Enhancement of Power Efficiency and Stability of P3HT-Based Organic Solar Cells under Elevated Operating-Temperatures by Using a Nanocomposite Photoactive Layer

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With the aim to find out an enhanced operating-temperature range for photovoltaic device parameters, two types of the photoactive layer were prepared: poly(3-hexylthiophene) (P3HT) and P3HT+nc-TiO$_2$ (PTC) thin films. The enhancement obtained for the photoelectrical conversion efficiency of the composite based OSCs is attributed to the presence of nanoheterojunctions of TiO$_2$/P3HT. For the temperature range of 30–70°C, the decrease of the open-circuit potential was compensated by an increase of the fill factor; and the increase in the short-circuit current resulted in an overall increase of the energy conversion efficiency. At elevated temperatures of 60–80°C the efficiency of the P3HT- and PTC-based cells reached a maximum value of 1.6% and 2.1%, respectively. Over this temperature range the efficiency of P3HT-based OSC decreased strongly to zero, whereas for the PTC cells it maintained a value as large as 1.2% at the temperature range of 110–140°C. The improved thermal stability of the composite-based device was attributed to the lowered thermal expansion coefficient of the nanocomposite photoactive layer.

1. Introduction

Recently, conducting polymers and polymer-based devices have found applications in many fields such as optoelectronics, organic light emitting diodes (OLEDs), and solar flexible cells [1–3]. Poly(3-hexylthiophene) (P3HT) is a type of conducting polymer that is used for flexible polymer electronic devices like organic solar cells (OSCs). P3HT with an energy bandgap of 1.9 eV [4] is often used as the electron donor in a bulk heterojunction [5], while the electron acceptor was [6,6]-phenyl C$_{61}$-butyric acid methyl ester (PCBM) [6]. The enhanced solubility of PCBM compared to C$_{60}$ allows a high fullerene/conjugated polymer ratio and strongly supports the formation of bulk donor-acceptor heterojunctions. As compared to inorganic solar cells like Si-single crystalline cells, the production technology for either materials or devices of OSCs is much simpler. However, the efficiency of an organic solar cell until now is considerably low; this is usually attributed to the strong decay of the excitons which are generated in the donors/acceptors junctions owing to the illumination of solar radiation. The exciton decay can be diminished by the creation of either appropriate heterojunctions or nanocomposite layers. This results in charge separation, that is, generated electrons and holes moving in opposite directions, and consequently the luminous quenching occurs [7]. It has been known that, by embedding inorganic nanocrystalline oxides like TiO$_2$ nanoparticles (nc-TiO$_2$) into polymer matrices, one can enhance the efficiency and service duration of the organic devices. The embedded oxides can substantially influence both the electrical and optical properties of the polymer; for instance, MEH-PPV + nc-TiO$_2$ composite thin films were studied as a photoactive material [8, 9]. Thomas et al. [10] and Liu [11] gave reviews on the recent progress of hybrid/composite photovoltaic systems of inorganic semiconductors and organic conducting polymers. Nanostructures and their influence on the photovoltaic performance of these hybrid materials have been analyzed. By using hybrid or nanocomposite materials for the photoactive...
layer, one can enhance the power conversion efficiency of composite-based OSC. The temperature dependence of the photovoltaic device parameters has been investigated for both the inorganic [12] and organic [13] solar cells. It was found that with increasing temperature the photovoltaic conversion efficiency increased. For conjugate polymers, the results were discussed with respect to possible mechanisms for photovoltaic generation and charge carrier transport in the photoactive layer and, in particular, thermally activated charge carrier mobility. However, as far as we know, there was no evidence of the impact of thermal expansion properties on the device performance.

For OSCs, it is very important to improve the thermal stability of the device performance under operating conditions. In particular the thermal expansion of the polymeric layer plays an important role in the thermal stability of the devices. In a very recent work [14] by using a laser beam diffraction method we have shown that the thermal expansion coefficient (α) of pure P3HT films is almost one order of magnitude larger than that of a P3HT+nc-TiO$_2$ composite.

In this paper, we demonstrate the advantage of the composite-based OSC under operating conditions of high temperatures. For this, we have prepared two types of solar cells: one is the polymeric (P3HT) and the other is the P3HT-nanocomposite-based. The temperature dependence for the photovoltaic device parameters of these solar cells has been studied in detail.

2. Experimental

The bulk donor-acceptor heterojunction solar cells were produced by spin-coating. The fabrication method is described in detail elsewhere [15]. To compare the photoactive behavior of the pure P3HT and a composite consisting of P3HT and TiO$_2$ nanoparticles (abbreviated to PTC) and also the performance of the devices, P3HT and PTC thin films were prepared, using ITO with a sheet resistance of 10Ω per square. In our work ITO-coated glass substrates used for spin-coating nanocomposite films were ultrasonically cleaned in distilled water, followed by cleaning in ethanol and acetone. For improvement of the ITO contact as shown in [16], the ITO was coated with a 70 nm thick layer of polyethylene dioxythiophene (PEDOT). To deposit the active layers onto PEDOT, the P3HT solution was prepared by dissolving 8 mg of P3HT powders in 1 mL of chlorobenzene. For the composite, TiO$_2$ nanoparticles of 5 nm in size were embedded in the P3HT solution according to a weight ratio TiO$_2$/polymer of 0.05 (5 wt.%). This ratio, as reported in [17], is the optimal content for both the generation and separation of charges (electrons and holes) under illumination of solar energy radiation. To obtain a homogenous dispersion of TiO$_2$ in polymer, the solutions were well mixed together for 8 hours by using magnetic stirring. Further, these P3HT and PTC solutions were used for spin-coating. The conditions for spin-coating were as follows: a delay time of 120 s, a rest time of 30 s, a spin speed of 1500 rpm, and an acceleration of 500 rpm and finally a drying time of 2 min. For the acceptor layer, a 50 nm thick PCBM layer was spin-coated onto the P3HT and PTC layers. The thickness of the P3HT:PCBM and PTC:PCBM active layers was about 100 nm. The samples were put in a flow of dried gaseous nitrogen for 12 hours. As electrodes, a PEDOT/ITO film on one side and a LiF/Al bilayer contact on the other side were used. A LiF/Al electrode (shallow contact) was chosen instead of pure Al in order to ensure a good ohmic contact between the metal and the organic layer [18]. An 80 nm thick Al-electrode on the top was thermally evaporated in a vacuum of $1.33 \times 10^{-5}$ Pa, using a mask with windows of 2.5 mm × 3 mm in size. Therefore, the active area of a cell was 0.09 cm$^2$. By this way, two types of organic solar cells (OSC) with respective structures of ITO/PEDOT/P3HT:PCBM/LiF/Al and ITO/PEDOT/P3HT:PTC/LiF/Al (resp., abbreviated to OSC-1 and OSC-2) were prepared, where the active layers of the OSC-1 and OSC-2, respectively, are P3HT and PTC films.

To heat up the devices, we used a thermoelectric heater plate, the temperature of which can be setup and automatically controlled. A schematic drawing is shown in Figure 1.

The surface morphology of the samples was characterized by using a NT-MDT Atomic Force Microscope (AFM) operating in a tunnel current mode. The performance of the OSCs or current-voltage (I-V) characteristics were carried out on an AutoLab-Potentiostat PGS-30 electrochemical unit connected to "Sol 1A" Newport source which provides an energy spectrum similar to the solar one.

3. Results and Discussion

3.1. Thin Films Morphology. The surfaces of P3HT and PTC nanocomposite samples were examined by AFM techniques. Figure 2 shows AFM images of a pure P3HT and a PTC with an embedding of 5 wt.% nc-TiO$_2$ (∼5 nm in size). The surface of the P3HT sample appears rather smooth whereas, in the composite sample considered, a distribution of completely dispersive TiO$_2$ nanoparticles can be seen. After being annealed at temperatures up to 150°C the morphology of the composite sample remained almost unchanged, while from 70°C in the pure P3HT surface there appeared nanosized cracks, which grew in both number and size (their AFM images were not introduced here).
3.2. Characterization of Device Performance. Characterization of the device parameters such as the open-circuit voltage ($V_\text{oc}$), the short-circuit current density ($J_\text{sc}$), and the fill factor (FF) was carried out with the AutoLab-Potentiostat using cyclic voltammetry (CV) measurements in both the dark and illumination states. The CV curves shown in Figure 3 revealed the current-voltage ($I-V$) characteristics of the two devices, OSC-1 and OSC-2, under an illumination with a power density of 56 mW/cm$^2$. In this figure the light-gray and deep-gray rectangles, respectively, illustrate the fill factor for OSC-1 and OSC-2 that is determined by the charge carriers reaching the electrodes, when the built-in field is lowered toward the open-circuit voltage. In fact, there is a competition between charge carrier recombination and transport. The FF can be determined by

$$\text{FF} = \frac{(J \times V)_{\text{max}}}{J_\text{sc} \times V_\text{oc}},$$

(1)

where $(J \times V)_{\text{max}}$ is the rectangle having the largest area. Then the photoelectrical conversion efficiency ($\eta$) can be determined by

$$\eta = \frac{\text{FF} \times J_\text{sc} \times V_\text{oc}}{P_\text{in}},$$

(2)

where $P_\text{in}$ is the density of the illuminating power, in mW/cm$^2$. In our experiments $P_\text{in} = 56$ mW/cm$^2$.

The fill factor and photoelectrical conversion efficiency which were calculated by (1) and (2), together with $V_\text{oc}$ and $J_\text{sc}$ taken from the $I-V$ curves, are displayed in Table 1. The $V_\text{oc}$ of the two cells have almost the same value (namely, 710 and 715 mV), but the $J_\text{sc}$ of the composite cell, OSC-2, is larger (2.34 mA/cm$^2$) than that of the polymer cell, OSC-1 (2.13 mA/cm$^2$). The fact that the FF of the OSC-2 is larger than that of OSC-1 proves that the PTC nanostructured composite is a good matrix where TiO$_2$ particles are tightly surrounded. This is because, during the spinning process (in the spin-coating technique), the TiO$_2$ nanoparticles can adhere to strong electrostatic forces to the polymer, and the capillary forces can then draw the P3HT solution around the nanoparticles into cavities without opening up pinholes through the device. This results in an increase of the $J_\text{sc}$ and consequently the efficiency, $\eta$, of the composite-based devices. The $\eta$-value (1.73%) is small in comparison with solid-state PbS-QDs/TiO$_2$ heterojunction solar cells which have a value for $\eta$ of 3.5% under AM1.5 illumination [19]. However, it can be comparable to the efficiency of a solid-state photovoltaic device using a surface-adsorbed dye complex for light absorption and electron injection to the TiO$_2$ layer, in which an extremely thin absorber is sandwiched between two.
3.3. Temperature Dependence of Device Parameters. In this section we report the temperature dependence for the photovoltaic device parameters of two types of organic solar cells (i.e., OSC-1 and OSC-2) under different operating conditions. Current-voltage measurements were performed under irradiation by using the “Sol 1A” Newport solar simulator at light intensity of the above-mentioned power (56 mW/cm²) and a cell temperature ranging from 20 to 80°C. Figure 4 summarizes the temperature dependency of the principal cell parameters ($V_{oc}$, $J_{sc}$, $\eta$, and FF) derived from the indoor I-V measurements of two devices. The measurements of $V_{oc}$ show a linear decrease with increasing temperature up to 70°C (Figure 4). For all samples, the observed linear decrease had an average temperature coefficient $dV_{oc}/dT = -1.45$ mV/K which is similar to the results reported in [13] for polymer-fullerene solar cells. This is comparable to corresponding values observed for common inorganic solar cells in this temperature range.

From the analysis of the $V_{oc}$ behavior of conventional inorganic semiconductor solar cells with a p-n junction [23], Katz et al. [13] obtained the $V_{oc}$ versus $T$ expression, as follows:

$$V_{oc} = a - bT,$$

where $a$ is the $V_{oc}$ at 0 K and $a \sim E_g/q$ ($E_g$ is the bandgap of the semiconductor used); $b = -dV_{oc}/dT$. In our work $dV_{oc}/dT$ was found to be of $-1.45$ mV/K.

In the range of 20–70°C for both the devices, the decrease of $V_{oc}$ with the temperature increase is almost the same, whereas a relatively large increase with temperature for $J_{sc}$ and FF reaches a saturation, respectively, at 60°C and 70°C for OSC-1 and OSC-2 (Figure 4). A similar but smaller increase in $J_{sc}$ with temperature is also often observed in inorganic solar cells [24]. From Figure 4 one can see that the relative decrease of $V_{oc}$ is compensated by a relative decrease of FF. Thus, the increase of $J_{sc}$ can be seen as a main part which contributed to the increase of $\eta$ for both the polymeric and composite-based devices. As a result, there is an absolute increase of the photoelectrical conversion efficiency ($\eta$) with temperature, reaching a maximum value at temperature $T_{max} = 60°C$ for OSC-1 and $T_{max} = 70°C$ for OSC-2. Over these temperatures all the photovoltaic parameters of the devices decreased with temperature. The fact that $T_{max}$ of OSC-2 is larger than that of OSC-1 proves a better thermal stability for the composite-based solar cells.

Recently it was demonstrated theoretically and experimentally that $J_{sc}$ in conjugated polymer-fullerene solar cells is controlled to a considerable extent by the mobility of the majority charge carriers in the cell’s active layer [25]. Moreover, the expressed activated behavior of charge carrier mobility in conjugated polymers is known to result in higher mobility at higher temperatures [26]. In our work the observed temperature dependence of FF is similar to that of $J_{sc}$. Thus, owing to the increase in carrier mobility, the improvement in FF and $J_{sc}$ with increased temperature occurred.

Our results are concordant with the ones obtained by Kim et al. [27] who observed a significant improvement in device performance at a temperature near the glass-transition temperature of P3HT. The behavior in the FF and $J_{sc}$ parameters with increasing temperature was related to an evolution in the thin film morphology toward a graded composition (vertical phase segregation). It was also shown to be consistent with improved transport properties in the wide-bandgap semiconductors, one n-type and the other p-type [20–22].
blend films upon annealing at 75°C, as confirmed from time-of-flight measurements for carrier mobility.

A positive temperature dependence of \( J_{sc} \) was also observed for organic solar cells based on Zn-phthalocyanine (ZnPc)/perylene(M-PP) heterojunction [28]. In [13] Katz et al. suggested that positive temperature dependencies of \( J_{sc} \), FF, and \( \eta \) may be characteristic for solar cells with expressed temperature activated behavior for charge transport, resulting in higher mobility/conductivity at higher temperatures. Similar properties were also obtained for some types of amorphous silicon solar cells.

Figure 5 illustrates the detailed temperature dependence of \( \eta \) for OSC-1 and OSC-2 in a temperature range of 30–140°C. A similar positive dependence of \( \eta \) for OSC-1 and OSC-2 is observed in a temperature range of 30–60°C. From 60°C, \( \eta \) of OSC-1 decreased with \( d\eta/dT = 0.04\%/K \) with increased temperature and almost diminished to zero at 140°C. For the composite-based OSC-2 the maximum efficiency was reached at 70°C and then decreased with \( d\eta/dT = 0.02\%/K \) which is much smaller than that of OSC-1. Moreover, \( \eta \) had a critical value of ca. 1.2%. This means that the performance of the OSC-2 was maintained at temperatures as large as 120–140°C. This clearly demonstrates the advantage of the nanocomposite-based solar cells when the devices are exposed outdoor at high temperatures of solar illumination.

The difference in the performance parameters of the polymeric and composite-based solar cells is closely related to morphology and thermal expansion of the active layers. In a recent work by our group [29], it was shown that in the pure conjugate polymer film like MEH-PPV a few nanoscale cracked spots were often created during the postannealing, whereas, for the composite film with embedded TiO\(_2\) nanoparticles, no similar spots could be observed. Similarly to this, for the as-prepared P3HT film, some spots were formed. After annealing at high temperatures these spots were considerably expanded. AFM images of the P3HT and PTC films conducted at 130°C are presented in Figure 5, showing large size cracks in the pure P3HT film, whereas, in the PTC film, there were no similar features.

It is clearly seen that the nanocracks in the polymeric active layers can be considered as linear defects (or dislocations) in inorganic single semiconducting crystals, and they play a role in charge trapping for both electrons and holes.

In the P3HT+nc-TiO\(_2\) film, the TiO\(_2\) nanoparticles filled up the cracks, creating numerous heterojunctions of TiO\(_2\)/polymers. These junctions favor the injection of the generated electrons from the active layers (P3HT) to the Al-electrode (Figure 1), resulting in an enhancement of the so-called charge separation. This would enable performance parameters of the OSC such as \( V_{oc}, J_{sc}, \) and FF to be improved. Thus \( \eta \) of the OSC-2 is much larger than that of OSC-1 (Figure 6).
The fact that over 70°C the efficiency of OSC-1 decreased strongly and the device stopped working at over 110°C, while by OSC-2 the photoelectrical energy conversion process was continued with a value $\eta = 1.2\%$ (at 140°C), demonstrates an excellent thermal stability of the composite-based devices. Indeed, since the thermal expansion coefficient of the P3HT film ($7.60 \times 10^{-5} \, \text{K}^{-1}$) is much larger than that of the PTC film ($\alpha = 0.91 \times 10^{-5} \, \text{K}^{-1}$) as shown in [15], at such a large temperature of 140°C, the nanocracks in P3HT would grow further, creating numerous large canals which can block the charge transport in the P3HT active layer. For the composite film (namely, P3HT+nc-TiO$_2$) where nanocracks do not exist and $\alpha$ is very small, the increase of temperature up to 140°C did not affect much the performance of this active layer. Thus, $\eta$ of OSC-2 decreased about 30% from 1.73% (at room temperature) to 1.20% (at 140°C) and possessed the largest $\eta$ at 70°C (namely, ~2.1%). These results showed that the effective temperature range (60–80°C) for polymeric photovoltaic devices is much lower than that for some types of inorganic solar cells (100–170°C) [12].

As in the work by Ma et al., regarding the achievement of thermally stable and efficient polymer solar cells [30], it is expected that, in the case of our OSC-2 samples, the heating has resulted in an optimized and stable separation for efficient charge generation and an improved crystallinity within the phase-separated networks that facilitates charge transport to electrodes.

4. Conclusion

We investigated the temperature dependence of photovoltaic parameters for organic solar cells based on P3HT and P3HT+nc-TiO$_2$ nanocomposite with fullerenes. With increasing temperatures, the open-circuit voltage of both the polymer and composite cells decreased with $dV_{oc}/dT$ of $-1.45 \, \text{mV/K}$ in the operating-temperature range from 30 to 140°C. A larger photoelectrical conversion efficiency of the composite-based OSCs was attributed to the presence of nanoheterojunctions of TiO$_2$/P3HT. For the temperature range under investigation, the increase of the fill factor compensated the decrease of the open-circuit voltage, and the increase in the short-circuit current resulted in an overall increase of the energy conversion efficiency with increasing temperature. At elevated temperatures of 60–80°C the efficiency of the polymeric and composite cells reached a maximum value of 1.6% and 2.1%, respectively. Over these temperatures the efficiency decreased strongly; however for the composite cells, it maintained a critical value of 1.2% in a temperature range from 110 to 140°C. Compared to polymeric devices, composite-based solar cells exhibited much better thermal stability. This fact is closely related to the lowered thermal expansion coefficient of the photoactive P3HT+nc-TiO$_2$ layer in the composite-based devices.

Conflict of Interests

The authors declare that there is no conflict of interests related to this paper.

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