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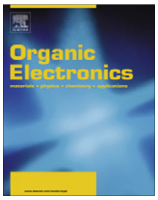

Morphological modification induced by external electric field during solution process of organic solar cells

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ABSTRACT

An electric field was externally applied on the poly(3-hexylthiophene)/[6,6]-phenyl C_{61} butyric acid methyl ester (P3HT:PCBM) blend film during the fabrication of the bulk-heterojunction (BHJ) solar cells to induce morphological modification. It influences the vertical ratio of P3HT:PCBM molecules. Because the field is applied externally to the device, its direction can be altered. When the electric field of 5.0×10^5 V m^{-1} was applied with the specific direction, it formed a P3HT-rich and rougher surface, compared with that of pristine active layer, to improve the performance of the inverted polymer solar cells. Hence, the current density was improved from 9.15 mA cm^{-2} to 9.83 mA cm^{-2}, and power conversion efficiency increased from 3.16% to 3.51%. This finding provides guidance for morphology engineering in organic materials for higher power conversion efficiency of organic solar cells.

1. Introduction

Organic solar cells (OSCs) are advantageous over inorganic photovoltaic devices because of their light weight, low production cost, mechanical flexibility, and the large-area manufacturing approach [1–3]. The most common structure is that of donor–acceptor (D/A) bulk heterojunction (BHJ) organic solar cells [4–6]. The BHJ device provides an interpenetrating network of donor and acceptor materials to increase the interface area for exciton dissociation and to overcome short exciton diffusion length [7]. In the D/A systems, the most widely used materials are poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) [8,9]. Because P3HT has a high degree of crystallinity, it can provide the advantage of high mobility [10], and environmental stability [11]. However, because the nanostructure of heterojunction is a random distribution of donor and acceptor materials, it could occasionally lead to isolated islands and prevent the carrier from migrating to the electrodes [12]. Therefore, modifying the order of donor and acceptor materials distribution to improve the efficiency of cells is an important issue in recent studies.

The most commonly used techniques for improving the morphology are thermal annealing [13–15] and solvent annealing [16]. These post-annealing processes mainly focus on the further increase of the molecular crystallinity and the fine improvement of the morphology after the solid film was derived. A more direct way to manipulate the morphology is to control the film evolution kinetics during the drying process, for instance, by creating a solvent-saturated atmosphere to slow down the as-cast film formation. Under the solution-process, the thickness of the active layer, the vertical composition of P3HT:PCBM, the crystalline grain size, and the surface roughness are mainly adjusted in the solution drying period. Recent studies show that treatment during the drying process is more effective than treatment afterward [17].

This study introduces a method to manipulate the surface of the organic layer by externally applying electric field treatment in the critical moment of film formation.

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Sariciftci et al. reported that applying a bias and annealing the devices simultaneously can improve the power conversion efficiency (PCE) of cells [6]. Some studies have also applied bias voltage on devices to establish a large electric field, which can order the arrangement of conjugated polymers to improve the performance of organic solar cells [18,19]. However, in such studies, the electric field was applied directly through the electrodes of the devices. In contrast, here the present study uses an external electric field instead of conducting a huge bias voltage directly on the electrodes of the device. The vertical external electric field was established by two parallel metal plates. The electric field applied during the drying process induced increased orderliness in the polarity of organic polymer materials and improved the performance of organic solar cells. This "no contact" method reduces the possibility of damage and essentially influences the polymer to be more ordered than the original BHJ active layer.

2. Experimental details

Inverted BHJ solar cells, made from indium tin oxide (ITO)/ZnO/P3HT:PCBM/NiO/Ag, were fabricated in this study. Devices were fabricated on cleaned glass substrates coated with ITO. For the transparent electrode, 7Ω/□ ITO glass was used. The ZnO seed layer was fabricated on the ITO glass by spin-coating ZnO sol–gel (0.5 M) and subsequently was baked at 200 °C for 30 min. The ZnO thin film was deposited onto the substrate as the electron selective layer [20,21]. Then a polymer thin film of P3HT/PCBM (1:1 by weight) dissolved in 1,2 dichlorobenzene (DCB) with a concentration of 1.5 wt.% was spin-coated on at a spin rate of 600 rpm for 40 s under a nitrogen atmosphere. The polymer thin film was kept in a petri dish for slow drying in dark conditions.

In the period of slow drying, an electric field was exerted on P3HT:PCBM until it dried. In electric field treatments, devices were placed between two parallel metal plates with bias voltage applied to them, forming an electric field perpendicular to the devices. The vertical electric field treatment was divided into two conditions according to the direction of the electric field: forward and backward electric field. The diagram of the device that exerted the electric field is shown in Fig. 1. In this experiment, the direction from glass to active layer was defined as the forward direction and the direction from active layer to glass was defined as the backward direction. The differences between opposite electric field orientations treatment was observed on the devices. This was followed by spin coating a thin layer of NiO nanoparticle as the electron blocking layer [22]. Finally the anode, 200 nm of Ag, was thermally evaporated in a deposition chamber under a vacuum of 3×10^{-4} Pa. The active layer of the device, defined by shadow mask, was 0.06 cm^2. Devices were measured under air atmosphere at room temperature. A Sun 2000 solar simulator (ABET technologies) with a Keithley 2400 source meter were used to measure the current density–voltage (J–V) curve under AM 1.5(100 mW cm^{-2}) illumination. The surface ratio of the polymer compositions in the devices was determined by electron spectroscopy for the chemical analysis (ESCA), which was performed on a VG Scientific ESCALAB 250 spectrometer under the measurements of spectral areas of C-1s and S-2p photoelectrons emitted by Al-K_α radiation (1486.6 eV). A Solver P47-PRO scanning probe microscope (NT-MDT) was used to observe atomic force microscopy (AFM) images.

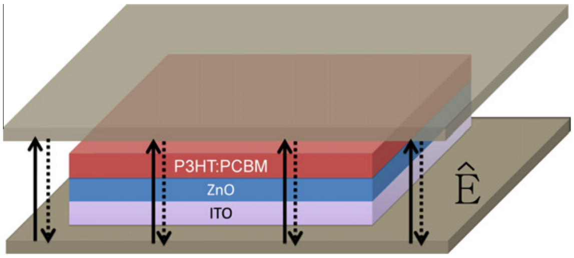

Fig. 1. Schematic structure of vertical electric field treatment (the solid line means the electric field is in the forward direction; the dashed line is backward).

3. Results and discussion

The J–V curves of devices under different electric field treatments are shown in Fig. 2. The characteristic parameters of the devices are shown in Table 1. The PCE of the device without the electric field treatment was 3.16%. After the device was treated by a backward electric field of 2.5×10^5 V m^{-1}, its PCE increased to 3.23%. When the treated electric field was enhanced to 5.0×10^5 V m^{-1}, PCE increased to 3.51%. The treatment increased the performance of device efficiency by 11%. On the contrary, when the treated electric field was forward 2.5×10^5 V m^{-1}, its PCE decreased to 3.09%. When the electric field was forward 5.0×10^5 V m^{-1}, the PCE was 3.04%. The method of treating with an external electric field to induce the polarity of organic polymer materials to be more orderly was able to increase the performance of organic solar cells. However, there was also an impact on the device when applied in different directions. In a comparison of the solar cells with

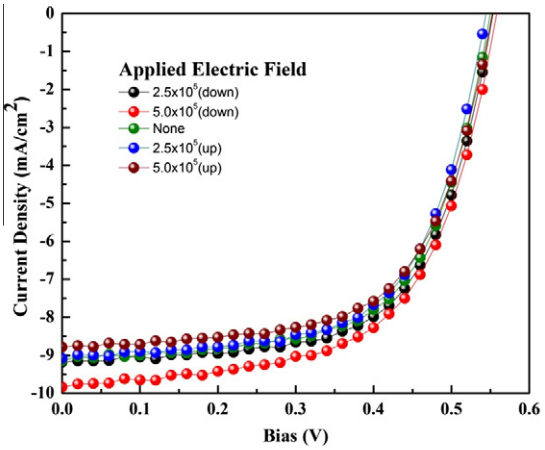

Fig. 2. J–V characteristics of the photovoltaic devices with different electric field treatments under 100 mW cm^{-2} AM 1.5 G irradiation.

Table 1
Average performance of P3HT:PCBM OSCs under different electric field treatments.

Applied Field (V/m)	Voc (V)	J_{SC} (mA cm^{-2})	PCE (%)	FF (%)	R_S (Ω cm^2)	R_{SH} (Ω cm^2)
Pristine film	0.56	9.147	3.16	61.7	1.1	886.0
2.5×10^5 (backward)	0.56	9.184	3.23	62.8	1.0	955.4
5.0×10^5 (backward)	0.56	9.829	3.51	63.8	0.8	949.8
2.5×10^5 (forward)	0.55	9.079	3.09	61.9	1.2	872.6
5.0×10^5 (forward)	0.56	8.786	3.04	61.8	1.1	878.6

forward and backward electric field treatments, the biggest different was the short-circuit current. With the backward electric field treatment, the short circuit density (*Jsc*) increased up to 9.829 mA cm^{-2}, and the *Jsc* of the device with forward electric field treatment is 8.786 mA cm^{-2}. The significant upgrade of photocurrent is due to the backward electric field treatment.

Unlike previous methods which applying electric field directly through the electrodes of devices, in this study, the electric field was applied externally to the active layer before the deposition of electrodes. Therefore, this study was able to investigate the film property directly by using AFM and ESCA that will be described below.

The AFM images of the surface of the polymer layer are shown in Fig. 3. The AFM images and the surface roughness measurement revealed different morphology after treatment with the electric field. When the device was treated by a backward electric field of 5.0×10^5 V m^{-1}, the root mean square (RMS) roughness increased from 9.96 to 13.87 nm. The rough P3HT/PCBM blend provides more contact area with the electrode and can lead to lower series resistance; further, the *Jsc* of solar cells can be significantly increased. Instead, the treatment with a forward electric field increased the surface roughness of the blend layer, which led to decreasing *Jsc*.

The surface ratio of the polymer compositions in the devices was determined by ESCA to further analyze the reasons for morphology change in the electric field treatment. Using ESCA, the ratio of carbon and sulfur could be observed. Using the amount of sulfur, the amount of P3HT molecules could be calculated. The amount of carbons in PCBM could be calculated by removing the carbons of P3HT in all carbons. Then, the number of PCBM molecules was obtained. Multiplied by the molecular weight of each polymer, the weight ratio of the polymer compositions in the devices was determined. The weight ratio of the P3HT/PCBM on the surface is shown in Fig. 4.

The result of the ESCA measurement and calculation shows the weight ratio of P3HT will increase when treated with a backward electric field. The weight ratio of P3HT increased from 47% to 52% when the treating electric field was backward 5×10^5 V m^{-1} and decreased from 47% to

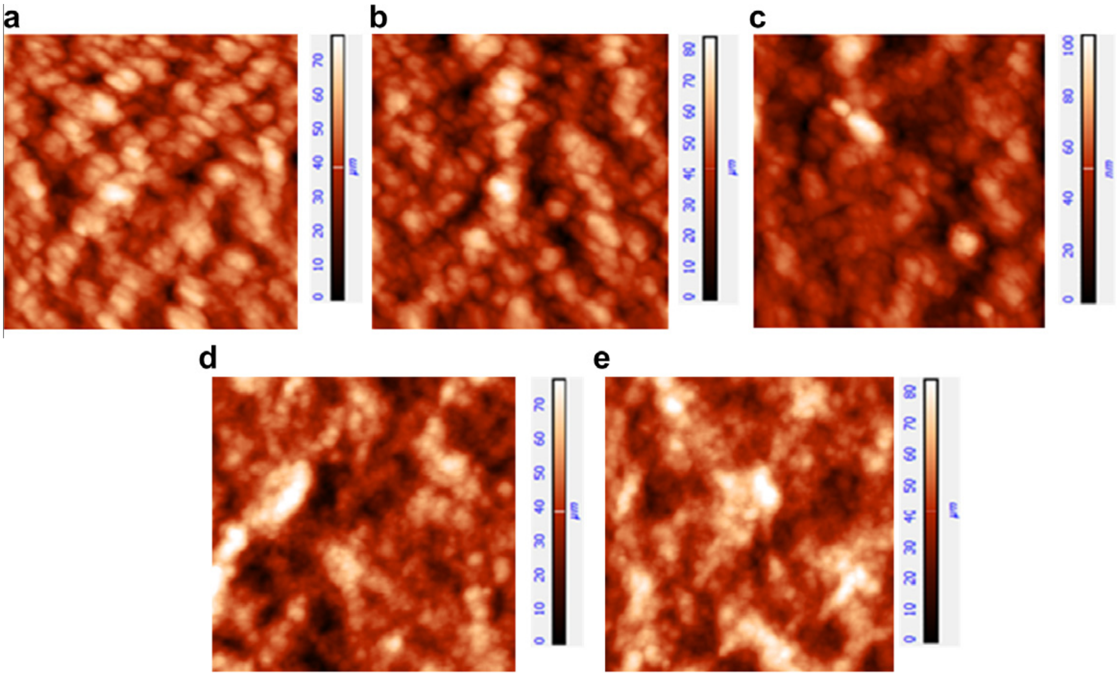

Fig. 3. AFM height images of the surface of P3HT:PCBM thin films (a) with no electric field treatment (rms roughness ~9.96 nm); (b) backward 2.5×10^5 V m^{-1} (rms roughness ~12.19 nm); (c) backward 5.0×10^5 V m^{-1} (rms roughness ~13.87 nm); (d) forward 2.5×10^5 V m^{-1} (rms roughness ~11.18 nm); (e) forward 5.0×10^5 V m^{-1} (rms roughness ~11.81 nm).

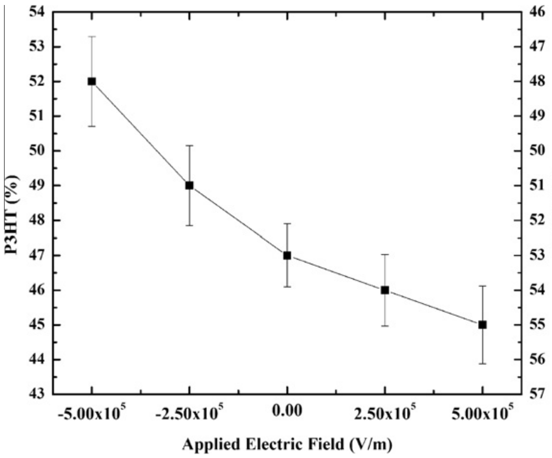

Fig. 4. The P3HT and PCBM molecules' weight ratio on the surface of the active layer after applied the vertical electric field treatment, where the horizontal axis shows the strength of the electric field, in which (−) is the symbol for backward and (+) indicates forward.

Table 2
The surface P3HT/PCBM weight ratio and roughness treated in different conditions.

Applied field (V/m)	RMS roughness (nm)	P3HT:PCBM	J_{SC} (mA cm^{-2})
Pristine film	9.96	47:53	9.147
2.5×10^5 (backward)	12.19	49:51	9.184
5.0×10^5 (backward)	13.87	52:48	9.829
2.5×10^5 (forward)	11.18	46:54	9.079
5.0×10^5 (forward)	11.81	45:55	8.786

45% when it was forward 5.0×10^5 V m^{-1}. In the process of fabricating inverted polymer solar cells, the anode is the Ag electrode. The ideal condition in the consideration of band theory is that P3HT lies closer to the Ag electrode than to PCBM. This may explain why both forward and backward electric fields could lead to surface roughness increase but the effects on *Jsc* are different. The electric-field treatments changed the vertical composition of the active layer and led to the variations of distribution between P3HT and PCBM. Both the P3HT-rich surface and the PCBM-rich surface could increase the surface roughness. In the inverted structure OSCs, the P3HT-rich surface would lead to better carrier transport. The surface P3HT/PCBM weight ratio and roughness of different conditions are shown in Table 2. In the forward bias condition, when the electric field was 5.0×10^5 V m^{-1}, the *Jsc* was 8.786 mA cm^{-2} and the P3HT:PCBM ratio was 45:55. For the reverse bias with an electric field of 5.0×10^5 V m^{-1}, the *Jsc* was 9.829 mA cm^{-2} and the P3HT:PCBM ratio was 52:48.

In recent studies, P3HT and PCBM had a vertical phase distribution in the active layer [23–25]. The tendency of the PCBM molecules is to distribute near the bottom, with P3HT near the top. However, PCBM molecules would form a cluster structure on the surface. When drying the P3HT:PCBM blend layer, P3HT molecules formed in crystals first. Then PCBM filled the vacancies by diffusion. The downward PCBM molecules tended to lie near the ZnO layer and the upward PCBM would diffuse to the surface to form clusters. Therefore, the active layer without treatment would have PCBM-rich distribution on the blend surface, leading to restriction of hole transport.

Some studies provided ways to solve the problem, for example, by using argon plasma to etch the PCBM clusters [26]. In this study, the treatment of the backward electric field also reduced the tendency for self-assembled PCBM clusters to form on the surface. Inducing the electric field causes the polarity of the organic polymer materials to align in an orderly fashion so that the PCBM molecules will disperse and not form cluster structures. The polarity direction of PCBM points to its fullerene structure. Thus, if treated with a backward electric field, the side chain of PCBM may be aligned upward, and this then restrains the diffusion of PCBM molecules to the top surface. In addition, the ratio of P3HT molecules increases after the backward electric field treatment. The schematic diagrams of P3HT:PCBM vertical separation after electric field treatment are shown in Fig. 5. The P3HT-rich surface provides more channels for holes to transport and thus reduced the probability of electron hole recombination. For this reason, the leakage of current, shunt resistance, and *Jsc* demonstrated better performance. On the other hand, treatment with a forward electric field had the opposite effect on the P3HT:PCBM vertical phase distribution. The effect was not conducive

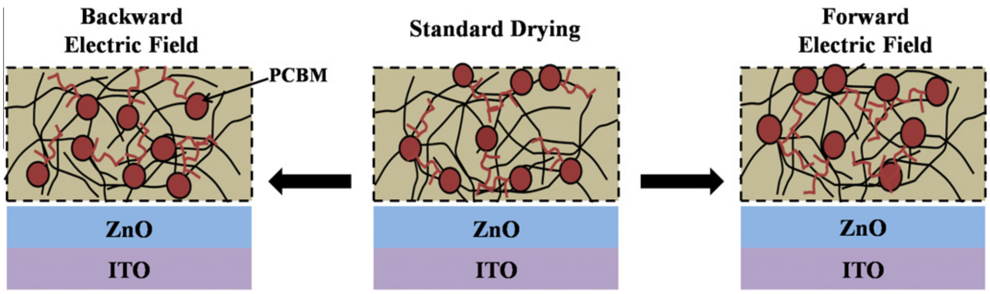

Fig. 5. The schematic representation of PCBM distributions adjacent to the top surface after treating with electric field. When treating with a backward electric field, the PCBM side chains are aligned upward and restrain the diffusion of PCBM molecules to the top surface. When treating with a forward electric field, it will have the opposite effect to the PCBM and still form a cluster structure on the surface.

to the bulk structure of inverted type polymer solar cells and decreased the devices' PCE.

4. Conclusion

In summary, the experimental results show that backward electric field treatment can improve the performance of P3HT:PCBM BHJ polymer solar cells. Applying the treatment on devices makes polymers arrange in a more orderly fashion and modulates the weight ratio of P3HT and PCBM molecules on the surface. It can form a P3HT-rich surface to improve the inverted polymer solar cells. Furthermore, the distribution also causes the surface to become rougher. The rough active layer provides more contact area with the electrode and improves the current transmission. After treatment by a backward electric field ($5.0 \times 10^5\ \mathrm{V\,m^{-1}}$), the devices had the largest RMS roughness of 13.87 nm, the current density improved from $9.15\ \mathrm{mA\,cm^{-2}}$ to $9.83\ \mathrm{mA\,cm^{-2}}$, and power conversion efficiency increased from 3.16% to 3.51%.

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