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<td>Author(s)</td>
<td>Li, X; Choy, WCH; Xie, F; Zhang, S; Hou, J</td>
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Room-Temperature Solution-Processed Molybdenum Oxide as Hole Transport Layer with Ag Nanoparticles for Highly Efficient Inverted Organic Solar Cells

Xinchen Li, Wallace C. H. Choy, Fengxian Xie, Shaoqing Zhang and Jianhui Hou

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While metal oxide film are typically formed by high-temperature and sputtering processes, we report an approach with the features of room-temperature, water-free and solution-based process for forming molybdenum oxide (MoOx) film of inverted organic solar cells (OSCs) by proposing vacuum treatment at room temperature and selecting appropriate solvent. Remarkably, our results indicate that the vacuum treatment can introduce oxygen vacancies in the molybdenum oxide film and modify its work function for functioning as an efficient hole transport layer. To further improve OSCs performances, silver nanoparticle-molybdenum oxide (Ag NP-MoOx) composite film is demonstrated by the introduction of Ag nanoparticles in the solution. Evidences and explanations confirm that OSCs performance enhancement is mainly due to the improvement of the electrical properties of Ag NP-MoOx composite film. With the optimized composited film, inverted OSCs with power conversion efficiency (PCE) of 7.94% are achieved. Through the demonstration of high performance inverted OSCs with different polymer materials, the water-free, room-temperature and solution-processed MoOx can contribute to the evolution of high performance OSCs such as inverted and tandem OSCs and other optoelectronic devices.

1. Introduction

In organic optoelectronic devices such as organic light emitting diodes (OLEDs) and organic solar cells (OSCs), metal oxides have been widely used as charge transport layers due to the universal energy-level alignment trends between the active layer and the electrodes. For hole transport layer, one of the most promising metal oxide materials is molybdenum oxide (MoOx), which has good alignment of energy-level and more stability as compared to other commonly used hole transport materials such as acidic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Besides the typical methods such as sputtering and thermally evaporation, solution processed MoOx has drawn great attention for applications in different structures of OSCs, which acts as the interfacial layer between the anode and the active layer. However, there are a number of challenges in processing solution MoOx film on the active layer of inverted OSCS at room-temperature. First, instead of the commonly used water and the electrodes, the conventional precursor methods for forming MoOx film with good hole transport properties usually require thermal annealing process. Unfortunately, many polymer materials cannot sustain such high annealing temperature, which would subsequently cause inherent modifications in crystallization or molecular scission and thus deteriorate device performances. Recently, metal oxides from low-temperature solution-process methods used as hole transport layer for inverted OSCs have been reported by others. However, the device performances of these OSCs are not yet comparable to those of inverted OSCs using other efficient hole transport layers. Meanwhile, there is not clear study on metal nanoparticle-metal oxide composites by room-temperature and solution-based process as efficient hole transport layer in organic optoelectronic devices.

In this work, a water-free, room-temperature and solution-processed approach to form MoOx film is demonstrated. The film can be used as an efficient hole transport layer of inverted OSCs. We propose to (1) introduce vacuum treatment to modify the work function of solution-processed MoOx film to form efficient hole transport layer without any annealing process. Meanwhile, for the practical application of the film and elimination of water induced degradation, we (2) target for water-free in forming the film. In order to favor the MoOx film formation from hydrogen molybdenum bronzes, we (3) dedicate to select a solvent with low boiling point for our solution process. Isopropanol which has low boiling point and does not degrade the underneath active polymer layer is adopted. The inverted OSCs using our solution-processed MoOx have comparable performances as those using thermally evaporated MoOx film. Moreover, we can (4) further improve the electrical properties of the MoOx hole transport layer by introducing silver nanoparticles (Ag NPs) for forming Ag NP-MoOx composite film which is difficult to be realized by conventional evaporation approaches. The analyses...
show that the proposed vacuum approach can create oxygen vacancies in the film and thus modify the work function of MoOx film for favoring its hole transport properties in OSCs. By further introducing the Ag NP-MoOx composite interfacial layer in the inverted structure OSCs, average power conversion efficiency (PCE) of 7.94% is achieved. Consequently, through the demonstration of high performance inverted OSCs with different polymer materials, the water-free, room-temperature and solution-processed MoOx efficient hole transport layer can contribute to the evolution of high performance OSCs such as inverted and tandem OSCs and other optoelectronic devices.

2. Results and Discussion

To form molybdenum oxide film from proper solution approach, we oxidize molybdenum powder by using hydrogen peroxide in ethanol. Importantly, ethanol is used to control the oxidation rate of molybdenum by hydrogen peroxide to obtain hydrogen molybdenum bronze solution as described in experimental section. The synthesized hydrogen molybdenum bronze solution is dried and dissolved into IPA without any water. After spin-coating the solution directly onto the active layer of OSC, the sample is treated at room temperature in 10 Pa vacuum chamber for 10 min. Finally inverted OSCs are completed with thermal annealing, achieving good hole transport properties, and realizing suitable work function. Here, with the strategic selection of IPA (i.e. low boiling point and not degrading the polymer underneath active layer), we propose to use vacuum treatment.

To investigate the reason of the room-temperature solution-processed MoOx film working as an efficient hole transport layer on the active layer of inverted OSCs, the properties of MoOx thin film formed before and after the vacuum treatment have been studied. The energy band structure of the MoOx film is investigated by ultraviolet photoelectron spectroscopy (UPS) measurement. The UPS spectra of the MoOx film after 10 minutes of vacuum treatment at 10 Pa and control MoOx film without the vacuum treatment are shown in Fig. 2. The results illustrate that MoOx thin film with the vacuum treatment has clear shift at Fermi edge and secondary-electron cut-off as compared with the control film, depending on Fermi Level (E_F) shift of MoOx thin film. The energy difference between conduction band (CB) and valance band (VB), i.e. the optical band gap (E_g), can be determined from the extrapolated line of the linear part of photon energy curve in the plot of (αhν)^1/2 and hν (see ESI Fig. S2). E_g is the intersection of the extrapolated performance, while our approach have the features of water-free, room-temperature, and solution based process. As shown in Table 1 and Fig. 1, the PCE of the optimized solution-processed MoOx inverted OSCs using robust poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) active layer is 3.84% with the comparison to 3.87% of the control devices. The structure of inverted OSCs is ITO/TiO2/P3HT:PCBM/ MoOx/Ag. Their short-circuit current density (J_sc) are 9.34 mA cm^-2 (solution-processed MoOx) and 9.44 mA cm^-2 (evaporated MoO3). The fill factors (FF) are 65.19% (solution) and 64.79% (evaporated), with the same open-circuit voltage (V_oc) 0.63 V. By incorporating Ag NPs to form the Ag NP-MoOx composite film, the device performances of the inverted OSCs can be further enhanced and perform better than control devices, as will be described later.

2.1. Contributions of the vacuum treatment

The challenges to make the solution-based process MoOx at room temperature functioning as highly efficient hole transport layer for inverted OSCs lie at (1) forming the MoOx layer without any thermal annealing, (2) achieving good hole transport properties, and (3) realizing suitable work function. Here, with the strategic selection of IPA (i.e. low boiling point and not degrading the underneath active layer), we propose to use vacuum treatment.

Table 1 P3HT:PCBM OSCs performances of thermally evaporated MoO3 and solution-processed MoOx film.

<table>
<thead>
<tr>
<th>Devices</th>
<th>J_sc(mA cm⁻²)</th>
<th>V_oc(V)</th>
<th>FF(%)</th>
<th>PCE(%)</th>
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<tr>
<td>Evap. MoO3</td>
<td>9.44±0.037</td>
<td>0.63±0.007</td>
<td>64.79±0.372</td>
<td>3.87±0.038</td>
</tr>
<tr>
<td>Solution MoOx</td>
<td>9.34±0.163</td>
<td>0.63±0.008</td>
<td>65.19±0.951</td>
<td>3.84±0.065</td>
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Fig. 1 J-V characteristics of P3HT:PCBM OSCs with evaporated MoO3 (black cube) and solution-processed MoOx (red circle). (Inset: Dark current density-Voltage (J dark-V) characteristics of OSCs with thermally evaporated MoO3 (black cube) and solution-processed MoOx (red circle).)
Fig. 3 (a) Schematic band diagram of inverted OSCs with the structure of ITO/TiO$_2$/P3HT:PCBM/MoO$_x$/Ag. (b) Energy-level diagrams in details of no treatment MoO$_x$ (left) and vacuum treatment MoO$_x$ (right).

Fig. 4 XPS results of (a) MoO$_x$ layer with no treatment and (b) MoO$_x$ layer with vacuum treatment. The black dot lines are experimental XPS results. The solid lines are decomposed XPS data results.

MoO$_x$ film is mainly featured in two 3d doublet Gaussian peaks. They are centered at 232.9 eV and 236.1 eV and close to the 3d5/2 and 3d3/2 Mo$^{6+}$ oxidation states with values of 232.8 eV and 235.9 eV respectively.31-33 Interestingly, the vacuum treated MoO$_x$ film not only shows major Gaussian peaks at 232.8 eV and 236 eV, but also shows clear minor Gaussian peaks at 231.7 eV and 235 eV. The major and minor peaks separately reveal 3d doublet of Mo$^{6+}$ and Mo$^{5+}$ oxidation states. In addition, the atomic concentration ratio of the two states is nearly 5:1. These results indicate that the vacuum treatment offers oxygen vacancies into the molybdenum oxide film.34, 35 The introduction of vacancies in MoO$_x$ film can form complex aggregate centers, which will modify the Fermi level and enhance the charge transfer in the thin film,36, 37 as confirmed by the band structure and work function determined by UPS. Consequently, it is remarkable to note that the vacuum treatment can functionalize the MoO$_x$ film into an efficient hole transport layer of OSCs.

The performances of inverted OSCs using the solution-processed MoO$_x$ thin film as hole transport layer have been investigated with device structure of ITO/TiO$_2$/P3HT:PCBM/MoO$_x$/Ag. As compared to the optimized control inverted OSCs using thermally evaporated molybdenum oxide, the optimized solution processed MoO$_x$ device shows similar performance. In fact, the inverted OSC with solution-processed MoO$_x$ has better diode characteristics and less leakage current under reverse bias voltage (see the inset of Fig. 1). The incident photon-to-current conversion efficiency (IPCE) spectra of the inverted OSCs with thermally evaporated molybdenum oxide and solution processed MoO$_x$ are also similar as shown in ESI Fig. S3. Beside the polymer blend of P3HT:PCBM, the inverted OSCs made from high performance low band gap material of poly[(4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl]-alt-[2-(2'-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyl]] (PBDTTT-C-T)38, 39 blended with [6,6]-phenyl C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) are also investigated. The J-V and dark current density (J$_{dark}$)-V characteristics show similar characteristics as compared with the low band gap inverted OSCs.
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Using thermally evaporated molybdenum oxide. With our solution-processed MoOx film, the PCE of OSCs using low band gap material can reach 7.15%. Consequently, through the vacuum treatment, the water-free, room-temperature and solution-process MoOx layer can function as an efficient hole transport layer in various inverted OSCs made from different polymer blends including robust P3HT:PCBM and low band gap polymer blend of PBDTTT-C-T:PC71BM. The results illustrate that our vacuum approach highly efficient hole transport MoOx film can be suitable for a variety of donor materials in OSCs with its universal energy-level alignment ability.

2.2. Ag NP-MoOx composite film for high performance inverted OSCs

To achieve further performance improvement of our room-temperature solution-processed MoOx, we introduce Ag NPs into the solution to form Ag NP-MoOx composite film. Since the optimized solution-processed MoOx thin film is about 8 nm, we would like to have the Ag NPs with size (4 nm) smaller than the thickness of the MoOx film. The device performances of P3HT:PCBM and PBDTTT-C-T:PC71BM inverted OSCs with different concentrations of Ag NPs are shown in Table 2 and Table 3, and their J-V characteristics are shown in Fig. 5a (P3HT:PCBM) and Fig. 5b (PBDTTT-C-T:PC71BM). The Jdark-V characteristics are shown in ESI Fig. S4 (P3HT:PCBM) and Fig. S5 (PBDTTT-C-T:PC71BM) respectively. The optimized concentration of Ag NPs in the composites solution is 0.125 mg ml⁻¹ for both P3HT:PCBM and PBDTTT-C-T:PC71BM inverted OSCs. The results show that JSC and FF are significantly increased while VOC remains almost unchanged. As a result, by introducing the Ag NPs with the optimized concentration into the solution-processed MoOx, PCE of P3HT:PCBM based OSCs and PBDTTT-C-T:PC71BM based OSCs can be increased from 3.84% (no Ag NPs) to 4.37% and from 7.15% (no Ag NPs) to 7.94%, respectively.

By using the polymer blend of P3HT:PCBM, we investigate the reasons of the performance enhancement. With the incorporation of Ag NPs, the optical properties of the MoOx film and OSCs are firstly studied. Recently, plasmonic resonances due to metal NPs have been widely investigated for enhancing the optical absorption of OSCs. Fig. 6a and Fig. 6b successively reveal the transmission spectra of MoOx film and the absorption spectra of the active layer with a top layer of MoOx film. The average diameter of the Ag NPs is 4 nm, which is measured by Transmission electron microscope (TEM) and captured in the inset of Fig. 6b. Nevertheless, the incorporation of Ag NPs in the...
Fig. 6 (a) Transmission spectra of pristine MoO$_x$ film (black line) and Ag NP-MoO$_x$ composite film (red line). (b) Absorption spectra of P3HT:PCBM film (black line), P3HT:PCBM coated with pristine MoO$_x$ film (red line), P3HT:PCBM coated with Ag NP-MoO$_x$ composite film (blue line). (Inset: TEM result of 4 nm Ag NPs, the white scale bar is 5 nm in left bottom.)

Fig. 7 IPCE spectra (left axis) of P3HT:PCBM OSCs with pristine MoO$_x$ and Ag NP-MoO$_x$ composite layer and the enhancement factor (right axis) in the core absorption region from 350 nm to 650 nm, i.e., (IPCE of OSCs with Ag NP-MoO$_x$ composite)/(IPCE of OSCs with pristine MoO$_x$).

Ag NP-MoO$_x$ composite film does not show obvious change in the transmission and absorption. We did not observe clear optical enhancement in the active layer of the inverted OSCs (i.e. no clear absorption enhancement due to plasmonic resonances). Consequently, optical enhancement is not likely a contributing factor to the improvement of device performance.

Interestingly, there is a wide wavelength band increment of IPCE as shown in Fig. 7, covering the core absorption region from 350 nm to 650 nm of P3HT:PCBM based OSCs. In addition, no clear peak in the enhancement factor spectrum, i.e. (IPCE of OSCs with Ag NP-MoO$_x$ composite)/(IPCE of OSCs with pristine MoO$_x$), can be observed in the core absorption region. The wideband enhancement suggests that the increase of $J_{SC}$, FF and PCE are contributed by the improved electrical properties due to the incorporation of Ag NPs in the Ag NP-MoO$_x$ composite interfacial layer. Another IPCE spectra of OSCs using low band gap material as active layer and solution-processed Ag NP-MoO$_x$ composite film also show wideband enhancement as shown in ESI Fig. S6.

To further verify this claim, we investigate hole dominated devices with the structure of ITO/PEDOT:PSS/P3HT:PCBM/MoO$_x$/Ag with and without Ag NPs in the MoO$_x$ film. As shown in ESI Fig. S7, the current of the hole dominated device with Ag NP-MoO$_x$ composite film is much larger than the pristine solution-processed MoO$_x$ and evaporated MoO$_3$ film. This indicates the holes are more efficiently extracted to anode by using the Ag NP-MoO$_x$ composite as the hole transport layer. Another evidence can be obtained from transient photo-generated voltage (TPV) measurement. The TPV measured using the excitation source of 532 nm picoseconds laser pulse shows that the transient voltage of the device with Ag NP-MoO$_x$ composite film decays faster than that of those devices without Ag NPs, which are shown in ESI Fig. S8. This indicates that the carrier will transfer faster through the Ag NP-MoO$_x$ composite film to anode as compared to that of the pristine MoO$_x$ and evaporated MoO$_3$ film. It should be noted that the hole dominated device and TPV measurement of the OSCs with the solution-processed MoO$_x$ film overlap with that of the evaporated MoO$_3$ film. This re-confirms that the room-temperature solution-processed MoO$_x$ film functions as good as the evaporated MoO$_x$ film as described before. Consequently, our results show that the room-temperature solution-process MoO$_x$ composite film can clearly work as efficient hole transport layer and improve the PCE of inverted OSCs. We also demonstrate that the improvement is mainly due to the enhanced electrical properties of the hole transport layer by introducing Ag NPs to form the Ag NP-MoO$_x$ composite film.

3. Conclusion

In conclusion, a new approach with the features of water-free, room-temperature and solution-based process MoO$_x$ film is proposed and demonstrated as efficient hole transport layer for inverted OSCs. Interestingly, the UPS and XPS results indicate that oxygen vacancies can be introduced in the molybdenum
oxide thin film by vacuum treatment, which functionalize the MoOx film to be an efficient hole transport layer. Remarkably, further improvement of the electrical properties of the MoOx film is achieved by incorporating Ag NPs to form Ag NP-MoOx composite film. Inverted OSCs with PCE of 7.94% are achieved by using the Ag NP-MoOx composite film as hole transport layer. Consequently, through the demonstration of high performance inverted OSCs with different polymer materials, the water-free, room-temperature and solution-processed MoOx film can function as efficient hole transport layer for high performance organic optoelectronic devices, and with the further potential contribution to OLEDs and OSCs with inverted and tandem structured devices.

4. Experimental Section

4.1 Molybdenum bronze solution synthesis and preparation

Molybdenum powder was purchased from Aladdin. First 0.2 g metal powder was dispersed into 20 ml ethanol with ultrasound bath. Then solution was mixed with 0.7 ml hydrogen peroxide (30%). Ethanol was used to control the reaction rate between metal powders and hydrogen peroxide. During the reaction, ethanol will provide e- and H+ for the reduction of the metal peroxide, meanwhile H+ can be inserted into the metal oxide lattice to form metal oxide bronzes. After 20 hour reaction, molybdenum oxide solution turned from gray to blue attributed to H+ insertion into the metal oxide lattice and then the reduction of metal element (Mo6+) into sub-state (Mo5+), forming hydrogen molybdenum bronzes (H2MoOx). Finally, the remained solvent was exhausted in dry box, after which the obtained molybdenum bronze was dissolved into IPA with a concentration of 1 mg ml⁻¹.

4.2 Inverted OSCs device fabrication

The device structure of inverted OSCs was ITO/TiO2/polymer blend active layer/MoOx/Ag. The sheet resistance of the ITO was 15 Ω sq⁻¹. The glass substrate was cleaned with detergent, acetone and ethanol, and then treated under UV-ozone for 15 min. The TiO2 film with a thickness of ~20 nm was made by spin-coating TiO2 nanocrystals onto the ITO followed by 150 °C baking for 10 min. TiO2 nanocrystals solution was prepared by the nonaqueous method in previously reported paper. In our inverted OSCs, the active layer was the robust polymer blend of P3HT:PCBM and small band material of PBDTTT-C-T:PC71BM. The P3HT:PCBM solution (20 mg ml⁻¹ : 20 mg ml⁻¹, in 1,2-dichlorobenzene) was filtered and spin-coated. The sample was solvent annealed for 1 hour and annealed at 120 °C for 10 minutes to form a film with a thickness of ~220 nm. For small band gap materials, PBDTTT-C-T:PC71BM solution (10 mg ml⁻¹ : 18 mg ml⁻¹, in chlorobenzene, with 3% volume ratio 1,8-diiodooctane (DIO)) was filtered and spin-coated to form a film with a thickness of ~100 nm. After spin-coating the active layer, it was put in the vacuum chamber of ~10 Pa for 1 hour to remove the DIO. Our newly synthesized molybdenum bronze solution was spin-coated onto the active layer with an optimized 3000 rpm. Then the sample was quickly put into 10 Pa vacuum chamber for 10 min treatment. The control device was fabricated by using thermally evaporated molybdenum oxide layer with an optimized thickness of 10 nm.

Silver anode of thickness 100 nm was finally evaporated onto the interfacial layer with a mask of 0.045 cm² area. In fabricating the hole dominated devices with the structure ITO/PEDOT:PSS(30 nm)/P3HT:PCBM/MoOx/Ag, the same fabrication process of active layer as in the inverted structure OSCs has been used and the active layers thickness ~220 nm for all hole dominated devices.

4.3 Synthesis of Ag NPs and Ag NP-MoOx composite film

To improve electrical properties of our solution processed MoOx film, Ag NPs were incorporated into molybdenum bronze solution. Ag NPs were synthesized by mixing 1 mmol Ag acetate, 3 mmol oleylamine, 3 mmol oleic acid, 20 ml phenyl ether and steary alcohol. The mixture was magnetically stirred and dispersed under nitrogen ambiance at 80 °C. Heat the mixture in 195 °C for 1 hour. After cooling to room temperature, it was added with 50 ml ethanol and centrifuged to precipitate the Ag NPs. The precipitated Ag NPs can be well dispersed into non-polar solvent hexane. Then the Ag NPs was further dispersed into IPA with a concentration of 0.5 mg ml⁻¹. The Ag NPs synthesized by this method had an average diameter of 4 nm, which can be verified by the TEM result. To optimize the concentration of Ag NPs, molybdenum bronze solution was first concentrated to 2 mg ml⁻¹, after which, it was mixed with the same volume of different diluted concentration of Ag NPs solution.

4.4 Measurement and characterization

UPS measurement was taken by He I discharge lamp (Kratos Analytical) with energy of 21.22 eV and a resolution of 0.15 eV. A -10 V bias was added on samples to enhance the measured signals. XPS measurement was performed using Physical Electronic 5600 multi-technique system (monochromatic Al Kα X-ray source). The J-V characteristics were measured using ABET AM 1.5 G solar simulator with a light intensity of 100 mW cm⁻² and a Keithley 2635 source meter. TEM was measured by FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope. The thickness of film was measured by ellipsometer.

The SEM was measured by LEO 1530 FEG Scanning Electron Microscope.

Acknowledgements

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Notes and references

* Corresponding author: chchoy@eee.hku.hk (Choy)

† Electronic Supplementary Information (ESI) available: [Additional information details about optimized thickness of solution-processed MoOx, interfacial layer, optical band gap, IPCE of compared OSCs using P3HT:PCBM polymer blends with different interfacial layers, Jdark–V](#)
characteristics of OSCs with Ag NP-MoO₃ composites, IPCE of compared OSCs using small band gap material polymer blends with different interfacial layers, J-V characteristics of hole dominated devices with different interfacial layers, and SEM images of pristine MoO₃ film and Ag NP-MoO₃ composite film). See DOI: 10.1039/b000000x/