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The effect of active layer thickness on P3HT:PCBM nanoparticulate organic photovoltaic device performance

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Abstract. The effect of active layer thickness on the performance of nanoparticulate organic photovoltaic (NP-OPV) devices based on Poly (3-hexylthiophene) (P3HT) as electron donor and 6,6-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) as electron acceptor is reported. Power conversion efficiency (PCE) is observed to peak for active layer thickness of around 100 nm, which is very similar to that obtained for bulk heterojunction devices. Increasing the thickness of the active layer beyond of 100 nm decreases the short circuit current, lowering PCE. Decrease in short circuit current and hence device efficiency of NP-OPV devices is due to the serial resistance of the device increase.

1. Introduction

Nanoparticulate organic photovoltaic (NP-OPV) devices are one of organic photovoltaic which are made from water based solution. As an organic photovoltaic, NP-OPV devices cheap and easy to fabricate, solution processed, printable, flexible and since they are made from water based solution they also friendly to environment. However, compare to bulkheterojunction organic photovoltaic (BHJ-OPV) devices, power conversion efficiency (PCE) of NP-OPV devices still lower suggesting that more investigation are needed to improve NP-OPV devices efficiency. One of important thing to be investigated is the thickness of the active layer [1-4].

Increasing the thickness of the active layer of organic photovoltaic devices will increase their light absorption. However, increasing the active layer thickness will not increase the performance of the devices continuously. There is an optimum thickness of the active layer, which strikes a balance between light absorption and exciton diffusion length [3], and increasing the active layer thickness beyond this optimum thickness will decrease the performance of the device [4]. In bulk heterojunction organic photovoltaic devices, the optimum thickness is around 100 nm [2] while in NP-OPV devices, the optimum thickness is currently unknown. So far, thickness of the active layer of NP-OPV devices used based on the optimum thickness of the active layer of bulk heterojunction devices. However, the active layer of NP-OPV devices [5, 6] and bulkheterojunction devices [7] has different structure.

In this paper we report that although the optimum thickness of the active layer of P3HT:PCBM NP-OPV devices around 100 nm which is very similar to bulkheterojunction devices, there is different mechanism from the active layer thickness in affecting the performance of devices. In bulkheterojunction devices, device performance dominated by the fill factor FF [2] while in P3HT:PCBM NP-OPV devices dominated by the current density.

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2. Research Method

Nanoparticle dispersions of P3HT:PCBM (Lumtec) NPs (1:1 blend) was prepared using the miniemulsion technique as outlined previously [8]. The NP-OPV devices were fabricated as outlined in our previous paper [5] and six devices were made for each different active layer thickness. Thickness was altered by varying spin coater speed. The thickness of the film was measured by a KLA-Tencor Alpha Step 500 profilometer. To measure the film thickness, the film on the glass was scratched diagonally and a profilometry scan was conducted perpendicular to the direction of the scratch. Five locations were measured (1 at the middle and 4 at the corners) then the results were averaged together to get the final thickness. Since the film is soft, we used a stylus force of 0.2 mg.

For UV-vis spectroscopy measurement, only five samples were made because we only want to see the relationship between the absorption and the film thickness obtained by varying spin coater speed. Samples were fabricated by spin casting 25 μ l of nanoparticle dispersion onto quartz substrates (1 cm x 2 cm) with different spin coater speed. Drying temperature and drying time used were the same as with NP-OPV devices preparation.

3. Results and Discussion

Figure 1a shows the UV-vis spectra of different film thicknesses produced from a 1:1 P3HT:PCBM nanoparticle dispersion and figure 1b shows the relationship between the absorption and the thickness of a 1:1 P3HT:PCBM NP film at wavelength 552 nm.

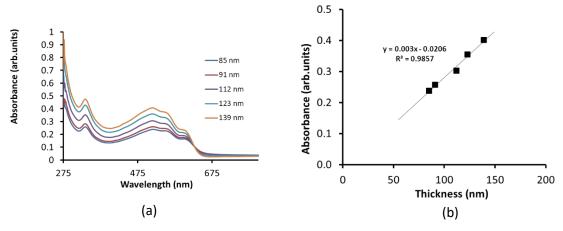


Figure 1. (a) UV-Vis spectra of different film thickness of P3HT:PCBM nanoparticles. (b) Absorption (522 nm) versus film thickness obeys Beer's Law.

As can be seen in figure 1b, it is clear that increasing the film thickness will increase the light absorption of both P3HT and PCBM according to Beer's Law. However, as can be seen in table 1, the average power conversion efficiency (PCE) of the devices increases only until an active layer thickness of around 100 nm and based on our previous paper [5] it is about three layers of nanoparticle. Increasing the film (active layer) thickness beyond these thicknesses resulted in decreased power conversion efficiency. This change arises since, whilst absorption is a function of amount of material present, PCE is a complex function of absorption, exciton mobility, charge separation and charge transport. Increasing the thickness of the active layer increases the charge transport pathway, which may increase recombination in the device, lowering PCE. To see the trend of devices characteristics, the IV characteristic data in table 1 was plotted in graphs as shown in figure 2.

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Table 1. I-V characteristics of P3HT:PCBM NP-OPV devices with different active layer thickness for best devices, with the averages (± standard deviation) of a minimum of 6 devices in brackets.

Thickness	V_{oc}	$oldsymbol{J_{sc}}$	EE	Efficiency
(nm)	(mV)	(mA/cm ²)	FF	(%)
60	$413.0 (396.6 \pm 10.4)$	$3.60 (3.35 \pm 0.24)$	0.44 (0.43±0.005)	$0.651 \ (0.577 \pm 0.055)$
66	$428.2 \ (411.6 \pm 10.4)$	$3.60 (3.42 \pm 0.14)$	$0.44 \ (0.43 \pm 0.006)$	$0.657 \ (0.609 \pm 0.038)$
78	$439.5 (429.7 \pm 9.4)$	$3.68 (3.51 \pm 0.09)$	$0.45 \ (0.44 \pm 0.010)$	$0.711 \ (0.661 \pm 0.032)$
100	$456.3 (443.4 \pm 6.8)$	$3.86 (3.79 \pm 0.06)$	0.44 (0.44±0.003)	$0.761 \ (0.732 \pm 0.016)$
107	$429.6 (429.1 \pm 0.8)$	$3.97 (3.89 \pm 0.11)$	0.43 (0.43±0.004)	$0.740 \ (0.720 \pm 0.029)$
113	$446.2 (442.2 \pm 3.4)$	$4.06(3.93 \pm 0.09)$	$0.43 \ (0.42 \pm 0.006)$	$0.760~(0.727\pm0.022)$
121	$458.9 (444.0 \pm 11.7)$	$3.85 (3.67 \pm 0.13)$	$0.43 \ (0.42 \pm 0.011)$	$0.735 \ (0.679 \pm 0.047)$
128	$454.2 (441.8 \pm 14.3)$	$3.51 (3.42 \pm 0.10)$	$0.42 (0.41 \pm 0.006)$	$0.632 \ (0.621 \pm 0.013)$
136	$464.1 \ (450.2 \pm 10.2)$	$3.18(2.99 \pm 0.16)$	$0.41 \ (0.40 \pm 0.007)$	$0.602 \ (0.540 \pm 0.044)$
145	$469.3 \ (455.8 \pm 8.10)$	$3.25~(2.88\pm0.32)$	$0.41~(0.40\pm0.003)$	$0.607 \ (0.530 \pm 0.065)$
170	$453.6 (449.5 \pm 4.10)$	$2.62 (2.47 \pm 0.16)$	$0.40 \ (0.40 \pm 0.004)$	$0.470~(0.440\pm0.030)$

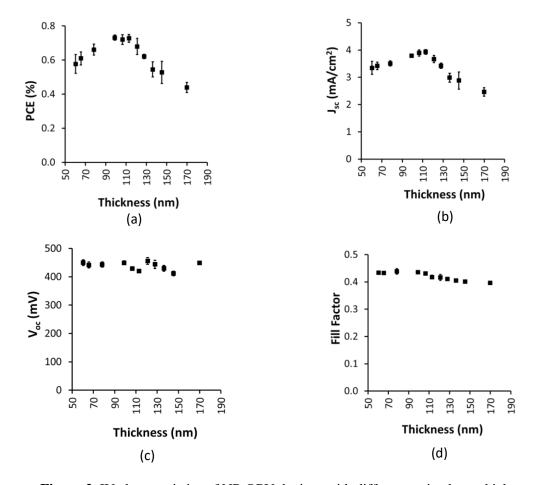


Figure 2. IV characteristics of NP-OPV devices with different active layer thickness. All of the characteristics are the average values with error bars showing the STDEV devices. (a) Power conversion efficiency, (b) current density, (c) open circuit voltage, and (d) fill factor.

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The open circuit voltage shown in figure 2c and the fill factor shown in figure 2d show no significant change upon increasing the active layer thickness. The trend in current density is similar to the PCE trend. Therefore, the performance of these devices is dominated by their current density. The trend in current density shows that the balance between charge generation and charge transport is optimal at an active layer thickness of around 100 nm [9]. This optimal active layer thickness is very similar to that obtained for bulk heterojunction devices suggesting that the nanoparticulate active layer does not really seem to affect the optimal thickness.

Figure 3 shows the IV curve of each highest efficiency device. Fitting the IV curves using an equivalent circuit model [10], we have series resistance, R_s and shunt resistance, R_{sh} in graphs as can be seen in figure 4. Trend line in figure 4a shows that the shunt resistance seem has no significant change while trend line in figure 4b shows that the series resistance increases upon increasing the active layer thickness. Therefore, power conversion efficiency decreased upon increasing the active layer thickness beyond thickness of around 100 nm, which is thought to be due to increased series resistance.

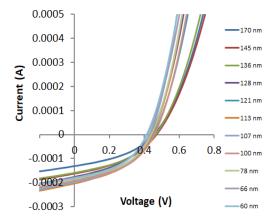


Figure 3. IV characteristic of each highest efficiency

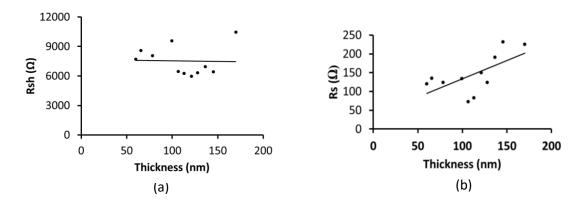


Figure 4. Plot of the active layer thickness versus (a) the shunt resistance and (b) the series resistance.

4. Conclusions

Investigations to determine appropriate active layer thickness in NP-OPV P3HT:PC₆₁BM devices have been performed. Optimal active layer thickness was found to be around 100 nm. Increasing the active layer thickness beyond of 100 nm, will increase device series resistance, reduce the current density and hence device efficiency. Since the optimal thickness of P3HT:PCBM NP-OPV devices very similar to

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the optimal thickness of bulk heterojunction devices, the nanoparticulate active layer does not really seem to affect the optimal thickness.

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