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Organic light emitting diodes using magnesium doped organic acceptor as electron injection layer and silver as cathode

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Organic light emitting diodes employing magnesium doped electron acceptor 3, 4, 9, 10 perylenetetracarboxylic dianhydride (Mg : PTCDA) as electron injection layer and silver as cathode were demonstrated. As compared to Mg : Ag cathode, the combination of the Mg : PTCDA layer and silver provided enhanced electron injection into tris (8-quinolinolato) aluminium. The device with 1 : 2 Mg : PTCDA and Ag showed an increase of about 12% in the maximum current efficiency, mainly due to the improved hole-electron balance, and an increase of about 28% in the maximum power efficiency, as compared to the control device using Mg : Ag cathode. The properties of Mg : PTCDA composites were studied as well.

Keywords: organic light emitting diodes, Mg : PTCDA, electron injection
PACC: 7860F, 7280L, 7200

1. Introduction

Organic light emitting diodes (OLEDs) have been generally considered as a promising candidate for next-generation solid-state light sources. Although great progresses have been achieved for OLEDs,[1−4] it is of importance to develop improved electron injection techniques and thereby achieve enhanced device performance. In general, Mg : Ag alloy and LiF/Al are two most frequently used cathode contacts in OLEDs. In order to improve electron injection from the cathode into organic layer, alkaline metal doped organic electron transport materials, e.g., lithium doped 4, 7-diphenyl-1, 10-phenanthroline (Li : Bphen), have been fast developed.[5−7] Here, we fabricate a class of functional composite films, i.e., magnesium doped organic electron acceptor 3, 4, 9, 10 perylenetetracarboxylic dianhydride (Mg : PTCDA), and demonstrate that the OLED utilizing 1 : 2 Mg : PTCDA composite as electron injection layer and silver as cathode has increased performance as compared to the control OLED using conventional Mg : Ag cathode.

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2. Experimental details

Copper phthalocyanine (CuPc) and Mg doped PTCDA were used as hole injection and electron injection layers, respectively, and N,N'-bis-(1-naphthl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and tris (8-quinolinolato) aluminium (Alq3) were used as hole transport and emitting/electron transport layers, respectively. Alq3 was home-made; NPB was used as received, while CuPc and PTCDA were purified by a home-made sublimation system after purchase. ITO substrates with a sheet resistance of 30 Ω/□ were treated 15 minutes in UV-ozone before the usage. The base vacuum pressure for the device preparation was 1×10^{-5} Pa. Three OLEDs using Mg : PTCDA with different weight ratios of Mg to PTCDA and one control OLED were fabricated as follows :

Device 1 : ITO/CuPc 5 nm/ NPB 75 nm/ Alq3 50 nm/ 1 : 1 Mg : PTCDA 10 nm/ Ag;

Device 2 : ITO/CuPc 5 nm/ NPB 75 nm/ Alq3 50 nm/ 1 : 2 Mg : PTCDA 10 nm/ Ag;

Device 3 : ITO/CuPc 5 nm/ NPB 75 nm/ Alq3

50 nm/ 1 : 4 Mg : PTCDA 10 nm/ Ag;

Device C : ITO/CuPc 5 nm/ NPB 75 nm/ Alq3 60 nm/ Mg : Ag.

The current–voltage ($I-V$) characteristics of the devices were measured by the Programmable Keithley Electrometer 617, and the luminance was recorded by an ST-86LA Spot Photometer. The optical absorption spectra and x-ray diffraction (XRD) spectra of organic thin films were obtained using a UV–visible spectrometer (UV-3100) and an x-ray diffractometer (D/max-RB), respectively.

3. Results and discussion

3.1. The structural and optical properties of Mg : PTCDA composites

Figure 1(a) indicates that the three composites of Mg : PTCDA of 1 : 1, 1 : 2, and 1 : 4 by mass are almost amorphous, demonstrating Mg can effectively destroy PTCDA (102) stacks[8,9] during the vacuum co-deposition.

The optical properties of PTCDA and the three Mg : PTCDA thin films have also been investigated. As shown in Fig.1(b), all the three Mg : PTCDA thin films show increased transmittance in the 400 nm to 650 nm range, as compared to pure PTCDA thin film. Furthermore, the transmittance of Mg : PTCDA composite increases with increasing Mg weight percentage from 20% to 50%, implying that PTCDA is the major light-absorbing constituent in Mg : PTCDA composite: y when Mg concentration increases, the mass fraction of PTCDA decreases, resulting in the reduction of the absorption correspondingly.

Mg is likely to react with PTCDA molecules during the co-deposition, expressed as

$$\frac{1}{2}\mathrm{Mg} + \mathrm{PTCDA} \rightarrow \frac{1}{2}\mathrm{Mg}^{2+} + \mathrm{PTCDA}^{-}, \qquad (1)$$

which is believed to contribute to the variation of the UV–vis absorption. Note that, the molar ratios of Mg to PTCDA used are 4.1 : 1, 8.2 : 1, and 16.3 : 1, respectively. We therefore deduce that quite an amount of Mg atoms form neutral micro-aggregates in Mg : PTCDA fabricated in the experiment.

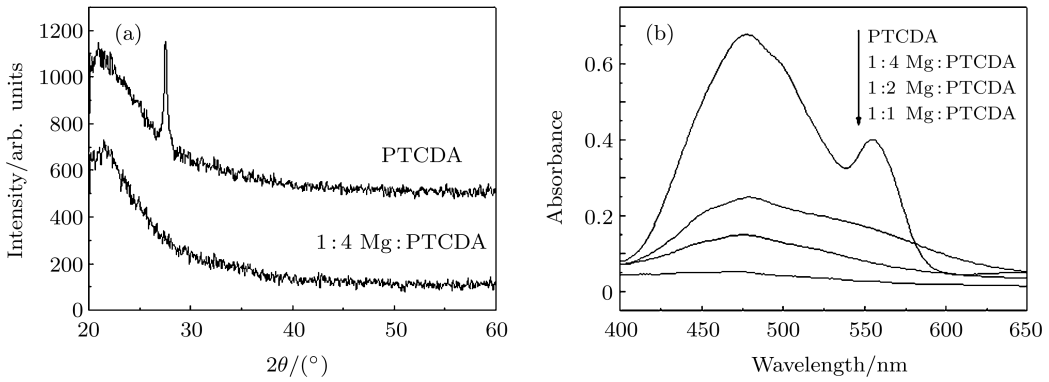


Fig.1. XRD measurements (a) and optical absorption spectra (b) for 50 nm PTCDA and 50 nm Mg : PTCDA of 1 : 1, 1 : 2, and 1 : 4 by mass on quartz glasses. The three Mg : PTCDA composites exhibited the same XRD pattern.

3.2. The electrical properties of Mg : PTCDA composites

Strong electroluminescence has been observed from the device with structure of ITO/PTCDA 20 nm/Alq3 100 nm/ LiF 1 nm/Al, indicating that PTCDA can function as a hole transporter.[10] However, no light is obtained from all the devices with structure of ITO/ Mg : PTCDA x nm/ Alq3 120-x nm/LiF 1 nm/Al ($X \geq 20$), suggesting that Mg : PTCDA composites of 1 : 1, 1 : 2, and 1 : 4 by mass cannot conduct holes effectively and the current in Mg : PTCDA/Alq3 bilayer device is electron-dominated. Figure 2(a) shows that the current of the device with structure of ITO/Mg : PTCDA (1 : 2) x nm/Alq3 120-x nm/LiF1 nm/Al increases with increasing Mg : PTCDA (1 : 2) thickness, indicating that the electron conductivity of 1 : 2 Mg : PTCDA is much higher than that of Alq3.

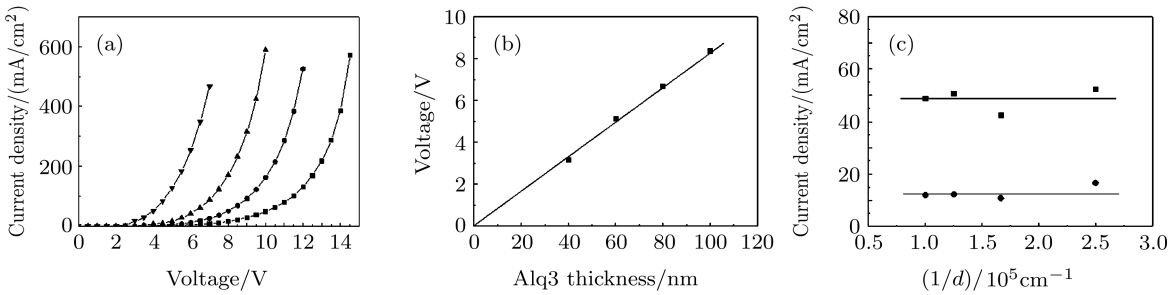


Fig.2. (a) $I-V$ characteristics of the devices of ITO (anode)/Mg : PTCDA (1 : 2) x nm/Alq3 120-x nm/LiF 1 nm/Al (cathode), where $x = 20$ (squares), 40 (circles), 60 (triangles), and 80 nm (inverted triangles), respectively. (b) Driving voltage of Mg : PTCDA (1 : 2)/Alq3 bilayer device (at $I = 20\,\mathrm{mA/cm^2}$) as a function of Alq3 thickness. The voltage drop across Mg : PTCDA is neglected for all devices. The linear dependence of driving voltage on Alq3 thickness is also obtained when $I = 40$ and $60\,\mathrm{mA/cm^2}$. (c) Current density of Mg : PTCDA (1 : 2)/Alq3 bilayer device versus the inverse of Alq3 thickness d at $F = 1\times10^6$ V/cm (squares) and 0.75×10^6 V/cm (circles). The voltage drop across Mg : PTCDA is neglected in both cases.

Charge transport in amorphous organic semiconductors can be considered as injection-limited.[11] In the model, the charge at the organic/cathode interface determines the electric field F, and voltage V, viz,

$$V = \frac{qn_{\mathrm{T}}d_{\mathrm{I}}d}{\varepsilon}, \tag{2}$$

where n_{T} is the interfacial charge density, q is electron charge, d_{I} is the thickness of the interfacial zone containing filled sites, d is the thickness of organic layer, and ε is organic permittivity. In Fig.2(b), driving voltage of Mg : PTCDA (1 : 2)/Alq3 bilayer device [shown in Fig.2(a)] at $I = 20\,\mathrm{mA/cm^2}$ shows a linear dependence on Alq3 layer thickness, consistent with the prediction of Eq.(2). Current density of Mg : PTCDA (1 : 2)/Alq3 bilayer device is plotted as a function of the inverse of Alq3 thickness at two different electric fields. As shown in Fig.2(c), at a electric field of $F = 1\times10^6$ or 0.75×10^6 V/cm, the current is approximately independent of the inverse of Alq3 thickness, further confirming that $I-V$ characteristics of the Mg : PTCDA (1 : 2)/Alq3 bilayer devices are injection-limited. Figures 2(b) and 2(c) strengthens the point that Mg : PTCDA (1 : 2) has a much higher electron conductivity than Alq3, as the voltage drop across Mg : PTCDA (1 : 2) is neglected in the consideration. It also testifies that the electron conductivities of 1 : 1 and 1 : 4 Mg : PTCDA are much higher than that of Alq3.

The Fermi levels of metals are necessarily pinned close to the lowest unoccupied molecular orbit of PTCDA.[12] Thus, electrons can expectedly be donated from Mg into PTCDA in Mg : PTCDA, as expressed by Eq.(1), leaving it highly N-conductive. We further investigated the influence of Mg concentration on the conductivity of Mg : PTCDA. As shown in Fig.3, the electron current of the device with structure of ITO/Mg : PTCDA 20 nm/Alq3 100 nm/LiF 1 nm/Al increases with Mg weight percentage decreasing from 50% to 20%. This clearly demonstrates that in Mg : PTCDA composite, PTCDA forms the main path of conducting electrons and Mg micro-aggregates play the role of trapping electrons : the more Mg micro-aggregates, the more electrons trapped during the conduction, and the lower electron conductivity of composite correspondingly.

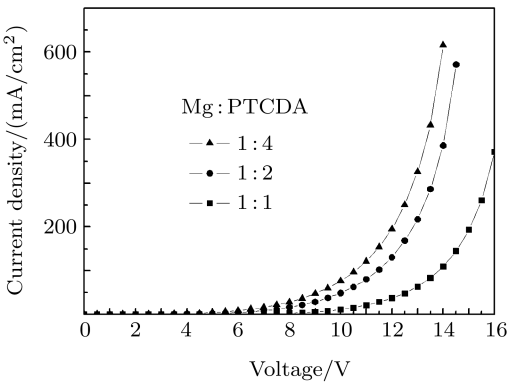


Fig.3. $I-V$ characteristics of the bilayer devices of ITO (anode)/Mg : PTCDA 20 nm/Alq3 100 nm/LiF 1 nm/Al (cathode) with various Mg : PTCDA weight ratios.

3.3. Characterization on OLEDs using Mg : PTCDA

The electrical and luminous properties of devices 1–3 and device C have been compared. At a driving voltage of 10 V, devices 1–3 achieve current densities of 170.1, 152.4, and $139.0\,\mathrm{mA/cm^2}$, respectively,

higher than that of 100.5 mA/cm^2 obtained in device C. Figure 4(a) suggests that the combination of Mg : PTCDA composite and silver cathode may provide enhanced electron injection into Alq3, compared to conventional Mg : Ag cathode. The process of electron generation into Alq3 in devices 1–3 is comprised of the following three steps : (1) electron injection from Ag into Mg : PTCDA, (2) electron transport through Mg : PTCDA, and (3) electron injection from Mg : PTCDA into Alq3. Because Mg incorporation can form an ohmic contact between Mg : PTCDA and Ag[13,14] and Mg : PTCDA is much more N-conductive than Alq3 (Fig.2), step 3 is regarded crucial to control the process of electron generation into Alq3 for the three OLEDs. As there is a big electron injection barrier from PTCDA to Alq3,[1)] it is reasonable to consider that Mg micro-aggregates take up the role of injecting electrons into Alq3 at the Alq3/Mg : PTCDA interface. As a result, the more Mg at the Alq3/Mg : PTCDA interface, the more efficient electron injection into Alq3, and the higher device current accordingly. In devices 1–3, the high-resistance region of electron conduction (equal to Alq3 in thickness) is thinner than that in device C, which might account for the enhanced current of devices 1–3 over device C.

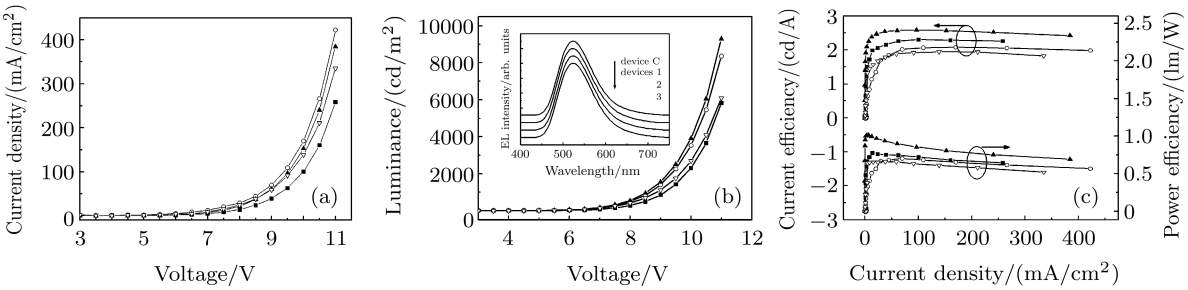


Fig.4. The $I-V$ (a), $L-V$ (b) and efficiency-current density (c) characteristics of device C (filled squares), devices 1 (open circles), 2 (filled triangles) and 3 (inverted open triangles). The inset shows the electroluminescent (EL) spectra of these four OLEDs.

Figure 4(b) shows that the luminance of devices using Mg : PTCDA is higher than that of device C. For example, at a driving voltage of 10 V, devices 1–3 achieve luminance of 3531, 3914, and 2697 cd/m^2, respectively, higher than that of 2310 cd/m^2 in device C. The inset of Fig.4(b) shows all of the devices have nearly identical electroluminescent spectra of Alq3.

Figure 4(c) shows a comparison of the device efficiencies. Device 2 with 1 : 2 Mg : PTCDA shows an increase of about 12% in the maximum current efficiency (MCE), compared to device C, which is mainly ascribed to the improvement of hole-electron balance in device 2 since the average reflectivity from 450 nm to 700 nm of Ag measured to be about 95% is slightly higher than that of Mg : Ag calculated to be 92%,[15,16] nevertheless devices 1 and 3 show lower MCEs than device C, implying the device efficiency using Mg : PTCDA is subject to the doping concentration of Mg.1 : 4 Mg : PTCDA thin film possesses the strongest absorption over Alq3 emission among the three Mg : PTCDA thin films (Fig.1(b)), and hence the MCE of device 3 is the lowest among devices 1–3. Though 1 : 1 Mg : PTCDA has smaller absorption over Alq3 emission and generates higher current density than 1 : 2 Mg : PTCDA [Fig.4(a)], the diffusion of Mg into adjacent Alq3 layer, driven by Mg concentration, is more severe in device 1 than in device 2, quenching more excitons in device 1 than device 2 and thereby making MCE of device 1 lower than that of device 2.

Device 2 gives an increase of about 28% in the maximum power efficiency compared with device C. There is a decrease of the power efficiency in the order of device 2 > device C > device 1 > device 3 when the current density is greater than 50 mA/cm^2. Device 2, using 10 nm 1 : 2 Mg : PTCDA as electron injection layer and silver as cathode, exhibits increased performance, as compared to the control device using conventional Mg : Ag cathode.

4. Conclusions

The optical, structural, and conduction properties of Mg : PTCDA have been studied. An electron injection technique comprising Mg : PTCDA as electron in-

[1)] It can be concluded from the fact that the maximum efficiency of the device of ITO/CuPc 5 nm/ NPB 75 nm/ Alq3 50 nm/ PTCDA 10 nm/ Ag fabricated in the experiment was only 0.08 cd/A.

jection layer and silver as cathode has been proposed and the resulting device (device 2) shows increased performance, as compared to the control device using Mg : Ag cathode. The current research is focused on fabricating Li doped PTCDA to further improve electron injection from PTCDA composite into Alq3.

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