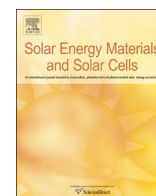




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Manipulation of discrete porphyrin–fullerene nanopillar arrays regulated by the phase separated infiltration of polymer in ternary blended organic thin-films

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ABSTRACT

Fabrication of nanostructure in various typed solar cell is of great importance in terms of the improvement of charge carrier collection and junction area. Here, we report that well-aligned nanopillar arrays are spontaneously developed in the process of the spin coating when a polymer is added to specific porphyrin–fullerene complexes. The nanopillars embedded in the polymers are composed of donor–acceptor assembled systems, based on J-type aggregation of a low-molecular zinc porphyrin derivative and subsequent integration of pyridylated fullerene derivative with coordination and orientation. The diameter and the height of the nanopillars can be controlled by the side chain-length and the concentration of the polymer as well as drying time after the spin coating. Structural, optical, and electrical properties of the nanopillar are also investigated. Finally, improved power conversion efficiency in the porphyrin–fullerene nanopillar is experimentally observed compared to that of the planar thin film prepared under similar conditions.

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1. Introduction

Organic photovoltaics (OPVs) have been developed remarkably since bulk heterojunction system based on poly (3-hexylthiophene) (P3HT) and fullerene derivatives such as [6] phenyl-C₆₁-butyric acid methyl ester (PCBM) [1–3]. Photoactive layers with bulk heterojunction of donor–acceptor (D–A) brought more efficient photo-induced charge separation of exciton at the interface of the D–A system [4,5]. However, it is simultaneously required to construct sufficient percolation pathways for the rapid charge transportation to electrodes while the electron and the hole do not disappear by recombination. Higher crystallized and ordered P3HT by thermal annealing, slow drying and various additives modified the nanomorphology inside the D–A blended active layer [6–10]. In order to obtain an ideal and optimum heterojunction structure, vertical composition gradients and nanoimprinted array were also introduced [11–17].

Meanwhile, as substituents of the polymer–fullerene system, the porphyrin–fullerene combination has been employed due to

high electron transfer and low charge recombination [18–23]. The combination of porphyrins and fullerenes forms supramolecular complexes, which result from strong interaction energy [24–26]. Moreover, the type of metal ion in a porphyrin ring can enhance electron transport properties for photodevices [27,28]. Hasobe et al. constructed novel organic photovoltaic systems using supramolecular complexes of porphyrin–peptide oligomers with fullerene clusters [29]. Hatano et al. reported the design of porphyrin donors possessing high solubility and strong intermolecular interactions, which attained the power conversion efficiency of 2.5% [30]. However, compared to the polymer–fullerene system, there has been no reference to morphology manipulation such as vertical nanostructures of porphyrin–fullerene complexes. Herein, we demonstrate the well-aligned nanopillar array in a ternary blend system based on porphyrin–fullerenes, where various polymers act as an additive. For this purpose, our research has been proceeded in consecutive order as follows: (i) the investigation of bicontinuous porphyrin–fullerene complexes with high electron-transfer efficiencies [31,32], (ii) the development of the phase separation between L-glutamide derivatives and polymers based on a low-molecular-weight gelation phenomenon [33,34]; and (iii) the formation of nanopillars of L-glutamide-functionalized tetraphenylporphyrinate zinc(II)

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chloride (*g*-TPP/Zn) and pyrrolidinofullerene (*py*-C₆₀) in the presence of polymer through spin coating process. Here, we present a comprehensive study on discrete *g*-TPP/Zn:*py*-C₆₀ nanopillars made by the phase separated infiltration of various polymers with different side chain-length as well as concentration of the polymer, drying time of the thin-films after coating process. The films have been investigated with atomic force microscope (AFM), transmission electron microscope (TEM), field-emission scanning electron microscope (FE-SEM), X-ray diffractometer (XRD), and UV–vis spectrophotometer to reveal the origin and properties of the nanopillars. The same films have also been incorporated into devices and have been fully characterized under the illumination with solar simulator. By combining the morphological and electro-optical characterization, we have been able to understand the mechanism of carrier transport and optimum composite ratio of the polymer in *g*-TPP/Zn:*py*-C₆₀:P3HT ternary solar cell.

2. Experimental section

2.1. Materials

N₁, N₅-didodecyl-L-glutamide zinc porphyrin-derivatives (*g*-TPP/Zn), and pyridine-substituted pyrrolidinofullerene (*py*-C₆₀) were synthesized by previously reported procedures [32,35].

2.2. Device preparation

In the preparation of solar cell devices, indium-tin-oxide (ITO) coated glass substrates (Geomatec, 5 Ω 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 μm filtered PEDOT: PSS solution (Clevios P), purchased from HC Starck, at 4000 rpm for 60 s to produce a 40 nm thick layer. 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*-C₆₀, were prepared separately with a concentration of 0.15 mg ml⁻¹ in chlorobenzene and stirred in ultrasonic bath at 50 °C for 2 h. The mixture of each solution was stirred in ultrasonic bath at 50 °C for 1 h. P3HT (Rieke Metal) with the concentration of devices with contents of 1, 5, 10, 20 and 50 wt% P3HT in *g*-TPP/Zn:*py*-C₆₀ complex was blended to the *g*-TPP/Zn:*py*-C₆₀ solution. The sample was then heated at 40, 80, 120 and 160 °C for 6 min in air, respectively. The titanium tetraisopropoxide in ethanol (10 μl/3 ml) solution was at 4000 rpm spin-cast in air on top of the *g*-TPP/Zn:*py*-C₆₀:P3HT composite layer. Subsequently, during 0.5 h in air at room temperature, the precursor converted to TiO_x by hydrolysis. Subsequently the device was pumped down in vacuum (5 × 10⁻³ Pa), and a ~100 nm thick Al electrode was deposited by thermal evaporation. The same procedure except for TiO_x layer and Al evaporation was used to prepare samples for morphological and spectroscopic studies with ~200 nm composite layers on ~40 nm PEDOT:PSS for the morphological studies.

2.3. Device measurements

TEM images were observed by JEM-2000X (JEOL). The solution was cast on a carbon-coated copper grid and dried under reduced pressure. The accelerating voltage of the TEM was 80 kV. The AFM topography is employed to trace samples between the surface and nanopillars by 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 nanopillars were characterized by FE-SEM (SU-8000; Hitachi High Technologies, Co. Ltd., Tokyo, Japan). UV–visible absorption spectra were obtained using a Shimadzu UV-1601 PC UV–visible spectrophotometer. Energy diagram were calculated from HOMO by PYS-201 (Sumitomo Heavy Industries Ltd.). The devices are examined by XRD using SMART-LAB (Rigaku). Thin polymer films were deposited onto previously cleaned quartz slides with the same settings used for the production of solar cells. The photovoltaic characteristics were measured under nitrogen atmosphere 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

3.1. Molecular design

In our previous work, the D–A complex is based on J-type assembly of porphyrin as a donor and subsequent coordination and orientation of fullerene as an acceptor on the donor assembly, as shown in Fig. 1(a) modified from the molecular model of Ref. [32]. From the experiments, it is confirmed that the following three-step molecular ordering and assembly: (1) highly ordered J-type aggregation resulting from both intermolecular hydrogen bonding among the *g* moieties and intermolecular coordination of the *g* carbonyl group on zinc porphyrin. (2) *py*-C₆₀ interacting with zinc by axial coordination; significant enhancement in the binding constant due to the ordered structures of the *g*-TPP/Zn aggregates. (3) Complementary interaction of *py*-C₆₀ promoted on the *g*-TPP/Zn aggregates [32]. At the same time, the quenching efficiency of 99% was realized by addition of only 1.0 equivalents of the acceptor (*py*-C₆₀) to a solution of *g*-TPP/Zn.

In order to obtain a high performed solar cell using these *g*-TPP/Zn:*py*-C₆₀ complexes with high electron transfer efficiency, it is required to keep strong aggregation of the complex as well as to create pathways for higher mobility of the charge carriers. Here, we also found a highly oriented nano-sized phase separation in a polymer matrix using a low-molecular gelation technique [36,37]. On the basis of these phase separation, we investigated to build discrete nanopillars making the best use of phase separation phenomenon between these *g*-TPP/Zn:*py*-C₆₀ complex and the polymer. Considering cascade charge transport mechanism expected in the ternary blend system, P3HT was preferentially selected for the additive polymer as shown in Fig. 1(b). Interestingly, after P3HT was inserted to *g*-TPP/Zn:*py*-C₆₀, well-aligned nanopillars of *g*-TPP/Zn:*py*-C₆₀ surrounded by the additive P3HT was obtained.

3.2. Manipulation of nanopillars

Fig. 2 shows AFM images of surface morphology according to the concentration of the additive P3HT and the speed of spin coating. To match the conditions used for typical device preparation and to exclude any possible influence of the substrate, all films in this study were spin cast from chlorobenzene on indium tin oxide (ITO)-coated glass substrates covered an additional layer of a transparent conducting polymer (poly(3,4-ethylenedioxythiophene)poly(styrene sulfonic acid) (PEDOT:PSS)). Devices with the different weight ratios of H-P3HT (1:1:0.2) and L-P3HT (1:1:0.1) in terms of *g*-TPP/Zn:*py*-C₆₀:P3HT were prepared. The speed of spin coating was changed from low-speed rotation (*l*: 500 rpm) to high-speed rotation (*h*: 750 rpm). The height images reveal no remarkable change in the *g*-TPP/Zn:*py*-C₆₀ blends film, even if root-mean-square (RMS) values is 2.2 nm. Contrast to spike shape of pristine P3HT film in Fig. 2(b), small aggregation is

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