F₄TCNQ Doping of P3HT:PCBM Photovoltaic Devices

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Photovoltaic properties of a conventional bulk heterojunction organic solar cell composed of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) were investigated as a function of the addition amount of a p-type doping reagent, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ). Addition of a small amount of F₄TCNQ to P3HT induced spectral changes with the appearance of low energy polaron bands, suggesting the efficient doping of the p-type semiconductor. The doping also resulted in the improved hole conduction, as revealed by current density-voltage (*J-V*) curves in the dark. A systematic study of the devices indicated that the soft doping with F₄TCNQ and the utilization of a hole-transporting PEDOT:PSS layer on an ITO electrode sometimes improve the short-circuit current density (*J*_{SC}) and fill factor (FF). In contrast, the hard doping always generates hole-trapping sites. Based on this knowledge, the device performances were successfully optimized.

Keyword: charge-separation, doping, organic device, photovoltaic cell

1. Introduction

Chemical doping is an efficient method for improving organic polymer properties and their device performances [1]. For example, doped aromatic polyamines showed better electric conductivities or magnetic properties compared to the parent polyamines [2–7]. This feature was successfully applied to hole-transport layers of organic devices. Organic light-emitting diodes (OLEDs) using doped polyamines in the hole-transport layer have been fabricated, and their good luminance driven at low voltages was reported [8–14]. In particular, Leo et al. demonstrated that 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) is one of the most effective p-type doping reagents because of the stronger electron-accepting power and the extended π -system, which stabilizes an anionic radical generated

through an electron transfer [1].

Bulk heterojunction organic solar cells have attracted increasing attention, because they can be prepared by the straightforward and low cost wet processes. An active layer of these devices are generally composed of p-type semiconducting polymers, such as poly(3-hexylthiophene) (P3HT), and n-type fullerene derivatives, such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). However, there are, to our knowledge, few reports of the chemical doping of this layer [15].

In this paper, we report F₄TCNQ doping of P3HT:PCBM photovoltaic devices. Effects of the doping amount on photovoltaic properties are investigated. The necessity of a PEDOT:PSS layer is also reported.

2. Experimental

2.1. Materials

Poly(3-hexylthiophene) (P3HT) ($M_w = 23800$, $M_n = 14100$) was prepared according to the reported procedure [16]. F₄TCNQ, PCBM, and *o*-dichlorobenzene were purchased from Tokyo Kasei, Frontier Carbon, and Aldrich, respectively, and used without further purification.

2.2. General measurements

UV-Vis spectra of polymer films were recorded on a JASCO V-670 spectrophotometer. After polymer solutions in *o*-dichlorobenzene (7 g L⁻¹) were passed through a 0.2 μ m filter, they were spin-coated on a quartz substrate at 1000 rpm for 60 s.

2.3. Photovoltaic cells

Bulk heterojunction photovoltaic cells were prepared on a patterned ITO-coated glass substrate by a wet process. An ITO substrate (Geomatec, 5 Ω sq⁻¹) was first patterned by etching, followed by ultrasonication in an aqueous detergent solution, distilled water, and isopropanol for 15 min each. The ITO was exposed to a UV-ozone (Technovision, UV208) for 15 min. After an aqueous PEDOT:PSS solution (H.C.Starck, P VP.AI 4083) and DMSO (50:50 v/v) were passed through a 0.2 μ m filter, they were spin-coated on the ITO at 2500 rpm for 60 s and dried at 200 °C for 10 min under air. A solution of P3HT (7 g L⁻¹) and F₄TCNQ in *o*-dichlorobenzene was mixed with a solution of PCBM (Frontier Carbon, nanom spectra E100H, 21 g L⁻¹) in *o*-dichlorobenzene. After the mixed solution was filtered, it was spin-coated on the PEDOT:PSS layer at 1000 rpm for 60 s, followed by annealing at 140 °C for 10 min in a glovebox. Subsequently, an Al electrode with a thickness of ca. 100 nm was deposited. The active area of the device was 4 mm².

Current density-voltage (J - V) curves were measured under air using a source meter (Keithley, 2400) with a solar simulator (Peccell, PEC-L11) under the illumination of AM 1.5G at 100 mW cm⁻². A lamp was calibrated using a standard Si cell (Peccell, PECSI01).

3. Results and Discussion

3.1. Chemical doping

Successful p-type doping of P3HT by F₄TCNQ was confirmed by UV-Vis-NIR spectroscopy. The first reduction potential of F₄TCNQ was reported to be 0.16 V (vs. Fc⁺/Fc in CH₂Cl₂), suggesting a much stronger oxidant than TCNQ [17]. P3HT films showed the most intense peak at 555 nm and a longer wavelength shoulder at ca. 600 nm

Figure 1. UV-Vis-NIR spectra of P3HT films with various F₄TCNQ amounts.

Figure 2. (a) Molecular structures of P3HT, F₄TCNQ, and PCBM. (b) A schematic representation of the photovoltaic devices.

(Figure 1). When F₄TCNQ was added to the polymer films, these original bands decreased and new low energy bands appeared at 770 and 860 nm. These new bands are probably derived from a polaron (cationic radical). The spectral change was continuous until 5 mol% of F₄TCNQ was added, a

Figure 3. J - V characteristics of ITO/P3HT:PCBM/Al devices with different F_4TCNQ doping amounts, measured (a) in the dark and (b) under illumination of AM 1.5G.

fact that ensured the sufficient stability of generated cationic radicals during the absorption measurements at room temperature.

3.2 Photovoltaic properties without PEDOT:PSS

Bulk heterojunction photovoltaic devices were fabricated with a sandwich structure of ITO/(PEDOT:PSS)/active layer/Al (Figure 2). The active layer was composed of P3HT

Figure 5. J - V characteristics of ITO/PEDOT:PSS/P3HT:PCBM/Al devices with different F_4TCNQ doping amounts, measured under illumination of AM 1.5G.

Figure 4. Effects of the F_4TCNQ doping on the photovoltaic properties of PEDOT:PSS-free P3HT:PCBM devices: (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Figure 6. Effects of the F₄TCNQ doping on the photovoltaic properties of PEDOT:PSS-coated P3HT:PCBM devices: (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE

doped with various F₄TCNQ amounts and PCBM, in which the weight ratio of P3HT and PCBM was 1:3. The previous OLED studies suggests that no PEDOT:PSS layer was necessary when the hole-transport layer was doped with acceptors. Therefore, we first fabricated the device without PEDOT:PSS, namely ITO/active layer/Al, and the current density-voltage (J - V) curves were measured. The J - V characteristic measured in the dark suggested that a hole injection barrier was reduced and the hole conduction was facilitated as more F₄TCNQ were added (Figure 3a). Illumination of AM 1.5G light improved these features due to the occurrence of photo-induced charge-separation (Figure 3b). Therefore, effects of doping on the photovoltaic parameters, such as short-circuit current densities (J_{sc}), open circuit voltages (V_{oc}), fill factors (FF), and power conversion efficiency (PCE), were investigated under the light illumination. The J_{sc} value increased from 1.71 to 1.90 mA cm⁻² in the case of soft doping ~1 mol% (Figure 4a). However, when more F₄TCNQ were added, the J_{sc} values gradually decreased to 1.13 mA cm⁻². This was probably due to the unbalanced generation of holes and electrons. This

doping-induced disproportion also resulted in a decrease in the V_{oc} values (Figure 4b). In addition, hard doping generally produces hole trapping sites. Thus, FF of the devices also decreased upon doping (Figure 4c). Consequently, the PCE dramatically decreased from 0.33% (no doping) to 0.04% (5 mol% doping) (Figure 4d).

3.3. Photovoltaic properties with PEDOT:PSS

In order to mainly improve the J_{sc} values, PEDOT:PSS was newly introduced as a hole-transport layer (for the device structure, see Figure 2b), and the photovoltaic properties were measured under the illumination of AM 1.5G as a function of F₄TCNQ doping amount (Figure 5). As expected, the J_{sc} was improved to ca. 3.3 mA cm⁻² in the case of soft doping ~1 mol% (Figure 6a). However, similar to the PEDOT:PSS-free devices, a significant decrease in the J_{sc} was observed when hard doping was performed. The V_{oc} also showed a slight decrease upon doping, but the extent of the decrease was not significant in this case (Figure 6b). In contrast, FF displayed a well-defined increase upon 1 mol% of F₄TCNQ doping, probably due to the formation of novel interfaces facilitating efficient charge-transports (Figure 6c). When

the doping amount was increased to 3 mol%, more charge-trapping sites were formed, resulting in the low FF value. Based on these competing parameters, the best PCE of 0.58% was achieved in the case of 1 mol% F₄TCNQ doping (Figure 6d).

4. Conclusion

In summary, the photovoltaic performances of the P3HT:PCBM devices were significantly affected by the chemical doping with F₄TCNQ as well as the PEDOT:PSS layer. The *J-V* characteristics in the dark suggested the improved injection and conduction of holes upon doping. However, it was difficult to optimize the actual device parameters, because there was an appropriate balance between holes and electrons. The best PCE was achieved by soft doping of ~1 mol% F₄TCNQ in the presence of PEDOT:PSS.

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