Effect of slow-solvent-vapour treatment on performance of polymer photovoltaic devices*

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In this work, enhanced poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk-heterojunction photovoltaic devices are achieved via slow-solvent-vapour treatment. The correlations between the morphology of the active layer and the photovoltaic performance of polymer-based solar cell are investigated. The active layers are characterized by atomic force microscopy and optical absorption. The results show that slow-solvent-vapour treatment can induce P3HT self-organization into an ordered structure, leading to the enhanced absorption and efficient charge transport.

Keywords: polymer solar cell, solvent-vapour treatment, self-organization
PACC: 8630J, 6855, 4270

1. Introduction

Polymer photovoltaic (PV) devices have attracted considerable attention because of their unique advantages including low-cost fabrication, easy processing, mechanical flexibility and versatility of chemical structure.[1] Power conversion efficiency (PCE) has steadily increased over the past decade, and achieved 7.73% recently reported for devices based on a bulk-heterojunction of polymer and methanofullerene blends.[2] Of all the polymeric systems reported in the literature for the fabrication of bulk-heterojunction cells, the poly (3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) blend represents the state-of-art.[3−5]

Many studies showed that the nanoscale phase-separation morphology, which itself depends on the fabrication processes, plays a decisive role in the optoelectronic properties and device performance.[6] A number of approaches to the control of the blend morphology have been developed, including both deposition and post-deposition procedures, for example, thermal and electrical annealing,[5−10] appropriate solvent choice,[11,12] slow drying of spin-coated films,[3,13,14] melting of bilayers,[15] and solvent vapour annealing of blends.[16−18] In this work, spin-coated P3HT:PCBM blend layers are treated with different organic solvent vapours to enhance the self-organization of P3HT chains and phase separation of the blend. The results indicate that the slow-solvent-vapour treatment can induce P3HT self-organization into ordered structure, which enhances optical absorption and efficient charge transport. The devices with the slow-solvent-vapour treated active layers present enhanced PCE. Simultaneously, the effects of different organic solvent vapours on the morphology of P3HT:PCBM blend films are investigated.

2. Experiment

The PV devices used in this experiment were fabricated by spin-coating and thermal evaporation on indium tin oxide (ITO) glass substrates with a sheet resistance of 30 Ω/□. The ITO substrates were first cleaned in an ultrasonic bathes with detergent, alcohol, and deionized water, and then treated with an ultraviolet lamp for 5min. The cleaned substrates were spin-coated with a 40 nm film of poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS), and dried at 140 °C for 10 min in

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air. Subsequently, the solution of P3HT:PCBM (1:1 in weight) in 1,2-dichlorobenzene (DCB) was spun on the top of the PEDOT:PSS layer. The samples were transferred into a sealed container filled with organic solvent vapour and stayed for 6 h. Organic solvents including chlorobenzene (CB) and DCB were used in this study. Finally, the cathode aluminum (Al) was deposited through a shadow mask on the top of the active layer by thermal evaporation at a pressure of less than 10^{-3} Pa. The shadow mask determined an active area of 3 mm× 3mm. Post-thermal annealing was carried out at 140° for 10 min on a hot plate inside a vacuum chamber.

All the devices were illuminated through ITO electrode, and the forward bias was defined as positive voltage applied to the ITO electrode. Current–voltage curves were recorded by a Keithley 2410 Source Measure Unit under illumination. A xenon lamp with an illumination intensity of 86 mW/cm^2 was used as an illumination source. The atomic force microscopy (AFM) images were measured by Digital Instruments Nanoscope IIIa. UV/V is absorption spectra were measured on a UV-3101 PC UV–VIS–NIR Scanning Spectrophotometer.

3. Results and discussion

Figure 1 shows the photocurrent density–voltage (J–V) curves under 86 mW/cm^2 white-light illumination for the PV devices with P3HT:PCBM active layer treated in different solvent vapours. The performances of these devices are summarized in Table 1.

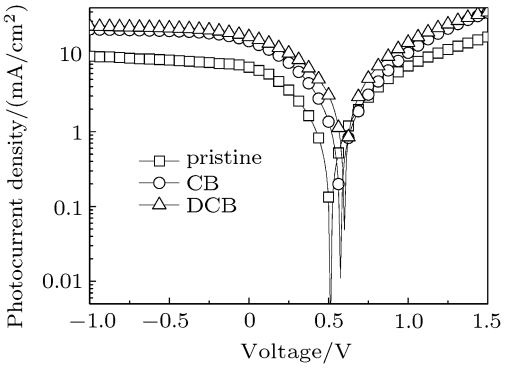


Fig. 1. J–V curves of the PV cells treated with different organic solvent vapours.

The devices with the active layers of P3HT:PCBM blend treated in solvent vapour behave better than the device with as-spun active layer. The short circuit current density (J_{sc}) of the PV devices with solvent-vapour treatment can increase more than twofold. And the open circuit voltage (V_{oc}) also shows significant enhancement. The PCEs of the PV devices treated by CB and DCB vapours are enhanced about 2.3 and 3.1 times, respectively.

In order to further elucidate the effects of solvent vapour treatment on the morphology of P3HT:PCBM films, the microstructures of the P3HT:PCBM blend films were studied via measuring AFM and UV–V is absorption spectra.

Table 1. Summary of the performances of the PV cells with the active layers treated with different solvent vapours under white light illumination with an intensity of 86mW/cm^2.

	V_{oc}/V	J_{sc}/(mA/cm^2)	FF	PCE/%
pristine	0.525	7.28	0.239	1.06
CB	0.575	16.2	0.223	2.42
DCB	0.600	18.5	0.257	3.32

Figure 2 shows the AFM height images of the P3HT:PCBM blend films without and with solvent-vapour treatment. For the as-spun film, PCBM molecules disperse well in P3HT and the P3HT:PCBM blend film shows smooth surface. But the P3HT:PCBM films treated by solvent vapour are much rougher. The root-mean-square (rms) roughness of the as-spun, CB and DCB vapour treated films are 0.62, 2.62 and 2.71 nm in a 2 μm×2 μm scan area, respectively. Normally, the increase in roughness is attributed to polymer self-organization and phase separation of the blend.[3] P3HT chains self-organization into ordered structure can significantly enhance the hole mobility.[19−22] Meanwhile, the aggregation of PCBM molecules can form separate paths for electron transport.[16] The vertical phase separation can finally result in the enhancement of J_{sc} of the PV devices.[23] It can be demonstrated that crystallization induced by slow-solvent-vapour treatment controls the nanoscale organizations of P3HT and PCBM in the photoactive layers. And then a large interfacial area for efficient charge generation and the crystalline order for improving charge transport are obtained.[20,21,24]

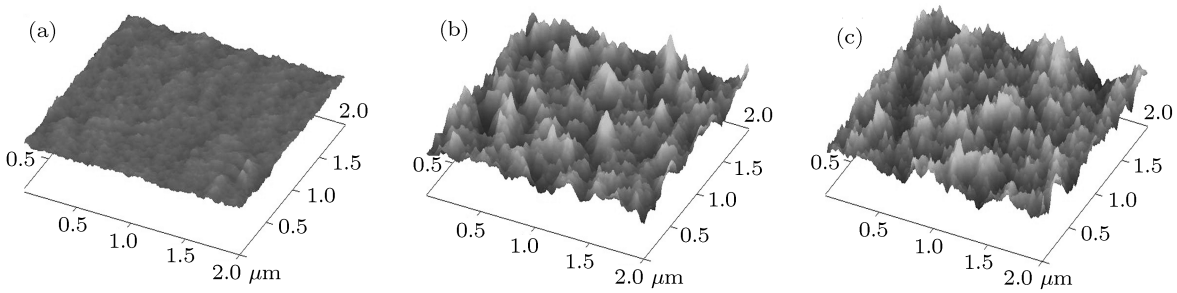


Fig. 2. AFM height images of (a) as-spun P3HT:PCBM film, (b) CB-vapour treated P3HT:PCBM film, and (c) DCB-vapour treated P3HT:PCBM film.

The AFM phase images of the P3HT:PCBM thin films are shown in Fig. 3. The phase image of the as-spun film (Fig. 3(a)) shows a smooth surface, in which the phase separation is not obvious. But the CB vapour treated film (Fig. 3(b)) features coarse chain-like fibrils running across the surface, which represent P3HT crystallites. The region between these features is a disordered region which may accumulate disordered P3HT and PCBM molecules.[19] Furthermore, the fibrils are thicker and the interspace between two fibrils is bigger. And for the DCB vapour treated film (Fig. 3(c)), the crystalline domains of pure P3HT chains are much more ordered and denser. The fibrils are thinner and the separation distance between the fibrils is also less, which suggests tighter packing of P3HT crystallites in the DCB vapour treated film. The reduced crystallite size and inter-crystallite spacing are believed to be the consequence of higher ordering,[19] which is the main reason for the highly improved performance of the PV devices with DCB vapour treated active layers.

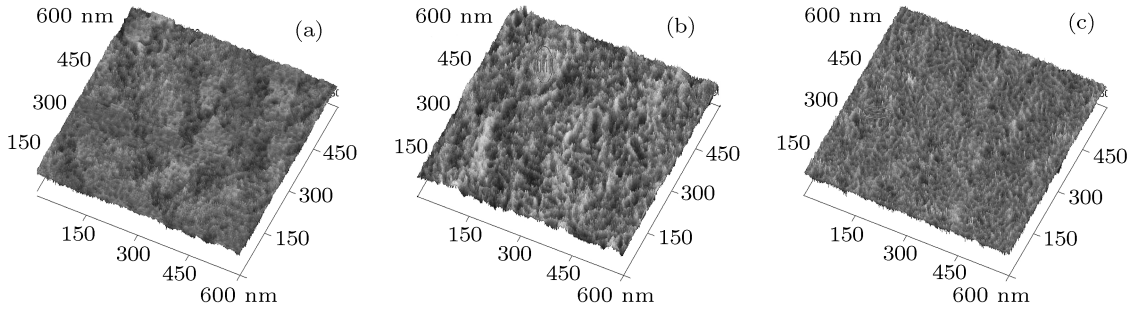


Fig. 3. AFM phase images of (a) as-spun P3HT:PCBM film, (b) CB-vapour treated P3HT:PCBM film, and (c) DCB-vapour treated P3HT:PCBM film.

Figure 4 shows the UV–V is absorption spectra of the P3HT:PCBM blend films. For the blend film treated by CB vapour, its profile of absorption spectrum is roughly the same as that of the as-spun film. However, some distinguishable differences are still found. After treatment of CB vapour, the intensity of the peak approximately at 550 nm, which represents the intrinsic $\pi - \pi^*$ transitions of P3HT,[17,19] obviously increases. The peak at 600 nm, associated with the interchain interaction,[17,19] also increases, which implies an enhancement in molecular ordering. For the blend film treated by DCB vapour, the absorption intensity of PCBM significantly increases compared with that of P3HT, which may be correlated to the blend film morphology.

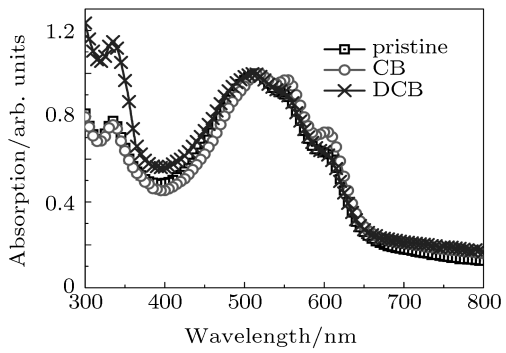


Fig. 4. UV–Vis absorption spectra of the P3HT:PCBM films treated in slow-solvent-vapour treated with different organic solvents.

4. Conclusion

The performance of the PV devices based on P3HT:PCBM blend can be obviously enhanced by slow-solvent-vapour treatment. An improved film morphology and self-organized P3HT are obtained. Different solvent vapours can induce different morphologies of the blend films, which directly influences the performances of the PV devices.

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