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Reappraising the validity of poly(3-hexylthiophene) nanostructures in interdigitated bilayer organic solar cells

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ABSTRACT

Interdigitated nanostructures can increase power conversion efficiency (PCE) by providing large interfaces for the dissociation of excitons and arrays for carrier transportation without recombination. Here, we reappraise the validity of donor–acceptor nanostructures composed of well-aligned porphyrin–fullerene nanopillars based on their contribution to the PCE compared with bulk heterojunction (BHJ) and bilayer (BL) organic photovoltaic solar cells (OPVs) with high efficiencies. Contrary to expectations, the results showed that poly (3-hexylthiophene) (P3HT):[6, 6]-phenyl C_{61} butyric acid methyl ester (PCBM) interdigitated nanostructures hardly enhanced the PCE. We suggested three reasons focused on the morphological characteristics: the misbalanced carrier transit time caused by differences in the travel distances and carrier mobilities, detrimental effects on carrier transportation due to the overlap of the pathways to the electrodes, and the dependence of the PCE on the shapes and sizes of the nanostructures.

1. Introduction

Poly(3-hexylthiophene) (P3HT):[6, 6]-phenyl C_{61} butyric acid methyl ester (PCBM) bulk heterojunction solar cells are the most investigated polymer solar cells in the form of OPVs based on solution-processed BHJs of semiconducting polymers [1–11]. Under optimized conditions, this material system has achieved PCEs of approximately 3–5%. Generally, the PCEs are affected by the regioregularity (RR) [12] and molecular weight (M_w) of P3HT [13], the ratio of P3HT to PCBM [14–21], the annealing conditions [22–26], the thickness of the active layer [27–29] and the morphology. Among these factors, the BHJ morphology requires an optimized design in which the phase separation length scale is comparable to the exciton diffusion length [30–32], which is ∼10 nm for most polymer semiconductors. However, some domain regions deviate from this condition, causing problems such as carrier recombination.

In this regard, interdigitated donor–acceptor nanostructures, such as nanopillars, nanopores, nanoparticles, etc., play an important role in determining the PCE for devices based on donor–acceptor composites [33–36]. A large donor–acceptor interface enable the dissociation of photogenerated excitons, and arrays of nanostructures allow the holes and electrons to transport to their respective electrodes, while also providing pathways for charge carriers to reach the

electrodes without recombination. A variety of experimental methods, which offer control over nanostructures, have been developed. One type of promising nanostructure is vertically well-aligned inorganic semiconductor nanopillars [33,34]. ZnO nanostructures are applied for P3HT:PCBM photovoltaic devices due to the high electron mobility and transparency as well as vertical growth. The hybrid inorganic/polymer solar cells based on ZnO/P3HT are also investigated in terms of ZnO morphology and wettability of the P3HT surface [35,36]. Although ZnO nanopillars promote electron transport and collection, the poor contact of the organic semiconductor with the ZnO nanopillars revealed the limit in the improvement of PV performance [37–42]. To overcome the drawbacks of the insufficient contact at the inorganic/organic interface, other efforts have been devoted to the development of direct conjugation with nanostructured polymers. The polymer nanopillars were obtained using the template-assisted synthesis method. The process includes nanoimprint lithography using a mold [43–45], porous alumina templates [46–52] or specifically designed polymers, such as cylindrically phase-separated and conducting block copolymers [53–55]. Recently, optional elimination of polymers via phase segregation has also been reported [56–62], including a simple method of self-assembly with polystyrene (PS) [63].

However, these methods require time and cost for the development of controlled nanostructures; they also have complicated processes compared with the fabrication of BHJ and bilayer organic solar cells. In this regard, organic solar cells with P3HT nanostructures

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should meet the high expectations for the enhancement of PCE. Intensive research has been focused on the preparation of well-aligned and controllable nanostructure, which is based on the assumption that the nanostructures will lead to the enhancement of PCE via more efficient charge separation. Interestingly, for some unexplained reason, the PCEs of nanostructured devices have been comparable to those of bilayer devices with low efficiencies [64–66]; therefore, the validity of nanostructured devices has been reviewed favorably. However, the PCEs enhanced with nanostructures never outperform the general BHJ and elaborated bilayer solar cells, which show efficiencies of 3–4% [67,68]. These facts raise questions about whether P3HT nanostructures are effective in P3HT:PCBM photovoltaic devices.

We reappraise the validity of P3HT nanopores obtained from well-aligned porphyrin–fullerene nanopillars with regard to the contribution to PCE and directly compare them with BHJ and bilayer solar cells with high efficiencies. Nanoporous P3HT on (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) layers is obtained after removal of the porphyrin–fullerene nanopillars, which are embedded in P3HT via *J*-type ordered assembly and phase aggregation [62]. The films were investigated using atomic force microscopy (AFM) to confirm the structural features, such as depth and size of the nanopores. The same films were also incorporated into devices and fully characterized under illumination from a solar simulator. By combining the morphological and electro-optical characterizations, we were able to suggest factors that limit the PCE enhancement.

2. Experimental section

2.1. Materials

N_1,N_5-Didodecyl-L-glutamide zinc porphyrin-derivatives (*g*-TPP/Zn) and pyridine-substituted pyrrolidinofullerene (*py*-C_{60}) were synthesized by previously reported procedures [69,70].

2.2. Device preparation

In the preparation of the solar cell devices, indium-tin-oxide (ITO)-coated glass substrates (Geomatec, Japan, $5 \Omega \, cm^{-2}$) were first patterned by etching and then cleaned thoroughly with a sequence of solvents: detergent, deionized water, acetone and isopropanol, for 10 min each in an ultrasonic bath. The cleaned substrates were purified further by oxygen plasma treatment for 10 min. The substrates were then spin coated with a $0.45 \, \mu m$ filtered PEDOT:PSS solution (Clevios P), purchased from HC Starck, at 4000 rpm for 60 s to produce 40 nm thick layers. The substrates were subsequently heated on a hotplate in air at 200 °C for 10 min to remove excess water. Solutions of the active layer components, *g*-TPP/Zn:*py*-C_{60}, were prepared separately with a concentration of $0.15 \, mg \, mL^{-1}$ in chlorobenzene (CB) and stirred in an ultrasonic bath at 50 °C for 2 h. The mixtures of each solutions were stirred in ultrasonic baths at 50 °C for 1 h. The mixed solutions with concentrations of 10, 20 and 40 wt% *g*-TPP/Zn:*py*-C_{60} complex in P3HT (Rieke Metal) were prepared. The *g*-TPP/Zn:*py*-C_{60} complex was flushed out after rinsing with dichloromethane (DCM). For coating of the PCBM layer, the PCBM solution (Nano C) in DCM at a concentration of $3 \, mg \, mL^{-1}$ was spin-casted at 2000 rpm. The samples were then heated at 160 °C for 6 min in air. For fabrication of P3HT:PCBM bilayer solar devices, solutions of P3HT in DCB at concentrations of $15 \, mg \, mL^{-1}$ were spin-casted at 1000 rpm (30 s), and solutions of PCBM in DCM at concentrations of $3 \, mg \, mL^{-1}$ were spin-casted at 2000 rpm (10 s). For BHJ solar cells, we obtained active layers using a 1:0.5 mixture of P3HT and PCBM dissolved in CB. After the active layer coating process, a

titanium tetraisopropoxide in ethanol (10 μL/3 mL) solution was spin-cast at 4000 rpm in air. Subsequently, in air at room temperature for 0.5 h, the precursor was converted into TiO_x via hydrolysis. Then, the device was pumped down in a vacuum (5×10^{-3} Pa), and a ~100 nm thick Al electrode was deposited by thermal evaporation.

2.3. Device measurements

AFM topography is employed to trace samples between surface and nanopillars using a Dimension Icon-ES1001SPM (Veeco). The sample is scanned under the tip and the topography is reproduced with built-in software tools that translate this information into images. The photovoltaic characteristics were measured under nitrogen atmospheres using an Agilent 4156C parameter analyzer under AM1.5G (100 mW cm^{-2}) simulated illumination using a solar simulator with a 1000 W xenon arc lamp.

3. Results and discussion

The fabrication process of the nanostructured OPVs based on nanoporous P3HT is illustrated in Fig. 1. Well-aligned nanopillars of L-glutamide-functionalized tetraphenylporphyrinate zinc(II) chloride (*g*-TPP/Zn):pyrrolidinofullerene (*py*-C_{60}) embedded in P3HT were formed when *g*-TPP/Zn:*py*-C_{60}:additive P3HT was spin-coated on a PEDOT:PSS covered ITO substrate. In our previous work, we showed that the nanopillars are developed via donor–acceptor assembled systems based on *J*-type aggregation of *g*-TPP/Zn and subsequent integration of *py*-C_{60} with coordination and orientation [62]. The diameter and height of the nanopillars can be tuned by the side chain-length, drying time and concentration of polymers, such as P3HT [62]. The PCBM solution was spin-coated directly on the nanostructured P3HT layer, formed after removing porphyrin–fullerene nanopillars by dichloromethane (DCM). Most of the P3HT remained, while the porphyrin–fullerene complexes are flushed out [62]. In process (D), partial interpenetration of PCBM into the P3HT underlayer happens, although it is significantly less than typical BHJ [68,71–74]. However, the spin coating of PCBM does not cause any remarkable differences in the morphology of the underlayer [67,68].

Fig. 2 shows AFM images of the surface morphology and cross-section profiles of process (B), (C), and (E) of Fig. 1. The three devices of N_1, N_2 and N_3 are fabricated using ratios of 10, 20 and 40 wt% *g*-TPP/Zn:*py*-C_{60} complex to P3HT, respectively. The data on the depths (or heights) of processes (A)–(E) are summarized in Table 1 and Fig. 3. To minimize any influence of the P3HT concentration on the PCE measurement, the depths of the nanopillars are manipulated only by the ratio of the *g*-TPP/Zn:*py*-C_{60} complex to the P3HT concentration although the nanopillar size also varies with the concentration of P3HT as shown in Fig. S1 [62]. Because the *g*-TPP/Zn:*py*-C_{60} nanopillars embedded in P3HT in process (B) directly affect process (C), we could estimate a broad outline of the P3HT nanostructures before eliminating the nanopillars in process (B). As shown in Fig. 2(b), the size of nanoporous P3HT shows close correlation with the shapes of the nanopillars; for example, the depths of the P3HT nanostructures (8, 23 and 34 nm) correspond to half of the height of the *g*-TPP/Zn:*py*-C_{60} nanopillars (15, 42 and 69 nm), while the diameters remain unchanged. The nanoporous P3HT are completely filled with PCBM components via process (D), except for a few deep nanopores in the N_3 device. The uneven morphology of the N_3 device is attributed to the quick drying time of DCM and the depth of the P3HT nanopores.

Fig. 4(a) shows the *J*–*V* characteristics of solar cells incorporating nanopores of various depths. The ratios ($R_s/R_{s(BHJ)}$ and $R_{sh}/R_{sh(BHJ)}$) of each device to a BHJ solar cell in terms of series resistance