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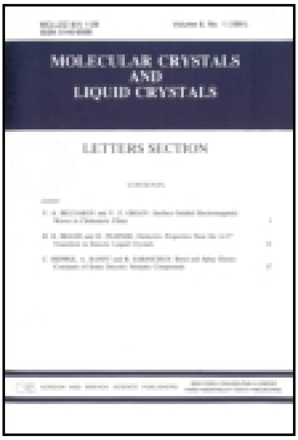

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Enhanced Photovoltaic Performance of P3HT:PCBM Cells by Modification of PEDOT:PSS Layer

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Enhanced Photovoltaic Performance of P3HT:PCBM Cells by Modification of PEDOT:PSS Layer

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In this study, the doped poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film was introduced as an anode buffer layer into the poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) system for organic photovoltaic devices (OPVs). The doped PEDOT:PSS films were prepared by (1) mixing of PEDOT:PSS solution with ethylene glycol (EG) solvent (referred as 'mixing') or by (2) dipping the PEDOT:PSS-coated film into the EG solution (referred as 'dipping'). The devices with the doped PEDOT:PSS layers showed significantly increased photovoltaic performanes upto 4.57% compared to the pristine P3HT:PCBM cells (1.27%), which can be explained by the increased conductivity of the doped PEDOT:PSS layer. The device performance of P3HT:PCBM cells showed a strong relationship with the film conductivity of PEDOT:PSS buffer layer and the surface morphology of the films.

Keywords Organic photovoltaic cells; organic solar cells; PEDOT:PSS

Introduction

Organic photovoltaic cells (OPVs) are promising sources of electrical power that have attracted considerable attention because of their efficiency, low cost, and potential renewable energy applications than ordinary silicon solar cell [1, 2]. In recent few years, the OPV field has progressed remarkably both in terms of device performance as well as understanding of the governing physical processes. The prototypical system comprising poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methylester (PCBM) is nearing its theoretically optimal device performance [3].

In OPV devices, the water soluble poly(3,4-ethylene dioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) layer is commonly used as an anode buffer layer to provide efficient hole extraction and improve device performance. Recently, there are several reports about the influence of the conductivity and morphology of the doped PEDOT:PSS on the OPV performance [4–8]. It is well-known that the conductivity of PEDOT:PSS film can be greatly increased by doping it with organic materials, which are mainly high-boiling and polar solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), sorbitol, or ethylene glycol (EG) [9–12]. A cationic

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surfactant (*N*,*N*,*N*-trimethyl-1-hexadecanaminiu bromide, CTAB) was also used for modification of PEDOT:PSS layer [4]. A 50% increase of power conversion efficiency was achieved with the CTAB-modified PEDOT:PSS layer in OPVs. In most cases, the modification of PEDOT:PSS layer can increase the conductive PEDOT enrichment on top surface of the PEDOT:PSS layer and also increase the surface roughness of the active layer, resulting in better absorption and charge extraction [5].

In this work, we introduced the doped PEDOT:PSS film as a buffer layer to achieve high-efficiency P3HT:PCBM OPV cells. The doped PEDOT:PSS films were prepared by (1) mixing of PEDOT:PSS solution with EG solvent (referred as 'mixing') and (2) dipping the PEDOT:PSS-coated film into the EG solution (referred as 'dipping'). The effect of film conductivity and surface morphology to the device performance will be described herein.

Experimental

Characterization Methods

Film thicknesses were measured using a TENCOR surface profiler. The conductivity of the PEDOT:PSS film was evaluated using four-point-probe measurements. Atomic force microscopy (AFM) images were obtained with a Digital Instruments D3100 microscope in the tapping-mode.

Device Fabrication

The organic photovoltaic devices (OPVs) were fabricated with the configuration indium-tin oxide (ITO)/PEDOT:PSS (45 nm)/P3HT:PCBM (1:0.8, 80–90 nm)/LiF (1 nm)/Al (100 nm). The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, isopropyl alcohol, and methanol. The PEDOT:PSS layer was spin-coated on the substrate and annealed at 120°C for 20 min. The doped PEDOT:PSS layers were prepared in two different ways. The PEDOT:PSS layer with EG addition (referred as 'mixing') was obtained by addition of certain amounts of ethylene glycol (EG) to a PEDOT:PSS solution and then spin-coating the mixed solution on the substrate. On the other hand, the PEDOT:PSS layer with dip-treatment (referred as 'dipping') was prepared by spin-coating and annealing the PEDOT:PSS layer and then dipping the PEDOT:PSS-coated film into the EG solution for certain time. The active layer consisting of P3HT and PCBM was spin-coated from a chlorobenzene solution (2000 rpm, 30 s). Prior to use, a chlorobenzene solution of P3HT and PCBM with the total concentration of 36 mg/mL was stirred at room temperature overnight to ensure complete dissolution. The solutions were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane syringe before applied dropwise onto the substrates. After annealing at 120°C for 10 min, the devices were completed by evaporating LiF/Al metal electrode. The area of the device was 4 mm^2. The current-voltage (J-V) characteristics of the P3HT:PCBM blend films were measured with a Keithley 2400 source-measure unit under white light illumination of AM 1.5, 100 mW/cm^2. All fabrication and characterizations were performed in an ambient environment.

Results and Discussion

Firstly, the PEDOT:PSS layer with EG addition (referred as 'mixing') was obtained by addition of a polar solvent, ethylene glycol (EG), to an aqueous solution of PEDOT:PSS

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(PH500) [6]. Different amounts of EG (5%, 10%, 15%, and 20%) were added to the PEDOT:PSS solution. Prior to use, a mixture of PEDOT:PSS and EG was stirred at room temperature overnight to ensure complete dissolution. The solutions were filtered through a 0.45 μm Teflon membrane syringe before applied dropwise onto the substrates (3000 rpm) and the PEDOT:PSS films were annealed at 120°C for 20 min. Figure 1 shows the conductivity of the PEDOT:PSS films modified with various amounts of added EG (0, 5, 10, 15, and 20%). The conductivity was varied by the amounts of EG. As more EG added, the conductivity of the film was dramatically increased. Similar phenomenon was reported previously, in which the enhanced conductivity of PEDOT:PSS films after the EG addition was explained by aggregating of gel particles, by removing excess PSS, leading to superior charge-transport pathways among the conducting PEDOT-rich regions [6]. In organic electronics such as OLED and OPV, the PEDOT:PSS layer is mainly used to provide efficient hole extraction. However, a high content of insulating species of PSS is formed after spin-coating on top surface of the PEDOT:PSS film that may prevent hole collection [4]. Therefore, the device performance can be improved by EG addition on PEDOT:PSS layer by removal of insulating PSS and increase of conductive PEDOT-rich regions. Figure 2 shows the thickness of the pristine PEDOT:PSS (black) and the PEDOT:PSS with 20% EG films (sky blue) spin-coated using various spin-coating speeds from 800 to 3500 rpm. In order to exclude an effect of the thickness of PEDOT:PSS layer to the conductivity and/or device performance, the thickness of both treated and untreated PEDOT:PSS films was optimized as about 45 nm [5]. The 45 nm-thick film from PEDOT:PSS solution with 20% EG (1500 rpm) showed increased conductivity of 429.6 S/cm, compared to the pristine PEDOT:PSS film (~45 nm, 3500 rpm).

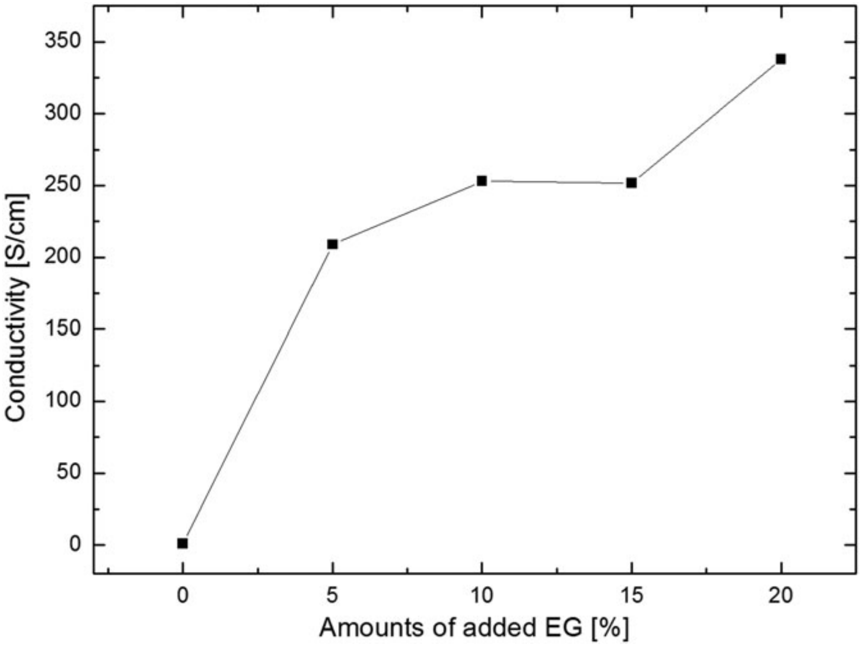

Figure 1. Conductivity of PEDOT:PSS films modified with various amounts of added EG (0, 5, 10, 15, and 20%).

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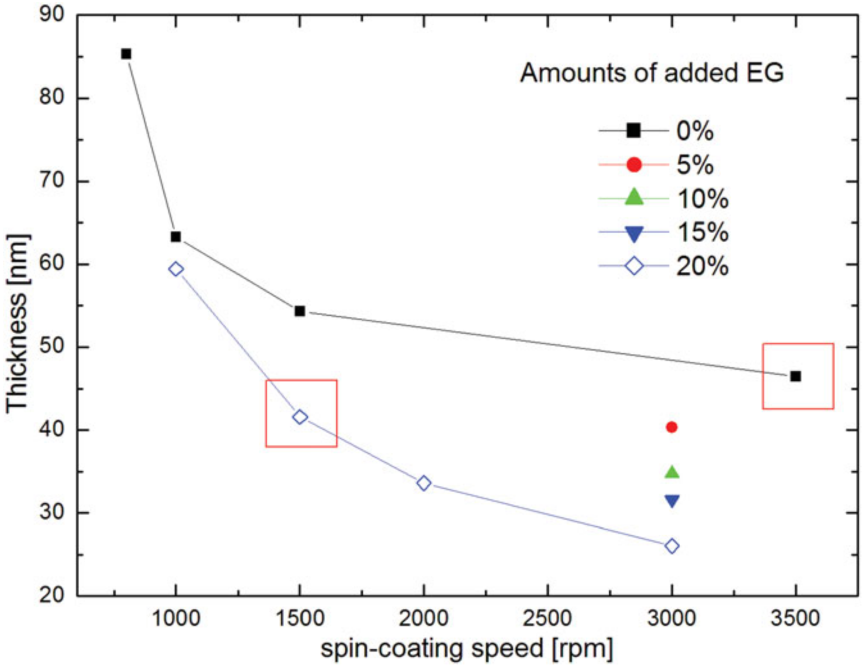

Figure 2. Thickness of the pristine PEDOT:PSS (black) and the PEDOT:PSS with 20% EG films (blue) using various spin-coating speeds (rpm) from 800 to 3500 rpm.

Secondly, we also prepared the highly conductive PEDOT:PSS film by dip-treatment in EG (referred as 'dipping'). The dip-treatment is also known to be a good method to increase the conductivity of PEDOT:PSS film. Okuzaki et. al. reported that the electrical conductivity of PEDOT:PSS was significantly increased by dip-treatment, in which there was about a 6-fold increase in film conductivity after dipping in EG for 3 min [12]. It was explained by removal of insulating PSS from the surface of the PEDOT:PSS grains and crystallization of PEDOT, which led to the formation of large numbers of higher conductive PEDOT-rich grains that enhanced the transport of charge carriers. The conductivity in our system was also increased by the increase of the dipping time (from 10 s to 5 min). In order to use the doped PEDOT:PSS layer with dip-treatment for OPV device, the dipping time and film thickness were optimized as 5 min and about 45 nm, respectively. The dipping time of 5 min resulted in the highest conductivity and the thickness of the pristine PEDOT:PSS film in OPV device was about 45 nm. Compared to the pristine film, the conductivity of the film after dipping (referred as 'dipping') was significantly increased to 463.0 S/cm. It is worth noting that the conductivity of PEDOT:PSS film after dipping is comparable to that of the PEDOT:PSS film prepared with EG addition (referred as 'mixing').

Finally, the organic photovoltaic devices (OPVs) were fabricated with the configuration of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al. In this work, the blending ratio of P3HT and PCBM was adjusted to be 1:0.8 (P3HT:PCBM) and the thickness of the active layer (P3HT:PCBM) was about 80–90 nm. For comparison, the P3HT:PCBM device with the pristine PEDOT:PSS layer was also prepared at the same time and the fabrication conditions for all devices were exactly same except the treatment of PEDOT:PSS layer. The PEDOT:PSS layers were prepared in three different ways as described above; (1) pristine,

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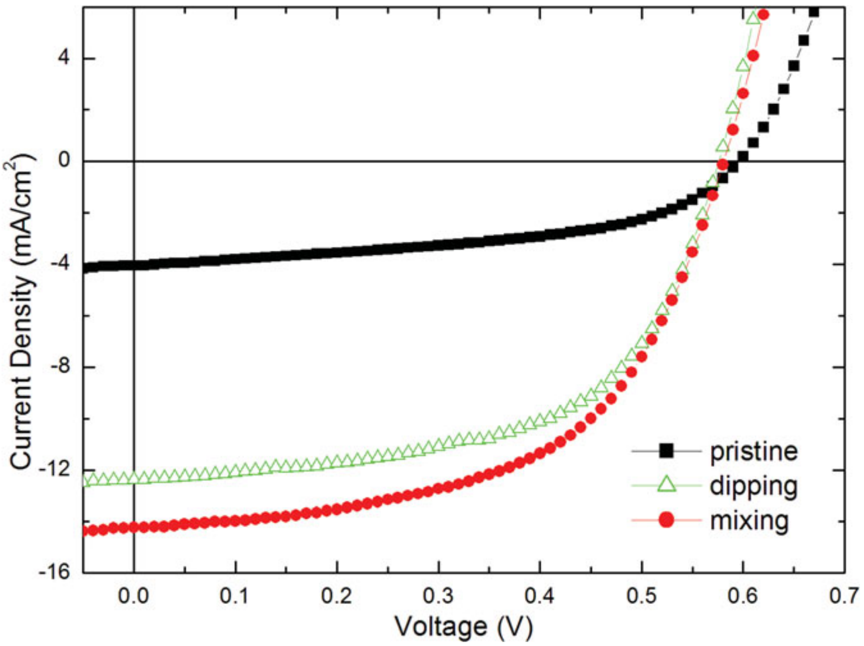

Figure 3. *I-V* Characteristics of P3HT:PCBM devices with the pristine PEDOT:PSS layers (a) and the doped PEDOT:PSS layer with dip-treatment in EG for 5 min (‘dipping’) (b) and 20% EG addition (‘mixing’) (c).

(2) mixed with 20% EG and (3) dipped in EG. After annealing PEDOT:PSS film at 120°C for 20 min, the active layer of P3HT and PCBM was spin-coated on top of the PEDOT:PSS film and annealed at 120°C for 20 min before *I-V* measurement.

Figure 3 shows the current density versus voltage (*I-V*) curves for P3HT:PCBM devices with the pristine or doped PEDOT:PSS layers. As shown in Fig. 3, device with the doped PEDOT:PSS layer by dip-treatment (referred as ‘dipping’) showed the higher device performance with PCE value of 4.15% compared to the pristine device (1.27%). Moreover, the device with the PEDOT:PSS layer with EG addition (referred as ‘mixing’) exhibited more pronounced improvement of PCE = 4.57% with a short circuit current (J_{SC}) = 14.2 mA/cm^2. The PCE value of ‘mixing’ device (4.57%) was about 3.6 times higher than that of the pristine film (1.26%). The device performances were mainly attributed from the increase of J_{SC} values rather than open circuit voltages (V_{OC}) and fill factors (FF). The J_{SC} values were increased from 4.21 (‘pristine’) to 12.37 (‘dipping’) and 14.22 mA/cm^2 (‘mixing’) and J_{SC} values of the devices with the modified PEDOT:PSS layer were nearly three times higher than that of the pristine film. The similar phenomenon was observed with the devices from PCz3TB:PCBM70, which could confirm doping effect on device performance. The device performance was increased from 2.15% to 2.50% by mixing PEDOT:PSS with 20% EG. In this case, the increased efficiency was mainly attributed from the increase of FF values (from 0.40 to 0.51). In addition, the almost constant V_{OC} indicated the well-established ohmic contact between the anode and active layer irrespective of the doped PEDOT:PSS [6]. Such a good performance by doping PEDOT:PSS layer can be explained by not only the increased conductivity of PEDOT:PSS layer but also improved surface morphology. The thin film morphology change of P3HT:PCBM films by

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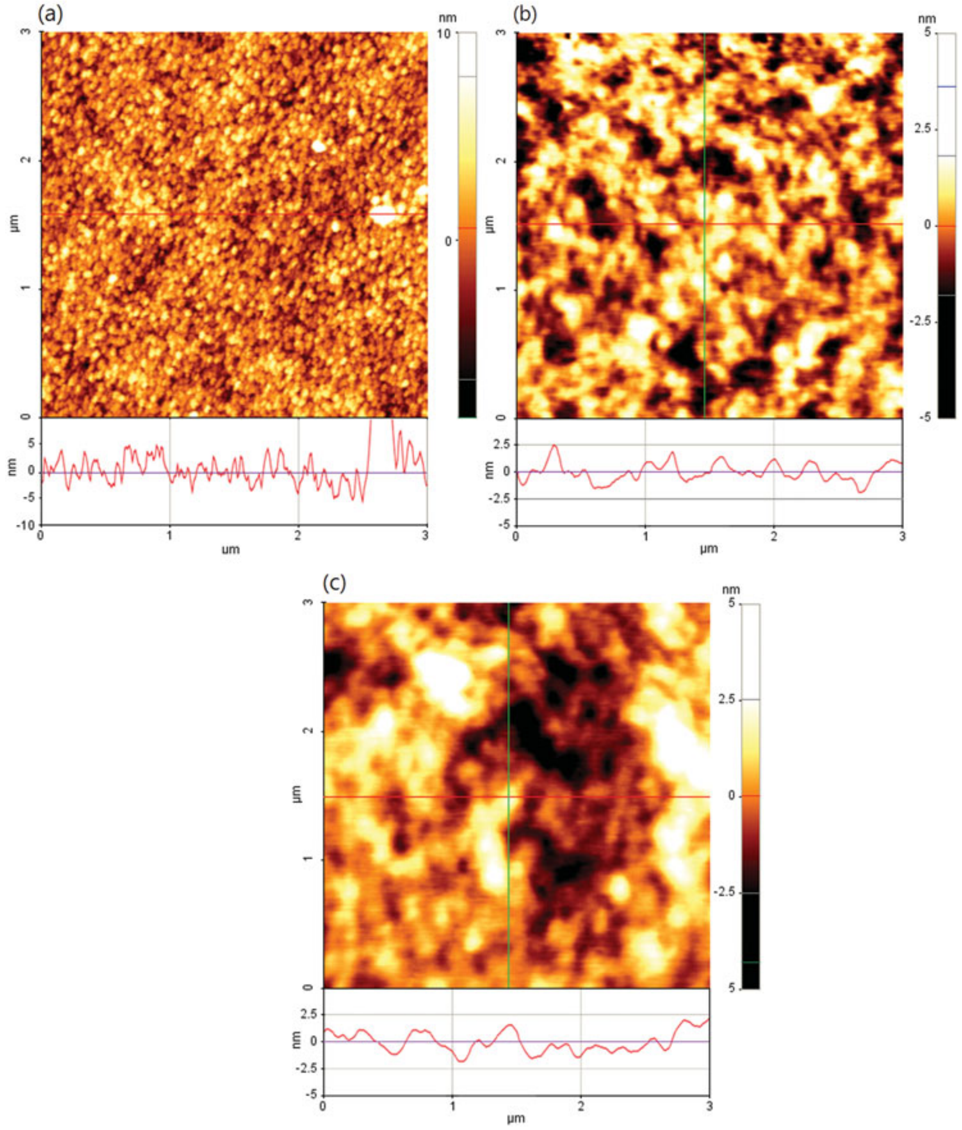

Figure 4. AFM images ($1\mu m \times 1\mu m$) of the P3HT:PCBM layers on top of the pristine PEDOT:PSS layers (a) and the doped PEDOT:PSS layer with dip-treatment in EG for 5 min (‘dipping’) (b) and 20% EG addition (‘mixing’) (c).

doped PEDOT:PSS layer were characterized by atomic force microscopy (AFM). AFM images were obtained from the films prepared similarly with the devices (glass/PEDOT:PSS (45 nm)/P3HT:PCBM (80–90 nm)). Figure 4 shows the AFM images of the P3HT:PCBM films prepared on top of (a) the pristine PEDOT:PSS layer and the PEDOT:PSS layers prepared (b) by dip-treatment in EG for 5 min and (c) with 20% EG addition. As shown in Fig. 4, the domain size of the P3HT:PCBM film was clearly increased by using the doped PEDOT:PSS layers ((b) and (c)) compared to that of the pristine film (a). The increased domain size is the signature of polymer self-organization, which indicates the formation of more extensively ordered structures in thin films [13]. Therefore, the doping of PEDOT:PSS layer by a polar solvent of EG can increase the extent of polymer aggregation and device performance. In addition, it was found that conductivity of PEDOT:PSS films and the OPV performance of the P3HT:PCBM devices prepared with the doped PEDOT:PSS layer are sensitive to the surface quality of the films. Further research on the optimization of device fabrication is currently underway.

Conclusions

Here we developed the simple strategy to increase device performance of P3HT:PCBM OPV devices by introduction of the doped PEDOT:PSS film. The doped PEDOT:PSS films were prepared by (1) mixing of PEDOT:PSS solution with EG solvent and (2) dipping the PEDOT:PSS-coated film into the EG solution. The P3HT:PCBM devices with doped PEDOT:PSS layer showed 3.6 times higher OPV performance than the pristine film due to the increased conductivity of PEDOT:PSS layer and improved surface morphology of the films. We also introduced this strategy into other photovoltaic polymer system and similar phenomenon was successfully observed with the devices from PCz3TB:PCBM70.

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