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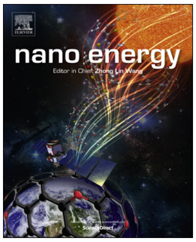

RAPID COMMUNICATION

Critical role of domain crystallinity, domain purity and domain interface sharpness for reduced bimolecular recombination in polymer solar cells

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Abstract
Inverted bulk heterojunction solar cells were fabricated using poly(3-hexylthiophene) (P3HT) blended with two different fullerene derivatives namely phenyl-C61-butyric acid methyl ester ($PC_{60}BM$) and indene-C_{60} bis-adduct ($IC_{60}BA$). The effects of annealing temperatures on the morphology, optical and structural properties were studied and correlated to differences in photovoltaic device performance. It was observed that annealing temperature significantly improved the performance of P3HT:$IC_{60}BA$ solar cells while P3HT:$PC_{60}BM$ cells showed relatively less improvement. The performance improvement is attributed to the extent of fullerene mixing with polymer domains. Energy filtered transmission electron microscopy (EFTEM) and x-ray diffraction (XRD) results showed that ICBA mixes with disordered P3HT much more readily than $PC_{60}BM$ which leads to lower short circuit current density and fill factor for P3HT:$IC_{60}BA$ cells annealed below 120 °C. Annealing above 120 °C improves the crystallinity of P3HT in case of P3HT:$IC_{60}BA$ whereas in P3HT:$PC_{60}BM$ films, annealing above 80 °C leads to negligible change in crystallinity. Crystallization of P3HT also leads to higher domain purity as seen EFTEM. Further it is seen that cells processed with additive nitrobenzene (NB) showed enhanced short circuit current density and power conversion efficiency regardless of the fullerene derivative used. Addition of NB led to nanoscale phase separation between purer polymer and fullerene

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domains. Kelvin probe force microscopy (KPFM) images showed that enhanced domain purity in additive casted films led to a sharper interface between polymer and fullerene. Enhanced domain purity and interfacial sharpness led to lower bimolecular recombination and higher mobility and charge carrier lifetime in NB modified devices.

Introduction

Due to increased demand for clean energy and depletion of fossil fuels, alternative energy sources such as solar and wind are of interest currently. Organic semiconductors have gained significant amount of interest for photovoltaic applications in the last several decades due to their lower cost [1] and processability from solution for lightweight and flexible devices [2]. Polymer–fullerene bulk heterojunction (BHJ) solar cells have shown photovoltaic efficiencies up to 11% [3,4]. Nanomorphology plays a crucial role in BHJ solar cells as it dictates both charge generation and transport [5–7]. Nanomorphological features such as donor/acceptor crystallinity [8], vertical/lateral phase separation [9,10], domain purity [11], orientation [12] and domain interfaces [13] can be tailored by optimizing the processing conditions to enhance device conversion efficiencies. Processing parameters such as solvent selection [8,14,15], annealing temperature [16], donor–acceptor mixing ratio [17,18], and coating techniques can be fine-tuned to attain high photovoltaic performance.

Molecular miscibility between polymer and fullerene is critical to acquire homogenous phase separation between polymer and fullerene components leading to efficient exciton dissociation [19]. However higher miscibility can lead to highly intermixed domains preventing ordering of polymer chains. These highly intermixed amorphous domains have shown to possess poor charge transport [20]. It is desired to have pure polymer domains having sharp interface between polymer and fullerene phase (less intermixing at domain boundaries) to improve charge transport and suppress trap assisted losses [21]. Several studies have focused on the mixing of donor polymers and fullerene blend films and have shown that domain purity and crystallinity [5,22,23] play an important role in enhancing device performance, but the physics behind efficient charge transport correlated to nanoscale morphology is still elusive. Further, the processing parameter required to achieve ideal morphology is dependent upon the material selection and needs to be studied. Such an insight will be beneficial to attain high power conversion efficiency at large scale.

P3HT:PCBM solar cells have been widely studied [24] in the past decade and efficiencies of 4–5% have been regularly achieved. Device efficiencies were further improved to 5–7% [25,26] by using a bis-adduct fullerene derivative namely indene-C_{60} bisadduct ($IC_{60}BA$) resulting in higher open circuit voltage due to the higher LUMO level in ICBA. One of the most prominent approaches to improve efficiency in P3HT based blends has been slow drying of cast films. Slow drying leads to structural ordering of P3HT and diffusion of fullerene to achieve nanoscale phase separation between crystalline P3HT and fullerene domains. This approach has demonstrated efficient solar cells, however, is not practical for roll to roll processing. Lower boiling point solvents are preferred to increase throughput and thickness uniformity for roll to roll printing implementation [27]. Further it has been shown that mixing behavior of fullerene with P3HT is dependent upon the fullerene derivative used [28]. There exists a need for understanding the correlation between processing conditions and resulting morphology and between complex nanoscale morphological features and charge transport/recombination to achieve faster commercialization of low cost plastic solar cells.

In this study we found that mixing behavior of P3HT and fullerene is dependent upon the fullerene derivative used. ICBA was found to mix with P3HT more readily and the blend films require higher thermal energy to segregate into pure polymer and fullerene phases. Inclusion of additives that are poor solvents for P3HT and good solvent for fullerene leads to formation of ideal morphology consisting of interconnected pure polymer domains that have sharper interfaces for exciton dissociation and lower bimolecular recombination.

Results and analysis

The chemical structures of the donor and acceptor materials used are shown in Figure 1a. The experimental procedures for film deposition, device fabrication and characterization are given in detail in Supporting Information. To evaluate the effect of annealing on the optical properties and structural properties of P3HT:$PC_{60}BM$ and P3HT:$IC_{60}BA$ blend films, UV–Visible absorption and XRD diffraction spectra were taken as shown in Figure 1b and Figure 1c respectively. In both cases films without thermal annealing (as deposited) showed a single peak at 476 nm. For P3HT:$PC_{60}BM$ films annealing at and above 80 °C, the peak red shifted to 504 nm and also showed formation of vibronic shoulders around 545 nm and 595 nm. These vibronic shoulders formation at 545 nm and 595 nm is related to intrachain and interchain packing of P3HT respectively [29–31]. When the P3HT:$PC_{60}BM$ films were subjected to thermal annealing these shoulders start to form suggesting interchain and intrachain stacking. In particular the intensity of the shoulder at 595 nm (0–0 transition) was low in the as deposited films indicating poor packing between chains. When the films were annealed these shoulders become more pronounced which indicated that the P3HT chains assemble to form ordered chains as supported by the XRD spectra. However in P3HT:$IC_{60}BA$ films, the vibronic shoulder at 595 nm had low intensities even when annealed below 120 °C. The absorption peaks of P3HT:$IC_{60}BA$ films also stayed at ~468 nm and did not show any red shift which represents less crystalline and defective P3HT when blended with $IC_{60}BA$ up to 120 °C. Annealing at and above 120 °C led to red shift of the peak to 486 nm and annealing beyond 150 °C, the vibronic shoulder at 595 nm became more pronounced leading to the conclusion that higher temperatures