

Improved hole injection and transport of organic light-emitting devices with an efficient p-doped hole-injection layer

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A 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine thin film doped with Fe₃O₄ has been demonstrated an efficient p-type hole-injection layer (HIL) in organic light-emitting devices (OLEDs). The tris-(8-hydroxyquinoline) aluminum-based OLEDs with the p-type HIL exhibit a very low turn-on voltage of 2.4 V and a high luminance of 29 360 cd/m² at 8 V, while it is 3 V and 6005 cd/m², respectively, for the nondoped devices. The improvement in the device performance is clarified as arising from the improved hole injection and transport by the results of ultraviolet/visible/near-infrared absorption, x-ray photoelectron spectra and current density-voltage characteristics of hole-only devices. © 2009 American Institute of Physics.

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Lowering driving voltage is crucially important to prolong the lifetime, increase the power efficiency, and reduce the power consumption of the organic light-emitting devices (OLEDs). Employing electrically doped transport layers and electrode buffers have been demonstrated powerful solutions to lower the driving voltage through improving the charge conductivity and reducing the injection barrier.^{1–6} Transition metal oxides such as MoO₃,^{7,8} WO₃,⁹ and ReO₃¹⁰ have been found as effective anodic buffers or p-dopants in improving the hole injection and transport in OLEDs. Fe₃O₄ as one of the transition metal oxides is a widely used material for spintronic devices due to its unique electrical and magnetic properties, such as 100% spin polarization and high Curie temperature. Very recently, we have demonstrated that Fe₃O₄ could be utilized as an effective anodic buffer layer in the OLEDs.¹¹ This, together with the fact that Fe₃O₄ are environmentally benign, inexhaustible, and cheap, would open up its unexplored potential application as the p-dopant in OLEDs. In this letter, we report use of Fe₃O₄ as an efficient electron-accepter dopant in 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA) to attain p-doped OLEDs. As results, the device performance is found significantly enhanced for the tris-(8-hydroxyquinoline) aluminum (Alq₃) based OLEDs. The effect is experimentally confirmed as due to that both hole injection and hole transport are improved induced by this p-dopant.

The OLEDs were fabricated by depositing 25 nm thick Fe₃O₄ doped hole injecting layer (HIL) of m-MTDATA, followed by deposition of 10 nm thick m-MTDATA, 5 nm thick hole transporting layer of N,N'-diphenyl-N,N'-bis(1,1'-biphenyl)-4,4'-diamine (NPB), 50 nm thick Alq₃ emitting layers and LiF (1 nm)/Al cathode on the indium tin oxide (ITO) coated glass substrates. The m-MTDATA doped with Fe₃O₄ serves as the p-doped HIL with varied molar ratios of m-MTDATA:Fe₃O₄ of 4:1, 2:1, and 1:1, respec-

tively. For comparison, the devices with undoped m-MTDATA (35 nm) as the HIL were fabricated as control. All layers were prepared by thermal evaporation at a vacuum pressure of less than 5×10^{-4} Pa. The atomic compositions of the evaporated Fe₃O₄ thin films have been analyzed by x-ray photoelectron spectroscopy (XPS) and are confirmed to stoichiometrically consist of Fe₃O₄.¹¹ The active area of the devices was 2×2 mm². Their current density-voltage-luminance (J-V-L) characteristics were measured by Keithley 2400 programmable voltage-current source and Photo Research PR-655 spectrophotometer. The absorption spectra were measured by means of ultraviolet/visible/near-infrared (NIR) absorption spectrometer (UV 3600, Shimadzu). The XPS measurements were performed with Mg K_α x-ray source (1253.6 eV, Specs XR50).

In general, the p-dopant acts as an electron acceptor to form the charge-transfer (CT) complex with the carrier-transporting materials, which could be verified by the emergence of the characteristic absorption in the NIR region.^{5,12–15} The absorption spectra of the Fe₃O₄ doped m-MTDATA (30 nm) films with different doping ratio of 4:1, 2:1, and 1:1 and the neat films of m-MTDATA (30 nm) and Fe₃O₄ (50 nm) deposited on quartz substrate are shown in Fig. 1. The strong absorptions of the neat m-MTDATA and Fe₃O₄ films are all located at the wavelength less than 400 nm, while the m-MTDATA:Fe₃O₄ films exhibit additional broad absorption peak at around 1200 nm. It is increased with increasing concentration of the Fe₃O₄ and shows saturation up to the concentration ratio of 1:1. The existence of this peak is a proof of the electron transfer from m-MTDATA to Fe₃O₄, and the formation of the CT complex. Free holes would generate through the electron transfer process in these doping films, which would improve the electrical conductivity in the doped layer of the OLEDs.

The J-V-L characteristics of the devices with the different doping ratio of m-MTDATA:Fe₃O₄ are shown in Fig. 2(a). Both the current density and the luminance of the doped devices strikingly increase compared to the undoped devices, indicating an optimum doping ratio of 2:1. For example, the

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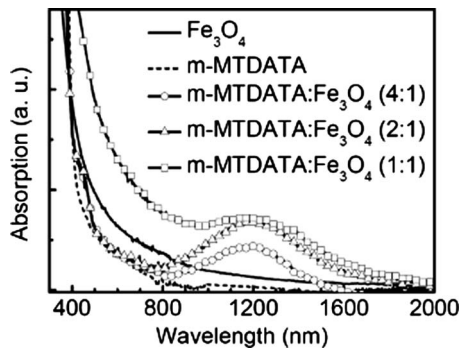


FIG. 1. Ultraviolet/visible/NIR absorption spectra of the neat films of Fe_3O_4 (50 nm) and m-MTDATA (30 nm), and the Fe_3O_4 doped m-MTDATA films (30 nm) with different doping ratio of 4:1, 2:1, and 1:1 deposited on quartz substrate.

operating voltage is 5.4 V for the doped device with the doping ratio of 2:1, while it is 7.2 V for the undoped device at the current density of 100 mA/cm^2 . The turn-on voltage is 2.4 V and the luminance is $29\,360 \text{ cd/m}^2$ at 8 V for the doped devices, which are much improved compared to those obtained from the undoped device (3 V of turn-on voltage and 6005 cd/m^2 at 8 V). The power efficiency-current density characteristics of the OLEDs with the doped and undoped HIL are shown in Fig. 2(b). The devices with doped HIL show higher power efficiency (2.6 lm/W at 20 mA/cm^2) compared to the undoped device (1.5 lm/W) due to the lowering of the operating voltage.

Fe_3O_4 has been demonstrated an efficient anodic buffer,¹¹ and therefore its effects as the p-dopant are further examined by comparing to its effects as the anodic buffer in improving the electroluminescence performance of the OLEDs. The J-V-L characteristics of the doped and buffered devices are compared in Fig. 3(a). The characteristics of the control devices are also plotted for comparison. The doping ratio for the doped devices is 2:1 with the same structure as described above. The structure of the buffered device is ITO/ Fe_3O_4 (1 nm)/m-MTDATA (35 nm)/NPB (5 nm)/Alq₃

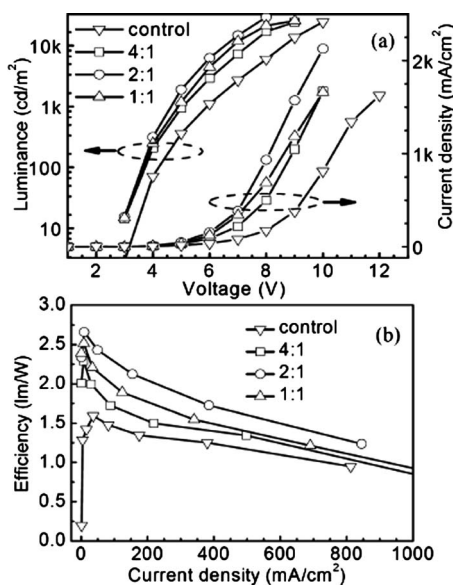


FIG. 2. (a) Current density-voltage-luminance characteristics and (b) power efficiency-current density of the devices with various doping ratio of the m-MTDATA: Fe_3O_4 .

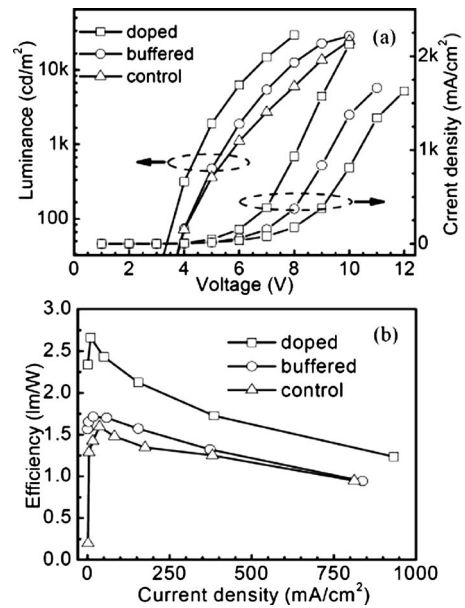


FIG. 3. (a) Current density-voltage-luminance characteristics and (b) power efficiency-current density of the devices with Fe_3O_4 as the p-dopant and the anodic buffer, and the control devices.

(50 nm)/LiF (1 nm)/Al. The 1 nm thickness of the buffer is the optimum thickness demonstrated in the previous letter.¹¹ It can be clearly seen that the buffered devices exhibit higher current density, luminance, and power efficiency compared to the control devices, which is attributed to the lowering of the injection barrier on ITO/m-MTDATA interface by insertion of the Fe_3O_4 as the anodic buffer. However, in case of the doped devices, the current density and luminance are even higher than that of the buffered devices. The power efficiency [Fig. 3(b)] for the doped devices also shows much enhancement compared to that of the buffered devices. Therefore, the p-doped devices exhibit superior performance than the buffered devices.

In order to study the origin of the superior performance of the doped devices, the XPS was performed to analyze the ITO/m-MTDATA: Fe_3O_4 interface. The XPS spectra of the Indium 3d peaks were measured from the bare ITO and ITO/m-MTDATA: Fe_3O_4 (2 nm, 2:1), ITO/ Fe_3O_4 (1 nm), as shown in Fig. 4. It can be seen that the Indium 3d peaks shift toward higher binding energy ($\sim 0.3 \text{ eV}$) after depositing either Fe_3O_4 (1 nm) or m-MTDATA: Fe_3O_4 (2 nm, 2:1) on ITO. The peak shift indicates an electron transfer from ITO

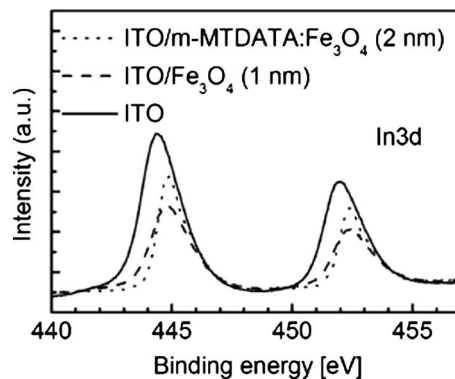


FIG. 4. XPS spectra of ITO (solid), ITO/m-MTDATA: Fe_3O_4 (2 nm, 2:1) (dotted), and ITO/ Fe_3O_4 (1 nm) (dashed).

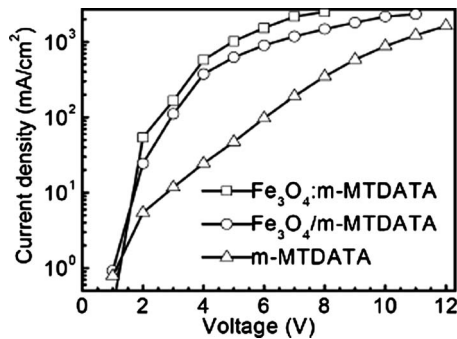


FIG. 5. The current density-voltage characteristics of the hole-only devices with Fe_3O_4 as the p-dopant, anodic buffer, and undoped m-MTDATA HIL.

to Fe_3O_4 and m-MTDATA: Fe_3O_4 at the interface, 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.^{4,8} Therefore, the hole injection barrier is reduced as a result of the potential shift. The XPS results exhibit that the Fe_3O_4 doped HIL on ITO has the same effect as the anodic buffer to lower the energy barrier. Therefore, in case of the p-doped devices, not only the increased electrical conductivity of the HIL but also the improved hole-injection efficiency can be obtained, which results in its superior performance.

The hole injection and transport improvements of the p-doped devices are further approved by the J-V characteristics of the hole-only devices.^{3,7} The hole-only devices with Fe_3O_4 as either buffer or p-dopant are fabricated. The structure is ITO/MTDATA: Fe_3O_4 (2:1, 25 nm)/m-MTDATA (10 nm)/NPB (5 nm)/Al, and ITO/ Fe_3O_4 (1 nm)/m-MTDATA (35 nm)/NPB (5 nm)/Al. A device of ITO/m-MTDATA (35 nm)/NPB (5 nm)/Al is fabricated for comparison. The electron injection from the Al cathode to the m-MTDATA is prohibited, because the work function of Al is around 4.3 eV, while the lowest unoccupied molecular orbital level of the NPB is around 2.4 eV and there exists a large injection barrier. It is clearly shown in Fig. 5 that the current density of the hole-only devices with Fe_3O_4 as either p-dopant or anodic buffer is much higher than that of the device without the Fe_3O_4 , and the devices with the p-dopant layer exhibit the highest current density, which confirms that the enhance-

ments of both the hole transport and the hole injection obtained for the p-doped OLEDs.

In summary, improved performance of OLEDs was obtained by using the Fe_3O_4 as the p-dopant in the HIL. Reduced driving voltage, increased current density, and power efficiency were obtained for the p-doped OLEDs. The doping of the Fe_3O_4 in the HIL resulted in the formation of the CT complex with the m-MTDATA, which resulted in the generation of the free holes in the p-doped HIL. In addition, enhanced hole injection was demonstrated for the doped devices. Both the enhanced hole injection and improved hole transport induced by the p-doped HIL lead to the improvements of the device performance.

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