enough, so that only a second drop of ZnO sol can cause a remarkable reduction in the dye adsorption and light harvest efficiency. Thereby, the DSSC photocurrent (**Figure 3**, green curve) shifts well below that of the uncoated TiO₂ case (**Figure 3**, black curve), and the DSSC efficiency reduces to about 0.5% (**Table 1**). Further increase of the ZnO amount to 3 and 5 drops will vanishingly reduce the dye-adsorption efficiency, resulting in absorbance spectra even lower than that of the bare TiO₂ film (**Figure 5**, purple and brown curves). The ZnO layer will entirely screen the dye and one should rather consider dye adsorption by the ZnO which is known to be of much lower efficiency than that of the TiO₂ [20].

An estimation of the amount of adsorbed dye in the ZnO-coated TiO₂ electrodes can be achieved by pro-ceeding with the dye desorption technique [21,22]. **Figure 6** shows the absorbance spectra for solutions of desorbed dye from these ZnO-coated TiO₂ electrodes. The solution for dye desorption consists of 4 ml of 0.1M NaOH and ethanol, mixed at equal volumes, in which the dye-loaded electrode is immersed. As can be observed, the lower the amount of ZnO, the higher is the absorbance of the desorbed dye. Since the absorbance intensity is proportional to the amount of desorbed dye in the solution, this means that the amount of adsorbed dye is higher in the TiO₂ film with lower amount of coating ZnO. However, the decrease of TiO₂ dye-adsorption efficiency with increasing ZnO amount is not the only factor to account for the sharp fall of the DSSC efficiency, but also the increase of light loss due to absorption by ZnO particles and Zn-dye aggregates (**Figure 5**).

While the present study has led to an optimization of the ZnO amount in terms of number of drops of the coating sol, further work for more enhancement of the DSSC efficiency can be achieved by decreasing the ZnO precursor concentration below 0.4 M [12].

4. Conclusion

The sol-gel spin-coating method is applied to deposit a ZnO layer on the surface of TiO₂ electrode in order to increase the efficiency of the corresponding DSSC. The influence of ZnO amount, as monitored by the number of coating sol drops is emphasized. I-V characteristics of five ZnO-coated TiO₂ DSSCs with different ZnO amounts (1 - 5 drops) are compared to that of uncoated TiO₂ DSSC. The results show an increase of η at a single sol drop with enhancement of about 40% followed by a sharp decrease to 0% with further increase of ZnO amount. The efficiency increase is due to the energy barrier created by the coating thin ZnO layer, which reduces the rate of electron back-recombination to dye molecules
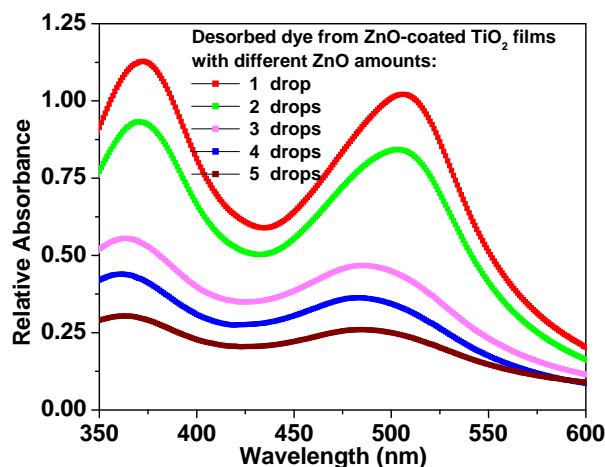
Figure 6. Absorbance spectra of desorbed dye from ZnO-coated TiO₂ electrodes with different ZnO amounts.

and electrolyte species. The sharp decrease of η is attributed to reduced dye adsorption efficiency of the TiO_2 film due to screening by larger ZnO amount.

5. Acknowledgements

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