Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2013, Article ID 612095, 8 pages
http://dx.doi.org/10.1155/2013/612095

Research Article

Nanostructured ZnO, TiO_2, and Composite ZnO/TiO_2 Films for Application in Dye-Sensitized Solar Cells

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Received 24 May 2013; Revised 28 June 2013; Accepted 29 June 2013

Academic Editor: Gaetano Di Marco

The effects of using composite semiconductor films on the efficiency and stability of dye-sensitized solar cells (DSSCs) were investigated. Four different types of composite ZnO/TiO_2 cells were developed and sensitized with the organic molecules Coumarin 343 (C343) and Rose Bengal (RB). A comparative assessment of the different composite cells was conducted, and the photovoltaic performance of single-semiconductor ZnO and TiO_2 solar cells was also compared to that of the composite ZnO/TiO_2 cells. It was observed that composite cells with ZnO/TiO_2 ratio equal to 90/10 have comparable efficiency to single-semiconductor cells and have the advantage of higher stability. The effects of using various multicomponent electrolytes on the efficiency and stability of the ZnO/TiO_2 cells were also investigated. It was observed that the combined properties of the materials used in these electrolytes enhance the efficiency of the composite ZnO/TiO_2 cells.

1. Introduction

Dye-sensitized solar cells (DSSCs), with highest efficiencies approximately 11%, are considered a promising alternative to conventional silicon solar cells [1] since they can be developed using low-cost production processes and non-toxic materials, are less sensitive to ambient temperature changes and have good performance in low-light conditions [2].

The basic structure of dye-sensitized solar cells consists of a nanostructured mesoporous semiconductor film deposited on a glass or a flexible substrate, a platinum or platinised counter electrode and a liquid, and gel or solid electrolyte containing a redox couple, which fills the space between the two electrodes [3]. A monolayer of dye is adsorbed on the surface of the semiconductor and acts as the sensitizer. In dye-sensitized solar cells the conversion of visible light to electricity is achieved through the spectral sensitization of wide bandgap semiconductors such as TiO_2 [4], ZnO [5], and SnO_2 [6].

The most efficient sensitizers for wide bandgap semiconductors are the well-known metalloorganic ruthenium complexes [2]. Several simple organic dyes though, and especially xanthene dyes (Eosin Y, Rose Bengal, etc.), yield efficiencies comparable to those achieved with ruthenium complexes, especially when used to sensitize ZnO films [7–9]. Organic dyes such as these are inexpensive [10, 11], can be easily recycled [12], and do not rely on the availability of precious metals such as ruthenium. They also have high extinction coefficients, and their molecular structures contain adequate anchoring groups to be adsorbed onto the oxide surface. However, solar cells sensitized with such dyes tend to have low stability and efficiency compared to cells sensitized with ruthenium-based dyes [13, 14]. Xanthene dyes have also been used in solar cell applications in the form of hybrid core-shell nanoparticles where photoinduced electron transfer occurs for charge separation, and it has been observed that the rate of photoinduced electron transfer depends on the electron-accepting nature of the organic xanthene molecule on the shell layer [15, 16].

The development and optimization of solar cells is of great interest, both commercially and scientifically. However, dye-sensitized devices are still not commercially available in large volumes. Disadvantages such as their low efficiency and stability pose a hindrance to their commercialization.

The main parameters that affect dye-sensitized solar cell performance, with emphasis on their efficiency and stability,

are examined here, and an attempt is made to improve their overall performance. Nanostructured ZnO, TiO_2, and composite ZnO/TiO_2 thin films were considered for this purpose. The composite ZnO/TiO_2 films were developed with the aim to produce solar cells with improved photovoltaic properties compared to those displayed by either ZnO or TiO_2 cells. Composite films of four different ZnO/TiO_2 concentrations were developed in order to determine which ZnO/TiO_2 ratio leads to the production of the more efficient type of dye-sensitized solar cell. In addition, the performance of ZnO solar cells was studied using four different electrolytes: three multicomponent electrolytes and a standard-type electrolyte, which was used for comparison. The effect of using these multicomponent electrolytes compared to using a standard-type electrolyte on the efficiency and stability of the cells was examined. The performance of the ZnO cells was also compared to that of corresponding TiO_2 cells. All cells presented here were sensitized with the low-cost organic dyes Coumarin 343 (C343) and Rose Bengal (RB).

2. Methodology

Nanostructured ZnO, TiO_2, and composite ZnO/TiO_2 films were prepared as described in [17]. Commercial ZnO or TiO_2 nanopowder (Aldrich) with nanoparticle diameter less than 100 nm was used to create a colloidal paste. The powder was mixed with a small amount of distilled water containing acetyl acetone (10% v/v) [18, 19] in order to prevent the coagulation of nanoparticles and improve the porosity of the film [20]. A small amount of Triton X-100 was added to the mixture to reduce surface tension and enable even spreading of the paste [21, 22].

Composite ZnO/TiO_2 films were also developed. The use of composite electrodes facilitates charge carrier separation [23] and can enhance cell performance. Composite thin films containing both ZnO and TiO_2 were developed by mixing ZnO and TiO_2 paste in different quantities in order to obtain pastes with the following ZnO/TiO_2 ratios: 90/10, 75/25, 50/50, and 25/75.

The semiconductor oxide paste was spread on conductive glass substrates (K-glass-SnO_2:F with sheet resistance 16,7 Ω/sq, 80% transmittance in the visible, 0.38 cm glass thickness) via a doctor blade technique, and the electrodes were annealed for 30 min at 450°C in air to enhance the electrical contact between the nanoparticles as well as between the nanoparticles and the conductive substrate [24]. The thickness of the resulting films was measured by a stylus XP-1 Ambios Technology profilometer. As the thickness of the films can affect the performance of the DSSCs, the results presented in the paper were obtained for samples of approximately the same thickness (equal to 7.5 μm) [4].

The semiconductor films were sensitized with the low-cost dyes Coumarine 343 and Rose Bengal. Coating of the semiconductor surface with the dye was conducted by soaking the film in a solution of the dye in methanol (0.01 M) for 12 h.

Four different types of electrolytes were developed and used: a standard-type electrolyte containing potassium iodide and iodine in propylene carbonate (PC) and three multicomponent electrolytes containing potassium iodide and iodine dissolved in varying mixtures of PC and EG (ethylene glycol). The standard-type electrolyte consists of 0.3 M potassium iodide and 0.03 M iodine in PC. The multicomponent electrolytes contain potassium iodide dissolved in a small amount of EG. Then, PC was added to the electrolyte in various quantities in order to obtain electrolyte solutions of different PC/EG concentrations. The following composite electrolytes were developed.

(i) An electrolyte containing 0.5 M potassium iodide and 0.05 M iodine in an 80% PC and 20% EG solvent (named the 80/20 electrolyte).

(ii) An electrolyte containing 0.5 M potassium iodide and 0.05 M iodine in a 90% PC and 10% EG solvent (named the 90/10 electrolyte).

(iii) An electrolyte containing 0.5 M potassium iodide and 0.05 M iodine in a 95% PC and 5% EG solvent (named the 95/5 electrolyte).

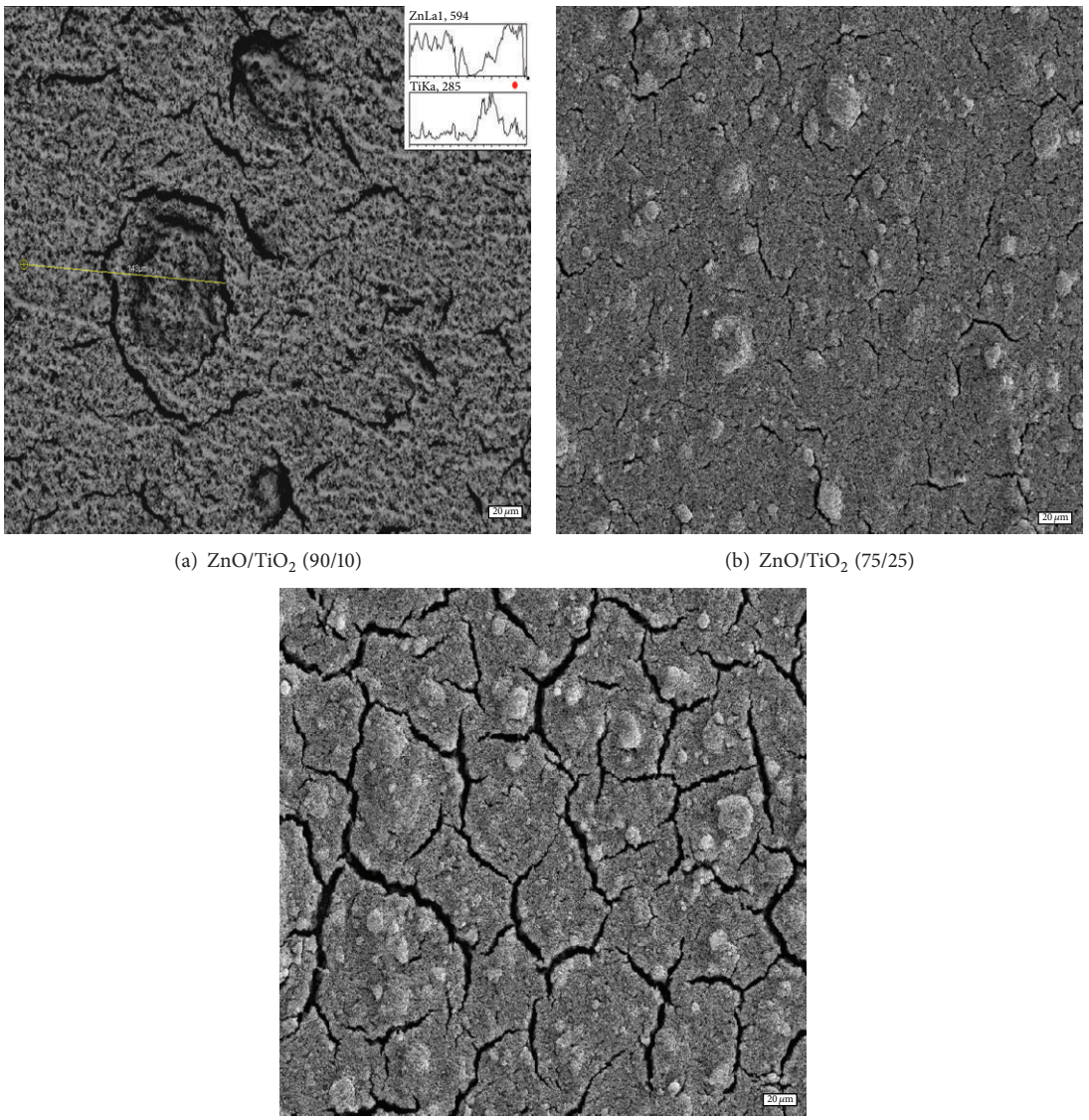
It has been demonstrated that the presence of EG in the electrolyte solution increases the solubility of potassium iodide as well as the presence of iodide ions, enhancing the current density of TiO_2 cells [17]. The combined properties of the two solvents in the multicomponent electrolytes improve the efficiency and stability of the TiO_2 cells. The effectiveness of these electrolytes in ZnO cells sensitized with various dyes is investigated here.

Counter electrodes were prepared through thermal decomposition of a 5 mM hexachloroplatinic acid in isopropanol solution on conductive glass substrates. The sensitized semiconductor electrode and the counter electrode were assembled as a sandwich-type cell (area 1 cm^2) sealed together with silicon, with the electrolyte filling the space between the two electrodes.

Scanning electron microscope (SEM) images were obtained with a JEOL JSM-6300 Scanning Electron Microscope in order to examine the morphology of the various semiconductor films. All SEM images were obtained with accelerating voltage equal to 20 kV. The elemental composition of the samples was determined through energy dispersive X-ray (EDX) analysis.

The properties of the solar cells were studied with emphasis on their efficiency and stability. Current-Voltage (I-V) curves of the cells were obtained using a computer-controlled AMEL Function Generator and a 50 W halogen lamp, which provides illumination intensity equal to 708 W/m^2. The main characteristics of the solar cells can be obtained from these I-V curves, namely, the open circuit voltage (V_{oc}), the short circuit current (I_{sc}), the fill factor (FF), and the efficiency (η) of the cell. The aforementioned properties were measured at regular intervals after the preparation of the cells in order to evaluate the stability of the devices over time.

Dark current measurements were also conducted for TiO_2, ZnO, and composite ZnO/TiO_2 solar cells. Dark current arises when triiodide ions from the electrolyte draw electrons from the semiconductor, reducing the triiodide to iodide. Since electrons are removed from the semiconductor,



(a) ZnO/TiO_2 (90/10)

(b) ZnO/TiO_2 (75/25)

(c) ZnO/TiO_2 (25/75)

Figure 1: SEM images of semiconductor films. Images are magnified ×300. The bar at the bottom right of the figures is 20 μm.

the overall current produced in the photovoltaic cell is reduced by a small amount [25].

Incident photon to current efficiency (IPCE) spectra were obtained using a Newport setup with an AM1.5 Xe-lamp solar simulator and a Newport (Oriel Cornerstone) monochromator. IPCE corresponds to the number of electrons measured as photocurrent in the external circuit divided by the monochromatic photon flux that strikes the cell.

The IPCE factor is given by the following equation:

$$\text{IPCE}\,(\%) = \frac{1240\,[\text{eV nm}] \times J_{\text{ph}}\left[\text{mA cm}^{-2}\right]}{\lambda\,[\text{nm}] \times \Phi\left[\text{mW cm}^{-2}\right]} \times 100, \quad (1)$$

where J_{ph} is the short-circuit photocurrent density for monochromatic irradiation and λ and Φ are the wavelength and the intensity, respectively, of the monochromatic light [26, 27].

3. Results and Discussion

SEM images of ZnO/TiO_2 films with ZnO/TiO_2 ratio equal to 90 : 10, 75 : 25, and 25 : 75 are shown in Figures 1(a), 1(b), and 1(c), respectively. In each of these figures dark patches can be observed throughout the surface of the film. Through SEM analysis, these patches were identified as areas with excess TiO_2, and the more bright spots that appear on the surface of the films were found to correspond to ZnO agglomerates. In addition, an analysis of the elemental composition of the films confirmed that the film shown in Figure 1(a) consists of approximately 90% ZnO and 10% TiO_2, the film shown in Figure 1(b) of approximately 75% ZnO and 25% TiO_2, and the film shown in Figure 1(c) of 25% ZnO and 75% TiO_2, as expected.

Figure 2 presents examples of the current density-voltage characteristics (I-V curves) of ZnO cells sensitized with Rose

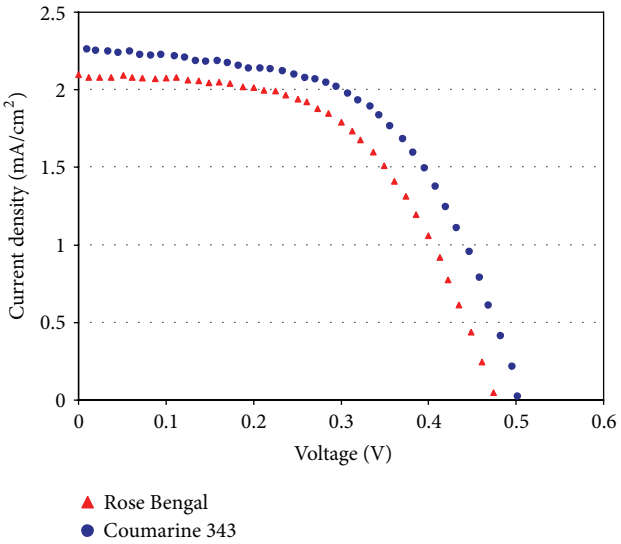


FIGURE 2: Current density (mA/cm^2) versus voltage (V) for ZnO cells sensitized with Rose Bengal and Coumarine 343.

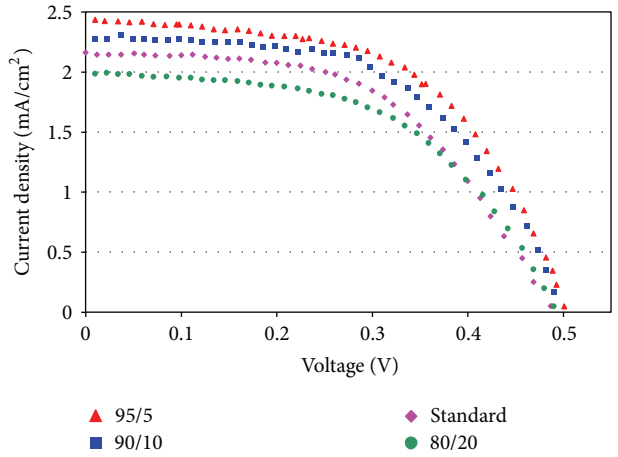


FIGURE 3: I-V characteristics of ZnO cells sensitized with Rose Bengal, each filled with one of the four different electrolytes.

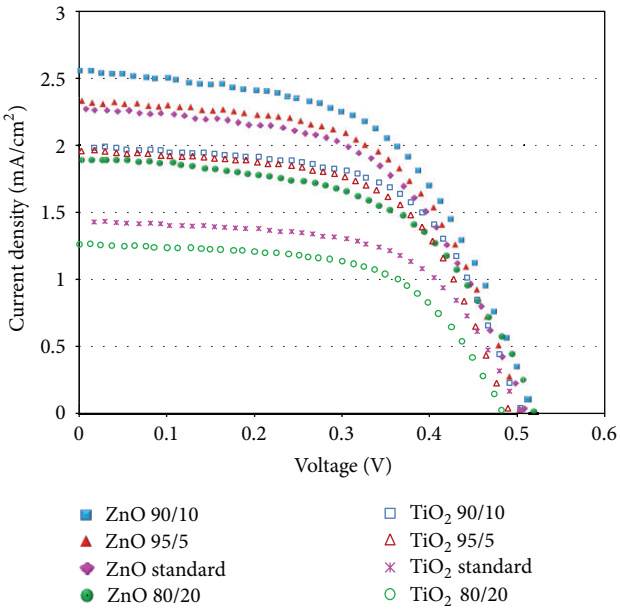


FIGURE 4: I-V characteristics of ZnO and TiO$_2$ cells sensitized with Coumarine 343, each filled with one of the four different electrolytes.

Bengal and Coumarine 343. The standard-type electrolyte was used, and the results displayed in this figure are representative of the cells prepared during this study. From Figure 2, it can be observed that both the voltage and the current density of cells sensitized with C343 are higher than those of corresponding cells sensitized with RB. In general, the current density of cells sensitized with RB was 25–30% lower than that of cells sensitized with C343.

The main parameters that characterize the performance of the cells shown in Figure 2 are summarized in Table 1. The uncertainty in the results of Table 1 is mainly due to small differences in the morphology of the various cells prepared.

The effect of the multicomponent electrolytes on the efficiency of the cells is shown in Figures 3 and 4. Figure 3 shows the current I-V curves of ZnO cells sensitized with Rose Bengal, and Figure 4 shows the I-V curves of ZnO and TiO$_2$ cells sensitized with Coumarine 343. The cells presented in these figures were prepared using the four different electrolytes considered and are representative of the majority of the cells prepared and tested. From Figure 3, it can be observed that, for ZnO cells sensitized with RB, the cells with the 95/5 electrolyte have the highest current density and voltage and, hence, the highest efficiencies. Cells with the 90/10 electrolyte have also slightly higher efficiency than those with the standard-type electrolyte, while the cells with the 80/20 electrolyte have the lowest efficiency.

From Figure 4, it can be observed that, in general, ZnO cells sensitized with C343 have higher efficiencies than TiO$_2$ cells. The performance of ZnO and TiO$_2$ cells sensitized with C343 has been investigated in a previous work through femtosecond upconversion spectroscopy measurements, and it has been observed that ZnO films sensitized with C343 display faster electron injection rates than TiO$_2$ ones [28]. The higher efficiencies observed in ZnO cells sensitized with C343 compared to TiO$_2$ ones have partly been attributed to the faster electron injection of C343 on ZnO than on TiO$_2$. In addition, TiO$_2$ cells sensitized with C343 have been shown to have considerably higher dark current than corresponding ZnO cells, indicating faster electron recombination with accepting states in the electrolyte. The more efficient carrier recombination in TiO$_2$ cells sensitized with C343 is also partly responsible for their lower efficiency compared to ZnO cells [28].

From Figure 4, it can also be observed that, for both ZnO and TiO$_2$ cells, the multicomponent electrolytes have higher efficiencies than the standard electrolyte, with the exception of the 80/20 electrolyte. Cells that contain either the 95/5 or the 90/10 electrolyte exhibit considerably higher performance than those that contain the standard-type electrolyte, as shown in Figure 4. The cells with the 90/10 electrolyte yield

Table 1: Photovoltaic properties of ZnO cells sensitized with Rose Bengal and Coumarine 343.

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
Rose Bengal	2.14 (±0.05)	0.49 (±0.02)	0.62 (±0.02)	0.88 (±0.04)
Coumarine 343	2.34 (±0.04)	0.51 (±0.03)	0.60 (±0.02)	0.97 (±0.03)

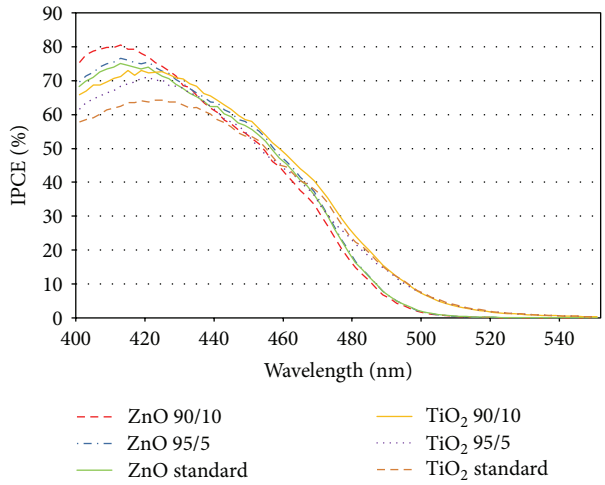


Figure 5: IPCE spectra of TiO_2 and ZnO cells sensitized with C343.

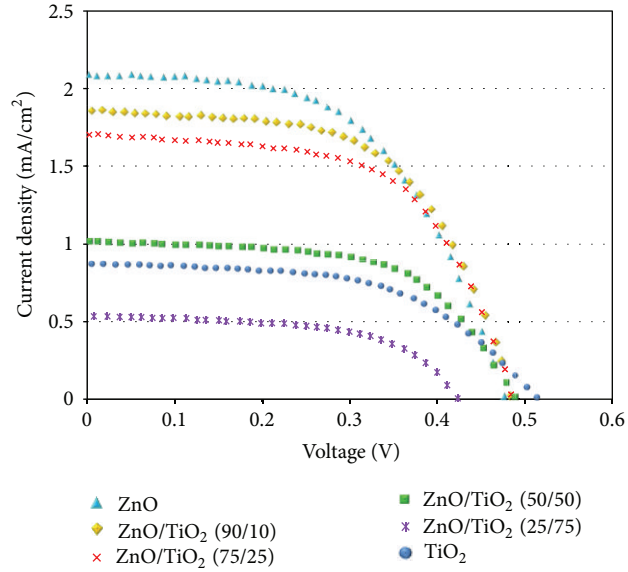


Figure 6: Current-Voltage characteristics of ZnO, TiO_2, and composite ZnO/TiO_2 cells sensitized with Rose Bengal.

the highest efficiencies, while cells filled with the 80/20 electrolyte have again the lowest efficiencies.

In a previous work we have discussed the performance of these multicomponent electrolytes in TiO_2 cells sensitized with Rhodamine B [17]. The increased efficiency of the cells with the multicomponent electrolytes was found to be mainly due to the aforementioned increase in the solubility of KI in the electrolyte. The increased solubility leads to increased ion concentrations in the mixture and, thus, to an increase in the conductivity of the electrolyte. The increase in the short-circuit current, which was observed for cells containing multicomponent electrolytes, is mainly due to this increase in the conductivity. Another factor that enhances the short-circuit current of cells containing the multicomponent electrolytes is the increased availability of anions, which reduce the oxidized dye from light absorption [17].

IPCE spectra of the various DSSCs were obtained in order to investigate the spectral response of the cells. Figure 5 shows the IPCE spectra of TiO_2 and ZnO cells sensitized with C343 and filled with different electrolytes. A small shift (less than 5 nm) of the spectral response to the blue was noticed in TiO_2 spectra with respect to ZnO ones. This shift was also confirmed through absorption measurements of TiO_2 and ZnO films sensitized with C343, obtained using a PerkinElmer Lambda 650 Spectrophotometer. From Figure 5, it is also apparent that the best photon-to-current conversion efficiency (resulting to the highest current) is given by cells filled with the 90/10 electrolyte, followed by those filled with the 95/5 electrolyte and then by those with the standard electrolyte. Those results are consistent with those presented in Figure 4 and show that the high efficiencies produced by both TiO_2 and ZnO cells filled with the 95/5 electrolyte are due to higher photon-to-current conversion. From Figure 5 we can also observe that ZnO cells have higher conversion efficiencies than TiO_2 ones, in line with the results presented in Figure 4. Moreover, the IPCE results presented in Figure 5 are in agreement with corresponding values for C343-based DSSCs presented in the literature [26].

The performance of the composite ZnO/TiO_2 cells was also investigated. Figure 6 shows the Current-Voltage characteristics of ZnO, TiO_2, and of composite ZnO/TiO_2 cells with the following ZnO/TiO_2 ratios: 90/10, 75/25, 50/50, and 25/75. All films were sensitized with the organic dye Rose Bengal. These results are representative of the majority of the results obtained during the study. As can be seen from this figure, ZnO cells sensitized with Rose Bengal have much higher efficiencies than corresponding TiO_2 cells. TiO_2 cells yield slightly higher voltage than ZnO ones, but ZnO cells have much higher current density than TiO_2 ones. In general, xanthene dyes such as Rose Bengal, Eosin Y, Mercurochrome, and Eosin B have a better performance when used to sensitize ZnO rather than TiO_2 cells [7]. The composite ZnO/TiO_2 cells with the 90/10 and 75/25 ratios follow closely the efficiency of the ZnO cells. The composite cells with the 50/50 and 25/75 ratios yielded considerably lower efficiencies, especially those with the 25/75 composition, which yielded very poor results.

Table 2: Photovoltaic properties of ZnO, TiO_2, and composite ZnO/TiO_2 cells sensitized with Rose Bengal.

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
ZnO	2.1 (±0.06)	0.48 (±0.02)	0.61 (±0.02)	0.87 (±0.03)
TiO_2	0.9 (±0.08)	0.51 (±0.02)	0.59 (±0.03)	0.39 (±0.05)
90/10	1.9 (±0.06)	0.48 (±0.03)	0.64 (±0.02)	0.81 (±0.03)
75/25	1.7 (±0.08)	0.49 (±0.03)	0.63 (±0.02)	0.76 (±0.06)
50/50	1.1 (±0.11)	0.49 (±0.04)	0.64 (±0.03)	0.49 (±0.08)
25/75	0.6 (±0.14)	0.43 (±0.07)	0.63 (±0.04)	0.23 (±0.11)

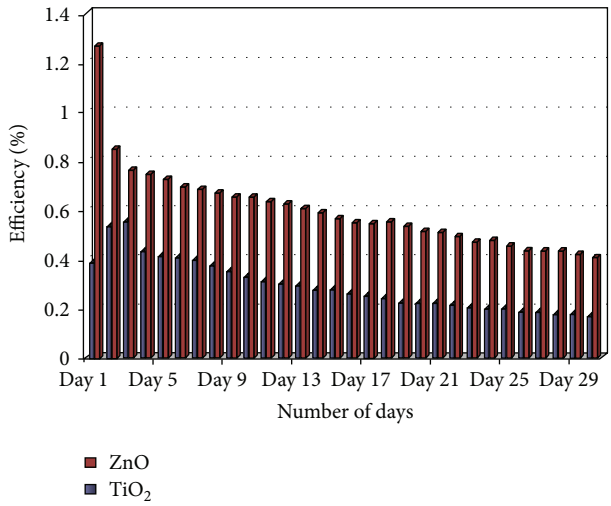


Figure 7: Evolution of cell efficiency with time over a 30-day period for a TiO_2 and a ZnO cell sensitized with Rose Bengal.

The main parameters that characterize the performance of the cells shown in Figure 6 are summarized in Table 2. Again, the uncertainty in the results originates from small differences in the morphology of the cells.

The stability of the solar cells plays a very important role in assessing their overall performance. The efficiency of DSSCs tends to decrease considerably with time mainly due to the degradation of the dye sensitizer [29, 30]. The stability of the cells was assessed by measuring their *I-V* characteristics daily for a 30-day period. Figure 7 shows the change in cell efficiency over a 30-day period for a TiO_2 and a ZnO cell, both sensitized with Rose Bengal. For TiO_2 cells it was observed that the efficiency reaches its maximum value on the 2nd or 3rd day after cell preparation and then gradually decreases. This decrease is mainly due to dye desorption and degradation. Only dye molecules which are adsorbed on the TiO_2 surface can sensitize spectrally the semiconductor and can, therefore, contribute to the photocurrent, so dye desorption causes a decrease in cell efficiency [31].

From Figure 7 it can also be observed that the most abrupt decrease in the current density of ZnO cells occurs between the first and the second day after cell preparation, mainly due to dye degradation. Dye degradation in ZnO films occurs more rapidly than in TiO_2 ones since protons originating from the dye may cause the dissolution of Zn surface atoms [32]. These Zn atoms then react with the protons from the dye, forming Zn^{+2}/dye complexes:

$$ZnO + 2H^+ \longrightarrow Zn^{+2} + H_2O. \quad (2)$$

The above reaction leads to the formation of inactive dye molecules which limits charge carrier injection and reduces the efficiency of the cells. The dissolution of Zn atoms depends on a number of factors, such as the dye concentration, the sensitization time, and the pH of the dye solution [33].

Table 3: Drop in efficiency over a 30-day period for ZnO, TiO_2, and composite ZnO/TiO_2 cells sensitized with Rose Bengal.

	ZnO	TiO_2	90/10	75/25	50/50	25/75
Efficiency decline (%)	68	52	51	58	69	76

By comparing the TiO_2 and ZnO efficiency results presented in Figure 7, it is apparent that TiO_2 films have higher stability than ZnO films. The efficiency of ZnO solar cells is reduced more rapidly with time, while TiO_2 cells maintain relatively high efficiencies for some time after cells preparation. Specifically, it was observed that, 30-days after preparation, ZnO cells experience a drop of up to 70% in their efficiency, while TiO_2 cells lose approximately 50% of their original efficiency during the same time. On the other hand, the efficiencies achieved during the first days after cell preparation were considerably higher for ZnO than for TiO_2 cells so that, even after the passing of 30-days, ZnO cells still yield higher efficiencies than TiO_2 ones.

The composite ZnO/TiO_2 films were developed in order to improve the properties of dye-sensitized solar cells. The aim of this work was to develop cells with high efficiencies, such as those exhibited by ZnO cells, but with the increased stability of TiO_2 cells. As shown previously, the composite ZnO/TiO_2 cells with the 90/10 and 75/25 ratios yield efficiencies comparable to those of ZnO cells.

The stability of the composite cells was also examined. Table 3 summarizes the average drop in efficiency of ZnO, TiO_2, and composite ZnO/TiO_2 cells over a 30-day period. The results presented in this table show that TiO_2 cells and composite ones with the 90/10 and 75/25 ratios have the highest stability. ZnO and composite cells with the 50/50 and 25/75 ratios have considerably lower stability.

Figure 8 shows the efficiency of ZnO and composite ZnO/TiO_2 cells with the 90/10 and 75/25 ratios over a 30-day period. These two types of composite cells were considered in this comparison since they have exhibited both high efficiency and stability. The performance of the composite cells in this figure is compared against the performance of ZnO cells. All cells were sensitized with Rose Bengal. From Figure 8, it is apparent that the efficiency of the ZnO cells on the day they were assembled was considerably higher than that of the composite cells. However, the efficiency of the composite cells does not decrease as rapidly with time, so that, at the end of the 30-day period, composite cells with the 90/10 ZnO/TiO_2 ratio have higher efficiency than ZnO cells. The composite

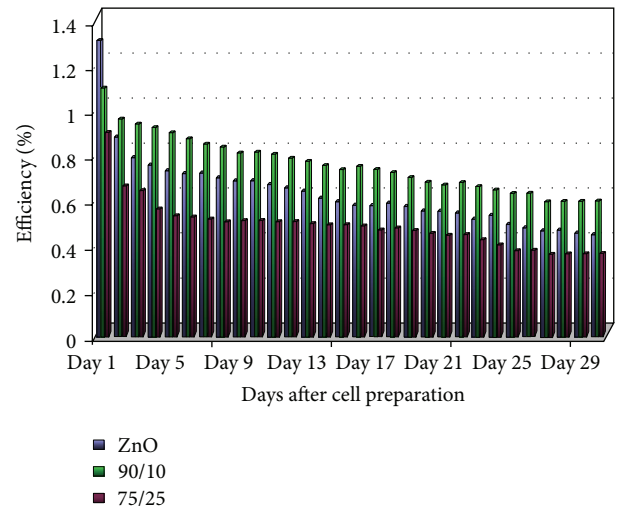


Figure 8: Cell efficiency over a 30-day period for a ZnO and two composite ZnO/TiO_2 cells sensitized with Rose Bengal.

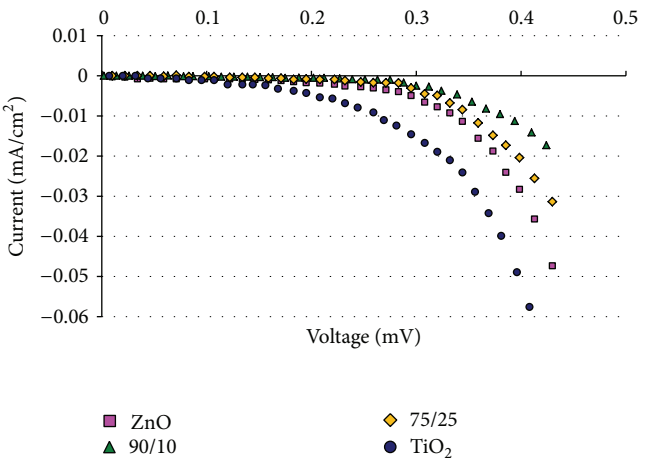


Figure 9: Dark current characteristics of ZnO, TiO_2, and ZnO/TiO_2 cells sensitized with Rose Bengal.

cells with the 75/25 ratio have only slightly lower efficiency than ZnO ones.

Dark current measurements were also conducted for ZnO, TiO_2, and composite ZnO/TiO_2 cells. Figure 9 shows dark current results for ZnO, TiO_2, and two types of composite ZnO/TiO_2 cells. All cells shown in this figure were sensitized with Rose Bengal. It was found that the composite cells have the lowest dark current, while the TiO_2 cells have the highest. The higher dark current in the TiO_2 cells is an indication of faster electron recombination than in ZnO and composite cells [34]. The relatively low current density produced by TiO_2 cells (Table 2) is partly due to higher recombination losses as evidenced by their higher dark current. As mentioned previously, similar measurements of ZnO and TiO_2 cells sensitized with C343 [28] have also shown that TiO_2 cells have higher dark current than ZnO ones when sensitized with C343. The higher recombination losses for TiO_2 cells sensitized with both C343 and Rose Bengal are partly responsible for their lower efficiency compared to corresponding ZnO cells.

4. Conclusions

The aim of this study was to improve the performance of solar cells sensitized with simple organic dyes. ZnO, TiO_2, and composite ZnO/TiO_2 films sensitized with Rose Bengal were prepared and tested. It was observed that, in general, ZnO cells sensitized with simple organic dyes yield higher efficiencies than corresponding TiO_2 cells. However, TiO_2 cells exhibit higher stability than ZnO cells.

Four different types of composite cells were also considered, with ZnO/TiO_2 ratios equal to 90/10, 75/25, 50/50, and 25/75. It was observed that composite cells with ZnO/TiO_2 ratio equal to 90/10 have higher efficiencies than other composite cells and only marginally lower efficiencies than ZnO cells. Moreover, these cells have a higher stability than the other cells tested, so that, a month after cell preparation, they maintain higher efficiency values than ZnO cells.

Finally, multicomponent electrolytes were developed and used in ZnO cells sensitized with a simple organic dye. The performance of the cells with the multicomponent electrolytes was assessed by comparison with cells using a standard-type electrolyte. It was found that the combined properties of the materials used in these electrolytes improve cell efficiency.

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