Effect of anode interfacial modification on the performance of laminated flexible ITO-free organic solar cells

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Funding information
Fundamental Research Funds for the Central Universities, Grant/Award Number: 21618308; Key Projects of Joint Fund of Basic and Applied Basic Research Fund of Guangdong Province, Grant/Award Number: 2019B1515120073, 2019B010132004 and 2019B090921002; NSFC Project, Grant/Award Number: 61774077 and 61804065; Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials Open Projects Fund, Grant/Award Number: KFVE20200006; Open Fund of the State Key Laboratory of Luminescent Materials and Devices (South China University of Technology), Grant/Award Number: 2019-skllmd-05

Abstract
Lamination technique is one of the most promising and effective approaches to produce flexible organic solar cells (OSCs), with the combination of high throughput and simultaneous encapsulation. In this study, flexible ITO-free OSCs were successfully fabricated by lamination technique under the optimized temperature and pressure. It is found that the introduction of hole interface layer of PEDOT:MoO3 helps to improve both the film hydrophobicity and the carrier extraction. A high efficiency improvement of about 30% is obtained in the interface-modified laminating flexible ITO-free OSCs compared to the conventional laminated device. This work illustrates that anode interface engineering has a significant effect on the improvement of performance of roll-to-roll laminated and self-encapsulated OSCs.

Keywords
flexible, interface layer, lamination, organic solar cells, self-encapsulation
1 | INTRODUCTION

Organic solar cells (OSCs) with excellent advantages of flexibility and light weight as well as low cost have attracted intense research interest for their potential applications in wearable energy generators and building-integrated photovoltaics.1,2 Toward the commercial manufacturing process, there are many techniques that can realize the high-speed and large-area production of OSCs, such as slot-die coating,3,4 doctor blading,5,6 spraying coating,7,8 Among them, the multilayer laminating approach is considered one of the most effective methods due to its simplicity and effectiveness.9-12 At the very beginning, lamination technology was adopted for device encapsulation either on the backside or on both sides of the device by using barrier foils with UV-curable epoxy resin or heat-sensitive adhesives.13,14 Then, it was applied to transfer printing the special solid film, which is hindered by poor surface wetting or dissolution of underlying layers, to partially fabricated devices using a stamp.15,16 Recently, in most cases it was used to produce devices in large volumes with high throughput allowing the simultaneous encapsulation, viz. the pressure and elevated temperature are applied in the lamination process to eliminate the tension-induced wrinkles and the trapped air bubbles at the melted interface.10,12,17 For example, Olle Inganäs et al12 reported laminated semitransparent flexible OSCs with nonadhesive additives, which is a great progress in the development of laminated OSCs. Since the soft-contact lamination technique is a versatile scalable technique, it has been successfully utilized in many applications such as supercapacitor,18 electrochromic devices,19 thermistor,20 LED,21 and sensor,22 showing great attracting prospects for future device manufacturing.

At present, there are still many remaining unsolved problems in laminated OSCs. The most obvious one is that the power conversion efficiency (PCE) lagged far behind that of the devices prepared via layer-by-layer deposition.12 As we know, highly conductive PH1000 is a promising candidate to replace ITO as the transparent electrode in flexible OSCs due to good flexibility and high transparency as well as solution processability.10 However, electron trap density will increase significantly upon ambient exposure for the inverted device structure,17 resulting in low short-circuit current density ($J_{SC}$) and fill factor (FF). Therefore, the approach to further improve the performance of the PH1000-based laminating OSCs should be investigated in conjunction with revealing the corresponding enhancement mechanism.

In this work, we reported a high PCE improvement of 30% in the laminating flexible ITO-free OSCs with the self-packaging structure of polyethylene terephthalate (PET)/Ag/ZnO/thieno[3,4-b]thiophene/benzodithiophene (PTB7):[6,6]-phenyl-C71-butyric acid methyl ester (PC71BM)/PTB7:PC71BM/PEDOT:MoO3/PH1000/PET compared to the conventional device without inserting PEDOT:MoO3 hole interfacial layer (HIL). PEDOT:MoO3 had been inserted between the ITO and active layer as a promising hole transport layer.23 The contacting interface between PTB7:PC71BM and PTB7:PC71BM is exactly the soft-contact lamination interface. It is found that the laminating pressure and temperature has a big effect on the compactness of the interface. More importantly, the insertion of an ultrathin anode-modified PEDOT:MoO3 HIL helps to improve not only the film hydrophobicity but also the carrier extraction, resulting in improved device performance. This work illustrates that under optimum lamination parameters, anode interface engineering is very important and necessary for laminated flexible ITO-free OSCs.

2 | RESULTS AND DISCUSSION

PTB7 and PC71BM are used as the electron donor and acceptor in this work (Figure 1A). The device is made of two parts, referred as anode side and the cathode side. The structure of the cathode side is PET/Ag/ZnO/PTB7:PC71BM, while the structure of the anode side is PET/PH1000/with or without PEDOT:MoO3/PTB7:PC71BM. Figure 1B illustrates the lamination process.

For obtaining the compact interface formed by laminating the anode side and the cathode side, the pressure (3.2-4.4 MPa) and temperature (100-140°C) were adjusted in turn. Lower pressure than 3 MPa results in inadequate adhesion, and higher pressure than 4.4 MPa can easily make the device shorted. The $J-V$ curves for the conventional OSCs without HIL are shown in Figure 2A,B. It can be seen that the optimized corresponding conditions of pressure and temperature are determined to be 3.8 MPa and 120°C with the highest PCE of 2.43%. The concrete device parameters are shown in Table 1.

As the previous reported result has demonstrated that the PH1000 anode has a serious current loss,17 therefore an ultrathin HIL of PEDOT:MoO3 is inserted between the PH1000 and PTB7:PC71BM for anode interface modification.24 The effect of the thickness of PEDOT:MoO3 on device performance was studied under the optimum conditions of pressure and temperature (Figure 3A and Table 1). It can be seen that the performance of the laminated OSCs is greatly improved after inserting different thicknesses of PEDOT:MoO3 HIL. When the PEDOT:MoO3 HIL is 10 nm, the best device performance is obtained. Moreover, it is found that once HIL is employed, the contact angle of the nonpolar n-hexadecane droplets is sharply decreased from 51.7 to 29.6° (inset in Figure 3A). The increased hydrophobicity is very beneficial to the deposition of the back active layer.25 Thus, more intimate interface contact in the HIL-modified laminating OSC should be achieved compared to the one without HIL. For better revelation of the
effect of HIL on device performance. Figure 3B presents the $J$-$V$ curves of the laminating OSCs with and without HIL (10 nm) under the AM 1.5 G illumination (1000 W/m²). The device without HIL exhibits a low short-circuit current density of 7.66 mA/cm², an open-circuit voltage ($V_{OC}$) of 0.75 V, an FF of 42.4% and a low PCE of 2.43%. After inserting 10 nm HIL, the $J_{SC}$, FF and PCE of the device are greatly increased to be 9.12 mA/cm², 46.1% and 3.16%, respectively. The increased $J_{SC}$ and FF with the similar $V_{OC}$ for the OSC with HIL result in a high PCE improvement of 30% compared to the one without HIL.

EQE of the device without HIL shows low response in the range of 300-500 nm, while the devices with HTL exhibit increased response in the corresponding range (Figure 3C). Then, we examined the absorption spectra of PET/ZnO/PTB7:PC$_{71}$BM/PEDOT:MoO$_3$ (with or without)/PH1000/PET. The samples were fabricated with the same processing condition as the devices. The addition of PEDOT:MoO$_3$ did not contribute to absorption in 300-500 nm (Figure 3D). Therefore, the EQE difference is possibly due to the difference in the charge transport/extraction efficiency. In our case, one of the possible reasons is that the photocurrent extraction capability is different according to active layer position. Then, the variation of internal quantum efficiency (IQE) of the device depending on the position could cause the EQE's shape to change. Jonas Bergqvist et al also found that the active layer in contact with PH1000 has a lower IQE than the laminated device with HIL, which is consistent with our results. This observation validates our conclusion that PEDOT:MoO$_3$ optimizes charge extraction for laminated devices. The calculated $J_{SC}$ values based on EQE spectra are in good agreement with the measured $J_{SC}$ ones.
In order to shed light on the steady and transient charge collection characteristics of the well-performed device, the electrical measurements were conducted in the laminating devices with and without HIL. Figure 4A, B show the light-intensity-dependent $J_{SC}$ and $V_{OC}$ curves of the devices with and without HIL, respectively. The relationship between $J_{SC}$ and light intensity ($L$) follows: $J_{SC} \propto L^\alpha$. Theoretically, $\alpha$ is equal to 1 if all dissociated free carriers are swept out from device without charge recombination. The higher $\alpha$ value about 0.99 for the laminating device with HIL than the one without HIL indicates the bimolecular recombination is negligible by inserting an ultrathin PEDOT:MoO$_3$ HIL. The semi-logarithmic plot of $V_{OC}$ as a function of light intensity shows a linear relationship with a slope of $n \cdot \kappa_B T / q$, where $n$ is the ideality factor, $\kappa_B$ is the Boltzmann constant, $T$ is the temperature and $q$ is the unit charge. In our case, $n$ is found out to be 1.48 for the HIL-modified laminating device while the high value of 1.59 for the conventional laminating device without HIL. The difference on the ideality factor between devices with and without HIL can be correlated to the degree of trap mediated recombination that has been observed in OSCs. Likely, the introduction of HIL helps to form an interface between PH1000 and the active layer with less traps. To probe the charge generation and decay dynamics, TPC and TPV measurements were carried out with the results shown in Figure 4C, D. It can be seen that the device with HIL shows a higher charge carrier density than that of the device without HIL (Figure 4C), agreeing well with the device $J_{SC}$ difference. The charge extraction time ($\tau_{ex}$) can be extracted by exponentially fitting the TPC curves. The HIL-modified laminating device shows a faster $\tau_{ex}$ of...
0.49 µs than 0.85 µs of the conventional laminating device without HIL. Furthermore, a longer carrier lifetime (τ) of 11.11 µs is obtained for the HIL-modified laminating device than 7.86 µs for the conventional laminating device without HIL (Figure 4D). The fact that fast τex and long τ for the HIL-modified OSC compared to the device without HIL implies that carrier extraction efficiencies are improved after inserting an ultrathin PEDOT:MoO3 layer, which is consistent with the observations in light-intensity-dependent JSC and VOC measurements (Figure 4A,B).

IS was performed to investigate the effect of the HIL on the electrical resistances of each layer in device. According to the laminating device structure, an equivalent circuit is defined, as shown in Figure 5A.26 R0 refers to the electrode resistance including Ag, ZnO, and PH1000; R1 and C1 refer to the resistance and capacitance from the interfaces; R2 and C2 refer to the resistance and capacitance from the BHJ layer. The experimental impedance data of two types of the laminating devices are presented in the Cole-Cole plot. When inserting the 10 nm thick HIL, all three resistance parameters of R0, R1,
and R2 decrease significantly from 125, 4950 and 7900 Ω to 65, 1600 and 3458 Ω, respectively, compared to the conventional device. The reduced resistances are correlated with the increase of JSC or the efficient charge extraction in the HIL-modified laminating OSC. In addition, the charge carrier mobility is improved after inserting an ultrathin PEDOT:MoO3 HIL. The extracted current, measured by photo-CELIV,30,31 is changed as a function of time delay after photo excitation (Figure 5B). The equivalent carrier mobilities are calculated to be $3.45 \times 10^{-5}$ and $4.14 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ for the devices without and with PEDOT:MoO3 HIL, respectively. The higher carrier transport of the HIL-modified laminating device than that of the conventional device without HIL is consistent with the reduction of trap mediated recombination and fast $\tau_{ex}$ as well as long $\tau$ (Figure 4).

3 | CONCLUSION

In this work, the self-encapsulated laminating flexible ITO-free OSCs are effectively optimized by introducing an anode HIL of PEDOT:MoO3. The HIL not only promotes the film forming property of active layer, but also reduces the trap mediated recombination, leading to the efficient transport and extraction of charge carriers with the low device resistance. As a result, a high PCE improvement of 30% is successfully achieved for the HIL-modified device compared to the conventional device. This work provides a promising way in the realization of high-performance plastic photovoltaic modules with the ease of encapsulation.

4 | EXPERIMENTAL SECTION

The PTB7 donor and PC$_{71}$BM acceptor were purchased from Derthon and Solenne, respectively. The active solution of PTB7:PC$_{71}$BM (1:1.5 wt.%) was dissolved in ternary solvent mixtures (chlorobenzene (CB):1-chloronaphthalene (CN):1,8-diiodooctane (DIO) = 94:3:3 by volume) with a concentration of 25 mg/mL. The high conductive PEDOT:PSS (PH1000, Clevios) was doped with 5% dimethyl sulfoxide (DMSO) and 0.5% surfactant (FS-30) for achieving high conductivity. The HIL of PEDOT:MoO3 and electron transport layer (ETL) of ZnO nanoparticle solutions were purchased from Avantama. The PEDOT:MoO3 solution was diluted with alcohol at a volume ratio of 1:3. The flexible PET substrate was purchased from Kaivo. The overall fabrication process was conducted in ambient conditions.

The PET substrate was ultrasonically cleaned in sequence with acetone, alkaline lotion, deionized water, and isopropanol. For the cathode side, a 100 nm thick Ag film was thermally evaporated on the UV plasma-treated PET under a pressure of $3 \times 10^{-4}$ Pa. Then, a 40 nm thick ZnO was spin-coated onto the top of Ag as the ETL. A 50 nm thick PTB7:PC$_{71}$BM active layer was spin-coated on top of the ZnO ETL. For the anode side, PH1000 was spin-coated onto another PET substrate with a thickness of 100 nm. Then, the PET/PH1000 film was annealed at 80°C for 60 seconds to remove the residual water. A 50 nm thick PTB7:PC$_{71}$BM active layer was spin-coated onto the PH1000 with or without inserting a 10 nm thick HIL of PEDOT:MoO3. Finally, the two sides were roll-to-roll laminated together into laminated devices with the structures of PET/Ag/ZnO/PTB7:PC$_{71}$BM/PTB7:PC$_{71}$BM/with or without HIL/PH1000/PET in air condition by using a roll laminator under high temperature and high pressure (Figure 1B). The device area is 14 mm$^2$, determined by a patterned mask.

The current density-voltage ($J$–$V$) characteristics were measured by a Keithley 2400 source meter under the AM 1.5 G illumination of 100 mW/cm$^2$ (Sun 2000, Abet). The external quantum efficiency (EQE) spectrum was measured by a QE-R test system (Enli. Technology Company). The light intensity dependence and spectroscopy (IS) as well as photo-induced charge extraction by linearly increasing voltage (photo-CELIV) measurements were performed using an all-in-one electrical and optical characterization platform of Paios system from FLUXiM AG. The transient photovoltage (TPV) and photocurrent (TPC) measurements were carried out under the open-circuit condition and a short-circuit condition, respectively, with a light bias nearly 100 mW/cm$^2$ and the same intensity laser pulse. The film thickness was measured by using a surface profiler (XP-2). The cross-section image of the laminated device was investigated by SEM (ULTRA55, Zeiss). Transmittance spectra were recorded using a Shimadzu UV-2600 UV-visible spectrophotometer. Contact angles were measured using a drop shape analyzer DSA100 instrument with the nonpolar solvent n-hexadecane as the testing liquid.

ACKNOWLEDGMENTS

The authors are grateful to the NSFC Project (61774077 & 61804065), Key Projects of Joint Fund of Basic and Applied Basic Research Fund of Guangdong Province, Research and Development Program in Key Areas of Guangdong Province (2019B1515120073, 2019B090921002 & 2019B010132004), the Open Fund of the State Key Laboratory of Luminescent Materials and Devices (South China University of Technology) (2019-skllmd-05), Guangzhou Key laboratory of Vacuum Coating Technologies and New Energy Materials Open Projects Fund (KFFE20200006) and the Fundamental Research Funds for the Central Universities for financial support (21618308).

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**How to cite this article:** Lin Z, Guan W, Cai W, et al. Effect of anode interfacial modification on the performance of laminated flexible ITO-free organic solar cells. *Energy Sci Eng*. 2021;9:502–508. [https://doi.org/10.1002/ese3.870](https://doi.org/10.1002/ese3.870)