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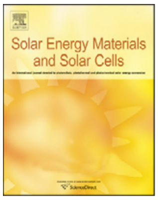

Yet another poor man's green bulk heterojunction photocells: Annealing effect and film composition dependence of photovoltaic devices using poly(3-hexylthiophene):C_{70} composites prepared with chlorine-free solvent

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ABSTRACT

Chemically modified fullerenes and chlorinated solvents have been predominantly chosen in the recent studies of the photovoltaic devices based on polymer bulk heterojunction composites. However, these items seem to be undesirable because of their potential impacts on the environment as well as the consumption of resources. In this context, a systematic study on the annealing effect and film composition dependence of bulk heterojunction photovoltaic devices based on composites consisting of poly(3-hexylthiophene) (P3HT) and neat C_{70} prepared with a chlorine-free solvent 1,2,4-trimethylbenzene has been carried out. For the device using P3HT:C_{70} composite (2:1 by weight) film as an active layer, power conversion efficiency of 1.47%, with open-circuit voltage of 0.52 V, short-circuit current density of 6.2 mA/cm^2 and fill-factor of 45%, has been obtained after post-production annealing at 160 °C. The combination of neat fullerenes with naturally obtained solvents will open up a new way to produce cost-effective and environmentally-friendly photovoltaic devices based on polymer:fullerene bulk heterojunction composites.

1. Introduction

Since the discovery of the photoinduced electron transfer in conjugated polymers doped with fullerenes such as C_{60} and C_{70}, huge effort has been devoted to the study on the polymer photovoltaic devices based on polymer–fullerene composites [1–4]. The doping of polymers with just a few mol% of fullerene is enough to observe phenomena peculiar to the photoinduced electron transfer such as drastic quenching of photoluminescence and dramatic enhancement of photoconductivity [5–7]. However, if we targeted the polymer photovoltaic devices, so-called bulk heterojunction composites, which contain comparable amounts of conjugated polymers and fullerenes, are desired, because we need to install the pathways for electrons and holes throughout the composite.

The lack of knowledge in the community of researchers of polymer photovoltaic devices about solvents which can dissolve neat fullerenes such as C_{60} and C_{70} at a concentration high enough to prepare bulk heterojunction composites almost omitted them from the researchers' list of "fullerenes." Instead, chemically modified fullerenes such as [6,6]-phenyl-C_{71}-butyric acid methyl ester (C_{70}-PCBM) have been predominantly chosen as counterparts of conjugated polymers [8–11]. Therefore, the photovoltaic devices based on bulk heterojunction composites using neat C_{70} have been rarely reported though, there is no question that neat fullerenes are the most cost-effective fullerenes in terms of economical and environmental viewpoints, because they are the starting materials of all chemically modified fullerenes known so far.

Recently, it has been demonstrated that a not-so-common organic solvent 1,2,4-trimethylbenzene (TMB) can dissolve both poly(3-hexylthiophene) (P3HT) and neat fullerenes at a concentration high enough to make bulk heterojunction composites for photovoltaic devices [12,13]. Since TMB is produced by distillation of natural oil, this solvent must be more favorable than chloroaromatic solvents such as chlorobenzene and 1,2-dichlorobenzene (ODCB), which have been predominantly used in the preparation of bulk heterojunction composites for photovoltaic devices, in terms of economical and environmental viewpoints. Not only the toxicity of chlorinated solvents but also the chlorination process, which is a heavily energy consuming process, is not favorable in terms of the environmental friendliness [14,15].

In our previous study, it has been demonstrated that the photovoltaic devices based on P3HT:C_{70} composite (1:1 by weight) prepared from TMB solution showed power conversion efficiency (PCE) of 0.45% [13], 10 times lower than those of state-of-the-art devices, although it is higher than the previously reported value for P3HT:C_{70}-based devices from ODCB solution [16] by an order of magnitude. Here, a systematic investigation on

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the annealing effect and film composition dependence of P3HT:C_{70} bulk heterojunction photovoltaic device is reported. For the device using P3HT:C_{70} composite (2:1 by weight) film as an active layer, maximum power conversion efficiency (PCE) of 1.47%, with open-circuit voltage (V_{OC}) of 0.52 V, short-circuit current density (J_{SC}) of 6.2 mA/cm^2 and fill-factor (FF) of 45%, has been obtained after a post-production annealing at 160 °C for 20 min.

2. Material and methods

Regioregular P3HT and C_{70} were purchased from Rieke Metals and Nano-C, respectively. TMB was a product of Tokyo Kasei. All chemicals were used as received. The films of P3HT:C_{70} composite were deposited on appropriate substrates by spin-coating. For example, a film of P3HT:C_{70} composite (1:1 by weight) was prepared at a spin-rate of 750 rpm for 60 s from a solution containing 15 g/l of P3HT and 15 g/l of C_{70}. The thicknesses of the films were in the range of 80–90 nm, except for P3HT:C_{70}=1:3 composite films which were approximately 60 nm. The mixture solution was once warmed on a hot plate heated at 90 °C for 1 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 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 mm^2 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 photovoltaic devices were characterized using a Keithley 6517A electrometer under AM 1.5G 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 P3HT:C_{70} composite films with various mixing ratios without annealing. The optical absorption spectra of the films annealed at 160 °C, which is the best annealing temperature for this system, are also shown in Fig. 1(b). It is known that the thermal annealing of bulk heterojunction composites based on C_{60} and C_{60}-PCBM induces strong modulation in the optical absorption spectra, because of an increase in optical absorption in the 500–600 nm region due to improved interchain interaction as well as crystallinity of the polymer [17–19]. However, the modulation of the optical absorption spectra in the composites based on C_{70} is rather moderate, because the spectra of P3HT and C_{70} substantially overlap, especially in the composites with relatively high C_{70} content [20]. The most significant spectral change was observed in the 1:1 composite film, which has been published in the preceding report [13].

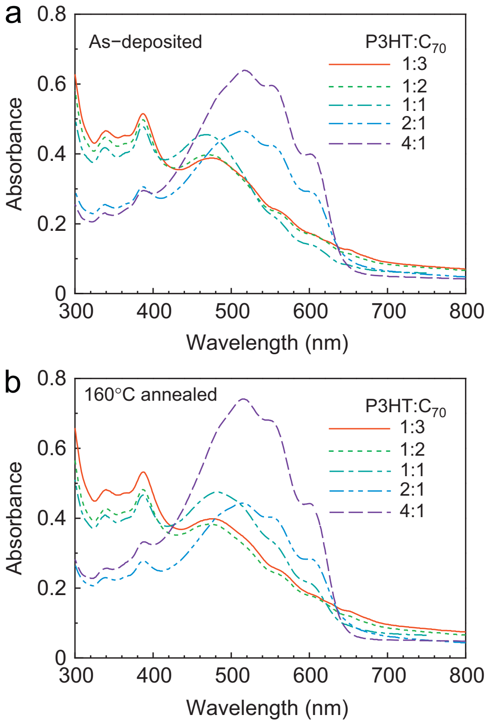

Fig. 1. Optical absorption spectra of P3HT:C_{70} composite films with various compositions; (a) and (b) show the spectra of as-deposited and 160 °C annealed films, respectively.

It is known that C_{70} forms aggregates in a mixture solvent containing certain amount of poor solvent, which effectively enhance absorption in the 700–800 nm region, where molecularly dissolved C_{70} shows negligible optical absorption [21]. In the case of P3HT:C_{60} bulk heterojunction composites, the formation of C_{60} aggregates, which accompanies noticeable red-shift as well as broadening of the absorption peak, is induced by the thermal annealing [12]. On the other hand, the minor change induced by the thermal annealing suggests that additional formation of C_{70} aggregates in the present system is negligible.

Fig. 2(a) shows the EQE spectra of the photovoltaic devices based on P3HT:C_{70} composites without thermal annealing. The onset wavelengths are found to be 700 nm and 650 nm for the devices with P3HT:C_{70}=1:3 and 4:1 composites, respectively. Similar difference in the onset wavelengths can be found in the optical absorption spectra of the two composites.

Although the thermal annealing did not increase the optical absorption in the composites, it drastically enhanced the EQE of the photovoltaic devices, as shown in Fig. 2(b). For all cases but the P3HT:C_{70}=4:1 composite, the EQE almost doubled without significant modulation of its spectral shape upon annealing at 160 °C. Since the number of photons absorbed in the composites does not change, this result is attributed to the improved carrier separation and transport properties in the composites. That is, improved phase segregation and enhanced interchain interaction of the polymer upon annealing, similar to those reported for other bulk heterojunction composites based on conjugated polymers and fullerenes, also take place in the present P3HT:C_{70} composite system [17–19]. In the cases of the devices containing more amount of P3HT than C_{70}, annealing at elevated temperature such as 190 °C resulted in significant reduction of EQE, which can be attributed to excessive mixing of the polymer and fullerene.