

Tunable of Open-circuit Voltage in Bilayer Hybrid Solar Cells by Binary Polymer Blends

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Abstract. The different concentration of BPEI were blended into the MEHPPV, and then respectively be composed into the MEHPPV/ ZnO PHJ solar cells. Through calculating the dark reverse saturation current, we found that the interface barrier Φ_B was changed. Interestingly, the open circuit voltage V_{oc} was observed that changed linearly with the Φ_B . Through studying the relation of the V_{oc} and Φ_B , we found that the open circuit voltage V_{oc} can be tuned by the variation of Φ_B .

Introduction

Hybrid polymer-based solar cells (HPSCs) that use conjugated polymers as electron donor (D) and inorganic semiconductor nanocrystals as electron acceptor (A) had evoked a great wave of enthusiasm for the past few years. [1, 2] The working principles, as well as the device performance and charge transfer modeling had also been studied gradually. [3, 4] Despite some achievements were obtained for understanding the mechanism of HPSCs in recent years, however, there was also not forming a complete and unified system in theoretical recognition on device physics, for example, there are some different viewpoints to recognize the factors that affect the open-circuit voltage (V_{oc}): the V_{oc} can be enhanced by the superposition of the built-in field with the interfacial dipole of the interlayer; [5] the dissociation rate and decay rate of photo-induced electron-hole pairs also influence the open-circuit voltage; [6] the origin of this difference in the V_{oc} has been proven to be directly related to the crystallization properties of active layer. [7]

In this paper, we fabricated the MEH-PPV/ ZnO bilayer planar heterojunction solar cells, and added different concentration of branched-poly (ethylene mine) (BPEI) in MEH-PPV. Some new physical insights for the HPSCs were studied, which are not only simply reported the strategy of tuning V_{oc} for HPSCs, but also indicated some new physical quantity that closely related to V_{oc} .

Experimental

Device Fabrication

ITO glass was cleaned sequentially, prior to use, by ultrasonic agitation twice in acetone, isopropanol and distilled water for 10 min in each washing process. For ZnO PHJ device, The ZnO precursor was prepared from a mixture of zinc acetate aqueous solution (1 mL, 0.1 M), ethanol (4 mL, AR), and acetic acid (0.1 mL, GR). The precursor was stirred for 1 hour after mixing. An etched ITO substrate was spin-coated with the precursor at 2000 rpm for 50 s in ambient conditions (about 40 nm). Then the ZnO film was annealed in air at 350 °C for 20 min. The TiO_2 sol-gel was prepared from a mixture of titanium tetraisopropoxide, absolute ethanol and acetic acid (GR, $\geq 99.8\%$), in a volume ratio of 2:20:0.1. An etched ITO substrate was spin-coated with the TiO_2 sol at 2000 rpm for 50 s in ambient conditions. Then layer of MEH-PPV was spin coated (3000 rpm, 40 s) on oxide layer from a solution of MEH-PPV with BPEI of different concentration (weight ratio $W_{BPEI/PPV} = 0\%, 0.5\%, 1\%, 5\%$) in trichloromethane (15 mg/mL). After being dried in vacuum at room temperature for 24 h, they are dried in vacuum at 100 °C for 30 min under vacuum. An Au top contact (100 nm thick) was deposited as 4 mm² via thermal evaporation through a shadow mask.

Characterization

The steady-state current–voltage (J–V) characteristic of the devices was measured on a controlled intensity modulated photo spectroscopy (CIMPS) (Zahner Co. Germany) in ambient conditions under an illumination through ITO glass side, using a blue light-emitting diode (LED) as light source (BLL01, $\lambda_{\max} = 470$ nm, spectral half-width = 25 nm, Zahner Co.) driven by a frequency response analyzer and the light intensity of dc component (15.85 mW/cm^2) was controlled by the bias voltage at the LED with a proportionality factor $FP = 315.7 \text{ W}\cdot\text{m}^{-2}\cdot\text{V}^{-1}$, which was calibrated using an IL1400A photometer with a SEL 033/W detector (International Light, Inc., USA). Cyclic voltammetric (CV) measurements were performed on an IM6e electrochemical workstation (Zahner Co., Germany) in N_2 atmosphere at a scan rate of 50 mV s^{-1} , with a platinum counter electrode.

Results and Discussion

Table 1. Performance of devices with different BPEI concentration measured under monochromatic illumination (15.85 mW/cm^2) at 470 nm.

MEH-PPV/ZnO different BPEI concentration	with V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η (%)	Φ_B (eV)
$W_{BPEI/PPV} = 0.0 \%$	0.54	0.02	31.0	0.049	2.40×10^{-7}
$W_{BPEI/PPV} = 0.5 \%$	0.56	0.01	36.8	0.013	2.63×10^{-7}
$W_{BPEI/PPV} = 1.0 \%$	0.51	0.05	34.6	0.052	5.25×10^{-7}
$W_{BPEI/PPV} = 2.5 \%$	0.38	0.04	36.5	0.056	1.60×10^{-6}
$W_{BPEI/PPV} = 5.0 \%$	0.33	0.15	33.2	0.100	6.58×10^{-6}
MEH-PPV/ TiO_2 with no BPEI	0.69	0.01	26.3	0.009	1.68×10^{-9}

The performance of MEH-PPV/ZnO PHJ devices with different BPEI concentration were seen in the Table 1. The device performance is changed remarkably after addition BPEI into MEH-PPV matrix. After adding a BPEI concentration of 0.5 wt% in weight ratio, the short-circuit current increased slightly from 0.02 mA/cm^2 to 0.04 mA/cm^2 , but when adding to 1.0 wt% in weight ratio, the short-circuit current enhanced to 0.15 mA/cm^2 , which is the highest short-circuit current among the above ZnO devices. When the BPEI concentration surpass the 1.0 wt%, the short-circuit current gradually decreased. The open-circuit voltage also changed after BPEI addition, basically, open-circuit voltage reduced as BPEI concentration increased from 0 to 1.0 wt%, and the continue adding the BPEI, the open–circuit voltage will back–up. The changed device performance are similar to those found in the P3HT/ TiO_2 bulk heterojunction cells with different concentration of PMMA as an additive to blending into P3HT and the P3HT/ TiO_2 bilayer cell with BPEI addition. [8, 9]

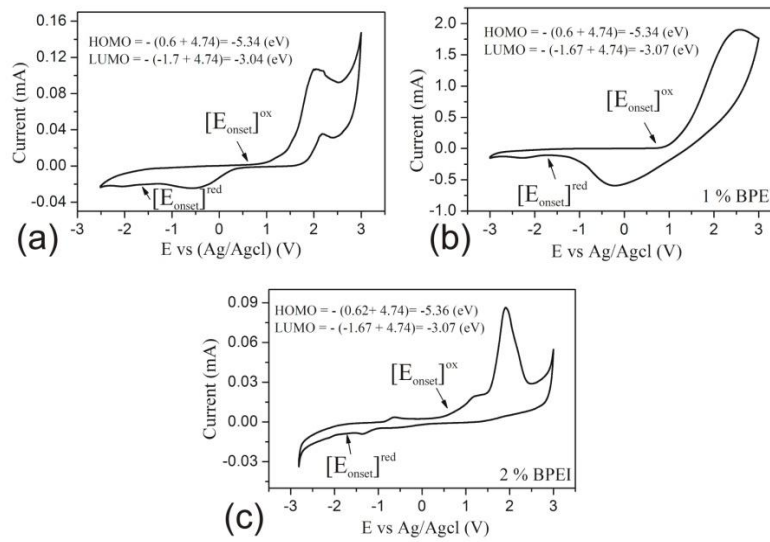


Fig. 1 The cyclic voltammetry characteristics for MEH-PPV/BPEI blends with different BPEI concentrations.

The various current had been explained as the different interfacial contact by adding proper the BPEI or the enhanced electrical conductivity by adding small amount of PMMA. [8, 9] However, the V_{oc} had not been attentive researched, which causes us to search for the reason that why the voltage will changed after BPEI addition. First, the electrode materials unchanged in this experiment. Therefore, the effect of electrode work-functions on the V_{oc} should be ruled out. Others had also experimentally demonstrated that the electrode work-function has no significant effect on the device V_{oc} . [10] In this case, we take the cyclic-voltammetry ($C-V$) measurements for MEH-PPV/BPEI blends to sure that whether the change of the open-circuit voltage is by the change of the energy levels of MEH-PPV/BPEI blends. From the $C-V$ curve (in the Figure 1), we can see that the HOMO and LUMO of MEH-PPV were not largely changed by BPEI addition. Thus, it cannot help to ask that which factor play the key role on the open-circuit voltage.

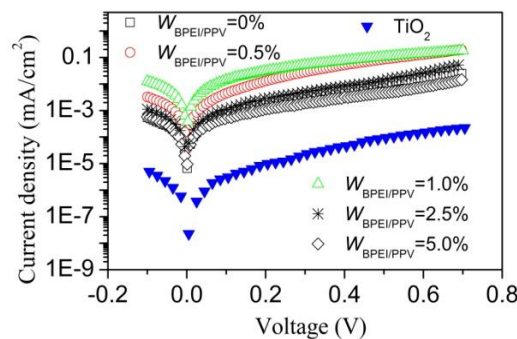


Fig. 2 Dark $J-V$ of the device for various $W_{BPEI/PPV}$ of MEH-PPV/ZnO bilayer solar cells and MEH-PPV/TiO₂ bilayer solar cells with no BPEI.

For answer this question, we deeply analysis the dark $J-V$ characteristic curves of our cells (Figure 2). The changed of reverse dark current which similar to the change of open-circuit voltage, which aroused our much interest. It has been demonstrated that there is often an interface activation energy barrier Φ_B at the heterojunction. At present, the formation of the Φ_B are usually explained as a result of the energy level bending by the vacuum level misalignments at the heterojunction or the formation of interface charge-transfer states, [11] and Φ_B can be evaluated from the dark reverse saturation current in dark $J-V$ characteristic by: [12, 13]

$$J_0 = B \exp\left(\frac{-q\phi_B}{kT}\right) \quad (1)$$

Where B is a coefficient with a value in the range of 1000 A cm^{-2} , J_0 is dark saturation current, k is the Boltzmann constant, T is the temperature constant, q is the electron charge. Therefore, we extracted the approximate value of dark saturation current J_0 from the dark J - V curve, which listed in Table 1. Based on eq 1, we calculated the interface energy barrier Φ_B values of all devices, the results also be listed in Table 1.

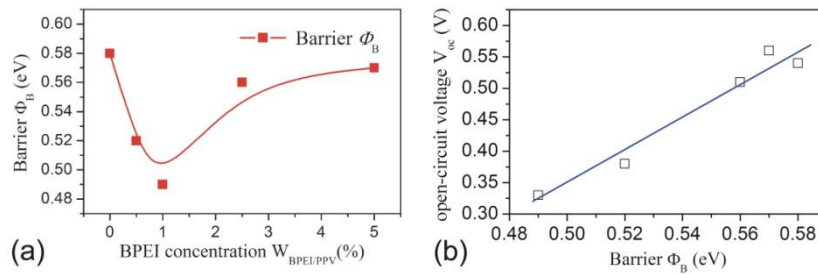


Fig. 3 (a) The plot of the relation of interface barrier Φ_B with BPEI concentration. The inset Figure in (a) is the plot of the relation of open-circuit voltage with BPEI concentration. (b) The linear correlation of open-circuit voltage and the Φ_B .

As shown in Fig. 3a, the dependence of Φ_B on BPEI concentration is the same as that of V_{oc} . The V_{oc} vs Φ_B plot in Fig. 3b exhibits a good linear ship. These results indicate a direct correlation between V_{oc} and Φ_B . The mechanism of BPEI how to change the interface energy barrier Φ_B had not clear; probably it caused the interface energy level bending by different degrees or the formation of interfacial hybrid charge-transfer states. [14] Although the mechanism is not very distinct, however, it not affects to conclude the relation of the V_{oc} and Φ_B . For further confirming the correlation of V_{oc} and Φ_B , we studied the MEH-PPV/TiO₂ PHJ cells without adding the BPEI. As the energy levels of TiO₂ are the same to the ZnO, if the V_{oc} depended on the energies of the relevant energy levels at the D/A heterojunction, the V_{oc} in TiO₂ cell should be close to the ZnO cell. However, the open-circuit voltage of TiO₂ cell is much bigger than ZnO cells. The V_{oc} of TiO₂ cell is 0.69 V, which is 0.15 V higher than the ZnO cell. According this deduce, the interface barrier in TiO₂ cell should be higher than ZnO celling. Be as expected, the interface barrier in TiO₂ cell is 0.71eV which is 0.13eV higher than the ZnO cell, even that the difference of Φ_B values is close to the difference of V_{oc} values. That also explained that why the open-circuit voltage in TiO₂ composed cells is higher than the ZnO composed cells.

Table 2 Listed device performances and J - V characteristics parameters of P3HT/PCBM solar cells from literature. [15]

Anneal	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)	Φ_B (eV)
Before	0.42	6.9	46	1.3	9.0×10^{-7}
After	0.59	7.7	58	2.7	3.6×10^{-9}

Otherwise, other group studies on the effects of thermal annealing before and after Al deposition on poly(3-hexylthiophene)(P3HT)/[6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) blend solar cells also certificate our conclusion. [15] The device performance datum which extracted from the paper is listed in Table 2. From the J_0 values in Table 2, the Φ_B value can be calculated by eq (1),

which are also shown in the Table 2. Obviously, the bigger of the barrier Φ_B , the higher of the V_{oc} , and the growth amplitude of the V_{oc} is 0.17 V, the Φ_B is 0.14 eV, and the values are very close. This result effectively certificates our conclusion.

Conclusions

The different concentration of BPEI were blended into the MEH–PPV, and then respectively be composed into the MEH–PPV/ZnO PHJ solar cells. Through calculating the dark reverse saturation current, we found that the interface barrier Φ_B was changed. Simultaneously, the open–circuit voltage V_{oc} are also found that changed parallelly with the interface barrier Φ_B . Through studying the relation of the V_{oc} and Φ_B , we found that the V_{oc} more correlated with the Φ_B .

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