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Performance Characteristics of Polymer Solar Cells with an Additive-Incorporated Active Layer

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*Bulk heterojunction (BHJ) polymer solar cells, based on phase-separated blends of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl C₆₁butyric acid methyl ester (PCBM) as an active layer, have been fabricated. During active layer forming process, single solvent, chlorobenzene or 1,2-dichlorobenzene, and a processing additive, 1,8-octanedithiol or 1,8-diiodooctane, were introduced. The effects of additives on the performance characteristics of polymer solar cells have been discussed based on the results from current density-voltage (*J-V*) measurements, UV-Vis absorption, X-ray diffraction spectra (XRD), and scanning probe microscope (SPM). At the presence of processing additives, the performance characteristics of polymer solar cells have been significantly improved and the peaks in UV-Vis absorption band of P3HT:PCBM films were apparently red-shifted, resulting in the enhancement of device efficiency due to the red-shifted absorption band. Furthermore, well ordered polycrystalline structure of P3HT molecules positively affected on the device efficiency in this work.*

Keywords Additive; P3HT; PCBM; PEDOT:PSS; polymer solar cells

Introduction

Clean and renewable energy have been considerable issues in the last decade. For this reason, organic photovoltaic cells have been attractive devices as next generation substitute energy sources [1–4]. Currently, the power conversion efficiencies of organic photovoltaic cells have been steadily improved around 6% through polymer solar cells [5]. There have been reports that polymer solar cells have many advantages of cost effectiveness in fabrication process and a wide field of applications due to the mechanical flexibility and low weight of polymer materials [6,7].

Bulk heterojunction (BHJ) solar cells, based on phase-separated blends of polymer semiconductors and fullerene derivatives, typically consist of conjugated polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT) as electron donor and fullerene derivatives, [6,6]-phenyl C₆₁butyric acid methyl ester (PCBM) as electron acceptor [8–12]. Especially, P3HT has attracted lots of interest due to the high crystallinity and self-assembling property. For supporting P3HT crystallite formation, PCBM

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should be dispersed between P3HT chains [13]. For this, thermal and solvent annealing can be used to improve their roles between P3HT and PCBM [14,15]. Recently, a small volume ratio of additives such as 1,8-octanedithiol has been incorporated into P3HT:PCBM system to achieve improved interactions between P3HT and PCBM [16].

In this work, we have fabricated BHJ solar cells based on P3HT and PCBM, which were dispersed using single solvent, chlorobenzene and 1,2-dichlorobenzene. The effects of additives, 1,8-octanedithiol and 1,8-diiodooctane, on the performance characteristics of polymer solar cells have been investigated. The results of current density-voltage (J-V) measurements, UV-V is absorption, X-ray diffraction spectra (XRD), and scanning probe microscope (SPM) will be intensively used to discuss the performance characteristics of polymer solar cells fabricated in this study.

Experimental

BHJ films were prepared via solution process. P3HT (Rieke Metals) and PCBM (Nano-C) with 1:1 wt/wt ratio was dissolved in chlorobenzene and 1,2-dichlorobenzene to make 2.4 wt% solution. The blend solution was stirred for 24 hr at 40°C in a shaking incubator. 1,8-octanedithiol (formula: $C_8H_{18}S_2$, molecular weight: 178.36 g/mol, boiling point: 269–270°C, density: 0.97 g/mL at 25°C, Sigma Aldrich) and 1,8-diiodooctane (formula: $C_8H_{16}I_2$, molecular weight: 366.02 g/mol, boiling point: 167–169°C at, density: 1.84 g/mL at 25°C, Sigma Aldrich) were selected as additives and 2.5 vol % additives were then added to the base solution. A solution containing a mixture of P3HT:PCBM with processing additives was stirred for 10 min.

Polymer solar cells were fabricated on the pre-patterned indium-tin oxide (ITO) glass substrate. PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was spin-coated on to the ITO substrate at 3000 rpm for 30 s, and the prepared thin film was then baked at 120°C for 10 min on the hotplate in an air. The prepared solution was spin-coated on to the PEDOT:PSS layer at 1000 rpm for 30 s and then the spin-coated thin film was dried in the Petri dish. As a final step, Al electrode was deposited on to the spin-coated layer by thermal evaporation. The fabricated devices were annealed at 120°C for 30 min. An active area of device, 2 mm × 2 mm in dimension, was made using a shadow mask. The current density-voltage (J-V) and power conversion efficiency (η_e) characteristics were measured using Keithley 2400 multi-source meter unit. The Xenon lamp (100 mW/cm²) was used as a light source and light intensity has been measured by a silicon photo-diode calibrated for an AM 1.5 spectrum. The absorption spectrum were taken using an Optizen 2120 UV spectrophotometer (Mecasys) and XRD images were obtained using a high resolution X-ray diffractometer (Philips) and SPM images were obtained using a scanning probe microscope (Digital Instruments Multimode).

Result and Discussion

The current density-voltage (J-V) curves of the devices solution-processed using different processing additives, 1,8-octanedithiol and 1,8-diiodooctane, are shown in Figure 1. By introducing a small amount of processing additives to solution-processed active layer, the current density-voltage (J-V) characteristics of the active layer were improved and consequently higher power conversion efficiency (PCE) of

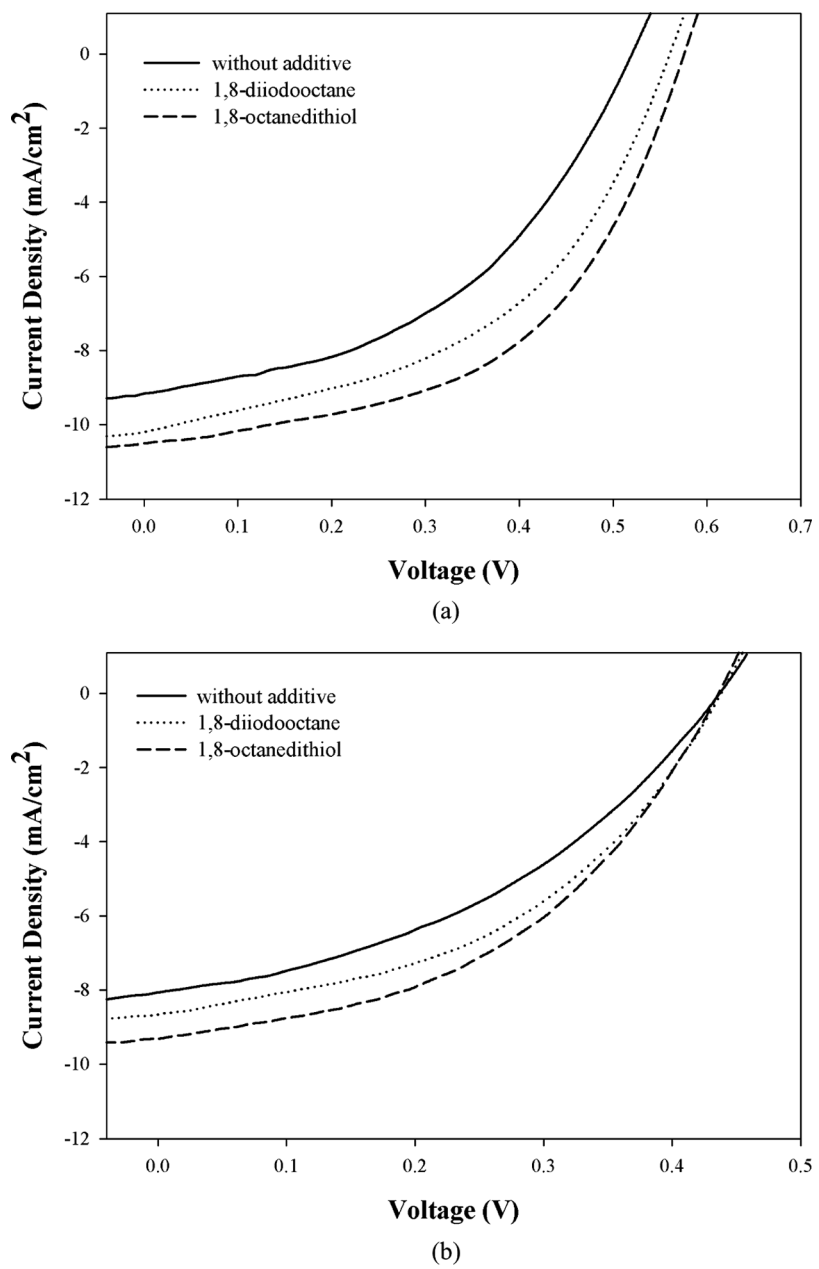


Figure 1. Current density-voltage (J-V) curves of the devices solution-processed with a solvent; chlorobenzene (a) and 1,2-dichlorobenzene (b).

the device was achieved. When chlorobenzene as a solvent and 1,8-octanedithiol as a processing additive were employed in solution process, the performance characteristics of the device were highly improved, showing that a short-circuit current density $J_{sc} = 10.53 \text{ mA}/\text{cm}^2$, a fill factor $FF = 0.51$, an open-circuit voltage $V_{oc} = 0.58 \text{ V}$, and

Table 1. Device performance of the devices solution-processed with a solvent; chlorobenzene (a) and 1,2-dichlorobenzene (b)

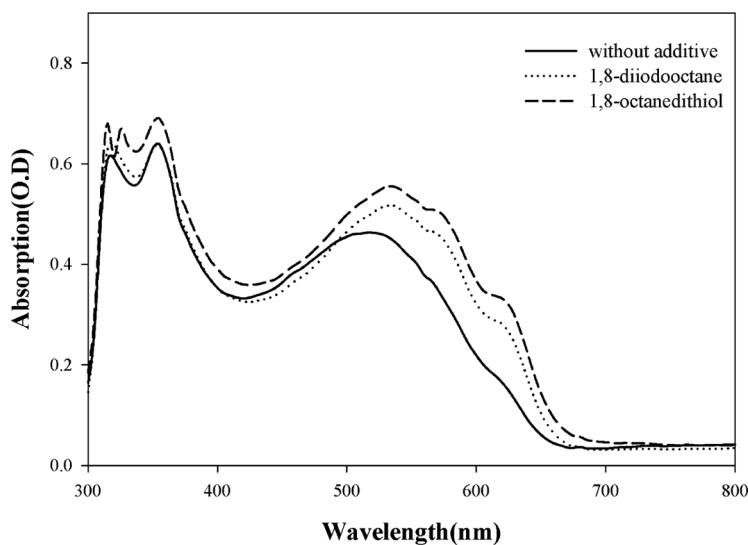
	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
(a)				
Without Additive	0.52	9.16	0.45	2.16
1,8-diiodooctane	0.57	9.89	0.48	2.69
1,8-octanedithiol	0.58	10.53	0.51	3.12
(b)				
Without Additive	0.43	8.06	0.40	1.42
1,8-diiodooctane	0.51	8.90	0.47	2.12
1,8-octanedithiol	0.54	9.61	0.49	2.50

a PCE of 3.12%. Also, when 1,8-diiodooctane were employed in the same solvent, chlorobenzene, a short-circuit current density $J_{sc} = 9.89 \text{ mA/cm}^2$, a fill factor $FF = 0.48$, an open-circuit voltage $V_{oc} = 0.57 \text{ V}$ and a PCE of 2.69% were measured. For a cell solution-processed using 1,2-dichlorobenzene and 1,8-octanedithiol, as a solvent and processing additive, respectively, a short-circuit current density $J_{sc} = 9.61 \text{ mA/cm}^2$, a fill factor $FF = 0.49$, an open-circuit voltage $V_{oc} = 0.54 \text{ V}$ and a PCE of 2.50% were measured. When 1,8-diiodooctane were added in the same solvent, 1,2-dichlorobenzene, a short-circuit current density $J_{sc} = 9.89 \text{ mA/cm}^2$, a fill factor $FF = 0.48$, an open-circuit voltage $V_{oc} = 0.57 \text{ V}$ and a PCE of 2.69% were obtained.

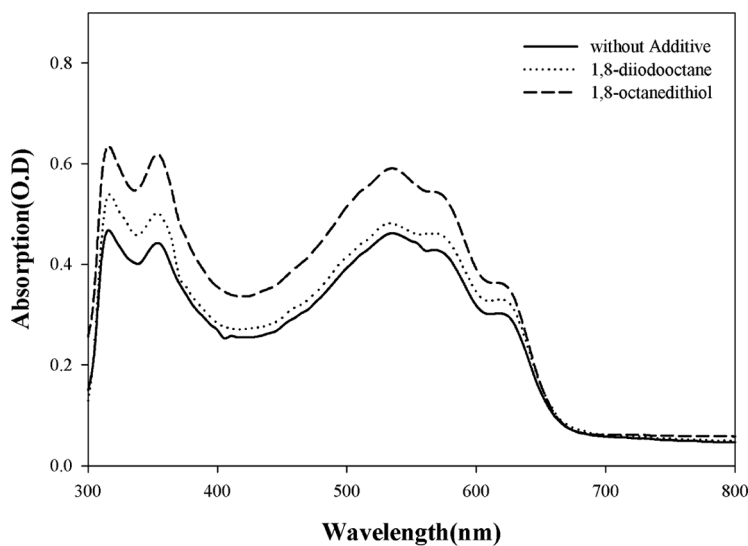
The UV-Vis absorption spectra of P3HT:PCBM films, processed with additives of chlorobenzene and 1,2-dichlorobenzene, are shown in Figure 2. As two processing additives were introduced to the BHJ films, P3HT:PCBM composite films, the absorption intensities were significantly increased. At the presence of processing additives, furthermore, the peaks in the absorption band of P3HT:PCBM composite films processed with a chlorobenzene solvent were especially red-shifted, eventually much higher device efficiency could be achieved by using those composite films as an active layer in solar cells. The absorption intensity increase of the film associated with π - π^* transition indicates that the P3HT chains interact more strongly and that there is improved local structural order compared with films processed with pure chlorobenzene.

The X-ray diffraction spectra of active layers, P3HT:PCBM films, are shown in Figure 3. Polycrystalline structure of P3HT molecules in P3HT:PCBM composite films should be preferred to improve the mobility in the films because of enhanced interactions of P3HT molecules, which form uniformly dispersed polycrystalline structure at the presence of processing additives. Furthermore, P3HT in active layer with additives has longer time to solidify due to the difference of boiling point between solvent and additive, and this helps to form higher self-organized structure. So, it was observed that peak intensities were slightly increased at the presence of additives, indicating that well ordered polycrystalline P3HT molecules existed in the composite films.

SPM images of P3HT:PCBM films are shown Figure 4. By introducing additives, the surface roughness and grain size were significantly increased. When 1,8-octanedithiol was used as processing additives, the grain boundaries were very



(a)



(b)

Figure 2. UV-Vis absorption spectra of the devices solution-processed with a solvent; chlorobenzene (a) and 1,2-dichlorobenzene (b).

clearly distinguished on the surface of P3HT:PCBM films. In those grains, there should be well ordered those polycrystalline structures of P3HT molecules.

Conclusions

BHJ polymer solar cells based on P3HT and PCBM films as an active layer, which was formed using both single solvent, chlorobenzene or 1,2-dichlorobenzene, and a

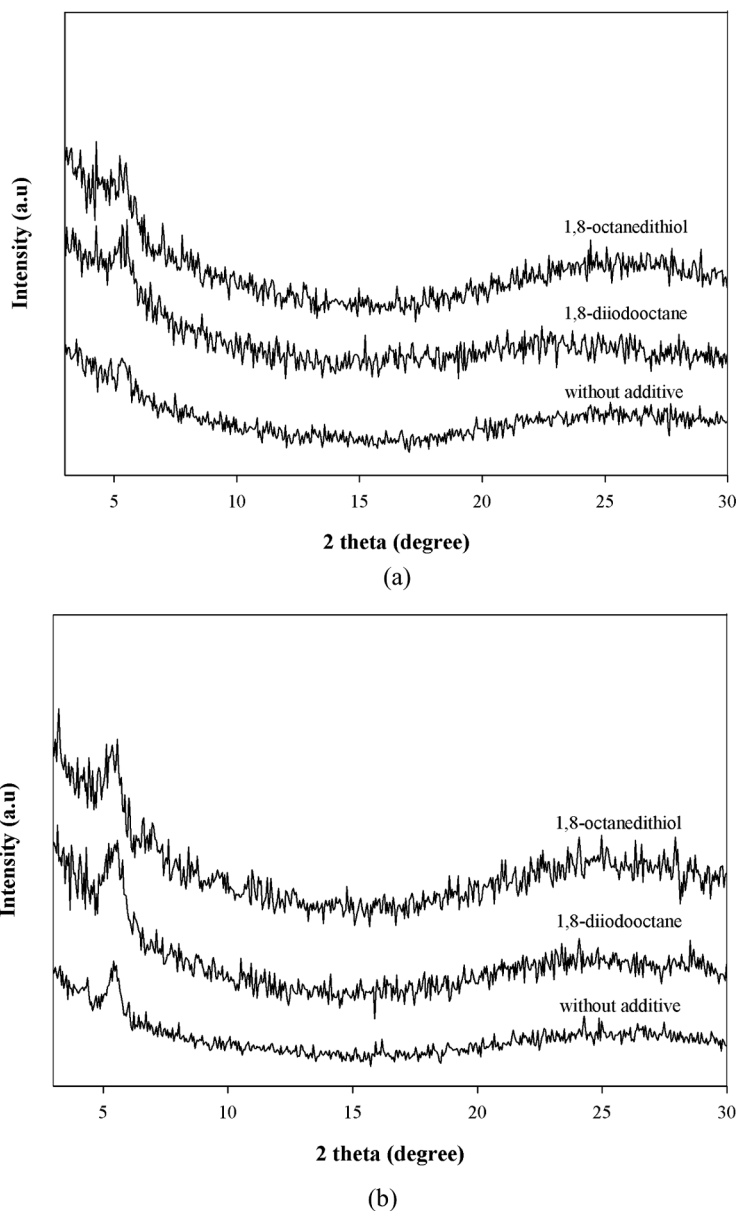


Figure 3. X-ray diffraction spectra of the devices solution-processed with a solvent; chlorobenzene (a) and 1,2-dichlorobenzene (b).

processing additive, 1,8-octanedithiol or 1,8-diiodooctane, were fabricated. By introducing processing additives, the performance characteristics of polymer solar cells have been significantly improved and the peaks in UV-Vis absorption band of P3HT:PCBM films were apparently red-shifted, consequently achieving the enhanced device efficiency due to the red-shifted absorption band. Well ordered polycrystalline structure of P3HT molecules in uniformly dispersed grains positively affected on the device efficiency in this work.

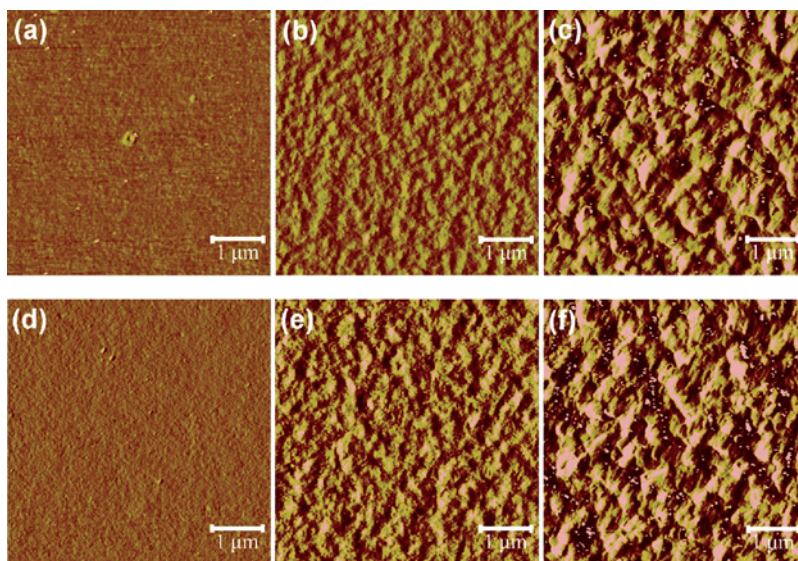


Figure 4. SPM images of P3HT:PCBM films formed using chlorobenzene alone (a), chlorobenzene and 1,8-diiodooctane (b), chlorobenzene and 1,8-octanedithiol (c), 1,2-dichlorobenzene alone (d), 1,2-dichlorobenzene and 1,8-diiodooctane (e), and 1,2-dichlorobenzene and 1,8-octanedithiol (f), as a solvent and processing additive, respectively.

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