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Relation between morphology and performance parameters of poly(3-hexylthiophene):Phenyl-C61-butyric acid methyl ester photovoltaic devices

Xiuxiu Zhao, Nana Yuan, Yue Zheng, Danhui Wang, Lin Li, Zhishan Bo, Jianjun Zhou, Hong Huo[*]

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Xinjiekouwai Street No. 19, Beijing 100875, PR China

A B S T R A C T

Poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction (BHJ) solar cells are one of archetypal polymer photovoltaic devices. Understanding the relationship between electronic properties and active layer morphology is essential to obtain high-performance electronic devices. The magnitudes of the short circuit current (J_{SC}), the fill factor (FF) and the open circuit voltage (V_{OC}) will vary on the basis of changes in phase purity, interfacial region area and domain size of the active layer. We investigated the device characteristics of the samples having comparable phase purity and found that the performance parameters were better in the device having larger interfacial region area. In another case the phase purity decreases, the interfacial area increases and the recombination rate increases, resulting FF and V_{OC} increase, J_{SC} first increases then decreases. Power conversion efficiency (PCE) increases with the increase of interfacial region area, although at the same time associates with the decrease of the phase purity. The device efficiency reaches optimal value by balance the phase purity and the interfacial area. We finally investigated the two devices where, in spite of significant difference between domain dimensions, the PCEs were quite similar. Especially, the devices having large micrometer scale PCBM crystals also obtain good PCEs if they have enough interfacial areas.

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1. Introduction

In recent years BHJ organic photovoltaic (OPV) cells have attracted a lot of attentions. They show many advantages comparing to inorganic solar cells, including easily fabricated, low cost and their adaptability to flexible substrates which makes them viable for large-scale applications using roll-to-roll processing methods [1—3]. Another important advantage of organic solar cells is that the organic semiconductor materials used for cells have high light absorption efficiency, and the range of absorption wavelength can be adjusted by changing the molecular structure.[2] So the thickness of the film can be made very thin to realize the complete absorption of light. Single BHJ devices have achieved PCEs in the range of 7—10% [4—6].

Controlling the morphology of polymer/fullerene BHJ is one of the key strategies to obtain high PCE. The active layer generally consists of the acceptor (A)-rich and donor (D)-rich phases, with an intermixed phase (the interfacial region) between them [7]. When the active layer absorbs sunlight, the excitons produce. Then the excitons diffuse to the interfacial region and separate into electrons and holes and they transform to the cathode and the anode respectively. Hence, a three-phase morphology of aggregated A, pure polymer D, and a mixed D:A interfacial domain might be a more favorable morphology than initially thought, as long the pure D and A phase are sufficiently connected, and dispersed pure phases will trap holes or electrons. Interfacial region area, phase purity and domain size are the critical factors to affect the active layer morphology [8—11]. A large interfacial area will increase the generation of photo carrier, so the short circuit current (J_{SC}) is high and the recombination is low [12,13]. But the recombination also takes place at the interfacial region, so the structure and area of the interfacial region are important. Improving the crystallization of D

and A can increase the phase purity of both of them. For donor polymer, the crystallized form has longer conjugation length and lower ionization potential than an amorphous phase [14,15]. For acceptor PCBM, crystallization is shown to result in an increase in its electron affinity and providing an energetic driving force for spatial separation of electrons and holes [16]. These generally favorable electronic landscapes make them more probable for electrons and holes to exit the mixed regions and move to purer fullerene and purer polymer domains. Due to the small exciton diffusion length of ca. 10 nm, small scale nano-phase separation is suitable for efficient exciton dissociation efficiency, so the optimal domain size is about 10 nm [17–19]. But the interfacial region area, phase purity and domain size can not achieve the best values at the same time in the active layer. Recent simulations suggest that the phase purity and the structure of the D:A interfacial region could be of greater importance than the domain size toward determining the exciton dissociation and carrier collection process and consequently the J_{SC} [20,21]. Above all, understanding and balancing the relation of phase purity, domain size and interfacial area are critical to morphological design of active layer for optimum device performance.

The BHJ consisting of P3HT and PCBM was the most studied OPV active layer in recent years, as PCE approaching 5% has been reported. In P3HT:PCBM active layer, it includes crystalline P3HT phase, aggregated PCBM phase and intermixed phase that PCBM dissolving in the amorphous P3HT [22]. The improvement of P3HT crystallization facilitates the phase separation of PCBM from P3HT crystalline region, and the excluded PCBM tends to form large agglomerates. P3HT provides adequate hole mobility in P3HT:PCBM BHJ OPV devices. If increasing the in-plane stacking of P3HT, charges can easily transport from one grain to another, and charge carrier mobility increases [23–27]. Understanding and controlling the phase purity or crystallinity of P3HT is essential to increase charge carrier mobility and charge collection, and improve the PCE of the solar cell. Many groups clearly demonstrate that the cell efficiency is directly correlated to the P3HT crystallinity, where the decrease in P3HT crystallinity leads to directly lower cell efficiency [11,28,29]. On the other hand, the effect of PCBM aggregation or crystallization on the PCE of OPV device is subject to debate. Such aggregate or crystallite formation has been related to the formation both of electron percolation pathways and of enhanced charge separation [30–32]. It has also been considered that the formation of large PCBM crystals are detrimental to the solar cell performance [33,34]. The large scale phase separation leads to small interfacial region area. In a word controlling the crystallization of P3HT and PCBM can modify phase purity, domain size and interfacial region area, finally determine the morphology of the active layer. The morphology of the active layer affects the magnitudes of J_{SC}, FF, and V_{OC}. The interrelations among aspects of interfacial region area, phase purity, domain size and the device performance parameters are worth to study in detail.

In this paper, we produced fundamentally different morphologies of P3HT:PCBM BHJ system by using different processing strategies: solvent casting; super-critical carbon dioxide (scCO$_2$) processing; CS$_2$ vapor annealing; and scCO$_2$ processing first, then CS$_2$ vapor annealing. ScCO$_2$ was used to make P3HT and PCBM plasticize and crystallize, leading large domain size and high phase purity. CS$_2$ vapor annealing was used to properly dissolve P3HT and PCBM crystals, decrease phase purity but increase interfacial region area. Here, the variation ranges of phase purity, interfacial area and domain size are wide after excessively scCO$_2$ treatment (for 12 h) and CS$_2$ vapor treatment, which can be clearly observed and compared by using optical microscope (OM), UV–vis absorption spectrum and grazing incidence X-ray diffraction (GIXRD).

2. Experimental methods

2.1. Materials

P3HT (M_w = 45,000 g/mol and regioregularity ≥ 90%) was purchased from Rieke Metals. PCBM was purchased from Nano-C. 1, 2-dichlorobenzene (ODCB) was purchased from Sigma–Aldrich Chemicals. Carbon disulfide (CS$_2$) was purchased from Fine Chemical Research Institute of Tianjin Jinke. All materials were used without further purification.

2.2. Sample preparation

P3HT:PCBM blends with the weight ratio of 1:1 were dissolved in ODCB and the blend concentration is 40 mg mL^{-1}. The solution was stirred overnight at 40 °C in a nitrogen-filled glovebox. The indium tin oxide (ITO)-coated glass substrate with a conductivity of 20 Ω/sq was cleaned in detergent, deionized water, isopropyl alcohol and acetone and then activated at 160 °C in the mixed solution of deionized water, hydrogen peroxide and ammoniumhydroxide with the volume ratio of 5:1:1. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron Al 4083, H.C. Starck) was filtered through a 0.45 μm PVDF film before use. It was spin-coated onto the well-cleaned ITO substrates and baked at 130 °C for 30 min, then getting a 30 nm thick PEDOT:PSS layer. The active layer was spin-coated at 800 rpm for 30s, followed by spinning at 1500 rpm for 1s, then they were dried by continued spinning at 600 rpm for 30s under ambient temperature in the glove box. The thickness of the active layer is about 160 nm.

2.3. ScCO$_2$ treatment

Samples were put into a sealed stainless steel container connected with a CO$_2$ cylinder (Air Liquid, 99.99% purity). The pressure of CO$_2$ was controlled by the high pressure fluid injection system. The temperature was controlled by water bath. First CO$_2$ was purged into the stainless steel container and deflated, the process was repeated twice to remove air. Then the cell which containing the samples and CO$_2$ was immersed in a water bath and heated to 50 °C, and the pressure was kept at 11 MPa. Based on the density–pressure phase diagram of CO$_2$ [35], it identifies that CO$_2$ at 11 MPa and 50 °C is the scCO$_2$.

2.4. CS$_2$ vapor treatment

CS$_2$ vapor pressure was controlled by pouring 5 mL CS$_2$ in a long glass tube (5 cm in diameter and 22 cm in length). Solvent vapor can diffuse from bottom to the top and stable vapor gradient along the tube could be obtained after CS$_2$ was placed in the tube for 15 h. The solvent in the tube was allowed to evaporate thoroughly at 25 °C. The solvent vapor pressure (P) is given by L/L$_0$ where L is the distance from the upper edge of the setup to the specimen position and L$_0$ is the length given by the distance from the upper edge of the setup to the solvent surface at the bottom of the tube.[11]In CS$_2$ vapor annealing the required solvent vapor pressure P can be precisely chosen upon rapidly placing the blend film at the given position in the tube. In this work, we fixed P as 0.9.

2.5. X-ray photoelectron spectroscopy (XPS)

The S element and O element content of the film were measured by the XPS (ESCALAB MK II). The X-ray was excited by a monochromatic Al Kα (1486.6 eV) X-ray source. The pressure of the measurement chamber was less than 10^{-9} mbar. Binding energies