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Letter

Bulk heterojunction photocells utilizing neat C₇₀ and low energy-gap polymer prepared with halogen-free solvent

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ABSTRACT

The combination of halogen-free solvent and neat fullerene is expected to provide a way to develop environment-friendly and cost-effective polymer photocells. Here, polymer photocells using neat C₇₀ and a low energy-gap polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]â[3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) prepared by using 1,2,4-trimethylbenzene as a halogen-free solvent have been studied. After a preliminary optimization, a device with the power conversion efficiency of 3.02% has been obtained. The C₇₀-based composites contain less amount of fullerene than the composites using C₇₀-PCBM at their optimal compositions, reflecting the different electron mobility and/or the aggregation tendency of the fullerenes.

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1. Introduction

Photocells based on bulk heterojunction composites consisting of organic materials such as conjugated polymers and fullerenes are attracting much attention as the large-area photocells in the next generation, because the composites can be deposited by solution-based technologies such as spin-coating and printing [1–5]. The state-of-the-art organic photocell marked a certified power conversion efficiency (PCE) over 10% [6].

The study on the optoelectronic properties of polymer:fullerene composites was initiated by the discovery of unique phenomena, namely efficient quenching of the photoluminescence as well as drastic enhancement of photoconductivity, in conjugated polymers doped with a few mol% of neat fullerene [7–9]. These phenomena come from the photoinduced charge transfer between the conjugated polymer and the fullerene. That is, photoexcited electrons in the conjugated polymer are transferred to the fullerene because the energy level of the lowest unoccupied molecular orbital (LUMO) in the fullerene is lower than that in the polymer, resulting in the dissociation of electrons and holes before luminescent decay as well as efficient generation of photocarriers. In this type of systems, the conjugated polymer functions as an electron donor and the fullerene works as an electron acceptor.

To make the polymer photocells efficient, so-called bulk heterojunction composites, in which both donor and acceptor materials continuously distribute to all regions of composites to provide pathways for the both carriers, are required [10]. The lack of knowledge about appropriate solvents which can dissolve enough

amounts of neat fullerene and polymer to produce the bulk heterojunction composites has made neat fullerenes be almost forgotten by the researchers of polymer photocells. However, since all fullerene derivatives known so far are derived from neat fullerenes, the usage of neat fullerenes is potentially minimizes the economic and environmental costs of polymer photocells.

Although the preparation of composites with halogenated solvents such as chlorobenzene or *o*-dichlorobenzene seems to be a common practice in the field of polymer photocells, the halogenated solvents are basically not preferred because they are highly toxic and their production processes consume a lot of energy [11,12]. Thus, the realization of efficient polymer photocells with neat fullerenes and halogen-free solvents may be an interest target to investigate.

Recently, it has been clarified that a halogen-free solvent 1,2,4-trimethylbenzene (TMB, pseudocumene) is useful to prepare bulk heterojunction composites with neat fullerenes [13–15]. However, the power conversion efficiencies of the device based on poly(3-hexylthiophene) (P3HT) and neat fullerenes reported so far were approximately 1% and have not been attracted serious attentions of researchers. Here, a polymer photocell using neat C₇₀ and a low energy-gap polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]â[3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) [16–18] showing PCE over 3% is reported.

2. Material and methods

PTB7 and C₇₀ were purchased from 1-Material Chemscitech and Nano-C, respectively. TMB was a product of Tokyo Kasei. All

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chemicals were used as received. The films of PTB7:C₇₀ composite were deposited on appropriate substrates by spin-coating. For example, a film of PTB7:C₇₀ composite (1:1 by weight) was coated at a spin-rate of 1000 rpm for 60 s from a solution containing 15 g l⁻¹ of PTB7 and 15 g l⁻¹ of C₇₀. The thicknesses of the films were approximately 100 nm. The concentration of the polymer in the solutions was kept constant throughout the study. The mixture solution was once warmed on a hot plate heated at 100 °C for 3 min to be homogeneous and was cooled to room temperature before deposition. The samples were annealed on a hot plate at a specified temperature in the range of 130–190 °C for 20 min after the deposition.

Photocells based on the composites were fabricated as follows. Films of poly(3,4-dioxythiophene):poly(styrene sulfonate) salt (PEDOT) were deposited on prepatterned ITO electrodes by spin-coating from an aqueous suspension purchased from Aldrich, followed by annealing at 130 °C for 60 min. The thickness of the PEDOT films was approximately 80 nm. After the spin-coating of the composite films, Al electrodes were vacuum deposited to complete the devices with 3 × 3 mm² square active area. The preparation as well as post-production thermal annealing of the devices was carried out in a glove-box filled with nitrogen.

The optical absorption spectra of the composite films coated on glass plates were recorded using a Shimadzu UV-1800 spectrophotometer. The photocells were characterized using a Keithley 6517A electrometer under AM 1.5 G 100 mW cm⁻² (1 sun) illumination from an Asahi Spectra HAL-C100 solar simulator. Photocurrent spectra were collected by irradiating light from a 300 W Xe-lamp passing through a monochromator as well as appropriate long-pass glass filters. The photocurrent spectra were converted to external quantum efficiency (EQE) spectra using a photocurrent spectrum of a calibrated Hamamatsu S1337BQ Si-photodiode under the same irradiation. All measurements were carried out in air.

3. Results and discussion

Fig. 1(a) shows the optical absorption spectra of PTB7:C₇₀ composite films with various compositions. The absorption peaks at around 365 nm and 485 nm correspond to the optical transitions in C₇₀. It is known that the absorption spectrum of C₇₀ is sensitive to the aggregation degree of C₇₀ [19], namely the absorption peaks undergo substantial broadening and red-shift due to aggregation. Since the absorption peaks shown in Fig. 1 (a) do not indicate large modulation and the peak at 365 nm is relatively sharp, the aggregation degree of C₇₀ in the composites seems moderate and independent to the polymer:fullerene ratio. It should be worth to note that this sharp peak is absent in composite films consisting of PTB7 and phenyl-C₇₁-butyric acid methyl ester (C₇₀-PCBM) [16]. Unlike P3HT:fullerene composites in which the thermal annealing results in the color change due to the recovery of the optical absorption of the polymer in a composite film is easily visible by the naked eye, [13,14,20,21] the thermal annealing treatment gives only negligible effect on the optical absorption spectra of the present PTB7:C₇₀ composites as shown in Fig. 1(b). This suggests that the thermal annealing does not induce noticeable rearrangement of polymer main chains.

As shown in Fig. 2(a), the short-circuit photocurrent density (J_{SC}) strongly depends on the polymer:fullerene ratio. The thermal annealing gave a slight positive effect on the devices showing high J_{SC} such as those with PTB7:C₇₀ = 1:1 and 3:2, while it deteriorated J_{SC} in the devices with PTB7:C₇₀ = 2:3 and 2:1. On the other hand, the composition change yields relatively small variation within 0.05 V, with negligible effects from the thermal annealing, in the open-circuit voltage (V_{OC}) as shown in Fig. 2(b). For the devices

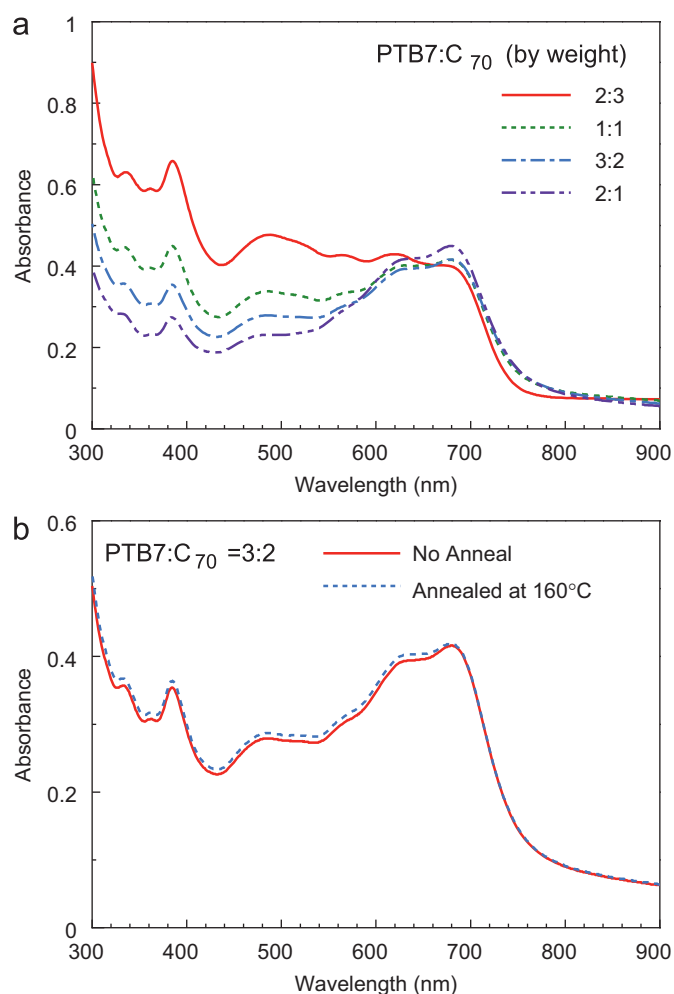


Fig. 1. (a) Optical absorption spectra of PTB7:C₇₀ composite films with various compositions and (b) optical absorption spectra of PTB7:C₇₀ = 3:2 composite films with and without the annealing at 160 °C.

with PTB7:C₇₀ = 1:1 and 3:2, the fill-factor (FF) moderately increased by the thermal annealing, as shown in Fig. 2(c). Since the tendencies of FF and J_{SC} are almost the same, these can be attributed to the improved carrier transport nature of the composites. Relatively minor effects of the thermal treatment on the device performance are consistent with the negligible annealing effect on the optical absorption spectra. As a result of the preliminary tuning of the composition and annealing condition, the highest PCE of 3.02% in this study was obtained in a device with PTB7:C₇₀ = 3:2 after annealing at 160 °C for 20 min.

While the optimal composition for the device using PTB7:C₇₀-PCBM composite is reported as polymer:fullerene = 2:3, [16] the optimal composition for the present system was found to be PTB7:C₇₀ = 3:2. It is pointed out that the balanced mobility for hole and electron in polymer:fullerene bulk heterojunction composite is a key to obtain high photovoltaic performance [3,22,23]. Since the electron mobilities of neat C₇₀ and C₇₀-PCBM are reported as 0.003–0.066 cm² · V⁻¹ s⁻¹ [24] and 1–2 × 10⁻³ cm² V⁻¹ s⁻¹ respectively, [25] it seems reasonable that the C₇₀-based composite contains less amount of fullerene than the composite using C₇₀-PCBM at their optimal compositions. Similar difference has been also found in the composites based on P3HT [15].

Recently, Jamieson et al. has pointed out the importance of the aggregation of fullerene in the polymer:fullerene bulk heterojunction composites on the charge separation [26]. According to their theory, the formation of aggregated fullerene domains is a key to

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