Improvement of Photovoltaic Properties for Unmodified Fullerene C$_{60}$-Based Polymer Solar Cells by Addition of Fusible Fullerene

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We fabricated the organic thin-film solar cells consisting of poly(3-hexylthiophene-2,5-diyl) (P3HT) and unmodified fullerene (C$_{60}$). Since our devices performance was not good, we tried to improve the photovoltaic (PV) properties by means of adding fusible fullerene derivative (PCBM). The addition of PCBM improved the compatibility of C$_{60}$ and modified the bulk-hetero junction structure of active layer and the PV properties could be improved twice.

Keywords: Organic thin-film solar cell, Unmodified fullerene, Fusile fullerene, Aggregation, Poly(3-hexylthiophene-2,5-diyl) (P3HT)

1. Introduction

Organic photovoltaic cells (OPVs) have developed since Tang’s bilayer-type cell in 1986 [1]. This bilayer-type cell consisted of a copper-phthalocyanine (CuPc) and a perylene diimide derivative (PTCBI) as donor and acceptor materials, respectively. This structure is called a heterojunction type, which is also called Tang-type cell with the kind of respect. The power conversation efficiency (PCE) of the first cell is reported to be almost 1 % under 1 sun. This value is much higher than those of Schottky-type OPVs. In 1991, Hiramoto et al. proposed the bulk-heterojunction type consisting of the mixture layer of donor and acceptor materials [2]. Famous fullerene as an acceptor was discovered in 1985 by Kroto et al. [3]. After establishing the isolation and purification processes of fullerene, the photo-induced interaction between a conducting polymer and fullerene was discovered [4,5]. Fullerene was recognized as a typical acceptor material in the OPV field. Hummelen et al. developed a fusible fullerene derivative, phenyl-C$_{51}$-butyric-acid-methyl Ester (PCBM) in 1995 [6]. Yu et al. fabricated the OPV of 1.5 % PCE using PCBM [7]. Using poly (3-hexylthiophene-2,5-diyl) (P3HT) and PCBM, Brabec et al. reported the OPV of 3.3% PCE in 2002 [8] and Padinger et al. reported the OPV of 3.5% PCE in 2003 [9]. The combination of P3HT and PCBM was typical OPV materials in the early research.

In 2013, Prof. Tada have firstly reported the fabrication and properties of OPVs consisting of P3HT and C$_{60}$ using a green solvent (halogen-free solvent)[10]. Their power conversation efficiency was reported to be 1.47%. The price of PCBM is almost 10 times more expensive than that of C$_{60}$. If the low-cost C$_{60}$ and a green solvent are used widely, they will be very effective for the practical use of OPVs [11]. However, the solubility of C$_{60}$ is not always good to both halogen and halogen-free solvent.

In addition, the compatibility of fullerene to organic materials is also not good. Since the fullerene aggregates easily, the additives such as 1,8-diodeoctane (DIO) are often mixed in polymer:fullerene solutions [12,13]. DIO is very effective for the improvement of compatibility of
fullerene. However, the addition of DIO improves the initial device performance of OPV but is not effective for the prolongation of device lifetime [14]. If high performance OPVs can be fabricated without any additive, the additive-free process will be better than the additive-use process.

We reported the organic alloy which is the mixture material by a co-evaporation method [15-17]. The hole or electron transport layer fabricated by the organic alloy shows a good mechanical and increases a heat-resistance without reducing electrical properties in spite of the combination of low glass point ($T_g$) molecules. In a liquid crystal (LC) field, a molecular alignment and $T_g$ are often adjusted by the mixture of two LC materials. Mixture is a simple method but can change physical properties.

In this study, we fabricate the P3HT:C$_{60}$-based OPV by adding a small amount of PCBM in place of DIO in order to improve the compatibility and heavy aggregation of C$_{60}$.

2. Experimental

2.1. Materials and fabrication

We used poly(3-hexylthiophene-2,5-diyl) (P3HT) (lot# 20121010, Jilin Optical and Electronic Materials Co. Ltd.) as a donor material, a fullerene C$_{60}$ and phenyl-C$_{61}$-butyric-acid-methyl Ester (PCBM) as acceptor materials, and poly(3,4-ethylenedioxy thiophene)-poly(styrene sulfonate) (PEDOT:PSS) as a buffer layer in Fig. 1. 1,2,4-trimethylbenzene (TMB) was used as a solvent.

Fig. 1. Chemical structures of our organic materials.

We prepared active layers (Fig. 2) from 4 kinds of solutions. The weight-ratios of these solutions in 1 mL-TMB were shown in Table 1.

| Specimens | P3HT [mg] | C$_{60}$ [mg] | PCBM [mg] |
|-----------|-----------|---------------|-----------|
| 0 wt%     | 10        | 7             | 0         |
| 10 wt%    | 10        | 6.3           | 0.7       |
| 20 wt%    | 10        | 5.6           | 1.4       |
| 30 wt%    | 10        | 4.9           | 2.1       |

Table 1. The weigh-ratios of 4 kinds of specimens

Fig. 2. The structure of specimens: ITO/ PEDOT:PSS (20 nm)/ active layer (~100 nm)/Al.

2.2. Measurements

Microscopic images were taken by a microscope, Nikon, Optiphoto-2 and a digital camera DS-5M. Atomic force microscopy (AFM) images were obtained using Keyence, VN-8000 viewer. Current-voltage (J-V) measurements were recorded by applying external potential biases to the cells and recording the output photocurrent with a digital source measure meter (Agilent B2901A). A 150 W xenon lamp (Bunkoukeiki Otento-SUN3 Xe-S150) was used as the light source under AM 1.5 G, 100 mW/cm$^2$. Figure 3 shows a typical photo current curve of photovoltaic cells. The maximum current density at 0 V is the short-circuit current density, J$_{SC}$. The maximum voltage at 0 A/m$^2$ is the open voltage, V$_{OC}$. The fill factor, FF is defined as the equation (1).

$$\text{FF} = \frac{P_{\text{max}}}{J_{\text{SC}} \cdot V_{\text{OC}}} \quad (1)$$

And the power conversation efficiency, PCE is defined as the equation (2).

$$\text{PCE} = \frac{P_{\text{max}}}{100 \text{ [mW/cm}^2\text{]}} = \frac{J_{\text{SC}} \cdot V_{\text{OC}} \cdot FF}{100 \text{ [mW/cm}^2\text{]}} \quad (2)$$

Incident photon-to-electron conversion efficiency (IPCE) measurement was conducted in
the wavelength range of 350-900 nm with a 300 W xenon light source and a monochromator (Asahi Spectra, PVL 3300). Ultraviolet-visible (UV-vis) absorption spectra were measured using an UV-vis spectrophotometer (Shimadzu, UV 2450). We used a thickness tester (Kosaka Laboratory, Surfcoeder, ET200).

**3. Results and discussion**

3.1. OPV properties

Figures 4 (a) and (b) show the photo and dark currents of the 0 and 30 wt% specimens, respectively. In the fourth quadrant (J<0, V>0), the photo current is overlapped with the dark current. A leakage current due to electrical defects is not observed. We believe pinhole-free OPVs can be fabricated. Figure 5 shows the PCBM content dependence of photo current for various specimens. In addition, Table 2 summarizes PV parameters of Fig. 4.

As the content of PCBM increases, both $J_{SC}$ and $V_{OC}$ increase. Consequently, the PCE also increases with the content of PCBM. The authors’ group have already reported the performance of the P3HT:PCBM based OPVs [18]. The OPV parameters of $J_{SC}$, $V_{OC}$, FF and PCE were 8.1 mA/cm², 0.55 V, 0.48 and 2.2 %, respectively. The performance of our C$_{60}$-based OPV are poorer than those of P3HT:PCBM OPVs. However, the FF of the former is higher than that of the latter.

Figure 6 shows the absorbance spectra of 4 kinds of active single layer on glass. These absorbance spectra are not normalized by a local maximum. The absorption due to P3HT is observed in the wavelength range of 400-650 nm and all peak strengths are almost same. On the other hand, the absorption due to fullerene is observed in the wavelength range of 330-400 nm, although it is...
overlapped with the absorption of a glass substrate. It decreases with the content of PCBM. Since PCBM has a soluble substitute, the molecular weight of PCBM is higher than that of C\textsubscript{60}. If the weight of solute is same, the molar number of C\textsubscript{60} in PCBM is less than that of C\textsubscript{60}. The absorption of C\textsubscript{60} reduces with the content of PCBM in place of C\textsubscript{60}.

Table 2. Summary of PV parameters

| PCBM wt\% | $J_{SC}$ [mA/cm$^2$] | $V_{OC}$ [V] | FF | PCE [%] |
|-----------|----------------------|--------------|----|---------|
| 0         | 1.92                 | 0.408        | 0.583 | 0.462 |
| 10        | 2.21                 | 0.443        | 0.552 | 0.544 |
| 20        | 3.04                 | 0.447        | 0.573 | 0.7921 |
| 30        | 2.62                 | 0.463        | 0.590 | 0.723 |

Figure 7 shows the IPCE spectra of 4 kinds of OPVs with a different PCBM’s content. With increasing the content of PCBM, the IPCE increases in the absorption regions of both P3HT and C\textsubscript{60}. The external quantum efficiency of OPV, $\eta_{\text{EQE}}$, is described as the equation (3).

$$\eta_{\text{EQE}} = \eta_A \eta_{\text{ED}} \eta_{\text{CT}} \eta_{\text{CC}},$$  \hspace{1cm} (3)

where $\eta_A$ is the optical absorption efficiency in the active layer, $\eta_{\text{ED}}$ is the diffusion efficiency of exciton to the donor/acceptor (D/A) interface, $\eta_{\text{CT}}$ is the generation efficiency of free carrier at the D/A interface, and $\eta_{\text{CC}}$ is the ejection efficiency to the electrode connected with an external circuit, respectively. Since the absorbance spectra of the 4 kinds of specimens are same, the $\eta_A$ is thought to be same and depend on the content of PCBM. The generation efficiency of free carrier at the D/A interface will be mainly controlled by the energy gap between donor and acceptor and the area of the D/A interface. The $\eta_{\text{ED}}, \eta_{\text{CT}}$ and $\eta_{\text{CC}}$ are influenced by the morphology and aggregation conditions of donor and acceptor materials. If donor molecules are mixed with acceptor molecules perfectly, it is thought that $\eta_{\text{CT}}$ will be the maximum but $\eta_{\text{ED}}$ and $\eta_{\text{CC}}$ will be the minimum. Because the D/A interface area is the maximum and the pass and region formed by homo materials decrease. On the other hand, if the device structure is a hetero junction which is the bilayer structure consisting of donor and acceptor layers, $\eta_{\text{CC}}$ will be the maximum but $\eta_{\text{CT}}$ and $\eta_{\text{ED}}$ will be a small value. Because the D/A interface area is the minimum and the large pass and region are effective for the carrier transport but prevent excitons with a short diffusion length from dissociating. In Fig. 8 (a), donor and acceptor regions are block-like structure and many discrete blocks. The D/A interface are much wide and excitons may be able to diffuse to the D/A interface within a diffusion length. However, dissociated carriers will be recombined on the way to electrodes.

As shown in Fig. 8 (b), the bulk-hetero junction has an absorption layer with nano-sized dispersed mixture layer. The D/A interface are comparatively wide and excitons can diffuse to the D/A interface within a diffusion length at the dispersed area. In the bulk-hetero junction structure, there are enough passes for carriers. Therefore, all $\eta_{\text{CC}}, \eta_{\text{CT}}$ and $\eta_{\text{ED}}$ will be large or not small. The bulk-hetero junction is be thought to be an ideal structure for OPVs.

We speculate that the improvement of IPCE is caused by the change of morphology of active layer.

Fig. 6. PCBM concentration dependence of absorbance spectra of active single layers on glass substrate.

Fig. 7. PCBM concentration dependence of IPCE spectra of OPVs.
3.2. Morphology of active layers

Figure 9 shows the microscopic images of active layers with various the content of PCBM. C₆₀ easily aggregates. Many black points (>10) are observed in the microscopic image of 0 wt%. These black points are thought to be the aggregation regions of C₆₀. The average number of black points to PCBM content is shown in Fig. 10.

The number of black point decreases with increasing the content of PCBM. The addition of PCBM improves the dispersibility of fullerene, C₆₀.

Fig. 9. Microscopic images (100 µm x 100 µm) of 4 kinds of active layers: top left, 0 wt%; top right, 10 wt%; bottom left, 20 wt%; bottom right, 30 wt%. Black dotted circles are aggregation points.

Fig. 10. The PCBM content dependence of the average number of aggregation point.

Fig. 11. AFM images of active layer surface for 4 kind of specimens: top left, 0 wt%; top right, 10 wt%; bottom left, 20 wt%; bottom right, 30 wt%.

Figure 11 shows the AFM images of active layer surface for 4 kinds of specimens. Only 0 wt% specimen shows the different surface morphology of 4 kinds of specimens. These aggregation is thought to be due to C₆₀. However, the aggregation of C₆₀ is diminished by the addition of PCBM. Although PCBM has the unit of C₆₀, the occupied volume of fusible part of PCBM is regarded not to be small. When C₆₀ molecules align by their own molecular interaction, the fusible parts, which get through the aggregation position, disturb the alignment of C₆₀. Consequently the compatibility of fullerene, C₆₀ to P3HT will become higher. The film morphology of P3HT:C₆₀ is close to a bulk-hetero
junction by the addition of PCBM. But the film morphology of PCBM-added P3HT:C₆₀ is regarded as incomplete bulk-hetero junction. We must polish up this method for further.

4. Conclusion
We found that the addition of PCBM improved the film morphology of P3HT:C₆₀ active layer without any additive such as DIO and the PCE of PCBM-added P3HT:C₆₀ increased. The existence of PCBM prevented C₆₀ from aligning and enhanced the compatibility of C₆₀ to the donor polymer.

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