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Optimization of Ethylene Glycol Doped PEDOT:PSS Transparent Electrodes for Flexible Organic Solar Cells by Drop-coating Method

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 Electronic Supplementary Information

Abstract Fabrication of flexible transparent electrodes (FTEs) is one of the core technologies in the field of flexible electronics. Among multiple choices of FTEs, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonic acid) (PEDOT:PSS) has shown its promising application in roll-to-roll manufacturing. A simple yet effective method for substantially boosting the conductivity of these conducting polymer films without causing large-domain aggregations is by adding ethylene glycol (EG) as dopant. Herein, we investigated in detail the effects of the secondary solvent of ethylene glycol (EG) on the optical and electrical characteristics of PEDOT:PSS films. The modified PEDOT:PSS FTEs were deposited using drop-coating techniques as it had greater compatibility for large-area samples than the conventional spin-coating method did. The 6% EG-doped PEDOT:PSS FTE via drop-coating method achieved a high figure of merit (FoM) value of 47.24 and the devices fabricated using the optimal PEDOT:PSS FTE yielded a high power conversion efficiency (PCE) of 8.89%, mostly attributed to the modified PEDOT:PSS films that had excellent optical and electrical characteristics with low surface roughness. These results suggested that EG-doping could effectively boost the conductivity of PEDOT:PSS films and that the modified PEDOT:PSS FTE is suitable for roll-to-roll manufacturing in the future.

Keywords PEDOT:PSS; Doping; Conductivity; Flexible transparent electrodes; Organic solar cells

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INTRODUCTION

To date, numerous studies have been directed towards flexible electronics as it possesses grand advantages of wearable, portable, light-weight, and bendable properties.^[1–3] Due to these exceptional features, flexible electronics have remarkable potential for large-scale production via jet-printing and roll-to-roll manufacturing.^[4–6] One of the core technologies to be considered, if such large-scale next-generation flexible electronics could be realized, is the development of flexible transparent electrode (FTE). Typically, indium tin oxide (ITO) electrodes are used as the anodes in most organic electronics such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic thin-film transistors (OTFTs), etc.,^[7–10] mostly because of the high optical transmittance and electrical conductivity. However, ITO films are rather brittle and fragile, which indicate that they have a high

probability of cracking during flexing. Moreover, the film productions are conducted through high-temperature sputtering that gives rise to high fabrication cost. The high cost of ITO is further added by the fact that indium is rare and expensive.^[11,12] All these facts limit the applications of ITO as FTE in cost-effective and large-area flexible electronics.

In recent years, numerous efforts have been devoted to developing high-performance electrodes as ITO alternatives for FTEs application, which include conducting polymers (CPs),^[13–16] carbon-based materials,^[17–19] metal grids,^[20,21] metal nanowires,^[22–24] and many other. Compared to other ITO alternatives, CPs have the advantages of low cost, solution processability, satisfactory flexibility, etc. As a classic CP, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (see chemical structure in Fig. S1, in electronic supplementary information, ESI) is deemed as a promising FTE due to its high transparency, good flexibility, high work function (≈ 5.0 eV), excellent thermal stability,^[25] etc. However, intrinsic PEDOT:PSS films suffer from a low conductivity because the ambiguous phase segregation and the excessive components of insulating PSS in PEDOT:PSS matrix.

To enhance the electrical conductivity of the typical

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PEDOT:PSS films, several methods have been employed, for instance, doping the PEDOT:PSS aqueous solutions with secondary solvents of ethylene glycol (EG),^[26] dimethyl sulfoxide (DMSO),^[27] glycerol,^[28] and methanol,^[13] or using other dopants (e.g., ionic liquids, zwitterions, and salts).^[29–31] Among them, EG doping is considered as a simple and effective method for substantially boosting the conductivity of the CP films without causing large-domain aggregations. Nevertheless, typical spin-coating methods are unsuitable to make large-area and uniform FTE films on plastic substrates. Herein, we used EG-doping as a modification approach to produce PEDOT:PSS FTE film and adopted a drop-coating method to fabricate those FTEs. This method is feasibly confirmed by our previous work.^[32]

In this study, we investigated the effects of the secondary solvents of ethylene glycol (EG) on the optical and electrical characteristics of PEDOT:PSS films in detail. By doping PEDOT:PSS aqueous solutions with different concentrations of EG followed by drop-coating processing, the optimal PEDOT:PSS films with a large area ($\approx 5.0 \text{ cm}^2$) exhibited a favorable phase segregated morphology as well as excellent optical and electrical characteristics. The flexible devices with 6% EG-doped PEDOT:PSS films based on PBDB-T and IT-M were fabricated and achieved an efficiency as high as 8.89%.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (PET) plastic substrates (180 μm -thick) and ITO glass with a sheet resistance of 15 Ω/sq were purchased from Polytron Technologies Inc. of Southern China and Wuhu Changxin Technology Co., Ltd., respectively. PEDOT:PSS aqueous solution (Clevios PH1000) and

PEDOT:PSS (Clevios P VP AI 4083) were purchased from Heraeus, Germany. PBDB-T and IT-M were purchased from Solarmer Materials Inc.

Preparation of PEDOT:PSS FTEs

Flexible ITO substrates were etched by hydrochloric acid (HCl) solution. The residual ITO was defined as the anode. The substrates were then cleaned in an ultrasonic bath using deionized water, acetone, and isopropanol, each for 20 min, respectively. The PEDOT:PSS aqueous solution (Clevios PH1000) with different amounts of EG doping (1%, 3%, 5%, 6%, 7%, or 9%) and with 1 vol% Zonyl FS300 was filtered through a syringe filter (0.45 μm pore size), and then drop-coated on a pre-cleaned PET substrate. The films (Fig. 1) were then annealed on a hot plate at 100 $^\circ\text{C}$ for 30 min in ambient atmosphere.

Fabrication of Flexible OSC Devices

The flexible organic solar cell (Fig. 1) was fabricated with the anode consisting of PEDOT:PSS and different concentrations of EG *via* drop-coating method on PET substrates. Firstly, PEDOT:PSS (Clevios P VP AI 4083), as hole transporting layer, was spin-coated on ITO or PEDOT:PSS FTEs films at 3000 or 2500 $\text{r}\cdot\text{min}^{-1}$ for 60 s, followed by annealing at 130 $^\circ\text{C}$ for 15 min or 100 $^\circ\text{C}$ for 30 min. The active layer of PBDB-T (poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b'*]dithiophene))-*alt*-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-*c*:4',5'-*c'*]dithiophene-4,8-dione))] and IT-M (3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-*d*:2',3'-*d'*]-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene) was spin-coated on the top of PEDOT:PSS buffer layer at 2150 $\text{r}\cdot\text{min}^{-1}$ for 60 s using a solution of PBDB-T:IT-M (10 mg:10 mg) in 1 mL of chlorobenzene, followed by annealing at 120 $^\circ\text{C}$ for 10 min.

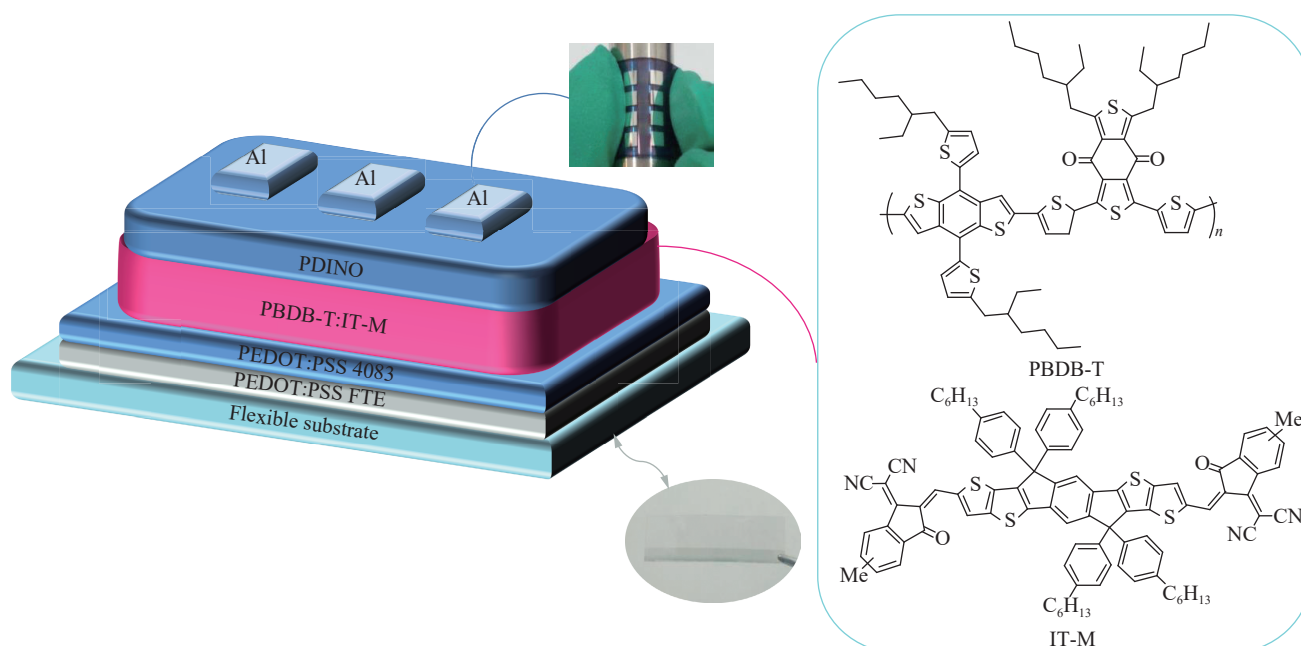


Fig. 1 Schematic diagram of the flexible OSC device. Insert figures are the physical presentation of PEDOT:PSS/PET substrate and device, as well as the molecular structures of IT-M and PBDB-T, respectively.

Subsequently, perylene diimide functionalized with amino N-oxide (PDINO) dissolved in methanol ($1.5 \text{ mg} \cdot \text{mL}^{-1}$) as electron-transporting layer was spin-coated onto the active layer. Finally, Al (100 nm) electrode was deposited through a shadow mask to define the effective area of the devices.

Characterization

Optical transmission spectra of PEDOT:PSS films on glass slides were measured using a Perkin-Elmer Lambda 950 spectrophotometer. Morphology of the PEDOT:PSS films was observed using atomic force microscopy (AFM, VEECO Dimension 3100 V). An ohmmeter was used to measure the sheet resistance (R_{sq}) of PEDOT:PSS films. X-ray photoelectron spectroscopy (XPS) (Kratosanalytical, Manchester, U.K.) was used to analyze the compositions and chemical states of PEDOT:PSS films.

Current density-voltage (J - V) characteristics of the device were measured in Ar atmosphere without encapsulation, using the simulated solar light ($100 \text{ mW} \cdot \text{cm}^{-2}$; AM 1.5 G) provided by a Newport-Oriels Sol3A 450 W solar simulator. Film thickness was measured using a surface profiler (Dektak 150).

RESULTS AND DISCUSSION

Effects of EG Content on the Performance of PEDOT:PSS Films

In order to investigate the effect of EG solution concentration on the morphology of PEDOT:PSS films, AFM images of different PEDOT:PSS films are presented in Fig. 2. In Fig. 2(a), the pristine PEDOT:PSS film shows a typical phase image in which the bright (positive) regions refer to conducting rigid PEDOT-rich domains, while the dark (negative) regions refer to soft PSS-rich areas.^[33] The pristine PEDOT:PSS film showed physically disconnected PEDOT-rich grains that were wrapped by PSS chains, which resulted in a weak phase separation and thus led to low conductivity of the film. As shown in Figs. 2(b)–2(d), by doping different contents of EG, the favorable phase separation of PEDOT:PSS films was achieved, which created a continuous con-

ductive pathway in the films. However, when the concentration of EG was increased to 9%, the PEDOT:PSS film (Fig. 2d) portrayed a rise in electrical conductivity while the film had a relatively high root-mean-square (RMS) roughness of 2.57 nm. It was found that the PEDOT:PSS film doped with 6% EG (as shown in Fig. 2c) displayed good uniformity with a low RMS of 1.83 nm, giving an intimate connection of the PEDOT-rich grains and optimized phase separation, which contributed to high conductivity.

Fig. 3(a) shows the measured transmission spectra of all PEDOT:PSS films doped with different contents of EG. All PEDOT:PSS films exhibited high transmittance in the visible-light regions at λ of 400–800 nm. In particular, the transmittance of the PEDOT:PSS film with 6% EG-doping was as high as 96% at $\lambda = 550 \text{ nm}$, which was higher than those of any other EG-doped films partly due to its favorable phase separation. With the increase of EG-doping concentration over 6%, the transmittance of PEDOT:PSS films decreased significantly, which was possibly due to the inferior film quality. Transparent conductive electrodes are often evaluated by the figure of merit (FoM). The value of FoM is influenced by film transmittance and sheet resistance. The relationship between the three parameters is governed by the following equation:^[34]

$$\text{FoM} = \frac{\sigma_{\text{dc}}}{\sigma_{\text{op}}(\lambda)} = \frac{188.5\Omega}{R_{\text{sq}}(T(\lambda)^{-1/2} - 1)} \quad (1)$$

where $T(\lambda)$ is the transmittance at $\lambda = 550 \text{ nm}$, σ_{op} and σ_{dc} are the optical conductivity and direct current conductivity, respectively. Higher values of FoM suggest better optical and electrical properties. Typically, a value over 35 indicates commercial viability. Fig. 3(b) plots the FoM values of the EG-treated PEDOT:PSS films. Table 1 summarizes the transmittance at 550 nm, sheet resistance (R_{sq}), and FoM values of the films. From the results, the PEDOT:PSS film doped with 6% EG exhibited the highest value of 47.24, which was much higher than those of the films with lower concentration EG-doping (e.g. the FoM value of 1% EG-doped films was as low as 10.75). This is mainly because of its high transmittance and high conductivity. Notably, when EG-doping concentration was over 3%, the modified PEDOT:PSS films showed a considerably low sheet resistance and high transmittance value, leading to a high FoM of over 40. This scenario suggested that these conducting polymers could be a potential ITO alternative for photo-electronic applications.

In order to investigate the mechanical stability of modified PEDOT:PSS films, we carried out bending (bending radius $\approx 5.6 \text{ mm}$) and folding tests for these FTEs. Figs. 3(c) and 3(d) plot $R_{\text{sq}}/R_{\text{sq}}(0)$ of PEDOT:PSS films with or without EG as a function of bending cycles. After 1000 cycles of bending, R_{sq} of the PEDOT:PSS films with 6% EG increased by 4.9% compared to the initial value. Meanwhile, the pristine PEDOT:PSS films showed a 15.8% increment under the same conditions. In terms of its foldability, 6% EG-doped PEDOT:PSS film exhibited a growth ratio of 11.5%, whereas pristine PEDOT:PSS films escalated by 28.0% after 1000 cycles of folding tests. From these bending and folding analysis, it could be concluded that the EG-doping treatment

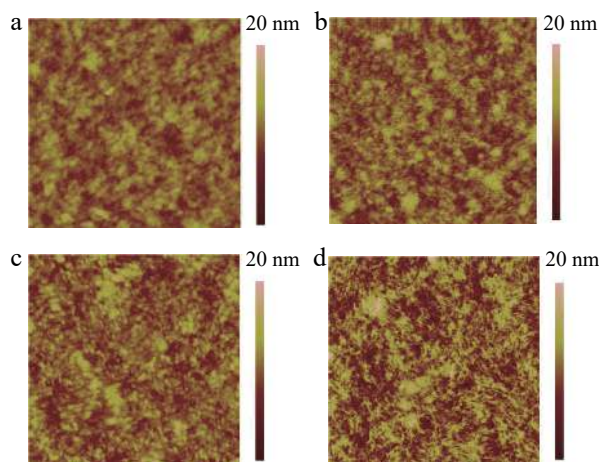


Fig. 2 Topography images of PEDOT:PSS electrodes (a) without EG dopant, (b) with 1% EG dopant, (c) with 6% EG dopant, and (d) with 9% EG dopant. All the samples were obtained through tapping-mode AFM at a scale of $2 \mu\text{m} \times 2 \mu\text{m}$.

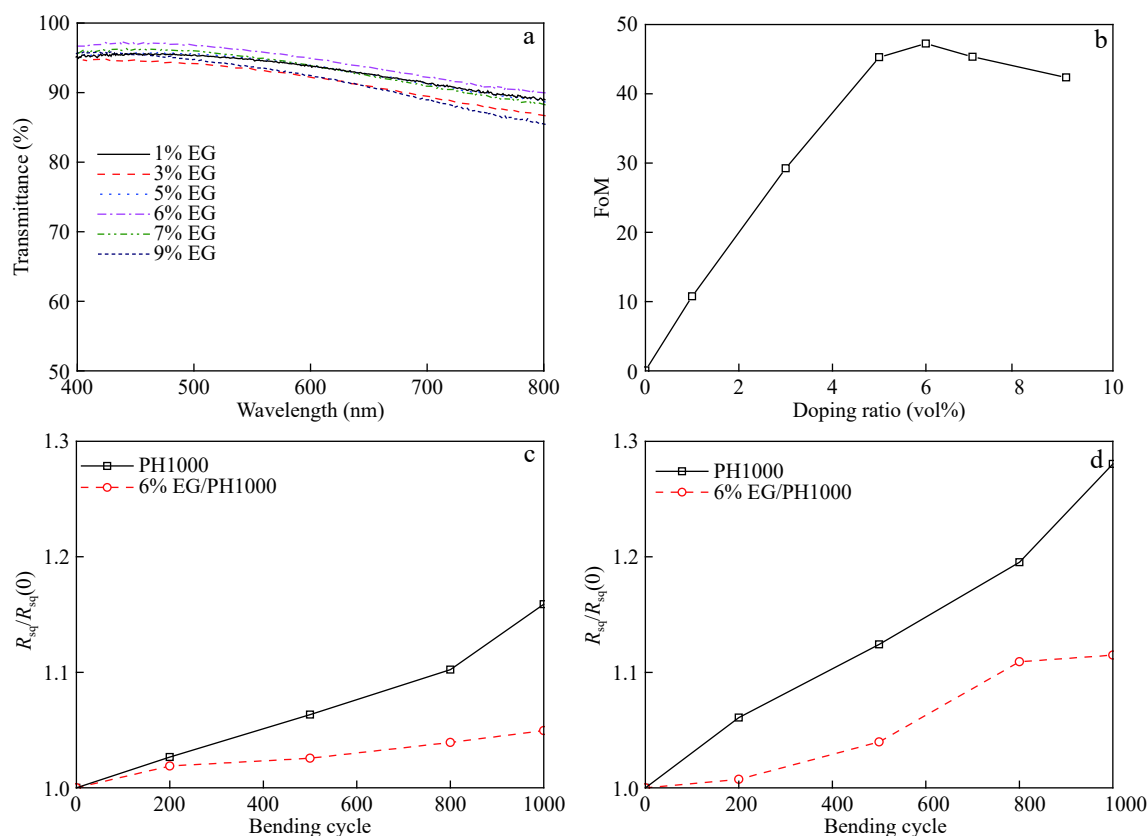


Fig. 3 (a) Transmittance spectra of various flexible PEDOT:PSS FTEs; (b) FoM values of different PEDOT:PSS FTEs; (c) $R_{sq}/R_{sq}(0)$ of PEDOT:PSS film without EG and with 6% EG as a function of bending cycles (bending radius ≈ 5.6 mm); (d) $R_{sq}/R_{sq}(0)$ of PEDOT:PSS film without EG and with 6% EG as a function of bending cycles (completely folded)

Table 1 Transmittance, sheet resistance, and FoM value of PEDOT:PSS films

Film	Transmittance at 550 nm (%)	R_{sq} (Ω/sq)	FoM
PH1000 + 1% EG	94.8	470	10.75
PH1000 + 3% EG	93.4	187	29.25
PH1000 + 5% EG	94.9	147	45.27
PH1000 + 6% EG	96.0	195	47.24
PH1000 + 7% EG	94.3	140	45.34
PH1000 + 9% EG	93.7	135	42.36

could improve the mechanical stability of PEDOT:PSS film for FTE applications.

XPS was conducted to observe the S atom contents and elemental states in PEDOT:PSS films. Fig. 4 shows the XPS spectra of sulfur 2p (S2p) for the pristine PEDOT:PSS film and 6% EG-doped PEDOT:PSS film. The S2p peaks at the lower binding energy of 164.2 and 165.3 eV corresponded to the sulfur atom of PEDOT. Meanwhile, the S2p peaks at the higher binding energy near 169 eV were originated from the sulfur atom in PSS. Based on the measured area ratio of PEDOT to PSS, the S2p intensity ratio was increased after doped with EG as the relative intensity of $-\text{S}-$ (PEDOT)/ $-\text{S}-$ (PSS) was increased from 0.528 to 0.709. This indicated that EG-doping is able to largely remove the insulating PSS/PSSH chains from the PEDOT:PSS matrix, thereby leading to the high conductivity of the modified PEDOT:PSS films.

Effects of EG Content on the Photovoltaic Performance of OSCs

In light of the high transmittance and electrical conductivity of the modified PEDOT:PSS films, these conducting polymer films showed great potentials to replace the commercial ITO products as transparent conductive electrodes in organic electronics. Hence, flexible organic solar cells were fabricated using these modified FTEs drop-coated on PET substrates. Table 2 illustrates the performance parameters of the flexible ITO-free PBDB-T:IT-M bulk-heterojunction solar cells. The data for the devices based on ITO electrodes are also included for comparison.

The device structure of PET/PEDOT:PSS FTEs/PEDOT:PSS (Clevios P VP Al 4083)/PBDB-T:IT-M/PDINO/Al is shown in Fig. 1. Fig. 5(a) illustrates the $J-V$ curves of the flexible organic solar cells with different transparent electrodes under $100 \text{ mW}\cdot\text{cm}^{-2}$ AM 1.5 G irradiation. The device with 1% EG-doped PEDOT:PSS anode exhibited a poor performance with V_{oc} of 0.90 V, J_{sc} of $12.67 \text{ mA}\cdot\text{cm}^{-2}$, and FF of 52.91%. As a result, the power conversion efficiency (PCE) was 6.05% due to the high series resistance of the devices. When the EG-doping ratio reached 6%, the device displayed an optimal performance with V_{oc} of 0.918 V, J_{sc} of $14.63 \text{ mA}\cdot\text{cm}^{-2}$, FF of 66.12%, and PCE of 8.89%, which was comparable to 9.36% of the reference devices by spin-coating method. The obvious enhancement of device performance was attributed to a significant improvement in the

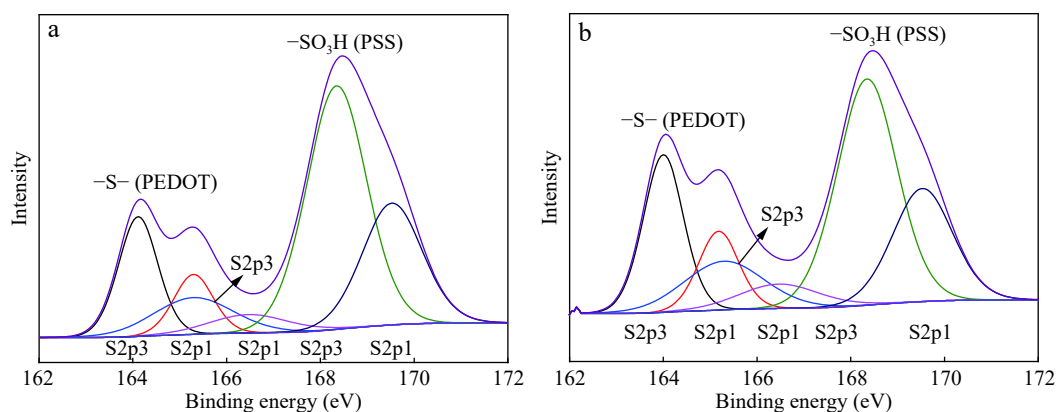


Fig. 4 XPS S2p spectra of PEDOT-PSS films (a) without EG and (b) with 6% EG

Table 2 Device performance of PBDB-T:IT-M solar cells with different electrodes *

Device	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	PCE (Ave.) (%)	R_{sq} (Ω·cm ²)
ITO (110 nm) (Glass)	0.932	16.30	72.40	11.01 (10.88)	3.90
PH1000 + 1% EG (PET)	0.902	12.66	52.91	6.05 (5.90)	21.34
PH1000 + 3% EG (PET)	0.909	13.13	63.17	7.54 (7.43)	10.84
PH1000 + 5% EG (PET)	0.919	14.08	68.00	8.80 (8.69)	6.11
PH1000 + 6% EG (PET)	0.918	14.63	66.12	8.89 (8.75)	6.26
PH1000 + 7% EG (PET)	0.911	14.57	65.39	8.68 (8.49)	7.31
PH1000 + 9% EG (PET)	0.911	14.20	65.70	8.51 (8.43)	7.59
ITO (185 nm) (PET)	0.885	13.88	64.72	7.90 (7.77)	6.22

* Data for the average values of PCE were obtained from 10 devices; The effective area of all devices was 0.04 cm².

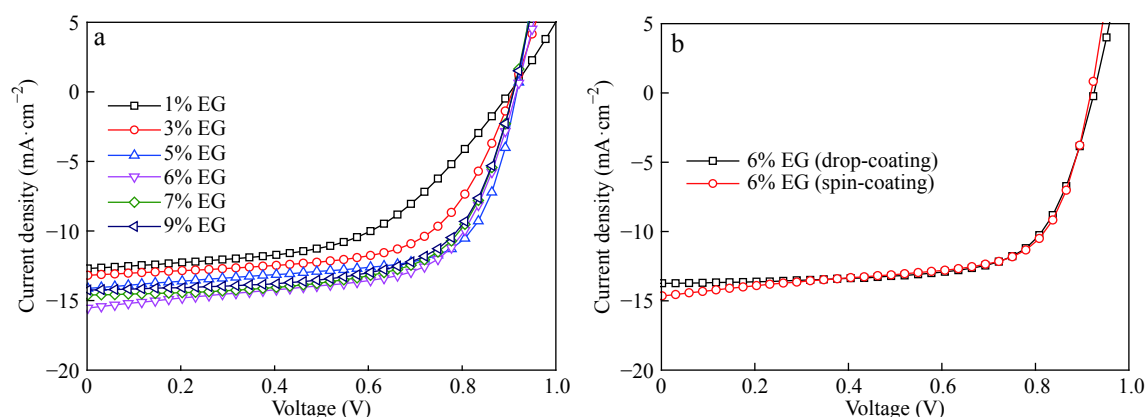


Fig. 5 J - V curves of the flexible devices using PEDOT:PSS FTEs (a) with different EG contents by drop-coating method and (b) with 6% EG by drop- or spin-coating method

conductivity of doped PEDOT:PSS films, which had been confirmed by higher J_{sc} and FF. However, when the EG content was further increased to 7% and 9%, PCE of the devices decreased to 8.68% and 8.51%, respectively. These were most probably due to the poor morphology of those modified PEDOT:PSS FTEs. Fig. 5(b) shows the J - V curves of devices with 6% EG-doped PEDOT:PSS film fabricated by spin-coating and drop-coating technique, respectively. Based on the J - V curve results, the photovoltaic performance of devices with drop-coating method was comparable to that of the devices with PEDOT:PSS films prepared through spin-coating. We also fabricated the device using PEDOT:PSS FTE with 6% EG and an effective area of 1.0 cm², where the optimized performance of 4.61% was obtained (Fig. S3, in ESI), indicating that EG-doped PEDOT:PSS FTE is practicable for printing and roll-to-roll manufacturing.

Hole transport and collection are both affected by the choice of buffer layer coatings and FTEs. Hole mobility (μ_h) was calculated using the space charge limited current (SCLC) method by fitting the Theott-Gurney square law:[35]

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \quad (2)$$

where ε_r is the dielectric constant of the BHJ systems, ε_0 is the dielectric constant of free space, and L is the thickness of active layer in the device. The hole-only devices with the configuration of PEDOT:PSS FTE/PEDOT:PSS (4083)/PBDB-T:IT-M/MoO₃/Ag were fabricated to study device's hole mobility. Fig. S4 (in ESI) illustrates the J - V characteristics of the hole-only devices. The calculated values of μ_{hs} were 4.20×10^{-5} , 6.63×10^{-5} , 1.81×10^{-4} , 1.95×10^{-4} , 1.14×10^{-4} , and 9.88×10^{-5} cm²·V⁻¹·s⁻¹ for device with

different EG-doped FTEs (1%, 3%, 5%, 6%, 7%, and 9%), respectively. The device with 6% EG-doped FTE exhibited the highest hole mobility that facilitated the charge-carrier transport and collection, giving higher efficiency of the flexible OSC, which was consistent with the result of J - V curves for flexible device.

For further comparison, the device with commercial ITO (≈ 180 nm)-coated PET substrate as anode was also fabricated. Compared to the flexible ITO-free OSC devices, the reference device exhibited a lower PCE of 7.90% with V_{oc} of 0.885 V, J_{sc} of $13.88 \text{ mA}\cdot\text{cm}^{-2}$, and FF of 64.72% (as shown in Fig. S2, in ESI). This might be attributed to the rough surface and low-quality sputtering of ITO/PET.^[36] Fig. 6 shows the average normalized efficiencies of these flexible devices with commercial ITO (≈ 180 nm)-coated PET substrate and optimized PEDOT:PSS films as anode. The reference device displayed a sharp drop in PCE in the bending test at $r = 5.6$ mm and just maintained about half the initial PCE due to the intrinsic fragility of the sputtered ITO films. Compared to the reference device, the device with the optimized PEDOT:PSS film maintained over 80% of the initial PCE values after 1000 cycles of bending, which demonstrated an excellent mechanical property of our ITO-free flexible OSCs using the EG-doped PEDOT:PSS electrodes.

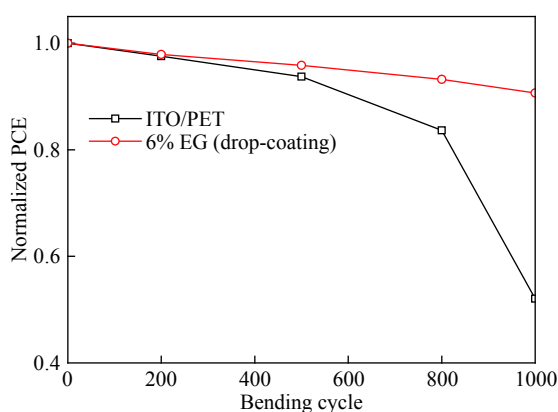


Fig. 6 Decays of normalized PCE of the reference devices with ITO (≈ 180 nm)/PET and our flexible ITO-free devices using the PEDOT:PSS FTEs doped with 6% EG as a function of bending cycle

CONCLUSIONS

In conclusion, the effects of EG-doping on the optical and electrical characteristics of PEDOT:PSS FTEs were investigated. The morphology and chemical states of EG-modified PEDOT:PSS films were analyzed as well to support the change in optical and electrical characteristics upon EG-doping. It was found that 6% EG-doping resulted in the best performance of PEDOT:PSS FTE with high optical and electrical characteristics ($T = 96\%$ at $\lambda = 550$ nm, FoM = 47.24). This is mainly due to the removal of insulating PSS/PSSH chains from PEDOT:PSS matrix, which thereby caused a more favorable phase separation with continuous conductive pathway. Flexible OSCs based on this FTE was

fabricated *via* drop-coating method, where we obtained an excellent photovoltaic performance with V_{oc} of 0.918 V, J_{sc} of $14.63 \text{ mA}\cdot\text{cm}^{-2}$, FF of 66.12%, and PCE of 8.89%. This device with EG-doped PEDOT:PSS FTE showed a superior performance than that of the device with ITO electrode on a flexible PET substrate. Interestingly, devices fabricated *via* drop-coating method still showed a comparable performance to those fabricated *via* spin-coating method. Overall, these results implied that the 6% EG-doping method could effectively modify PEDOT:PSS film towards a more desirable use as FTEs and that drop-coating method could be practically utilized to deposit this FTE for future large-scale roll-to-roll manufacturing.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2257-5>.

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