MoO3-induced oxidation doping of PEDOT:PSS for high performing full-solution-processed inverted quantum-dot light emitting diodes

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MoO$_3$-induced Oxidation Doping of PEDOT:PSS for High Performing Full-solution-processed Inverted Quantum-dot Light Emitting Diodes

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KEYWORDS: full-solution processed composite anode; inverted QD-LEDs; ohmic contact; conductivity; charge transfer; oxidation doping
ABSTRACT

Full-solution processed inverted quantum dot light-emitting diodes (QD-LEDs) are promising candidates for application in next generation active matrix displays, due to their low-cost solution fabrication processes and easy integration with n-type thin-film transistor backplanes. In this work, we report high performing transparent inverted QD-LEDs using a full-solution processable hybrid composite anode, formulated using poly(3,4-ethylendioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), solution-processed molybdenum trioxide (s-MoO₃), and silver nanowires. The effect of the aqueous s-MoO₃ additive in PEDOT:PSS anode on efficient operation of the QD-LEDs was systematically investigated. Our results show that the s-MoO₃ additive not only enhances the wettability of PEDOT:PSS surface, but also improves the conductivity of the PEDOT:PSS layer, leading to an ohmic contact between the composite anode and hole transporting layer for efficient hole injection. With an optimal s-MoO₃ addition in PEDOT:PSS anode, the full-solution processable inverted QD-LEDs with a maximum current efficiency of 1.39 cd/A and a visible light transparency over 70% were demonstrated. The composite transparent anode enables a 27% increase in current efficiency of the full-solution processable QD-LEDs as compared to that of the structurally identical control device without s-MoO₃ additive. The encouraging results suggest that our investigation paves a way for the development of efficient vacuum-free transparent inverted QD-LEDs.
1. Introduction

Colloidal quantum-dot light emitting diodes (QD-LEDs) are promising candidates for next generation displays due to the unique properties of quantum dots (QDs), such as solution-processibility, high color purity, size-tunable emitting color and high quantum yield. [1-5] Significant advancements and improvements have been made in the development of high performance QD-LEDs. [6,7] QD-LEDs with the highest external quantum efficiency (EQE) of ~20% have been reported, realized through optimizing both QD materials and device architectures. [7] QD-LEDs with an inverted structure, e.g., having a stack of the functional layers sandwiched between a high work function top anode and a bottom cathode, possess higher luminous efficiency and better stability. The inverted QD-LEDs also enable an easy integration with the thin film transistor backplanes for use in display applications. [8-10] Thus, much effort has been devoted to developing high efficient solution-processed inverted QD-LEDs, [10-13] However, most of these QD-LEDs were made by the thermal evaporation process, [13] which is not a commercial viable approach for low-cost manufacturing.

With respect to large-area display applications, it is desirable to have not only the active layers but also the electrodes in the inverted QD-LEDs that can be formed by solution fabrication process. The development of solution processable metal oxide-based interlayers, such as molybdenum oxide (MoO₃), [14] tungsten oxide, [15] zinc oxide (ZnO), [9,14,15] and titanium oxide, [16] has attracted increasing attention for application in QD-LEDs. The solution-processed electron/hole injection layers can be readily adopted using these metal oxides. [17-23] However, high quality full-solution processed top electrode is still one of the challenges the QD-LEDs face today. Various solution-processable top contact materials, including metal nanowires, graphene, carbon nanotubes, conductive polymers, have been developed to replace the top metal
electrode formed typically using thermal evaporation process. [24] Among these materials, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) is one of the favorite anode choices due to its easy accessibility and suitable work function (~5.0 eV) for efficient hole injection. However, the conductivity of PEDOT:PSS-based electrode is less than satisfactory, limiting the performance of all solution-processed QD-LEDs. Lee et al. have demonstrated that the conductivity of PEDOT:PSS can be improved by adding some liquid organic compounds, e.g., ethylene glycol, N,N-dimethylformamide, and dimethyl sulfoxide. [25] The use of the organic compound additives helps to remove the PSS component, resulting in better connection between the PEDOT units. However, the addition of the organic additives generally decreases the work function of the PEDOT:PSS layer, leading to an undesirable increase in the energy barrier between the anode and the hole transport layer.

Another method for enhancing the conductivity of the PEDOT:PSS top electrode is to combine the PEDOT:PSS with a stochastic silver nanowire (AgNW) mesh to form a composite electrode. Such a bilayer composite electrode may allow for an ohmic contact between the hole transport layer and top anode, and thereby decreases the sheet resistance between the nanowires. [26] However, the wettability of the PEDOT:PSS surface is another crucial problem for subsequent coating of a uniform AgNW contact to form a high quality PEDOT:PSS/AgNWs bilayer composite electrode. Although the wettability of PEDOT:PSS can be improved by doping isopropanol (IPA) or other surfactants, the reduction in the conductivity and work function of PEDOT:PSS is often observed. [27] Until now, the solution-processed top electrode with high conductivity and good wettability is still an open issue towards full-solution inverted QD-LEDs.
In this work, we demonstrate that the high quality hybrid composite PEDOT:PSS:s-MoO$_3$/AgNWs electrode with a superior electric conductivity and an excellent process wettability can be readily formulated by adding proper amount of solution-processed MoO$_3$ nanoparticles (s-MoO$_3$ NPs). By adopting such a hybrid composite top anode, vacuum-free, full-solution processed transparent inverted QD-LEDs with a large improvement in luminance and current efficiency were successfully achieved. The effects of s-MoO$_3$ additive on the optical, electric and surface electronic properties of the PEDOT:PSS: s-MoO$_3$/AgNWs composite anode were systematically studied by infrared (IR) absorption, X-ray Photoelectron Spectroscopy (XPS), and Raman spectroscopy measurements. The results show that the use of s-MoO$_3$ NPs additive promotes the networking between the conducting PEDOT units, and thereby greatly increases the electric conductivity of hybrid PEDOT:PSS: s-MoO$_3$ layer. A maximum luminance of 4839 cd/m$^2$ and a luminous efficiency of 1.39 cd/A were obtained for the transparent inverted QD-LEDs having a PEDOT:PSS:s-MoO$_3$/AgNWs composite top anode, which are significantly higher than the maximum luminance of 3622 cd/m$^2$ and luminous efficiency of 1.09 cd/A obtained for a structurally identical control QD-LEDs having a pristine PEDOT:PSS/AgNWs bilayer anode.

2. Experimental Section

Materials. ZnO nanoparticles were synthesized following the procedure reported in a previous work. [28] High conductivity PEDOT:PSS (Heraeus-Clevios, PH1000), silver nanowires (diam.× L 60 nm × 10 μm, 0.5%, dispersion in IPA, Sigma-Aldrich), poly(9-vinylcarbazole) (PVK) (from Nichem Fine Technology, Taiwan), and the colloidal CdSe-ZnS core-shell quantum dot (620 nm, 5 mg/ml in Toulene, from Najingtech, China) were used as received.
without further purification. The formulation solutions were optimized to meet the process compatibility and requirement for high performing QD-LEDs.

Preparation of aqueous composite solution of PEDOT:PSS: s-MoO₃. MoO₃ NPs solution (~5 mg/mL in IPA) was synthesized according to a previous work. [29] The aqueous composite solutions were prepared through blending the s-MoO₃ NPs solution into PEDOT:PSS (PH1000) solution, with different volume ratios of PEDOT:PSS to s-MoO₃ of 1:1, 2:1, 3:1 and 4:1. Meanwhile, PEDOT:PSS and IPA mixture with a volume ratio of PEDOT:PSS to IPA of 3:1 was also prepared.

Device fabrication and characterizations. The full-solution processed inverted QD-LEDs have a device configuration of glass/indium tin oxide (ITO)/ZnO/CdSe-ZnS QDs/PVK/s-MoO₃/PEDOT:PSS: s-MoO₃ (3:1)/AgNWs. The cross-sectional view of the QD-LED is shown in Figure 1a. The ZnO modified ITO serves as a cathode to inject electrons and the top PEDOT:PSS: s-MoO₃/AgNWs hybrid composite electrode acts as an anode to inject holes. A 40 nm thick ZnO electron transporting layer and a 30 nm thick PVK HTL were used to improve the hole-electron current balance in the QD-LEDs. A ~5 nm thick s-MoO₃ interlayer was deposited between the PVK hole transport layer and PEDOT:PSS: s-MoO₃/AgNWs composite anode to enhance the hole injection, due to the matching between its comparable minimum electron conduction level and the highest occupied molecular orbital (HOMO) of the PVK HTL, as illustrated in Figure 1b. All these functional layers were spin coated layer-by-layer on the pre-patterned ITO/glass substrate. After each layer deposition, the samples were then annealed at a low temperature of <100 °C to remove the residual solvents in the films. The control QD-LED with a pristine PEDOT:PSS/AgNWs bilayer electrode was fabricated following the same procedure for comparison studies.
Surface electronic properties of PEDOT:PSS: s-MoO$_3$ hybrid layers were analyzed using XPS measurements, with a monochromatic Mg $K_x$ line having a photon energy of 1253.6 eV, operated at 10 kV and an emission current of 15 mA. Ultraviolet Photoelectron Spectroscopy (UPS) measurements were performed in an ultra-high vacuum system with a base pressure of $<2 \times 10^{-9}$ mbar, equipped with an electron spectrometer (Sengyang SKL-12) and an electron energy analyzer (VG CLAM 4 MCD). The UV-visible absorption spectra were measured by UV-visible spectrophotometer (Shanghai Metash Instruments, UV-6100). The Raman spectra for different hole transport layers were recorded by the MicroRaman photoluminescence system (InVia Renishaw). After fabrication, the QD-LEDs were encapsulated in the glove box before they were taken out for characterization in ambient condition. The electroluminescence (EL) spectra were measured by spectra colorimeter (Photo Research Inc., Model 650) spectrophotometer. Current density–voltage–luminance ($J–V–L$) characteristics of the vacuum-
free QD-LEDs were measured by a Keithley source unit (Keithley Instruments Inc., Model 236 SMU), which was calibrated using a silicon photodiode. The surface hydrophobicity of the hybrid PEDOT:PSS: s-MoO$_3$ and PEDOT:PSS thin films, fabricated on the surface of s-MoO$_3$/ITO/glass, was characterized by the contact angle measurements.

3. Results and Discussion

The electric conductivity measured for the PEDOT:PSS: s-MoO$_3$ layers, prepared with different volume ratios of PEDOT:PSS to s-MoO$_3$ NPs, is shown in Figure 2a. It is clearly shown that the conductivity of the resulting PEDOT:PSS:s-MoO$_3$ layers can be largely modulated by varying the ratio of PEDOT:PSS to s-MoO$_3$ NPs in the mixed solution. The highest electric conductivity of $>1100$ S/cm was obtained for PEDOT:PSS: s-MoO$_3$ layer, prepared using a volume ratio of PEDOT:PSS to MoO$_3$ (3:1) in the formulation. As s-MoO$_3$ contains IPA, in order to exclude the possible effect of IPA on the improvement in conductivity of the PEDOT:PSS layer, the conductivity of pristine PEDOT:PSS layer, prepared using the PEDOT:PSS-IPA mixture having the same volume ratio of PEDOT:PSS to IPA (3:1), was also measured, revealing a much lower conductivity of $<900$ S/cm, indicated by the blue dashed line in Figure 2a. It is demonstrated that the significant increase in the electric conductivity of PEDOT:PSS: s-MoO$_3$ hybrid film is mainly contributed due to the use of the s-MoO$_3$ NPs additive.

The effect of MoO$_3$ NPs additive on the solution wettability was analyzed by the contact angle measurements. The contact angles measured for the droplets of PEDOT:PSS: s-MoO$_3$ (3:1) and pristine PEDOT:PSS solutions on the surfaces of s-MoO$_3$/ITO/glass are 29° and 59°, as shown in Figures 2b and 2c. The results suggest that the wettability of the PEDOT:PSS is significantly
improved by adding a small amount of s-MoO$_3$ NPs additive. Thus, the transparent electrode PEDOT:PSS: s-MoO$_3$(3:1)/AgNWs can then be easily coated on the surface of an underlying hydrophobic s-MoO$_3$ hole injection layer, improving the interfacial contact quality, and thereby facilitating charge injection at the electrode/function layer interface.

![Graph](image1.png)

**Figure 2** (a) Conductivity of PEDOT:PSS: s-MoO$_3$ blend layers prepared using different volume ratios of PEDOT:PSS to s-MoO$_3$ NPs. The contact angles measured for the droplets of (b) PEDOT:PSS: s-MoO$_3$ (3:1) and (c) pristine PEDOT:PSS solutions on the surfaces of s-MoO$_3$/ITO/glass substrates. (d) UPS spectra measured for the PEDOT:PSS:s-MoO$_3$ and PEDOT:PSS films fabricated on ITO/glass substrates; (e) Transparency spectra measured for pristine PEDOT:PSS (70 nm)/glass, PEDOT:PSS: s-MoO$_3$ (70 nm)/glass, and ITO/glass.
Since the work function of the electrode plays an important role in controlling the carrier injection properties, the work function of the PEDOT:PSS: s-MoO\textsubscript{3} layer was also studied by UPS. **Figure 2d** displays the UPS spectra and the secondary electron cut-offs (insert in **Figure 2d**) measured for hybrid PEDOT:PSS: s-MoO\textsubscript{3} (3:1) layer and pristine PEDOT: PSS layer. A work function of 5.3 eV for PEDOT:PSS: s-MoO\textsubscript{3} (3:1) layer was obtained, which is 0.3 eV higher than that of pristine PEDOT:PSS film (5.0 eV). The increase in the work function of the hybrid PEDOT:PSS: s-MoO\textsubscript{3} layer is more favorable for hole injection, due to the reduced interfacial barrier, as seen in **Figure 1b**. The transparency of the hybrid PEDOT:PSS: s-MoO\textsubscript{3} (3:1) thin film was recorded above 86 % over the wavelength range from 400-800 nm (as shown in **Figure 2e**), which is similar to that of the pristine PEDOT:PSS layer (87 %) and that of the ITO (110 nm)/glass. The use of the s-MoO\textsubscript{3} additive in the PEDOT:PSS anode does not cause observable change in its optical transparency.

Based on the above discussion, the hybrid PEDOT:PSS: s-MoO\textsubscript{3} anode contact, developed in this work, with high conductivity, good wettability, and suitable work function would be very suitable for fabricating full-solution processed, transparent, inverted QD-LEDs. A hybrid composite anode of PEDOT:PSS: s-MoO\textsubscript{3} (3:1)/AgNWs (as shown in **Figure 1**) was used to strengthen the mechanism properties of the transparent anode. The $J$–$V$ characteristics measured for the QD-LEDs with different composite anodes of PEDOT:PSS: s-MoO\textsubscript{3}/AgNWs and PEDOT:PSS/AgNWs are plotted in **Figure 3a**. The QD-LEDs with a PEDOT:PSS: s-MoO\textsubscript{3}/AgNWs composite anode have an obvious higher current density than that of the QD-LEDs with a PEDOT:PSS/AgNWs top electrode. The turn-on voltage, defined as the applied bias required for the QD-LEDs emitting light achieving a luminance of 100 cd/m\textsuperscript{2}, of ~6.7 V is obtained for the QD-LEDs with a PEDOT:PSS: s-MoO\textsubscript{3}/AgNWs composite anode, which is...
lower than that of a control QD-LED with a PEDOT:PSS/AgNWs top contact (7.1 V). The lower turn-on voltage for QD-LEDs with a PEDOT:PSS: s-MoO\textsubscript{3}/AgNWs composite anode reflects the improvement in the hole injection, agrees with the analyses made with the UPS measurements in showing that PEDOT:PSS: s-MoO\textsubscript{3} is more favorable for hole injection, as illustrated in Figures 2b, 2c and 2d. The QD-LEDs with a PEDOT:PSS: s-MoO\textsubscript{3}/AgNWs composite anode also exhibit a remarkable enhancement in luminance (Figure 3b).

**Figure 3** (a) Current density–voltage, (b) luminance–voltage characteristics, and (c) normalized EL spectra measured for QD-LEDs with a PEDOT:PSS: s-MoO\textsubscript{3}/AgNWs hybrid composite anode and a PEDOT:PSS /AgNWs composite anode at 5.0 V; (d) Transparency spectrum measured for a QD-LED with a PEDOT:PSS:s-MoO\textsubscript{3}/AgNWs composite anode over the wavelength range from 300-1000 nm. The inserts in figure 3(d): Photo pictures taken for a transparent QD-LED, emitting light (left) and illustrating the transparent feature without power (right).
The corresponding luminance and current efficiency of two types of QD-LEDs were summarized in Table 1. It can be seen that the luminance and current efficiency of QD-LEDs made with a PEDOT:PSS: s-MoO₃/AgNWs composite anode are much higher than those of a control QD-LED having a PEDOT:PSS/AgNWs composite anode, measured from the ITO side (black line) and the AgNWs side (dark blue line). The total luminance of the devices, taking the sum from both sides is also plotted (red line). The corresponding results obtained for a control QD-LED made with a PEDOT:PSS/AgNWs anode are given in the insert of Figure 3b. The maximum luminance and current efficiency of QD-LEDs with a PEDOT:PSS: s-MoO₃/AgNWs composite anode were recorded to be 4839 cd/cm² and 1.39 cd/A, which show 33.6% increase in luminescence and 27% increase in current efficiency as compared to those of a control QD-LED without s-MoO₃ additive. The current efficiency of 1.39 cd/A obtained for the full-solution-processed transparent QD-LEDs in this work is quite respectable as compared to that of the transparent QD-LEDs made with a pair of top and bottom graphene contacts (0.45 cd/A) [30] or with a laminated graphene top anode (0.32 cd/A) [31] reported recently.

Table 1 Device characteristics of full-solution-processed inverted QD-LEDs with different anodes.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Parameters</th>
<th>Anode side</th>
<th>Cathode side</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS/AgNWs</td>
<td>Luminance (cd/m²)</td>
<td>1851</td>
<td>1770</td>
<td>3622</td>
</tr>
<tr>
<td></td>
<td>Current efficiency</td>
<td>0.56</td>
<td>0.53</td>
<td>1.09</td>
</tr>
<tr>
<td>PEDOT:PSS: s-MoO₃/AgNWs</td>
<td>Luminance (cd/m²)</td>
<td>2547</td>
<td>2292</td>
<td>4839</td>
</tr>
<tr>
<td></td>
<td>Current efficiency</td>
<td>0.73</td>
<td>0.66</td>
<td>1.39</td>
</tr>
</tbody>
</table>
The normalized EL spectra measured for the QD-LEDs with a PEDOT:PSS:s-MoO$_3$/AgNWs composite anode and a control device with a PEDOT:PSS/AgNWs anode are shown in Figure 3c, showing a narrow emission feature with an EL peak at ~620 nm. The EL measured for both types of QD-LEDs are overlapping. The QD-LEDs with a PEDOT:PSS: s-MoO$_3$/AgNWs composite anode possess very good visible light transparency of >70% (as shown in Figure 3d). The inserts in Figure 3d are the photo pictures taken for a transparent QD-LED, emitting light (left) and illustrating the transparent feature without power (right). These results indicated that the transparent QD-LEDs developed in the present work are very suitable for applications in transparent displays where light optical transparency is desired.

The remarkable improvement in luminous efficiency of the QD-LEDs with a PEDOT:PSS: s-MoO$_3$/AgNWs composite anode arises from the better carrier injection, better wettability and higher conductivity of the composite anode, which favors the efficient operation of the QD-LEDs. However, the origin of the enhancement in the conductivity of the composite anode with additive of s-MoO$_3$ NPs has not yet been fully explored. To unveiling the origin of the improvement in the conductivity of the PEDOT:PSS: s-MoO$_3$ hybrid layer, the structural and electronic properties of the composite conductive layer PEDOT:PSS: s-MoO$_3$ (3:1) were characterized by XPS, IR absorption, and Raman spectroscopy measurements.

The change in the chemical and electronic properties of PEDOT:PSS layers before and after the addition of s-MoO$_3$ were characterized by XPS measurements. S 2p XPS spectra measured for the pristine PEDOT:PSS and hybrid PEDOT:PSS: s-MoO$_3$ thin films over the binding energy range from 160~170 eV are shown in Figure 4a. The S 2p XPS peaks over the binding energy range from 162~166 eV are contributed by S atoms in the PEDOT chains, and S 2p XPS peaks over the binding energy range from 166~172 eV are assigned to the S atoms in the PSS. [32] The
area ratio of the S 2p XPS spectrum (over the binding energy range from 162~166 eV, for PEDOT) to the S 2p XPS spectrum (over the binding energy range from 166~172 eV, for PSS) was calculated to estimate the change in the ratio of PEDOT to PSS in the contact. It is seen that the ratio of PEDOT to PSS in the PEDOT:PSS: s-MoO₃ hybrid layer (red line) is 0.13, which closes to 0.12 obtained for a pristine PEDOT:PSS layer. Thus, the XPS results indicate that the insulting PSS component in the PEDOT:PSS cannot be removed by adding the s-MoO₃ additive in the mixed solution. We suggest that the interaction between PEDOT:PSS and s-MoO₃ in the hybrid electrode contributes to the improvement in the conductivity of the film.

Figure 4 (a) S 2p XPS spectra, (b) visible and NIR absorption spectra and (c) Raman spectra measured for a pristine PEDOT:PSS and a hybrid PEDOT:PSS: s-MoO₃ thin films (~200 nm). The UV-visible absorption spectrum measured for a 200 nm thick pure s-MoO₃ film also is presented in (b) for comparison.

The optical properties of p-doped conjugated polymers, e.g., the PEDOT:PSS layer, are closely associated with their optical band gap, relating to the excitation of the electrons from π to π* band. Appropriate doping in the PEDOT:PSS creates the extra sub-states in the band gap, thus electronic transitions in lower energies are allowed. As shown in Figure 4b, the shoulder appeared near 590 nm is the result of the absorption by the π–π* transition in neutral chains.
(NC), the absorption near 750 nm is due to the radical cations (RC), and the absorption band at wavelength >1200 nm is associated to the appearance of di-cations (DC) in PEDOT:PSS. [33] Therefore, the variation in the near infrared (NIR) absorption region of the film reflects the change in the confirmation of the PEDOT chains in the hybrid PEDOT:PSS: s-MoO₃ film.

The UV-Vis absorption spectra of a 200 nm thick pure PEDOT:PSS layer and a PEDOT:PSS: s-MoO₃ hybrid layer, [34] deposited on the quartz substrate and formed with a post annealing treatment at 120 °C for 10 min in air, are shown in Figure 4b. There is no apparent change in the absorption spectra measured for the PEDOT:PSS and PEDOT:PSS: s-MoO₃ films over the visible region, exhibiting a good optical transparency. However, the PEDOT:PSS: s-MoO₃ layer has a significant absorption enhancement in the wavelength range from 700 nm (red) to NIR. The results in Figure 4b illustrate clearly that the contribution to the evident increase in the NIR absorption of the PEDOT:PSS: s-MoO₃ film is not due to the addition of s-MoO₃, as a 200 nm thick s-MoO₃ film has a very weak absorption in this wavelength region. We suggest that the enhancement in NIR absorption is related to the change in the confirmation of the PEDOT chains, leading to the generation of additional charge carriers in the hybrid PEDOT:PSS: s-MoO₃ films. The evident increase in the NIR absorption of the PEDOT:PSS: s-MoO₃ film is attributed to the oxidation doping of PEDOT:PSS by the s-MoO₃ NPs, which results in the change in the chemical structure of PEDOT:PSS: s-MoO₃ film.

The change in the conformation of PEDOT components in the PEDOT:PSS chains was further analyzed using Raman spectroscopy measurements. PEDOT contains two resonating benzoid and quinoid structures. The transition from benzoid to quinoid configurations, manifested by the Raman spectroscopy measurements, reflects the change in the internal structures of the PEDOT:PSS thin film. The transition between benzoid and quinoid
configurations is closely related to the change in the conductivity of PEDOT:PSS film. The shift in the wavenumber of the Raman peak 1432 cm$^{-1}$, measured for the hybrid film, as compared to that of the pristine PEDOT:PSS (1447 cm$^{-1}$) reveals that there is an increase in the quinoidal configuration in the PEDOT:PSS: s-MoO$_3$, and thus the film is more conductive. [35] The transition from benzoid to quinoid configurations is very sensitive to the oxidation doping in the PEDOT:PSS. Raman spectroscopy results reveal an obvious transition from benzoid to quinoid configurations in the hybrid PEDOT:PSS:s-MoO$_3$ films, leading to an increase in the number of polarons.

The MoO$_3$ NPs have special electronic chemical potential and absolute electro-negativity, the interaction between the PEDOT and PSS chains is disturbed due to the coulombic attraction between the positively charged PEDOT chains and negatively charged MoO$_3$. The change in the resonant structure of the PEDOT chains, e.g., from benzoid to quinoid configurations, converts the PEDOT from its coil shaped configuration to the linear structure. Therefore, the stretch of PEDOT chains, due to the oxidation doping by the s-MoO$_3$ nanoparticles, improves the networking between the conducting PEDOT units, an increase in the conductivity of hybrid PEDOT:PSS:s-MoO$_3$ layer is obtained. The above discussion agrees well with the analyses of the valence electronic states of Mo atoms in the PEDOT:PSS: s-MoO$_3$ blend system, reported in a previous work. [29] There is an apparent presence of the Mo$^{5+}$ electronic state in the Mo 3d XPS spectrum measured for the thin film of PEDOT:PSS with an s-MoO$_3$ additive. The presence of the Mo$^{5+}$ valence electronic state associates with the oxidation of PEDOT. This implies that the charge transfer and chemical reaction between the PEDOT units and MoO$_3$ NPs take place, leading to an increase in the work function of the hybrid PEDOT:PSS:s-MoO$_3$ layer, supported by the UPS measurements, as seen in Figure 2d.
Based on the above discussions, the charge transfer processes between PEDOT, with a low ionization energy, and s-MoO$_3$, with a high electron affinity, resulting in a partial oxidation of the PEDOT and the partial reduction of s-MoO$_3$, are illustrated in Figure 5. The interaction between PEDOT units and MoO$_3$ NPs results in an oxidation of PEDOT. The formation of Mo$^{5+}$ electronic state becomes an electron acceptor due to the charge transfer between PEDOT and MoO$_3$, forming quinoid structure to enhance the conductivity. As a result, such a high conductivity solution processable transparent conductive layer, combining with a layer of silver nanowires, can then be used as a suitable top electrode for application in solution-processed inverted QD-LEDs.
4. Conclusions

In summary, the use of s-MoO$_3$ additive in PEDOT:PSS anode improves its electric conductivity, work function and process wettability. The full-solution-processed inverted QD-LEDs, made with a PEDOT:PSS: s-MoO$_3$/AgNWs composite anode, exhibit great performance improvement, e.g., having >33% increase in the maximum luminance and 27% enhancement in the luminous efficiency. These results indicate that the oxidation doping of the PEDOT:PSS by s-MoO$_3$ NPs is mainly responsible for the improvement in performance and process compatibility of solution-processed inverted QD-LEDs.

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