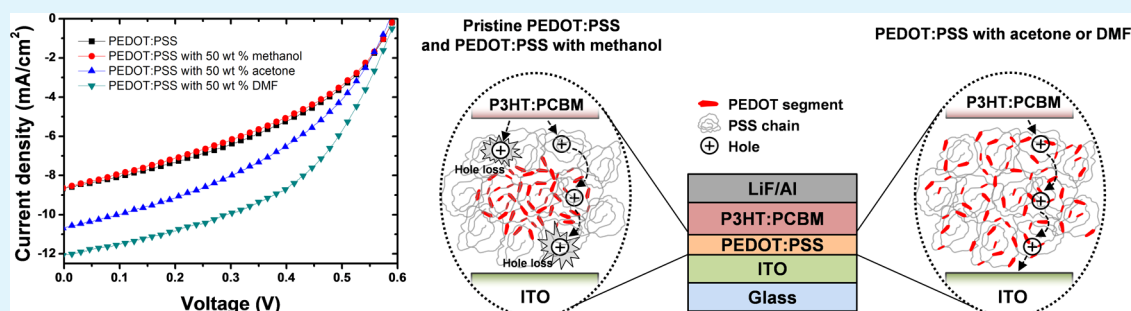# Hole Transport Enhancing Effects of Polar Solvents on Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonic acid) for Organic Solar Cells

Jeong Suk Yang, Sang Hoon Oh, Dong Lim Kim, Si Joon Kim, and Hyun Jae Kim*

School of Electrical, Electronic Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea

Ⓢ Supporting Information

ABSTRACT: This study analyzed the properties of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) thin-films prepared by spin-coating solutions made with the polar solvents methanol, acetone, or N,N-dimethylformamide (DMF). A characteristic analysis was carried out for poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM)-based organic solar cells (OSCs) having these modified PEDOT:PSS thin-films as the hole transport layer. The resistivity of the PEDOT:PSS thin-film obtained from the DMF solution was 4.89×10^{-3} Ω·cm with a roughness of 3.23×10^{0} nm, compared to 3.51×10^{-1} Ω·cm and 7.72×10^{-1} nm for a pristine PEDOT:PSS thin-film. The dipole moment increase of the solvent led to the decreased resistivity and the increased roughness and transparency of PEDOT:PSS thin-films on the structural arrangement of the polymers. Highly efficient OSCs with a power conversion efficiency of 3.47% were obtained when DMF-treated PEDOT:PSS thin-film was used as the hole transport layer.

KEYWORDS: organic solar cells, PEDOT:PSS thin film, polar solvent, dipole moment, hole transport layer

1. INTRODUCTION

Organic solar cells (OSCs) are of particular interest because of their low cost, high flexibility, and ease of mass production.[1−4] Although they are receiving a lot of attention as potential next-generation alternative energy sources, they have low power conversion efficiencies (PCEs), which significantly hinder their commercialization. The way to increase the PCEs of OSCs is to enhance the short-circuit current density (J_{SC}) and fill factor (FF).[3,5]

Enabling larger numbers of photons to be absorbed in the active layer to increase the photon absorption efficiency (η_{abs}) will increase the J_{SC}.[6] To accomplish this, photon absorption in the buffer layer between the electrode and the active layer must be minimized. Another way to increase the J_{SC} is to raise the carrier transport efficiency (η_{tr}) by enabling the carriers formed in the active layer to be more easily transported to the electrode without loss within the device.[6] In OSCs, excitons, which are formed by incident light, are generally dissociated in the active layer. Electrons and holes generated in the active layer flow to the cathode and the anode, respectively.[7,8] The total amount of photogenerated charge carriers to reach the electrodes determines a FF.[3] However, carriers become lost due to recombination and trapping within the interface or the transport layer and fail to reach the electrode, thus giving rise to reduced solar cell efficiencies.[9] To solve these problems, polymer films such as poly(3,4-ethylenedioxythiophene):poly-(styrene sulfonic acid) (PEDOT:PSS) have been used as the hole extraction layer in OSCs due to their high work function, conductivity, and transparency.[10−12] PEDOT:PSS has been widely used as an interfacial layer or organic electrode in polymer electronic devices such as OSCs and organic light emitting devices (OLEDs).[13−15] PEDOT:PSS as the hole transport layer (HTL) in OSCs is coated between the indium tin oxide (ITO) and the active layers and serves to facilitate transport of the holes to the anode. However, to fabricate highly efficient OSCs, the conductivity of the PEDOT:PSS thin-film must be improved.[16] PEDOT:PSS is composed of PEDOT, which is hydrophobic and conductive, and PSS, which is hydrophilic and insulating; the conductivity of the thin-film is directly related to the way in which the PEDOT is formed.[17]

Many studies have focused on enhancing the conductivity of PEDOT:PSS by adding solvents.[18−21] There are many theories that explain why these solvents enhance the conductivity, but the precise mechanism is still unclear.[22,23] In addition to conductivity increase, other fundamental properties of solvent-modified PEDOT:PSS thin-film should be studied to improve the efficiency of OSCs.

In this work, the polar solvents such as methanol, acetone, or *N*,*N*-dimethylformamide (DMF) were used to modify the PEDOT:PSS. We proposed the better mechanism of the higher conductivity and transparency of PEDOT:PSS modulated with polar solvents. Changes in the resistivity of PEDOT:PSS thin-films that resulted from the addition of various amounts of polar solvents having different dipole moments were investigated to understand the nature of the polar solvent-treated PEDOT:PSS thin-film. Furthermore, a characteristic analysis of OSCs prepared using these modified PEDOT:PSS thin-films as HTL was then carried out, and ways to enhance the efficiency of OSCs were considered.

2. EXPERIMENTAL SECTION

Solutions were prepared by mixing each of methanol, acetone, and DMF to PEDOT:PSS (Clevios P) in the range from 0 wt % to 80 wt %. These solutions were stirred for 12 h to obtain homogeneous solutions. Each solution was spin-coated on a glass substrate and then annealed in air at 150 °C for 10 min. The resistivity of each 50-nm-thick film was measured using the Hall technique in the van der Pauw configuration (HMS-3000, Ecopia). Surface analysis of the thin-films was performed using an atomic force microscope (AFM, XE-150, Park Systems) in the noncontact mode. The transparency of each thin-film was determined using an ultraviolet−visible spectrophotometer (UV−vis, V-650, JASCO). The thickness of the thin-films was measured using an Alpha-Step (XP-2 surface profiler, Ambios). X-ray photo-electron spectroscopy (XPS) measurements were performed in a base pressure of 4×10^{-9} Torr using monochromated Al $K\alpha$ X-rays, at $h\nu$ = 1486.6 eV (XPS, Theta Probe AR-XPS System, Thermo Fisher Scientific). To fabricate OSCs, solutions consisting of PEDOT:PSS mixed with 50 wt % of each solvent were spin-coated on glass substrates patterned with ITO and then annealed in air at 150 °C for 10 min. They were then moved to an argon-filled glovebox. Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) in a 1.0:0.8 ratio were mixed in chlorobenzene and stirred for 12 h to produce the active-layer solutions. These solutions were deposited by spin coating onto the HTLs, and the assembly was annealed at 120 °C for 10 min in the glovebox. LiF and Al were deposited using a thermal evaporator to form electrodes that were 3 and 150 nm thick, respectively. The devices were annealed at 120 °C for 10 min to enhance the interfacial contact between the photoactive layer and the electrode. To assess the performance of the devices, a solar simulator (Sun 2000, Abet Technologies) with AM 1.5 G illumination was used. The OSCs' layout in this paper is a structure which includes the unpatterned PEDOT:PSS and active layer between the patterned and crossed ITO and Al. The area that actually receives light and produces energy is the nominal area where patterned ITO and Al electrodes form the crossing area. Its size is 0.04 cm². If a part other than this area receives light, extra current will be produced due to an edge effect.[24] To solve this problem, we used a black mask to eliminate the unwanted extra current.[24]

3. RESULTS AND DISCUSSION

3.1. Analysis of Modified PEDOT:PSS Thin-Films. The resistivity of each thin-film fabricated from the various PEDOT:PSS solutions is shown in Figure 1. The results show that the resistivity of the pristine thin-film (PEDOT:PSS only) and that made with methanol were very similar. However, when DMF was used, there was a significant reduction in the
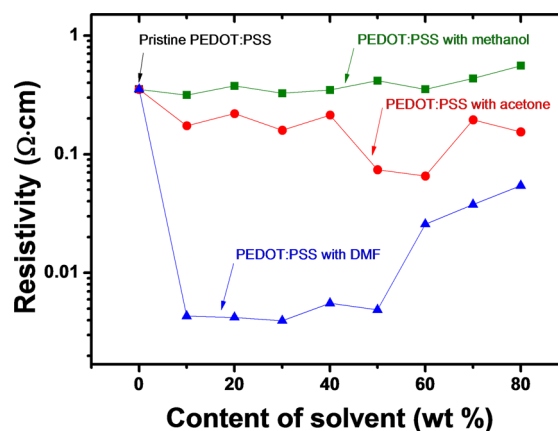

Figure 1. Resistivity of PEDOT:PSS thin-films after treatment with different concentrations of various polar solvents ranging from 0 to 80 wt %. Polar solvents are methanol, acetone, and DMF.

resistivity. Positively charged PEDOT is a conductive polymer with a low molecular weight (MW) of 1×10^3 to 2.5×10^3 g/mol, and negatively charged PSS is an insulating polymer with a high MW of about 4×10^5 g/mol.[17] A PEDOT:PSS thin-film is composed of PEDOT:PSS grains, where each individual grain is spherical and about 30 to 50 nm in diameter.[17] The thicknesses of the PEDOT:PSS thin-films fabricated in this study were about 40−50 nm, and a thin-film is a single layer of PEDOT:PSS grains. PEDOT is insoluble in water, but the addition of the water-soluble PSS improves its dispersibility.[21] For this reason, PSS is used as the charge-balancing dopant during polymerization.[21] As shown in Figure 2a, the conductive and hydrophobic PEDOT is equally distributed inside the PEDOT:PSS grains, whereas the insulating and hydrophilic PSS surrounds the outside.[17] In this type of structure, the insulating PSS reduces the conductivity of the thin-film because the outer insulating region prevents carrier transport. If a polar solvent having a high dipole moment is added inside the grains of PEDOT:PSS, the PEDOT segments separate from the inner PSS chains. The PEDOT concentrated inside the grain becomes evenly distributed radially from the grain center and thereby provides a continuous conductive pathway. Therefore, as shown in Figure 2b, the resistivity of the thin-film is reduced through the conductive PEDOT segment pathways. This makes efficient movement of carriers possible because of the shortened distance between the PEDOT segments. This phenomenon is demonstrated by XPS measurement (see Figure S1 in the Supporting Information). In Figure S1, we show the S 2p core level spectra of the pristine PEDOT:PSS thin-film and PEDOT:PSS thin-films with each solvent added. In PEDOT:PSS thin-films treated with acetone or DMF, the PEDOT/PSS ratio is increased more in the surface region compared to the pristine PEDOT:PSS thin-film and PEDOT:PSS thin-film treated with methanol (see Table S1 in the Supporting Information). This proves that the PEDOT segments were distributed onto the thin-film surface by the solvents with high dipole moment. Through this, we confirmed that conductive pathways were formed by PEDOT segments throughout the entire thin-film.

The PEDOT:PSS thin-film made from methanol solution did not show any noticeable reduction in resistivity (Figure 1) because methanol does not have a sufficiently high dipole moment (1.68 D)[25] to change the orientation in PEDOT:PSS. As shown in Figure 1, when less than 50 wt % of acetone was
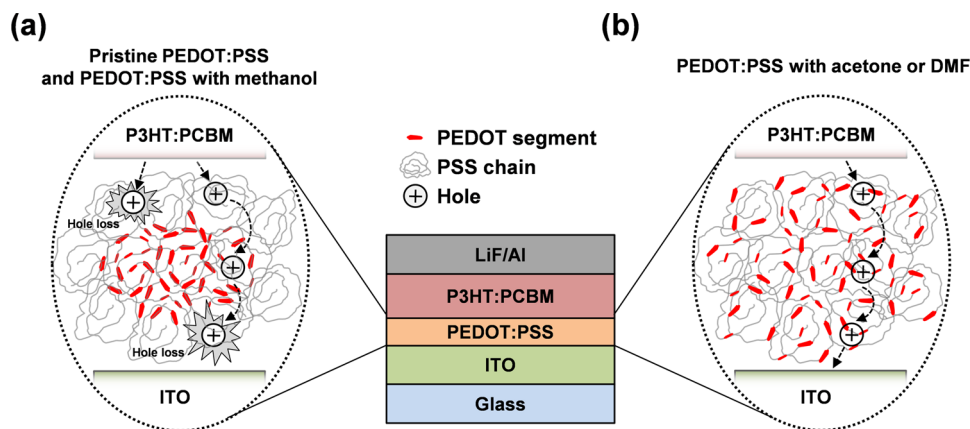
Figure 2. Carrier transport mechanism of (a) the pristine PEDOT:PSS and PEDOT:PSS with methanol and (b) PEDOT:PSS with acetone or DMF.
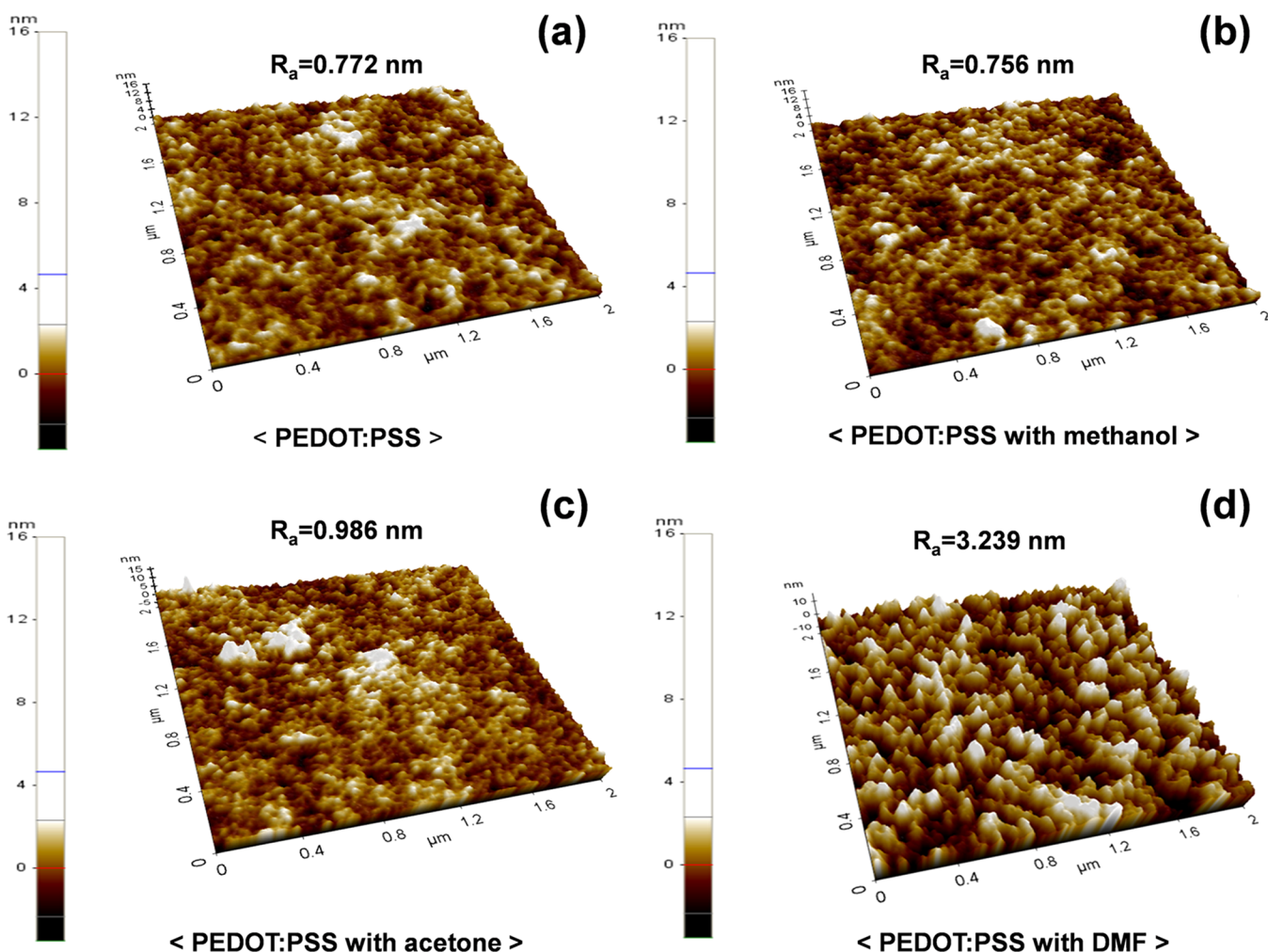

Figure 3. AFM topography of (a) PEDOT:PSS thin-film, (b) PEDOT:PSS thin-film with 50 wt % methanol, (c) PEDOT:PSS thin-film with 50 wt % acetone, and (d) PEDOT:PSS thin-film with 50 wt % DMF.

used, there was no change in the resistivity of the PEDOT:PSS thin-film. When over 50 wt % was used, however, the amount of acetone was sufficient to evenly distribute the PEDOT segments in the PEDOT:PSS thin-film and reduce its resistivity to 7.40×10^{-2} $\Omega \cdot$cm or about 10 times less than that of the pristine film. Acetone, a polar solvent with a high dipole moment (2.88 D),[25] affected the PEDOT:PSS resistivity, but sufficient (50 wt %) acetone needed to be used in order to

effect any change in the PEDOT:PSS film. Of the three solvents, DMF has the highest dipole moment (3.86 D),[25] and it causes the largest phase separation in PEDOT:PSS. DMF distributed the positively charged PEDOT segments over the entire thin-film to the greatest extent. This solvent significantly increased the conductivity by increasing the probability that carriers would be transported through the conductive pathway without being recombined or trapped in the thin-film. Figure 1

shows the changes in the resistivity as a function of DMF content. Even a small amount of DMF (i.e., 10 wt %) lowered the resistivity (4.33×10^{-3} Ω·cm). Minimum resistivities of DMF-treated PEDOT:PSS thin-films were observed at 10−50 wt %. When 50 wt % DMF was used, the resistivity (4.89×10^{-3} Ω·cm) of the film decreased by about 100 times compared to the pristine film (3.51×10^{-1} Ω·cm). In contrast, when large amounts of DMF were used (i.e., >60 wt %), the resistivity consequently increased to 2.57×10^{-2} Ω·cm.

Figure 3 depicts the topography of the thin-films spin-coated from the 50 wt % solutions. The thin-film of PEDOT:PSS made from the methanol solution was very smooth; its surface roughness was almost the same as that of the pristine film, 7.72×10^{-1} nm. The thin-films made from acetone or DMF solutions, however, showed significant differences in their surface characteristics, as shown in Figure 3c,d. The size of the bright area corresponding to the PEDOT greatly increased with the grain size.[17] Particularly, the surface roughness (3.24×10^{0} nm) of DMF-modulated PEDOT:PSS thin-film was much greater than that of the pristine film (7.72×10^{-1} nm). These results suggest that the PEDOT segments that are concentrated inside the grains separate from the PSS chains and become widely distributed over the surface of the PEDOT:PSS thin-film because of the high dipole moment of the solvents, as discussed above. In addition, the surface becomes more hydrophobic because the proportion of the insoluble PEDOT on the surface of the PEDOT:PSS thin-film is greater when a solvent with a high dipole moment is used.[26] These results follow the changes in the resistivity. The rough surface increases the surface contact area between the active layer and the HTL.

Figure 4 shows the transmittance of the various PEDOT:PSS thin-films. The transparency of PEDOT:PSS thin-films made
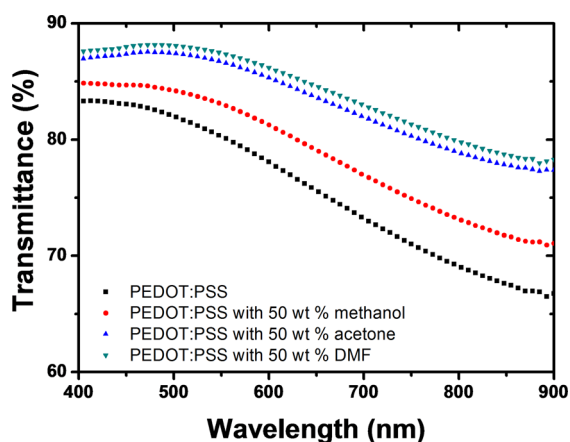

Figure 4. Transmittance spectra of PEDOT:PSS thin-films with various solvents compared to the pristine PEDOT:PSS thin-film.

from DMF or acetone solutions was enhanced by about 6−7% in the visible range compared to that of the pristine PEDOT:PSS film. This increase of transmittance is associated with forming evenly distributed PEDOT segments in PEDOT:PSS thin-film treated with acetone or DMF. When PEDOT segments aggregate, this produced a high level of light scattering and reduced transmittance of PEDOT:PSS thin-film.[27] However, in PEDOT:PSS thin-film treated with acetone or DMF that have a high dipole moment, the PEDOT:PSS segments are evenly distributed throughout the entire thin-film and the light scattering could be effectively reduced. Hence, the

transmittance of the thin film could be further increased. Furthermore, the refractive index (n) increases when the transmittance of a PEDOT:PSS thin-film increases.[28] The increased n by solvent having a high dipole moment raises the density of PEDOT:PSS thin-film.[29] As seen in Figure 2b, the enhancement in density by a polar solvent confirms that the PEDOT segments were spread throughout the PEDOT:PSS thin-film.

3.2. J−V Characteristics of OSCs.
Figure 5 shows the current density−voltage ($J−V$) characteristics of OSCs in which
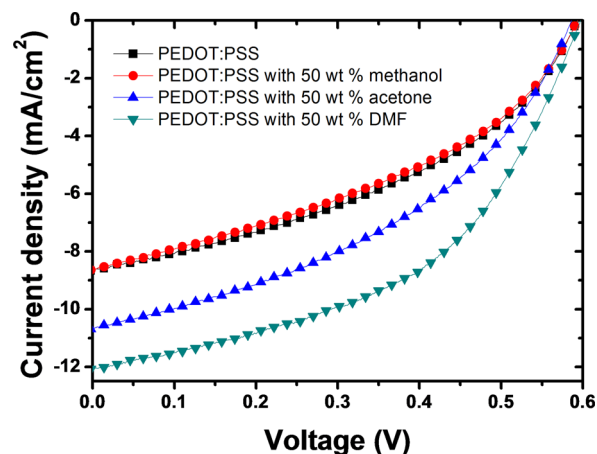

Figure 5. $J−V$ characteristics of OSCs using the pristine PEDOT:PSS and PEDOT:PSS thin-films with 50 wt % of each solvent added.

the PEDOT:PSS thin-films made from 50 wt % solutions were used as the HTL. The OSC made with the PEDOT:PSS thin-film modulated by 50 wt % DMF had a PCE of 3.47%, much greater than the 2.10% for the OSC made with the pristine PEDOT:PSS thin-film (Table 1). The PEDOT:PSS thin-film

Table 1. Performance of OSCs with Different HTLs under AM 1.5 G Illumination

condition	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
PEDOT:PSS	8.65	0.59	40.92	2.10
PEDOT:PSS with 50 wt % methanol	8.64	0.59	39.49	2.02
PEDOT:PSS with 50 wt % acetone	10.69	0.59	41.63	2.61
PEDOT:PSS with 50 wt % DMF	12.05	0.60	48.39	3.47

made from DMF solution also had a resistivity about 100 times lower than that of the pristine PEDOT:PSS thin-film. Rearrangement of the PEDOT segments occurs with polar solvents and leads to higher conductivity of the prepared thin-film. An evenly distributed conductive PEDOT pathway forms, as shown in Figure 2b. Concurrently, holes created in the active layer easily reach the electrode without being recombined or trapped within the HTL. Thus, this reaction increases a FF of OSCs.[3] Furthermore, conductive pathways are more extensive with solvents that have a large dipole moment and increase η_{tr}, which enhances J_{SC}. As a result, PEDOT:PSS thin-films modulated with solvents having large dipole moments enhanced the PCEs of OSCs.

The surface roughness increased when solvents were used (Figure 3). This increases the interface contact area between the active layer and PEDOT:PSS thin-film, which in turn

increases the possibility that the created holes are transported to the PEDOT:PSS.[30] The increased efficiency of the OSCs thus corresponds to the increased roughness and the decreased resistivity.

UV−vis results indicate that, when solvent-modulated PEDOT:PSS thin-films with higher transparency were used as the HTL, an increased number of photons were absorbed into the donor P3HT, thereby enhancing η_{abs}. This effect contributed to the increased efficiency of the OSCs.

4. CONCLUSIONS

We investigated the effect of added solvents on the characteristics of PEDOT:PSS thin-films and monitored the changes in the efficiency of OSCs when those thin-films were used as the HTL. The dipole moment magnitude of polar solvent affected the thin-film characteristics; the higher dipole moments of polar solvents caused a reduction in the resistivity of the PEDOT:PSS thin-films. The degree of reduction depended on how well the polar solvent dispersed the PEDOT segments concentrated inside the thin-film to the outside. Increased dispersion increased the conductive pathways of the carriers. The DMF-modulated (50 wt %) PEDOT:PSS thin-film had the lowest resistivity and highest transparency and roughness of the solvent-modulated films. The OSC having this PEDOT:PSS thin-film as the HTL had the highest PCE of 3.47%, J_{SC} of 12.05 mA/cm^2, an open circuit voltage (V_{OC}) of 0.60 V, and a FF of 48.39%. These results contribute to the research on the effect of solvents on the conductivity of PEDOT:PSS and to the development of highly efficient next-generation OSCs.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Details of XPS analysis; figure of S 2p XPS spectra; table of PEDOT:PSS ratios. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: hjk3@yonsei.ac.kr. Tel.: +82-2-2123-5865.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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