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Analysis of ITO-Free Organic Solar Cells Using a Highly Conductive Polymer Anode

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We have fabricated organic solar cells using highly conductive poly 3,4-ethylene-dioxythiophene: poly styrenesulfonate (PEDOT:PSS), which are modified by adding 5 wt.-% ethylene glycol (EG) as an anode without using transparent conducting oxide (TCO). The conductivity of the modified PEDOT:PSS (PEDOT:PSS-EG) film with ethylene glycol (EG) additive was enhanced by three orders of magnitude. With the modified PEDOT:PSS film, we investigated the transmittance of visible range light at various film thicknesses and device performance levels on ITO-free organic solar cells-based highly conductive polymer anodes. The power conversion efficiency (PCE) was governed by the series resistance, which directly determines a short circuit current density (J_{sc}).

1. Introduction

Organic solar cells (OSCs) based on the solution process have attracted much academic and industrial attention in the last couple of years due to their great advantages of low cost and easy fabrication processes on flexible substrates. However, in most cases, indium tin oxide (ITO) film is routinely used as an anode even though ITO works against the advantages of OSCs in terms of low cost and easy fabrication. There are several alternatives for replacing ITO, such as a solution-processed carbon nanotube network film [1], a metal nanowire mesh [2], or a highly conductive PEDOT:PSS film [3,4]. When using carbon nanotube network film or a metal nanowire mesh, it is not easy to avoid shorting the device while preparing the film. So, the modification of PEDOT:PSS is the most promising material at present due to its high transparency in the visible light spectrum, easy aqueous solution processing, and application for flexible devices. It is well known that the addition of a high-dielectric solvent with a high boiling point, such as sorbitol, dimethyl sulfoxide (DMSO), *N*-methyl pyrrolidone (NMP), and ethylene glycol (EG), into an aqueous solution of PEDOT:PSS can drastically improve the conductivity of the film [4–6]. It is generally considered that the addition of high-dielectric solvent improves the morphology of the films, providing good current pathways among the PEDOT:PSS

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domains and transforming the molecular structure. Recently, several research groups successfully demonstrated that the device performance of OSCs based on modified PEDOT:PSS film is comparable to ITO-based OSCs by using highly conductive PEDOT:PSS as an anode instead of the ITO material [4,7,8].

In this paper, we argue that the conductivity of the modified PEDOT:PSS films increases by three orders of magnitude and that the morphological variation strongly affects the increase of the conductivity when the EG was added to the aqueous PEDOT:PSS solution prior to film preparation. Furthermore, modified PEDOT:PSS films are used as an anode for fabrication of OSCs instead of ITO.

2. Experimental

In this work, 5 wt.-% of EG was used to modify the conductivity of commercial PEDOT:PSS (PH 500, H. C. Stark) in aqueous colloidal dispersions. Before film preparation, the modified PEDOT:PSS dispersions were magnetically stirred for at least 24 hrs. The modified PEDOT:PSS-EG was spin coated onto glass and annealed in air. Before the deposition of PEDOT:PSS-EG or pristine PEDOT:PSS, the glass substrates were treated with UV ozone plasma to improve the wetting property of the PEDOT:PSS solutions onto the glass surface. Aqueous PEDOT:PSS dispersions were filtered using a 0.45 μm syringe filter. Various spinning speeds were used to make the different thicknesses of the PEDOT:PSS-EG films, and the thickness of the film was measured by an Alpha step (Tencor Instruments, Alpha-step IQ) with an accuracy of ± 1 nm. PEDOT:PSS-EG films on glass were annealed at various temperatures for 10 min to determine an optimum annealing temperature. Film conductivity was measured using a standard four-point probe method with a Keithley 224 current source and a Keithley 197 microvolt DMM. The conductivity evaluated at different annealing temperatures is shown in Figure 1. In order to obtain the morphological information from the modified PEDOT:PSS films, tapping mode imaging

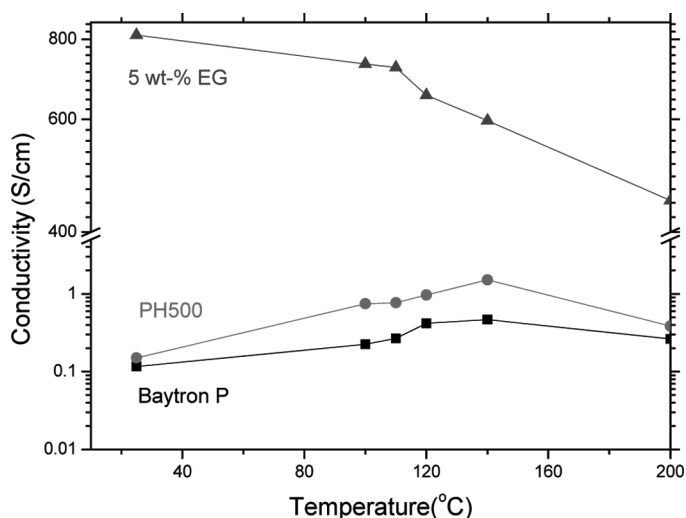


Figure 1. Conductivities of PH 500, Baytron P, and PEDOT:PSS-EG films on glass versus annealing temperature.

of AFM (DI3100, Veeco) was used. The light transmittance of films having different thicknesses was measured with a UV/VIS spectrometer (PERKIN ELMER, Lambda 20).

For the fabrication of active layers composed of poly(3-hexylthiophene) (P3HT) and phenyl [6,6] C61 butyric acid methyl ester (PCBM), the composite solution of P3HT and PCBM with 1:0.7 wt ratio was prepared in chlorobenzene as a solvent and stirred overnight. The active layer was spin coated onto the glass after the modified PEDOT:PSS film deposition. Since the same spinning speed was used, the thickness of the P3HT:PCBM layer for the whole measured devices was the same with 80 nm. To remove some residual solvents in the active layer at the end of the spin coating, the sample was baked at 120°C for 1 min. The device structure was completed by depositing about 0.6 nm of LiF and 110 nm of Al material as the top cathode electrode onto the polymer active layer under 3×10^{-6} torr vacuum in the thermal evaporator. Finally, fabricated devices were annealed at 150°C for 30 min to improve the morphology of the active layer and the performance of the devices [9,10].

The current density-voltage ($J-V$) characteristics of all polymer photovoltaic cells were measured under the illumination of simulated solar light with 100 mW/cm² (AM 1.5 G) by an Oriel 1000 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit, and all characterizations were carried out in an ambient environment. The illumination intensity used was confirmed by a standard Si photodiode detector from PV Measurements Inc., which was calibrated at the National Renewable Energy Laboratory, USA.

3. Results and Discussion

PEDOT:PSS films modified with EG were prepared as described in the experimental section, and the conductivities were measured using the four-point probe technique at different annealing temperatures on each film. An average of the measured values was taken, and the results are presented in Figure 1. The pristine PEDOT:PSS (PH 500 and Baytron P) film has around 10^{-1} S/cm of conductivity before annealing, and the conductivities of the films were slightly increased. But modified films showed an increase in conductivity by three orders of magnitude upon the addition of EG and a slow decrease in the conductivity with the increasing annealing temperature. In order to determine the reason for the conductivity enhancement of the PEDOT:PSS films, a morphological study was performed by atomic force microscopic imaging; the results are shown in Figure 2. From the morphological image in Figure 2(a) (pristine PEDOT:PSS) and Figure 2(b) (PEDOT:PSS-EG), the surface morphology of the pristine PEDOT:PSS and PEDOT:PSS-EG films is similar, while the phase images are quite different as shown in Figure 2(c) and (d), which corresponds with the pristine PEDOT:PSS and PEDOT:PSS-EG film, respectively. The pristine PEDOT:PSS film shows a clear separation of PEDOT rich domains and PSS rich domains, where the latter corresponds to dark. But the EG-modified PEDOT:PSS film reveals that PEDOT rich domains form networks made of lamellar-like, one-dimensional chains as in previous works [6,8]. This is probably due to the rearrangement of the PEDOT:PSS cluster as proposed by Nardes *et al.* [11]. The one-dimensional PEDOT rich chain and many cross points between these long chains afford a good current pathway and ultimately improve the conductivity of the film.

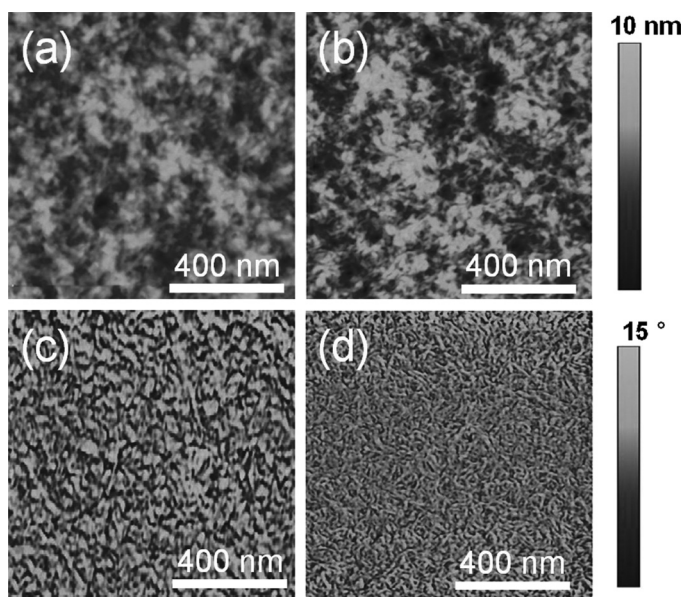


Figure 2. AFM topographic and phase images. (a), (b) Topographic image of pristine PEDOT:PSS and PEDOT:PSS-EG films. (c), (d) phase image of pristine PEDOT:PSS and PEDOT:PSS-EG films.

In Figure 3(a), the light transmittances of the EG-modified PEDOT:PSS films having different thicknesses are shown in comparison with that of ITO, which is 200 nm thick. Except for 340 nm thickness, more than 90% of the transmittances were observed in the main absorption region (from 300 nm to 600 nm) of P3HT:PCBM-based OSCs. Films having less than 200 nm of thickness are better than 200-nm-thick ITO, especially in the range from 300–600 nm, excluding the glass substrate. Figure 3(b) shows a transmittance of 550 nm wavelength light. The transmittance linearly increases with the decreasing film thickness and reaches 94% at

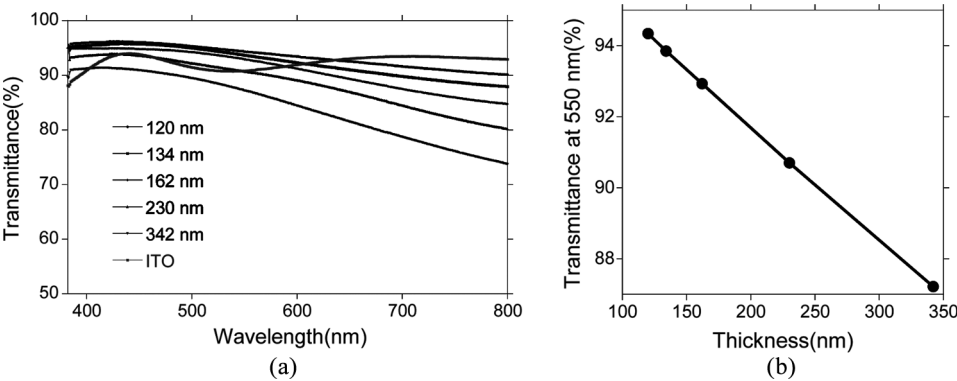


Figure 3. (a) Optical transmittance of ITO and the various thicknesses of PEDOT:PSS-EG films. (b) Optical transmittance versus film thickness at 550 nm of light wavelength.

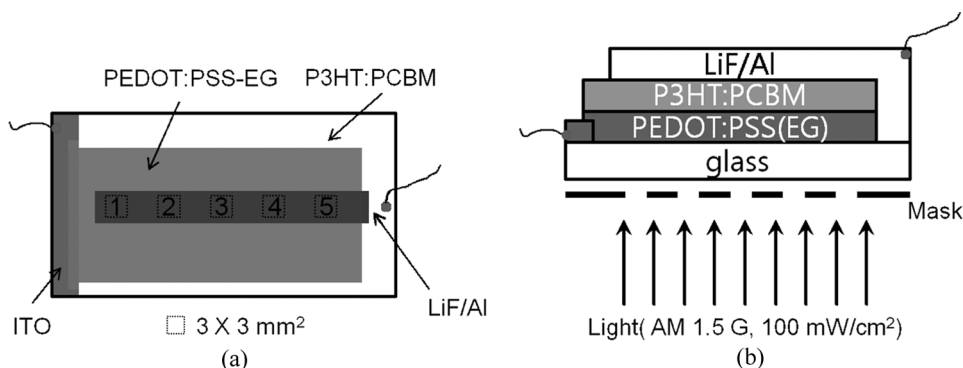


Figure 4. (a) The device structure of PEDOT:PSS-EG-based OSC. (b) Side view of device and measurement scheme.

120 nm of film thickness. This high transparency is also advantageous in the light harvest of the active layer, and it increases the photocurrent.

Figure 4(a) and (b) display the device structure of modified PEDOT:PSS-based organic solar cells and measurement schemes. The devices were prepared as described in the experimental section, and the active layer was defined by using the mask to limit the unwanted photocurrent generated from the outside region of the overlapped electrode area. The position of the mask window was changed from 1 to 5 and the size of the mask window for light illumination is $3 \times 3 \text{ mm}^2$. The distance between the centers of adjacent mask windows is 4.5 mm. Figure 5(a) and Table 1 summarize the device performances of ITO-free OSC, which has 270 nm of PEDOT:PSS-EG film thickness as measured at various positions. The PCE, fill factor, open circuit voltage (V_{oc}), and short circuit current density (J_{sc}) decrease with the increasing hole-collecting electrode length. In earlier investigations it has been demonstrated that the cell series resistance affects the cell performance and

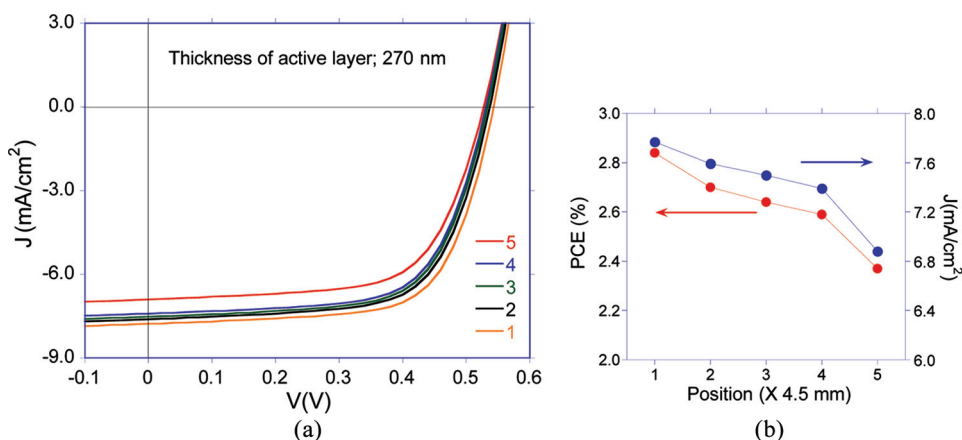


Figure 5. (a) Current density-voltage ($J - V$) characteristics of the device having 270 nm of the PEDOT:PSS-EG anode. (b) PCE and J_{sc} versus the mask window position.

Table 1. Performance of ITO-free OSCs with 270 nm of PEDOT:PSS-EG film thickness at various positions

Position	Jsc (mA/cm ²)	Voc (V)	FF (%)	PCE (%)	R _{SA} (Ωcm ²)
1	7.77	0.54	67	2.84	2.60
2	7.59	0.54	66	2.70	2.67
3	7.50	0.53	66	2.64	2.72
4	7.39	0.53	66	2.59	2.77
5	6.88	0.53	65	2.37	2.99

efficiency [12,13]. The series resistance includes the resistance of the electrodes, the contacts between each layers and active layer. In our case, the resistance of PEDOT:PSS-EG film mainly attributed to the cell series resistance with the increasing hole-collecting electrode length. Because, the resistance of the contacts and active layer should be identical and the conductivity of Al metal is much higher than PEDOT:PSS-EG film. Hence, the resistance of the PEDOT:PSS-EG film for hole current flowing strongly suppresses the current density in our device and the changing of PCE is directly proportional to the change of Jsc as shown in Figure 5(b).

4. Conclusions

In summary, we studied the influence of EG on the conductivity of PEDOT:PSS and surface morphology of PEDOT:PSS films modified with EG. The addition of EG increases the conductivity by three orders of magnitude by means of producing long PEDOT rich chains and increasing cross points between the chains to obtain better charge carrier transport. PEDOT:PSS-EG film thickness thinner than 250 nm are more transparent than ITO, and the optical transmittance is more than 90% in the main absorption region (from 300–600 nm) of P3HT:PCBM-based OSCs.

We fabricated OSCs using a highly conductive and transparent PEDOT:PSS-EG film as an anode. The device performance of OSCs based on the modified PEDOT:PSS film is strongly correlated to series resistance, which limits the current density and Jsc on the device.

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