Morphological engineering via processing additive in thin film bulk-heterojunction photovoltaic cells: A systematic understanding of crystal size and charge transport

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ABSTRACT

In this research, organic photovoltaic devices based on bulk-heterojunction (BHJ) from Poly(3-hexylthiophene-2,5-diyl) (P3HT)/[6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) were successfully fabricated to determine the optimization of solvent additive of 1,8-diiodooctane (DIO). The BHJ devices with DIO show improved short circuit current (J_{SC}) correlated to the improved device performance, since the DIO in P3HT:$PC_{71}BM$ BHJ affects the morphology in terms of the surface roughness and crystal size. Furthermore, the DIO contributes to the enhanced charge carrier transport of the BHJ device, because the decreased fluorescence and increased hole mobility as found through Raman spectra analysis and SCLC measurement, respectively. The device with optimized concentration (1 vol %) of DIO accomplishes 5% improved photovoltaic performance due to the favorable structural property and enhanced carrier mobility.

1. Introduction

Organic photovoltaic cells (OPVs) are an established and increasingly important technology for the production of renewable energy [1,2]. Research on OPVs is therefore an important issue. OPVs have several advantages, including light weight, flexibility, and the potential for being formed into large-area devices [3–5]. For a high efficiency OPV, a bulk heterojunction (BHJ) with an active layer made from a blend of a conducting polymer and a fullerene derivative is usually needed [6,7]. Among the photovoltaic materials used in OPVs, regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) are the most representative donor and acceptor compounds, respectively. The power conversion efficiency (PCE) of OPVs based on P3HT:$PC_{71}BM$ can reach over 4% [8–11]. Recently, many research groups have reported P3HT:$PC_{71}BM$ solar cells to further increase the PCE as a way to control the active layer morphology [12,13]. Among several methods used to control the nano-morphology, solvent additive processing is a pre-electrode deposition technique that has been implemented in many high-performance and breaking the record of BHJ OPVs [14]. An attractive feature of this technique is that is does not necessitate an extra processing step for device optimization and solvent or thermal annealing [15,16]. First, the morphology of the donor and acceptor compound phases is significantly altered; thereby a dramatic morphological variation is achieved [17–20].

For these reasons, in this work we report the effect of a systematically increased amount of 1,8-diiodooctane (DIO) on the photophysical and morphological characteristics of P3HT:$PC_{71}BM$ solar cells. First, structural studies of this type provide important insight into the final effects that occur due to solvent additive processing. However, information on the crystals of the compound domains in terms of the structural changes that lead to optimized morphologies remains unclear. Therefore, we carefully monitored the crystal sizes of the blend domains that have a crystalline packing structure and correlated information on these structural morphologies with the physical properties of the device by

determining the J-V characteristics and the charge carrier mobilities. The results of this study will be important in determining the specific interaction of the additive in P3HT:PC$_{71}$BM blends and aid future studies by explaining the specific crystal size of the structural rearrangement induced by DIO use.

2. Experimental details

2.1. Device fabrication

Organic solar cells based on P3HT:PC$_{71}$BM bulk heterojunction were fabricated on ITO/glass substrates. The substrates were washed with detergent and then ultrasonicated, and were then cleaned in a solution of water, acetone, and isopropyl alcohol. To convert the state of the surface, the ITO was exposed to UV-ozone for 20 min. The PEDOT-PSS (AI 4083), which is a hole transporting material, was then spin-coated on top of the ITO (thickness of ~40 nm). The substrate was dried at 140 °C for 10 min in air, and then transferred to a glove box. The P3HT:PC$_{71}$BM solution with a concentration of 26 mg/ml was then added to chlorobenzene (CB) without 1,8-diiodooctane (DIO) and with DIO (1 vol%, 3 vol%, 7 vol %), respectively. This solution was spin-coated on the PEDOT-PSS layer at 1500 rpm for 60 s. Subsequently, a metal cathode (Al) was deposited with a thickness of ~100 nm under a pressure of 4.0×10^{-6} Torr, using a thermal evaporator. All the cells were then annealed at 150 °C for 30 min in a glove box.

2.2. Characterization

The performances of the organic solar cells were measured using a solar simulator, with Air Mass 1.5 Global (AM 1.5 G) at an intensity of 100 mW/cm^2, and the current density-voltage characteristics of the solar cells was measured using ZIVE SP1. The total cell area was 0.15 cm^2. The incident photon-to-current efficiency (IPCE) spectra (PV measurement) for the solar cells was determined to prove the short-circuit current of J_{SC} related to the J-V curves. The surface morphology and roughness of the blend of P3HT:PC$_{70}$BM without and with DIO (1 vol%, 3 vol%, 7 vol%) were observed by atomic force microscopy (AFM) (Park NX10), using non-contact mode. X-ray diffraction (XRD) was performed using the 9C beamline (wavelength = 1.382 Å) at the Pohang Accelerator Laboratory (PAL) in Korea. Samples for the XRD measurements were prepared by spin-coating the polymer:PC$_{71}$BM:DIO solution on a PEDOT:PSS-coated Si-wafer. The Raman spectra were measured using a Raman microscope (Xperam200 (Nanobase.inc)). The laser wavelength was 642 nm and power was 0.3 mW for each device. The magnification of object lens was a power of 40×. We calculated an average of ten datasets of Raman spectra in the same position for each sample. For the charge carrier mobility measurements, hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/P3HT:PC$_{71}$BM/Au. The Au layer was deposited at low speed (1 Å/s) to avoid the penetration of Au atoms into the active layer. The J-V characteristics of the single charge carrier devices were measured by modeling the dark current under an applied forward bias and analyzed in the space charge limited region. The mobilities were determined from the modified Mott-Gurney equation:

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \exp\left(\frac{0.89\beta}{\sqrt{L}} \sqrt{V}\right)$$

where J represents the current density, L is the thickness of the active layer, μ is the hole carrier mobility, ε_0 and ε_r are the electric permittivity of free space and the relative dielectric constant of the active layer, respectively, and β is the electric field-activation factor. $V = V_{appl} - V_r - V_{bi}$, where V_{appl} is the applied voltage, V_r represents the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage.

3. Results and discussion

Fig. 1(a) shows the typical structure of the P3HT and PC$_{71}$BM BHJ device with an additive, DIO. Adding DIO assists the P3HT:PC$_{71}$BM blend to gain an optimized morphology [21–23], which seems to have an influence on the solar cell performance. The inset of Fig. 1(a) and (b) also show the molecular structures of P3HT, PC$_{71}$BM, and DIO, and an energy diagram of the component materials, respectively. A detailed explanation of the fabrication of the devices is given in the experimental section. We fabricated the
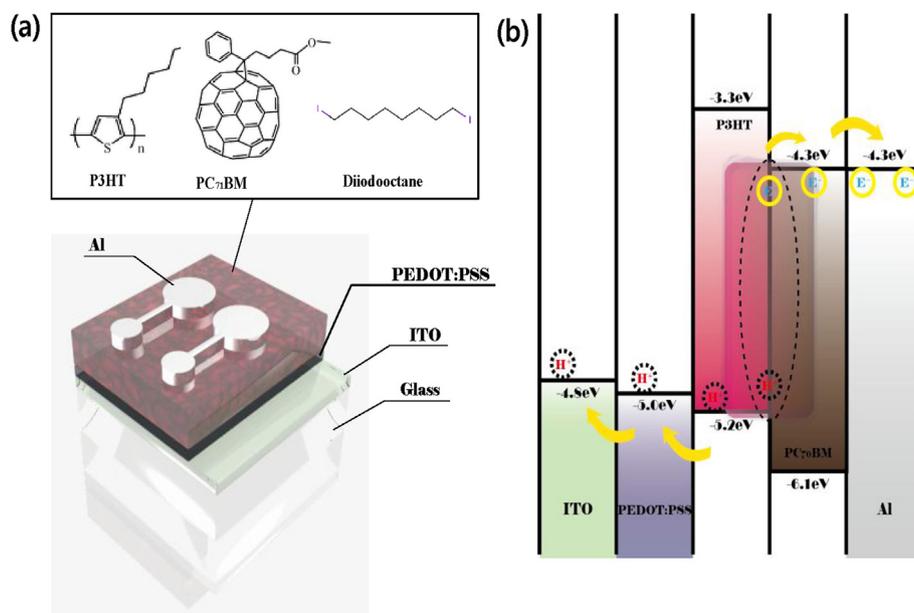
Fig. 1. (a) Schematic structure of P3HT and PC$_{71}$BM BHJ with the addition of DIO. (b) Energy level diagram of the solar cell used in this research.