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# Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)/MoO<sub>3</sub> composite layer for efficient and stable hole injection in organic semiconductors

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We report a composite hole injection layer (HIL) composed of an ultrathin film of MoO<sub>3</sub> on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) for efficient and stable hole injection in organic semiconductors. The optimized thickness of MoO<sub>3</sub> layer was determined to be about 0.5 nm, which was enough to increase the work function of the underlying films substantially. The composite HIL can inject holes efficiently into a variety of hole transport layers (HTLs), even that with very deep highest occupied molecular orbital (HOMO) levels. Moreover, the utilization of PEDOT:PSS/MoO<sub>3</sub> composite HIL greatly improved the stability of hole injection in organic devices, as compared to those based on pure PEDOT:PSS or MoO<sub>3</sub> HILs, beneficial to practical applications. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3687933>]

## I. INTRODUCTION

Owing to their easy processing and potential for low-cost fabrication,<sup>1</sup> organic semiconductors have attracted much attention recently as new candidates for electronic devices, including organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), and organic solar cells (OSCs). One of the fundamental requirements for efficient operation of these organic electronic devices is the effective carrier injection from the electrodes into the active region or carrier extraction from the active region into the electrodes.<sup>2</sup>

The energy barrier for carrier injection/extraction depends on the energy level difference between the electrode work function and the ionization potential/electron affinity of the organic semiconductors. Small energy barrier or match of energy levels between electrodes and active layers is highly desired to achieve good device performance. However, the most commonly used electrodes, such as ITO, Au, or Ag, usually have difficulties to inject/extract carriers into/from organic active layers. To solve the energy level mismatch, electrodes modification is usually adapted. One successful demonstration<sup>3</sup> is using a thin layer of LiF (0.5 nm thick) to modify the electron injection interface between Al and Alq<sub>3</sub>. After that, a large variety of cathode and anode modification materials have been worked out. Among them, the application of transition metal oxides (TMOs) has attracted much attention. TMOs combine properties such as high transparency, good electrical conductivities, tunable morphology, and possibility of deposition on large areas with low-cost techniques.<sup>4</sup> At the anode side, TMOs, such as MoO<sub>3</sub> (Ref. 5), WO<sub>3</sub> (Ref. 6), and V<sub>2</sub>O<sub>5</sub>,<sup>7</sup> were introduced to improve the hole injection properties. It was reported that MoO<sub>3</sub> thin films had a valence band edge

at 5.3 eV and the conduction band edge at 2.3 eV,<sup>8</sup> so that the device improvement relied on a more favorable energy level alignment. More recently, however, detailed ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES) investigations<sup>9–11</sup> revealed that MoO<sub>3</sub> was an n-type semiconductor with a large electron affinity (EA) (6.7 eV) and ionization potential (IP) (9.7 eV) as well as a high work function (WF) (6.8 eV). Based on that, the hole injection mechanism was revised to rely on electron extraction from the organic semiconductors adjacent to MoO<sub>3</sub>. Moreover, many UPS investigations of MoO<sub>3</sub> on different materials showed that a very thin MoO<sub>3</sub> was capable of increasing the work function of the underlying films to

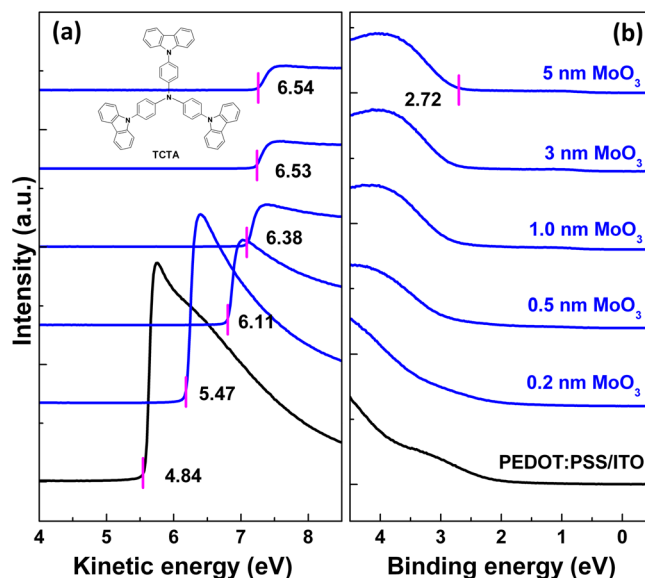


FIG. 1. (Color online) UPS spectra of different thickness of MoO<sub>3</sub> on PEDOT:PSS/ITO. (a) The low kinetic energy regions showing the secondary electron cut-off; (b) valence band region near the Fermi energy. Also shown is the molecule structure of TCTA.

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sufficiently high values.<sup>12–14</sup> All these demonstrations fully indicate the advantage of thin MoO<sub>3</sub> film in improving hole injection in organic devices.

Poly(phenylenevinylene):poly(styrene-sulfonate) (PEDOT:PSS) has been widely used as hole injection layers (HILs) in OLEDs and OSCs because of its superior conductivity and good energy level match with ITO. The work function of ITO/PEDOT:PSS anode was reported to be 4.8 eV to 5.15 eV.<sup>15,20</sup> Efficient hole injection from PEDOT:PSS into hole transport layers (HTLs) such as N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB),<sup>16</sup> Di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) (Ref. 17) or 4,4',4''-Tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (m-MTDATA) (Ref. 16) have been demonstrated. However, there is hardly an example that shows good hole injection from PEDOT:PSS into HTLs with deep highest occupied molecular orbital (HOMO) levels of larger than 5.7 eV. Recently, a composite PEDOT:PSS/MoO<sub>3</sub> (1 nm) electrode was used in OLEDs, and found that the operational

voltage of fabricated OLEDs is greatly reduced, thus the power efficiency is significantly enhanced compared to that based on ITO/MoO<sub>3</sub> (1 nm) electrode.<sup>18</sup> The improved performance was attributed to the higher work function, lower refractive index, and decreased surface roughness of PEDOT:PSS versus ITO, and Ohmic hole injection from PEDOT:PSS to HTL via the MoO<sub>3</sub> interlayer.

In this paper, we investigated in details the mechanism of PEDOT:PSS/MoO<sub>3</sub> composite film as HIL in improving hole injection and found that the utilization of PEDOT:PSS/MoO<sub>3</sub> composite HIL greatly improved the stability of hole injection in organic devices, as compared to those based on single PEDOT:PSS or MoO<sub>3</sub> HILs. The UPS measurements show that an ultrathin film of 0.5 nm MoO<sub>3</sub> on PEDOT:PSS can increase the work function of ITO to more than 6.0 eV, which is sufficiently high to inject holes to most of organic semiconductors with high HOMO levels, such as generally used large bandgap hole transporting material 4,4',4'''-tri(N-carbazolyl) triphenylamine (TCTA) [as shown in Fig. 1].

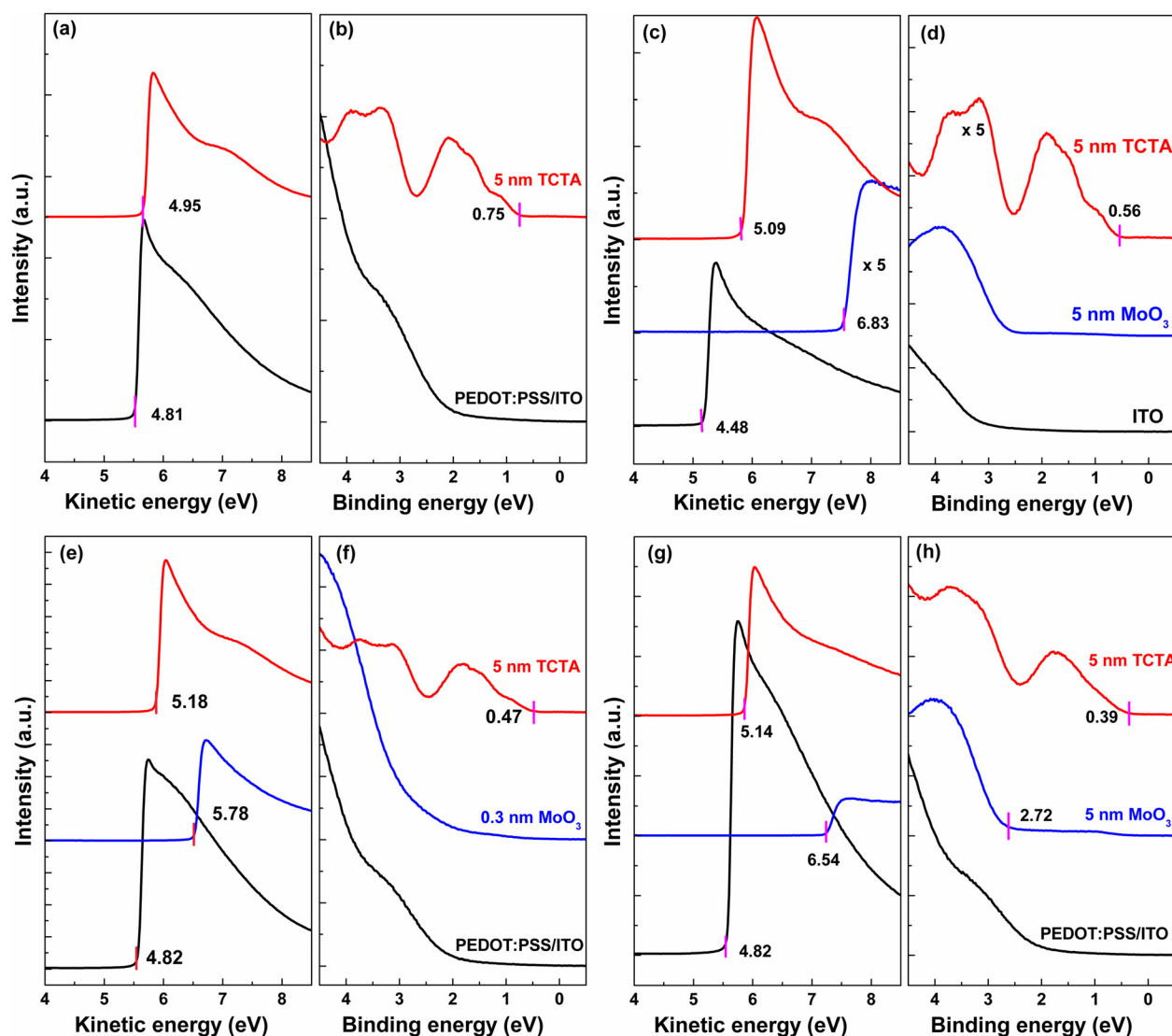


FIG. 2. (Color online) UPS spectra for TCTA on different ITO modification layers: (a), (b) PEDOT:PSS/ITO; (c), (d) MoO<sub>3</sub>/ITO; (e), (f) thin-MoO<sub>3</sub>/PEDOT:PSS/ITO and (g), (h) thick-MoO<sub>3</sub>/PEDOT:PSS/ITO.

## II. EXPERIMENTAL

The fabricated devices were grown on cleaned glass substrates pre-coated by a 180 nm thick-ITO with a sheet resistance of  $10 \Omega$  per square. The ITO surface was treated by oxygen plasma for 2 min, followed by a degrease in an ultrasonic solvent bath and dried at  $120^\circ\text{C}$ . PEDOT:PSS (Clevious<sup>TM</sup> P VP AI 4083) film was formed by spin-coating at 3000 rpm and then baked at  $120^\circ\text{C}$  for 30 min. Other organic layers and metal layer were grown by thermal evaporation in a high-vacuum system with a pressure of less than  $5 \times 10^{-4}$  Pa without breaking the vacuum. The evaporation rates were monitored by a frequency counter and further calibrated by a Dektak 6M profiler (Veeco). The overlap between ITO and Al electrodes was  $4 \text{ mm} \times 4 \text{ mm}$  as the active emissive area of the devices. Current-voltage characteristics were measured by using a Keithley 2400 unit. UPS measurements were performed in a custom designed ultra-high vacuum (UHV) system with a base pressure better than  $2 \times 10^{-8}$  Pa, and He I ( $h\nu = 21.2 \text{ eV}$ ) as the excitation source.<sup>19</sup> Vacuum level shifts were measured from the linear

extrapolation from the onset of secondary electron cutoff at the low kinetic energy part with  $-5 \text{ V}$  sample bias.

## III. RESULTS AND DISCUSSION

### A. UPS investigation of PEDOT:PSS/MoO<sub>3</sub> composite film on ITO electrode

Figure 1(a) shows the evolution of UPS spectra at the low-kinetic energy region during the deposition of MoO<sub>3</sub> on ITO/PEDOT:PSS electrode. The vacuum level of PEDOT:PSS upon the deposition of MoO<sub>3</sub> was measured by linear extrapolation of the low-kinetic energy onset (secondary electron cutoff) in the UPS spectra. The work function of the pristine ITO/PEDOT:PSS electrode was measured to be  $4.84 \text{ eV}$ , in good agreement with previous results.<sup>15,20</sup> As can be seen, after fractional coverage of PEDOT:PSS with  $0.2 \text{ nm}$  MoO<sub>3</sub>, the work function of PEDOT:PSS is increased to about  $5.5 \text{ eV}$ . This value is already larger than the IPs of common HTLs in OLEDs, such as NPB ( $5.4 \text{ eV}$ ), TAPC ( $5.3 \text{ eV}$ ),  $\alpha$ -NPD ( $5.4 \text{ eV}$ ), and m-MTDATA ( $5.1 \text{ eV}$ ). After depositing

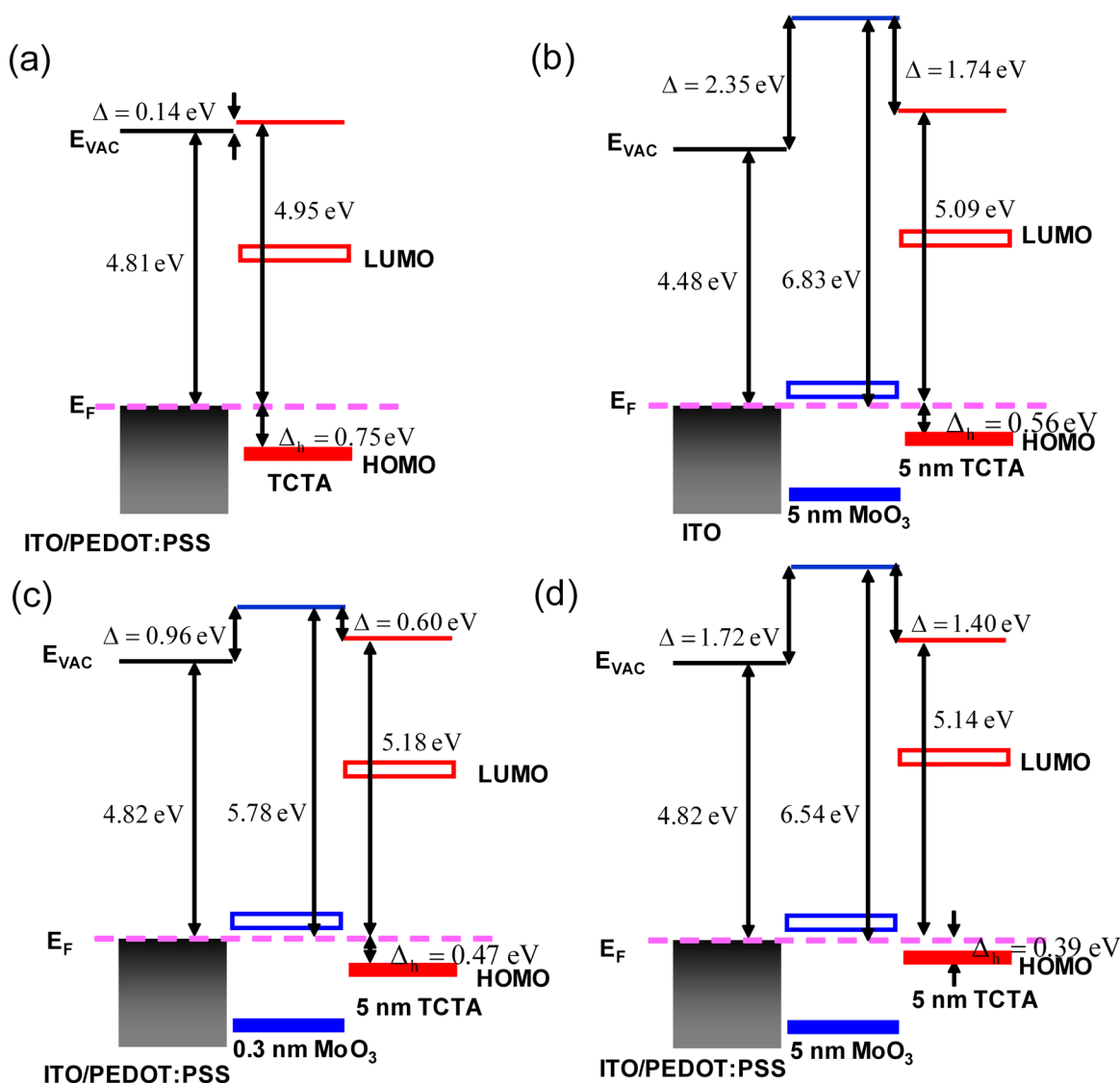


FIG. 3. (Color online) Energy level diagram for ITO/HIL/TCTA: (a) PEDOT:PSS, (b) MoO<sub>3</sub>, (c) PEDOT:PSS/thin MoO<sub>3</sub> and (d) PEDOT:PSS/thick MoO<sub>3</sub>.



0.5 nm MoO<sub>3</sub> the work function of PEDOT:PSS approaches 6.10 eV, which is even higher than IPs of most large bandgap HTLs, such as TCTA (5.7 eV), 1,3-Bis(carbazol-9-yl)benzene (mCP) [5.7 eV], and 4,4'-Bis(carbazol-9-yl)biphenyl (CBP) [6.0 eV]. The work function saturates at 6.54 eV after enough thick MoO<sub>3</sub> is deposited on PEDOT:PSS. The observed vacuum level evolution at PEDOT:PSS/MoO<sub>3</sub> interface is very similar to other MoO<sub>3</sub>/Metal or MoO<sub>3</sub>/organic interfaces. As shown in Fig. 1(b), the valence band edge of MoO<sub>3</sub> layer with respect to the Fermi level is determined to be about 2.72 eV, indicating the n-type nature of thermal evaporated MoO<sub>3</sub>.

From the above analysis, we can assume that a thin MoO<sub>3</sub> on PEDOT:PSS should be enough to efficiently inject holes to most HTLs due to its high work function. We systematically investigated the energy level alignment at the interface between ITO/PEDOT:PSS/MoO<sub>3</sub> and TCTA and compared it with the cases for TCTA on ITO/MoO<sub>3</sub> and ITO/PEDOT:PSS. The results are shown in Fig. 2. For TCTA on pristine ITO/PEDOT:PSS, there is a small upward vacuum level shift of 0.14 eV [shown in Fig. 2(a)] and a relatively deep lying HOMO edge at 0.75 eV [shown in Fig. 2(b)]. Since the hole injection barrier can be measured as the energy difference between the HOMO edge and the Fermi level, this value is much larger than that of commonly observed for  $\alpha$ -NPD (0.4 eV),<sup>15</sup> pentacene (0.25 eV),<sup>15</sup> and CuPc (0.4 eV) (Ref. 20) on PEDOT:PSS. As a comparison, the energy level alignment at TCTA and MoO<sub>3</sub> modified ITO anode is given in Figs. 2(c) and 2(d). With 5 nm MoO<sub>3</sub> on ITO, a high WF of 6.83 eV was achieved and the resulting injection barrier between TCTA and ITO/MoO<sub>3</sub> was found to be 0.56 eV, which is similar to TCTA on WO<sub>3</sub>.<sup>13</sup> We can see that the injection barrier at TCTA and ITO/MoO<sub>3</sub> interface was about 0.2 eV less than that of TCTA/PEDOT:PSS interface, which implies that MoO<sub>3</sub> modified ITO should have better hole injection ability than ITO/PEDOT:PSS. The UPS results of ITO/PEDOT:PSS/MoO<sub>3</sub> are shown in Figs. 2(e)–2(h). As seen in Fig. 2(e), a coverage of 0.3 nm MoO<sub>3</sub> on PEDOT:PSS increases the work function to 5.78 eV. Although this value is smaller than that of ITO/MoO<sub>3</sub>, the resulting hole injection barrier, as shown in Fig. 2(f), however, is determined to be 0.47 eV, which is reduced by 0.1 eV relative to the case of ITO/MoO<sub>3</sub> anode. When the thickness of MoO<sub>3</sub> on PEDOT:PSS was increased to 5 nm, the work function was further increased to 6.54 eV and the hole injection barrier was further decreased to 0.39 eV, indicating the superior effect of PEDOT:PSS/MoO<sub>3</sub> composite film on reducing hole injection barrier. We assume the reason for this may be due to the dual function of PEDOT:PSS (Ref. 15) and MoO<sub>3</sub> since both of them were reported to be able to reduce the hole injection barrier compared with bare ITO or metal anode. To give a good perception, the energy level diagrams for the above four cases are shown in Fig. 3.

## B. Effect of PEDOT:PSS/MoO<sub>3</sub> composite film on current density-voltage property

As shown above, the utilization of PEDOT:PSS/MoO<sub>3</sub> composite film on ITO anode greatly reduced the hole injection barrier, indicating that hole current should be signifi-

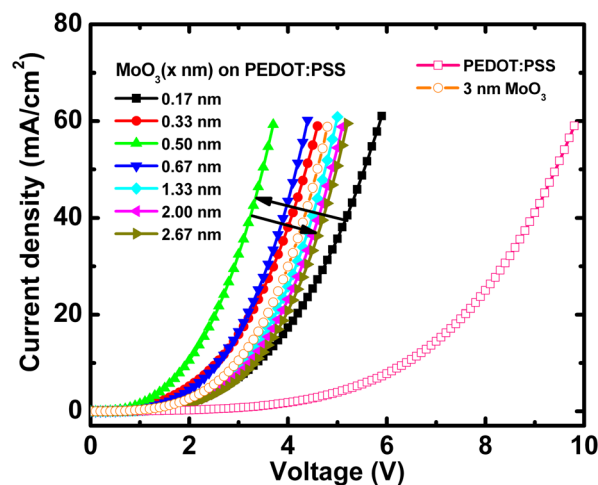


FIG. 4. (Color online) Current density-voltage characteristics of TCTA hole-only devices with different HILs on ITO anode.

cantly enhanced in the devices. To demonstrate this, some hole-only devices with different HILs were fabricated and the current density-voltage (J-V) characteristics of them were compared. The hole-only device structures are ITO/HIL/TCTA(100 nm)/MoO<sub>3</sub>(5 nm)/Al. The 5 nm MoO<sub>3</sub> between TCTA and Al is used as electron blocking layer. The results are shown in Fig. 4. It can be seen that the optimized thickness of MoO<sub>3</sub>, such as 0.5 nm, shows much more high hole injection current with respect to the cases of individual MoO<sub>3</sub> or PEDOT:PSS as HIL. This also indicates that it is necessary to optimize the thickness of MoO<sub>3</sub> in PEDOT:PSS/MoO<sub>3</sub> composite film as HIL for achieving large hole injection current. Very thin MoO<sub>3</sub> film seems not to play the effective role of enhancing hole injection current due to the partial coverage, thus not enough high work function. Furthermore, however, since the hole injection process is due to electron extraction from the HOMO of HTL through the MoO<sub>3</sub> conduction band,<sup>11</sup> the thicker MoO<sub>3</sub> film may make the electron extraction through MoO<sub>3</sub> film difficult, thus larger driving voltage is needed to efficiently extract the electrons. No matter what, the utilization of PEDOT:PSS/MoO<sub>3</sub> composite film as HIL greatly improves the hole injection property, which should be in favor of reducing operational voltage, thus enhancing device efficiency.

## C. Effect of PEDOT:PSS/MoO<sub>3</sub> composite film on hole injection stability

We further investigated the effect of PEDOT:PSS/MoO<sub>3</sub> composite film as HIL on hole injection stability. For comparison, the hole-only devices with only MoO<sub>3</sub> or PEDOT:PSS as HIL were also included. The measurement was conducted by performing J-V sweep at several time intervals in air. The voltage evolution of the three devices with time at fixed current density of 100 mA/cm<sup>2</sup> was extracted and plotted in Fig. 5. For the hole-only device with PEDOT:PSS as HIL, the J-V stability is much poorer as already pointed out by others.<sup>21</sup> When MoO<sub>3</sub> or PEDOT:PSS/MoO<sub>3</sub> is used as HIL, much better air stability can be

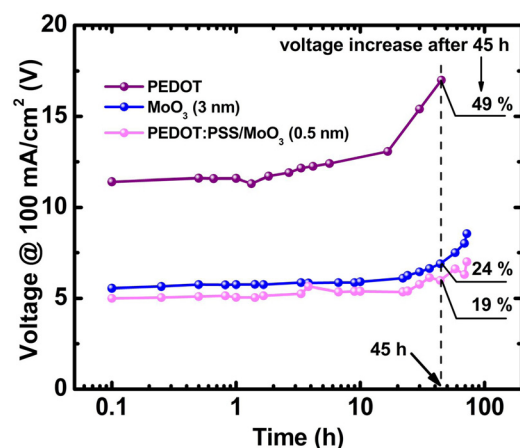


FIG. 5. (Color online) I-V air stability of HODs with three different HILs.

achieved. For example, after stored in air for about 45 h, the voltage increase percentages with respect to the initial values were 49%, 24%, and 19% for PEDOT:PSS, MoO<sub>3</sub>, and PEDOT:PSS/MoO<sub>3</sub> HILs, respectively. It can be seen that the hole injection stability of device with PEDOT:PSS/MoO<sub>3</sub> composite film as HIL is greatly improved. This means that the instability of device with PEDOT:PSS as the HIL mainly come from the degradation of PEDOT:PSS/organic semiconductor interface rather than from the ITO/PEDOT:PSS interface. The insertion of MoO<sub>3</sub> between anode and organic semiconductor greatly improves the device stability,<sup>5</sup> which should also work for the PEDOT:PSS/organic semiconductor interface. This also indicates that the drawback of instability of PEDOT:PSS as HIL observed in real devices may be well resolved by employing this method.

#### IV. CONCLUSIONS

In conclusion, we have developed an effective hole injection layer material, a composite film composed of MoO<sub>3</sub> and PEDOT:PSS. We have shown that the utilization of the PEDOT:PSS/MoO<sub>3</sub> composite film as HIL not only enhances greatly hole injection current, but also significantly improves the stability of hole injection. It is found that the instability of devices with PEDOT HIL should mainly result from the degradation of PEDOT/organic semiconductor interface rather than from ITO/PEDOT. We also find that very thin MoO<sub>3</sub> film modified on PEDOT:PSS is enough to reduce the hole injection barrier and the optimum thickness of MoO<sub>3</sub> was determined to be 0.5 nm. It is expected that the

PEDOT:PSS/MoO<sub>3</sub> composite film would show large potential in real devices.

#### ACKNOWLEDGMENTS

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