Thickness and Solvent influence on the photo-active layer in Organic photovoltaic devices

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Abstract: Today, organic photovoltaic (OPV) devices made from a blend of conjugated polymers such as poly(3-hexylthiophene-2,5-diyl), (P3HT) and fullerene derivative [6,6]-phenyl C_{60} butyric acid methyl ester (PCBM) have attracted much attention because of their promising improvement of power conversion efficiencies. In this study, we investigate the effect of solvent on the photo-active (P3HT:PCBM) blend in OPV devices performance. Dissolving the photo-active materials in Chloroform, 1,2-dichlorobenzene and chlorobenzene solvents, optical absorption of the blended films, external quantum efficiencies (EQE) and photovoltaic properties of devices were evaluated. The films prepared by using chloroform showed intense absorption compared to those prepared by 1,2-dichlorobenzene and chlorobenzene solvents. The thickness of the films determined from the surface profile using Alpha-step IQ was about 138.8 nm (chloroform), 56,1 nm(1,2-dichlorobenzene) and 75.2 nm (chlorobenzene). The current-density (J-V) characteristics showed a maximum power conversion efficiency of ~ 3.45 % was obtained from the device fabricated using chloroform, while the power conversion efficiencies of ~2.94 % and ~2.86 % were obtained when chlorobenzene and 1,2-dichlorobenzene were used, respectively, as solvents.

1. Introduction

Conventional bulk heterojunction (BHJ) organic solar cells (OSCs) are of great interest nowadays due to their potential applications as sources of renewable energy and for being able to reach power conversion efficiencies of 3-8 % [1,2]. Among all possible materials that have been used as photo-active layers, the most widely used material system in BHJ-OSCs, is the blend of poly(3-hexylthiophene-2,5-diyl) polymer or P3HT and [6,6] phenyl butyric acid methyl ester fullerene or PBCM and the layer is commonly referred to as P3HT:PCBM. Investigations shows that OSCs made from this blend have power conversion efficiencies that can go up to 3-5% and this indicate the reasonable capability of the P3HT:PCBM blend to attain high efficiencies in future [3,4].

High performance can be achieved by the optimization of phase segregation in the polymer-fullerene blend and the development of new materials allowing better p-n interfaces and balanced charge transport [3]. In OSCs the efficient photo-induced charge separation strongly depends on the processing conditions used in depositing the photo active layer, morphology of the photo active layer, drying time, nature of solvent and thermal annealing [5]. Moreover, maximum photovoltaic response are obtained by optimizing processing parameters in the P3HT:PCBM blend system and the thickness of the active layer is important in this regard. The use of thin layers of about $50 - 110$ nm can lead to efficient cells due to the good absorption coefficient of P3HT:PCBM blend and this leads to the percolation paths and enhanced charge transport. However, thicker layers of about 350 nm are necessary for optimum light absorption and short circuit current without affecting bulk recombination [6]. Solvents such as cholorobenzene and chloroform have been explored by many researchers as feasible to improve the film morphology thereby enhancing the conversion efficiencies in OSCs. *Y. kim et al* found that active layers cast from chlorobenzene demonstrated more ordered mesophase morphology and ultimately performed more efficiently than those cast from dichlorobenzene [7]. The

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aim of this study is to investigate the characteristics of the OSCs processed from dissolving the photo-active materials in chlorobenzene, 1,2-dichlorobenzene and chloroform. In addition, we also discuss the active layer thickness effects on the light absorption and power conversion efficiencies of the OSCs.

2. Experimental

2.1 Device Fabrication **:** A glass substrate was cleaned ultrasonically using isopropanol, acetone and isopropanol again, consecutively for 10 minutes, was dried at ~ 80°C for 20 minutes and then treated in an ultraviolet ozone generator for 20 minutes. A thin layer of poly(3,4-ethylenedioxythiophene):polystyrenesulfonic acid (PEDOT:PSS) (CLEVIOS™ AI 4083) was spin coated on a substrate at the speed of 4000 rpm for 35 seconds then followed by drying at 110°C for 10 minutes. The photo active P3HT:PCBM blend layer (P3HT, Aldrich/ PCBM, Nano-C), with weight ratio of 1:0.6, dissolved from a blend solution of chlorobenzene , 1,2 dichlorobenzene and chloroform was spin coated on the substrate at the speed of 1000 rpm for 15 seconds. This was followed by the deposition of the Al layer (~ 100 nm) thermally evaporated at ~ 1x10^{-6} Torr pressure through a shadow mask defining the device area of 0.12 cm^2. The devices were then heat treated at 155°C for 10 minutes.

2.2 Films and device Characterization: The UV-Vis absorption spectrum of the P3HT:PCBM blend films was recorded using Perkin – Elmer Lambda 35 UV-Vis spectrophotometer. The SEM images of the films were captured using the Field-emission Scanning Electron microscope (FE-SEM, Nova-nano SEM^{200}, FEI). Film thicknesses were determined by Alpha-step IQ surface profiler. The current density-voltage (J-V) curves were measured in air by a Keithley 2400 source meter and an Oriel Xenon lamp (150 W, Newport) coupled with an AM1.5 filter to simulate sunlight. The light intensity was calibrated with a silicon reference cell with a KG2 filter following standard solar cell testing procedures. The light intensity used in this study was 100mW/cm^2. The external quantum efficiencies (EQE) as a function of wavelength were measured using incident photo-to-current efficiency (IPCE) measurement system (PV measurement, Inc). The wavelength of the bias light was controlled with optical filters (Andover Corporation).

3 Results and discussion

FE-SEM cross-sectional view in Figure 1(a) shows the layers of a ITO-coated glass, a thin layer of highly conducting PEDOT:PSS (~30 nm) and an active layer blend (P3HT:PCBM) spin-cast from the solution of chlorobenzene (~75.2 nm) or 1,2-dichlorobenzene (~56.1 nm) or chloroform (~138.8 nm). Film thickness is the key factor in the fabrication of the device, i.e. thicker the active layer greater is the chance of the film to harvest more photons. The thicknesses of the active layer films prepared from different solvents are listed in table 1. We found that the P3HT:PCBM blend from chloroform solution gives the best performance because of its thicker layer compared to chlorobenzene and 1,2-dichlorobenzene. Figure 1(b) shows the UV-vis absorption spectrum of P3HT:PCBM films prepared from different solvents. The absorption band at ~ 510 nm is attributed to the π-π* transition of P3HT while the shoulders at ~557 nm and ~609 nm are due to the inter-chain interactions. The two shoulders at ~557 nm and ~609 nm become prominent on the devices made from the blend of chorobenzene and 1,2-dichlorobenzene solutions, indicating the highly crystalline nature of the P3HT in the blend [8,9].
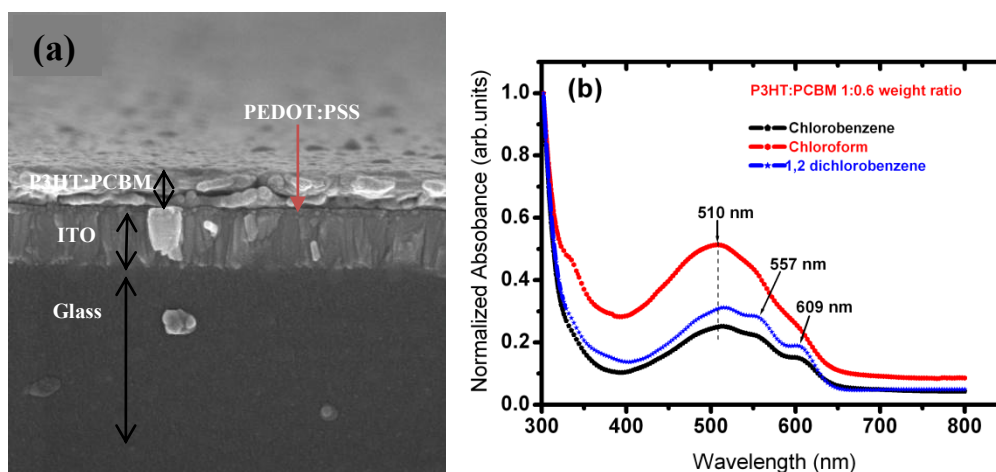
Figure 1: (a) FE-SEM Cross-sectional view images of OSC, (b) UV-visible spectra of P3HT:PCBM blend from chlorobenzene, chloroform and 1,2-dichlorobenzene solutions.

The photovoltaic characteristics of OSCs are summarized in Table 1. The power conversion efficiency (PCE), short-circuit current (J_{sc}) and fill factor (FF) of OSCs processed from each solvent increases with an increase of film thickness and V_{oc} remain constant. This could be due to properties like carrier mobility, conductivity of active layer film and charge collection to the respective electrodes [10]. P3HT:PCBM blend prepared from chlorobenzene, 1,2-dichlorobenze solutions gave the FF of 50.42%, 48.25%, respectively, and with maximum of 62.23% from chloroform solution, indicating an effective and efficient energy conversion system, this is evident in Figure 2(a). Furthermore, the increase of J_{sc} is also attributed to a better packing of P3HT chains as well as structural re-organization of the blend film. The thicker film is able to generate the highest short circuit current (Jsc) due to increased light absorption and therefore best performance. Figure 2(b) shows the current density-voltage (J-V) curves of OSCs with the active layer dissolved in different solvents. Maximum PCE of 3.45% was obtained from the cell with the thickness of 138.8 nm and chloroform solution. In addition, the absorption is enhanced and phase separation in the P3HT:PCBM blend is more prominent providing better carrier pathways as compared to blends from chlorobenzene and 1,2-dichlorobenze with PCE of 2.94% and 2.86%, respectively.

Our results indicate that the photovoltaic response of OSCs depends on the thickness of the active layer film, which is influenced by the respective solvent used. Factors like solution viscosity, balancing of solvent evaporation rate and solubility of materials in these solvents also influence the general performance of OSCs [11]. As mentioned, the significant improvement in photocurrent was observed when the chloroform solvent was used. This could also be due to the different degree of material mixing which provides better P3HT/PCBM interface [12]. It also possible that the PCBM nanocrystals in chloroform processed film constitutes appropriate pathways for enhanced electron transport to the respective electrode compared to the chlorobenzene and 1,2-dichlorobenzene processed films.
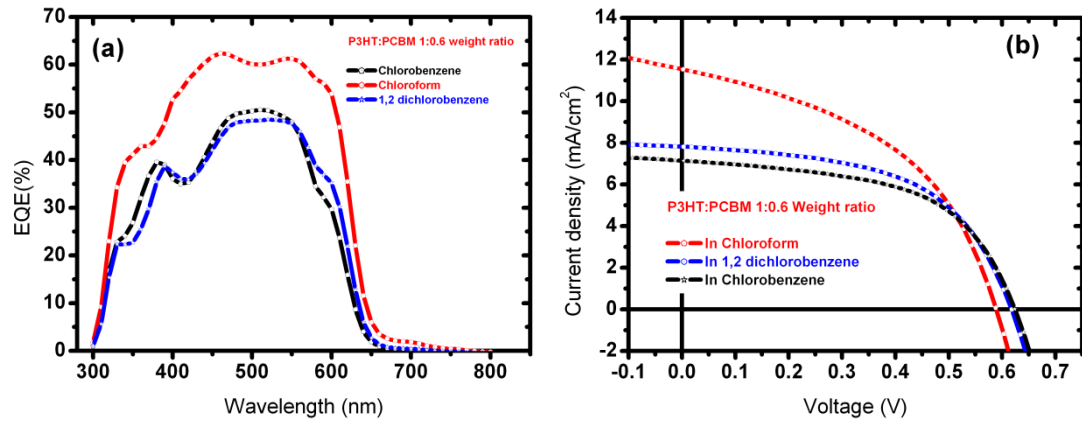
Figure 2: (a) external quantum efficiencies (b) Current-density curves of P3HT:PCBM blends OSCs.

Table 1: Photovoltaic characteristics of organic solar cells

P3HT:PCBM Thickness(nm)	P3HT:PCBM Solvent	J_{sc}(mA/cm^2)	V_{oc}(V)	FF(%)	PCE(%)
75.2	Chlorobenzene	7.524	0.653	50.42	2.94
138.8	Chloroform	9.260	0.655	62.23	3.45
56.1	1,2diChlorobenzene	7.333	0.657	48.25	2.86

4   Conclusion

We have demonstrated that J_{sc}, FF and PCE of the OSCs significantly depends on the solvent used and the thickness of the photoactive film. The OSC devices fabricated from a chloroform solution showed an enhanced absorption coefficients compared to chorobenzene and 1,2-dichlorobenzene and this indicates that the efficient light harvesting can be obtained from thicker P3HT:PCBM blend films in a device.

5   Acknowledgement

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