Donor acceptor ratio effect on P3HT:PCBM nanoparticulate organic photovoltaic device performance

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Abstract. The Effect of blending ratio between Poly (3-hexylthiophene) (P3HT) as donor electron and phenyl C61 butyric acid methyl ester (PCBM) on Nanoparticulate Organic Photovoltaic has been investigated. A series of P3HT:PCBM nanoparticle dispersions with blending ratio by mass of P3HT:PCBM 2:1, 1:1, and 1:2 were prepared as an active layer of nanoparticulate organic photovoltaic devices. The highest efficiency of both pre-annealed and annealed P3HT:PCBM nanoparticulate organic photovoltaic devices is at blending ratio of 1:1. The highest efficiency was driven by the highest current density (J_sc) and the highest fill factor (FF) indicating that optimal balance between charge generation and charge transport occurred at blending ratio of 1:1.

1. Introduction

Nanoparticle organic photovoltaic is an alternative way to harvest sun energy using organic materials and attracting many researchers since it is containing no toxic solvent and add a level of morphological control of the active layer. However, the efficiency of NP-OPV devices still lower compare to standard organic photovoltaic suggesting more factors need to be investigated.

One of important factors which need to be investigated in NP-OPV devices is the blending ratio of polymer to fullerene, since blending ratio are likely to play a significant role in improving device performance as has been observed in bulk heterojunction devices [1, 2]. Chirvase D, et al. [1] investigated the blend ratio effect on bulk heterojunction devices performance, specifically the P3HT:PCBM systems in 2004. They found that ratios between 1:1 and 1:0.9 exhibit maximum power conversions. Ratio between 1:1 and 1:0.9 were found to be optimal because maximum photocurrent was achieved in this range ratio, suggesting that the charge carrier mobility of both donor and acceptor components is matched for these concentrations [3].

In this paper we report that the best blending ratio between P3HT as electron donor and PCBM as electron acceptor in nanoparticulate organic photovoltaic devices is 1:1 which is very similar to standard OPV although they have different structures [4-6]. In this blending ratio, both pre-annealed and annealed devices have the highest current density (J_sc) and the highest fill factor (FF) and hence the efficiency. The highest current density and the highest fill factor indicating that the optimal balance between charge generation and charge transport occurred in this blending ratio.
2. Research Method

Nanoparticle dispersions were prepared as outlined in earlier paper [7]. However, blending ratio (by mass) of P3HT:PCBM used in this investigation was 2:1, 1:1, and 1:2. Devices were fabricated by spin coating PEDOT:PSS with a thickness of ~60 nm on pre-cleaned patterned ITO glass slide and then dried on a hotplate at 140 °C for 30 minutes. P3HT:PCBM nanoparticle layers were deposited by spin coating 75 µl of dispersion in air with thickness of ~100 nm. The active layers then were dried on a hotplate at a temperature of 130 °C for 4 minutes (in air). Following deposition of calcium and aluminium (in nitrogen) with thicknesses of ~30 nm and ~100 nm respectively. Photocurrent density–voltage (J–V) measurements were conducted using a Newport Class A solar simulator AM 1.5 with light intensity of 100 mW/cm² and the J–V data were recorded with a Keithley 2400 source meter. Photocurrent density–voltage (J–V) measurements were conducted before devices were annealed (pre-annealed) and after devices were annealed (annealed). Devices were annealed on a hotplate at a temperature of 140 °C for 4 minutes (in nitrogen). There were six devices for each treatment.

For Uv-vis characterisation, the nanoparticle dispersions were spin coated onto glass slide to form nanoparticulate films with thickness of ~100 nm. An ultraviolet-visible absorption spectrophotometer (UV–vis, Varian Cary 6000i) was used to study the absorption of the nanoparticulate films. For particle size measurement, the nanoparticle dispersions were dilute until it becomes transparent. Dynamic light scattering (Zetasizer Nano-ZS, Malvern Instruments, UK) was used to measure the distribution of particle sizes in the aqueous dispersion.

3. Results and discussions

Table 1 shows the Z-average diameter in average (Z-average) of nanoparticle solutions as measured by dynamic light scattering (DLS). Different ratios gave different sizes of nanoparticle with increasing amounts of PCBM (i.e. smaller ratio) systematically reducing the particle size.

| Material Ratio     | Z-Average Size (nm) | STDEV   |
|--------------------|---------------------|---------|
| Pure P3HT          | 39.62               | 0.268   |
| P3HT:PCBM 2:1      | 33.81               | 0.585   |
| P3HT:PCBM 1:1      | 30.27               | 0.267   |
| P3HT:PCBM 1:2      | 25.35               | 0.223   |
| Pure PCBM          | 19.95               | 1.077   |

Figure 1 shows UV-vis spectra of P3HT:PCBM nanoparticle films produced from P3HT:PCBM blends of different mass ratios. The total mass of P3HT and PCBM was kept constant at 30 mg. It is clear from figure 1 that increasing the ratio of P3HT increases the relative light absorption due to P3HT at wavelengths of between approximately 450-650 nm and likewise, PCBM absorption increases relatively between 200-400 nm as the ratio is reduced.

Table 1 and figure 2 show the I-V characteristics of P3HT:PCBM NP-OPV devices with different mass ratios of P3HT and PCBM. Figure 2a shows that the highest efficiency of P3HT:PCBM NP-OPV devices were obtained at a mass ratio of 1:1, driven primarily by the current density of the devices (figure 2b). This optimum current density implies that an optimal balance between charge generation and charge transport occur at a ratio of 1:1.
Table 2. I-V characteristics of P3HT:PCBM NP-OPV devices with different blended ratio for best devices, with the averages (± standard deviation) of a minimum of 6 devices in brackets.

| Ratio  | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | $FF$ | Efficiency (%) |
|--------|---------------|----------------------|------|----------------|
| **Pre-annealed** | | | | |
| 2:1 | 412.2 (395.4 ± 16.7) | 3.02 (2.50 ± 0.50) | 0.36 (0.35±0.017) | 0.437 (0.347 ± 0.093) |
| 1:1 | 397.4 (395.3 ± 02.9) | 4.47 (3.97 ± 0.42) | 0.47 (0.45±0.019) | 0.822 (0.713 ± 0.088) |
| 1:2 | 435.8 (422.1 ± 11.1) | 3.40 (2.83 ± 0.52) | 0.45 (0.44±0.010) | 0.662 (0.524 ± 0.118) |
| **Annealed** | | | | |
| 2:1 | 496.9 (472.0 ± 16.7) | 2.63 (2.50 ± 0.14) | 0.36 (0.35±0.014) | 0.448 (0.414 ± 0.034) |
| 1:1 | 557.4 (543.0 ± 11.1) | 4.40 (3.81 ± 0.48) | 0.42 (0.41±0.014) | 1.009 (0.840 ± 0.132) |
| 1:2 | 579.7 (574.1 ± 05.7) | 3.67 (3.10 ± 0.48) | 0.39 (0.37±0.019) | 0.827 (0.665 ± 0.132) |

It is interesting that at a mass ratio 1:1, the overall efficiency of devices increase after annealing although their current density and fill factor decreased after annealing. Therefore, the reason the efficiency of 1:1 devices increased upon thermal annealing was due to an increase in open circuit voltage ($V_{oc}$).

Figure 2c shows that the $V_{oc}$ of pre-annealed devices does not change significantly with the change in material ratio. However, after devices are annealed, the $V_{oc}$ increases systematically with increasing PCBM mass. XPS depth profile data of a 1:1 P3HT:PCBM nanoparticle device in our previous paper [8] shows the vertical material composition of devices from cathode to anode. There are few changes in the film composition between the pre-annealed and annealed devices. In both cases a partial layer of Al$_2$O$_3$ is observed at the Al/active layer interface. The size of this layer does not change dramatically upon annealing. The S and the Na peaks reach a maximum at the anode interface where the S and Na rich PEDOTT:PSS layer is located. However a systematic change in the carbon to sulphur ratio (C:S ratio) is observed for annealed devices across the active layer. This implies that there is a concentration gradient of PCBM within the device with more located near the cathode. Furthermore, the XPS depth profile data shows that after device annealing, more PCBM moves to the interface between Al and the active layer. This movement can be seen from the ratio of carbon to sulphur (C:S) at interface which increases upon annealing. This PCBM movement is advantageous for device performance since it creates a gradient in the electron conduction pathway that is maximised at the cathode, and will result in a greater charge carrier density and reduced recombination in the device [9]. As a result, $V_{oc}$ will increase [10]. Therefore this migration of PCBM concentration within the device increases the $V_{oc}$ after annealing.
Figure 2 shows that the FF of devices that have smaller ratio of P3HT:PCBM (1:1, 1:2) decreased after annealing. As we discussed in our previous paper about XPS depth profile data [8], PCBM will move to Al-active layer interface after annealing. We assume that if the concentration of PCBM is higher, then more PCBM will move to the Al-active layer interface. Consequently, more PCBM will crystallite at Al-active layer interface, which damages the interface [1, 11].

Figure 3. IV curves of the best nanoparticle P3HT:PCBM devices for each different mass ratio.
Moreover, fitting the IV curve of the devices (figure 3) using equivalent circuit model [12] shows that series resistance of the devices increased and their shunt resistance decreased (table 2) after annealing which is in good agreement with interface damage. This interface damage is thought to be the reason the FF decreased after annealing.

| Ratio | Pre-annealed | Annealed |
|-------|--------------|----------|
|       | R_s(Ω) | R_sh(Ω) | R_s(Ω) | R_sh(Ω) |
| 2 : 1 | 3489 | 277 | 5733 | 218 |
| 1 : 1 | 6759 | 115 | 6730 | 131 |
| 1 : 2 | 7702 | 223 | 6711 | 247 |

4. Conclusion

We have study the effect of blending ratio between P3HT as donor electron and PCBM as acceptor electron on P3HT:PCBM NP-OPV devices and shows that the best blending ratio is 1:1. In this ratio, both pre-annealed and annealed P3HT:PCBM NP-OPV devices have the highest efficiency. The highest efficiency was primarily driven by the highest current density and the highest fill factor suggesting that an optimal balance between charge generation and charge transport occurs at these optimum values. For pre-annealed devices, increasing PCBM concentration does not affect the open circuit voltage significantly. However, for annealed devices, the open circuit voltage was increase upon PCBM concentration increase.

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