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Role of tungsten oxide in inverted polymer solar cells — Source link

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Role of tungsten oxide in inverted polymer solar cells

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Tungsten oxide (WO₃) was inserted as an anode interfacial layer between the photoactive layer and top electrode in inverted polymer solar cells (PSCs) with nanocrystalline titanium dioxide as an electron selective layer. The device with WO₃ exhibited a remarkable improvement in power conversion efficiency compared with that without WO3, which indicated that WO3 efficiently prevented the recombination of charge carriers at the organic/top electrode interface. The dependence of the device performances on WO₃ film thickness and different top metal electrodes was investigated. Transparent inverted PSCs with thermally evaporable Ag/WO₃ as a transparent anode were also investigated when introducing a WO₃ buffer layer. © 2009 American Institute of *Physics*. [DOI: 10.1063/1.3076134]

Interest in solar cells to capture sunlight and generate electricity is increasing due to oil energy crisis and rising concerns over global climate change. Inorganic solar cells can yield high power conversion efficiency but the expensive fabrication process makes them infeasible in common use. Instead, polymer solar cells (PSCs) are a good candidate because semiconducting polymers can be dissolved in common solvents and printed like inks so that economical roll-in-roll fabrication process can be realized. 1,2 The photoactive layer composed of electron donating and accepting materials absorbs light and generates excitons. Then electrons and holes can be efficiently separated from each other due to the nanometer-scale interpenetrating network of electron donor and acceptor within the whole photoactive layer.³ However, a simple structure that sandwiched the photoactive layer between two electrodes (anode and cathode) is not perfect enough. The low efficiency of charge collection at the interface between the photoactive layer and electrodes results in poor performance of PSCs. In order to solve this problem, interfacial layers, such as a combination of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and lithium fluoride (LiF), are commonly introduced between the active layer and electrodes to improve charge carrier collection and to enhance the open-circuit voltage $(V_{\rm oc})$.

Nevertheless, PEDOT:PSS has been demonstrated to have a side effect on the performance of PSCs due to its corrosion to indium tin oxide (ITO) and electrical inhomogeneities.⁶⁻⁸ In order to overcome this problem, one might simply introduce interfacial layer materials to improve the performance of PSCs. Recently, molybdenum oxide (MoO₃), vanadium oxide (V_2O_5), and nickel oxide (NiO) have been demonstrated to effectively substitute PEDOT:PSS as the anodic buffer layer in PSCs. 9,10 An alternative approach is to reverse the device architecture and hence to form inverted PSCs, in which MoO₃ and V₂O₅ were usually inserted between the active layer and top electrode. 11,12 In this letter, we introduce a low-cost, nontoxic, and easily evaporable tungsten oxide (WO₃) as a holeextraction layer in inverted PSCs with nanocrystalline titanium dioxide (nc-TiO₂) as an electron selective layer. The device architecture is shown schematically in Fig. 1(a), and the energy level diagrams of different materials used in the device fabrication are shown in Fig. 1(b). Meanwhile, transparent inverted PSCs are fabricated with thermally evaporable Ag(13 nm)/WO₃(40 nm) as a transparent anode when introducing a 10 nm WO₃ buffer layer.

Detailed processes of preparing TiO2-sol have been described in our previous paper. 12 After a cleaning step, TiO₂-sol was spin coated on ITO-coated glass substrates at 3000 rpm. Then the samples were moved to a muffle furnace and annealed at 450 °C for 2 h. After annealing treatment,

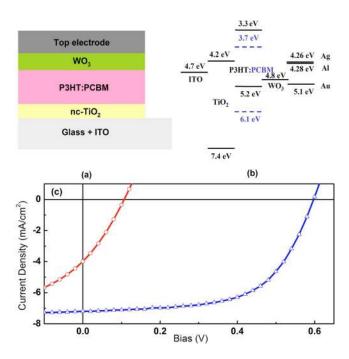


FIG. 1. (Color online) (a) The device structure of the inverted PSCs. (b) Scheme of the energy levels of the materials involved in the inverted PSCs. (c) The J-V characteristics of the devices under 100 mW/cm² white light illumination in air: ITO/nc-TiO₂/P3HT:PCBM/Ag (circle) and ITO/nc-TiO₂/P3HT:PCBM/WO₃(10 nm)/Ag (triangle).

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nc-TiO $_2$ was formed. In this letter, poly(3-hexylthiophene) (P3HT) (Rieke Metals) was used as electron donor material, and 6,6-phenyl C $_{61}$ butyric acid methyl ester (PCBM) (Solenne BV) was used as electron acceptor material. The mixed chlorobenzene solution composing of P3HT (10 mg/ml) and PCBM (8 mg/ml) was then spin coated on top of the nc-TiO $_2$ layer at 700 rpm in ambient air. Then the samples were heated in low vacuum (vacuum oven) at approximately 150 °C for 10 min. Subsequently, the samples were pumped down in vacuum (<10 $^{-3}$ Pa). Finally WO $_3$ and 60 nm top electrode (Ag, Au, and Al) were thermally evaporated in sequence. The active area of the device was about 0.064 cm 2 .

Current density-voltage (*J-V*) characteristics of the devices were measured by a computer-controlled Keithley 2601 source meter in air without any encapsulation. The light source is a 500 W xenon lamp (CHF-XM-500W, Beijing Changtuo). The light intensity was calibrated with a Si photodetector (FZ-A, Photoelectric Instrument Factory of Beijing Normal University).

Figure 1(c) shows the current density-voltage (J-V) characteristics of the device with and without WO₃ under 100 mW/cm² white light illumination. In the absence of WO₃, the simple device (ITO/nc-TiO₂/P3HT:PCBM/Ag) exhibits a power conversion efficiency of 0.13% with a very low fill factor (FF) of 30.4%. The short-current density (J_{sc}) and V_{oc} are 3.99 mA/cm² and 0.107 V, respectively. However, by introducing a 10 nm WO₃ layer between the active layer and Ag, the device exhibits a power conversion efficiency of 2.58% with J_{sc}=7.20 mA/cm², V_{oc}=0.597 V, and FF=60.0%.

By inserting a 10 nm WO₃ buffer layer, the device $(ITO/nc-TiO_2/P3HT:PCBM/WO_3/Ag)$ gives rise to a significant increase in J_{sc} from 3.99 to 7.20 mA/cm². This indicates that WO₃ efficiently prevents the recombination of charge carriers at the organic/Ag interface. Considering the device without WO₃, both P3HT and PCBM are in direct contact with Ag. It is possible for PCBM to transfer electrons to Ag electrode, thereby increasing the recombination rate of photogenerated charges. However, inserting a WO₃ layer will introduce two additional interfaces (P3HT:PCBM/WO₃ and WO₃/Ag). The high work function of WO₃ (-4.8 eV) (Ref. 4) will enhance hole collection at the photoactive layer/Ag interface.

It is known that the bulk resistance of the active materials and the contact resistance contribute to the series resistance. The contact resistance originates from the interface between the photoactive layer and electrodes. The series resistance, defined by the slope of the J-V curve at $J=0~\text{mA/cm}^2$, is estimated to be $\sim\!15.2~\text{and}\sim\!20.0~\Omega~\text{cm}^2$ for the devices with and without WO₃, respectively. Although most of the carriers are generated in the photoactive layer, their collection is relative to the contact resistance at the organic/top electrode interface. The decrease in series resistance indicates that the insertion of the thin WO₃ film suppresses the contact resistance remarkably.

It is observable that the device without WO₃ exhibits a very low $V_{\rm oc}$ of 0.107 V, which is a main factor for the low power conversion efficiency. However, by incorporating a WO₃ interfacial layer, the $V_{\rm oc}$ has an obvious improvement and reaches up to 0.597 V. This might be caused by the increased built-in potential when introducing a WO₃ interfacial layer, for the $V_{\rm oc}$ is the voltage where the applied bias

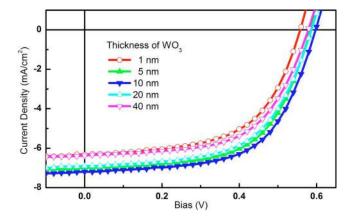


FIG. 2. (Color online) The J-V characteristics under 100 mW/cm² white light illumination in air for devices with different thickness of WO₃ used as the buffer layer between the active layer and Ag electrode.

equals the built-in potential in an ideal diode.

Similar to $J_{\rm sc}$ and $V_{\rm oc}$, the FF also increases remarkably from 30.4% to 60.0% due to the incorporation of WO₃, leading to a significant improvement in power conversion efficiency. The decrease in series resistance from 20.0 to 15.2 Ω cm² contributes partly to the increase in FF. Meanwhile, the shunt resistance, defined by the slope of the J-V curves near 0 V under illumination, is estimated to be \sim 1200.4 and \sim 39.6 Ω cm² for the devices with and without WO₃, respectively. The elevated shunt resistance also makes contribution to the improvement in FF.

It is necessary for the WO₃ interfacial layer to cover the active layer fully and uniformly to reduce the leakage current. However, introducing a WO3 layer will generally contribute to the series resistance of the device and the higher thickness of WO₃ will result in a lower current. Therefore, the effect of WO₃ film thickness on device performance is investigated and shown in Fig. 2. The detailed result is summarized in Table I. The optimum thickness of WO₃ is 5–10 nm. When the thickness of WO₃ is 1 nm or less, the active layer will not be fully covered by WO₃, which tends to form some small islands instead of a uniform film. Thereafter, two additional interfaces (polymer/Ag and polymer/WO₃/Ag) are introduced. The J-V curve of the device with 1 nm WO₃ can be regarded as the overlapping of two independent J-Vcurves of the devices with Ag and WO₃/Ag as top electrode, respectively. Due to the bad performance of the simple device (ITO/nc-TiO₂/P3HT:PCBM/Ag), the overlapping of the two independent J-V curves will result in a worse performance than that of a device with WO₃/Ag.

Figure 3 shows the device performance dependences on different top metal electrodes (Ag, Au, and Al) when the

TABLE I. Short-circuit current density ($I_{\rm sc}$), open-circuit voltage ($V_{\rm oc}$), FF, and power conversion efficiency (PCE) of inverted PSCs dependent on the thickness of WO₃.

WO ₃ (nm)	$J_{\rm sc}$ (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
1	6.33	0.557	57.3	2.02
5	6.99	0.584	60.0	2.45
10	7.20	0.597	60.0	2.58
20	6.91	0.586	58.5	2.37
40	6.38	0.578	58.6	2.16

FIG. 3. (Color online) The J-V characteristics under 100 mW/cm² white light illumination in air for devices with different top metal electrodes (Ag, Au, and Al).

thickness of WO₃ is 10 nm. Au devices exhibit a power conversion efficiency of 2.31% with $J_{\rm sc}$ of 6.57 mA/cm² and $V_{\rm oc}$ of 0.592 V. Al devices exhibit a power conversion efficiency of 2.37% with $J_{\rm sc}$ of 6.93 mA/cm² and $V_{\rm oc}$ of 0.577 V. Compared with Ag devices, Au devices show a lower efficiency because of the small absorption of incident light by Au electrode. ¹⁴ Since the test of J-V characteristics is carried out in ambient air, the oxidization of Al results in a larger series resistance, which induces a slightly lower efficiency in Al devices. However, devices with different top electrodes have a $V_{\rm oc}$ of \sim 0.59 V with a variation of 20 mV, which indicates that the $V_{\rm oc}$ is relatively irrespective of the choice of top metal electrodes when introducing a 10 nm WO₃ interfacial layer.

Recently, a WO₃/Ag/WO₃ electrode structure has been demonstrated to have a high transparency and a low sheet resistance in organic light emitting diodes due to an optical effect in the WO₃/Ag/WO₃ structure and the low resistance of the Ag layer, respectively. 15 Considering the device structure with Ag as top electrode mentioned above, it is easy to realize transparent inverted PSCs with a device structure of ITO/nc-TiO₂/P3HT:PCBM/WO₃(10 nm)/Ag(13 nm)/ \times WO₃(40 nm). The 10 nm WO₃ layer here is used as a buffer layer. Both ITO and Ag/WO₃ are highly transparent. The J-V curves for this transparent inverted PSC are shown in Fig. 4 when illuminated from ITO or Ag/WO₃ side. The device shows a power conversion efficiency of 1.80% with $J_{\rm sc}$ of 4.89 mA/cm² and $V_{\rm oc}$ of 0.592 V when illuminated from ITO side. However, the power conversion of the device is 0.96% with $J_{\rm sc}$ of 2.69 mA/cm² and $V_{\rm oc}$ of 0.572 V when illuminated from Ag/WO₃ side. The difference in power conversion efficiency is attributed to the different transparency between ITO and Ag/WO₃. Compared with the device with a reflected top electrode, the light absorption in the photoactive layer is less in transparent inverted PSC and hence to result in a lower power conversion efficiency.

In summary, we have explored the use of WO_3 in inverted polymer solar cells. Due to the high work function (-4.8 eV), WO_3 efficiently extracts holes and suppresses

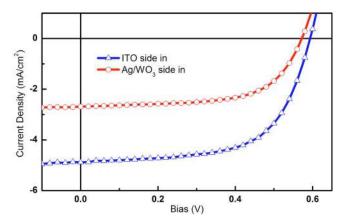


FIG. 4. (Color online) The J-V characteristics under 100 mW/cm² white light illumination in air for transparent inverted polymer solar cells illuminated from two transparent electrodes-ITO and Ag/WO₃.

electrons from the active layer. The thicknesses of WO_3 and different top metal electrodes on device performances are also investigated. Transparent inverted PSCs are fabricated with $Ag(13 \text{ nm})/WO_3(40 \text{ nm})$ as a transparent top electrode when introducing a 10 nm WO_3 buffer layer, which have the potential to realize a multiple device structure to absorb more solar photons by the multiple photoactive layers to achieve high device performance.

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