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Efficient top-emitting organic light-emitting devices using Fe_3O_4 modified Ag anode

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ABSTRACT

Highly efficient top-emitting organic light-emitting devices (TOLEDs) using a Fe_3O_4 modified Ag anode have been demonstrated. The tris-(8-hydroxyquinoline) aluminum-based TOLEDs exhibit a very low turn-on voltage of 2.5 V and a high current efficiency of 8.1 cd/A. The improved properties for the TOLEDs is mainly due to the enhanced hole injection by introducing the anodic buffer. The mechanism of this enhanced hole injection is studied by the X-ray and ultra-violet photoemission spectroscopy, which demonstrated that the dipole layer is formed at the anode/organic interface and the hole-injection barrier is therefore reduced after introducing the thin Fe_3O_4 film between the Ag anode and the hole-transport layer.

1. Introduction

Top-emitting organic light-emitting devices (TOLEDs) are of considerable interest for their application in high resolution active matrix display because they provide better image quality, higher aperture ratio and allows fabrication on an opaque substrate, such as Si wafers [1]. The bottom anode with both high reflectivity and high work function are essential for achieving efficient TOLEDs. Ag is an excellent candidate due to its highest reflectivity in visible light range among various metals. However, its work function (4.3 eV) [2] is not sufficient high for efficient hole injection. Serious efforts, therefore, have been devoted to overcome the problem. For example, MoO_x [3], Ag_2O [4], V_2O_5 [5], CFx [6], etc. have been reported to modify the Ag anode and improve the hole injection from the Ag anode. A self-assembled monolayer appears to be another way of tuning the work function of the Ag anode [7]. Therefore, using an anodic buffer in the TOLEDs is effective in realizing its high performance, and more works are needed to explore other materials as the anodic buffer to further improve the performance of the TOLEDs.

In previous work [8,9], we have reported that Fe_3O_4 is not only an effective buffer on the ITO anode but also an effective p-dopant in hole-transport layer in bottom emitting OLEDs. In this work, the application of the Fe_3O_4 was further explored into the TOLEDs and much improved performance due to the anodic modification of the Fe_3O_4 on the Ag anode was observed. Systematic investigation on the role of Fe_3O_4 as the buffer in the TOLEDs was performed by *in situ* ultra-violet photoemission spectroscopy (UPS) and X-ray photoemission spectroscopy (XPS) measurements, as well as the characteristics of the hole-only devices. These studies reveal that the hole-injection efficiency is enhanced due to the reduction of the injection barrier after introducing the ultra thin film of Fe_3O_4 at the Ag anode and the hole-transport layer interface. As a

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result, the brightness, the current density and the efficiency of the TOLEDs are highly improved.

2. Experimental details

The TOLEDs were fabricated by depositing 80 nm thick Ag as the reflective anode onto 1600 nm thick SiO_2-covered Si substrate. An ultra thin film of Fe_3O_4 as the anode buffer with the different thickness changing from 1 nm to 4 nm was then deposited, followed by deposition of 50 nm thick hole-transporting layer of *N*,*N*′-diphenyl-*N*,*N*′-bis(1,1′-biphenyl)-4,4′-diamine(NPB), 50 nm thick emitting layer of tris-(8-hydroxyquinoline) aluminum (Alq_3), and semi-transparent cathode of LiF (1 nm)/Al (1 nm)/Ag (20 nm). Here, all layers were prepared by thermal evaporation in a high vacuum system with the pressure of less than 5×10^{-4} Pa. The active area of the devices was 2×2 mm^2. Their current density–luminance–voltage (*J*–*L*–*V*) characteristics were measured by Keithley 2400 programmable voltage–current source and Photo Research PR-655 spectrophotometer. The UPS data were measured with a Thermo ESCALAB 250, and the samples were biased at −4.0 V to observe the low energy secondary cutoff during the measurement. The XPS measurements were performed with Mg Kα X-ray source (1253.6 eV) (Specs XR50).

3. Results and discussion

3.1. Effects of Fe_3O_4 modified Ag anode on electroluminescence performance of TOLEDs

The *J*–*L*–*V* characteristics of the TOLEDs with the various thickness of Fe_3O_4 as the anodic buffer are shown in Fig. 1. The inset of Fig. 1a shows the electroluminescence (EL) spectra of the TOLEDs at viewing angle of 0°, 20°, and 40° off the surface normal. The EL spectra of the TOLEDs with the various Fe_3O_4 thickness are similar, and the TOLEDs show narrowed and angular shift of the peak wavelength and intensity of the EL spectra due to the existence of microcavity effects. Both the current density and the luminance in the normal direction are strongly dependent on the presence and the thickness of the Fe_3O_4 buffer layer. They markedly increase when increasing the Fe_3O_4 thickness, and reach the maximum at 3 nm. With further increment of the Fe_3O_4 layer thickness, the current density and the luminance are decreased. The devices without the buffer layer shows much lower EL properties compared to the Fe_3O_4 buffered devices. The turn-on voltage of 2.5 V to obtained the luminance of 1 cd/m^2 and the maximum luminance of 108,297 cd/m^2 at 14 V have been observed from the TOLEDs with an optimum Fe_3O_4 thickness of 3 nm, while it is 5.0 V and 13,680 cd/m^2 at 13 V for the TOLEDs without the anodic buffer. The current efficiency versus voltage in the normal direction of these TOLEDs shows a similar behavior to that of *J*–*L*–*V* performance (Fig. 2b), and also exhibits an optimum thickness of 3 nm. The maximum current efficiency is around 8.1 cd/A for the Fe_3O_4 buffered TOLEDs, while it is only around 4.0 cd/A for the devices without the anodic buffer. These results indicate

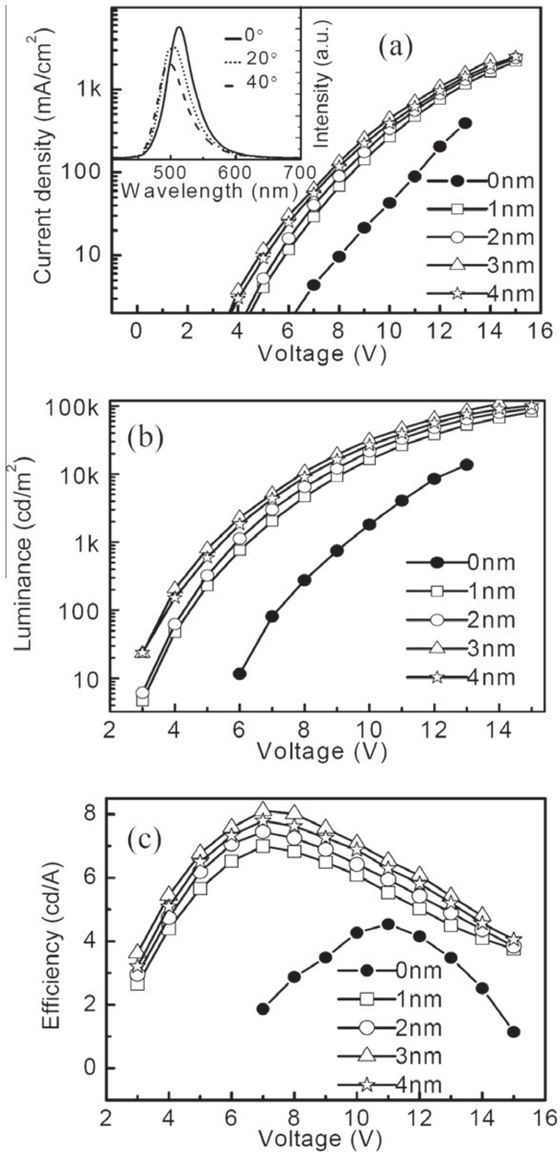

Fig. 1. EL performance of the Fe_3O_4 buffered OLEDs. (a) Current density–voltage, (b) luminance–voltage, and (c) current efficiency–voltage characteristics of the devices with various thickness of Fe_3O_4 film as the buffer layer. Inset in (a) shows the EL spectrum of the Fe_3O_4 buffered device at different observation angle.

that high EL performance of the TOLEDs is obtained by employing the Fe_3O_4 modified Ag anode.

Various metal oxides have been demonstrated as effective anodic buffer in the TOLEDs [3–5]. In order to study the relative effectiveness of the anodic modification of the Fe_3O_4, we have fabricated the devices with MoO_3 as the buffer layer for comparison, which is one of the most effective anodic buffer for the Ag anode [3,10]. The *J*–*L*–*V* characteristics of both Fe_3O_4 and MoO_3 buffered TOLEDs with the same device structure and optimized thickness of the buffer layer are compared in Fig. 2a. The optimized thickness is 3 nm and 4 nm for the buffer of Fe_3O_4 and MoO_3, respectively. The operating voltage at the current

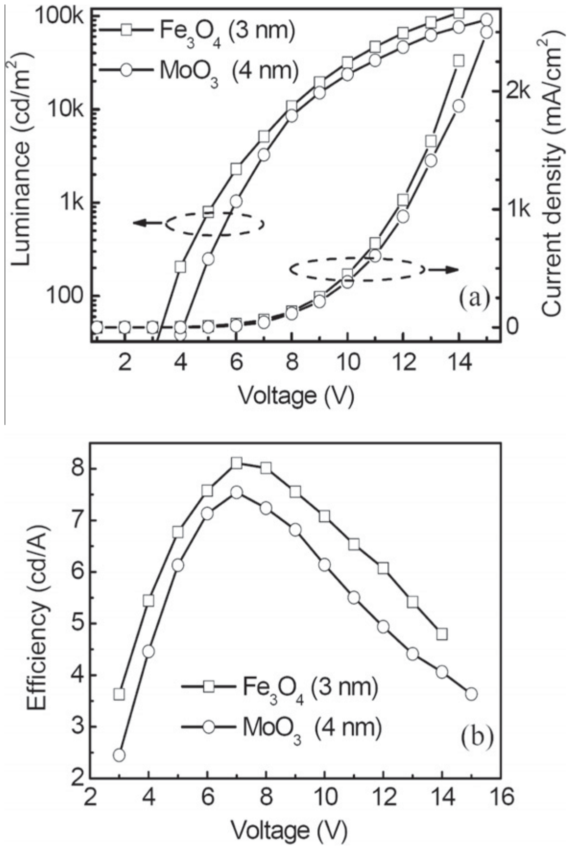

Fig. 2. (a) Current density–luminance–voltage and (b) current efficiency–voltage characteristics of the Fe_3O_4 and MoO_3 buffered devices.

density of 100 mA/cm^2 is 9.1 V and 9.3 V, and the operating voltage for obtaining a luminance of 300 cd/m^2 is 4.3 V and 5.1 V for the Fe_3O_4 and MoO_3 buffered devices, respectively. The turn-on voltage of the Fe_3O_4 buffered devices (2.5 V) is 0.2 V lower than that of the MoO_3 buffered devices (2.7 V), and its current efficiency is also higher than that of the MoO_3-based device as shown in Fig. 2b. These results indicate that Fe_3O_4 has comparable and even appreciably superior effect in modifying the Ag anode and improving the properties of the TOLEDs to the MoO_3.

3.2. Effects of Fe_3O_4 as anodic buffer on hole injection of TOLEDs

Generally, the reduced operating voltage and enhanced EL performance in OLEDs with the insertion of the anodic buffer are attributed to the reduced hole-injection barrier and therefore enhanced hole-injection efficiency. We have carried out the XPS measurements to analyze the interface between the anode and the hole-transport layer. The XPS spectra of the Ag 3*d* peaks are measured from the bare Ag (80 nm), Ag (80 nm)/Fe_3O_4 (3 nm) and Ag (80 nm)/MoO_3 (2 nm) as shown in Fig. 3a. It can be seen that the Ag 3*d* peaks shift towards higher binding energy by approximately 0.25 eV after depositing the ultra thin Fe_3O_4 layer on the Ag film, while it is ~0.15 eV in case of

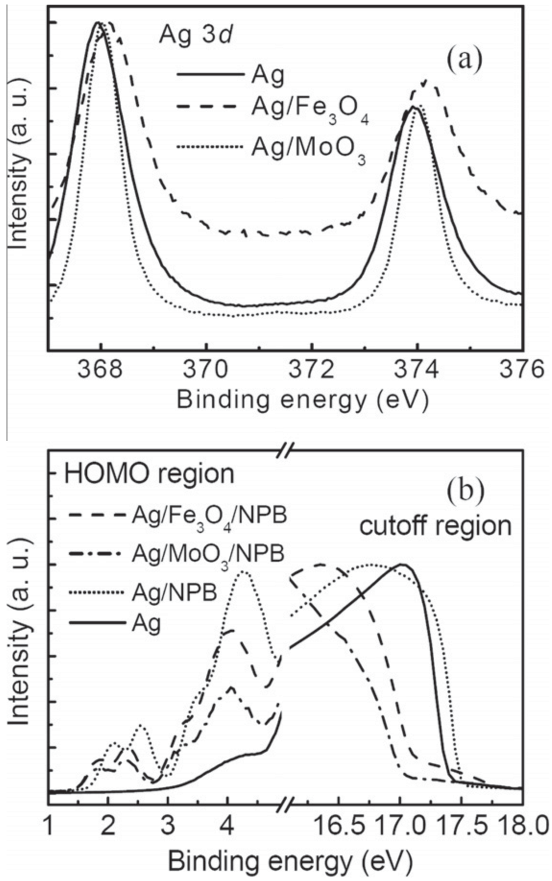

Fig. 3. (a) XPS spectra of Ag (80 nm) and Ag (80 nm)/Fe_3O_4 (3 nm). (b) UPS spectra of Ag (80 nm), Ag (80 nm)/NPB (15 nm) and Ag (80 nm)/Fe_3O_4 (3 nm)/NPB (15 nm).

MoO_3 buffered Ag film. The peak shift indicates an electron transfer from Ag to Fe_3O_4 at the interface [10], which would result in a formation of a dipole layer at the interface and leading to an abrupt shift of the potential across the dipole layer [11,12]. Therefore, the hole-injection barrier is reduced as a result of the potential shift.

To further clarify the effects of the Fe_3O_4 on the hole injection, UPS spectra are investigated to evaluate the reduction of the hole-injection barrier. Fig. 3b shows the UPS spectra of the Ag (80 nm), Ag (80 nm)/Fe_3O_4 (3 nm)/NPB (15 nm), Ag (80 nm)/MoO_3 (4 nm)/NPB (15 nm) and Ag (80 nm)/NPB (15 nm). There are clear spectra changes after the insertion of the ultra thin film of Fe_3O_4 or MoO_3 between Ag and NPB compared to that of Ag/NPB sample. Both the highest occupied molecular orbital (HOMO) onset position and the cut off position shift towards the lower binding energy. The shift of the HOMO onset position indicates that the HOMO level of NPB is reduced after introducing the Fe_3O_4 or MoO_3 buffer layer, which will result in the reduction of the hole-injection barrier [12]. Moreover, it is noticeable that the shift of the secondary electron cutoff position indicates the formation of the interface dipoles at the Ag/NPB interface, which is coincident with the XPS results. The energy diagrams of the Ag/NPB, Ag/Fe_3O_4/

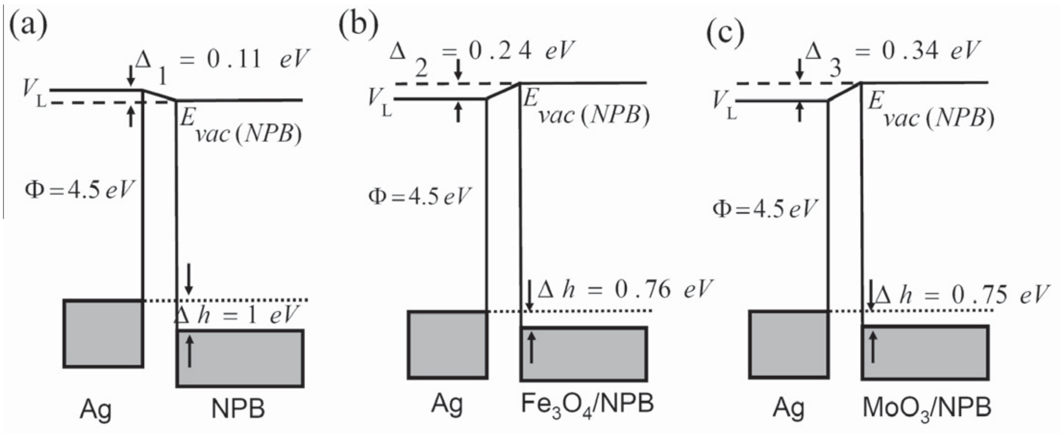

Fig. 4. Schematic energy diagram of Ag/NPB (a), Ag/Fe_3O_4/NPB (b), and Ag/MoO_3/NPB (c).

NPB, Ag/MoO_3/NPB extracted from the UPS spectra [13–15] are shown in Fig. 4. The work function of Ag is calculated to be 4.5 eV from the UPS spectra. The hole-injection barrier from Ag to NPB is reduced by 0.24 eV after inserting the Fe_3O_4 buffer. While in case of the MoO_3, the injection barrier is reduced by 0.25 eV. Both the XPS and UPS results demonstrate that the Fe_3O_4 as the anodic buffer has similar effect to MoO_3 in lowering the energy barrier of the hole injection at the interface, which should contribute to the reduction of the operating voltage and the improvement of the EL efficiency.

The efficient hole injection of the Fe_3O_4 modified devices are further confirmed by the *J–V* characteristics of the hole-only devices [16,17]. The hole-only devices with and without the anodic buffer were fabricated to demonstrate the role of the anodic buffer in the hole-injection ability of the TOLEDs. Fig. 5 shows the current density versus voltage characteristics of the hole-only devices with the structures of Ag (80 nm)/Fe_3O_4 (3 nm)/NPB (80 nm)/Ag (20 nm), Ag (80 nm)/MoO_3 (4 nm)/NPB (80 nm)/Ag (20 nm) and Ag (80 nm)/NPB (80 nm)/Ag (20 nm). The electron injection from the Ag cathode to the NPB is prohibited, because the work function of Ag is around 4.5 eV while the lowest occupied molecular orbital level of the NPB is around 2.4 eV, and there exists very large injection barrier. It can be seen that the current density of the hole-only devices with the anodic buffer is obviously higher than that of the device without the buffer, and the Fe_3O_4 buffered devices shows even higher current density than that of the MoO_3 buffered devices. It further confirms that Fe_3O_4 is an efficient anodic buffer in enhancing the hole injection of the TOLEDs.

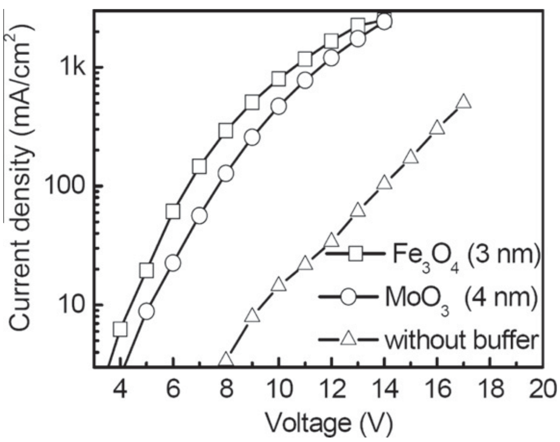

Fig. 5. The current density–voltage characteristics of the hole-only devices with and without the anodic buffer.

4. Conclusions

In summary, we report the thin film of Fe_3O_4 as the Ag anodic buffer for efficient TOLEDs. The Fe_3O_4 exhibits its effect in lowering the driving voltage and improving the brightness and current efficiency of the TOLEDs. The XPS and UPS measurements indicate that the introduction of the thin film Fe_3O_4 can greatly reduce the hole-injection barrier, and the enhancement of the hole injection has been further confirmed by the investigation of *J–V* characteristics of the hole-only devices. Our results reveal that Fe_3O_4 is a prospective material in modifying the Ag anode and realizing the high performance of the TOLEDs.

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