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Effect of Fabrication Conditions on the Performance of MEH-PPV: PCBM Photovoltaic Devices

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In this article, we fabricated photovoltaic devices based on poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV), as a donor and [6,6]-phenyl C₆₁-butyric acid methyl ester(PCBM) as an electron acceptor materials. The effect of different solvents such as chlorobenzene, o-dichlorobenzene, chloroform, and cosolvent systems prepared with 1:1 ratio of chlorobenzene:o-dichlorobenzene, chlorobenzene:chloroform and o-dichlorobenzene:chloroform on the performance of devices was studied. Further, the effect of a thin electron transport layer of Alq₃ inserted between active layer and cathode in the device structure, on the performance of devices was studied with the best solvent.

Keywords: Alq₃; MEH-PPV; PCBM; photovoltaic devices

INTRODUCTION

Polymer solar cells [1] are a new type of photovoltaic conversion devices with high potential applications in the future energy market since their unique advantages in potential low production costs because of roll-to-roll production, their flexibility, and lightweight. Bulk-heterojunction solar cells obtained by blending the donor and

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acceptor materials within a single bulk yield photovoltaic power converting efficiencies up to 5% [2–4]. While semi-conducting fullerene (C_{60}) derivatives are traditionally used as acceptor materials, donor properties are usually supplied by conjugated polymers. Since the report of poly(*p*-phenylenevinylene) (PPV) based electronic devices by Friend's group [5], π -conjugated polymers have attracted much attention because of their applications in flexible and wearable displays [6], organic thin film transistors [7], and photovoltaic cells [8,9]. Among the several conjugated polymers poly(*p*-phenylene vinylene) (PPV) or polythiophene (PT) are widely used in photovoltaic applications. With in the PPV based polymers, high-molecular weight poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) is widely used in the fabrication of polymer light emitting diodes. Several studies demonstrated the use of MEH-PPV as donor materials in the fabrication of bulk-heterojunction photovoltaic cells [8–10].

In order to increase the power conversion efficiency of the bulk-heterojunction solar cells, many research groups are using different approaches, fabrication conditions and device geometries [2–4,11]. There are many parameters, which can affect the performance of the photovoltaic cells. Among them the composition between donor and acceptor, the solvent used to make blend solutions, the solution concentration, controlled phase separation, and crystallization are having significant influence. In this article, we fabricated MEH-PPV and [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM) based bulk-heterojunction photovoltaic cells using different solvents and solvent mixtures. The choice of solvent not only affects the thickness of the film at a given spin speed, but also effects the morphology of the layer [12]. Different solvents have different solubilities and different mixing of the components in the blend. This results in both a larger internal donor–acceptor interface area and/or an increased charge mobility in one of the components. This solvent effect influences the morphology of the interpenetrating network structure formed between donor and acceptor in continuous active layer [13,14]. We inserted a thin Alq₃ layer as electron transporting layer between the active layer and cathode and its effect on the efficiency of photovoltaic cells was studied.

EXPERIMENTAL

Materials

Lithium fluoride, aluminum and Alq₃ were purchased from Aldrich Co. All solvents used in this study were of HPLC grade and the other reagents were also purchased from Aldrich Co. Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,

4-phenylenevinylene [15] and [6,6]-phenyl C₆₁-butyric acid methyl ester [16] were prepared according to the procedures published earlier.

Photovoltaic Device Fabrication

Glass substrate coated with ITO, whose conductivity was about 15 Ω /square (from Samsung Corning) served as anode electrode. ITO substrates were cleaned ultrasonically with detergent followed by distilled water, acetone, and 2-propanol sequentially. A 40 nm thick layers of PEDOT:PSS (Baytron P, AP Al 4083) was spin-coated on a cleaned ITO substrates after exposing the ITO surface to Ozone for 10 min. The PEDOT:PSS layer is baked on a hot plate at 120°C for 10 min. Active layer of polymer was spin coated from 1.0 wt% solution prepared in different solvents and solvent mixtures after filtering through 0.45 μ m PP syringe filters. We used chlorobenzene, *o*-dichlorobenzene and chloroform and the mixtures prepared in 1:1 ratio of chlorobenzene:chloroform, *o*-dichlorobenzene:chloroform and chlorobenzene:*o*-dichlorobenzene as solvents for this study. The thickness of the active layer was maintained at 75 nm. The device structure was completed by depositing either Al (150 nm) or LiF (1 nm)/Al (200 nm) cathode as top electrode onto the polymer active layer under 2×10^{-6} torr vacuum in thermal evaporator. The overlap of the two electrodes defined the active area of the photovoltaic device and is 4 mm². The photovoltaic devices were characterized under the illumination of simulated solar light with 100 mW/cm² (AM1.5) by Orel 300 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit. All other fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. Thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm.

RESULTS AND DISCUSSION

It has been demonstrated that by changing the solvent from xylene to 1,2-dichlorobenzene, high-quality spin cast MEH-PPV:PCBM films can be achieved [9]. In an another study by Liu et al. [17], they correlated the photovoltaic device parameters with different solvents such as xylene, chlorobenzene, 1,2-dichlorobenzene, chloroform and tetrahydrofuran. In case of poly(2-methoxy-5-(3',7'-dimethyloctyloxy))-1,4-phenylene vinylene (MDMO-PPV), a analogues to MEH-PPV and PCBM devices, it has been shown that a three-fold increased in PCE was achieved simply changing the solvent used for spin coating from toluene to chlorobenzene.

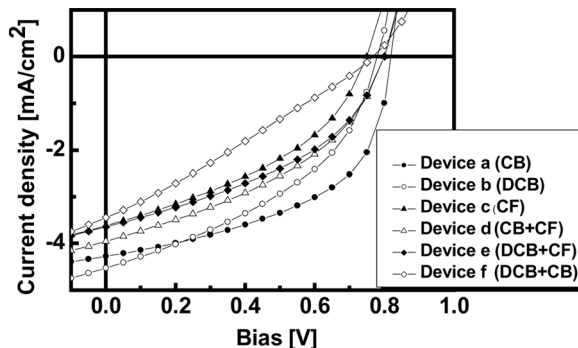


FIGURE 1 J-V curves of the MEH-PPV:PCBM devices, fabricated using different solvents and cosolvent systems, measured under at 100 mW/cm^2 light illumination.

Recently Zhang et al. [18] showed that addition of a small amount of low vapor pressure solvent to high vapor pressure solvent greatly influences the performance of poly(2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)) (APFO-3) and PCBM devices.

Here, we fabricated MEH-PPV:PCBM (1:4) photovoltaic cells using chlorobenzene (**device a**), *o*-dichlorobenzene (**device b**) and chloroform (**device c**) solvents and chlorobenzene:chloroform (**device d**), *o*-dichlorobenzene:chloroform (**device e**) and *o*-dichlorobenzene:chlorobenzene (**device f**) cosolvent systems. The current density versus voltage curves for these devices are presented in Figure 1. The photovoltaic parameters of the devices presented in Table 1 varied with the solvent used to make the blend solutions. It was reported [17] that aromatic solvents are better solvents for MEH-PPV based devices for obtaining good solubility and proper mixing of the blend components.

TABLE 1 Photovoltaics Parameters of the MEH-PPV:PCBM Devices Fabricated with Different Solvents and Cosolvent Systems

Device	Solvent	Cathode	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
a	CB	LiF/Al	0.82	4.28	52.0	1.82
b	DCB	LiF/Al	0.78	4.53	42.0	1.48
c	CF	LiF/Al	0.75	3.62	40.1	1.09
d	CB+CF	LiF/Al	0.80	3.95	40.8	1.29
e	DCB+CF	LiF/Al	0.80	3.65	41.4	1.21
f	DCB+CB	LiF/Al	0.77	3.45	27.1	0.72
g	CB	Alq ₃ /LiF/Al	0.82	4.03	43.9	1.45

In the present case, we also observed better photovoltaic performance for the **devices a** and **b** prepared with aromatic solvents chlorobenzene and *o*-dichlorobenzene, respectively compared with **device c** made using non-aromatic chloroform solvent. In case of APFO-3:PCBM [18] and P3HT:PCBM [19] devices, the cosolvent systems showed better photovoltaic properties than the pristine solvents. But, in the present case, pristine aromatic solvents showed better performance than cosolvent systems. Among the different solvents and cosolvent systems used, the **device a** fabricated using the solutions prepared in chlorobenzene has shown the highest PCE of 1.82% with open-circuit voltage (V_{OC}) of 0.82 V, short-circuit current density (J_{SC}) of 4.28 mA/cm² and fill factor (FF) of 0.52. Short-circuit current density (J_{SC}) 4.53 mA/cm² of the **device b** is higher than **device a**. The higher FF of 52.0% of the **device a** compared to **device b** (42.0%) might be responsible for the higher PCE observed with **device a** than **device b**.

The effect of drying conditions on device performance was studied using the best solvent, chlorobenzene (results not shown). After spin coating the active layer, devices were immediately dried on hotplate at 120°C for different length of time, 1, 3, 5, 7 and 20 min. After drying, devices were removed from the hotplate and further dried in covered petri dishes for 20–25 min. Along with these devices, one more device was made without drying on hotplate and only dried in covered petri dish for 20–25 min. The photovoltaic properties of all these devices did not show any further improvement of the performance compared to **device a**, which is made by drying the active layer on hotplate at 120°C for 10 min. In case of P3HT:PCBM devices [3,19], the slowly dried film has shown improved photovoltaic performance due to the increased crystallinity of P3HT chains in thin films during slow drying. In the present case the donor MEH-PPV is amorphous in nature. So, such a orderly arrangement of polymer chains is not possible with amorphous MEH-PPV polymer. Hence, the change of solvent drying time did not improve the performance MEH-PPV:PCBM devices.

In polymer light emitting diodes (PLED) many researchers [19,20] used a thin layer of tris(8-quinolinolate)aluminum (Alq₃) between the emitting layer and cathode to improve electron injection into the device. Use of such electron transport layers in photovoltaic devices is less known. After judging the best solvent for MEH-PPV:PCBM system from our study, a 10 nm layer of Alq₃ was inserted between the active and LiF layers by vapor deposition. The J-V curves of the devices made with (**device g**) and without Alq₃ (**device a**) using chlorobenzene solvent are presented in Figure 2 and the data is included in Table 1. Similar V_{OC} was observed for both **devices a** and **g**.

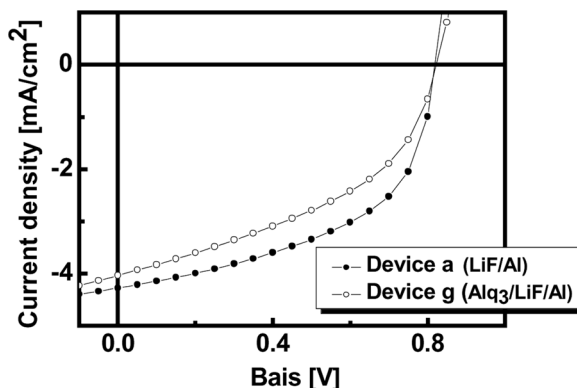


FIGURE 2 J-V curves of the MEH-PPV:PCBM devices, fabricated with and without Alq₃ layer with chlorobenzene solvent, measured under 100 mW/cm² light illumination.

But, lower J_{SC} and FF values were observed for **device g**. The PCE of **device g** is only 1.42% lesser than the **device a** (1.82%).

CONCLUSIONS

In the article, we studied the effect of different solvents and cosolvent systems on the photovoltaic performance of MEH-PPV:PCBM devices. Devices fabricated using chlorobenzene solvent showed better photovoltaic properties than the devices made with other solvents and cosolvent systems employed in this study. The solvent drying time of active layer has not shown any effect on the performance of the devices. Further, insertion of a thin electron transporting Alq₃ layer between active layer and cathode did not improve the photovoltaic properties compared with the devices made without Alq₃ layer.

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