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Inter-diffused ordered bulk heterojunction organic photovoltaics: optimized morphology for efficient exciton dissociation and charge transport

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ABSTRACT

Effective control of the morphology can enhance the performance of organic photovoltaics. The morphology of an active layer needs to have a large interfacial area between donors and acceptors for efficient exciton dissociation and continuous, direct charge transport paths to electrodes for high charge transport efficiency. These two requirements are usually contradictory. Here, we propose a morphology that meets these requirements nearly simultaneously, called an inter-diffused ordered bulk heterojunction (IDOBHJ). This novel structure exhibited 9% higher performance based on the Monte Carlo simulation than an optimized disordered bulk heterojunction. The main reasons for superior performance were attributed to the comparable short circuit current density and a higher fill factor. We also implemented the IDOBHJ morphology by the experimental nanoimprint technique combined with thermal annealing process to confirm simulation results. Our experimental results are indeed consistent with the theoretical analysis.

1. Introduction

Organic photovoltaics (OPVs) have been gaining attention due to their light weight, flexibility, and low manufacturing cost [1–4]. The performance of OPVs is proportional to the integration of external quantum efficiency (EQE) *versus* photon wavelength, also called the incident photon to current efficiency (IPCE). The EQE at certain photon wavelengths, λ, is calculated from the ratio of light absorption (η_{abs}), exciton diffusion (η_{extD}), charge transfer (η_{chrT}), and charge collection efficiency (η_{chrC}) [5–8].

$$EQE(\lambda) = \eta_{abs}(\lambda) \times \eta_{extD}(\lambda) \times \eta_{chrT}(\lambda) \times \eta_{chrC}(\lambda) \quad (1)$$

As shown in Eq. (1), a high *EQE* is required for high light absorption, exciton diffusion, charge transfer, and charge collection. We let $\eta_{chrT}=1$ due to the rapidity ($\sim$10–100 dfs) of the process in organic donor–acceptor photovoltaics [8]. However, other parameters are usually interdependent, wherein increasing one parameter decreases the others [9]. While the light absorption mostly depends on the active layer thickness, both the exciton diffusion and charge transport show strong dependency on the active layer morphology [10]. Thus, the active layer morphology is critical for high EQE, *i.e.*, power conversion efficiency (PCE). The OPVs can be categorized by various morphologies, but, in this study, we will focus on disordered bulk heterojunction (DBHJ) and ordered bulk heterojunction (OBHJ).

The DBHJ possesses a large interfacial area, which leads to high exciton diffusion efficiency. When the interfacial area between a donor and acceptor is large, the exciton diffusion to the interface is efficient; the generated Frenkel excitons, which possess limited diffusion length [11,12], can only be dissociated into the interfacial area. However, when the interfacial area is large, the charge transport path to the electrodes is generally long and non-straight, which reduces the charge collection efficiency. Thus, most DBHJ studies have focused on morphology control to ensure efficient charge colleciton while maintaining high exciton diffusion [13–18]. So, various computational simulation including Monte Carlo method [8,19–25] and drift-diffusion modeling [26,27] are conducted to reveal the correlation of morphology and performance. Maturová et al. [26] calculated current–voltage characteristics on different degrees of nanoscale phase separation in MDMO-PPV: PCBM system. In the modeling, they observed that the short-circuit current is enhanced in finer phase separation due to a reduction in bimolecular recombination caused by lateral movement of photo generated electrons to the fullerene-rich phase. However, at high bias, vertical electron transport is enhanced and lateral movement is reduced, causing a significant field-dependent

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carrier extraction for coarse morphologies. In their other paper [28], they concluded that the BHJ should have a phase separated morphology with feature sizes that are smaller than ~50 nm for best performance. All of these simulations represent that, through morphology control on DBHJ, charge collection can be enhanced. Also, there are various experimental morphology control methods to achieve this aim, [29–32] such as the thermal annealing [13,33,34], solvent annealing, [14] slow cooling by controlling the spin coating time [17], using a solvent additive [35], and solid additives as block-copolymer [36,37]. While these methods enhance the charge transport efficiency of DBHJ [28,38,39], we found that the charge transport efficiency of DBHJ is still less than 0.8 yet that of OBHJ is close to 1.0 (see Fig. 3).

Coakley et al. suggested the use of OBHJ to overcome the poor charge collection efficiency of DBHJ [40]. Unlike DBHJ, charges are collected through straight pathways in the OBHJ. Additionally, Aryal et al. reported that the vertical chain alignment of P3HT formed in the OBHJ can enhance the charge-carrier mobility [41]. This argument was supported by Zhou et al. [42], who reported that P3HT nanogratings showed 60 times greater hole mobility than a non-optimized shape. On the other hand, interfacial area per unit volume between donors and acceptors of OBHJ, which directly influencing to the exciton diffusion efficiency, is generally an order of magnitude smaller than that of DBHJ, which will be shown later in this paper (see Fig. 3).

In this study, we propose a morphology satisfying both the previously contradictory high exciton diffusion and high charge collection efficiency. We called this morphology the inter-diffused ordered bulk heterojunction (IDOBHJ). This morphology hybridized advantages of both DBHJ and OBHJ; high exciton diffusion efficiency and high charge collection efficiency. A schematic of the IDOBHJ structure is shown in Fig. 1. Both morphologies of DBHJ (Fig. 1(a)) and OBHJ (Fig. 1(b)) coexist in the IDOBHJ (Fig. 1(c)); straight pillars, *i.e.*, the morphology of OBHJ, for which the width is not greater than the exciton diffusion length, are observed. Near the pillar structures, the morphology of DBHJ, *i.e.*, the inter-diffused layer, are present as shown in Fig. 1(d). In our theoretical analysis, we confirmed that this IDOBHJ can achieve higher power conversion efficiency over those of OBHJ and DBHJ. Also, we presented experimental proofs supporting this analysis.

2. Theoretical analysis and experimental demonstration

2.1. Theoretical analysis

Morphology can be simulated in a few different ways such as Ising–Hamiltonian method [20,43], modified Cahn–Hilliard method [19,24,25], etc. The Ising–Hamiltonian method [20,43] was used for generating DBHJ morphologies. In DBHJ, two different materials, which were initially mixed randomly in an active layer, were combined with the same materials and these evolved to larger domains. Donor and acceptor sites were equally generated in the $60 \times 60 \times 30$ sites (x, y, z) of a Cartesian coordinate. The length of each site was 3 nm [44], and only one material was assigned to a site. According to the swap probabilities, two materials could swap, and these swap events occurred at neighboring site pairs. By repeating the swapping event, DBHJ morphologies were generated. This method is consistent with experimental data showing that domain size grows proportionally to thermal annealing time [45,46]. For example, Lei et al. [21] demonstrated the consistency of the Ising–Hamiltonian method with the P3HT/PCBM system. The domain size is defined as the distance at which the pair distribution probability, the ratio of the same material located in the distance, becomes 0.5 [25]. The domain sizes of generated DBHJ are evaluated from 3 to 14 nm which corresponds to the interfacial area per unit volume of 0.48 to 0.13 nm^{-1}, respectively.

The morphologies of OBHJ were constructed with pillar sizes of 18, 30 and 45 nm. Intervals between pillars are set to be the same as the respective pillar sizes. In the IDOBHJ morphologies, we chose to insert DBHJ morphologies into the OBHJ morphologies. This is because of the reasons as follows; we suspect that inter-diffusion occurs during the post-annealing process mainly because of the very rapid diffusion of fullerene derivatives into the amorphous polymer region [47,48] along with accompanying the polymer-chains-crystallization [41]. However, this cannot be captured well enough by the existing morphology generation methods such as the Ising–Hamiltonian method [20,43] or the modified Cahn–Hilliard method [19,24,25]. Also, although it is known that phase separation in organic photovoltaics is usually a consequence of solvent evaporation and thermal annealing [25], the relevant modeling on evaporation driven processes is still at an early phase [49].

Once the morphology was generated, light absorption was calculated. Analysis on the light absorption was conducted by solving Maxwell's equation using the finite differential time domain method for a glass/ITO/PEDOT:PSS/active layer/Al [50,51]. Uniform light absorption everywhere in the active layer was not assumed as it is not valid for OBHJ. The location of the light absorption is very important because it determines the position of the exciton generation and influences the exciton dissociation. If light is absorbed far from the donor/acceptor interface, generated excitons typically recombine due to their limited diffusion length of approximately 10 nm [11,12]. Alternatively, if light is absorbed near the donor/acceptor interface, the possibility of dissociation is high. In the simulation, excitons were generated with the rate of $1000\ s^{-1}\ nm^{-2}$ corresponding to 1 sun condition, *i.e.*, 100 mW/cm^2.

The lattice-based kinetic Monte Carlo (MC) method which traces movement of each charge or exciton has been developed to characterize photovoltaic performance in a device. Nelson et al. [52] initially applied the MC method to simulate charge transport in MDMO-PPV/PCBM system. They found that charge recombination is slow enough not to hinder short circuit current and claimed that space charge effects may be the reason for observing dependency of photocurrent on temperature. One of the main advantages of the MC method is that this method can be used even under complex morphology. Watkins et al. [20] utilized this fact and studied the dependence of the internal quantum efficiency (IQE) of an organic bulk heterojunction solar cell on the device morphology. They used the Kawasaki spin-exchange dynamics to create various DBHJ morphologies. They found that the IQE is indeed a strong function of the morphology and that OBHJ possesses 1.5 times higher IQE than that of DBHJ. Marsh et al. [43] updated the Monte Carlo modeling by including dark injection, so their modeling can present the full current–voltage characteristics including short-circuit current, open-circuit voltage, and fill factor. They examined that the morphology, light intensity, charge mobility, and recombination rate are key parameters on OPVs performance. Interestingly, they have shown that a tenfold increase in mobility produces a double increase in the maximum power output in a bilayer device. Meng et al. [23] compared the MC simulation results to experimental data and found that the fill factors are identical. They suggested a feature size has to be around ~10 nm to achieve an optimal energy conversion efficiency. Later, they improved the MC method by incorporating the Poisson equation to consider a nonuniform electrostatic potential that depends on the charge distribution [53]. The *I–V* curve based on this modeling showed good agreement with experimental results. Recently, Heiber et al. [54] further improved the exciton dissociation mechanism in DMC modeling by including exciton delocalization and hot charge separation effect. They found that both delocalized exciton and hot charge separation effect could reduce recombination so these effects should be considered. Kipp et al. [55] updated the