Front. Optoelectron. 2015, 8(3): 269–273
DOI 10.1007/s12200-015-0531-x

RESEARCH ARTICLE

ITO surface modification for inverted organic photovoltaics

Mingzhang DENG, Weina SHI, Chen ZHAO, Bingbing CHEN, Yan SHEN (✉)

Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China

Abstract The work function (*WF*) of indium-tin-oxide (ITO) substrates plays an important role on the inverted organic photovoltaic device performance. And electrode engineering has been a useful method to facilitate carrier extraction or charge collection to enhance organic photovoltaic (OPV) performance. By using self-assembly technique, we have deposited poly(dimethyl diallylammonium chloride) (PDDA) layers onto ITO coated glass substrates. The results indicate that the surface *WF* of ITO is reduced by about 0.3 eV after PDDA modification, which is attributed to the modulation in electron affinity. In addition, the surface roughness of ITO substrate became smaller after PDDA modification. These modified ITO substrates can be applied to fabricate inverted OPVs, in which ITO works as the cathode to collect electrons. As a result, the photovoltaic performance of inverted OPV is substantially improved, mainly reflecting on the increase of short circuit current density.

Keywords organic photovoltaic (OPV), indium tin oxide (ITO), inverted structure, surface modification, work function (*WF*)

1 Introduction

Organic photovoltaics (OPVs) have attracted much attention during the last decades due to their potential application for their light weight, low cost, and flexibility [1]. The simplest form of organic solar cells can be fabricated by sandwiching a layer of an organic electronic material between two metallic conductors, typically a layer of indium-tin-oxide (ITO) with high work function (*WF*) (~ 4.7 eV) and a layer of low *WF* metal such as aluminum (Al) (~ 4.1 eV). However, single layer organic solar cells do not work well, showing low quantum efficiencies ($< 1\%$) and low power conversion efficiencies ($< 0.1\%$), mainly due to an insufficient light absorption. The diffusion length of excitons in organic electronic materials is typically on the order of 10 nm for most excitons diffusing to the interface of layers and splitting into carriers. Therefore, the layer thickness should be in the same range as the diffusion length [2]. Now, most of OPV devices with high efficiency took the form of bulk heterojunction, which has an absorption layer consisting of a nanoscale blend of donor and acceptor materials. The large donor-acceptor interfacial area results in a higher likelihood for the short-lived excitons to reach an interface and dissociate [3]. Bulk heterojunctions have an advantage over layered photoactive structures because they can be made thick enough for effective photon absorption without the difficult processing involved in orienting a layered structure. ITO films are commonly used as an electrode in OPV devices, on which an acidic poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) layer is deposited as the hole selective contact. It is known that PEDOT:PSS layer was detrimental to the ITO substrates due to the instability of PEDOT:PSS/ITO interface. In addition, the PEDOT:PSS is acid and will etch the ITO, making this interface unstable [4]. And OPV with inverted structure is an effective way to improve the devices' stability by avoiding the contact between PEDOT:PSS and ITO substrates [5]. The inverted device architecture, in which ITO collects electrons and a high *WF* metal electrode collects holes, has proven to be effective in improving both the power conversion efficiency (PCE) and durability of OPV devices. Recent years, inverted OPV with modified ITO as the transparent cathode has received increasing attention and various kinds of OPV devices with inverted structure have been reported to improve the devices' efficiency and stability. However, this kind of optoelectronic device requires an electrode with a low *WF* to either facilitate the injection or collection of electrons from the lowest unoccupied molecular orbital (LUMO) of a given organic semiconductor [6]. So it is vital to use appropriate materials or modification to match the energy level in an inverted OPV structure. As the electronic potential of ITO surface has been proved to be very

Received May 22, 2015; accepted July 17, 2015

E-mail: ciac_sheny@hust.edu.cn

sensitive to the presence of self-assembled molecular layers via tuning the surface dipole, doping and electric field effect, the surface *WF* can be changed by applying different methods of modification [7].

In this paper, we demonstrate an effective method to reduce the *WF* of ITO films by electrostatic absorption with poly(dimethyl diallylammonium chloride) (PDDA) via self-assembly deposition method [8]. PDDA is a kind of cationic polymer with high charge density, which has been commonly used in layer-by-layer self-assembly technique [9]. Self-assembly deposition of polyelectrolytes is a widely used surface modification technique, which provides benefits of controlled thickness at nanometer scale. The result reveals that after the PDDA modification, the surface of ITO substrates become smoother, and the *WF* can be decreased by 0.3 eV. When these modified ITO substrates are applied to fabricate inverted OPV devices, the photovoltaic performance of inverted OPV can be improved. The resulting improvement in the photocurrent is analyzed and discussed according to the energy level and photovoltaic performance.

2 Experimental

The ITO substrates were first cleaned in an ultrasonic bath sequentially with detergent, deionized water, acetone and ethanol solution for 15 min each, followed by being washed with deionized water and then dried by N_2. The washed ITO glasses were prepared by sonicating in 10% NaOH and distilled water to obtain a negatively charged surface before putting into the PDDA solution. And the PDDA solution needed to be diluted to 1% wt before use. The ITO substrates were then immersed in this PDDA solution for 20 min to grow PDDA layer. After 20 min, the PDDA-coated ITO substrates were washed with deionized water again in order to remove all non-bound materials. Then they were dried by N_2 before transferring into the golve box for the next step.

The next step is to fabricate active layer on the ITO/PDDA substrates. In this study, the active materials used are poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) mixture with a weight ratio of 1:0.8 in 1,2-dichlorobenzene. The organic active layer was prepared on ITO/PDDA substrates by spin-coating at a speed of 600 r/min for 60 s. This step was carried out in a nitrogen glove box to avoid hydrolysis and oxidation of organic materials and the thickness of P3HT:PCBM active layer was targeted at about 200 nm. 15-nm-thick MoO_3 and 90-nm-thick Al layers were further thermally evaporated onto the substrates at a base pressure of 4×10^{-4} Pa. This MoO_3 layer was inserted between the active layer and Al electrode as an electron blocking layer and hole transport layer (HTL) in the inverted OPV structure. Finally, the OPV devices were annealed at 150°C for 10 min in the nitrogen glove box in order to attain an optimized morphology of the active layer [10].

Ultraviolet photoelectron spectroscopy (UPS) and atomic force microscopy (AFM) measurements were carried out after all the procedure. And the current density-voltage (*I-V*) characteristics were measured under AM 1.5 G at an intensity of 100 mW cm^{-2} (device area = 0.09 cm^2) by using a Keithley 2400 sourcemeter.

3 Results and discussion

Figure 1 illustrates the surface modification of ITO substrates with PDDA. In this study, the attractive force between the negatively charged ITO surface and the positively charged PDDA polymer leads to the growth of PDDA layer through self-organization or association of charge pairs [8]. Figure 2 compares AFM images of the ITO surface with and without PDDA modification. After the PDDA modification, the root-mean-square (*RMS*) roughness of the ITO surface decreases from 4.81 to 3.0 nm, which indicates that the PDDA layer uniformly covers the ITO surface. This PDDA layer can be used to improve the interlayer contact between ITO and active layer. This is beneficial to decrease the series resistance and improve the fill factor (*FF*) of the devices.

UPS measurements were performed to study the changes in the effective *WF* of ITO surface. Either electron affinity or Fermi level can be simultaneously changed for

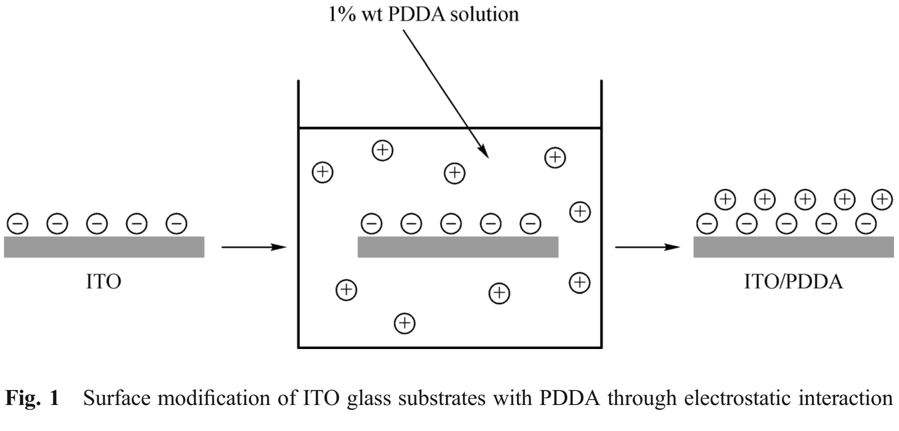
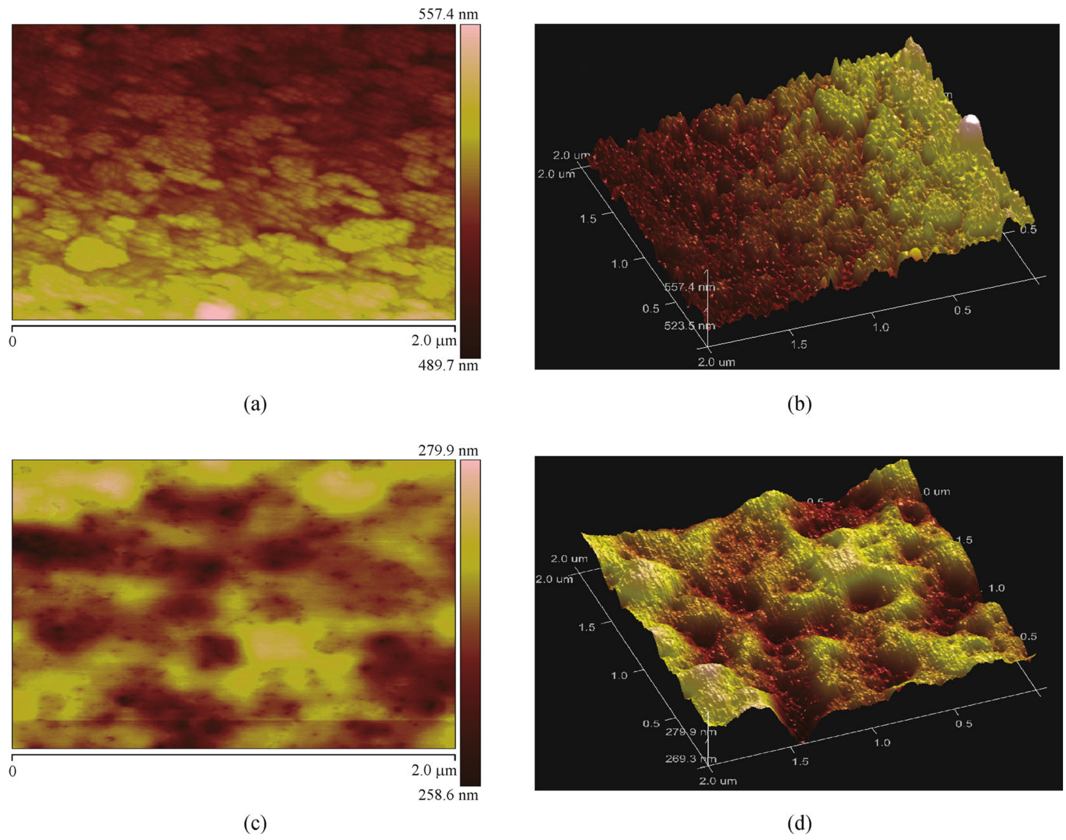


Fig. 1 Surface modification of ITO glass substrates with PDDA through electrostatic interaction



(a) (b)

(c) (d)

Fig. 2 AFM images of ITO surface with and without PDDA: (a) and (b) are 2D and 3D AFM images of pristine ITO; (c) and (d) are 2D and 3D AFM images of ITO surface after PDDA modification

the ITO surface if a dipole layer interacts with its adjacent material strongly. The UPS result indicates that the *WF* of ITO is determined by the energy positions of the lowest binding energy onsets of the secondary electrons. No obvious changes are observed in the electron density at the Fermi region, which stays at nearly 22.10 eV. The UPS spectra in the secondary electron cut-off ($E_{\text{cut-off}}$) are shown in Fig. 3. The secondary electron cut-off in the ITO film shifts toward a lower kinetic energy after the PDDA modification on the surface by 0.32 eV, from 5.80 to 5.48 eV. According to the *WF* calculation: $WF = h\nu - |E_{\text{cut-off}} - E_{\text{f}}|$, we can deduce the *WF* of ITO surface can be decreased by 0.32 eV [11].

To further validate if the ITO with PDDA modification could efficiently facilitate the collection of electrons from the photoactive layer, organic photovoltaics with the structure of glass/ITO/PDDA/P3HT:PCBM/MoO_3/Al (Fig.. 4) have been fabricated. For comparison, solar cells with bare ITO electrodes are also fabricated. Figure 5 presents the photocurrent-voltage curves of both kinds of devices tested under 100 mW/cm^2 AM 1.5G simulated irradiation. The photovoltaic parameters, open circuit voltage (V_{OC}), *FF*, short circuit current density (J_{SC}) and PCE are tabulated in Table 1. Encouragingly, the ITO/PDDA-based device displayed a J_{SC} of 7.38 mA/cm^2, a *FF* of 0.45, an V_{OC} of 0.64 V, amounting to a PCE of 2.14%. For comparison, the device based on ITO was also fabricated under the same conditions and showed a power conversion efficiency of 1.91% with a J_{SC} of 6.86 mA/cm^2, an V_{OC} of 0.62 V and a *FF* of 0.43. Comparison of the J_{SC} value of ITO/PDDA-based device with that of ITO-based device shows that photocurrent can be

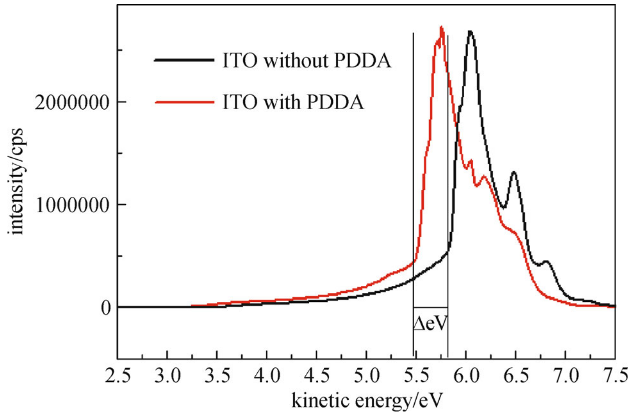


Fig. 3 Cut-off region in UPS spectrum of ITO modified with and without PDDA in kinetic energy scale

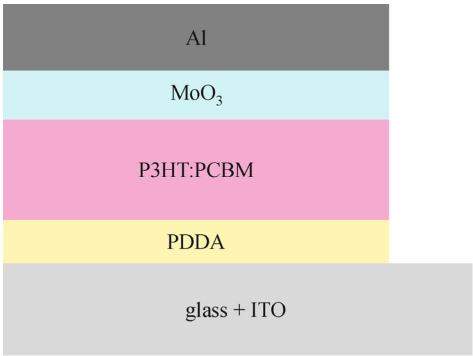


Fig. 4 Structure for an inverted organic photovoltaic device using the PDDA modified ITO glass substrate

Table 1 Photovoltaic performance of the organic solar cell device using ITO with and without PDDA modification

device	V_{OC}/V	J_{SC}/(mA· cm^{-2})	*FF*	PCE/%
OPV without PDDA	0.62	6.86	0.43	1.91
OPV with PDDA	0.64	7.38	0.45	2.14

Notes: V_{OC}: open circuit voltage; J_{SC}: short circuit current density; *FF*: fill factor; PCE: power conversion efficiency

increased from 6.86 to 7.38 mA/cm^2 simply by modifying the substrate with PDDA in the same device structure. There is no evident change on open circuit voltage (staying at nearly 0.6 eV) as shown in Fig. 5. Though there might be differences on *WF* of ITO after PDDA modification, the V_{OC} of the cells show no evident changes. This is because the open-circuit voltage, according to the p-n junction, is mainly determined by the difference between the quasi Fermi levels of the two charge carriers [12]. And when the *WF* of the electrode approaches the limit of the bandgap or electron affinity, there will be a substantial charge transfer between the electrode and the active layer, leading to interfacial dipoles and pinning of the Fermi level at an energy. So we can deduce that the improvement mainly results from the enhancement on J_{SC}.

By analyzing the energy level diagram, we can figure out how to low *WF* of ITO in the devices (Fig. 6). The energy levels of relevant materials in this inverted OPV structure are taken from previous reports [13,14]. ITO works as cathode to collect electrons while the MoO_3 interlayer acts as the hole transport layer to help prevent the recombination of charge carriers at the interface between active layer and Al electrode [15]. And it is known that this kind of optoelectronic devices require conductors with a *WF* that is sufficient low to facilitate the electrons injection and collection. As indicated in the UPS result, the *WF* of ITO with PDDA is reduced by nearly 0.3 eV. As *WF* refers to the level of difficulty in transferring electrons from a solar cell's photoactive layer to the metal electrode, a lower *WF* means easier electron transport. So the reduction on the *WF* of ITO is able to facilitates electron injection and collection from the LUMO of PCBM. And this improved injection results in an increase on J_{SC}, making the PCE of this device higher.

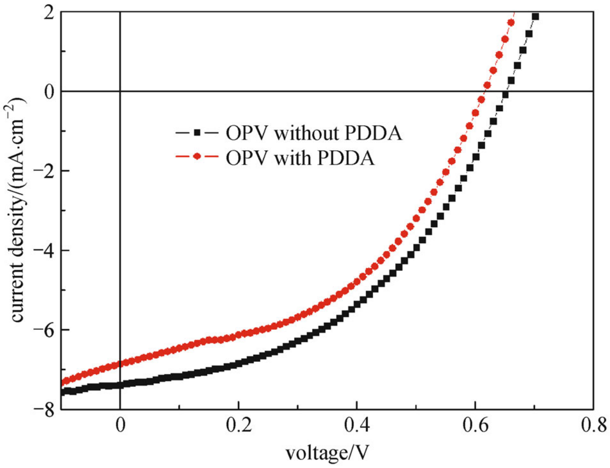


Fig. 5 *I-V* curves of organic solar cell devices using ITO modified without/with PDDA

The efficiency of the OPVs with ITO/PDDA is lower than some reported P3HT:PCBM-based solar cells. This is mainly attributed to our devices with inverted structure in semitransparent structure that uses no electrons transport layer (ETL) to either facilitate the electrons collection or block hole transfer on ITO surface. And this study mainly focus on the influence of *WF* of ITO electrodes on electrons collection in inverted OPV devices. The absence of proper ETL results in lower J_{SC} and *FF*, leading to a lower PCE.

4 Conclusions

In summary, we demonstrated a simple method to reduce the effective surface *WF* of a transparent ITO film with self assembled PDDA layer. The UPS and AFM measurement results suggest that the PDDA is uniformly deposited on the ITO substrates, which is able to reduce the *WF* of this kind of conducting materials. By modifying the ITO with PDDA, the surface *WF* of ITO can be reduced by 0.3 eV. This change is supposed to facilitate the electrons collection on ITO surface when these ITO substrates with low *WF* were applied to fabricate inverted OPV devices. As a result, the PCE of the inverted OPV can be improved, mainly reflecting on the increase of photocurrent, due to a lowering of the effective cathode interfacial barrier. The modification is simple, fast, and suitable to produce low *WF* electrode for inverted OPV devices. And the devices with ITO/PDDA are relatively stable and reliable kept in air. It could be expected that this simple and effective method will be widely applied to improve electron injection or collection.

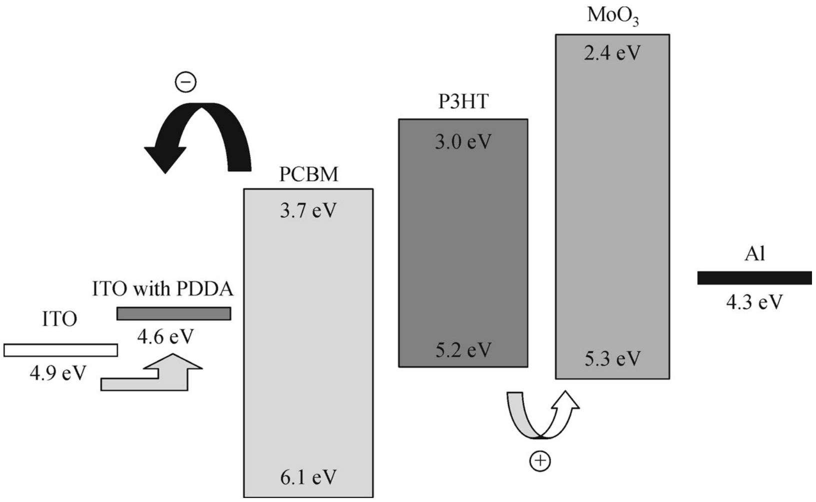


Fig. 6 Energy levels in the organic solar cell using ITO modified without/with PDDA

Acknowledgements The financial support from the Director Fund of the Wuhan National Laboratory for Optoelectronics, the Major State Basic Research Development Program of China (Nos. 2014CB643506 and 2013CB922104) is acknowledged.

References

1. Hoppe H, Sariciftci N S. Organic solar cells: an overview. Journal of Materials Research, 2004, 19(7): 1924–1945
2. Cnops K, Rand B P, Cheyns D, Verreet B, Empl M A, Heremans P. 8.4% efficient fullerene-free organic solar cells exploiting long-range exciton energy transfer. Nature Communications, 2014, 5: 3406
3. Cao W, Xue J. Recent progress in organic photovoltaics: device architecture and optical design. Energy & Environmental Science, 2014, 7(7): 2123–2144
4. Jørgensen M, Norrman K, Krebs F. Stability/degradation of polymer solar cells. Solar Energy Materials and Solar Cells, 2008, 92(7): 686–714
5. He Z, Zhong C, Su S, Xu M, Wu H, Cao Y. Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure. Nature Photonics, 2012, 6(9): 591–595
6. Zhou Y, Fuentes-Hernandez C, Shim J, Meyer J, Giordano A J, Li H, Winget P, Papadopoulos T, Cheun H, Kim J, Fenoll M, Dindar A, Haske W, Najafabadi E, Khan T M, Sojoudi H, Barlow S, Graham S, Brédas J L, Marder S R, Kahn A, Kippelen B. A universal method to produce low-work function electrodes for organic electronics. Science, 2012, 336(6079): 327–332
7. Min X, Jiang F, Qin F, Li Z, Tong J, Xiong S, Meng W, Zhou Y. Polyethylenimine aqueous solution: a low-cost and environmentally friendly formulation to produce low-work-function electrodes for efficient easy-to-fabricate organic solar cells. ACS Applied Materials & Interfaces, 2014, 6(24): 22628–22633
8. Guo Z, Shen Y, Wang M, Zhao F, Dong S. electrochemistry and electrogenerated chemiluminescence of SiO$_2$ nanoparticles/Tris (2,2-bipyridyl)ruthenium(II) multilayer films on Indium Tin oxide electrodes. Analytical Chemistry, 2004, 76(1): 184–191
9. Li L S, Li A D Q, Jia Q X. Effects of self-assembled multilayers on the evolution of surface physical properties of indium-tin-oxide. Applied Surface Science, 2003, 219(3–4): 199–202
10. Ma W, Yang C, Gong X, Lee K, Heeger A J. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. Advanced Functional Materials, 2005, 15(10): 1617–1622
11. Park Y, Choong V, Gao Y, Hsieh B R, Tang C W. Work function of indium tin oxide transparent conductor measured by photoelectron spectroscopy. Applied Physics Letters, 1996, 68(19): 2699–2701
12. Manor A, Katz E A. Open-circuit voltage of organic photovoltaics: Implications of the generalized Einstein relation for disordered semiconductors. Solar Energy Materials and Solar Cells, 2012, 97: 132–138
13. Zhang C, You H, Lin Z, Hao Y. Inverted organic photovoltaic cells with solution-processed zinc oxide as electron collecting layer. Japanese Journal of Applied Physics, 2011, 50(8R): 082302
14. Zhao D W, Sun X W, Jiang C Y, Kyaw A K K, Lo G Q, Kwong D L. Efficient tandem organic solar cells with an Al/MoO$_3$ intermediate layer. Applied Physics Letters, 2008, 93(8): 083305
15. Tao C, Ruan S, Zhang X, Xie G, Shen L, Kong X, Dong W, Liu C, Chen W. Performance improvement of inverted polymer solar cells with different top electrodes by introducing a MoO$_3$ buffer layer. Applied Physics Letters, 2008, 93(19): 193307