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Thermally robust bulk heterojunction photocells based on PTB7:C₇₀ composites

Kazuya Tada¹

Division of Electrical Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2201, Japan



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ABSTRACT

Bulk heterojunction (BHJ) photocells using low energy-gap polymers such as poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) and modified fullerenes such as [6,6]-phenyl-C₇₁-butyric acid methyl ester (C₇₀-PCBM) show relatively high power conversion efficiency. It is known that the thermal annealing, which effectively improves the photovoltaic performance of BHJ photocells with semi-crystalline polymers such as poly(3-hexylthiophene), is not applicable to BHJ photocells with amorphous-type polymers such as PTB7. In this study, it is found that PTB7:C₇₀-PCBM BHJ photocells degrade shortly at 80 °C, which is within the range of the temperature shock cycling test condition specified in IEC 61646, the international standard for testing thin-film photovoltaic module. On the other hand, the photovoltaic performance of PTB7:C₇₀ BHJ photocells composite has been found to significantly improve after the thermal annealing at 160 °C. The results strikingly indicate not only that the lack of thermal robustness in PTB7:C₇₀-PCBM BHJ photocells does not mainly arise from the nature of the polymer but the substituents of the fullerene used, but also that neat fullerenes should not be considered as just cheap and nasty substitutes of fullerene derivatives.

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1. Introduction

Photocells based on wet-processed bulk heterojunction (BHJ) composites, which consist of comparable amounts of conjugated polymers and fullerenes, have been attracting considerable attentions of researchers, partly because of their compatibility with the printing technology which is believed to enable high-throughput production of flexible and large-area photovoltaic panels at low cost [1–5]. Although the discovery of the efficient and ultrafast photoinduced electron transfer from conjugated polymers to neat C₆₀ slightly-doped in the polymers opened up this area [6–8], the realization of wet-processed BHJ composites with neat fullerene was hindered by the lack of knowledge about solvents which dissolve enough amounts of neat fullerenes and conjugated polymers. Thus, the use of chemically modified fullerene derivatives with high solubility such as [6,6]-phenyl-C₇₁-butyric acid methyl ester (C₇₀-PCBM) has been a common practice in this field [9].

Another common practice in this field is the utilization of halogenated solvents such as *o*-dichlorobenzene [10]. However, the toxicity of halogenated compounds is known to be relatively

high. Other than toxicity, the production of halogenated compounds is known to be a process with massive energy consumption, giving another drawback in terms of environmental cost [11]. In this context, the exploration of halogen-free solvents suitable for wet-processed photocells is becoming a crucial issue [12–14].

Recently, it has been reported that a halogen-free solvent 1,2,4-trimethylbenzene (TMB) dissolves enough amount of neat fullerenes to prepare BHJ composites with conjugated polymers such as poly(3-hexylthiophene) (P3HT) [15,16]. This finding potentially lofts neat fullerenes back onto center stage of the wet-processed BHJ photocells. Since all fullerene derivatives known so far are synthesized from neat fullerenes, photocells based on neat fullerenes seem to be attractive in term of the minimization of the cost of materials. Besides the economical issue, neat fullerenes are inherently attractive electron acceptor material in photocells, because they are known to have superior electron mobility compared with their derivatives [17,18]. It is also worth to note that commercial TMB is produced by refinement of mineral oil, offering another advantage for the material systems utilizing neat fullerenes and TMB in terms of economical and environmental views.

While the BHJ photocells based on neat fullerenes and P3HT show relatively low power conversion efficiency (PCE) less than 2%, it has been recently found that the photocells employing a low energy-gap

E-mail address: tada@eng.u-hyogo.ac.jp¹ Tel.: +81 79 267 4966; fax: +81 79 267 4855.

polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) [19,20] with neat C_{70} show PCE over 3% [21]. The application of interlayer of the conjugated polyelectrolyte poly(9,9-bis(3'-(N,N-dimethyl)-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)) (PFN) at the composite/cathode interface substantially has been found to improve the performance of the photocells, yielding PCE over 4% [22]. Nevertheless, the PCE realized with PTB7: C_{70} system is far less than state-of-art PTB7: C_{70} -PCBM BHJ photocells for which PCE over 6% is repeatedly reported [19,20,23]. This has made one consider neat fullerenes to be cheap and purely nasty substitutes for the fullerene derivatives so far.

On the other hand, it is known that the thermal treatment of BHJ photocells based on low energy-gap amorphous-type polymers yielding high power conversion efficiency such as PTB7 and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) causes serious deterioration of their photovoltaic performance [24,25], raising doubts about the thermal robustness of this type of photocells. In the present study, it is first shown that the BHJ photocells based on PTB7: C_{70} -PCBM degrade shortly at 80 °C which is lower than the upper limit in the temperature shock cycling test condition specified in IEC 61646, the international standard for testing thin-film photovoltaic module [26]. Then it is demonstrated that BHJ photocells based on PTB7: C_{70} composite show significant improvement of photovoltaic performance after the thermal annealing at 160 °C. This suggests that neat C_{70} is no longer just a cheap and nasty substitute of C_{70} -PCBM but a superior acceptor material for the realization of thermally robust BHJ photocells based on low energy-gap amorphous-type polymers such as PTB7.

2. Materials and methods

PTB7 and PFN were purchased from 1-Material. Fullerenes and TMB were products of Nano-C and Tokyo Kasei, respectively. All chemicals were used as received. Photocells based on PTB7: C_{70} BHJ composites were fabricated as follows. Films of poly(3,4-dioxathiophene):poly(styrene sulfonate) salt (PEDOT:PSS) 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 50 nm. The films of PTB7: C_{70} composite were deposited on appropriate substrates by spin-coating. That is, a film of PTB7: C_{70} composite (4:3 by weight) was coated at a spin-rate of 2000 rpm for 30 s from a solution containing 15 g l⁻¹ of PTB7 and 11 g l⁻¹ of C_{70} . The thicknesses of the films were approximately 70 nm. 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.

A 0.3 g l⁻¹ PFN solution was prepared by dissolving 1.0 g l⁻¹ of PFN in methanol containing 2 vol% of acetic acid, followed by dilution with pure methanol. The spin-coating of a PFN layer on a composite film was carried out with the 0.3 g l⁻¹ solution at a spin-rate of 3000 rpm for 5 s. The PFN film was so thin that the thickness was unknown. After the spin-coating of the polymer films, Al cathodes were vacuum deposited to prepare the devices with 3 × 3 mm² square active area. Photocells based on PTB7: C_{70} -PCBM composite (2:3 by weight) were prepared by a similar manner except for the usage of a TMB solution containing 15 g l⁻¹ of PTB7 and 23 g l⁻¹ of C_{70} -PCBM. Some devices were subject to post-production thermal annealing on a hot-plate heated at a specified temperature for 20 min. Finally, the active area of the photocell was covered by a glass plate and a UV-curable resin for the moderation of prompt degradation. The preparation of the devices was carried out in a glove-box filled with nitrogen.

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. The Solver add-in program of Microsoft Excel was employed for fitting the current-voltage characteristics with the equivalent circuit shown in Fig. 1 to extract circuit parameters. The procedure to extract the circuit parameters are described in a previous report [22].

To collect the data for statistical analysis of BHJ photocells based on PTB7: C_{70} , 12–13 devices were prepared on separated glass plates in four batches, each of which consisted of 3–4 samples under all conditions tested to avoid systematic bias in data. Statistical analysis was carried out by using R [27] and R Commander [28].

3. Results and discussion

3.1. Thermal annealing effect on PTB7: C_{70} -PCBM photocells

Fig. 2(a) shows typical current density–voltage characteristics of the BHJ photocells based on PTB7: C_{70} -PCBM=2:3 composite before and after the thermal annealing at 80 °C. Any additives to improve the photovoltaic performance such as 1,8-diiodopptane (DIO) were not applied in the present study. The pristine device shows the PCE of 2.97% with the photocurrent density (J_{SC}) of 7.14 mA cm⁻², the open-circuit voltage (V_{OC}) of 0.77 V and the fill-factor (FF) of 54.1%. The value of PCE is comparable with the value reported for a similar device prepared from chlorobenzene solution without DIO [23], indicating that the usage of TMB instead of chlorobenzene as a solvent does not alter the device performance.

The thermal annealing at 80 °C in nitrogen atmosphere resulted in a serious deterioration of the photovoltaic performance of the device, yielding the PCE of 1.33%, less than half of the pristine one, with the J_{SC} of 5.73 mA cm⁻², the V_{OC} of 0.72 V and the FF of 32.3%. This poses a serious question about the thermal robustness of the photocells with this particular material system, since the upper limit of the temperature shock cycling test condition specified in IEC 61646 is 85 °C [26].

To get deeper insight on the thermal treatment effect, fitting the current density–voltage characteristics of the photocells with the equivalent circuit shown in Fig. 1 was carried out to extract the circuit parameters. The relationship between current (I) and voltage (V) of the circuit is expressed as follows.

$$I = I_s \left(e^{\frac{V - I \cdot R_s}{n \cdot V_t}} - 1 \right) + \frac{V - I \cdot R_s}{R_p} - I_{ph}$$

In this equation, I_{ph} denotes the ideal photocurrent, and the saturation current I_s and $n \cdot V_t$ are the parameters of the internal diode. R_s and R_p stand for the series resistance and parallel (shunt) resistance, respectively. The thermal voltage V_t is 26 meV at room temperature. As reported in the previous paper, the ideal factor n of the internal diode was obtained by the fitting of the current–voltage characteristics under dark condition shown in Fig. 2(b), and then other parameters under illumination were determined by using the value of n [22].

As mentioned in Table 1, in which the parameters extracted by the fitting are listed as a normalized form, significant changes are found in the parameters corresponding to the internal diode, in addition to the 16% reduction in J_{ph} . The reduction in J_{ph} is too

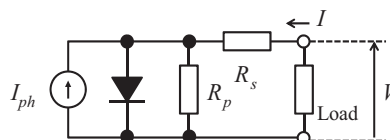


Fig. 1. Equivalent circuit model used for fitting the current voltage characteristics of photocells.

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