Feature article

Toward high performance inverted polymer solar cells

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1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) that can be fabricated by solution processing techniques are under intense investigation in both academic institutions and industrial companies because of their potential to enable mass production of flexible and cost-effective alternative to silicon-based solar cells. A combination of novel polymer development, nanoscale morphology control and processing optimization has led to over 8% of power conversion efficiencies (PCEs) for BHJ PSCs with a conventional device structure. Attempts to develop PSCs with an inverted device structure as required for achieving high PCEs and good stability have, however, met with limited success. Here, we report that (1) solution-processed zinc oxide (ZnO) thin film as an electron extraction layer for inverted polymer solar cells. Operated at room temperature, no obviously degradation was observed from the PSCs with ZnO layer after continuously illuminating the devices for 4 h. However, a significantly degradation was observed from the PSCs without ZnO buffer layer after illuminating the devices only for 1 h. Furthermore, PSCs with ZnO buffer layer also show very good shelf stability; only 10% degradation observed in PCEs after 6 months; (2) a high PCE of 8.4% under AM 1.5G irradiation was achieved for BHJ PSCs with an inverted device structure. This high efficiency was obtained through interfacial engineering of solution-processed electron extraction layer, ZnO, leading to facilitate electron transport and suppress bimolecular recombination. All these results provided an important progress for solution-processed PSCs, and demonstrated that PSCs with an inverted device structure are comparable with PSCs with the conventional device structure.

Abstract

Bulk heterojunction (BHJ) polymer solar cells (PSCs) that can be fabricated by solution processing techniques are under intense investigation in both academic institutions and industrial companies because of their potential to enable mass production of flexible and cost-effective alternative to silicon-based solar cells. A combination of novel polymer development, nanoscale morphology control and processing optimization has led to over 8% of power conversion efficiencies (PCEs) for BHJ PSCs with a conventional device structure. Attempts to develop PSCs with an inverted device structure as required for achieving high PCEs and good stability have, however, met with limited success. Here, we report that (1) solution-processed zinc oxide (ZnO) thin film as an electron extraction layer for inverted polymer solar cells. Operated at room temperature, no obviously degradation was observed from the PSCs with ZnO layer after continuously illuminating the devices for 4 h. However, a significantly degradation was observed from the PSCs without ZnO buffer layer after illuminating the devices only for 1 h. Furthermore, PSCs with ZnO buffer layer also show very good shelf stability; only 10% degradation observed in PCEs after 6 months; (2) a high PCE of 8.4% under AM 1.5G irradiation was achieved for BHJ PSCs with an inverted device structure. This high efficiency was obtained through interfacial engineering of solution-processed electron extraction layer, ZnO, leading to facilitate electron transport and suppress bimolecular recombination. All these results provided an important progress for solution-processed PSCs, and demonstrated that PSCs with an inverted device structure are comparable with PSCs with the conventional device structure.

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Moreover, ZnO thin film can be easily deposited from corresponding solution via various solution processes following thermal annealing treatment. All these features make ZnO an ideal material as a buffer layer for PSCs with an inverted device structure [18, 39]. Here we summarize the strategies we have developed to approach high performance inverted polymer solar cells. In section II, we report solution-processed ZnO thin film as an electron extraction layer for inverted polymer solar cells. Operated at room temperature, no obviously degradation was observed from the PSCs with ZnO layer after continuously illuminating the devices for 4 h. However, a significantly degradation was observed from the PSCs without ZnO buffer layer after illuminating the devices only for 1 h. Furthermore, PSCs with ZnO buffer layer also show very good shelf stability; only 10% degradation observed in PCEs after 6 months. In section III, we report high performance BHJ PSCs with an inverted structure. By casting a thin conjugated polyelectrolyte layer onto the solution-processed ZnO thin film, the interface between ZnO electron extraction layer and BHJ active layer is re-engineered, as a result, a record PCE of 8.4% under AM 1.5 G irradiation is achieved for BHJ PSCs with the inverted structure. All these results demonstrate that electron extraction layer plays an important role in enhancement of PSCs performance with an inverted device structure.

2. Solution-processed ZnO thin film as an electron extraction layer for inverted polymer solar cells

2.1. ZnO thin film

2.1.1. Preparation

ZnO thin films coated on top of ITO glass were obtained from solution by sol–gel method. Before coating ZnO thin films, the ITO glass substrates were cleaned by ultrasonic treatment in acetone, detergent, deionized water and isopropyl alcohol sequentially. ZnO precursor was prepared by dissolving zinc acetate (ZnAc: Sigma–Aldrich) and ethanolamine in the solution of 2-methoxyethanol with a concentration of 0.5 mol L–1. Approximately 40 nm ZnO thin films were obtained by spin-casting above solution following annealed at 200 °C for 10 min. Then the thin films were continuously annealed in air at 200 °C for 1 h. Note that the ZnO precursor was not heated gradually from room temperature to the temperature being treated [37]. ZnO thin films were then ultrasonicated in acetone and isopropyl alcohol, and subsequently dried in an oven for fabrication PSCs.

2.1.2. Characterization

2.1.2.1. Absorption spectra. The absorption spectrum of ZnO thin film was measured by an HP 8453 UV–vis spectrophotometer. Fig. 1 shows the absorption spectrum of ZnO thin film thermally annealed at 200 °C. ZnO thin films are transparency from 400 nm to 1000 nm. This indicated that ZnO thin films only block the light with wavelength shorter than 400 nm.

2.1.2.2. X-ray diffraction patterns. The ZnO thin films for x-ray diffraction (XRD) patterns were obtained by spin-coating the ZnO precursor on top of the SiO2 substrate following thermal annealing at temperature of 200 °C and 500 °C, respectively. Fig. 2 shows the XRD patterns of ZnO thin films annealed at 200 °C and 500 °C for 1 h. No diffraction peaks were observed from this pattern. To confirm the structure of the ZnO thin film, the XRD patterns of ZnO thin films annealed at 500 °C for 1 h was also shown in Fig. 2. Three peaks located at 31.7°, 34.4°, and 36.3° were observed. These indicated that the ZnO thin film annealed at 500 °C formed a polycrystalline structure.
\[ \text{hv} - E_v = E_{\text{vbe}} - E_{\text{cutoff}} \]  

where \( \text{hv} \) is the energy of photoelectron, \( E_v \) is the position of valence band of sample, \( E_{\text{vbe}} \) is valence-band edge, and \( E_{\text{cutoff}} \) is inelastic cutoff. The energy position of valence-band relative to vacuum energy is \(-7.61 \text{ eV}\). The absorption edge of ZnO was located at 390 nm, which was observed from its absorption spectrum. The optical bandgap of ZnO is \( 3.19 \text{ eV} \). Therefore, the conduction band of ZnO is \( 4.42 \text{ eV} \).

2.1.2.4. AFM images. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument) to observe the surface morphology of ZnO. Fig. 5 shows the surface roughness of ZnO thin film thermally annealed at 200 °C. The surface roughness of ZnO thin films is 1.32 nm. Such smooth surface allows high quality polymer films to be fabricated onto the top of ZnO thin films.

2.1.2.5. TEM images. The bright field (BF) transmission electron microscopy (TEM) images of the ZnO thin film annealed at 200 °C is shown in Fig. 6. Three diffraction rings were observed which indicates that the ZnO thin film forms a polycrystalline structure even though the annealing temperature is as low as at 200 °C. The BF image shows that the ZnO thin film is quite uniform. Many nanoscale fibrils with a diameter of \( \sim 10 \text{ nm} \) were observed. No visible pinhole was observed in this BF TEM image. This indicated that the ZnO thin film was quite dense.

2.1.2.6. Electron mobility. In order to investigate the electron transporting properties of ZnO thin film, we have fabricated ZnO filed-effect transistors (FETs). Fig. 7a shows the FETs device structure. The current–voltage characteristics of ZnO FETs are shown in Fig. 7b. Electron mobility, \( \mu \), was extracted from the linear regime of transfer characteristics, using

\[
\mu = \left( \frac{2L}{WC_i} \right) \left[ \frac{I_{ds}}{(V_g - V_{th})} \right]^2
\]

where \( W \) and \( L \) are the channel width and length, respectively. \( C_i \) is the silicon dioxide gate capacitance (which is \( 1.0 \times 10^{-9} \text{ F cm}^{-2} \) for a gate oxide thickness of 300 nm). \( V_{th} \) is threshold voltage, \( I_{ds} \), \( V_{ds} \), and \( V_g \) are source-drain current, source-drain voltage and gate voltage, respectively. From the \( I_{ds}-V_g \) curves, the electron mobility in the saturation regime was found to be 4.46 \( \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \).
for the ZnO thin film annealed at 200 °C. This indicated that the electron transporting property of this ZnO composite layer is not as good as that of bulk ZnO layer. However, such electron mobility is compatible to the electron mobility from most of organic materials used as the electron transporting layer in organic electronics [40]. More important, the low-temperature treatment can be potentially used for making PSCs on plastic substrates because it requires a low-temperature treatment [41]. Therefore, we have chosen ZnO thin films with thermally annealed at 200 °C as a buffer layer for fabrication inverted PSCs.

2.2. Inverted BHJ PSCs

2.2.1. BHJ composite

PSiF-DBT and PCBM are poly[(2,7-dioctylsilfluorene)-2,7-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5-diyl]] [42] and [6,6]-phenyl C 61-butyric acid methyl ester, respectively. The molecular structures of PSiF-DBT and PCBM are shown in Scheme 1. PSiF-DBT with PCBM together with a ratio of 1.0:2.0 (by weight) was dissolved into o-xylene with a concentration of 20 mg mL⁻¹; continuously stirred above solution at room temperature for 24 h for fabrication polymer solar cells.

2.2.2. Inverted PSCs fabrication

PSCs with an inverted device structure were fabricated by following steps. Approximately 100 nm PSiF-DBT:PCBM layer was deposited by spin-coating PSiF-DBT:PCBM solution onto top of ZnO thin films. The pre-devices were pumped down in the vacuum (≈ 2 × 10⁻⁴ Pa). A ≈ 4 nm thickness of molybdenum oxide (MoO₃) was thermally deposited onto the top of PSiF-DBT:PCBM layer at an evaporation rate of 0.1 Ås⁻¹. Ultimately, a ≈ 50 nm Au film was deposited on the top of MoO₃ layer through shade mask. The active layer of the device was 0.16 cm². All the devices were encapsulated with resin then exposed to ultraviolet light for 3 min and thermally heated at 60 °C for 30 min before characterization.

2.2.3. Inverted PSCs characterization

PCEs were measured under an illumination of 80 m W cm⁻² with an AM 1.5 solar simulator (Oriel model 91192). For PSCs with ZnO buffer layer, the light intensity was 72 m W cm⁻² since UV light was blocked by ZnO thin layer (see Fig. 1). The current-density-voltage (J–V) characteristics were measured with a Keithley 240 source-measure unit.

2.2.4. Performance of inverted PSCs

The device architectures under our investigation are: ITO/ZnO/PSiF-DBT:PCBM/MoO₃/Au (Device A) and ITO/PSiF-DBT:PCBM/MoO₃/Au (Device B). Scheme 2 depicts the energy diagrams of ITO, ZnO, PSiF-DBT, PCBM, and Au. The current density-voltage (J–V) characteristics of PSCs were shown in Fig. 8. PSCs with ZnO buffer layer show J_sc of 5.03 mA cm⁻², V_oc of 0.90 V and FF of 0.60, resulting in PCEs of 3.8%; PSCs without ZnO buffer layer, only show J_sc of 4.23 mA cm⁻², V_oc of 0.81 V, FF of 0.39, resulting in PCEs of 1.67%. The PCEs observed from PSCs with ZnO buffer layer is more than two times larger than that observed from PSCs without ZnO buffer layer. Therefore, ZnO buffer layer plays an important role in enhancement of PCEs for inverted PSCs.

Table 1 summarized the performance characteristics of inverted PSCs with and without ZnO buffer layer. It was found that inverted PSCs have significant improvements in FF (from 0.39 to 0.60) and V_oc (from 0.81 V to 0.90 V) by introduction of ZnO buffer layer. This indicated that ZnO efficiently suppresses the leakage current at the organic/ITO interface, originated from smooth ZnO surface (see Fig. 5).

Considering the devices without ZnO, both PSiF-DBT and PCBM are directly in contact with ITO. It is possible for hole to transfer from PSiF-DBT to ITO, thereby increasing the leakage currents. As shown in Scheme 2, the HOMO (highest occupied molecular orbital) of ZnO (−7.6 eV) is lower than the HOMO of PSiF-DBT (−5.4 eV), showing that ZnO can block the reverse hole flow from PSiF-DBT to ITO. Thereby, ZnO can effectively prevent the leakage current at the organic/ITO interface. In addition, the LUMO (lowest
unoccupied molecular orbital) of ZnO (−4.4 eV) is close to the LUMO of PCBM, revealing that ZnO will help collecting electrons.

Based upon the equivalent circuit of and the current density versus voltage characteristics of photovoltaic cells, solar cells must have small series resistance, $R_S$, and larger shunt resistance, $R_{SH}$, for obtaining high short-circuit current, $J_{sc}$ [43,44]. As shown in Table 1, the increase in $J_{sc}$ from Device B to Device A, implies significant decrease in $R_S$, and increase in $R_{SH}$. From numerical analysis [43–45], we found that $R_S$ decreased from $R_S = 56 \ \Omega \ \text{cm}^2$ to $R_S = 13 \ \Omega \ \text{cm}^2$; $R_{SH}$ increased from $R_{SH} = 600 \ \Omega \ \text{cm}^2$ to $R_{SH} = 1400 \ \Omega \ \text{cm}^2$ from Device B to Device A, respectively.

Fig. 9 shows the current density vs. voltage characteristics of inverted PSCs measured without illumination. It is also known that the high $R_{SH}$ indicates less leakage current across the solar cells [46]. The current density at reversed biases from Device A is approximately two orders of magnitudes smaller than that from Device B. The low leakage current and elevated $R_{SH}$ are strong evidence showing that the ZnO layer can serve as both an electron-transporting layer and a hole-blocking layer to effectively prevent the leakage currents, resulting in the dramatic improvement in PCEs.

We have further investigated both operation and shelf stabilities of inverted PSCs with and without ZnO buffer layer. The operational stabilities of inverted PSCs with and without ZnO buffer layer were shown in Fig. 10a. Inverted PSCs with ZnO buffer layer did not show obviously degradations in $J_{sc}$, $V_{oc}$ and FF after continuously illuminating the devices for 4 h. However, for the inverted PSCs without ZnO buffer layer, significant degradations in $V_{oc}$, FF and $J_{sc}$ were observed after continuously illuminating the devices only for 1 h. All these results indicate that inverted PSCs by using ZnO as the buffer layer have a good operational stability, and the inverted PSCs without ZnO buffer layer are unstable under the illumination condition.

A good operational stability of inverted PSCs with ZnO buffer layer is probably originated from the ZnO block the UV light (see Fig. 1) resulting in a negligible UV light induced photodegradation of organic materials. A significant degradation observed from inverted PSCs without ZnO buffer layer is attributed to the UV light induced photodegradation because UV light directly shining the organic layer through ITO electrode.

Figs. 10b and c show the shelf lifetimes of inverted PSCs with ZnO buffer layer. No obviously degradations in $J_{sc}$, $V_{oc}$, FF and PCEs are observed after the devices stored in glove-box for 47 days. Only 5% degradation in PCEs was observed from the devices after 47 days as compared with the fresh devices. We further continually
investigated the shelf stability of inverted PSCs. Fig. 10d shows the shelf stability of devices after 160 days. Only 10% degradation in PCEs was observed from the devices after 160 days as compared with the fresh devices. All these results demonstrated that inverted PSCs by using ZnO as a buffer layer have very good shelf stability.

2.3. Conclusion

Solution-processed ZnO thin film as a buffer layer for inverted PSCs has been demonstrated. PCEs of 3.8% was observed from inverted PSCs with a device structure of ITO/ZnO/PSiF-DBT:PCBM/MoO3/Au. Without ZnO layer, PSCs only show PCEs of 1.67%, which is less than half value observed from inverted PSCs with ZnO buffer layer. We also found that inverted PSCs with ZnO buffer layer have both good operation and shelf stabilities. Operated at room temperature, there is no obviously degradation observed from the inverted PSCs with ZnO layer after continuously illuminating the devices for 4 h. There is only 10% degradation observed in PCEs after 160 days. All these results demonstrate that inverted PSCs by using ZnO as the buffer layer have high PCEs and good stabilities.

3. Interfacial engineering via conjugated polyelectrolyte for high performance inverted polymer solar cells

3.1. Preparation of ZnO thin film and ZnO/PFN-Br thin film

ZnO thin film was prepared by the method described above. The ZnO/PFN-Br thin film was prepared by deposition ~5 nm thick of PFN-Br from PFN-Br water-alcohol (1:1 by volume) solution on the top of ZnO thin film.

Table 1

<table>
<thead>
<tr>
<th>Device</th>
<th>Active layer</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCEs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PSiF-DBT:PCBM</td>
<td>5.03</td>
<td>0.90</td>
<td>0.60</td>
<td>3.80</td>
</tr>
<tr>
<td>B</td>
<td>PSiF-DBT:PCBM</td>
<td>4.23</td>
<td>0.81</td>
<td>0.39</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Device A: ITO/ZnO/PSiF-DBT:PCBM/MoO3/Au.
Device B: ITO/PSiF-DBT:PCBM/MoO3/Au.

3.2. Characterization of ZnO and ZnO/PFN-Br thin films

3.2.1. Absorption spectra

the absorption spectra of solid thin film, ZnO and ZnO/PFN-Br were measured by an HP 8453 UV–vis spectrophotometer. Fig. 11 show the absorption spectrum of ZnO and ZnO/PFN-Br thin films. The ZnO/PFN-Br thin film only absorbs UV light and is transparency from 400 nm to 1000 nm which is similar to the absorption spectrum of ZnO thin film. This indicated that the visible light is allowed to pass through ZnO/PFN-Br thin layer into BHJ composite active layer. Therefore, the photodegradation of polymer active layer is reduced; as a result, a good stability from inverted PSCs is anticipated [19].

3.2.2. Energy levels

In order to verify the effect of PFN-Br on ZnO thin layer, UPS was carried out to study the energy levels of ZnO thin layer and ZnO/PFN-Br thin layer. The UPS measurements were carried out in a Thermo Fisher Scientific Ultra Spectrometer (ESCALAB 250) using He I (21.22 eV) discharge lamp. A bias of −5.0 V was applied to the samples for separation of the sample and the secondary edge for the analyzer.

The UPS measurements were carried out to study the energy levels of ZnO thin layer and ZnO/PFN-Br indicated that the LUMO energy levels of ZnO was 0.26 eV energy difference between ZnO/PFN-Br thin layer and ZnO thin layer. This difference indicated that a dipole was formed [48,49] between PFN-Br layer and ZnO layer.

The highest occupied molecular orbital (HOMO) energy levels for ZnO and ZnO/PFN-Br thin layers were shown in Fig. 12b. The HOMO energies are determined by

\[
E_{\text{HOMO}} = \frac{h\nu}{c} - \left( \frac{E_{\text{HOMO} \text{cutoff}} - E_{\text{cutoff}}}{r_{\text{ZnO/PFN-Br}}} \right)_{\text{onset}}^{48}
\]

where \( h\nu \) is the incident photon energy, \( h\nu = 21.22 \text{ eV} \); \( E_{\text{cutoff}} \) is defined as the lowest kinetic energy of the measured electrons which can be obtained from Fig. 12a; \( E_{\text{HOMO} \text{cutoff}} \). The HOMO energy onset, generally referred to the high kinetic energy onset. From Fig. 12b, the \( E_{\text{HOMO} \text{onset}} \) of ZnO was 22.4 eV, and the \( E_{\text{HOMO} \text{onset}} \) of ZnO/PFN-Br was 22.9 eV. Thus, the HOMO energies for ZnO and PFN-Br/ZnO are ~7.65 eV and ~6.89 eV, respectively. Based on these HOMO energies and optical gaps obtained from the onset of absorption spectra (Fig. 11), the estimated LUMO energy levels were ~4.46 eV for ZnO thin layer and ~4.08 eV for ZnO/PFN-Br thin layer, respectively. The difference in LUMO energy levels between ZnO and ZnO/PFN-Br indicated the LUMO energy levels of ZnO was tuned by PFN-Br thin layer. More importantly, this energy difference implied that the band alignment in the inverted PSCs with and without PFN-Br interfacial layer is different [50–52]. Therefore, a large Voc from the inverted PSCs with PFN-Br interfacial layer is anticipated.

3.2.3. Electronic conductivities

the electronic conductivities of ZnO and ZnO/PFN-Br thin films were conducted on Bruker Dimension ICON system with Peak Force Tapping Tunneling AFM (PFTUNA) module. The probe was the PFTUNA probe with spring constant of ~0.5 N/m with 20 nm Pt/Ir coating on both front and back side. The spring was constantly measured using thermal tune method. The peak currents were measured with bias voltage applied to the sample. The ramp rate of 0.4 Hz and the force setpoint of ~60 N were for both thin films.
PFTUNA module was used to measure the peak currents with bias voltage applied to the ZnO and ZnO/PFN-Br thin layers [16]. The peak currents were shown in Fig. 13a and b. The maximum peak current observed from pristine ZnO thin layer is about 5 pA within a 7 μm zoom, however, the maximum peak current observed from ZnO/PFN-Br thin layer is about 25 pA within a 4 μm zoom. These qualitative studies indicated that the electronic conductivity of ZnO/PFN-Br thin layer is much higher than that of ZnO thin layer. This high electronic conductivity will facilitate electron transport from BHJ composite to corresponding electrode [35,53]. Therefore, higher $J_{sc}$ was observed from the inverted PSCs with PFN-Br interfacial layer rather than that without PFN-Br interfacial layer.

3.3. BHJ composite

The BHJ materials under this study are a D–A conjugated polymer, PBDT-DTNT [54] and PC$_{71}$BM. The molecular structures of PBDT-DTNT, PC$_{71}$BM and PFN-Br [55] are shown in Scheme 3. The synthesis and characterization of PBDT-DTNT and PFN-Br in details were reported elsewhere [54,55]. The PC$_{71}$BM was purchased from One-Material Inc. and used without further purification. Fig. 14 shows the absorption spectra of PBDT-DTNT, PC$_{71}$BM, BHJ composite of PBDT-DTNT:PC$_{71}$BM and ZnO/PFN-Br thin films. The bandgap of PBDT-DTNT is 1.48 eV, which is closer to the ideal bandgap for PSCs donor materials [56]. This is the reason that we selected PBDT-DTNT rather than PsF-DBT as the electron donor for approaching high performance inverted PSCs. PBDT-DTNT has absorption from 400 nm to 800 nm PC$_{71}$BM has absorption from 400 nm to 700 nm. The absorption spectrum of PBDT-DTNT:PC$_{71}$BM BHJ composite is the superposition of PBDT-DTNT and PC$_{71}$BM which implies that both PBDT-DTNT and PC$_{71}$BM will contribute photocurrent for PSCs fabricated by PBDT-DTNT:PC$_{71}$BM.

3.4. Inverted PSCs fabrication

Two types of inverted PSCs were fabricated on ITO-coated glass substrates. For the inverted PSCs with ZnO thin layer as an electron extraction layer, an approximately 40 nm ZnO thin film was deposited on the top of ITO glass using the method described in the
Section 2.1.1. For the inverted PSCs with ZnO/PFN-Br as an electron extraction layer, an approximately 5 nm thick PFN-Br layer was casted on the top of ~40 nm thick ZnO which was coated on the ITO glass. Photoactive layer PBDT-DTNT:PC71BM BHJ composite with an approximately 250 nm thick was then spin coated on either ZnO or ZnO/PFN-Br layer from 1,2-dichlorobenzene solution composed of PBDT-DTNT and PC71BM (PBDT-DTNT:PC71BM = 1:1.5, by weight). The photoactive layer was then thermally annealed at 110 °C for 10 min. After that, about 8 nm molybdenum oxide (MoO3) was thermally deposited on the top of PBDT-DTNT:PC71BM layer with an evaporation rate of 0.1 Å s⁻¹ under the vacuum of ~3 × 10⁻⁴ Pa. Ultimately, about 60 nm Ag film was deposited on the top of MoO3 layer through a shade mask. The device area was 0.16 cm². All the devices were encapsulated with resin and exposed to ultraviolet light for 5 min in the glove-box with nitrogen atmosphere before testing in air. Scheme 4 shows the device architecture of inverted polymer solar cells with PFN-Br interfacial layer.

3.5. Characterization of inverted PSCs

The current densities–voltage (J–V) characteristics were measured using a Keithley 2400 Source Measure Unit. The solar cells were characterized using a Newport Air Mass 1.5 Global (AM 1.5G) full spectrum solar simulator with an irradiation intensity of 95 m W cm⁻².

Fig. 12. UPS spectra of (a) the inelastic cutoff region and (b) the HOMO region of ZnO and ZnO/PFN-Br thin layers.

Fig. 13. The peak currents of ZnO (a) and ZnO/PFN-Br (b) surfaces measured by the peak force tapping tunneling AFM (PFTUNA).

Scheme 3. The molecular structures of PFN-Br, PBDT-DTNT, and PC71BM.
The Incident photon-to-current efficiency (IPCE) spectra of inverted PSCs were measured by Solar Cell Quantum Efficiency Measurement System (QEX10) from PV Measurements, Inc.

3.6. Performance of inverted PSCs

Photovoltaic characteristics were investigated for the inverted PSCs with device architectures of ITO/ZnO/PBDT-DTNT:PC71BM/MoO3/Ag and ITO/ZnO/PFN-Br/PBDT-DTNT:PC71BM/MoO3/Ag. J–V characteristics were shown in Fig. 15. Without PFN-Br interfacial layer, inverted PSCs showed a short-circuit current (Jsc) of 15.2 mA cm$^{-2}$, an open-circuit voltage (Voc) of 0.69 V, a fill factor (FF) of 55% and a corresponding PCE of 6.1%. After depositing a thin conjugated polyelectrolyte layer, PFN-Br, onto ZnO thin film to reengineering the interface between ZnO electron extraction layer and PBDT-DTNT:PC71BM, inverted PSCs showed a Jsc of 17.4 mA cm$^{-2}$, a Voc of 0.75 V, an FF of 61% and a corresponding PCE of 8.4%. Over 37% enhanced PCEs were observed. Device performance optimization involved over 500 identical devices fabricated from over 100 independently PBDT-DTNT:PC71BM, and ZnO/PFN-Br thin films; PCEs between 8.2% and 8.6% were obtained. The average device yields PCE of 8.4%, with Jsc of 17.4 mA cm$^{-2}$ (the calculated Jsc value from IPCE spectrum was 17.2 mA cm$^{-2}$). This highest efficiency reported from inverted BHJ PSCs was recorded by the colleagues from the South China University of Technology [57].

The Voc of 0.75 V from the inverted PSCs with PFN-Br interfacial layer was larger than Voc of 0.69 V from the inverted PSCs without PFN-Br interfacial layer. This difference was due to the different band alignments in the inverted PSCs with and without PFN-Br interfacial layer. This observation is in good agreement with the band alignment showed in Scheme 5. Scheme 5 shows the band alignment of BHJ composite and two buffer layers with the work function of ITO and Ag electrodes.

![Scheme 4. Architecture of inverted polymer solar cells with PFN-Br interfacial layer.](image4.png)

![Scheme 5. Energy-level diagram showing the HOMO and LUMO energies of each component material and the work functions of ITO cathode and Ag anode.](image5.png)
those without PFN-Br interfacial layer [53]. Toward the end, we have modeled the J–V characteristics of PSCs with an equivalent circuit, consisting of single diode with series resistance ($R_s$) and shunt resistance ($R_{sh}$). The addition of a parallel photocurrent source, $J_{ph}$, leads to the well-known equation [53],

$$J = J_0 \left[ \exp\left(\frac{q(V - R_s A J)}{n k T} \right) - 1 \right] + \frac{V - R_s A J}{R_{sh} A} - J_{ph} (V)$$

(4)

where $q$ is the electron charge; $k$ is Boltzmann’s constant; $T$ is the temperature; and $J_{ph}$ is the voltage–dependent photocurrent produced by the cell. By rearranging Eqn. 3 under open circuit condition ($J = 0$) and $J_{ph} = J_{sc}$, $V_{oc}$ can be described as

$$V_{oc} = \frac{n k T}{q} \ln \left( \frac{J_{sc}}{J_0} \right)$$

(5)

where $J_0$ is reverse dark current density. According to Eqn (5), lower $J_0$, higher $V_{oc}$. Therefore, inverted PSCs with PFN-Br interfacial layer possesses a higher $V_{oc}$ than that PSCs without PFN-Br interfacial layer.

Device performance parameters were summarized in Table 2. The enhanced $J_{sc}$ and FF in the inverted PSCs with PFN-Br interfacial layer implied that $R_s$ in the inverted PSCs with PFN-Br interfacial layer was smaller than that without PFN-Br interfacial layer, and $R_{sh}$ in the inverted PSCs with PFN-Br interfacial layer is larger than that without PFN-Br interfacial layer. In order to confirm this hypothesis, we have calculated $R_s$ and $R_{sh}$ based on the J–V curves shown in Fig. 3a. The $R_s$ for the inverted PSCs with and without PFN-Br interfacial layer are 6.1 $\Omega$ cm$^2$ and 10.3 $\Omega$ cm$^2$, respectively. The $R_{sh}$ for the inverted PSCs with and without PFN-Br interfacial layer are 757.6 $\Omega$ cm$^{-2}$ and 490.2 $\Omega$ cm$^2$, respectively. It is indeed that the $R_s$ in the inverted PSCs with PFN-Br interfacial layer is smaller than that without PFN-Br interfacial layer, and the $R_{sh}$ in the inverted PSCs with PFN-Br interfacial layer is larger than that without PFN-Br interfacial layer.

Table 2 Performance of inverted PSCs with and without PFN-Br.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ mA cm$^{-2}$</th>
<th>FF (%)</th>
<th>$R_s$ $\Omega$ cm$^2$</th>
<th>$R_{sh}$ $\Omega$ cm$^2$</th>
<th>PCE (%)</th>
</tr>
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<tbody>
<tr>
<td>Device A$^a$</td>
<td>0.69</td>
<td>15.2</td>
<td>55</td>
<td>10.3</td>
<td>490.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Device B$^b$</td>
<td>0.75</td>
<td>17.4</td>
<td>61</td>
<td>6.1</td>
<td>757.6</td>
<td>8.4</td>
</tr>
</tbody>
</table>

$^a$ ITO/ZnO/PBDT-DTNT:PC$_{71}$BM/MoO$_3$/Ag,

$^b$ ITO/ZnO/PFN-Br/PBDT-DTNT:PC$_{71}$BM/MoO$_3$/Ag.

Fig. 16. J versus V characteristics of inverted PSCs with the device architectures of ITO/ZnO/active layer/Ag and ITO/ZnO/PFN-Br/active layer/Ag in dark.

In order to confirm the surface morphologies of pristine ZnO and ZnO/PFN-Br thin films, AFM was carried out to further investigation of the influence of PFN-Br interfacial layer on the device performance. Fig. 18a and b compared the surface morphologies of pristine ZnO and ZnO/PFN-Br thin films. With scale of 10 μm × 10 μm, the root mean square (RMS) for ZnO/PFN-Br is 2.335 nm, and RMS for ZnO is 1.375 nm. The rough surface offers a better interaction between PBDT-DTNT:PC$_{71}$BM BHJ composite layer and ZnO electron extraction layer whereas the smooth surface indicated that interfacial adhesion between PBDT-DTNT:PC$_{71}$BM BHJ composite layer and ZnO electron extraction layer was weak [3,62]. Consequently, a better charge transport is expected from a good interfacial adhesion between MoO$_3$ hole extraction layer and PBDT-DTNT:PC$_{71}$BM layer.

3.7 Conclusions

Through a conventional active-layer processing methodology, efficient BHJ PSCs with the inverted device structure based on
PBDT-DTNT:PC71BM composites have been fabricated. Power conversion efficiency of 8.4% under AM 1.5 G illumination was achieved from the inverted PSCs by using a PFN-Br interfacial layer to engineering ZnO electron extraction layer. Without PFN-Br interfacial layer, the inverted PSCs only showed an efficiency of 6.1% under the same condition. The overall enhanced short-circuit current density, open-circuit voltage, fill factor and corresponding high efficiency in the inverted PSCs with a thin conjugated poly-electrolyte interfacial layer, were attributed to the good contact between ZnO electron extraction layer and PBDT-DTNT:PC71BM BHJ active layer, good interface adhesion between the electron extraction layer and PBDT-DTNT:PC71BM BHJ active layer, and enhanced charge transport via suppressed bimolecular recombination. These results provided an important progress for solution-processed PSCs, and demonstrated that PSCs with an inverted device structure are comparable with PSCs with the conventional device structure.

4. Summary

Solution-processed ZnO thin film as an electron extraction layer for inverted PSCs has been demonstrated. Operated at room temperature, no obviously degradation was observed from the PSCs with ZnO layer after continuously illuminating the devices for 4 h. However, a significantly degradation was observed from the PSCs without ZnO buffer layer after illuminating the devices only for 1 h. Furthermore, PSCs with ZnO buffer layer also show very good shelf stability; only 10% degradation observed in PCEs after 6 months. We further optimize the performance of inverted PSCs. A high PCE of 8.4% under AM 1.5G irradiation was achieved for BHJ PSCs with an inverted device structure. This high efficiency was obtained through interfacial engineering of solution-processed electron extraction layer, ZnO, leading to facilitate electron transport and suppress bimolecular recombination. All these results provided an important progress for solution-processed PSCs, and demonstrated that PSCs with an inverted device structure are comparable with PSCs with the conventional device structure.

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References
