Influence of solvent treatment with fluoro compounds on the properties of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) polymer as a hole transport layer in polymer solar cells

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Abstract. We prepared high conducting poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) by solvent additives for using as a hole transport layer (HTL) in polymer solar cells (PSCs). PEDOT:PSS films treated with fluoro compounds of hexafluoroacetone (HFA) and hexafluoroisopropanol (HFIPA) with various concentrations show a significant enhancement in electrical conductivity without compromising optical transparency. The conductivity increased from 0.2 to 1053 and 746 S/cm after 4 vol. % HFA and 6 vol. % HFIPA treatments, respectively. The high performance of the PEDOT:PSS layer is attributed to preferential phase segregation of PEDOT:PSS with HFA and HFIPA solvent mixture treatment methods. The improved performance of PSC was dependent on the structure of organic solvents and the concentration of fluoro compounds in PEDOT:PSS solution. Using these optimized layers, conjugated PSCs with a poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5 thiophenediyl] polymer:[6,6]-phenyl-C71-butyric acid methyl esters (PCDTBT:PC₇₁BM) bulk heterojunction have been produced. The high power conversion efficiency (PCE) of 4.10% and 3.98% were observed for PEDOT:PSS films treated with 4 vol. % HFA and 6 vol. % HFIPA treatments, respectively. The obtained results show that PEDOT:PSS optimized with HFA and HFIPA organic solvents can be a very promising candidate for transparent anode buffer layer in the low cost organic solar cell devices. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.JPE.4.043097](https://doi.org/10.1117/1.JPE.4.043097)]

Keywords: polymer solar cells; bulk hetero junction; poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate); spin coating; atomic force microscopy; Raman spectroscopy; PCDTBT; PC₇₁BM.

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1 Introduction

The rise in global energy consumption as a result of increase in the population of the world and the subsequent decrease in fossil fuel resources is a serious matter of concern. Renewable energy is considered to be one of the alternative solutions to reduce environmental issues such as global warming and climate change. Harvesting energy directly from solar radiation through photovoltaic technology is a well-established strategy of future global energy production.¹ The current research community is extensively involved in developing new materials for green and clean energy applications. Among them, polymer solar cell (PSC) is one of the most important applications. The striking achievements in photoconducting polymers have opened a new pathway, and researchers have found that organic semiconducting polymers play an important role in

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efficient solar energy conversion.² PSCs based on conjugated polymer materials have been the focus of intense research over the past 15 years through the development of bulk heterojunction (BHJ) architectures comprising a donor-acceptor (D-A) systems, where efficient exciton dissociation takes place. Continuous improvements of the solar cell structure and the power conversion efficiency (PCE) have resulted from the developments of low bandgap polymer materials, novel approaches to control the active layer morphology, and various combinations of D-A materials.^{3,4}

PSCs are the best alternative to their inorganic counterparts because of their attractive features, which include light weight, high flexibility, roll-to-roll process, ease of large-area fabrication, and potential for low-cost solution processing.^{5,6} These advantages are due to the preparation of solar cells using solution processes at room temperature such as spin or spray coating. The research activities and reports on PSC-based devices have been increased during the last two decades. Researchers have adopted many ways to achieve high PCE in PSCs and to cover a large area at low cost.⁷ Among the various polymers used, conjugated low bandgap polymer-based active layers yield high PCE of 5–9%^{8–11} while >10% are needed for commercial viability.¹² The performance of PSCs has been improved using new materials, new structures, and new techniques in devices.^{13,14} Recently, interest has been focused on fabricating solar cells utilizing low energy-gap polymers as the light absorbing and electron donating material combined with an electron accepting fullerene derivative. One such low energy-gap polymer is poly [N-9-heptadeca-nyl-2,7-carbazole-alt-5,5(4,7-di-2-thienyl-2,1,3-benzo-thiadiazole)] (PCDTBT).^{15–19} The extended red absorption of such materials can lead to improved performance by harvesting a greater fraction of the sun's radiation.

To achieve the optimal PCE of a solar cell, the use of an additional interface layer is essential. The interface layer modification on BHJ active layer/electrodes has been comprehensively carried out for the improvement of charge injection or collection, especially those due to mismatched energy levels between polymer materials and metal electrodes.^{20–22} In order to enhance the PCE, several buffer layers have been reported to modify the interface between the active layer and metal electrodes. Many materials such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), molybdenum trioxide (MoO₃), vanadium pentoxide (V₂O₅), nickel oxide (NiO₂), and tungsten oxide (WO₃) have been used as hole transport buffer layers,^{23–26} and titania (TiO_x), lithium fluoride (LiF), cesium carbonate (CsCO₃), and zinc oxide (ZnO) have been reported for electron extraction layers^{27–30} to improve the device performance. Among the several anode buffer layer materials, PEDOT:PSS is widely used as anode buffer layer due to its high transparency in the visible region, high thermal stability, and mechanical flexibility. PEDOT:PSS aqueous dispersions are commercially available and used as a hole transport layer (HTL) in PSCs due to high hole affinity and high work function. The insertion of a thin PEDOT:PSS layer can raise the cohesion and/or change the work functions of the electrodes, and thus lower the interfacial series resistance.³¹ However, PEDOT:PSS suffers from low conductivity, <1 S/cm, which is lower by one or two orders of magnitude than that of some other conducting polymers.³² The conductivity of the PEDOT:PSS film must be increased for many applications. Therefore, for various applications, modification in the preparation of the PEDOT:PSS layer is mandatory. PSCs using this low conductivity PEDOT:PSS as the interface layer yield poor device performances. Hence, it is necessary to increase the conductivity of PEDOT:PSS for an effective HTL. It is highly possible to enhance its conductivity by adding various high-boiling-point polar solvents.³³

Several methods have been applied to increase the conductivity of the PEDOT:PSS films, for example, solvent additives in the PEDOT:PSS solution or thermal postdeposition treatment of the PEDOT:PSS film.^{33–37} PEDOT:PSS solution by mixing of organic molecules, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), ethylene glycol (EG), etc., was performed in order to improve the conductivity.^{37,38} Treatment with certain salts, carboxylic acids, or inorganic acids have also significantly enhanced the conductivity of the PEDOT:PSS film.^{39–41} Several models have been reported, such as conformational change of conductive PEDOT chains,^{41,42} the bonds breaking between PEDOT and PSS and their phase segregation,⁴³ reduction of excess PSS layer for better connectivity between inter-PEDOT chains,⁴⁴ and PSS coils associated with large protons that weakens the electrostatic interaction, thus increasing the intramolecular conductivity in the PEDOT,⁴⁵ in order to understand the mechanism of conductivity enhancement in the PEDOT:PSS films.

In the present study, we report on the improvement of photovoltaic parameters of the BHJ PSCs by the incorporation of a thin layer of PEDOT:PSS mixed with fluoro compounds such as hexafluoroacetone trihydrate ($\text{HFA} \cdot 3\text{H}_2\text{O}$) and hexafluoroisopropanol (HFIPA) with various concentrations by spin coating technique. We studied the effect of HFA and HFIPA solvent additives in a PEDOT:PSS layer as an HTL. We obtained enhanced PEDOT:PSS films conductivities of about 1053 and 746 S/cm after treatment with 4 vol. % HFA and 6 vol. % HFIPA, respectively. The high performance of the HTL is attributed to preferential phase segregation of PEDOT:PSS with $\text{HFA} \cdot 3\text{H}_2\text{O}$ and HFIPA solvent mixture treatments. The improved performance of the PSC was dependent on the structure of organic solvents and the concentration of fluoro compounds in PEDOT:PSS solution. Using these optimized buffer layers, conjugated PSCs with a poly[[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5 thiophenediyl] polymer:[6,6]-phenyl-C71-butyric acid methyl esters (PCDTBT:PC₇₁BM) BHJ have been produced on indium-tin-oxide (ITO) coated glass substrate. PSC devices are exhibited with a maximum PCE of 4.10% and 3.98% for HFA4% and HFIPA6%, respectively, with enhanced current density-voltage (J - V) characteristics. The function of the HFA and HFIPA mixed PEDOT:PSS hole extraction layer will be discussed in the views of structural, optical transparency, and surface morphology.

2 Experimental Results

PEDOT:PSS (Clevios PH1000, H. C. Starck, Goslar, Germany), PCDTBT (1-Material, Quebec, Canada), and PC₇₁BM (American Dye Source, Quebec, Canada) are used without further purification. PEDOT:PSS aqueous solution (Clevios PH1000) was used as a host polymer. The solvent additive treatment was performed by 2, 4, and 6 vol. % of $\text{HFA} \cdot 3\text{H}_2\text{O}$ and HFIPA were added into PEDOT:PSS as additives. The solution mixture was stirred vigorously for 5 h, after which it was filtered using a 0.25- μm filter. The filtered PEDOT:PSS was then deposited by spin coating at 5000 rpm for 30 s on glass and ITO coated substrates, which were precleaned with detergent, pure water, ethanol, and methanol in ultrasonication. Pristine and additive-mixed PEDOT:PSS films were annealed at 140°C for 20 min in vacuum in order to remove the water. The electrical conductivities and the thicknesses of the films were measured using Vander Pauw four-point probe method with a Keithley 2400 sourcemeter and a Dektak II surface profilometer, respectively. Optical transmittance spectra of the films were recorded using a Shimadzu UV-2450 spectrometer. Micro-Raman scattering measurements were performed in the backscattering geometry using a Renishaw in Via Raman spectrometer (532 nm). AFM images were recorded with Seiko Instruments SPA 400-SPI 4000 operating under ambient conditions in dynamic force mode. Solar cells were fabricated using an active layer of PCDTBT and PC₇₁BM (having 1:1.4 wt.% %) in chlorobenzene by spin coating at 1000 rpm for 60 s. Then the film was dried at room temperature for 1 h and had a thickness around ~105 nm. Finally, a 100-nm-thick Al layer was thermally deposited in a high vacuum of 1.3×10^{-4} Pa. The active area of each device was 0.3 cm². The current-voltage characteristics of the fabricated PSC devices were measured by employing an Advantest R-6441 A.C. source meter and a 100 mW solar simulator (Newport Oriel, California) with a filter having an air mass of 1.5 G (AM 1.5 G). The contact angle was analyzed with an Excimer Inc., (Kanagawa, Japan) contact angle meter. Figures 1(a)–1(c) show the molecular structure of PEDOT:PSS, HFA, and HFIPA, the energy level diagram of the active layer, PEDOT:PSS, ITO, and Al electrode and schematic diagram of fabricated PSC structure (ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/Al).

3 Results and Discussion

The thickness and electrical conductivity (σ) of the pristine, $\text{HFA} \cdot 3\text{H}_2\text{O}$, and HFIPA treated PEDOT:PSS films are presented in Table 1. The pristine PEDOT:PSS film, with a thickness of around 52 nm, had a conductivity of 0.2 S/cm. On the other hand, the conductivity was significantly improved by three orders of magnitude after adding different concentrations of $\text{HFA} \cdot 3\text{H}_2\text{O}$ and HFIPA into PEDOT:PSS aqueous solution directly. From Table 1, we observed that the conductivity of the film depends on the concentration of fluoro compounds in the PEDOT:

Fig. 1. (a) Molecular structures of PEDOT:PSS, PCDTBT, and PC₇₁BM. (b) Energy level diagram of the solar cell devices and (c) schematic device structure of the organic solar cell.

PSS film. Further, the high conductivity of 1053 S/cm was observed in 4 vol. % HFA treated PEDOT:PSS film which is nearly close to the conductivity of PEDOT:PSS film treated with HFA · 3H₂O (1164 S/cm) reported by Xia et al.³³ For HFIPA treated films, the high conductivity is only 746 S/cm obtained for 6 vol. % of HFIPA. Ouyang et al.⁴² reported that PEDOT:PSS films conductivity enhancement is strongly dependent on the properties and structure of the organic compounds. The conductivity is negligible when organic solvent with only one –OH group is used, whereas significant conductivity enhancement can be observed for EG and other polyols, which has two –OH groups. The hydrolysis of HFA with water molecules results into hexafluoropropanal-2,2-diol (HFP2OH), a gem-diol with two –OH groups connected to one carbon atom. Moreover, HFP2OH is a highly amphiphilic compound with two hydrophobic CF₃ and two hydrophilic –OH groups. The hydrophobic nature of CF₃ can preferentially interact with hydrophobic PEDOT and the hydrophilic nature –OH groups preferentially interacts with the hydrophilic PSS. Consequently, some of the PEDOT chains are detached from the insulating PSS chain as a result of decrease in Coulombic attraction between PEDOT and PSS after HFA · 3H₂O treatment with various volume percentages.

Dimitriev et al. reported that the larger amount of protons associated with PSS chains equilibrate the negative charge on the PSS backbone and weaken its electrostatic interaction with the positively charged PEDOT. This leads to distortion of the planar PEDOT backbone and, therefore, to easier charge transfer along the PEDOT chain.⁴⁵ After the HFA · 3H₂O treatment, the PSS chains become PSSH chains by taking protons from other PSS chains, and PSSH phase segregation takes place. This further reduces the Coulombic attraction between the PEDOT and PSS chains and can give rise to conductivity enhancement.⁴⁶ For each HFA and HFIPA treated PEDOT:PSS film, we observed a reduction in film thickness (Table 1). The higher conductivity

Table 1 Thickness and conductivity of PEDOT:PSS polymer films of pristine, HFA, and HFIPA treated.

Compound	0%		2%		4%		6%	
	Thickness (nm)	σ (S/cm)	Thickness (nm)	σ (S/cm)	Thickness (nm)	σ (S/cm)	Thickness (nm)	σ (S/cm)
HFA	52	0.2	49	634	45	1053	44	971
HFIPA	52	0.2	52	399	50	518	48	746

of HFA-treated PEDOT:PSS film compared to that of HFIPA treatment can be attributed to the strong interaction between two $-OH$ groups in the $HFA \cdot 3H_2O$ and the insulating PSSH-rich phase, whereas HFIPA has only one $-OH$ group and we need further concentration of HFIPA in the film in order to increase the conductivity of the film.^{47,48}

We measured the surface morphology of the polymer films by AFM, in order to confirm the effect of additives. Figures 2(a)–2(g) show the AFM images of PEDOT:PSS polymer film mixed with a different volume ratio of HFA and HFIPA additives. For comparison, height image of pristine PEDOT:PSS film is also presented in Fig. 2(a). Pristine PEDOT:PSS film reveals that the surface presents spherical type grain structures with dimensions of about 80 to 100 nm and a root-mean-square (rms) roughness of 1.01 nm. These grains are attributed to phase separated PEDOT:PSS domains surrounded by an excess of PSS chains.⁴⁷ The effect of HFA compound on PEDOT:PSS surface morphology can be clearly seen in Figs. 2(b)–2(d). The rms roughness for 2%, 4%, and 6% HFA treated polymer films was 1.22, 1.76, and 1.55 nm, respectively. After HFIPA treatment, the PEDOT:PSS films show different surface morphologies when compared with pristine PEDOT:PSS as shown in Figs. 2(e)–2(g). The rms roughness for 2%, 4%, and 6% HFIPA treated polymer films was 1.35, 1.41, and 1.73 nm, respectively. A remarkable difference in the AFM image can be observed for the 4% HFA and 6% HFIPA treated PEDOT:PSS film.

The surface features in the AFM image of HFA4% and HFIPA6% appear as entangled nanofibrous structures with dimensions of some tens of nanometers. This indicates the

Fig. 2. Two-dimensional AFM images of PEDOT:PSS (a) pristine, (b) HFA2%, (c) HFA4%, (d) HFA6%, (e) HFIPA2%, (f) HFIPA4%, and (g) HFIPA6% thin films.

conformational change of polymer chains from coil to linear shape⁴⁹ after the HFA and HFIPA treatments, and these nanowires can promote charge transport more efficiently than spherical particles. In addition, the pristine PEDOT:PSS film had a roughness of 1.01 nm. The roughness was increased for PEDOT:PSS films treated with HFA and HFIPA compounds. The obtained roughness indicates that the interconnection channels between conductive PEDOT chains that spread out onto the planar substrate increased by the fluoro compounds treatment, thereby enhancing the conducting pathway.⁵⁰

The optical transmittance spectra of HFA and HFIPA added PEDOT:PSS films on glass substrates were analyzed, as displayed in Figs. 3(a) and 3(b), respectively. The PEDOT:PSS films were quite smooth and had a uniform flat surface after the additive process. Transmittance is around 90% in the visible range for one-layer pristine PEDOT:PSS film, whereas a small reduction in transmittance was observed in 4 vol. % HFA addition. HFIPA treated films show a decrease in transmittance while pristine PEDOT:PSS films show relatively good transmittance, around 80% in the range from 400 to 900 nm. Due to the colorless nature of the PSS, the optical absorption in PEDOT:PSS mainly originates from the presence of PEDOT.

Figure 4 shows the Raman spectra of pristine and 4 vol. % HFA and 6 vol. % HFIPA treated PEDOT:PSS films. Clear differences between the Raman spectra of the pristine and the additive processed PEDOT:PSS films are evident in the range from 1400 to 1500 cm^{-1} . A shift in Raman peak position and change in band shape were observed in the C=C band of PEDOT:PSS after solvent additives.^{51,52} Pristine PEDOT:PSS film exhibits a broad C=C symmetric stretching peak at 1445 cm^{-1} with a shoulder part, whereas HFA4% and HFIPA6% treated films exhibit a narrower band and are shifted to the lower wave number of about 1436 cm^{-1} . The variations in the band stem from the changes in the electronic structure of PEDOT chains in PEDOT:PSS film upon additive treatment.⁵³ This change in Raman spectra is similar to that of EG treated PEDOT:PSS film observed by Ouyang et al.⁴² They proposed that both coil and extended linear conformations present in a PEDOT:PSS film, and some of the coil conformations turn into linear conformation after EG solvent treatment. The benzoic structure may be favorable for a coil conformation and quinoid structure may be favorable for linear conformation. Therefore, the change in Raman spectra shape (Fig. 4) indicates that some PEDOT chains change from a benzoic to a quinoid structure. From the above analysis, the reduction of insulating PSS and the structural change of PEDOT in PEDOT:PSS films⁵⁴ upon mixing of HFA and HFIPA additives may enhance the conducting pathway in the PEDOT:PSS film.

To examine the effect of solvent-modified HTL layer on the device performance, the PSCs were fabricated with the structure of ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/Al. The pristine and additive mixed PEDOT:PSS were chosen as a hole transport buffer layer. The PEDOT:PSS was sandwiched between the ITO and the PCDTBT:PC₇₁BM active layer. Figures 5(a) and 5(b) show the current density (J)–voltage (V) curves of the PSC devices with PEDOT:PSS layer that had been processed with HFA and HFIPA. Tables 2 and 3 list their photovoltaic parameters, such as open-circuit (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE. Figure 5(a)

Fig. 3. UV–visible absorption spectra of the (a) HFA treated and (b) HFIPA treated PEDOT:PSS films on glass substrate.

Fig. 4. Raman spectra of PEDOT:PSS films of pristine, HFA4%, and HFIPA6% on glass substrate.

shows the J - V curves for devices incorporating PEDOT:PSS film treated with different concentrations of HFA. The V_{oc} did not change much whereas J_{sc} varied significantly after the additive process. The PCE increased from 2.72% for pristine to 3.36%, 4.10%, and 3.64% for 2, 4, and 6 vol. % of HFA treated PEDOT:PSS film, respectively. The series resistance (R_s) of the pristine, 2, 4, and 6 vol. % HFA treated PEDOT:PSS devices were 70.8, 55.2, 42.8, and 45.1 Ω , respectively. Note the lower FF for pristine PEDOT:PSS device, indicating poor contact quality and leading to more recombination loss at the interface between the PEDOT:PSS and the PCDTBT:PC₇₁BM active layer. This clearly indicates that a 4 vol. % HFA treated PEDOT:PSS layer forms a good electrical contact between the ITO and the active layer of PCDTBT:PC₇₁BM.

Furthermore, we fabricated PSCs with HFIPA treated HTL and analyzed its impact on the device characteristics. From Fig. 5(b), the PSC devices that incorporated PEDOT:PSS film treated with HFIPA exhibit better device performance with increase of the concentration of HFIPA. The J_{sc} of the device with 6 vol. % of HFIPA treated buffer layer exhibits higher than that of other devices along with a higher FF, leading to PCE of 3.98%. In the case of HFA treated films, the device shows performance increase up to 4 vol. % of HFA in the film and performance decrease for 6 vol. % of HFA. The R_s of the devices for 2, 4, and 6 vol. % HFIPA treated PEDOT:PSS buffer layers was 56.3, 57.8 and 43.6 Ω , respectively.

Fig. 5. The J - V plots for PCDTBT:PC₇₁BM organic solar cells fabricated with (a) HFA and (b) HFIPA treated PEDOT:PSS as hole transport buffer layers under 100 mW/cm² illumination.

Table 2 Photovoltaic parameters of PSC devices that incorporated pristine and HFA treated PEDOT:PSS as hole transport layer (HTL).

PEDOT:PSS	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor (FF)	PCE (%)	R_s (Ω)
Pristine	0.873	7.78	0.40	2.72	70.8
HFA2%	0.850	9.41	0.42	3.36	55.2
HFA4%	0.874	10.19	0.46	4.10	42.8
HFA6%	0.864	9.36	0.45	3.64	45.1

Table 3 Photovoltaic parameters of PSC devices that incorporated pristine and HFIPA treated PEDOT:PSS as HTL.

PEDOT:PSS	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor (FF)	PCE (%)	R_s (Ω)
Pristine	0.873	7.78	0.40	2.72	70.8
HFIPA2%	0.853	8.42	0.43	3.09	56.3
HFIPA4%	0.868	9.90	0.44	3.78	57.8
HFIPA6%	0.864	10.03	0.46	3.98	43.6

Since the J_{sc} and FF values dominantly influenced the PCE by the solvent additive process, the maximum PCE of 4.10% and 3.98% was obtained for 4 vol. % HFA and 6 vol. % HFIPA treated PEDOT:PSS. The observed trend is likely associated with the hole transport buffer layer characteristics, which depend on the structure and concentration of the fluoro compounds in the PEDOT:PSS layer. If the layer is without additive, the PSC would exhibit poor device efficiency because the hole transport characteristics between the ITO and the PCDTBT:PC₇₁BM active layer are poor. Moreover, poor adhesion between PEDOT:PSS HTL and the ITO substrate or with the PCDTBT:PC₇₁BM layer, often has resulted in devices with low efficiency.⁵⁵ In order to study the wettability of PEDOT:PSS on ITO substrate before and after HFA and HFIPA solvent treatments was analyzed from the static contact angle measurement. It is a simple, useful, and sensitive tool for quantifying the wetting property of different materials. Figures 6(a)–6(c) show the contact angle measurement of pure PEDOT:PSS and PEDOT:PSS treated with HFIPA and HFA solvents. The measurements were performed at 22°C and 48% relative humidity. We used PEDOT:PSS and solvent (HFA and HFIPA) treated PEDOT:PSS droplets to evaluate their adhesion to ITO substrate. The average contact angle for each sample was obtained by measuring four spots with PEDOT:PSS droplets with a volume of 10 μ L. The standard error of contact angle measurements is ± 1 deg. A droplet of PEDOT:PSS solution placed on ITO substrate shows a static contact angle of 27 deg [Fig. 6(a)]. The static contact angles measured for HFIPA and HFA solvents modified PEDOT:PSS solution on ITO substrate were 23 and 12 deg, respectively. This clearly indicates that the simple solvent mixing into PEDOT:PSS greatly improved the wetting effect between ITO and PEDOT:PSS treated with HFA. It is expected that the improved adhesion property of PEDOT:PSS with 6% HFA can decrease resistance at the interface and help better to transport holes from the active layer to ITO electrode. The increment in FF accompanied with the

Fig. 6. Static contact angle photographs of the droplet (10 μ L) of (a) PEDOT:PSS, (b) PEDOT:PSS with 6% HFIPA, and (c) PEDOT:PSS with 4% HFA on ITO substrate.

reduction in series resistance can be attributed to enhanced conductivity and the good adherence property of PEDOT:PSS with HFA and HFIPA treatments. The uniform film with close packing of fine nanofibrous structures improves the transport of charge carriers and decreases the series resistance due to better contacts.

4 Conclusion

We have investigated the surface, optical, and structural modifications of PEDOT:PSS films based on fluoro compound additive processes with various concentrations. The electrical conductivity of as-prepared PEDOT:PSS films can be significantly enhanced by the addition of HFA and HFIPA and the film transmittance is over 80%, compared to the commercial ITO substrate. The enhancement of the conductivity is attributed to preferential phase segregation of PSS chain induced by the HFA and HFIPA as well as a conformational change of the PEDOT chains in the PEDOT:PSS polymer films. AFM images showed the presence of entangled nanofibrous structures which enhance the conducting pathway. Thin layers of PEDOT:PSS treated with HFA and HFIPA as HTL provide an explanation for the interesting device characteristics of the PSC. The additive process has allowed the lowering of the series resistance of the obtained devices and this indicates that an optimized hole buffer layer can improve the device performance of OSCs. The PCE of the device with pristine PEDOT:PSS buffer layer was 2.72% together with low J_{sc} and FF. We obtained a high PCE of 4.10% and 3.98% in the PSC with a 4 vol. % HFA and 6 vol. % HFIPA treated PEDOT:PSS layer, respectively.

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