Contents lists available at ScienceDirect

# **Organic Electronics**

journal homepage: www.elsevier.com/locate/orgel

# Hybrid organic light-emitting device based on ultrasonic spray-coating molybdenum trioxide transport layer with low turn-on voltage, improved efficiency & stability

Shihao Liu<sup>a</sup>, Xiang Zhang<sup>a</sup>, Shirong Wang<sup>a</sup>, Haiwei Feng<sup>a</sup>, Jiaxin Zhang<sup>a</sup>, Huishan Yang<sup>b</sup>, Letian Zhang<sup>a,\*\*</sup>, Wenfa Xie<sup>a,b,\*</sup>

<sup>a</sup> State Key Laboratory on Integrated Optoelectronics, College of Electronics Science and Engineering, Jilin University, Changchun, 130012, People's Republic of China <sup>b</sup> Department of Physics, Quanzhou Normal College, Quanzhou, 362000, People's Republic of China

#### ARTICLE INFO

Keywords: MoO<sub>3</sub> Hybrid OLED Ultrasonic spray Vacuum thermal evaporating

# ABSTRACT

Hybrid organic light-emitting devices (OLEDs) employing inorganic oxides as carrier transport layer can further improve the performances of OLEDs, such as power efficiency, reduce turn-on voltage and enhance stability. Vacuum thermal evaporating (VTE) and ultrasonic spray coating (USC) molybdenum trioxide (MoO<sub>3</sub>) films with the thickness of 60 nm are used as hole transport layer (HTL) to realized hybrid OLEDs. USC-MoO<sub>3</sub> based OLED performs much better than VTE-MoO<sub>3</sub> based OLED. Atom forces microscope images shows that both VTE-MoO<sub>3</sub> film and emitting layer deposited on it have an extremely rough surface, offering convenient entrance ports for the intrusion of oxygen and water vapor into organic function layer. Nevertheless, USC MoO<sub>3</sub> film and emitting layer deposited on it exhibit much smoother surface so that oxygen and water vapor must completely destroy the metal cathode before they intrude in the organic function layers. Besides, to prevent MoO<sub>3</sub> quenching excitons, host material with excellent hole transport property is used to restrict exciton recombination region at the interface between emitting layer and electron transport layer. As a result, hybrid OLEDs employing USC-MoO<sub>3</sub> as HTL are realized with low turn-on voltage, improved efficiency and stability.

### 1. Introduction

During the last thirty years, the development of organic lightemitting devices (OLEDs) technology based on sandwich-structure is considerable and the OLEDs-related products have come to enter the daily life of ordinary people [1–6]. However, there are still some problems to be worked out, such as limited device lifetime and high manufacture cost [5,7,8]. Additionally, the electroluminescent performances are far below the theoretical maximum now and higher requirements are still needed.

To some extent, the issues faced by the OLEDs should be caused by the intrinsic physics and chemistry properties of small molecular organic materials, such as limited carrier transport mobility and low glass transition temperature ( $T_g$ ) [9,10]. Due to limited mobility, the thickness of OLEDs should be confined to about 100 nm to ensure high efficiency [1–6]. Besides, Joule heat of devices can easily cause crystallization of organic materials. Thus, a slight change of hole transport layer serving as a base of whole OLED, would lead to the failure of devices. Therefore, highly conductive and stable hole transport layer is beneficial to improve performances of OLEDs.

Metal oxides carrier transport layer has drawn attention by the researches [11,12]. Their atoms connect with each other by covalent bond or ionic bond so that metal oxides could have better carrier transport ability and thermal stability. Molybdenum trioxide (MoO<sub>3</sub>) has been widely used in OLEDs as hole injection layer due to its favorable energy level alignment [13]. Vacuum thermal evaporation (VTE) process is the conventional method to fabricate ultrathin MoO<sub>3</sub> films. However, the process is not suitable for thick MoO<sub>3</sub> films due to high melting point of MoO<sub>3</sub>. Due to the vapor growth mechanism, the thick VTE MoO<sub>3</sub> films always have rough film morphology [14]. Furthermore, MoO<sub>3</sub> also has a serious quenching effect on excitons since MoO<sub>3</sub> can introduce acceptor states for non-radiative transition [15,16]. The existence of these problems prevent the realization of efficient hybrid OLEDs employing MoO<sub>3</sub> as hole transport layer.

To solve the problems, ultrasonic spray coating (USC) process requiring low annealing temperature is used to fabricate much smoother

\*\* Corresponding author.

http://dx.doi.org/10.1016/j.orgel.2017.10.041 Received 25 September 2017: Received in revised for

Received 25 September 2017; Received in revised form 28 October 2017; Accepted 28 October 2017 Available online 31 October 2017 1566-1199/ © 2017 Elsevier B.V. All rights reserved.







<sup>\*</sup> Corresponding author. State key Laboratory on Integrated Optoelectronics, College of Electronics Science and Engineering, Jilin University, Changchun, 130012, People's Republic of China.

E-mail addresses: zlt@jlu.edu.cn (L. Zhang), xiewf@jlu.edu.cn (W. Xie).

(a) Solution MoO<sub>3</sub> Film Ultrasonic Nozzle **Film Forming Liquid Layer** Substrate **Ultrasonic Atomization Droplets Coalescence** Solvent Evaporation (b) Aqueous Solution 30s 200s **N**s **Methanol Dilute Solution** 20s 0s 5s

**Fig. 1. (a)** The schematic diagram of the USC process, (b) (c) the lateral static images of  $MoO_3$  aqueous and methanol dilute solution droplets after falling on substrate.

MoO<sub>3</sub> films, whose chemical composition, transmittance, conductivity, surface morphology and quenching effect on excitons are studied in detail. Additionally, 4,4',4"-Tris(carbazol-9-yl) triphenylamine (TCTA) with excellent hole transport ability [17] is used as host to keep excitons recombination region from the interface of MoO<sub>3</sub>. Finally, efficient hybrid OLEDs with simple structure is fabricated successfully. The hybrid OLEDs exhibit low turn-on voltage, improved efficiency and device stability.

#### 2. Experimental section

# 2.1. Device fabrication

MoO<sub>3</sub> powder, small molecular organic materials 4,7-Diphenyl-1,10-phenanthroline (Bphen), 4,4',4"-Tris (carbazol-9-yl) triphenylamine (TCTA) and green phosphorescent dopant tris (2-phenylpyridine) iridium (III) [Ir(ppy)<sub>3</sub>] are purchased from Luminescence Technology Corporation. The peroxo-polymolybdate solution is prepared by mixing 80 mg MoO<sub>3</sub> powder into 4 ml hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) aqueous solution (30 wt%, Aladdin) and the solution is refluxed for 2 h at 60 °C. And then 19 times volume methanol solvent is added to dilute the original aqueous solution. Before film deposition, the ITO glass substrates are subjected to a routine cleaning process. First, it is rinsed by Decon 90 and ultrasonic cleaned in deionized water three times for 5 min, and then dried in an oven at 120 °C for 10 min, and finally treated in a plasma cleaner chamber (PDC-32G, Harrick) for 3 min.

The peroxo-polymolybdate methanol aqueous solution (1 mg/mL) is used to form the MoO<sub>3</sub> HTL on ITO substrate through the USC process. The USC process is carried on in ultrasonic spray coating system (UC320, Siansonic Technology Co. Beijing, China) employing D series ultrasonic nozzle. In the USC process, the ultrasonic nozzle is about 10 cm over the heating plate. To be efficiently atomized to micrometerscale drops, the MoO<sub>3</sub> solution is injected into the ultrasonic spray nozzle with the speed of 3 ml/min under the effect of 1 MHz ultrasonic vibrational energy. To obtain MoO<sub>3</sub> film with suitable thickness, the injection volume is set to 100 µL. The temperature of the heating plate in the fabrication process is set at 40 °C, while the post-treatment temperature for MoO<sub>3</sub> film is 120 °C for 30 min to remove residual water and methanol. And then, the emitting layers, carrier transfer layers and cathode are evaporated on the substrate orderly by vacuum thermal evaporation (VTE) process in vacuum oven ( $\sim 6 \times 10^{-4}$  Pa). Monitored by quartz oscillators, the rate of the VTE films is controlled at 1–2 Å s<sup>-1</sup>.

#### 2.2. Device characterization

The contact angle goniometer (JC2000D, Powereach Co., Shanghai, China) is used to take the static lateral images. The surface morphologies of the films are measured by atomic force microscope (AFM, Dimension Icon, Bruker Co., Germany) in contact mode, while the fluorescence microscopy images of devices are obtained by the inverted fluorescence microscope (Mshot M53, Micro-shot Technology Co. Ltd., Guangzhou, China). Thermo ESCALAB 250 with Al Ka radiation is used to detect the X-Ray photoelectron spectroscopy (XPS) spectra and the binding energies are calibrated with the C1s peak at 284.8 eV. For the room temperature time-resolved transient PL decays, the measurements are carried on the IHR320 spectrometer (HORIBA, USA). The electroluminescent properties of unpackaged devices, such as luminance-current-voltage characteristics and emission spectra are measured simultaneously using Goniophotometric Measurement System based on spectrometer (GP-500, Otsuka Electronics Co. Osaka, Japan) in air at room temperature.

#### 3. Result and discussion

#### 3.1. The fabrication of $MoO_3$ films by USC process

The peroxo-polymolybdate solution is prepared according to the method reported by Wang et al. [18]. The schematic diagram of the USC process is shown in Fig. 1 (a). In the USC process, a continuous liquid layer must be formed on the substrate. To ensure high material utilization, instruments that produce centrifugal force to smooth the liquid layer are not used here. As a result, excellent wettability of the solution is the key condition to keep uniform liquid film during our USC process. That's because, a small amount of solution with excellent wettability could form a uniform liquid layer controlled by substrate surface forces, while solution with bad wettability could not. Besides, excellent wettability could also ensure the liquid film keep uniform distribution all the time.

However, as shown in Fig. 1 (b), the  $MoO_3$  aqueous solution droplet can't wet the ITO substrate very well. After the aqueous solution droplet falls on the substrate, the droplet keeps a hemispherical shape all the time and the water solvent is hard to be evaporated. To improve the wettability of  $MoO_3$  solution and accelerate the evaporation of solvent, methanol with low surface tension and boiling point is introduced. As shown in Fig. 1 (c), after the methanol dilute solution fall on the substrate, the droplets immediately spread out to form an ultra-thin liquid layer with uniform distribution. Additionally, due to the low boiling point of methanol, the solvent could be evaporated absolutely in a short time. Hence, based on the  $MoO_3$  methanol dilute solution, high quality  $MoO_3$  (s $MoO_3$ ) film is successfully realized by the USC process.

#### 3.2. The film properties of $sMoO_3$ films

#### 3.2.1. The chemical composition of sMoO<sub>3</sub> films

In order to clarify the chemical compositions of  $sMOO_3$  films, the Xray photoelectron spectroscopy (XPS) of these films are studied. The spectra of survey scan, Mo 3d and O 1s of  $sMOO_3$  films before annealing ( $sMOO_3$ -BA) and after annealing ( $sMOO_3$ -AA), and vacuum thermal evaporation (VTE)  $MOO_3$  film ( $eMOO_3$ ) are shown in Fig. 2 (a), (b) and (c), respectively. From the survey spectra, four intense peaks that correspond to O 1s, Mo 3p, C 1s and Mo 3d could be found in all three films. The C 1s peak at 284.8 eV used for calibration should arise from adventitious hydrocarbon contamination. The O 1s and Mo 3d peaks are much more intense in accordance with the characteristics of neat  $MOO_3$  layer. The O:Mo ratio of  $sMOO_3$ -BA,  $sMOO_3$ -AA and  $eMOO_3$  film is 3.24, 2.87 and 2.81, respectively.

Additionally, it could be seen from Fig. 2 (b) that the sMoO<sub>3</sub>-AA (after annealing) has two symmetric peaks Mo 3d<sub>5/2</sub> at 233.1 and Mo 3d<sub>3/2</sub> at 236.2 eV, which are identical to the eMoO<sub>3</sub>. It means that the Mo atoms mainly belong to the Mo<sup>6+</sup> oxidation state. With regard to the high resolution O 1s spectra, the performance of sMoO<sub>3</sub>-AA and eMoO<sub>3</sub> is also same. As indicated in Fig. 2 (c), both sMoO<sub>3</sub>-AA and eMoO<sub>3</sub> have a dominant Oa peak at 531.1 eV and a weak Ob peak at 532.3 eV. However, the intensity of Ob peak of sMoO<sub>3</sub>-BA (before annealing) is comparable to Oa peak. The Oa peak of the O1s should be attributed to the Mo-O bond, while the higher binding energy Ob usually arises from chemisorbed or dissociated oxygen or OH species on the surface of the MoO<sub>3</sub> thin film, such as adsorbed H<sub>2</sub>O or adsorbed O<sub>2</sub> [19]. Thus, the strong Ob peak in sMoO<sub>3</sub>-BA indicates the existence of residual water and methanol solvent, which also clarifies the higher O:Mo ratio of sMoO<sub>3</sub>-AA film. Nevertheless, it could be seen from the similar O 1s spectra of sMoO<sub>3</sub>-AA and eMoO<sub>3</sub> that the residual water or methanol could be mainly removed after a low temperature annealing. Considering the above results, we can conclude that MoO<sub>3</sub> film fabricated by the USC process has an identical chemical composition to the one obtained by the VTE process.

#### 3.2.2. The optical and electrical properties of sMoO<sub>3</sub> films

The optical and electrical performances of sMoO<sub>3</sub> films have an important influence on their application in OLEDs. Fig. 2 (d) shows the transmittance and Tauc plots of eMoO<sub>3</sub> and sMoO<sub>3</sub> films. It could be seen that transmittance curves of sMoO<sub>3</sub> and eMoO<sub>3</sub> has a similar tendency that the value is nearly same in the visible wavelength range. Additionally, based on the refractive index of amorphous MoO<sub>3</sub> from Kessels et al., a simulated transmittance is obtained [20]. Apparently, the simulated results coincide well with the experimental ones. Thus, the eMoO<sub>3</sub> and sMoO<sub>3</sub> should belong to amorphous films, and it is also proved by X-Ray Diffraction measurements since there is no any diffraction peak to be observed. Furthermore, the optical properties can be also used to determine the value of the band gap of the films. By using Tauc's plot  $[a_{hv} \approx (hv - \text{Eg})^{1/2}]$  calculated by the optical properties, the band gaps of eMoO<sub>3</sub> and sMoO<sub>3</sub> films are obtained as shown in Fig. 2 (d).

When the MoO<sub>3</sub> film is used as hole transport layer, its quenching effect on excitons should be considered. To explore the quenching effect, emitting layers (EMLs) consists of 90% TCTA and 10 wt% Ir(ppy)<sub>3</sub> is deposited on the eMoO<sub>3</sub> and sMoO<sub>3</sub> films and their time-resolved transient PL decays are measured as shown in Fig. 2 (e). Since the Ir (ppy)<sub>3</sub> is a phosphorescent material, the EML deposited on glass substrate exhibits a long decay time which could attain to 1.18  $\mu$ s. Weak quenching effect could be observed in the EML on MoO<sub>3</sub> films. Decay time of PL intensity from EML on eMoO<sub>3</sub> and sMoO<sub>3</sub> become to 831 and 841 ns. It should be attributed to that MoO<sub>3</sub> could introduce acceptor states for non-radiative transition. Nevertheless, after introducing the interlayer, the decay time could be restored to 1.03  $\mu$ s, indicating that quenching effect of MoO<sub>3</sub> on excitons away from it becomes much weaker.

Besides, hole injection and transport ability of the MoO<sub>3</sub> films under high electric field intensity is also investigated by the measurement about the electrical properties of single-carrier devices based on MoO<sub>3</sub> films. The current intensity of single-carrier devices based on sMoO<sub>3</sub>, eMoO<sub>3</sub> and TCTA films under different electric field intensity is shown in Fig. 2 (f). It could be seen that the current intensity of single-carrier device based on sMoO<sub>3</sub> films is similar to single-carrier device based eMoO<sub>3</sub>. However, the current intensity of TCTA-based devices is much lower. Additionally, the discharge time of residual charges accumulated in the electrode interface after turning off the positive bias voltage is also introduced to justify the hole transport ability as shown in Fig. 2 (f). In the measurement of discharge process, arbitrary waveform generator (Rigol, DG5102), high-speed switching diode (Philips, 1N4531) and single-carrier devices are connected in series orderly, and digital oscilloscope (Rigol, DS4054) is used to measure the voltage across single-carrier device. The circuit diagram used for the measurement is shown in the inset of Fig. 2(f). Due to the current-voltage characteristic of diodes, charge carriers can easily flow through the switching diode and transfer into the single-carrier device when the waveform generator outputs positive voltage. In addition, the existence of injection barrier leads to that a certain amount of holes or electrons are accumulated at the interface between function layer and anode or cathode. After the output of waveform generator turns to negative voltage, charge carriers are forbidden to flow through switching diode and the residual holes in the anode interface can only traverse the films of single-carrier device to neutralize the electrons of cathode interface. Hence, the discharge time is depended on the hole transport ability of the film in singlecarrier device. As seen in Fig. 2 (f), the residual charges in eMoO<sub>3</sub> and sMoO3-based devices are released completely and immediately after turning off the positive bias voltage. However, those in TCTA-based device exhibits relatively slow discharge process. With the consumption of residual charges, the internal resistance of device becomes too large to ignore the influence of the  $1M\Omega$  resistance of oscilloscope. Besides, as seen in Fig. 2 (f), the measured voltages of these single-carrier devices are different before the discharge stage. It should be attributed that forward resistance of switching diodes could not be ignored so that bias



Fig. 2. (a) Survey scan, (b) Mo 3d and (c) O 1s XPS spectra of eMoO<sub>3</sub>, sMoO<sub>3</sub>-BA and sMoO<sub>3</sub>-AA films; (d) transmittance and Tauc plots of eMoO<sub>3</sub> and sMoO<sub>3</sub> films; (e) room temperature time-resolved transient PL decays of emitting layers on glass, eMoO<sub>3</sub>, sMoO<sub>3</sub> and sMoO<sub>3</sub> and sMoO<sub>3</sub> with interlayer; and (f) the conductivity of TCTA, eMoO<sub>3</sub> and sMoO<sub>3</sub> films under high electric filed intensity.

voltage across the single-carrier devices is obviously affected by their internal resistances. These results shows that the  $MoO_3$  films have much better hole injection and transport ability than TCTA organic film.

#### 3.2.3. The surface topography of $sMoO_3$ films

The atom force microscope (AFM) images of  $eMoO_3$  and  $sMoO_3$ films are shown in Fig. 3(a) and (b), respectively. It can be seen that the  $sMoO_3$  films has an obviously different surface topography with the  $eMoO_3$  film. The  $eMoO_3$  film obtained by vapor-phase process has a rough surface, and its root-mean-square roughness (RMS) and maximum vertical distance between the highest and lowest points (R<sub>max</sub>) in the whole measured area (5 × 5 µm) is 3.60 and 35.9 nm, respectively. Nevertheless, the  $sMoO_3$  fabricated by liquid-phase process exhibits smoother surface since its RMS and R<sub>max</sub> is only 1.28 and 9.76 nm, respectively. Their cross-section plots could make the difference more visual. There are serious fluctuations in  $eMoO_3$  film while the fluctuations in sMoO<sub>3</sub> film are restricted within the limit of  $\pm$  3 nm. Additionally, the difference in film morphology could be also reflected in the contact angle of water. As seen in the insets of Fig. 3 (a) and (b), the contact angle of water on eMoO<sub>3</sub> and sMoO<sub>3</sub> film is 7.62° and 31.52°, respectively. According to Wenzel equation, when the contact angle is lower than 90°, the obvious decrease occurs in contact angle could indicate that the eMoO<sub>3</sub> film is much rougher than the sMoO<sub>3</sub> film.

The different surface topography should arise from the different film formation mechanism. In the VTE process based on vapor phase with long mean free path, the film growth is strongly dependent on the substrate surface energy and the interaction between atoms or molecules. Additionally, defects of substrate, material impurities and impact of the residual gas would still have an obvious influence on the film growth. Because the MoO<sub>3</sub> molecules have strong binding interaction with each other, they will follow island growth mode to form the film.



Fig. 3. (a) (b) AFM images of eMoO<sub>3</sub> and sMoO<sub>3</sub>, the insets are the contact angle of water on them; (d) (e) AFM images of emitting layer deposited on them, (c) (f) shows the cross-section plots.

And then, the continuous film formed by the connection of the growing islands exhibits rough and porous film morphology. However, the case is different for the film obtained from liquid phase since the mean free path of molecule is relatively short in liquid. The  $MoO_3$  solute could be homogeneously distributed in methanol aqueous solution because of the rapid random thermal motion.

Beyond that, the film morphology of MoO<sub>3</sub> films could also obviously affect the growth of EML deposited on them. Fig. 3 (d) and (e) the AFM images of EMLs deposited on eMoO<sub>3</sub> and sMoO<sub>3</sub> films. It could be seen that even the deposition of EML could not eliminate the rough surface of eMoO<sub>3</sub>. The surface of EML on eMoO<sub>3</sub> is still rough, and the value of its RMS and R<sub>max</sub> is 3.75 and 30.9 nm, respectively. However, as indicated in Fig. 3 (e), the introduction of EML results in the reduction of its RMS and R<sub>max</sub> to 0.78 and 7.39 nm, respectively.

#### 3.3. OLEDs employing $sMoO_3$ film as hole transport layer

# 3.3.1. The device structure of $sMoO_3$ -based OLEDs

Employing the  $sMoO_3$  as hole transport layer, hybrid OLEDs (sM-HT) are successfully fabricated and the device structure is shown in Fig. 4. Because the major component of low-temperature-annealed sol-gel-derived film is  $MoO_3$ , the work function of bulk  $MoO_3$  [21–23] are used to describe the energy levels of  $sMoO_3$ . Besides, two other devices are also fabricated for comparison. The device eM-HJ is a conventional device in which ultrathin vacuum thermal evaporating  $MoO_3$  (eMOO<sub>3</sub>) is used as hole injection layer. The device eM-HT is the device in which thick eMoO<sub>3</sub> film is used as hole transport layer.

#### 3.3.2. The EL performances of sMoO<sub>3</sub>-based OLEDs

Firstly, the current density-voltage-luminance characteristics of these devices are investigated and their performances are shown in Fig. 5 (a). The current density of hybrid device sM-HT doesn't show much lower current density than the conventional device eM-HJ. Additionally, the turn-on voltage of hybrid device sM-HT even becomes lower than device eM-HJ. The turn-on voltage of devices sM-HT, eM-HJ, and eM-HT is 2.66, 2.73 and 3.39 V respectively. The low turn-on voltage should be attributed to high conductivity of  $MoO_3$  film as described in Section 3.2.2.

Hybrid device sM-HT also shows superiority in efficiency. Fig. 5 (b) shows the current efficiency-luminance-power efficiency characteristics of these green devices. The maximum current efficiency of devices sM-HT, eM-HJ and eM-HT is 48.9, 42.4 and 37.2 cd/A, respectively. The

maximum power efficiency of device sM-HT is just comparable to device eM-HJ at low luminance. However, after the luminance surpasses 50 cd/m<sup>2</sup>, the superiority of device sM-HT in power efficiency could be observed. These results indicate that excellent luminescent performances could be also obtained by hybrid device sM-HT employing hole-transport material TCTA as host. When electron-transport material TPBi is used as host, its corresponding hybrid device sM-TPBi shows much worse performances than device sM-HT. It should be attributed to that the excitons formed at the interface between sMoO<sub>3</sub> and emitting layer as shown in Fig. 4 (b) can be easily quenched.

Additionally, according to the information of Fig. 5, hybrid device eM-HT performs much worse in turn-on voltage, current density and efficiency. The bad performances of device eM-HT should be attributed to the rapid formation of dark spots. As seen from the images shown in Figs. 4 (c) and 6 (a), there are lots of dark spots in the device eM-HT. The dark spots always indicate that there is no any exciton recombination in the area [24]. Thus, the charges at that location would be inhibited to inject into the organic layers by the non-emissive spots. The formation of dark spots in device eM-HT should be related to the rough morphology of eMO<sub>3</sub> and dark spot formation mechanisms in device sM-HT and eM-HT are shown in Fig. 6 (c).

According to the surface morphology shown in Fig. 3, there are many deep hollows caused by  $eMoO_3$  to offer convenient entrance ports for the intrusion of oxygen and water vapor into organic function layer of device eM-HT. However,  $sMoO_3$  film has extremely smooth surface and it could also ensure the films deposited on it possess smooth and compact surface. The oxygen and water vapor must completely destroy the metal cathode which is known as an oxygen and water vapor barrier before they intrude in the organic function layers of device sM-HT.

Besides, hybrid device sM-HT also performs much better in the device stability. To investigate the device stability, the luminance and bias voltage of devices at 1 mA/cm<sup>2</sup> after storing in air for some time are measured and shown in Fig. 5 (c). The EL luminance of device eM-HJ after storing in air for 8 h still keeps at 65.8% of the beginning, while that of the device sM-HT is 82.6%. However, due to rapidly emerging dark spots, hybrid device eM-HT could only keep at 53.6% of the beginning. According to the radar chart shown in Fig. 5 (d), compared to the conventional device eM-HJ, obvious enhancement in turn-on voltage, stability and efficiency could be observed in hybrid device sM-HT.

Finally, the spectral characteristics of emission from these OLEDs are studied. The normalized EL emission spectra of these devices at the



Fig. 4. (a) The device structure and (b) energy level diagram of  $MoO_3$ -based OLEDs, (c) images of sM-HT and eM-HT at 1 mA/

sM-HT

eM-HT



Fig. 5. (a) The current density-voltage-luminance characteristics and (b) the current efficiency-luminance-power efficiency characteristics of green OLEDs, (c) the luminance of these green devices at the current density of 1 mA/cm<sup>2</sup> after storing in air for some time and (d) the radar chart for comprehensive assessment on EL performances of these devices (L: luminance; TOV: turn-on voltage; EIS: EL intensity stability; PE: power efficiency; CE: current efficiency). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Microscope pictures of device (a) eM-HT and (b) sM-HT excited by UV lamp and the current of 10 mA/cm<sup>2</sup>, (c) schematic diagram of dark spot formation in devices sM-HT and eM-HT.



**Fig. 7.** (a) The normalized EL emission spectra of the green devices at the luminance of  $1000 \text{ cd/m}^2$ , (b) (c) the spectra distribution of sM-HT under different bias voltages and viewing angles, and (d) the spectra distribution of eM-HJ under different viewing angles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

luminance of 1000 cd/m<sup>2</sup> are shown in Fig. 7 (a). It could be found that all these devices exhibit intrinsic emission of  $Ir(ppy)_3$  and their peak wavelength are around 514 nm, proving the efficient formation of excitons in emitting layer. As seen in the angular distribution shown in Fig. 7 (a), the lateral emission from hybrid devices sM-HT and eM-HT is much weaker than the conventional device eM-HJ.

Furthermore, the spectral distributions of device sM-HT in the visible range are investigated to judge whether the MoO<sub>3</sub>-based hybrid OLEDs could keep stable under different bias voltages and viewing angle. As seen from Fig. 7 (b) and (c), the emission spectra of device sM-HT keep stable under different operating voltage and viewing angles. The stability exhibited by device sM-HT under viewing angle from 0° to 90° is even better than the conventional device eM-HJ. When the viewing angle increases from 0° to 90°, the CIE coordinates of device sM-HT shift less than (0.005,0.001), while those of device eM-HJ are (0.011, -0.011).

#### 4. Conclusions

In conclusion, the ultrasonic spray coating (USC) process is demonstrated to be an efficient method to fabricate high-quality  $MoO_3$ film. Employing the sMoO\_3 film as hole transport layer, efficient hybrid organic light-emitting devices is realized. The turn-on voltage of the hybrid organic-emitting devices (OLEDs) is much lower than the conventional devices. Due to its low turn-on and efficient carrier injection, high efficiency could be further improved by sMoO\_3-based hybrid OLEDs. Its maximum current and power efficiency could attain to 48.9 cd/A and 38.8 lm/W, respectively. Apparently, hybrid devices show superiority in turn-on voltage, efficiency and device stability.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 61774074, 61474054, 61475060).

## References

- C.W. Tang, S.A. VanSlyke, Organic electroluminescent diodes, Appl. Phys. Lett. 51 (1987) 913–915.
- [2] M. Helander, Z. Wang, J. Qiu, M. Greiner, D. Puzzo, Z. Liu, Z. Lu, Chlorinated indium tin oxide electrodes with high work function for organic device compatibility, Science 332 (2011) 944–947.
- [3] Q. Zhang, D. Tsang, H. Kuwabara, Y. Hatae, B. Li, T. Takahashi, S.Y. Lee, T. Yasuda, C. Adachi, Nearly 100% internal quantum efficiency in undoped electroluminescent devices employing pure organic emitters, Adv. Mater. 27 (2015) 2096–2100.
- [4] S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, K. Leo, White organic light-emitting diodes with fluorescent tube efficiency, Nature 459 (2009)

234-238

- [5] Z. Wu, D. Ma, Recent advances in white organic light-emitting diodes, Mater. Sci. Eng. R 107 (2016) 1–42.
- [6] H. Sasabe, J. Kido, Development of high performance OLEDs for general lighting, J. Mater. Chem. C 1 (2013) 1699–1707.
- [7] N. Aizawa, Y.-J. Pu, M. Watanabe, T. Chiba, K. Ideta, N. Toyota, M. Igarashi, Y. Suzuri, H. Sasabe, J. Kido, Solution-processed multilayer small-molecule lightemitting devices with high-efficiency white-light emission, Nat. Commun. 5 (2014) 5756.
- [8] T.-H. Han, M.-R. Choi, C.-W. Jeon, Y.-H. Kim, S.-K. Kwon, T.-W. Lee, Ultrahighefficiency solution-processed simplified small-molecule organic light-emitting diodes using universal host materials, Sci. Adv. 2 (2016) e1601428.
- [9] Y. Li, P. Sonar, L. Murphy, W. Hong, High mobility diketopyrrolopyrrole (DPP)based organic semiconductor materials for organic thin film transistors and photovoltaics, Energy Environ. Sci. 6 (2013) 1684–1710.
- [10] H. Sirringhaus, T. Sakanoue, J.F. Chang, Charge transport physics of high-mobility molecular semiconductors, in: W. Brütting, C. Adachi (Eds.), Physics of Organic Semiconductors, Verlag GmbH: KGaA, 2006, pp. 220–225.
- [11] M. Sessolo, H.J. Bolink, Hybrid organic-inorganic light-emitting diodes, Adv. Mater. 23 (2011) 1829–1845.
- [12] H.J. Bolink, H. Brine, E. Coronado, M. Sessolo, Phosphorescent hybrid organic-inorganic light-emitting diodes, Adv. Mater. 22 (2010) 2198–2201.
- [13] C. Girotto, E. Voroshazi, D. Cheyns, P. Heremans, B.P. Rand, Solution-processed MoO3 thin films as a hole-injection layer for organic solar cells, ACS Appl. Mater. Inter. 3 (2011) 3244–3247.
- [14] A. Arfaoui, S. Touihri, A. Mhamdi, A. Labidi, T. Manoubi, Structural, morphological, gas sensing and photocatalytic characterization of MoO<sub>3</sub> and WO<sub>3</sub> thin films prepared by the thermal vacuum evaporation technique, Appl. Sur. Sci. 357 (2015) 1089–1096.
- [15] D. Kabra, M.H. Song, B. Wenger, R.H. Friend, H.J. Snaith, High efficiency composite metal oxide-polymer electroluminescent devices: a morphological and material based investigation, Adv. Mater. 20 (2008) 3447–3452.
- [16] J. Maaβ, M. Wollenhaupt, H. Abrens, P. Fröbel, K. Bärner, The fluorescence of Sm<sup>3+</sup> in lithium molybdate borate glasses, J. Lumin. 62 (1994) 95–100.
- [17] L. Duan, L. Hou, T.-W. Lee, J. Qiao, D. Zhang, G. Dong, L. Wang, Y. Qiu, Solution processable small molecules for organic light-emitting diodes, J. Mater. Chem. 20 (2010) 6392–6407.
- [18] S.-Y. Lin, C.-M. Wang, K.-S. Kao, Y.-C. Chen, C.-C. Liu, Electrochromic properties of MoO<sub>3</sub> thin films derived by a sol-gel process, J. Sol Gel Sci. Technol. 53 (2010) 51–58.
- [19] P.-T. Hsieh, Y.-C. Chen, K.-S. Kao, C.-M. Wang, Luminescence mechanism of ZnO thin film investigated by XPS measurement, Appl. Phys. A Mater. 90 (2008) 317–321.
- [20] M.F. Vos, B. Macco, N.F. Thissen, A.A. Bol, W. Kessels, Atomic layer deposition of molybdenum oxide from (NtBu)<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>Mo and O<sub>2</sub> plasma, J. Vac. Sci. Technol. A 34 (2016) 01A103.
- [21] V. Shrotriya, G. Li, Y. Yao, C.W. Chu, Transition metal oxides as the buffer layer for polymer photovoltaic cells, Appl. Phys. Lett. 88 (2006) 073508–073503.
- [22] C. Tao, S. Ruan, X. Zhang, G. Xie, L. Shen, X. Kong, W. Dong, C. Liu, W. Chen, Performance improvement of inverted polymer solar cells with different top electrodes by introducing a MoO3 buffer layer, Appl. Phys. Lett. 93 (2008) 411.
- [23] T. Yang, M. Wang, Y. Cao, F. Huang, L. Huang, J. Peng, X. Gong, S.Z.D. Cheng, Y. Cao, Polymer solar cells with a low-temperature-annealed sol-gel-derived MoOx film as a hole extraction layer, Adv. Energy Mater. 2 (2012) 523–527.
- [24] M. Schaer, F. Nüesch, D. Berner, W. Leo, L. Zuppiroli, Water vapor and oxygen degradation mechanisms in organic light emitting diodes, Adv. Funct. Mater. 11 (2001) 116–121.