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ARTICLE

The Effect of Z907 Dye on the Performance of Solar Cells Based on the Nc-TiO₂ Semiconducting Polymer Heterojunction

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Abstract: This work studies the effect of cis-bis(isothiocyanato)(2,2'-bipyridyl-4,4'dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl) ruthenium(II) (Z907 dye) on the performance of nanocrystalline titanium dioxide (nc-TiO₂)/Poly3-hexylthiophene (P3HT) heterojunction solar cells. Specifically, the P3HT/Z907dye/nc-TiO₂ solar cells increase the short circuit current, J_{sc}, from 0.17 mA/cm² to 0.3 mA/cm², the open circuit voltage, V_{oc}, from 0.45 V to 0.7 V and the power conversion efficiency, η , from 0.03% to 0.08% compared with the P3HT/nc-TiO₂ solar cells. These changes are attributed to improvements in the absorption of the light falling on the device and the generation of electron–hole pairs in the presence of the dye layer. Additionally, the dye solar cells enhance the charge transport through the interface between the nc-TiO₂ and the P3HT. These results have been confirmed by studying the optical properties and the capacitance characteristics of the solar cells. **Keywords:** Solar cells; Capacitance; Short circuit current; Rectification; Power conversion efficiency.

Introduction

Over the past two decades, dye-sensitized solar cells (DSSCs) have attracted tremendous interest due to their high power conversion efficiency of up to 10 % and their low-cost photovoltaic cell [1]. A typical DSSC or Graetzel cell is composed of a chargetransporting electrolyte and nanocrystalline titanium dioxide (nc-TiO₂) coated by rutheniumbased sensitizers. After the light is absorbed by the sensitizer layer, an electron-hole pair (exciton) is generated at the interface and moves out of the cell to produce the photocurrent. The liquid electrolyte transports holes to the top electrode, while the nc-TiO₂ layer injects electrons into the bottom electrode. However, there has been considerable interest in using solid-state hole transport material instead of a liquid electrolyte, which causes several problems in a Graetzel cell, such as evaporation and leakage of the liquid electrolyte when sealing the cell [2-4]. For example, Wei-Zhang reported a

3.85% power conversion efficiency using organic indoline dve D131 as the sensitizer and poly(3-hexylthiophene) (P3HT) as the hole transport[5]. Our previous report demonstrated the effect of nanocrystalline TiO₂ morphology on the performance polymer of heterojunction solar cells. The results confirm that the properties of the semiconductor sensitized the solar cell interfaces such that the size and shape of the nc-TiO₂ particles affect its power conversion efficiency[6]. Such effects were also studied [7] by Serap Günes, who found that the compact TiO₂ layer between the bottom electrode and the nonporous TiO₂ layer improved the photovoltaic performance of dve-sensitized solar cells. Our recent report [8] shows the effects of molecularlevel insulation on the performance of a dyesensitized solar cell. The molecular-level insulation has led to a small enhancement in the energy-conversion performance of the fabricated DSSC, with the best result being an increase in the open circuit voltage (V_{oc}) from 0.7 to 0.8 V.

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Therefore, the interface properties play an important role in improving the performance of organic/inorganic solar cells. However, the efficiency of solid-state solar cells based on nc-TiO₂ semiconducting polymer heterojunctions like our devices is very low compared with a Graetzel cell [1] and Weishu's work [9] because of the differences in the hole transport layers and interfacial area.

The present paper focuses on the fabrication and characterization of a semiconductor solar cell sensitized using cis-bis(isothiocyanato)(2,2'bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'bipyridyl) ruthenium(II) (Z907 dye) between nc-TiO₂ and P3HT layers. Similar studies have used Z907 dye as a sensitizer with different hole transport layers [9, 10, 11, 12, 13]. However, they have not used P3HT as the hole transport layer or studied the negative capacitance characteristics of their devices. Therefore, the effect of Z907 dye on the performance of P3HT/nc-TiO₂ was investigated using capacitance measurements, current voltage measurements and optical properties.

Experimental

The solar cells were composed of five layers (see Fig. 1). The first layer was coated with fluorine-doped tin oxide $(SnO_2:F)$ electrodes, which were pre-coated with a thin, dense layer of TiO₂ (Solaronix, Switzerland). Using the doctor blade technique [14], a nc-TiO₂ paste was then spread over the cured substrates to form the anatase phase according to the procedures

described in our previous publication [6]. The cured nc-TiO₂ layer was immersed in a solution composed of 50 ml of pure ethanol and 10 mg of Z907 dye for 48 hours. Subsequently, the cell was removed from the solution, cleaned using ethanol and dried under a hot air stream. A drop of the p-type organic semiconductor P3HT in a chloroform solution (15 $mgmL^{-1}$) was placed onto the surface of the nc-TiO₂ for several seconds prior to spinning at 1000 rpm. It was difficult to measure the thickness of the P3HT, because the surface of the nc-TiO₂ thin film was very rough. According to the literature [15], the thickness of the P3HT film on a flat surface was approximately 100 nm for a coating using a P3HT solution with a spin coating speed of 1000 rpm. Finally, circular gold electrodes of an area of 3 mm² were evaporated on top of the P3HT film. Current-voltage (I-V) characteristics were obtained using a Keithley model 307 source measurement unit. A xenon lamp was used to illuminate the devices through the transparent electrode with the light (incident power 100 mW/cm^{-2}) constrained by an aperture to fall on an area coinciding with one of the gold top electrodes. For capacitance measurements, an Agilent E4980A precision LCR meter in air was used over the frequency range from 20Hz to 1 MHz with a signal amplitude of 100 mV. The Xray diffraction (XRD) patterns were obtained using a Seifert 3003 TT diffractometer operating at 40 kV and 40 mA. The microstructure of the nc-TiO₂ thin film was observed by scanning electron microscopy (SEM) using a Cambridge stereoscan-360 operating at 20 kV.



FIG. 1. Energy level diagram of the materials in the solar cells.

Results

Figures 2 and 3 show scanning electronic microscopy images of the nc-TiO₂/compact TiO₂ /SnO₂:Fn layer used in our solar cells. These figures show that the thickness of the nc-TiO₂/compact TiO₂/SnO₂:Fn layer used in our solar cells was approximately 1.5 μ m. The thickness of compact TiO₂/SnO₂:Fn is very small (less than 200 nm) and it is very difficult to distinguish the TiO₂/SnO₂:Fn layer from the nc-

 TiO_2 layer. From the top view image (see Fig. 3), it appears that the particle shape is almost uniform, with a small number of pin holes on the surface and particle size around 25 to 21nm. That may affect the amount of hole transport materials and dye that can penetrate the nc-TiO₂ thin film.



FIG. 2. Cross-section of the nc-TiO₂ /compact TiO₂ /SnO₂:Fn layer.



FIG. 3. Top view of the nc-TiO₂/compact TiO₂/SnO₂:Fn layer.

According to Park's paper [16], anatase-based solar cells produce short circuit currents at a rate greater than that of rutile-based solar cells. To determine the mineral form of the nc-TiO₂ thin films used in solar cells, X-ray diffraction measurements were conducted on the cells at room temperature. Figure 4 shows the XRD patterns of the nc-TiO₂ layer. This figure shows that the 2θ values at 25° were the strongest in the curve whereas smaller peaks were observed near 48° and 54° , and these three peaks are indexed to the (101), (200) and (105) lattice planes of the nc-TiO₂, respectively. These lattice planes occur in a tetragonal system and correspond to the anatase phase of TiO₂. The grain size of the

particle is determined by applying the Scherrer formula [17-18] to the largest diffraction peak:

$$G_{\rm S} = \frac{K\lambda}{\beta\cos\theta} \; ; \tag{1}$$

where λ =0.154 nm is the X-ray wavelength, G_s is the grain size and β is the full width at half maximum of the diffraction peak. As seen in Fig. 4, the largest peak occurs at $2\theta = 25.56^{\circ}$ for the reflection from the 101 lattice plane. By substituting the values $\beta = 0.0102$ radians, $\cos(12.78) = 0.975$ and K = 0.96 into equation (1), the grain size is estimated to be 15 nm.



FIG. 4. XRD patterns of the nc-TiO₂ layer.

The influence of the Z907 dye on the performance of the P3HT/nc-TiO₂ solar cells was studied. Figure 5 shows a semilog plot of the current density versus voltage (J-V) characteristics of a nc-TiO₂/P3HT solar cell without using the Z907 dye. In the dark, the device behaves like a good diode with a rectification ratio estimated to be 10^3 at ± 1 V. Additionally, the turn-on voltage of the nc-TiO₂/P3HT solar cell was found to be approximately 0.4 V. These values depend on the energy level alignment between the P3HT and the nc-TiO₂ and/or the work function of the bottom and the top electrodes. Under a positive bias voltage (forward bias condition), the electrons are injected from a low work function electrode made of gold, whereas the holes are injected from a low work function electrode made of SnO₂:Fn. The holes move toward the junction where the depletion region almost

vanishes when subject to a forward bias condition. Conversely, the negative region of voltage applied on the device produced a low current because of the increase of depletion region and the change in the energy level alignment of the electrodes' work function with respect to the P3HT and the nc-TiO₂ device.

Figure 6 shows the log J-V characteristics of the nc-TiO₂/P3HT solar cells with a Z907 dye layer. In the dark, the rectification ratio was estimated to be approximately 10^4 at ± 1 V, which is greater than the rectification ratio of the solar cells without dyes. Additionally, the turn-on voltage of the nc-TiO₂/Z907 dye/P3HT was found to be approximately 0.25 V, whereas the turn-on voltage was approximately 0.4 V for the solar cells without the dye. The differences between the two devices in a dark current are attributed to the removal of the depletion region, an interface and the decrease in the shunt resistance in the dye-containing solar cells. Under a reverse bias condition, the current was very low, because the energy level alignment of the materials was arranged in a way to prevent charge carrier transport through the junction. Under illumination, the two devices were affected by the light falling on them. The zero voltage current was enhanced more than 10^3 times compared with the dark current. At the same time, the rectification ratio was very small in the two devices because of the decrease in the series resistance of the device in the light.



FIG. 5. Log J-V characteristics of the nc-TiO₂/P3HT solar cells.



FIG. 6. Log J-V characteristics of the nc-TiO₂/Z907 dye /P3HT device.

Figure 7 shows the J-V characteristics of the P3HT/Z907 dye/nc-TiO₂ solar cells on a linear scale. This device produced an open circuit voltage (V_{oc}) of 0.7 V, a short circuit current (J_{sc}) of 0.28 mA/cm² and a maximum power output (P_{max}) of 0.08 mW/cm². The values for the fill factor, FF, and the power conversion efficiency, η , were determined using equations 2 and 3:

$$FF = \frac{P_{\text{max}}}{V_{oc}J_{Sc}} ; \qquad (2)$$

$$\eta = \frac{P_{\max}}{P_L} \quad ; \tag{3}$$

where P_L is the power of the incident light (100 mW/cm²). The performance of the P3HT/Z907 dye/nc-TiO₂ solar cells was observed on 10 devices. For the best device, the power conversion efficiency, η_e , was recorded to be approximately 0.08%, and the fill factor, FF, was 39%. Conversely, the response of the P3HT/nc-TiO₂ solar cells without dye to light

was less compared with the solar cells with the dye. Figure 8 shows the J-V characteristics of such a device, which produced a $V_{\text{oc}}\,\text{of}\,0,\!45$ V, a J_{sc} of 0.17 mA/cm and a maximum power output

 (P_{max}) of 0.035 mW/cm². Using equations (2) and (3), the power conversion efficiency was 0.035%, and the fill factor was 45 %.



FIG.7. J - V characteristics of nc-TiO₂/Z907 dye/P3HT solar cells.



FIG.8. J - V characteristics of nc-TiO₂ / P3HT solar cells.

The UV-vis absorption spectra of the SnO₂:Fn/nc-TiO₂/Z907dye/P3HT, SnO₂:Fn/nc-SnO₂:Fn/nc-TiO₂ TiO₂/P3HT, and nc- $TiO_2/Z907dye$ are shown in Fig. 9. It can be seen that, compared with the SnO₂:Fn/nc-TiO₂/P3HT with Z907 dye, the absorbance of the spectra of the SnO₂:Fn/nc-TiO₂/P3HT decreases in the 380

to 600 nm wavelength region. This result indicates that the Z907 dye improves the absorption of light falling on the device and explains the increase in the power conversion efficiency observed in the SnO2:Fn/nc-TiO₂/Z907 dye/P3HT solar cells. This result is similar to those published in [19-20].



FIG. 9. UV-Vis absorption spectra of the nc-TiO₂/Z907 dye /P3HT, nc-TiO₂/P3HT,nc-TiO₂/Z907 and nc-TiO₂ films

Fig. 10 shows the capacitance versus loss (conductance/frequency, G/w) curves over a wide range of frequencies for the P3HT/nc-TiO₂ solar cells at -1.5 V applied to the SnO₂:Fn electrode. At low frequencies (100 Hz to 10 kHz), the measured capacitance decreases because the frequency is less than the relaxation time of the charge carriers. In this case, the junction capacitance starts contributing to the overall capacitance. In the same range of frequency, the decrease of loss is also ascribed to charge carriers, which lag behind the AC field variation at the junction. With a decrease in the frequency, the loss remains almost constant from 100 Hz to 20 Hz. This result is due to a junction capacitance that is dominated by the depletion region capacitance and a reduction of the charge carriers that have accumulated at the junction. At high frequencies (f > 10 kHz), the capacitance represents the geometric capacitance of the device, where the charge carriers hardly follow the AC signal, which is coupled with a decrease in the loss.

In P3HT/dye/nc-TiO₂ solar cells, the capacitance *versus* loss curves over a wide range of frequencies are shown in Fig. 11. The low-frequency capacitance is dominated by the

junction capacitance, where the diffusion capacitance appears in the absence of the depletion region at the junction. The diffusion capacitance is generated by the accumulation of charge carriers at the interface due to the following: the dye layer easily accumulates at the injection of the charge carriers and the presence of the dipole at the junction [21]. These conditions lead to a decrease in the capacitance to the negative region and increase the loss in a manner that is more than three times than the loss in solar cells without the dye.

The difference in the capacitance measurements of the two devices emphasizes that the Z907 dye modified the interfacial layer between the $nc-TiO_2$ and the P3HT. Additionally, the formation of dipoles by the dye improves the power conversion efficiency by increasing the open circuit voltage from approximately 0.45 to 0.7 V, which agrees with Shvam's work [22]. This increase is accompanied by the appearance of a negative capacitance in the dye solar cells, which indicates a change in the position of the TiO₂ conduction band, the accumulation of charge carriers and a reduction in the resistance at the interface.



FIG. 10. Capacitance and loss versus frequency of SnO2:Fn/nc-TiO2/P3HT/Au solar cells.





Conclusion

Solar cells with dyes were found to exhibit a combination of a high concentration of charge carriers at the junction, an increase in the short circuit current density and an increase in the power conversion efficiency. These results were ascribed to the modification that occurred by adding the dye layer between the P3HT and the nc-TiO₂ layers.

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