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Hierarchical Modulation of PEDOT:PSS Buffer Layers for High Efficiency Organic Photovoltaic Devices

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The effects of solvent-modulated poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on the performance of organic photovoltaic devices (OPVs) were investigated. The PEDOT:PSS buffer layers were modulated by two different methods: blending and surface treatment. Both types of buffer layer modulation improved the power conversion efficiency (PCE) by reducing the series and contact resistances of OPVs. Compared with blending, which requires a carefully controlled doping level, surface treatment can be processed simply and exhibits much more obvious improvements after modulation. In short, efficient charge transport was possible after modulation, and high PCE values, 4.17% for blending and 5.14% for surface treatment, were obtained.

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Organic photovoltaic devices (OPVs) have attracted considerable interest as the next generation of solar energy conversion mechanisms due to their strong potential for low cost fabrication of lightweight, flexible, and ecofriendly equipment. However, their poor power conversion efficiency (PCE), typically 5 [1] and 6% even in tandem structures,[2] has remained an obstacle to commercial use.

Practically, one way to break through this drawback is to control the resistance of an OPV, which includes a series resistance (R_s) and a shunt resistance (R_{sh}). In the equivalent circuit of an OPV, R_s represents ohmic loss in the overall device and R_{sh} relates to leakage current.[3] Thus, a low value of R_s and a sufficiently high value of R_{sh} are preferred to achieve improved device performance. However, one problem is that photogenerated holes accumulate in an OPV because of the higher hole mobility in organic materials.[4,5] Moreover, high bulk resistivity and contact resistance (R_c) at the interface prevent some of the holes from being transported to the anode. This results in a reduction of the photocurrent and makes it difficult to control the resistance.

To resolve these issues, several attempts have been made to alternate a buffer layer, commonly poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Numerous researchers have studied the effects of added organic solvents, such as polyalcohols and ethylene glycol, on the characteristics of PEDOT:PSS, and the addition of these solvents can reduce the resistivity of PEDOT:PSS.[6-8] However, the doping level should be carefully controlled to avoid excess phase separation. Recently, Hsiao et al. reported that a highly conductive PEDOT:PSS anode could be obtained by surface modification with ethylene glycol.[9] Huang et al. showed that the conductivity of chemically synthesized PEDOT without PSS can be increased by cyclic voltammetry with a solvent.[10] Furthermore, Moujoud et al. demonstrated that UV irradiation on a PEDOT:PSS surface can increase the conductivity and work function.[11] These articles indicate that conformational changes in the surface condition contribute to the improvement in conductivity.

In this research, we modulated buffer layer characteristics by blending and surface treatment and investigated the effects of modulation on device performance. For improving device performance, surface treatment can be much more effective than blending, which has been studied in several previous studies.

N,*N*-dimethylformamide (DMF) (Aldrich) was used to modulate the buffer layer. PEDOT:PSS (Baytron P) was blended with DMF in a 3:1 volume ratio and surface treatment was carried out by spin-coating DMF onto a precoated PEDOT:PSS film (30 nm). The detailed modulation processes are illustrated in Fig. 1. To fabricate the OPVs, PEDOT:PSS or PEDOT:PSS/DMF (filtered through a 0.45 μm syringe filter unit) was spin-coated on patterned indium tin oxide glass substrates with a sheet resistance of 7 Ω/□ and annealed in air at 150°C for 10 min. For the surface treatment, DMF was spin-coated sequentially onto the PEDOT:PSS film and annealed in air at 150°C for 10 min. Next, the units were transferred to an argon-filled glove box (<0.1 ppm of O_2 and H_2O) and a photoactive layer composed of regioregular poly(3-hexylthiophene) (P3HT, Rieke Met., Inc.) and phenyl-C_{61}-butyric acid methyl ester (PCBM, Nano-c) in a 1:0.8 weight ratio was spin-coated from chlorobenzene to form a film with a thickness of ~ 200 nm. Finally, LiF (2 nm) and Al (150 nm) cathodes were deposited sequentially via a thermal evaporator with 0.04 cm^2 of the defined active area of the device. The devices were postannealed at 150°C for 10 min in the argon-filled glove box to enhance the interfacial contact between the photoactive layer and the electrode. Current density–voltage (*J-V*) measurements (Ivium Stats, Ivium Technologies) using a solar simulator (Sun 2000, Abet Technologies) in AM 1.5G, with an officially calibrated reference condition, were carried out to determine device performance.

The *J-V* characteristics of the devices with various buffer layers under an illumination of 100 mW/cm^2 are shown in Fig. 2. To assess the reproducibility of the devices, we fabricated six individual cells for each case and averaged their photovoltaic parameters (see Table I). The control device with a pristine PEDOT:PSS had an open-circuit voltage (V_{oc}) of 0.57 V, a short-circuit current density (J_{sc}) of 7.8 mA/cm^2, a fill factor (FF) of 55.3%, and a calculated PCE of 2.50% (with an optimum PCE of 2.61%). In contrast, obvious increases in J_{sc} and PCE were observed after modulating PEDOT:PSS with DMF. For devices with buffer layers modulated by blending, a clear improvement was seen in J_{sc} (to 13.5 mA/cm^2), whereas V_{oc} remained at 0.57 V and FF decreased slightly to 53.7%, leading to a calculated PCE of 4.17% (with an optimum PCE of 4.35%). In cases where surface treatment was used, the devices exhibit a much higher increase in J_{sc} (to 17.5 mA/cm^2) with the same V_{oc} of 0.57 V, leading to a higher PCE of 5.14% (with an optimum PCE of 5.35%) among the devices, whereas FF decreased to 51.1%. The clear increase in J_{sc} in both cases indicated efficient carrier transport due to the improvement of R_s and R_c.[3] The decrease in FF in both modulated devices could be caused by a lower value of R_{sh} (see Table I) induced by random leakage current in the highly conductive buffer layer or phase separation of PEDOT:PSS due to the added DMF.[7] However, because only small variations in FF ($<10\%$) and constant V_{oc} were observed, the R_{sh} values in our results seemed to be sufficiently high.

A clear effect of DMF modulation is seen in the R_s values listed in Table I. The R_s values of both modulated devices were lower than that of the control device, and surface treatment yielded a greater reduction in R_s (8.7 Ω cm^2) than blending (10.1 Ω cm^2). The reduction in R_s values was primarily due to the decreased resistivity of

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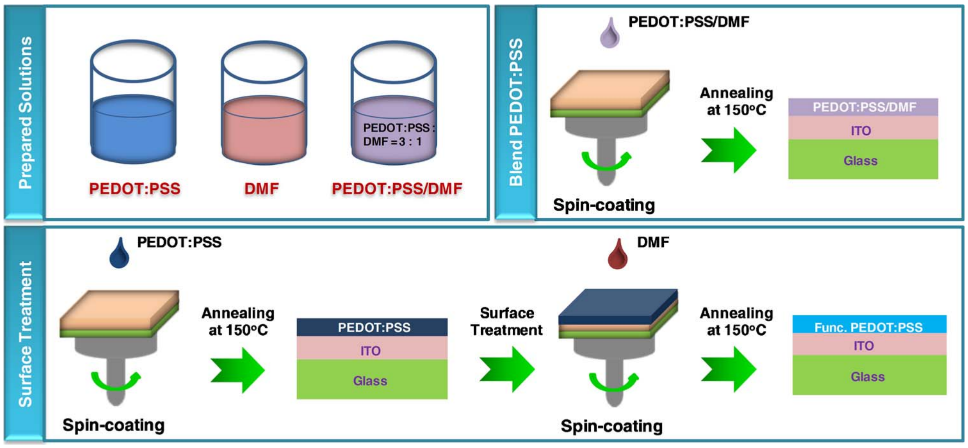

Figure 1. (Color online) The prepared solution and processing method of modulated buffer layer, blend PEDOT:PSS/DMF and surface-treated PEDOT:PSS using DMF.

PEDOT:PSS caused by DMF modulation. Furthermore, because charge transport in an OPV is greatly dependent on the internal electric field,[12] a lower R_s represents an increase in the effective internal electric field of the photoactive layer, leading to efficient charge collection at the electrode.

In fact, these results suggest that the R_s value of an OPV depends largely on the conductivity of PEDOT:PSS. The conductivity of PEDOT:PSS used in this work was specified at 1 S/cm, and our own measurement, via a four-point probe, yielded a similar value (1.27 S/cm). Furthermore, the conductivity of the modulated PEDOT:PSS was improved by 1 order of magnitude (69.2 S/cm) by blending and 2 orders of magnitude (152 S/cm) by surface treatment. These DMF-enhanced conductivities may originate from the transformation of the thiophene structures[8] and/or modified molecular arrangements to form conductive pathways.[13] Additionally, when chlorobenzene (with a lower dipole moment of 1.54 D) was used to modulate PEDOT:PSS in the manner described above, the photovoltaic parameters and the conductivity were not improved compared with the control device (data not shown). This indicates that the higher polarity of DMF (3.86 D) caused an interaction between the DMF dipoles and the dipoles of the PEDOT chains, which can contribute to conductivity enhancement.[14] Thus, the conductivity of the buffer layer controls the overall device performance, specifically improving the carrier transport and leading to increased J_{sc}.

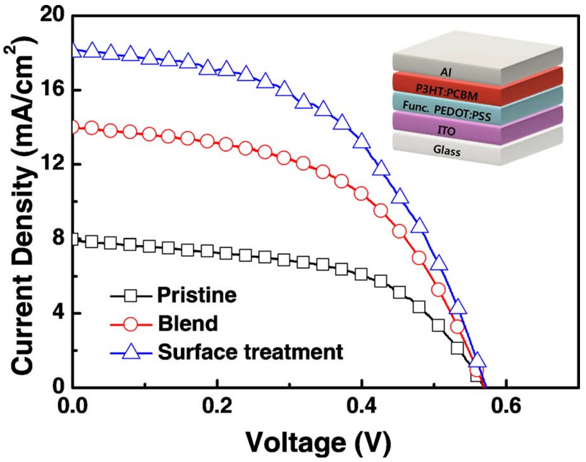

Figure 2. (Color online) The *J-V* characteristics of OPVs with different modulations onto buffer layer using DMF under the illumination of 100 mW/cm^2. Inset: The structure of OPVs.

To investigate the effect of DMF modulation on the contact between the buffer and photoactive layers of a device (represented by R_c), the alternating current impedance spectra (measured by Ivium Stats, Ivium Technologies) are shown in Fig. 3a at a voltage of 0.1 V over a frequency range from 0.1 Hz to 1 MHz in a dark condition.[15] The frequency response of the impedance exhibited a semicircular behavior and the R_c of the device is represented by the diameter of the semicircle of the real part (Z').[15] The R_c of the control device was ~ 100 kΩ. However, after DMF modulation, R_c was markedly decreased to 25 kΩ for blending and 22.5 kΩ for surface treatment. The decrease in R_c indicated that DMF modulation can reduce the interfacial resistance between the buffer and photoactive layers. Moreover, these reductions in R_c contribute to lower R_s values in modulated devices and can therefore promote extracting behavior and the release of accumulated holes in OPVs. Thus, charge loss can be clearly reduced, resulting in improved charge transport and increased J_{sc}.

Previously, Lee et al. reported that UV irradiation on PEDOT:PSS can reduce R_c. However, the corresponding PEDOT:PSS work function increased beyond the energy level of P3HT after UV irradiation, leading to trapped carrier loss due to the formation of an extraction barrier.[16] Thus, the PEDOT:PSS work function is crucial to reduce trapped carrier loss. In contrast, the work functions of DMF-modulated buffer layers measured by the Kelvin probe system (KP-6500, McAllister Technical Services) yield 5.08 eV for pristine, 4.92 eV for blend, and 5.06 eV for surface-treated. These results

Table I. Performance of OPVs with different buffer layers under illumination of AM 1.5G (100 mW/cm^2) and electrical properties of buffer layer. The average values are presented within six devices.

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s [a] (Ω cm^2)	R_{sh} [a] (kΩ cm^2)	Conductivity[b] (S/cm)	Work function[c] (eV)
Pristine	0.57	7.8	55.3	2.50	15.6	0.49	1.27	5.08
Blend	0.57	13.5	53.7	4.17	10.1	0.40	69.2	4.92
Surface-treated	0.57	17.5	51.1	5.14	8.7	0.38	152	5.06

[a] Calculated from the inverse slope of the *J-V* curves over $V > V_{oc}$ (R_s) and at 0 V (R_{sh}).
[b] Measured from the four-point probe.
[c] Measured from the Kelvin probe system.

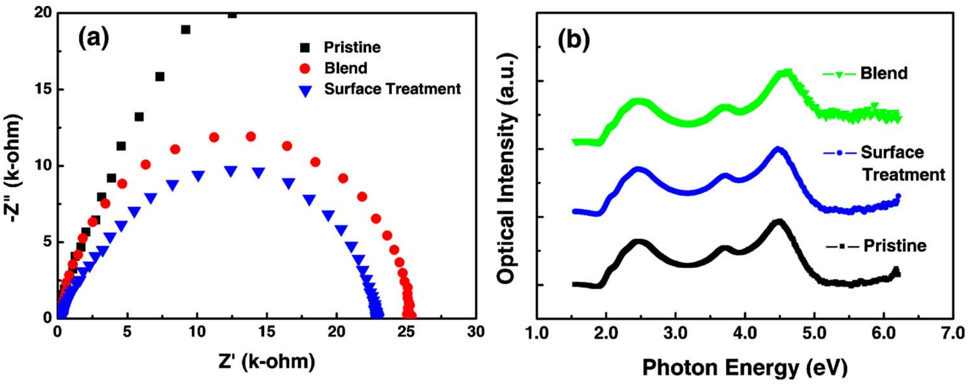

Figure 3. (Color online) (a) The ac impedance plot of the devices according to various PEDOT:PSSs in the dark. (b) UV-vis absorption spectra of the P3HT:PCBM photoactive layer for the various buffer layers.

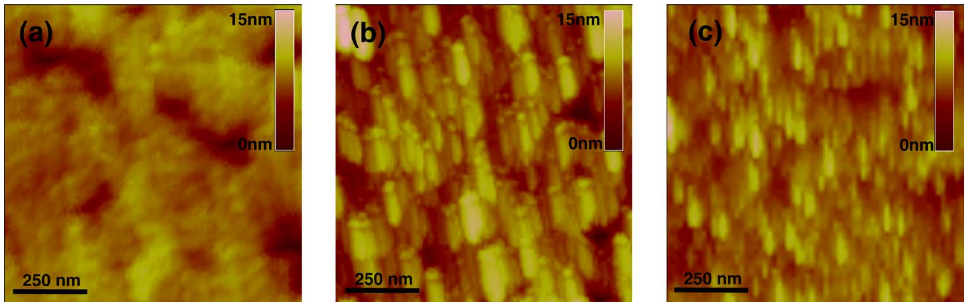

Figure 4. (Color online) The AFM images and root-mean-square values of PEDOT:PSS: (a) Pristine (rms = 1.512 nm), (b) blend (rms = 1.888 nm), and (c) surface-treated (rms = 1.258 nm).

indicate that the formation of a hole-extraction barrier does not occur following DMF modulation. Thus, trapped charge loss originating from an energy barrier at the interface between the buffer and photoactive layers could be effectively reduced.

To understand the optical properties of the photoactive layer on a modulated PEDOT:PSS film, ultraviolet-visible (UV-vis) absorption spectra were measured (Shimadzu UV 2401-PC Spectrophotometer) and are presented in Fig. 3b. The intensity and peak measurements from P3HT and PCBM were similar before and after DMF modulation. This indicates that modulation of the buffer layer had little effect on the optical properties of the photoactive layer and the increased PCE following DMF modulation may originate from the modified electrical properties of the OPV.

To further investigate these results, we examined the surface condition of each PEDOT:PSS film with an atomic force microscope (AFM, NanoScope IIIa, Veeco) in tapping mode. As shown in Fig. 4, DMF modulation generates significant changes in PEDOT:PSS in both cases. A slightly roughened morphology is exhibited in the blend case, whereas surface treatment produces a slightly flattened surface. Also, some small islands were observed on the surfaces in both cases. These effects resulted from conformational changes with increased interchain interaction.[10] In particular, the interaction between PEDOT:PSS and DMF can be a driving force, leading to a composition ratio of PEDOT to PSS that differs from that of the pristine layer, by the removal of PSS to form conductive pathways of continuous PEDOT-rich domains.[13,14] The surface treatment exhibits homogeneous phase separation due to a transition from compact to extended aggregated structure, to improve the ionic transport in the polymer as well as the hopping rate.[10] In contrast, when blending is used, excess DMF can induce inhomogeneity and serious phase separation and other defects that increase leakage current in OPVs. Thus, these results indicate that the surface condition and interface at the buffer layer are crucial to device performance.

In conclusion, we successfully demonstrated that the PCE of an OPV can be improved by a DMF-modulated buffer layer. From our investigations, DMF modulation of PEDOT:PSS let the carrier transport be efficient by reducing both the series and contact resistances of OPVs These phenomena result from the rearrangement of organic molecules and the formation of highly conductive pathways of continuous PEDOT-rich domains, leading to reduced resistivity of the buffer layer with no significant change in the work function. Compared with blending, which requires a carefully controlled doping level, surface treatment can be processed simply and exhibits much more obvious improvements. In short, efficient charge transport is possible in both cases, and high PCE values, 4.17% for blending and 5.14% for surface treatment, were observed. These investigations could be useful for improving the next generation of OPVs.

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