

CONTROLLING THE SURFACE COMPOSITION OF PCBM IN P3HT/PCBM BLEND FILMS BY USING MIXED SOLVENTS WITH DIFFERENT EVAPORATION RATES*

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Abstract The surface composition of poly(3-hexylthiophene-2,5-diyl) and fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (P3HT/PCBM) blend films could be changed by controlling the film formation process *via* using mixed solvents with different evaporation rates. The second solvent, with a higher boiling point than that of the first solvent and much better solubility for PCBM than P3HT, is chosen to mix with the first solvent with a lower boiling point and good solubility for both PCBM and P3HT. The slow evaporation rate of the second solvent provides enough time for PCBM to diffuse upwards during the solvent evaporation. Thus, the weight ratio of PCBM and P3HT ($m_{\text{PCBM}}/m_{\text{P3HT}}$) at surface of the blend films was varied from *ca.* 0.1 to *ca.* 0.72, *i.e.*, it increases about seven times by changing from single solvent to mixed solvents. Meanwhile, the mixed solvents were in favor to form P3HT nanofiber network and enhance phase separation of P3HT/PCBM blend films. As a result, the power conversion efficiency of the device from mixed solvents with slow evaporation process was about 1.5 times of the one from single solvents.

Keywords: P3HT; PCBM; Surface composition; Mixed solvents; Slow evaporation.

INTRODUCTION

Polymer and small molecule blend films have attracted much attention because of their application in many fields such as organic electronics and photovoltaics^[1], coatings^[2] and adhesives^[3]. Many different structures have been reported in the literature for different blend systems and different methods with both lateral and vertical segregation on the nano- to micrometer scale. Actually, vertical segregation is common for polymer and small molecule blend films. There are two driving forces can cause vertical segregation, one is surface energy and the other is entropic-push. If there is very different surface energies of the two materials, the one with the high surface energy will segregate at the substrate interface^[4]. If the two components are miscible, entropy drives small molecules to segregate at the substrate interface^[5].

Polymer and fullerene or fullerene-derivative mixtures are one of the most promising materials in terms of efficiency and stability in polymer solar cells. Among them, regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) and fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (C61-PCBM) are respectively one of the most important donor and acceptor materials. Recently, some groups have found that P3HT is enriched at the cathode interface and PCBM enriches at the anode interface of as spun films, due to the different surface energies of the two materials ($\gamma_{\text{PCBM}} = 37.8 \text{ mN/m}^2$, $\gamma_{\text{P3HT}} = 26.9 \text{ mN/m}^2$). ToF-SIMS^[6, 7], XPS^[8], VASE^[9] and

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neutron reflectivity^[10, 11] are used to characterize the surface or vertical structure of P3HT/PCBM blend films. A surface layer is relatively depleted in PCBM, while it is relatively rich in PCBM at the substrate interface. It is the inverted not the normal device architecture that is beneficial. It is surface-segregated PCBM not P3HT that can serve as a hole-blocking layer at the Al interface to reduce the electron extraction^[12] and enhance the internal quantum efficiency^[13].

The adverse surface-segregation can be suppressed by the way of traditional treatment, for example, thermal annealing and solvent vapor annealing^[13], but the effect is not notable. Other two approaches have been widely investigated^[14]. One is controlling the total energies, introduction of some acceptor materials with low surface energy^[15, 16] or surface treatment reducing the differences between interface energies^[17–19]. The other is controlling the kinetics of the process during the film formation^[20]. Actually, crystallization-induced vertical stratified structures can be constructed based on double-crystalline polymer systems^[21, 22]. Unfortunately, this method was not suitable in P3HT/PCBM blend films. In addition, the grad structure of bi-layer film has also been employed to obtain suitable vertical structure^[23–26].

However, little is known about the kinetics during the film formation. Time-resolved small-angle light scattering and light reflectivity^[27, 28] had revealed the structure evolution of a blend of two polymers during the spin-coating process. First vertical stratification formed, and then the interface between the stratified layers becomes unstable, leading to the final phase-separated thin film. It showed that desirable morphologies could be achieved by designing rational processing conditions. In this paper, mixed solvents with different evaporation rates, are applied to change the surface composition of P3HT/PCBM blend films. The second solvent, with a higher boiling point than that of the first solvent and much better solubility for PCBM than P3HT, carries PCBM molecules upwards after the first solvent evaporate. The slow evaporation process of film formation provides enough time for PCBM to diffuse upwards with the second solvent evaporation.

EXPERIMENTAL

Materials

Regioregular HT-HT P3HT (> 98.5%; HT: head-to-tail; M_n = 68 kDa) was purchased from Sigma-Aldrich Co. Ltd. PCBM with purity of 99% was purchased from Solenne Co. and used as received. Chlorobenzene (Beijing Chemical, China), acetophenone (Beijing Chemical, China) and chloronaphthalene (Sigma-Aldrich) were also used as received. Tetralin (Beijing Chemical, China) was purified before use.

Sample Preparation and Photovoltaic Devices

The solution used in this study for spin-coating active layer was prepared as following: P3HT and PCBM (1:1, W/W) were dissolved in chlorobenzene to make total 20 mg mL⁻¹ solution, followed by blending with the second solvent (tetralin, acetophenone or chloronaphthalene). The volume ratio of chlorobenzene and second solvent is 1:0.05. This solution was stirred for 12 h at room temperature in dark. The slow evaporated films were spin coated at 500 r/min and 10 s, and the fast evaporated ones were at 2000 r/min 30 s, and then placed on horizontal plate until the films were dried. The films were placed in vacuum more than 12 h after being dried.

The photovoltaic devices were prepared on glass/ITO substrates. The substrates were cleaned by ultrasonic treatment in detergent and deionized water, and then etched by oxygen plasma for 2.5 min. 45-nm-thick poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P4083) was deposited by spin-coating (2500 r/min and 60 s) and then dried for at 120 °C for 40 min. The solution of P3HT and PCBM was spin-coated as described above. Finally, the samples were transferred into an evaporator, 1-nm-thick LiF and 80-nm-thick Al electrodes were deposited by evaporation, respectively. The active surface area of typical device is 0.12 cm².

Characterization

The surface composition was measured by X-ray photoelectron spectroscopy. XPS experiments with argon sputtering were measured with a VG ESCALAB MK II instrument at room temperature by using an Al K α monochrom ($h\nu$ = 1486.6 eV) at 14 kV and 20 mA. The sample analysis chamber of the XPS instrument was

maintained at a pressure of 8×10^{-8} Pa.

The contact angles of water on the blend films were measured on a KRÜSS DSA10-MK2 (KRÜSS GmbH, Germany) drop shape analysis (DSA) system at ambient temperature.

The blend thin films UV-Vis absorption spectra were recorded with a Lambda 750 spectrometer (Perkin-Elmer, Wellesley, MA).

The morphology of P3HT films was characterized using atomic force microscopy (AFM) and transmission electron microscopy (TEM). AFM was used to study the surface topography of the films. Images were obtained using a SPI3800N AFM (Seiko Instruments Inc., Japan) with a Si tip with a spring constant of 2 N/m. The cantilevers were operated slightly below their resonance frequency of around 72 kHz. The image acquisition was performed at ambient condition. The AFM was used in tapping mode to reduce tip-induced surface degradation and sample damages. TEM was used to probe vertical direction information of P3HT film. Images were obtained using a JEOL JEM-1011 transmission electron microscope operated at 100 kV. Thin films were first floated on deionized water and then transferred onto copper grid. The samples were dried at room temperature for 12 h before TEM experiments.

Current density-voltage (J - V) curves of the photovoltaic devices under white light illumination were measured using a computer-controlled Keithley 236 source meter.

RESULTS AND DISCUSSION

The process of film formation is crucial to the surface composition of the blend films, which is controlled by the solvent evaporation rates. In this paper, mixed solvents with different evaporation rates (The solvents with high boiling point, tetralin, chloronaphthalene and acetophenone, were used to mix with chlorobenzene, as listed in Table 1) were chosen to change the surface composition of P3HT/PCBM blend films.

Table 1. The properties of the solvents

	Boiling point (°C)	Viscosity $\times 10^3$ (Pa·s)
Chlorobenzene	132	0.799 (20 °C)
Tetralin	207	2.02 (20 °C)
Chloronaphthalene	259	2.94 (25 °C)
Acetophenone	202	1.9 (20 °C)

X-ray photoelectron spectroscopy (XPS) was carried out to analyze the surface composition of P3HT/PCBM blend films. The weight or molar ratio of the components can be calculated directly from the peak intensities of individual elements. However, due to the short mean free path of the photoelectrons, the probing depth of XPS is only 6–8 nm. Figure 1 shows the XPS spectra of the P3HT/PCBM blend films prepared from chlorobenzene with slow evaporation or fast evaporation process, and from chlorobenzene/tetralin with slow evaporation or fast evaporation process. The peaks at *ca.* 164 eV and *ca.* 285 eV are attributed to the S 2p and C 1s, respectively. The weight ratio at surface of P3HT/PCBM blend films can be determined from the C/S atomic ratio obtained from XPS:

$$\frac{m_{\text{PCBM}}}{m_{\text{P3HT}}} = \frac{M_{\text{PCBM}} \times (N_{\text{C}} - 10N_{\text{S}}) \div 72}{M_{\text{P3HT}} \times N_{\text{S}}} = \frac{M_{\text{PCBM}}}{M_{\text{P3HT}} \times 72} \times \frac{I_{\text{C}} - 10I_{\text{S}}}{I_{\text{S}}} \quad (1)$$

where I is the peak area of elements in XPS, N_{C} and N_{S} are the number of carbon atoms and sulfur atoms and $N_{\text{C}}/N_{\text{S}}$ is equal to $I_{\text{C}}/I_{\text{S}}$, M_{PCBM} and M_{P3HT} are the molar mass of PCBM and repeat unit of P3HT, 10 comes from the mole ratio of carbon atoms and sulfur atoms in P3HT, and 72 is the number of carbon atoms in one PCBM molecule. The value of $m_{\text{PCBM}}/m_{\text{P3HT}}$ at surface of the blend films was different from different mixed solvents (tetralin/chlorobenzene, chloronaphthalene/chlorobenzene and acetophenone/chlorobenzene) (Table 2). With the same evaporation rate, the films deposited from chlorobenzene/chloronaphthalene and chlorobenzene/acetophenone solution had much lower PCBM concentration at surface of the blend films (0.09 and 0.20,

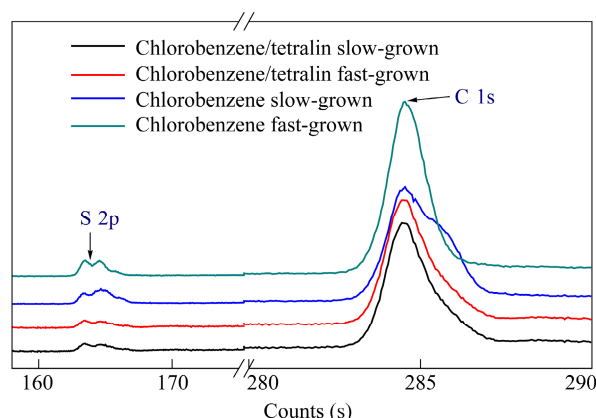


Fig. 1 Spectra of X-ray photoelectron spectroscopy (XPS)

Table 2. The weight ratio of PCBM and P3HT ($m_{\text{PCBM}}/m_{\text{P3HT}}$) at blend films' surface obtained from X-ray photoelectron spectroscopy

	Chlorobenzene		Chlorobenzene/Tetralin		Chlorobenzene/ Chloronaphthalene	Chlorobenzene/ Acetophenone
	Fast evaporation	Slow evaporation	Fast evaporation	Slow evaporation	Slow evaporation	Slow evaporation
$N_{\text{C}}/N_{\text{S}}$ (Glass)	11.9	10.7	12.0	19.5	11.2	12.4
$m_{\text{PCBM}}/m_{\text{P3HT}}$ (Glass)	0.14	0.05	0.15	0.72	0.09	0.20
$N_{\text{C}}/N_{\text{S}}$ (PEDOT:PSS)	12.4	10.8	10.9	18.0	—	—
$m_{\text{PCBM}}/m_{\text{P3HT}}$ (PEDOT:PSS)	0.18	0.06	0.072	0.61	—	—

respectively) than that from chlorobenzene/tetralin (0.72). Actually, tetralin and chloronaphthalene had better solubility for PCBM than acetophenone. But tetralin had poorer solubility for P3HT than chloronaphthalene^[29–31]. Thus, tetralin had the biggest difference between the solubility for the two constituents. So the high boiling point solvent chosen here should have much better solubility for PCBM than for P3HT. Except the solubility for P3HT and PCBM, solvent evaporation rate also played important roles in the value of $m_{\text{PCBM}}/m_{\text{P3HT}}$. It was *ca.* 0.1 regardless of the solvent evaporation rate when the films were spin coated from single solvent, chlorobenzene. The low ratio meant there was mainly P3HT at the film surface. On the contrary, the surface composition was dependent on the process of film formation when the film was spin coated from chlorobenzene/tetralin. The weight ratio at surface of the slow evaporated films was *ca.* 0.72, which was much higher than that of the fast evaporated one (0.072). The films from chlorobenzene/acetophenone were taken as another example. Figure 2 shows the change of surface composition with evaporation rate when acetophenone was used as the second solvent. The surface composition ratio of PCBM and P3HT decreased as the evaporation rate increased (from *ca.* 0.2 to *ca.* 0.08). Thus, the solvent slow evaporation during the film formation is also crucial to high surface composition ratio of PCBM and P3HT. In summary, there are two factors to increase surface segregation of PCBM. One was the second solvent had high boiling point and much better solubility for PCBM than for P3HT. The another was the slow evaporation rate during the process of films formation.

The static contact angles of water on the blend films were also measured to prove the change of surface composition of the blend films (Table 3). The contact angles of water on P3HT and PCBM were 108.34° and 89.13°, respectively. There were almost the same contact angles on the blend films prepared from chlorobenzene as the P3HT film no matter with the film formation process. It is attributed to the surface segregation of P3HT of these films as shown by XPS. But when the films were spin coated from chlorobenzene/tetralin, the contact

angles were dependent on the process of film formation. It was 103.4° , smaller than P3HT film, if the film formed with slow evaporation rate. It is believed the highest PCBM concentration at the film surface results in the smallest contact angle.

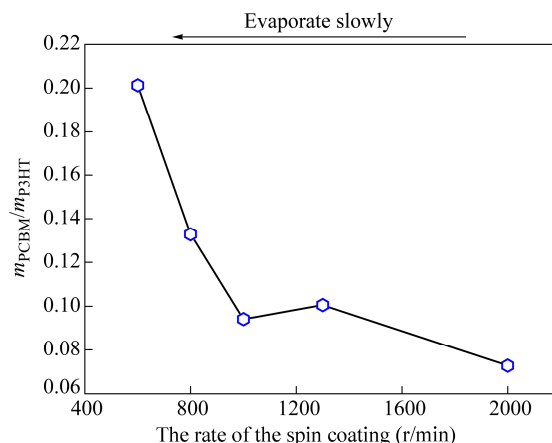


Fig. 2 The dependence of surface composition of P3HT/PCBM films ($m_{\text{PCBM}}/m_{\text{P3HT}}$) prepared from chlorobenzene/acetophenone on the spin coating rate

Table 3. Static contact angles of water on P3HT, PCBM and P3HT/PCBM blend films with fast and slow evaporation from chlorobenzene and chlorobenzene/tetralin

Film	P3HT (Chlorobenzene)	Chlorobenzene		Chlorobenzene/Tetralin		PCBM (Chlorobenzene)
		Fast evaporation	Slow evaporation	Fast evaporation	Slow evaporation	
Contact angle	108.3°	109.6°	108.8°	108.8°	103.4°	89.1°

The surface composition of P3HT/PCBM blend films deposited on PEDOT:PSS was almost the same as the ones deposited on glass (Table 2). The highest weight ratio at surface, about 0.65, was attributed to the slow evaporated film deposit from mixed solvent, in accordance with the films deposit on the glass. It means the PEDOT:PSS and glass, both hydrophilic substrates, had the same effect on the surface composition of P3HT/PCBM blend films in our results.

The effect of solvent and evaporation rate on surface composition of a polymer blend is discussed in terms of the solubility, phase separation and aggregation behaviors of two polymer components in a blend. First, the system transforms from one phase into two phases with the evaporation of solvent during the process of films formation. In this case, the first solvent, chlorobenzene, evaporated quickly, remaining the second solvent with high boiling point in the films. Because of much better solubility for PCBM than P3HT, most PCBM dissolved in the second solvent while P3HT began to precipitate. As a result, two phases appeared, a solid P3HT phase and a liquid phase including most PCBM molecules, few P3HT molecules and the second solvent. Then the diffusion of PCBM molecules in the liquid phase played an important role on surface-separation. According to the diffusion equation developed by Cahn and Hilliard^[14]:

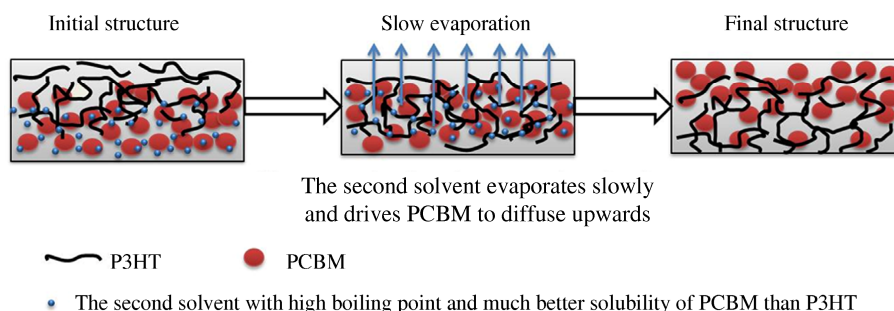
$$\phi - \bar{\phi} = \sum_{\beta} \{ \exp[R(\beta)t] \} [A \cos(\beta r) + B \sin(\beta r)] \quad (2)$$

where ϕ is the composition, $\bar{\phi}$ is the average, uniform concentration, β is the wave number of the sinusoidal composition fluctuation, r is the position variable, A and B are β -dependent parameters and

$$R(\beta) = -M\beta^2 [D + 2K\beta^2] \quad (3)$$

is the Rayleigh kinetic growth factor and M is the mobility parameter. According to Eqs. (2) and (3), the mobility

parameter, M , is crucial to the phase separation and can be manipulated by viscosity of the solution and drying conditions during the process of films formation. Because of better solubility for PCBM in the second solvent, the mobility parameter, M , increases in the liquid phase. Meanwhile, the solvent evaporated from the surface not the edges of the film. Furthermore, it allowed more time for molecules to be mobile and phase separate due to the high boiling point of the second solvent. Thus, PCBM molecules can diffuse upwards with the second solvent evaporation, resulting in a higher weight ratio at surface of PCBM and P3HT. This process is schematically given in Scheme 1. In a word, during the film formation, the second solvent drives PCBM molecules to upwards and slow evaporation of films formation provides enough time for PCBM to diffuse.



Scheme 1 P3HT/PCBM film formation process with mixed solvent and slow solvent evaporation

The crystallinity of P3HT is improved by mixed solvent. The UV-Visible absorption spectra clearly showed two peaks: one at 332 nm corresponds to the PCBM, the other peaks between 490 nm and 607 nm represent the P3HT (Fig 3). Among them the first peak is the absorption of P3HT main chain and the peak at 607 nm comes from the interchain transition of P3HT. The films prepared from mixed solvent had a red shift from 490 nm to 517 nm and two vibronic absorption shoulders at 558 nm and 607 nm were more distinct than the ones from single solvent. It means the crystallinity of P3HT was improved in the films from mixed solvent.

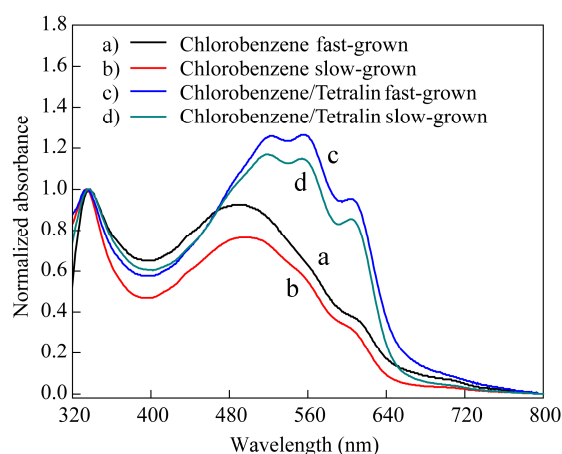


Fig. 3 UV-Vis absorption spectra for P3HT/PCBM films prepared from chlorobenzene/tetralin and chlorobenzene with different formation process

The morphologies of P3HT/PCBM films were also influenced by solvents, independent of the film formation conditions. Figures 4(a)–4(d) are the AFM phase images of the different films as discussed above. All of the film surfaces are covered by short nanofibers, formed by P3HT. But when the films were prepared from chlorobenzene/tetralin with slow evaporation rate, the nanofibers didn't arrange as tightly as others. We believe the high surface composition of PCBM disrupted the arrangement of nanofibers. Figures 4(a')–4(d') are the bright-field transmission electron micrographs of P3HT/PCBM blend films. Because PCBM (1.5 g/cm^3) has a

higher density than P3HT (1.1 g/cm^3), the dark and light region in TEM images respectively represented PCBM and P3HT domains. In bright-field TEM, the P3HT nanofiber networks, concerned with photon absorption and hole transport^[32], were present in the films from mixed solvents while not in the films from single solvent. Meanwhile, the phase separation was more obvious in the films from mixed solvents than the ones from single solvent. It is concluded that mixed solvents are in favor to form P3HT nanofiber network and enhance phase separation.

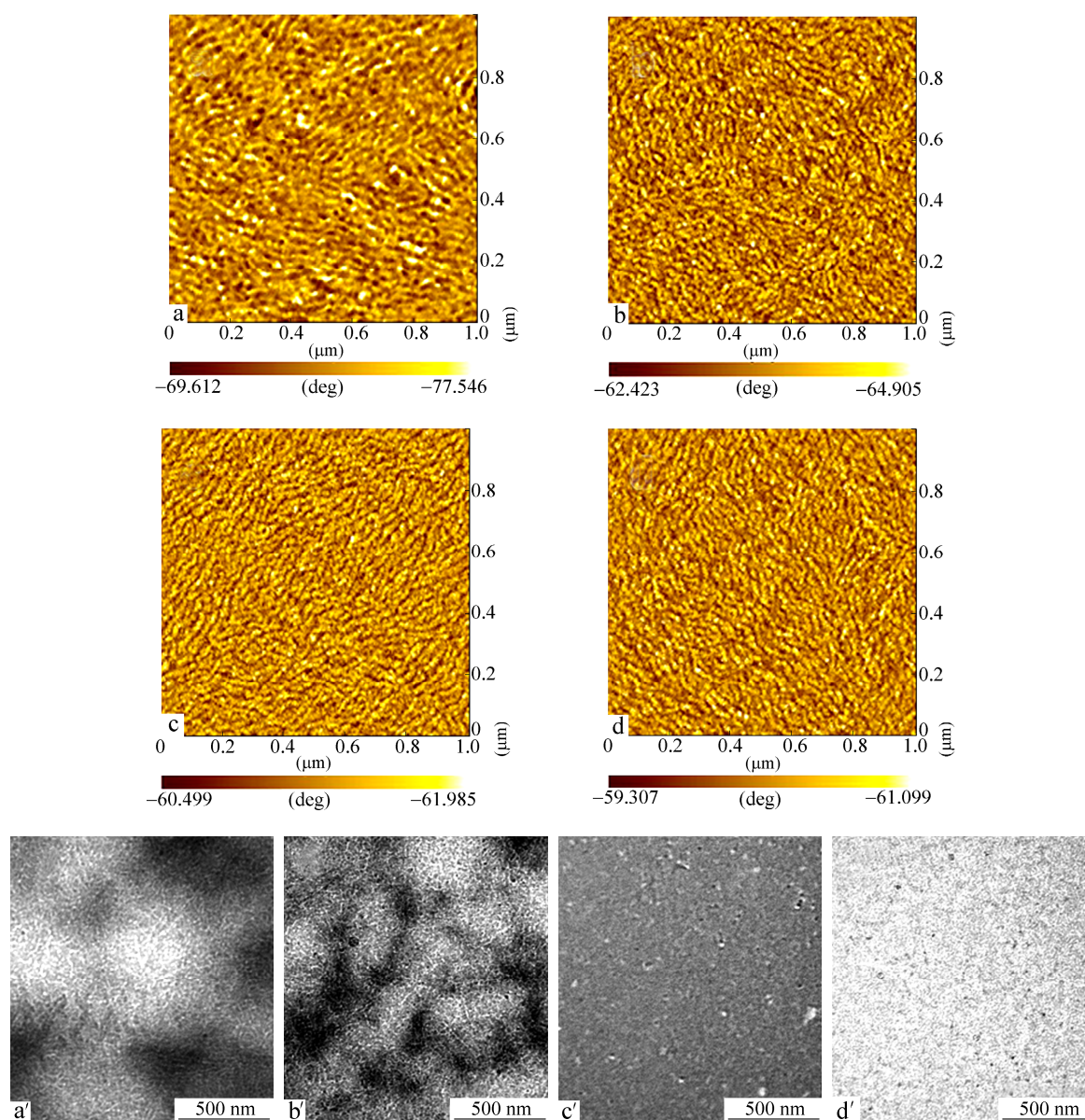


Fig. 4 Atomic force microscope phase images (a, b, c, d) and transmission electron microscope images (a', b', c', d') of P3HT/PCBM blend films prepared from chlorobenzene/tetralin with slow evaporation (a, a') and fast evaporation (b, b') and from chlorobenzene with slow evaporation (c, c') and fast evaporation (d, d')

Photovoltaic devices based on P3HT/PCBM blend films were made according to standard ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al architecture. The current density-voltage (J - V) curves of the devices,

prepared from chlorobenzene with slow evaporation or fast evaporation process, chlorobenzene/tetralin with slow evaporation or fast evaporation process, are shown in Fig. 5. There was no post-treatment or other optimization in these devices, so the performances were lower than the ones in other papers. The device, from chlorobenzene/tetralin with slow evaporation process, had the highest short-circuit current ($J_{SC} = 5.76$) and fill factor ($FF = 0.60$). The power conversion efficiency ($PCE = 1.96\%$) of it was almost three times of the one with fast evaporation process (0.67%) and about 1.5 times of the one from chlorobenzene solution (1.26%). We attributed it to the high surface segregation of PCBM and P3HT nanofiber network as discussed above.

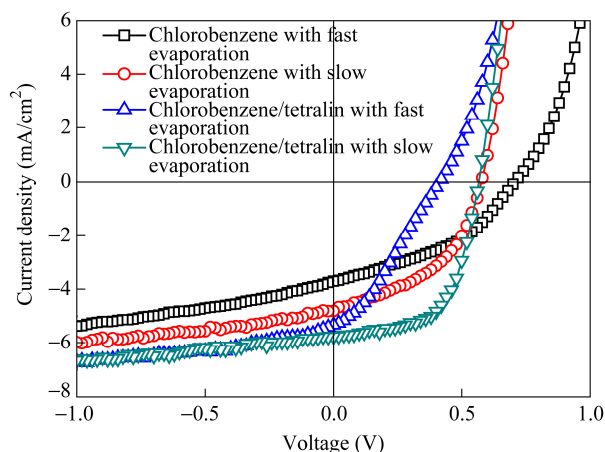


Fig. 5 J - V curves of P3HT/PCBM devices with films prepared from chlorobenzene/tetralin and chlorobenzene solutions with different film formation processes

CONCLUSIONS

In this paper, mixed solvents with a second solvent of slow evaporation rate, are applied to controlling the process of the film formation and change the surface composition of P3HT/PCBM blend films. The second solvent, with high boiling point and much better solubility for P3HT, can increase the mobility of PCBM molecules and drive PCBM molecules to move upwards. Slow evaporation provides enough time for PCBM to diffuse. As a result, the weight ratio of PCBM and P3HT (m_{PCBM}/m_{P3HT}) at surface of the blend films changed from *ca.* 0.1 to *ca.* 0.72, when films were prepared by chlorobenzene/tetralin with slow evaporation. Meanwhile, the mixed solvents are in favor to form P3HT nanofiber network and enhance phase separation of P3HT/PCBM blend films. As a result, the power conversion efficiency of the device using films from chlorobenzene/tetralin with slow evaporation process, was almost 1.5 times of the ones from chlorobenzene solution.

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