MoO$_3$ as a cathode buffer layer for enhancing the efficiency in white organic light-emitting diodes*

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Molybdenum trioxide (MoO$_3$) as a cathode buffer layer is inserted between LiF and Al to improve the efficiency of white organic light-emitting diodes (OLEDs) in this paper. By changing the MoO$_3$ thickness, a higher current efficiency of 5.79 cd/A is obtained at a current density of 160 mA/cm^2 for the device with a 0.8 nm-thick MoO$_3$ layer as the cathode buffer layer, which is approximately two times greater than that of the device without MoO$_3$. The mechanism for improving the device efficiency is discussed. Moreover, at a voltage of 13 V, the device with a 0.8 nm-thick MoO$_3$ layer achieves a higher luminance of 22370 cd/m^2, and the Commission Internationale de I'Eclairage (CIE) color coordinate of the device with 1 nm-thick MoO$_3$ layer is (0.33, 0.34), which shows the best color purity. Simple electron-only devices are tested to confirm the impact of the MoO$_3$ layer on the carrier injection.

Due to its potential applications for future flat panel display and lighting devices, much effort has been put into investigating organic light-emitting diodes (OLEDs). Optimizing luminescence efficiency of the organic materials is crucial to improve the performance of OLEDs, but it also depends on the carrier injection and transport. Recently, transition metal oxide (TMO), such as molybdenum, vanadium and tungsten oxide (MoO$_3$, V$_2$O$_5$, WO$_3$), placed between an anode electrode and a hole-transport layer could serve as an effective hole-injection layer in OLEDs[1-5]. Regarding cathode buffer-layer materials, it is well known that the insertion of a thin lithium fluoride (LiF) layer at the interface between the tri (8-quinolinolato) aluminum (Alq$_3$) and the aluminum (Al) cathode could obtain a good electron injection ability in OLED[6]. The study for enhancing the electron injection has attracted tremendous attention due to two main factors. On one hand, the electron mobility of electron-transport materials is much lower than the hole mobility of hole-transport materials[7]. On the other hand, the chemical process at the interface between metal electrodes and organic thin films affects the charge transportations, and has a strong effect on the efficiency of OLED[8].

In this paper MoO$_3$ is inserted between LiF and Al for the

further improvement of current efficiency in white OLED. The results show that the white OLED with MoO$_3$ as the cathode buffer layer can acquire a higher current efficiency than that without MoO$_3$. The mechanism for improving device efficiency is also discussed.

The device configuration used in this experiment is indium tin oxide (ITO)/4, 4', 4''-tris [2-naphthyl (phenyl) amino] triphenylamine (2T-NATA,15 nm)/N, N'-bis(naphthalene-1-y1)-N, N'-bis (phenyl)-benzidine (NPB, 25 nm)/ADN: DCJTB(1%): TBPe(2%) (30 nm) /Alq$_3$ (20 nm)/LiF(1 nm)/ MoO$_3$(X nm)/Al(100 nm). The thickness of the MoO$_3$ layer changes from 0 nm to 1.2 nm to investigate the effect of MoO$_3$ on current efficiency of OLEDs.

The ITO-coated substrates with a sheet resistance of 20 Ω/□ are used as the anode. Prior to the organic materials being deposited, the substrates were cleaned successively by utilizing acetone and ethanol in an ultrasonic bath for 10 min, and then treated with air plasma before these organic materials were deposited. All the layers of the devices were fabricated by thermal evaporation in a high-vacuum chamber with the vacuum of about 8×10^{-4} torr, and all the deposition experiments were continued without vacuum break.

The emitting layer is 9, 10-di (2-naphthy1) anthracene

(ADN) doped with 2% 2, 5, 8, 11-tetra-butyl-perylene (TBPe) and 1% 4-(dicyanomethylene)-2-t-butyl-6-(1, 1, 7, 7, - tetram-ethyljulolidyl-9-enyl)-4H-py-ran (DCJTB). The composite film was prepared by the simultaneous co-deposition of host and dopant from three separated sources. The deposition rate of the organic materials was 0.2–0.3 nm/s, and the thicknesses of all the layers were measured using quartz-crystal monitors.

The electroluminescent (EL) spectra and the CIE coordinates of the devices were measured by PR-655 spectrophotometer. The current-voltage and luminance-voltage characteristics were measured simultaneously with a programmable Keithley 2400 voltage-current source. All measurements were carried out at room temperature under ambient conditions.

For researching carrier injection, two different electron-only devices were fabricated. These devices have the following structures of ITO/Alq_3 (20 nm)/LiF (1 nm)/MoO_3 (0.8 nm)/Al (100 nm) named as E-A and ITO/Alq_3 (20 nm)/LiF (1 nm)/Al (100 nm) named as E-B.

Fig.1 depicts the characteristic of current density J versus voltage V for these devices. It is obvious that the device without the MoO_3 cathode buffer layer exhibits a lower current density at the same driving voltage compared with MoO_3 inserted devices. This indicates that the electron injection ability of device E-A is stronger than that of device E-B.
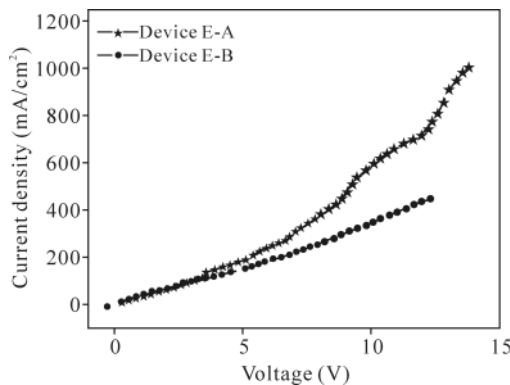
Fig.1 Current density versus voltage for the electron-only devices

In order to get the optimal thickness of the MoO_3 layer, several devices with different thicknesses of the MoO_3 layer were fabricated. The structures of the devices are ITO/2T-NATA (15 nm)/NPB (25 nm)/ADN:DCJTB(1%):TBPe (2%) (30 nm)/Alq_3 (20 nm)/LiF (1 nm)/MoO_3 (X nm)/Al (100 nm), where X=0 nm, 0.3 nm, 0.5 nm, 0.8 nm, 1.0 nm, 1.2 nm for devices A-E, respectively. To clearly compare the performance of these devices, characteristics of current density J and luminance L versus voltage V for these devices are obtained as shown in Fig.2. It is found that the behaviors of these devices are highly dependent on the thickness of the MoO_3 layer.
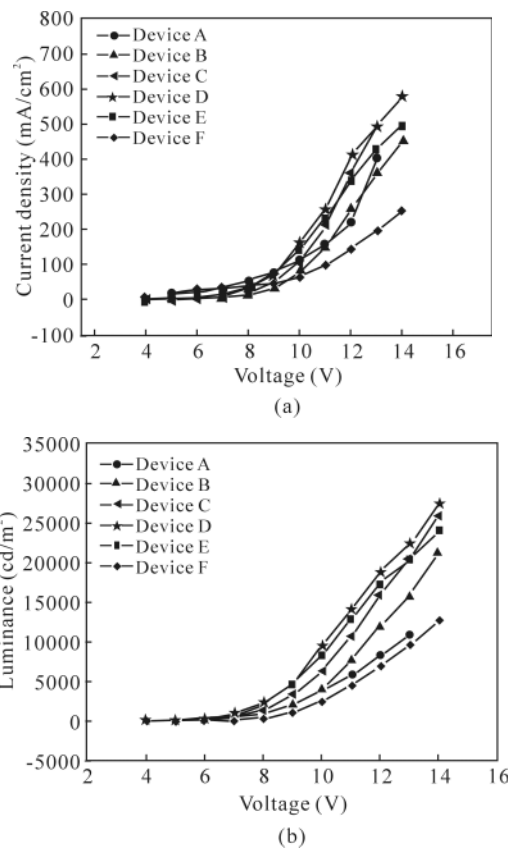
Fig.2 Characteristics of (a) current density and (b) luminance versus voltage for devices with different thicknesses of MoO_3 layer

It can be seen in Fig.2(a) that the device A has a higher current density than the others at the voltage of 9 V. For the OLED device, a current of electrons passes through the electron transport layer, and a current of holes travels in the opposite direction through the hole transport layer. This creates a concentration of oppositely charged species in the emissive layer. The electrons and holes then combine in the emissive layer. The amount of carrier injection is improved with the increase of voltage. Because the electron injection ability of device with MoO_3 is stronger than that of device without MoO_3, it can form more photons than the device without MoO_3. At 9 V, the device with MoO_3 has a lower current density because more photons are formed. As shown in Fig. 2(b), the insertion of MoO_3 results in the higher luminance of white OLED. For instance, at 9 V, the luminance of device D is 4910 cd/m^2, whereas the luminance of devices A is 2050 cd/m^2.

From Fig.2(b), we find that the luminance of device D is higher than that of other devices at any given voltage. Apparently, the device D also has the highest current density when the voltage is more than 9 V. This is because electron and hole combine in a relative balance with the increase of voltage, the current density of electron is increased, and hence the

total current density is increased. Therefore, the current density of device D is higher compared with other devices. Moreover, with the addition of MoO_3 into cathode, the current density and luminance of the devices are sharply increased by increasing the thickness of MoO_3 in cathode from 0.3 nm to 0.8 nm. With the thickness of the MoO_3 layer varying from 0.8 nm to 1.2 nm, current density and luminance are reduced. This is due to the unbalanced charge effect. With the increase of MoO_3 thickness, more electrons are generated in the cathode. But when the MoO_3 thickness increases to 1.2 nm, electrons are difficult to be transported from cathode to emitting layer. The balance of holes and electrons is destroyed. That is why device E has lower current density and luminance than other devices.

Fig.3(a) depicts the relationship between current efficiency and current density for the devices with different thicknesses of the MoO_3 layer. It can be seen that the white OLED with MoO_3 as a cathode buffer layer inserted between LiF and Al has a higher current efficiency than the white OLED without MoO_3. And the highest current efficiency is observed for the device with 0.8 nm-thick MoO_3 layer, i.e., in device D. At a current density of 160 mA/cm², the current efficiency of the device without the MoO_3 cathode buffer layer (device A) is 3.37 cd/A, and that of device D is 5.79 cd/A, which is approximately two times of that of the device A. The current efficiencies of devices B, C and D rise sharply at lower current density to the maximum, and then fall off gradually at higher current density ranging from 50 mA/cm² to 450 mA/cm². On the other hand, the current efficiencies of the devices A and F rise gradually at low current density to the maximum, and then display a nearly flat response from 150 mA/cm² to 300 mA/cm². In addition, the device efficiency is improved with the thickness of the MoO_3 layer varying from 0 to 0.8 nm. However, the device efficiency is reduced when the thickness of the MoO_3 layer varying from 0.8 nm to 1.2 nm.

There are some reasons for the difference between the white OLED with MoO_3 as a cathode buffer layer and that without MoO_3. Firstly, the electron injection ability of device with MoO_3 is stronger than that of device without MoO_3. It indicates that the device with the MoO_3 layer can generate carriers and inject them into emitting layers effectively. Secondly, it has been reported that the decomposition of LiF takes place due to the reaction of LiF and Al during the thermal deposition of Al onto LiF to liberate Li atoms which are subsequently doped into organic compounds. Therefore, a gap state is produced, which leads to exciton quenching in the emitting layer[9-11]. It is expected that the white OLED with MoO_3 layer as a cathode buffer layer inserted between LiF and Al can prevent the decomposition of LiF during the thermal deposition of Al[12]. The effects of the MoO_3 layer

result from the removal of gap states induced by the chemical process at the interfaces between metal electrodes and organic thin films[12]. So the device with the MoO_3 layer results in more electron and hole combining in emitting layer, and hence a higher current efficiency of white OLED is obtained. Finally, a better balance of electrons and holes can contribute to a good current efficiency for the device. The balance of holes and electrons in device E is destroyed, which leads to a low current efficiency.
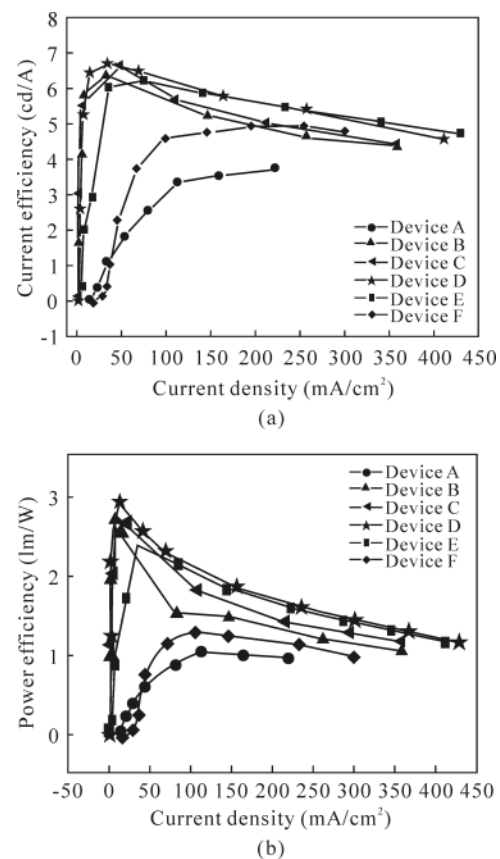

Fig.3 Characteristics of (a) current efficiency and (b) power efficiency versus current density for all devices with different thicknesses of MoO_3 layer

Fig.3(b) shows the characteristics of power efficiency versus current density for all devices. It is clear that device D shows the maximum power efficiency of 2.89 lm/W at current density of 13.77 mA/cm² compared with other devices. The superior performance of the device with MoO_3 is attributed to the high electron injection ability of cathode. The enhanced power efficiency of the device is useful to improve the device performance regarding power consumption.

Fig.4(a) shows the EL spectra of the devices with different thicknesses of the MoO_3 layer at the same voltage of 13 V. As can be seen, the EL spectra of all devices show two prominent peaks at 460 nm and 568 nm, meanwhile a shoulder peak of

about 488 nm. The peaks at 460 nm and 488 nm are attributed to TBPe, and the peak at 568 nm is attributed to DCJTB. From Fig.4(b), the CIE color coordinate of device E with the best color purity at the voltage of 13 V is (0.33, 0.34).
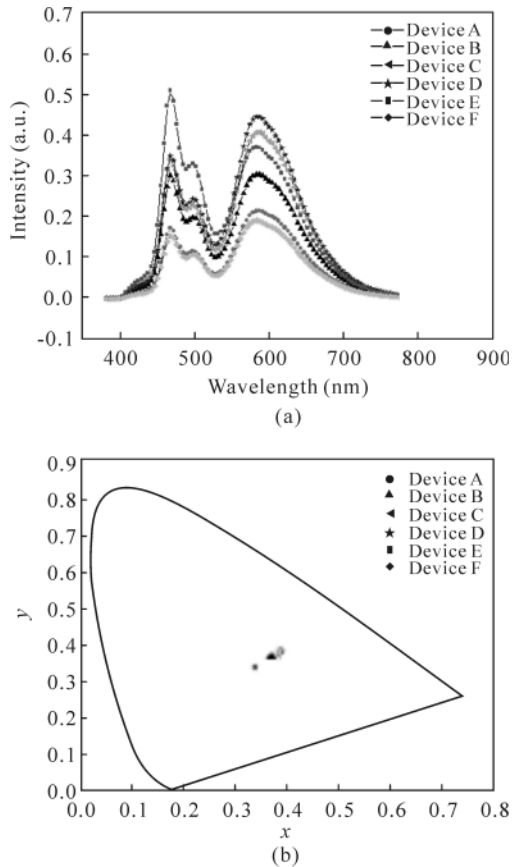
Fig.4(a) EL spectra and (b) CIE1931 color coordinate of the devices with different thicknesses of MoO₃ layer

In summary, we demonstrate that the use of MoO_3 as a cathode buffer layer inserted between LiF and Al can affect the performance of white OLEDs strongly. An optimal thickness of the MoO_3 layer can enhance the device efficiency. The superior efficiency of the white OLED with MoO_3 layer as cathode buffer layer is attributed to the reduction of exciton quenching at the emitting layer and the high electron-injection ability compared with the white OLED without MoO_3. In addition, the CIE color coordinate of the white OLED device with 1 nm-thick MoO_3 layer is (0.33, 0.34) at a voltage of 13 V, which shows the best color purity. The proposal contributes to the analyses and researches of correlated characteristics of OLED.

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