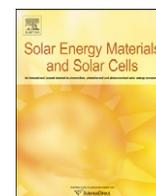




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## Efficient hole collection by introducing ultra-thin UV–ozone treated Au in polymer solar cells

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### ABSTRACT

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

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were then transferred to vacuum chamber immediately for Au evaporation. The ITO/Au (2 nm) samples were then treated by UVO for different durations including no 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<sub>61</sub> 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 the cathode with a device area of 5.77 mm<sup>2</sup> defined by a shadow mask. The conventional PEDOT-based device with the structure of ITO/PEDOT:PSS (Baytron AI 4083)/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<sup>2</sup> 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* (current density)–*V* (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 open-circuit voltage (*V*<sub>OC</sub>) increases from 0.41 V (UVO untreated) to 0.56 V, short-circuit current density (*J*<sub>SC</sub>) from 7.50 to 8.00 mA/cm<sup>2</sup>, and FF from 49.3% to 63.3%, resulting in the notable increase of power conversion efficiency (PCE) from 1.52% to 2.84%. The performance enhancement reaches a peak when the duration of UVO treatment is increased to 15 s. The PCE slightly decreases and then saturates when the treatment duration is further increased. Some reports state that the work function of a clean Au is about 5.1 eV [26], which is similar to that of the commonly used hole transport material PEDOT:PSS. However, the average *V*<sub>OC</sub> of the PEDOT-based conventional device is 0.60 V, which is about 0.2 V higher than that of the device with the untreated Au as the anode. Therefore, our results show that the work function of the untreated

**Table 1**

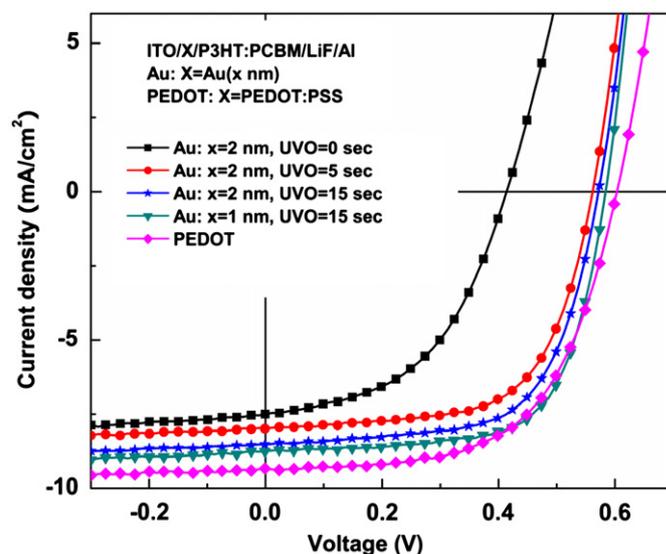
A summary of the performance of PSCs treated with different UVO time. The device structure is ITO/Au (2 nm)/P3HT:PCBM/LiF/Al.

| UVO duration | <i>J</i> <sub>SC</sub> (mA/cm <sup>2</sup> ) | <i>V</i> <sub>OC</sub> (V) | FF (%) | PCE (%) | <i>R</i> <sub>S</sub> (Ω cm <sup>2</sup> ) |
|--------------|--|----------------------------|--------|---------|--|
| 0            | 7.50   | 0.41                       | 49.3   | 1.52    | 8.6  |
| 5 s          | 8.00   | 0.56                       | 63.3   | 2.84    | 2.1  |
| 15 s         | 8.52   | 0.57                       | 63.9   | 3.10    | 2.0  |
| 30 s         | 7.84   | 0.56                       | 65.1   | 2.86    | 1.9  |
| 1 min        | 7.91   | 0.56                       | 64.7   | 2.87    | 2.2  |
| 2 min        | 7.76   | 0.55                       | 61.9   | 2.64    | 2.1  |
| 5 min        | 7.70   | 0.55                       | 62.5   | 2.65    | 1.8  |
| 8 min        | 7.65   | 0.55                       | 61.7   | 2.60    | 1.6  |
| 15 min       | 7.52   | 0.55                       | 62.3   | 2.58    | 1.5  |
| 30 min       | 7.51   | 0.55                       | 62.9   | 2.60    | 1.8  |
| 60 min       | 7.62   | 0.55                       | 61.8   | 2.59    | 2.2  |

**Table 2**

The performance of the PSCs with 15-s UVO treatment. The device structure is ITO/Au (*x* nm)/P3HT:PCBM/LiF/Al. The structure of the conventional PEDOT-based PSC is ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al.

| <i>x</i> (nm) | <i>J</i> <sub>SC</sub> (mA/cm <sup>2</sup> ) | <i>V</i> <sub>OC</sub> (V) | FF (%) | PCE (%) | <i>R</i> <sub>S</sub> (Ω cm <sup>2</sup> ) |
|---------------|--|----------------------------|--------|---------|--|
| 0             | 8.33   | 0.52                       | 55.9   | 2.42    | 2.8  |
| 1             | 8.75   | 0.59                       | 67.2   | 3.47    | 1.8  |
| 2             | 8.52   | 0.57                       | 63.9   | 3.10    | 2.0  |
| 3             | 6.94   | 0.56                       | 64.2   | 2.50    | 1.8  |
| 5             | 5.78   | 0.55                       | 62.2   | 1.98    | 2.1  |
| 8             | 4.59   | 0.55                       | 60.0   | 1.51    | 2.9  |
| 15            | 3.65   | 0.55                       | 58.0   | 1.16    | 4.8  |
| PEDOT-based   | 9.33   | 0.60                       | 60.4   | 3.38    | 3.2  |



**Fig. 1.** *J*–*V* characteristics of the representative PSCs.

Au is not likely to be 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 work function, which are determined to be 4.86 eV, 4.40 eV, 5.01 eV and 5.25 eV for samples A, B, C and D, respectively. The 4.86 eV of UVO treated ITO is similar to the reported 4.75 eV by UPS measurement [28] and also falls into the well recognized region of 4.7–4.9 eV [9]. The UVO untreated ITO/Au (2 nm) has work function of 4.40 eV, which agrees very well with those reported [29–31]. Different from the work function of the atomically clean Au surface (~5.2 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

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