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Polymer heterostructures with embedded carbon nanotubes for efficient photovoltaic cells

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ABSTRACT

Polymer photovoltaic cells (PVC) are intensely investigated because of their potential advantages over Si-based PVCs. Their present drawbacks are low conversion efficiency, limited exciton diffusion length, poor hole carriers transport and short lifetime. The highest conversion efficiency achieved so far in spin-coated polymer blends is close to 5%. Recently, efficiency growing has been demonstrated in multilayer architectures involving a donor/acceptor bulk heterojunction. Alternatively, a nanomaterial has been added to the polymer active layer to facilitate excitons dissociation and carriers transport through the polymer matrix. In this work we investigate both these approaches, first embedding single wall Carbon Nanotubes (SWCNT) in the polymeric matrix to improve the electrical transport and second studying the optical absorption of different polymer thin films to optimize the spectral response of the donor/acceptor heterojunction.

1. Introduction

Satisfying the world's growing demand for energy is one of the most significant challenges that our society is facing. Up to now, solar energy seems the easiest way to overcome this problem and free energy devices such as silicon-based solar cells play a fundamental role. Unfortunately, they suffer of low conversion efficiency and high production costs. Recently, organic solar cells received increasing attention. Indeed, the polymers used in photovoltaics offer many practical advantages. The fabrication techniques are cheap and consist in spin or dip coating, or in roll to roll processes. Moreover, the electronic properties of the polymers may be improved by adding or removing functional groups such as dye-sensitizing molecules. The simplest organic cell consists in a thin film conjugate polymer between one transparent electrode (usually Indium Thin Oxide—ITO) and one metal electrode (typically aluminium). A more complex topology consists in a heterojunction device obtained by depositing a donor over an acceptor polymer. The working principle of this polymer-based solar cell consists of three essential steps, i.e. light absorption, charge carrier generation and transport of the opposite charges to the contacts. Absorption of light results in excitons dissociation, therefore in charge carrier generation. In organic materials, the exciton binding energies exceeds kT at room temperature and efficient carrier generation is achieved when the relative energies of the HOMO and LUMO levels allow an energy offset larger than the exciton binding energy. The photo-generated charges must reach the donor-acceptor interface within their lifetime and the layer they have to cross to reach the electrode must be shorter than their diffusion length (about 10–20 nm). The electron-acceptor layer generates a path for electrons and a barrier for the holes transport [1]. Usually charge transfer occurs only in about 10% of the thickness of the contacting donor and acceptor layers, therefore the conversion efficiency of these devices is quite low [2–4]. Improvement of the conversion efficiency has been achieved with nanostructured materials embedded in the active layers [5–8]. They change either the absorption properties of the polymer or its conductivity. Carbon nanotubes improve electrical transport and increase the efficiency by trapping the photo-generated charges before their recombination [9,10]. The efficiency of the cell depends on the open circuit voltage (Voc). The maximum Voc is approximately equal to the energy difference between the HOMO and LUMO [11].

In the bi-layer polymers-based solar cell, both active materials forming the heterojunction play also the role of optical absorber. Improvement in internal conversion efficiency can be achieved choosing two polymers whose absorption cover complementary parts of the solar spectra. Thus, the choice of the material is a real

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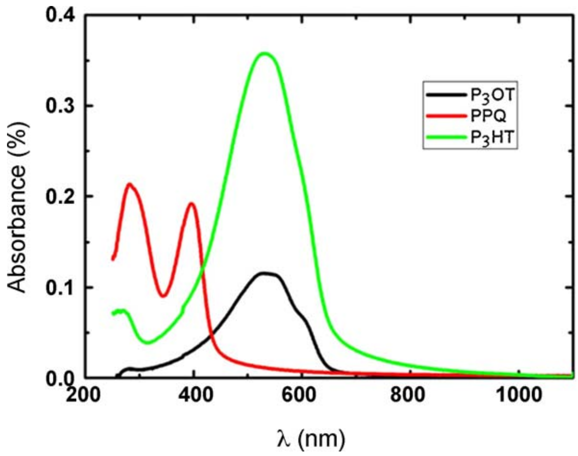

Fig. 1. Absorption spectra of a P_3OT (black line), P_3HT (green line) and PPQ (red line) 100 nm thin film, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

challenging task and plays a key role in the final efficiency [12]. In this work we compare the properties of two different p-type polymers, namely the poly(3-octylthiofene) (P_3OT) and poly(3-hexylthiophene) (P_3HT), when used in a bi-layer solar cell having poly(phenylquinoxaline) (PPQ) as n-type polymer.

2. Experimental

Fig. 1 shows the absorption spectra of a 100 nm thin film deposited by spinning a solution on a corning glass substrate, of P_3OT (black line), P_3HT (green line) and PPQ (red line), respectively. All polymers are dissolved in a solution with 10 mg/ml concentration, namely P_3OT and P_3HT in Toluene and PPQ in Chloroform. The same solutions were used to prepare the thin film for absorption spectra acquisition and devices. The P_3OT film exhibits an absorption band at 538 nm and a shoulder at about 600 nm. The P_3HT film shows a main large absorption band centered at about 530 nm and an UV band below 300 nm. To compare the spectral efficiency we have manufactured and investigated different devices using P_3OT and P_3HT polymers as electron donor.

To manufacture the device we first spin coated the donor polymer layers onto a ITO coated glass substrate (sheet resistance of 10 Ω/square). The PPQ is almost insoluble in toluene, therefore spinning the PPQ solution as last layer the heterostructure is easily realized [3]. The best results have been obtained by drying in Argon atmosphere at 70 °C for 1 h the first layer before spinning the second one. The bi-layer thin films were further dried in the same conditions. Finally, an aluminium top electrode was thermally evaporated in ultra high vacuum. In the last device, SWCNTs were added to the P_3HT solution and sonicated for 1 h before spin coating. The complete device structures are shown in Fig. 2. Light-beam-induced-voltage (LBIV) measurements give a map of the local external quantum efficiency [13,14]. LBIV method consists in measuring the Voc under local monochromatic illumination. The light beam, focused directly on the solar cell surface, scans the device both along the *X* and the *Y* axes. Thanks to the local voltage response of the cell, the measured *XY* voltage distribution can be arranged in the form of a voltage map; therefore, the behaviour of each individual part of the solar cell becomes visible. Our monochromatic light source is a halogen lamp filtered by a monochromator and modulated at 500 Hz. The Voc is detected point by point by a lock-in amplifier and the data are reassembled into a map. The same setup is able to give the spectral efficiency curve of the devices in the UV–vis range. To this purpose the focusing objective is removed to uniformly illuminate the active area of the cell.

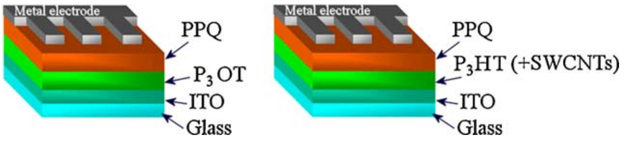

Fig. 2. A schematic of the devices with P_3OT/PPQ and P_3HT/PPQ thin film.

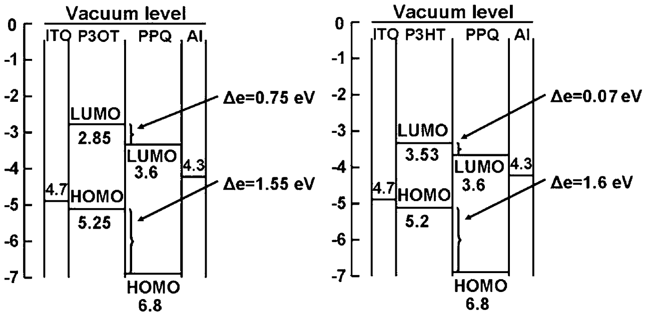

Fig. 3. Schematic energy diagrams for a P_3OT/PPQ and P_3HT/PPQ device with Al and ITO electrodes.

3. Results and discussion

A schematic energy diagrams for a P_3OT/PPQ and P_3HT/PPQ device with Al and ITO electrodes, are shown in Fig. 3. The energies of the LUMO and HOMO levels for the P_3OT are 2.85 and 5.25 eV, while the P_3HT energies are 3.53 and 5.2 eV. The PPQ is characterized by a LUMO level at 3.6 eV and a HOMO level at 6.8 eV [3,15]. The work functions of Al and ITO electrodes are about 4.3 and 4.7 eV, respectively [3]. The device working mechanisms is straightforward. The excitons photo-generated in the p-type layer diffuse to the interface between the two polymer layers. Since both LUMO levels of P_3OT and P_3HT lie above the PPQ one, the excitons are expected to efficiently dissociate by electron transfer to PPQ. Likewise, transfer of photo-induced holes from PPQ to donor layer

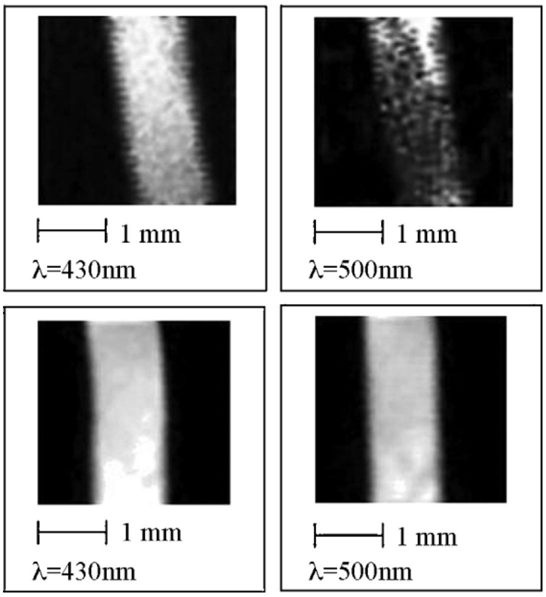

Fig. 4. Voc maps of the ITO-P_3OT-PPQ-Al (up) and ITO-P_3HT/SWCNTs-PPQ-Al (down) device obtained by exciting the cell at 430 nm (left) and 500 nm (right). The images reproduce the finger shape of the top Al electrode.

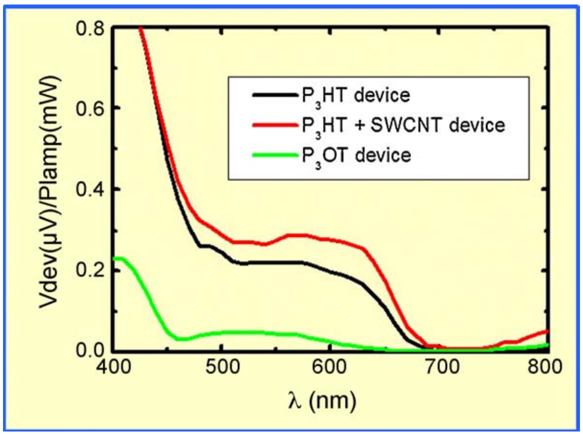

Fig. 5. Spectral responsivities of the three devices normalized to the lamp intensity.

is expected. Thus electrons are carried to one contact by PPQ, and holes are transported by the P_3OT or P_3HT layer to the opposite contact. The paths of oppositely charged carriers are separated and recombination should be prevented. Analytically, the interfacial barrier in the P_3OT/PPQ heterojunction is 0.75 eV for the holes and 1.55 eV for electrons while in P_3HT/PPQ device it is 0.1 and 1.5 eV, respectively. The LUMO level at 3.6 eV suggests that the use of PPQ gives rise to a significant enhanced electron transport from the donor layer to the acceptor one. Furthermore, the offset in the HOMO level at the interface between two polymer layers is significantly larger than the barrier at the ITO/donor interface, therefore the hole current is limited by the donor/PPQ interface.

Fig. 4 shows the Voc maps of the ITO-P_3OT-PPQ-Al and ITO-P_3HT/SWCNTs-PPQ-Al devices. The data are collected by illuminating the cell with 430 nm (left) and 500 nm (right) light. The images reproduce the finger shape of the top electrode. Interestingly, the map obtained by exciting the cell at the longer wavelength exhibits a poor charge collecting efficiency due both to inhomogeneities of the organic films and to a short diffusion length. Consistently, the map obtained at the shorter wavelength suggests a longer charge diffusion length and therefore a more efficient collection mechanism. A better result is obtained with the ITO-P_3HT-PPQ-Al device (not shown in Fig. 2) and ITO-P_3HT/SWCNTs-PPQ-Al device that exhibits a higher Voc and more homogeneous collection efficiency. The increase in the charge collection efficiency is due to the SWCNTs distributed inside the P_3HT layer that behave as charge collectors. Finally, we report in Fig. 5 the spectral response of the three devices normalized to the lamp intensity. Thanks to its absorption properties, the P_3HT-based device performs better than the P_3OT one. The device realized by embedding the SWCNTs inside the P_3HT active layer shows an increase in the charge collection efficiency at longer wavelength. This result is consistent with the hypothesis that SWCNTs work inside the polymeric layer as a preferential channel for charge collecting and transport.

4. Conclusion

The photovoltaic characteristics of organic devices based on P_3HT or P_3OT as donor and PPQ as acceptor have been investigated. The absorption spectra of the polymer active layer play a fundamental role in increasing the responsivity of the device. The LBIV measurements demonstrate that local inhomogeneities of the films decrease the cell performances. Embedding SWCNTs in the polymeric thin film matrix allows charge separation of the photogenerated excitons and an efficient electron transport through the nanotubes, improving the overall efficiency.

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