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Room-temperature solution-processed molybdenum oxide as a hole transport layer with Ag nanoparticles for highly efficient inverted organic solar cells†

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While metal oxide films are typically formed by high-temperature and sputtering processes, we report an approach with the features of a room-temperature, water-free and solution-based process for the formation of a molybdenum oxide (MoO_x) film for inverted organic solar cells (OSCs) by proposing a vacuum treatment at room temperature and selecting an 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 OSC performances, a silver nanoparticle–molybdenum oxide (Ag NP– MoO_x) composite film is prepared by the introduction of Ag nanoparticles into the solution. Evidence and explanations confirm that OSC performance enhancement is mainly due to the improvement of the electrical properties of the Ag NP– MoO_x composite film. With the optimized composite film, inverted OSCs with a 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 MoO_x can contribute to the evolution of high performance OSCs such as inverted and tandem OSCs and other optoelectronic devices.

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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 their universal energy-level alignment trends between the active layer and the electrodes.^{1–8} For hole transport layers, one of the most promising metal oxide materials is molybdenum oxide (MoO_x), which has good alignment of energy-levels and more stability as compared to other commonly used hole transport materials such as acidic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).^{9–11}

Besides the typical methods such as sputtering and thermal evaporation, solution processed MoO_x has drawn great attention for its applications in different structures of OSCs, which

acts as the interfacial layer between the anode and the active layer.^{12,13} However, there are a number of challenges in processing the solution MoO_x film on the active layer of inverted OSCs at room-temperature. First, instead of the commonly used water^{11,14} and organic solvents such as methanol,^{15,16} xylene,¹⁷ we select isopropanol (IPA) as the solvent of MoO_x solution, which has negligible influence on the active layer.^{18–21} Second, the widely used precursor methods^{15,22} for formation of the MoO_x film with good hole transport properties usually require a thermal annealing process. Unfortunately, many polymer materials cannot sustain such high annealing temperature, which would subsequently cause inherent modifications in crystallization or molecular scission,^{23–25} and thus deteriorate device performances. Recently, metal oxides from low-temperature solution-process methods used as hole transport layers for inverted OSCs have been reported by others.^{21,26} 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 no clear study on metal nanoparticle–metal oxide composites as efficient hole transport layers in organic optoelectronic devices by a room-temperature and solution-based process.

In this work, a water-free, room-temperature and solution-processed approach to form a MoO_x film is demonstrated. The film can be used as an efficient hole transport layer for inverted OSCs. We propose to (1) introduce vacuum treatment to modify the work function of a solution-processed MoO_x film to form an

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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 the formation of the film. In order to favor the MoO_x film formation from hydrogen molybdenum bronzes,²⁷ we (3) decided 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.²¹ The inverted OSCs using our solution-processed MoO_x have comparable performances to those using thermally evaporated MoO_3 films. Moreover, we can (4) further improve the electrical properties of the MoO_x hole transport layer by introducing silver nanoparticles (Ag NPs) for formation of the Ag NP- MoO_x 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 the MoO_x film for favoring its hole transport properties in OSCs. By further introducing the Ag NP- MoO_x composite interfacial layer in the inverted structure OSCs, an 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 MoO_x as an 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 the molybdenum oxide film by a 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 the Experimental section. The synthesized hydrogen molybdenum bronze solution is dried and dissolved in IPA without any water. After spin-coating the solution directly onto the active layer of OSCs, the sample is treated at room temperature in a 10 Pa vacuum chamber for 10 min. Finally, inverted OSCs are completed with a thermal deposit silver anode. More details on the synthesis and film formation can be found in the Experimental section. The optimized thickness of the MoO_x film for inverted OSCs is 8 nm through the device performances, which can be found in ESI Fig. S1.†

Inverted structure OSCs with their intrinsic stability and easy fabrication method are commonly formed by using thermally evaporated MoO_3 as a hole transport layer.^{28,29} Compared to the control devices with thermally evaporated MoO_3 , the solar cells with the solution-processed MoO_x thin film have similar device performances, while our approach has the features of a water-free, room-temperature, and solution based process. As shown in Table 1 and Fig. 1, the PCE of the optimized solution-processed MoO_x inverted OSCs using a robust poly(3-hexylthiophene):[6,6]-phenyl C_{61} -butyric acid methyl ester (P3HT:PCBM) active layer is 3.84% in comparison to 3.87% of the control devices. The structure of inverted OSCs is ITO/ TiO_2 /P3HT:PCBM/ MoO_x /Ag. Their short-circuit current densities (J_{SC}) are 9.34 mA cm^{-2}

Table 1 P3HT:PCBM OSC performances of a thermally evaporated MoO_3 film and a solution-processed MoO_x film

Devices	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
Evap. MoO_3	9.44 ± 0.037	0.63 ± 0.007	64.79 ± 0.372	3.87 ± 0.038
Solution MoO_x	9.34 ± 0.163	0.63 ± 0.008	65.19 ± 0.951	3.84 ± 0.065

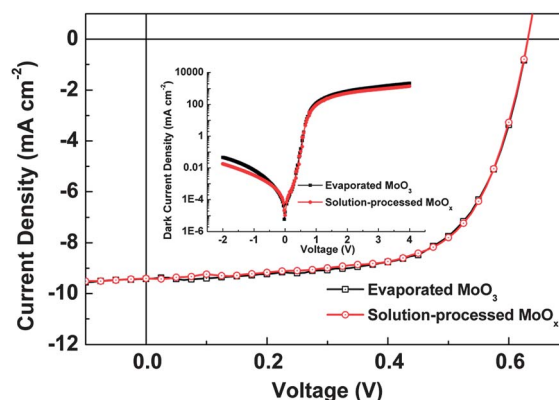


Fig. 1 J - V characteristics of P3HT:PCBM OSCs with evaporated MoO_3 (black cubes) and solution-processed MoO_x (red circles). (Inset: dark current density-voltage (J_{dark} - V) characteristics of OSCs with thermally evaporated MoO_3 (black cubes) and solution-processed MoO_x (red circles)).

(solution-processed MoO_x) and 9.44 mA cm^{-2} (evaporated MoO_3). The fill factors (FF) are 65.19% (solution) and 64.79% (evaporated), with the same open-circuit voltage (V_{OC}) of 0.63 V. By incorporating Ag NPs to form the Ag NP- MoO_x composite film, the device performances of the inverted OSCs can be further enhanced and perform better than those of the control devices, as will be described later.

2.1 Contributions of the vacuum treatment

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

To investigate the reason for the room-temperature solution-processed MoO_x film working as an efficient hole transport layer on the active layer of inverted OSCs, the properties of the MoO_x thin film formed before and after the vacuum treatment have been studied. The energy band structure of the MoO_x film was investigated by ultraviolet photoelectron spectroscopy (UPS) measurement. The UPS spectra of the MoO_x film after 10 minutes of vacuum treatment at 10 Pa and the control MoO_x film without the vacuum treatment are shown in Fig. 2. The results illustrate that the MoO_x thin film with the vacuum treatment has a clear shift at the Fermi edge and the

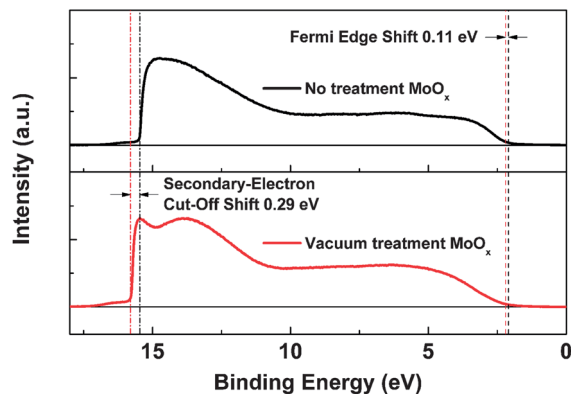


Fig. 2 UPS spectra of no vacuum treatment MoO_x film and vacuum treatment MoO_x film. The shifts of the Fermi edge and the secondary-electron cut-off are 0.11 eV and 0.29 eV, respectively.

secondary-electron cut-off as compared with the control film, depending on the Fermi level (E_F) shift of the MoO_x thin film.¹⁵ The energy difference between the conduction band (CB) and the valence band (VB), *i.e.* the optical band gap (E_{opt}), can be determined from the extrapolated line of the linear part of the photon energy curve in the plot of $(\alpha h\nu)^{1/2}$ and $h\nu$ (see ESI, Fig. S2†). E_{opt} is the intersection of the extrapolated line and the energy axis ($h\nu$). The energy-level of CB and VB can be calculated by following the description elsewhere.³⁰ So the schematic band diagram of the bulk heterojunction OSCs using blend P3HT:PCBM is shown in Fig. 3a. Details of the energy-level shift of the MoO_x films with and without vacuum treatment can be found in Fig. 3b. From the analysis, it indicates that the work function of the MoO_x film can be significantly modified from the original 5.75 eV to 5.43 eV by vacuum treatment, which is more suitable for applying as a hole transport layer for OSCs.

In order to determine the origin of the work function change of the MoO_x film due to the vacuum treatment, high-resolution X-ray photoelectron spectroscopy (XPS)

measurement is used to study the chemical characteristics and stoichiometry of the MoO_x films with and without vacuum treatment. Compared with the untreated MoO_x film, Fig. 4 shows that the vacuum treated film has different XPS peaks. According to the standard peak value of carbon 284.6 ± 0.1 eV, Mo peaks can indicate the stoichiometric composition of the MoO_x film. As shown in Fig. 4, the untreated 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 3d_{5/2} and 3d_{3/2} 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 a 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 the MoO_x film can form complex aggregate centers, which will modify the Fermi level and enhance the

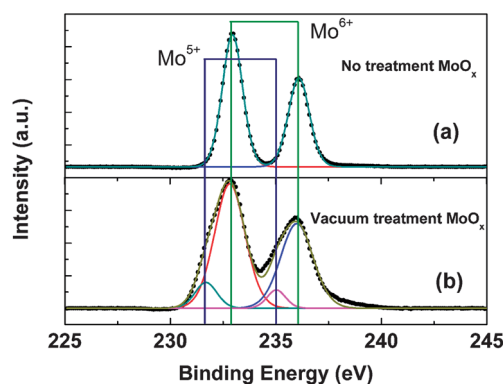


Fig. 4 XPS results of the (a) MoO_x layer with no treatment and (b) MoO_x layer with vacuum treatment. The black dot lines are experimental XPS results. The solid lines are decomposed XPS data results.

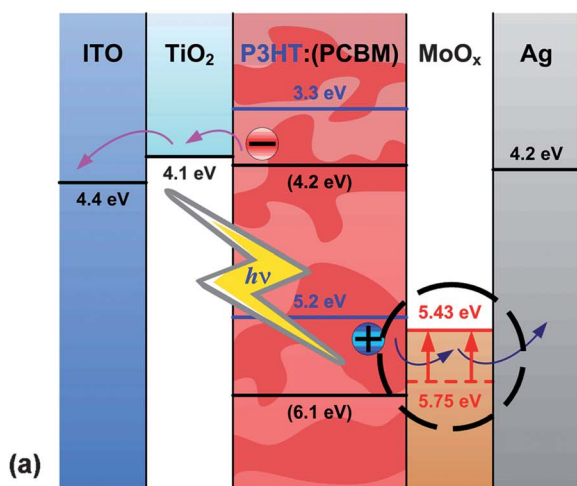
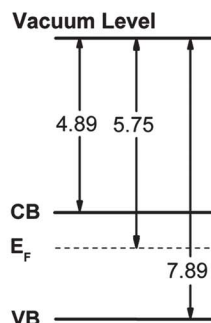
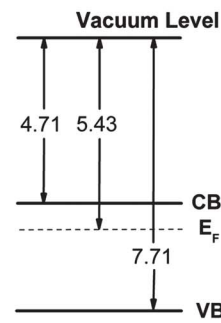


Fig. 3 (a) Schematic band diagram of inverted OSCs with the structure of ITO/ TiO_2 /P3HT:PCBM/ MoO_x /Ag. (b) Energy-level diagrams in detail of no treatment MoO_x (left) and vacuum treatment MoO_x (right).

Unit: eV



(b) No treatment MoO_x



Vacuum treatment MoO_x

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 as an efficient hole transport layer for OSCs.

The performances of inverted OSCs using the solution-processed MoO_x thin film as a hole transport layer have been investigated with the device structure of ITO/TiO₂/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 a 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 C₇₁-butyric acid methyl ester (PC₇₁BM) are also investigated. The *J*-*V* and dark current density (*J*_{dark})-*V* characteristics are similar as compared with the low band gap inverted OSCs using thermally evaporated molybdenum oxide. With our solution-processed MoO_x film, the PCE of OSCs using a low band gap material can reach 7.15%. Consequently, through the vacuum treatment, the water-free, room-temperature and solution-processed MoO_x 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 blends of PBDTTT-C-T:PC₇₁BM. The results illustrate that our highly efficient hole transport MoO_x film made by a vacuum approach can be suitable for a variety of donor materials in OSCs with its universal energy-level alignment ability.

2.2 Ag NP-MoO_x composite films for high performance inverted OSCs

To achieve further performance improvement of our room-temperature solution-processed MoO_x, we introduce Ag NPs into the solution to form Ag NP-MoO_x composite films. Since the optimized solution-processed MoO_x thin film is about 8 nm, we would like to have the Ag NPs with size (4 nm) smaller than the thickness of the MoO_x film. The device performances of P3HT:PCBM and PBDTTT-C-T:PC₇₁BM inverted OSCs with different concentrations of Ag NPs are shown in Tables 2 and 3, and their *J*-*V* characteristics are shown in Fig. 5a (P3HT:PCBM) and Fig. 5b (PBDTTT-C-T:PC₇₁BM). The *J*_{dark}-*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 composite solution is 0.125 mg ml⁻¹ for both P3HT:PCBM and PBDTTT-C-T:PC₇₁BM inverted OSCs. The results show that *J*_{SC} and FF are significantly increased while *V*_{OC} remains almost unchanged. As a result, by introducing the Ag NPs with the optimized concentration into the solution-processed MoO_x, the 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 for the performance enhancement. With the incorporation of Ag NPs, the optical properties of the MoO_x film and OSCs are first studied. Recently, plasmonic resonances due to metal NPs have been widely investigated for enhancing the optical absorption of OSCs.⁴⁰⁻⁴³ Fig. 6a and b successively reveal the transmission spectra of the MoO_x film and the absorption spectra of the active layer with a top layer of the MoO_x film. The average diameter of the Ag NPs is 4 nm, which is measured using a transmission electron microscope (TEM) and shown in the inset of Fig. 6b. Nevertheless, the incorporation of Ag NPs into the Ag NP-MoO_x composite film does not show any obvious change in the transmission and absorption. We did not observe any clear optical enhancement

Table 2 P3HT:PCBM OSCs with different weight ratios of Ag NPs in the Ag NP-MoO_x composite film

NPs concentration	<i>J</i> _{SC} (mA cm ⁻²)	<i>V</i> _{OC} (V)	FF (%)	PCE (%)
Pristine MoO _x	9.34 ± 0.163	0.63 ± 0.008	65.19 ± 0.951	3.84 ± 0.065
0.25 mg ml ⁻¹	10.25 ± 0.135	0.63 ± 0.007	65.56 ± 0.450	4.25 ± 0.045
0.125 mg ml ⁻¹	10.36 ± 0.101	0.63 ± 0.007	66.89 ± 0.984	4.37 ± 0.056
0.0625 mg ml ⁻¹	9.83 ± 0.196	0.63 ± 0.006	65.27 ± 0.555	4.07 ± 0.097
0.03125 mg ml ⁻¹	9.65 ± 0.083	0.63 ± 0.007	65.35 ± 0.151	3.97 ± 0.064

Table 3 PBDTTT-C-T:PC₇₁BM OSCs with different weight ratios of Ag NPs in the Ag NP-MoO_x composite film

NPs concentration	<i>J</i> _{SC} (mA cm ⁻²)	<i>V</i> _{OC} (V)	FF (%)	PCE (%)
Evap. MoO ₃	15.01 ± 0.409	0.77 ± 0.006	63.62 ± 0.249	7.31 ± 0.243
Pristine MoO _x	15.98 ± 0.155	0.77 ± 0.007	58.37 ± 0.373	7.15 ± 0.148
0.25 mg ml ⁻¹	16.51 ± 0.261	0.77 ± 0.007	60.73 ± 0.673	7.69 ± 0.107
0.125 mg ml ⁻¹	16.75 ± 0.146	0.77 ± 0.007	61.57 ± 0.712	7.94 ± 0.062
0.0625 mg ml ⁻¹	16.54 ± 0.290	0.77 ± 0.006	60.62 ± 0.722	7.65 ± 0.133
0.03125 mg ml ⁻¹	16.08 ± 0.171	0.77 ± 0.005	59.74 ± 0.781	7.41 ± 0.079

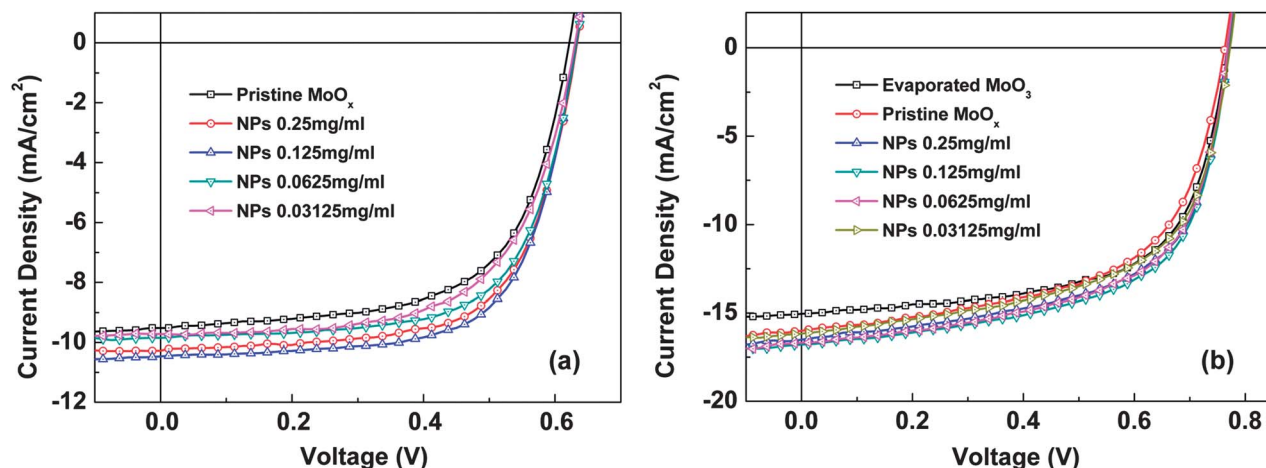


Fig. 5 (a) J - V characteristics of P3HT:PCBM OSCs with various weight ratios of Ag NPs in Ag NP-MoO_x composite layers. (b) J - V characteristics of PBDTTT-C-T:PC₇₁BM OSCs with various weight ratios of Ag NPs in Ag NP-MoO_x composite films.

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 attributed to the improved electrical properties⁴⁴ due to the incorporation of Ag NPs into the Ag NP-MoO_x composite interfacial layer. Other IPCE spectra of OSCs using the low band gap material as an active layer and the solution-processed Ag NP-MoO_x composite film also show wideband enhancement as shown in ESI Fig. S6.†

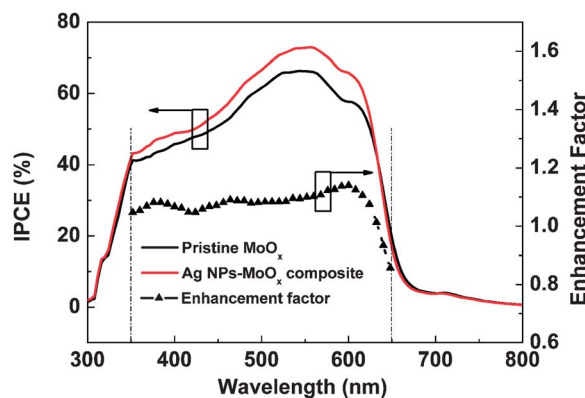


Fig. 7 IPCE spectra (left axis) of P3HT:PCBM OSCs with pristine MoO_x and Ag NP-MoO_x composite layers and the enhancement factor (right axis) in the core absorption region from 350 nm to 650 nm, *i.e.* (IPCE of OSCs with Ag NP-MoO_x composite)/(IPCE of OSCs with pristine MoO_x).

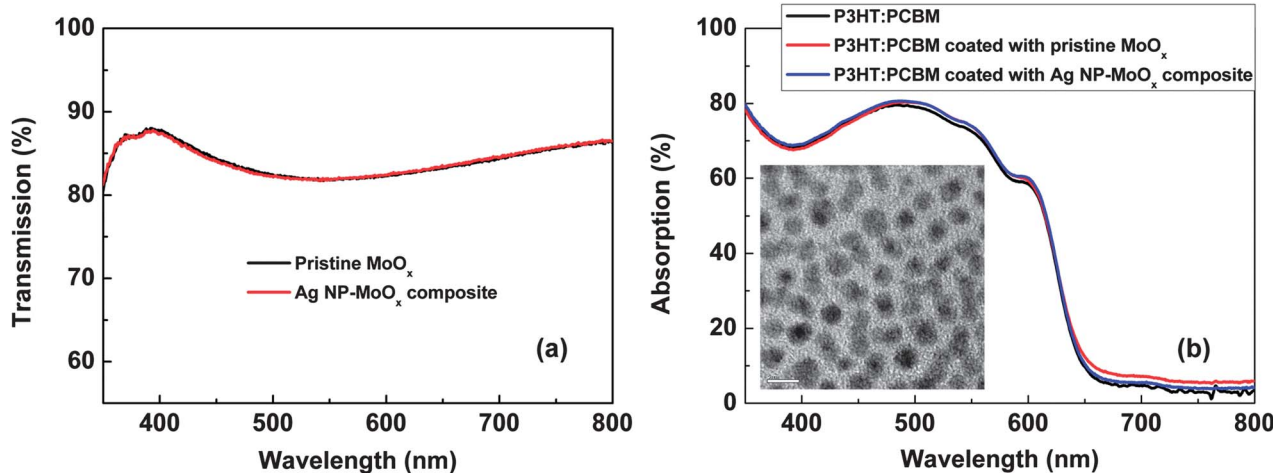


Fig. 6 (a) Transmission spectra of a pristine MoO_x film (black line) and an Ag NP-MoO_x composite film (red line). (b) Absorption spectra of a P3HT:PCBM film (black line), P3HT:PCBM coated with a pristine MoO_x film (red line), and P3HT:PCBM coated with an Ag NP-MoO_x composite film (blue line). (Inset: TEM result of 4 nm Ag NPs, the white scale bar is 5 nm in bottom left.)

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.^{45,46} As shown in ESI Fig. S7,† the current of the hole dominated device with the Ag NP–MoO_x composite film is much larger than that of the pristine solution-processed MoO_x and evaporated MoO₃ films. This indicates that the holes are more efficiently extracted to the anode by using the Ag NP–MoO_x composite as the hole transport layer. Another piece of evidence can be obtained from transient photo-generated voltage (TPV) measurement. The TPV measured using an excitation source of 532 nm picosecond laser pulse shows that the transient voltage of the devices with Ag NP–MoO_x composite films decreases 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 the anode than that of the pristine MoO_x and evaporated MoO₃ films.⁴⁷ It should be noted that the hole dominated device and TPV measurement of the OSCs with the solution-processed MoO_x film overlap with those of the evaporated MoO₃ film. This re-confirms that the room-temperature solution-processed MoO_x film functions as good as the evaporated MoO₃ film as described before. Consequently, our results show that the room-temperature solution-processed Ag NP–MoO_x composite film can clearly work as an 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 a water-free, room-temperature and solution-based process for the formation of a MoO_x film as an efficient hole transport layer for inverted OSCs is proposed and demonstrated. Interestingly, the UPS and XPS results indicate that oxygen vacancies can be introduced into the molybdenum oxide thin film by vacuum treatment, which functionalizes the MoO_x film to be an efficient hole transport layer. Remarkably, further improvement of the electrical properties of the MoO_x film is achieved by incorporating Ag NPs to form the Ag NP–MoO_x composite film. Inverted OSCs with a PCE of 7.94% are achieved by using the Ag NP–MoO_x composite film as a hole transport layer. Consequently, through the demonstration of high performance inverted OSCs with different polymer materials, the water-free, room-temperature and solution-processed MoO_x film can function as an 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 of metal powder was dispersed in 20 ml ethanol with an ultrasound bath. Then the 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.²⁷ After 20 hours of reaction, molybdenum oxide solution turned from gray to blue, which is attributed to H⁺ insertion into the metal oxide lattice and then the reduction of a metal element (Mo⁶⁺) to the sub-state (Mo⁵⁺), forming hydrogen molybdenum bronzes (H_xMoO₃). Finally, the remaining solvent was vaporized in a dry box, after which the obtained molybdenum bronze was dissolved in IPA with a concentration of 1 mg ml^{−1}.

4.2 Inverted OSC device fabrication

The device structure of inverted OSCs was ITO/TiO₂/polymer blend active layer/MoO_x/Ag. The sheet resistance of ITO was 15 Ω □^{−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 ITO followed by 150 °C baking for 10 min. TiO₂ nanocrystal solution was prepared by the nonaqueous method in previously reported paper.⁴⁸ In our inverted OSCs, the active layer was the robust polymer blend of P3HT:PCBM and the small band gap 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 a 3% volume ratio of 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 into the ~10 Pa vacuum chamber for 1 hour to remove 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 the 10 Pa vacuum chamber for 10 min treatment. The control device was fabricated by using a thermally evaporated molybdenum oxide layer with an optimized thickness of 10 nm. A silver anode of thickness 100 nm was finally evaporated onto the interfacial layer with a mask of 0.045 cm² area. In the fabrication of the hole dominated devices with the structure ITO/PEDOT:PSS (30 nm)/P3HT:PCBM/MoO_x/Ag, the same fabrication process of an active layer of thickness ~220 nm as in the inverted structure OSCs has been used for all hole dominated devices.

4.3 Synthesis of Ag NPs and Ag NP–MoO_x composite films

To improve the electrical properties of our solution processed MoO_x films, Ag NPs were incorporated into molybdenum bronze solution. Ag NPs were synthesized by mixing 1 mmol silver acetate, 3 mmol oleylamine, 3 mmol oleic acid, 20 ml phenyl ether and stearyl alcohol. The mixture was magnetically stirred and dispersed under a nitrogen atmosphere at 80 °C. The mixture was heated at 195 °C for 1 hour. After cooling to room temperature, it was added to 50 ml ethanol and centrifuged to precipitate the Ag NPs. The precipitated Ag NPs can be

well dispersed in non-polar solvent hexane. Then the Ag NPs were further dispersed in 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 concentrations of Ag NP solution.

4.4 Measurement and characterization

UPS measurement was performed using a He I discharge lamp (Kratos Analytical) with an energy of 21.22 eV and a resolution of 0.15 eV. A -10 V bias was applied on samples to enhance the measured signals. XPS measurement was performed using a Physical Electronic 5600 multi-technique system (monochromatic Al K α X-ray source). The *J-V* characteristics were measured using an ABET AM 1.5 G solar simulator with a light intensity of 100 mA cm⁻² and a Keithley 2635 source meter. TEM was performed using a FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope. The thickness of the film was measured using an ellipsometer. SEM was performed using a LEO 1530 FEG Scanning Electron Microscope.

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