Polymer solar cells (PSCs) have attracted much attention because of their light weight, low cost, and promising applications. However, to date the effect of molybdenum trioxide on the performance of PSCs has seldom been reported. In this letter, MoO$_3$ is introduced between the active layer and top electrode as buffer layer (nc-TiO$_2$) to ITO. In order to solve this problem, one feasible approach is to reverse the device structure by using a less air sensitive and high work function metal as the back hole-collecting electrode. This structure can avoid the use of PEDOT:PSS.

In inverted PSCs, vanadium oxide was usually introduced between the active layer and top electrode as buffer layer. However, to date the effect of molybdenum trioxide on the performance of inverted PSCs with different metal electrodes has seldom been reported. In this letter, MoO$_3$ is introduced between the active layer and top electrode in inverted PSCs with nanocrystalline titanium dioxide (nc-TiO$_2$) as an electron selective layer. The architecture of the device is shown schematically in Fig. 1(a). The performances of structurally identical PSCs with different top electrodes (Au, Ag, and Al) were investigated and compared. The interface between MoO$_3$ and different metals was studied by x-ray photoelectron spectroscopy (XPS). The results showed that the performances of devices with different metals are greatly improved due to the incorporation of MoO$_3$ and the open-circuit voltage of devices is relatively insensitive to the choice of the anode metal when MoO$_3$ is introduced.

Molybdenum trioxide (MoO$_3$) was inserted between the active layer and top electrode in inverted polymer solar cells (PSCs) with nanocrystalline titanium dioxide as an electron selective layer. The performances of structurally identical PSCs with different top electrodes (Au, Ag, and Al) were investigated and compared. The interface between MoO$_3$ and different metals was studied by x-ray photoelectron spectroscopy. The results showed that the performances of devices with different metals are greatly improved due to the incorporation of MoO$_3$ and the open-circuit voltage of devices is relatively insensitive to the choice of the anode metal when MoO$_3$ is introduced.

Performance improvement of inverted polymer solar cells with different top electrodes by introducing a MoO$_3$ buffer layer

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Polymer solar cells (PSCs) based on a blend of conjugated polymers and fullerene derivatives have attracted much attention because of their light weight, low cost, and promising applications. However, to date the effect of molybdenum trioxide on the performance of PSCs has seldom been reported. In this letter, MoO$_3$ is introduced between the active layer and top electrode in inverted PSCs with nanocrystalline titanium dioxide as an electron selective layer. The performances of structurally identical PSCs with different top electrodes (Au, Ag, and Al) were investigated and compared. The interface between MoO$_3$ and different metals was studied by x-ray photoelectron spectroscopy. The results showed that the performances of devices with different metals are greatly improved due to the incorporation of MoO$_3$ and the open-circuit voltage of devices is relatively insensitive to the choice of the anode metal when MoO$_3$ is introduced.

The performances of structurally identical PSCs with different top electrodes (Au, Ag, and Al) were investigated and compared. The interface between MoO$_3$ and different metals was studied by x-ray photoelectron spectroscopy (XPS). The results showed that the performances of devices with different metals are greatly improved due to the incorporation of MoO$_3$ and the open-circuit voltage of devices is relatively insensitive to the choice of the anode metal when MoO$_3$ is introduced.

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ITO/nc-TiO2/RR-P3HT:PCBM/Au, and ITO/nc-TiO2/RR-P3HT:PCBM/MoO3(1 nm)/Au under 100 mW/cm² white light illumination in ambient air. The detailed results are given in Table I. The experiment was carried out in ultrahigh vacuum environment.

Figure 2(a) shows the J-V curves of two types of devices, ITO/nc-TiO2/RR-P3HT:PCBM/Au, and ITO/nc-TiO2/RR-P3HT:PCBM/MoO3(1 nm)/Au under 100 mW/cm² white light illumination in ambient air. The detailed results are given in Table I. The experiment was carried out in ultrahigh vacuum environment.

TABLE I. Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), FF, and PCE of inverted PSCs with different anodes.

<table>
<thead>
<tr>
<th>Anode</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>3.90</td>
<td>0.463</td>
<td>38.2</td>
<td>0.69</td>
</tr>
<tr>
<td>1 nm MoO3/Au</td>
<td>5.61</td>
<td>0.608</td>
<td>58.6</td>
<td>2.00</td>
</tr>
<tr>
<td>Ag</td>
<td>3.11</td>
<td>0.085</td>
<td>26.5</td>
<td>0.07</td>
</tr>
<tr>
<td>1 nm MoO3/Ag</td>
<td>6.57</td>
<td>0.628</td>
<td>62.3</td>
<td>2.57</td>
</tr>
<tr>
<td>Al</td>
<td>2.44</td>
<td>0.300</td>
<td>19.1</td>
<td>0.14</td>
</tr>
<tr>
<td>1 nm MoO3/Al</td>
<td>5.60</td>
<td>0.541</td>
<td>42.9</td>
<td>1.30</td>
</tr>
<tr>
<td>3 nm MoO3/Al</td>
<td>5.90</td>
<td>0.581</td>
<td>51.9</td>
<td>1.78</td>
</tr>
<tr>
<td>5 nm MoO3/Al</td>
<td>5.89</td>
<td>0.608</td>
<td>56.4</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Considering the device without MoO3, both RR-P3HT and PCBM are in direct contact with Au. It is possible for PCBM to transfer electrons to the Au electrode, thereby compromising device efficiency. However, incorporating a MoO3 layer introduces two additional interfaces (RR-P3HT:PCBM/MoO3 and MoO3/Au). The highest occupied molecular orbital (HOMO) level of MoO3 is −5.3 eV [Fig. 1(b)], which is very close to the HOMO level of RR-P3HT (−5.2 eV). The energy level match reveals that MoO3 can extract holes from the active layer. The lowest unoccupied molecular orbital level of MoO3 is −2.3 eV, which is higher than that of PCBM (−3.7 eV). Inserting a MoO3 layer will prevent electrons from transferring from PCBM to Au. Thus, the MoO3 interlayer effectively prevents the recombination of the charge carriers at the organic/Au interface. The slope of the $J$-$V$ curve of the device with MoO3 near 0 V under illumination [Fig. 2(a)] is lower than that of the device without MoO3, leading to an increase in FF. The FF for the device with MoO3 is FF=0.586 compared to a value of FF=0.382 for the device without MoO3.

Similar to devices with Au top electrode, the MoO3 interlayer is also critical to those with Ag or Al top electrode. By incorporating a MoO3 buffer layer, the PCE increases from 0.07% to 2.57% for Ag devices [see Fig. 2(b) and Table I] and from 0.14% to 2.02% for Al devices [see Fig. 2(c) and Table I]. At the same time, both $J_{sc}$ and $V_{oc}$ have a significant improvement. All devices with different top electrodes exhibit a PCE of ~2%. The PCE of Ag devices is 0.57% larger than that of Au devices. The possible explanation for this phenomenon is that a small fraction incident light is absorbed by the thermally evaporated Au electrode in Au devices. At the same time, Ag has a higher reflectivity in the visible region compared with Au. The enhanced reflectivity of Ag makes the photocurrent of the devices slightly higher and hence to have a higher PCE. Owing to the oxidation of Al by O2 in air and the resultant increase of series resistance, Al devices exhibit a lower PCE than Ag devices although Al and Ag have comparable reflectivity in the visible region.

It is observable that for the simple devices, ITO/nc-TiO2/RR-P3HT:PCBM/top electrode, $V_{oc}$ appears to have considerable differences. $V_{oc}$ are 0.463, 0.085, and 0.3 V, respectively, for the simple devices with Au, Ag, and Al as top electrodes, which do not run parallel to the difference of the work function of these metals [Au (−5.0 eV), Ag (−4.6 eV), and Al (−4.28 eV) (Ref. 18)]. Meanwhile, the low $V_{oc}$ results in poor performance in the simple devices. However, by introducing a thin MoO3 layer, devices with different metal electrodes exhibit a $V_{oc}$ of ~0.61 V with a variation of 20 mV, leading to a significant improvement in device performance. This suggests that $V_{oc}$ of device with MoO3 is independent of the work function of the top electrodes.

It is known that $V_{oc}$ is the voltage where the applied bias equals the built-in potential in an ideal diode. In Au or Ag devices, 1 nm MoO3 is thick enough to increase the built-in potential. However, $V_{oc}$ does not reach to ~0.61 V in Al devices until the thickness of MoO3 is 5 nm. Prior to metal deposition, the fabrication conditions for devices are held constant. The sole differential is the interface between MoO3 and electrode metals. We deduce that the chemical reaction between MoO3 and Al occurs during thermal evaporation of Al. However, contact of MoO3 with Au or Ag is physical.
MoO$_3$ on Al substrate. In the fitting of complex signal by Swati et al. indicated by the additional spectral lines positioned at 231.15 eV, which are assigned to the Mo 3d$_{5/2}$ and 3d$_{3/2}$ spin-orbit components, respectively. However, compared with MoO$_3$ on Si, Au, and Ag substrates, both Mo 3d$_{5/2}$ and 3d$_{3/2}$ peaks for MoO$_3$ on Al substrate shift obviously toward a lower binding energy and the full width at half maximum (FWHM) broadens.

In order to investigate the interface between MoO$_3$ and different metals, XPS is introduced. Figure 3(a) shows Mo 3d spectra from XPS study of 5 nm MoO$_3$ film thermally evaporated on different substrates. For MoO$_3$ on Si, Au, and Ag substrates, the Mo 3d spectra show the presence of two well resolved spectral lines at 232.60–232.75 and 235.65–235.75 eV, which are assigned to the Mo 3d$_{5/2}$ and 3d$_{3/2}$ spin-orbit components, respectively. However, compared with MoO$_3$ on Si, Au, and Ag substrates, both Mo 3d$_{5/2}$ and 3d$_{3/2}$ peaks for MoO$_3$ on Al substrate shift obviously toward a lower binding energy and the full width at half maximum (FWHM) broadens.

Figure 3(b) shows XPS peak fitting of Mo 3d spectra for MoO$_3$ on Al substrate. In the fitting of complex signal shapes, the main constrain is that the binding energy difference $\Delta E_B$ of Mo 3d$_{5/2}$ and 3d$_{3/2}$ is 3.1±0.1 eV, which ensures that the results have the corresponding physical senses. The peak fitting results indicate that some of the MoO$_3$ present on the Al surface is transformed to MoO$_2$ as indicated by the additional spectral lines positioned at 231.15 and 234.25 eV. These double peaks represent Mo$^{4+}$ in MoO$_2$. Thus we infer that partial MoO$_3$ can be reduced to MoO$_2$ by Al during thermal evaporation of Al. This is consistent with the thermal analysis of Al–MoO$_3$ nanocomposites by Swati et al. MoO$_2$ is a conductor, which would not affect the charge transport in Al devices. As a result, it needs a thicker MoO$_3$ layer in Al devices than in Au or Ag devices due to the chemical reaction between MoO$_3$ and Al.

In summary, we have introduced an efficient structure of inverted PSCs with nc-TiO$_2$ as an electron selective layer by inserting a MoO$_3$ layer between the active layer and top electrode. The performances of structurally identical PSCs with different top electrodes (Ag, Au, and Al) are investigated and compared. All devices exhibit a PCE of ~2% under 100 mW/cm$^2$ white light illumination. The MoO$_3$ interlayer effectively prevents the recombination of charge carriers at the organic/top electrode interface, leading to the improvement of $J_{sc}$, $V_{oc}$, and FF. Devices with different top electrodes exhibit a $V_{oc}$ of ~0.61 V. It is suggested that $V_{oc}$ is irrespective of the work function of top electrode. XPS research indicates that the contact between MoO$_3$ and Al is different from that between MoO$_3$ and Au (or Ag). Due to chemical reaction between MoO$_3$ and Al, the thickness of the MoO$_3$ layer is thicker in Al devices than in Au or Ag devices when $V_{oc}$ reaches up to ~0.61 V.

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16. Note that the power conversion efficiencies of our devices are lower than the ones reported in the literature because of all devices being fabricated and tested in ambient atmosphere. However, the blended active layer was baked in low vacuum (vacuum oven).