Efficient hole collection by introducing ultra-thin UV–ozone treated Au in polymer solar cells

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A B S T R A C T

Efficient hole collection in polymer solar cells (PSCs) has been achieved by introducing an ultra-thin UV–ozone (UVO) treated Au on indium tin oxide (ITO) to substitute poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Through optimizing the Au thickness and the duration of UVO treatment, it is shown that the ITO/Au (1 nm) treated by UVO for 15 s improves the fill factor significantly to 67.2% and power conversion efficiency (PCE) to 3.47%, which is competitive to that of the PEDOT:PSS-based PSCs with PCE of 3.38%. The results of ultraviolet photoemission spectroscopy and the analysis of the current conduction mechanism show that the UVO-treated Au offers favorable band alignment at metal/polymer interface of the anode for efficient hole collection. Meanwhile, the series resistance of the device decreases drastically.

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1. Introduction

Polymer solar cells (PSCs) are the potential candidate for the next generation photovoltaic devices due to their low fabrication costs, flexible processing methods and large area applications [1–3]. In the past few years, many efforts have been made to improve the device performance towards 10% efficiency for commercialization. In fact, an efficiency of over 8% has been achieved [4].

In PSCs, the work function of anode should be larger than that of cathode for generating a built-in electric field with the right direction to benefit charge transport and collection [5]. Indium tin oxide (ITO) has been commonly used as the anode material due to its good optical transparency and robustness [6]. ITO itself has a relative low work function of about 4.4 eV [7], but this value can be modified to different levels to meet various requirements [8]. When ITO is used as anode to facilitate hole collection in the conventional devices, oxygen plasma or UV-ozone (UVO) treatment is often utilized to increase the ITO work function to about 4.7–4.9 eV [9]. Typically, poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), a hole transport material with work function of around 5.1 eV [6,10] is spin-coated on the ITO before fabricating the active layer for further adjusting work function alignment. In inverted cells, materials such as titanium oxide [11], zinc oxide [12], cesium carbonate [13], self-assembled monolayer [14], or low work function metals such as calcium [15,16] are widely used to favor electron collection.

Although PEDOT:PSS has been commonly used for PSCs, it has some negative effects. For instance, the ITO/PEDOT:PSS interface is not stable due to the strong acidic nature of PEDOT:PSS (pH ~1), which leads to the corrosion of ITO and indium diffusion into PEDOT:PSS and even into polymer layer [17–20]. Besides, the variation of morphology and microstructure of PEDOT:PSS causes anisotropic conductivity and electrical inhomogeneity [21,22]. Hence, it is desirable to have other approaches to modify the work function of ITO surface for efficient hole collection.

The presence of an ultra-thin layer of Au at the metal/organic interface at the anode has been shown to benefit the device performance for small molecule solar cells [23,24]. We found such strategy cannot apply to PSCs straightforwardly possibly due to the different material properties and fabrication process. However, when appropriate UVO is employed for further treatment, efficient hole collection can be obtained and device performance is improved significantly. In this paper, such UVO treated Au-based PSCs are demonstrated to have comparable power conversion efficiency to that of PEDOT-based ones. Ultraviolet photoemission spectroscopy (UPS) and current conduction mechanism are analyzed in details to explain the achievements.

2. Experiment

The ITO glass substrates with sheet resistance of 15 ohm per square were cleaned and then treated in a UVO cleaner for 15 min in an ambient atmosphere and room temperature. The substrates...
were then transferred to vacuum chamber immediately for Au evaporation. The ITO/Au (2 nm) samples were then treated by UVO for different durations instead of treatment. Meanwhile, samples with different Au thickness were also prepared and treated by UVO for 15 s. The samples were then transferred into a glove box filled with nitrogen for spin-coating the blend of poly(3-hexylthiophene) (P3HT from Luminescence Technology Corp) and [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM, from Nichem Fine Technology Ltd) with 1:1 weight ratio (20 mg/ml each dissolved in 1,2-dichlorobenzene). Before annealing at 110 °C for 10 min on a hotplate, slow growth was employed following the details stated elsewhere [25]. LiF(1 nm)/Al were finally thermally evaporated as a cathode with a device area of 5.77 mm$^2$ defined by a shadow mask. The conventional PEDOT-based device with the structure of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al was also fabricated for comparison. Current density ($J$)–Voltage ($V$) characteristics were obtained by using a Keithley 2635 sourcemeter and Newport AM 1.5 G solar simulator with 100 mW/cm$^2$ illumination. In addition, four samples including A: ITO only, B: ITO/Au (2 nm) without UVO treatment, C: ITO/Au (2 nm) with UVO treated for 15 s, D: ITO/Au (2 nm) with UVO treated for 20 min were prepared for UPS measurement. All the ITO surfaces were UVO treated for 15 min before Au evaporation for B, C and D. UPS was carried out using a He discharged lamp (He I 21.22 eV, Kratos Analytical). The samples were biased at −10 V to favor the observation of secondary-electron cut-off from the UPS spectra. Transmittance measurement was also performed under a dark ambient environment by using spectroscopic ellipsometry (Woollam).

3. Results and discussion

The performances of PSCs with the device structure of ITO/Au/P3HT:PCBM/LiF/Al are summarized in Tables 1 and 2, and the $J$ ($\text{current density}$)–$V$ ($\text{voltage}$) characteristics of the representative devices are shown in Fig. 1. The device performance improves remarkably by treating the Au with UVO for even only 5 s. The work function of ITO/Au (2 nm) increases to 5.01 eV, similar to the ionization energy of P3HT. The favorable band configuration should contribute to an ohmic contact for efficient hole collection between the anode and polymer and thus leads to better device performance. Extending UVO treatment to 15 s further increases the work function of ITO/Au (2 nm) to 5.25 eV, the work function of the vapor-deposited Au has reduced to (4.5 ± 0.1) eV attributing to “push-back” effect, namely, the compression of the electron-density tail possibly due to the physisorbed (mono)layer when Au surface is exposed to air or in contact with organic films [30,31]. After 15 s UVO treatment, the work function of ITO/Au (2 nm) increases to 5.01 eV, similar to the ionization energy of P3HT. The favorable band configuration should contribute to an ohmic contact for efficient hole collection between the anode and polymer and thus leads to better device performance. Extending UVO time to 20 min increases the work function of Au to 5.1 eV. In order to determine the work function of Au, we investigate the UPS spectra of the ITO/Au samples with different UVO treatments.

The UPS spectra of the four prepared samples are shown in Fig. 2. The secondary-electron cut-off (SECO) and Fermi edge are determined by the crosspoint of the slope of the spectra with the energy axis [27] as illustrated in insets (a) and (b) of Fig. 2. Considering the difficulty of determining the Fermi edge of ITO due to its small density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28]. The obvious shift of SECO indicates variations of density of states around Fermi level, the location is decided by measuring the Fermi edge of samples B, C and D as proposed by Sugiyama et al. [28].

![Fig. 1. J–V characteristics of the representative PSCs.](image)

Table 1
A summary of the performance of PSCs treated with different UVO time. The device structure is ITO/Au (2 nm)/P3HT:PCBM/LiF/Al.

<table>
<thead>
<tr>
<th>UVO duration</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.50</td>
<td>0.41</td>
<td>49.3</td>
<td>1.52</td>
<td>8.6</td>
</tr>
<tr>
<td>5 s</td>
<td>8.00</td>
<td>0.56</td>
<td>63.3</td>
<td>2.84</td>
<td>2.1</td>
</tr>
<tr>
<td>15 s</td>
<td>8.52</td>
<td>0.57</td>
<td>63.9</td>
<td>3.10</td>
<td>2.0</td>
</tr>
<tr>
<td>30 s</td>
<td>7.84</td>
<td>0.56</td>
<td>65.1</td>
<td>2.86</td>
<td>1.9</td>
</tr>
<tr>
<td>1 min</td>
<td>7.91</td>
<td>0.56</td>
<td>64.7</td>
<td>2.87</td>
<td>2.2</td>
</tr>
<tr>
<td>2 min</td>
<td>7.76</td>
<td>0.55</td>
<td>61.9</td>
<td>2.64</td>
<td>2.1</td>
</tr>
<tr>
<td>5 min</td>
<td>7.70</td>
<td>0.55</td>
<td>62.5</td>
<td>2.65</td>
<td>1.8</td>
</tr>
<tr>
<td>8 min</td>
<td>7.65</td>
<td>0.55</td>
<td>61.7</td>
<td>2.60</td>
<td>1.6</td>
</tr>
<tr>
<td>15 min</td>
<td>7.52</td>
<td>0.55</td>
<td>62.3</td>
<td>2.58</td>
<td>1.5</td>
</tr>
<tr>
<td>30 min</td>
<td>7.51</td>
<td>0.55</td>
<td>62.9</td>
<td>2.60</td>
<td>1.8</td>
</tr>
<tr>
<td>60 min</td>
<td>7.62</td>
<td>0.55</td>
<td>61.8</td>
<td>2.59</td>
<td>2.2</td>
</tr>
</tbody>
</table>
function of ITO/Au (2 nm) to 5.25 eV. This causes a larger deviation of work function from the ionization energy of P3HT and thus should result in an unexpected energy barrier at the metal/polymer interface and thereby account for the slight degradation in the device performance.

The increment of Au work function due to UVO treatment may be ascribed to the oxidation of Au and the conversion of physisorbed oxygen to chemisorbed oxygen [32], and also possibly due to removing of the organic contamination [28,33]. Studies show that the chemisorbed oxygen reaches a maximal value and then saturates with the extension of UVO time. However, a long UVO exposure may cause unexpected contaminations at the Au surface, such as C, S, and –OH [33], which may degrade interface properties. Such process probably also accounts for the slight performance degradation of the devices treated with the long UVO time.

The favorable band alignment at the anode arising from proper UVO treatment significantly reduces the energy barrier at the metal/polymer interface and thus increases FF. The series resistance (Rs) is derived from the slope of the illuminated J–V relationship at 1.0 V [34]. After UVO treatment for 5 s, Rs decreases remarkably from 8.6 to 2.1 Ω cm². The Rs remains at about 2.0 Ω cm² when the treatment time is further increased up to 60 min. According to Servaites et al. [35], if Rs is less than 10 Ω cm², the variation of Rs results in neglectable changes in JSC. In addition, neglectable transmittance change is observed as shown in Fig. 3 for ITO/Au after 15-s UVO treatment. Therefore, the variation of Rs as shown in Table 1 is most likely due to the different band alignment at the metal/polymer interface. As UVO treatment duration increases from 0 to 15 s, the work function of ITO/Au (2 nm) increases from 4.40 V to 5.01 eV, approaching to the ionization energy of P3HT, and thus benefits the generation of photocurrent. However, the work function of ITO/Au (2 nm) will further increase with the extension of UVO treatment, which will result in unfavorable band configuration and reduce the JSC.

Table 2 shows the performance of ITO/Au/P3HT:PCBM/LiF/Al with various the Au thicknesses ranging from 1 to 15 nm. All the ITO/Au samples are treated by UVO for 15 s before spin-coating the polymer blend. The performance of the conventional PEDOT-based device with the structure of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al is also listed for comparison. The reduction of JSC is attributed to less light transmitting into active layer owing to the thicker Au as shown in Fig. 3. Consequently, inserting 1 nm UVO treated Au leads to the best device with the average PCE of 3.47%, which is competitive to that of the conventional PEDOT-based device with the average PCE of 3.38%.

The dark J–V characteristics are shown in Fig. 4. The reverse saturation current for devices with ITO/Au (2 nm) as the anode is larger than that of the conventional devices with ITO/PEDOT:PSS as the anode. One reason may be from the localized short paths due to the roughness of ITO/Au surface. The other possible reason is the diffusion of Au into the active layer. Both situations will enhance recombination and thus increase the current leakage and reduce JSC and VOC [26]. However, such shortcomings resulting from the recombination should not be an issue for the present devices. It is because even the untreated ITO/Au PSCs has the rectification ratio over 300 at ± 1 V indicating a good rectifying behavior [36]. Importantly, the rectification ratio for devices with 15 s of UVO treated ITO/Au (2 nm) dramatically improves to nearly 10⁴, similar to that of the conventional PEDOT-based device with the value of 1.9 × 10⁵.

In addition, as shown in Table 2, the best UVO treated Au-based device has almost the same VOC as the conventional PEDOT-based device, i.e. 0.59 V (Au-based) vs. 0.60 V (PEDOT-based). Its obviously better FF (67.2%) compensates for its slightly reduced JSC and consequently offers its distinct advantage in device performance over the conventional PEDOT-based device as reflected by the PCE listed in Table 2. Furthermore, the series resistance of the best Au-based device is 1.8 Ω cm², which is lower than that of the PEDOT-based device with the value of 3.2 Ω cm². Hence, ultra-thin Au on ITO with a proper UVO treatment achieves a better metal/polymer interface at the anode favoring an efficient hole collection as compared to the PEDOT:PSS case.

It can also be observed that the short UVO treatment leads to a reduction in reverse saturation current indicating better diode characteristics. As the extended treatment of UVO, the increment of the reverse saturation current is probably due to the additional contamination and surface roughness enhancement induced by the long-time UVO exposure.

In addition, as observed from Fig. 4, under a forward bias, the shape of J–V curves is essentially similar to each other at the high-voltage region, but different at the low-voltage region. This phenomenon indicates that the work function of the ITO/Au anodes is different from each other. In other words, there are different

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**Table 2**

<table>
<thead>
<tr>
<th>Au Thickness</th>
<th>JSC (mA cm⁻²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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**Fig. 2.** UPS spectra of various samples: A: ITO only, B: ITO/Au (2 nm) without UVO treatment, C: ITO/Au (2 nm) with 15-s UVO treatment, D: ITO/Au (2 nm) with 20-min UVO treatment. The method of determining the secondary-electron cut-off and Fermi edge are illustrated in insets (a) and (b), respectively.

**Fig. 3.** Optical transmission spectra of various ITO/Au (x nm) with different UVO treatment time.
energy barriers at the metal/polymer interface of the anodes [37,38], which coincides very well with the UPS analysis stated above.

In the PSCs, three distinct regions are observed in the dark $J-V$ characteristics. Generally, at low voltage, the current is local-leakage dominated [29] and shows the ohmic behavior of $J \propto V$. At voltage near to build-in potential, the exponential relationship is observed as $J \propto \exp(qV/(nk_BT))$, where $n$ is the ideal factor. When $n < 1.5$, the current is considered to be drift-diffusion dominated. When $1.5 < n < 2$, the current is defect-assisted recombination dominated in the bulk or at the interface [39]. At higher voltage, the current follows the power law of $J \propto V^n$ [40]. When $n$ is around 2, the current is space-charge limited, which is a bulk effect, suggesting an ohmic contact at both electrodes [41]. Fig. 4(b) and (c) illustrate the fitted results of ITO/Au (2 nm)/P3HT:PCBM/LiF/Al with UVO treatment for 15 s. Such fitting was also conducted for other devices. For the PSCs with the same Au thickness (2 nm) without UVO treatment, $n = 2.1$ and $m = 3.0$ are extracted; while for the PSCs with various UVO treatment, $n$ is within the range between 1.3 and 1.5, and $m$ is within 1.9 to 2.5. This indicates a more drift-diffusion dominated current and a better ohmic contact for UVO treated devices. The recombination-dominated current and the larger deviation from the space-charge limited behavior of the UVO untreated devices should be due to the less favorable band alignment at the anode. This can be validated by another set of PSCs of ITO/Au(x nm)/P3HT:PCBM/LiF/Al device with UVO treatment for 15 s. For this set of PSCs, the fitted $n$ is within 1.3–1.5 and $m$ within 2.0–2.5. Although $J_{SC}$ and FF vary obviously, the slight variation of $V_{OC}$ means a slight variation of band alignment at the anode, and results in only a small variation in $n$ and $m$.

4. Conclusion

In this paper, a simple approach to achieve the efficient hole collection in polymer solar cells is demonstrated by inserting an ultra-thin UVO treated Au between ITO substrate and polymer blend layer. Through the appropriate UVO treatment on ITO/Au (1 nm), SCs with $V_{OC}$ 0.59 V, $J_{SC}$ 8.75 mA/cm², FF 67.2% and PCE 3.47% are obtained, which is competitive to that of the conventional PEDOT-based SCs. Further investigation including UPS measurement and conduction mechanism analysis suggests that the benefits of inserting ultra-thin UVO-treated Au are mainly explained by two achievements. Firstly, favorable band alignment and ohmic contact are achieved at the metal/polymer interface of the anode. Secondly, the series resistance is significantly reduced leading to remarkable FF improvement. Both aspects facilitate the efficient hole collection and hence render good device performance.

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