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RESEARCH ARTICLE

Organic electroluminescent characteristics of PS:NPB composite hole transporting layer

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Abstract Green organic light-emitting devices with a structure of indium-tin-oxide (ITO)/polystyrene (PS):*N*,*N*′-bis-(3-naphthyl)-*N*,*N*′-biphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB)/tris-(8-hydroxyquinoline)-aluminum (Alq_3)/Mg:Ag were fabricated. A doping system consisting of small-molecular hole transporting material NPB and polymeric matrix PS was applied as a composite hole transporting layer (HTL), and the thin film preparation was simplified via spin-coating technique. By adjusting the component ratio of the doping system, several devices with different concentration proportion of PS:NPB are constructed. The electroluminescent characteristics of the devices were investigated and discussed. This study demonstrated that the difference of doping concentration of NPB has a remarkable impact on the optoelectronic performance of both HTL and the devices. Optimum device performance can be obtained by choosing a suitable concentration proportion of PS:NPB at 1:1. This study contributes to the construction of composite functional layers of organic light-emitting diode (OLED) devices and to the technical modification.

Keywords organic light-emitting device, *N*,*N*′-bis-(3-naphthyl)-*N*,*N*′-biphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB), polystyrene, composite hole transporting layer, device performance

1 Introduction

The organic light-emitting diode (OLED) is a kind of optoelectronic device that transforms electric power directly into photonic energy. OLED has the distinguishing advantages of low drive voltage, high luminance, efficiency, wide viewing angle, quick response, simple fabrication process and potential application in full-color flat panel display [1–4]. After two decades of development, it has become one of the hottest research topics in the field of flat panel display [5,6]. The luminescent mechanism of OLED is generally considered to be as follows: driven by an applied electric field, the electrons and holes injected from the cathode and anode, respectively, drift towards each other. The excited states of molecules (i.e., excitons) might occur if the positive and negative carriers reach the emitting layer and engage in effective recombination. Excitons return back from excited states to ground states via radiative decay, which releases a certain amount of energy in the form of photons.

To enhance OLED's luminance efficiency, single heterojunction double-layer and double heterojunction multi-layer devices were evolved from a single-layer device. These novel device structures are beneficial to the balance of carrier injection, and contribute to more effective recombination process, which remarkably improves the device performance. In addition, excellent device performance is also attainable by the introduction of composite organic functional layers, e.g., composite hole transporting layer [7–9]. For instance, research work has been reported on enhancing device luminance and efficiency by introducing laminated TPD/m-MTDATA composite hole transporting layer, and the relevant mechanism of this TPD/m-MTDATA composite structure in device optimization has been discussed [7]. In fact, a doping system can be constructed by dispersing hole transporting materials with small molecular mass into the polymer matrix, and then the filming process is carried out by spin-coating or spray-coating techniques. This method can not only simplify the thin film preparation, but also control the rheologic and optoelectronic properties of film by adjusting the doping concentration, which combines the advantages of both small molecules and polymers. Therefore, the adoption of composite functional layers has become one of the most popular methods in the film process of OLED. In this paper, a doping

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system with hole transporting material *N*,*N*′-bis-(3-naphthyl)-*N*,*N*′-biphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) and polymer polystyrene (PS) as dopant and host, respectively, was realized, and the composite hole transporting layer (HTL) consisting of this doping system was fabricated by spin-coating method. The electroluminescent (EL) characteristics of devices were measured, and the impact of HTL with different PS:NPB concentration proportion on device performance was studied and discussed.

2 Experimental

2.1 Materials

The organic materials of NPB, Alq_3 and PS were all purchased from Sigma-Aldrich Co. Figure 1 shows their chemical structures. PS is a common polystyrene resin (GPPS) of good transparency, insulation, liquidity, water and light proof, etc. NPB is an ordinary hole transporting material with superior filming property and high stability. Alq_3, a fairly stable metallic coordination composite, is well known for its use in green light-emitting devices with ideal luminescent performance.

2.2 Device fabrication

The devices are of typical heterojunction double-layer structure (Fig. 1), where the PS:NPB doping system acts as a composite hole transporting layer and Alq_3 acts as both electron transporting and emitting layer. The emitting area was 0.5 cm × 0.6 cm. Chloroform solution (15 mg/ml) containing an appropriate amount of NPB and PS was prepared, and the mass ratio is 1:9, 3:7, 1:1, 7:3, 9:1, respectively. ITO-coated glass was employed as the anode substrate with a sheet resistance of 15 Ω/□. ITO glasses were routinely cleaned by a consecutive rinsing process of ultrasonic treatment for 20 min with acetone, ethanol, detergent and deionized water, respectively, and then dried with nitrogen flow. Afterwards, the glasses underwent an oxygen plasma treatment in the pretreatment chamber of OLED-V organic multifunctional vacuum deposition equipment for approximately 10 min in order to enhance the work function of ITO and thus improve its hole injecting capacity [10,11], which eventually contributes to the improvement of device performance. The PS:NPB composite film with a thickness of approximately 50 nm was formed by spin-coating the NPB-doped PS solution at a rotating rate of 2000 rpm for about 30 seconds. Then the substrate was transferred to the deposition chamber of OLED-V equipment for the following thermal evaporation of Alq_3 layer in vacuum background at 3×10^{-6} Torr. Its deposition rate was typically 0.1–0.2 nm/s. This process was monitored by a quartz crystal oscillator. The film thickness was 50 nm. After that, an alloy of Mg and Ag with a proportion of 10:1 was deposited as the cathode using a mask, and the thickness was 300 nm.

2.3 Device characterization

The luminescent characteristics such as current density-voltage (*J*-*V*), luminance-voltage (*L*-*V*) curves of the devices were measured with a KEITHLEY-4200 semiconductor characterization system and a luminance meter (ST-86LA) under a drive voltage in the range of 0–20 V at room temperature under ambient atmosphere. The EL spectra were also measured by using a spectrophotometer (OPT-2000).

3 Results and discussion

3.1 EL spectra measurement

For the convenience of description, the concentration proportion of PS and NPB is denoted *x*:*y*, and the devices A–E are decoded as follows:

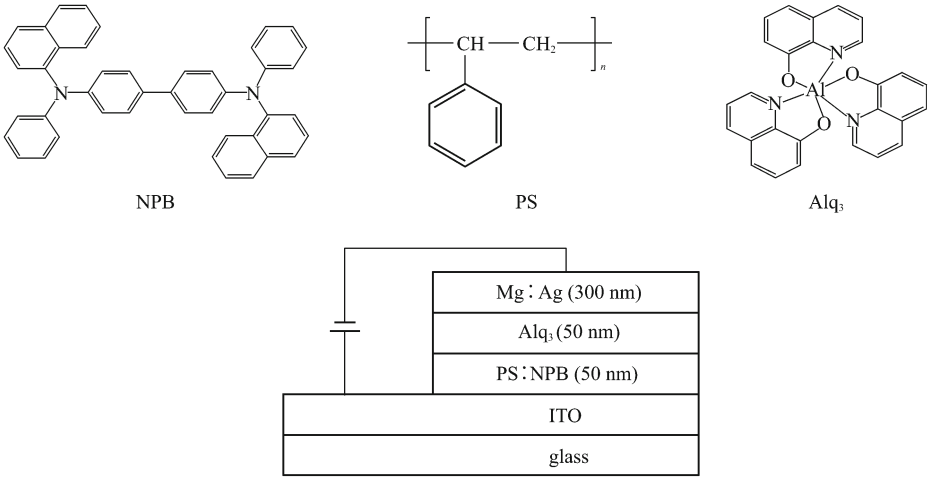

Fig. 1 Chemical structures of materials and device configuration

A: ITO/PS:NPB (x:y) (x:y = 1:9)/Alq_3/Mg:Ag
B: ITO/PS:NPB (x:y) (x:y = 3:7)/Alq_3/Mg:Ag
C: ITO/PS:NPB (x:y) (x:y = 1:1)/Alq_3/Mg:Ag
D: ITO/PS:NPB (x:y) (x:y = 7:3)/Alq_3/Mg:Ag
E: ITO/PS:NPB (x:y) (x:y = 9:1)/Alq_3/Mg:Ag

Figure 2(a) is the EL spectra of devices under a bias voltage (V_{bias}) of 15 V.

We can see that the EL spectrum peaks of the five devices are almost identical with all located at about 525 nm, which is in accordance with the characterizing spectrum of Alq_3 (520 nm) [12], and their CIE (the Commissions Internationale L'Eclairage) coordinates are quite close to each other. These results indicate that Alq_3 was the emitting layer. NPB acted here only as HTL, not involved in light emission. Meanwhile, the tiny deviation of the spectrum peaks of devices is originated from the intrinsic energy level structure of organic semiconductors; because they have only discretely distributed HOMO and LUMO states, unlike the inorganic semiconductors that have complete and continuous energy band, the width of the energy gap of organic semiconductors is relatively indefinite. According to the equation of intrinsic emission of semiconductors,

$$\lambda_0 = \frac{1.24}{E_g}\ (\mu m), \tag{1}$$

where λ_0 is the emissive wavelength of electron transition from the valence band to conduction band, and E_g is the gap energy. Therefore, a discrete energy band structure will lead to a certain deviation of emission wavelength. In addition, the emission zones of all the devices are located near the PS:NPB/Alq_3 interface within the Alq_3 layer, and this phenomenon can be explained from the energy level diagram showed in Fig. 2(b). 5.2 eV is the HOMO energy of pure NPB, and the dashed line stands for the HOMO energy of PS:NPB composite layer. The HOMO level of the doping system will exhibit a variation with different doping concentration of PS:NPB (as is indicated by the arrow). This variation results from two factors: on one hand, the hole drift mobility of the doped composite film varies with doping concentration, leading to a discrepancy of hole transporting ability of different films; on the other hand, the property of the interface formed between PS:NPB thin film with different doping concentration and Alq_3 layer is not totally the same, which indirectly affects the hole injection process. We can approximately estimate that the hole injection barrier is enhanced or lowered with regard to the energy level diagram. Generally speaking, the hole injection barrier at this interface (>0.5 eV and <0.9 eV) is relatively lower than that of electrons (0.9 eV), which is beneficial to hole injection from PS:NPB to Alq_3. It is difficult for electrons to tunnel through the high barrier at this interface to enter the NPB layer, thus most electrons are confined in the Alq_3 layer, accumulated near the PS:NPB/Alq_3 interface to form space charge, and recombine with holes attracted by the Coulomb force from PS:NPB to Alq_3 layer. Excitons are produced within the Alq_3 layer and Alq_3 emission is ultimately obtained through the radiative decay of excitons. The introduction of PS:NPB adjusts the injection and transportation level of hole carriers to a certain extent, gives rise to a more balanced distribution of holes and electrons inside devices, but has little impact on the location of the emitting layer. The above analysis of energy levels of the composite layer is merely a simplified model, not taking into account the internal micro-interaction between PS and NPB. As a matter of fact, because the structure of organic semiconductors is very complicated, the effect of PS:NPB composite hole transporting media is not a simple linear superposition of their respective nature. Further investigation should be carried out to explore the abstruse physical mechanism inside such devices.

3.2 Current density-luminance-voltage characteristics of EL devices

The current density-luminance-voltage (J-L-V) curves of devices are illustrated in Fig. 3. The current density and

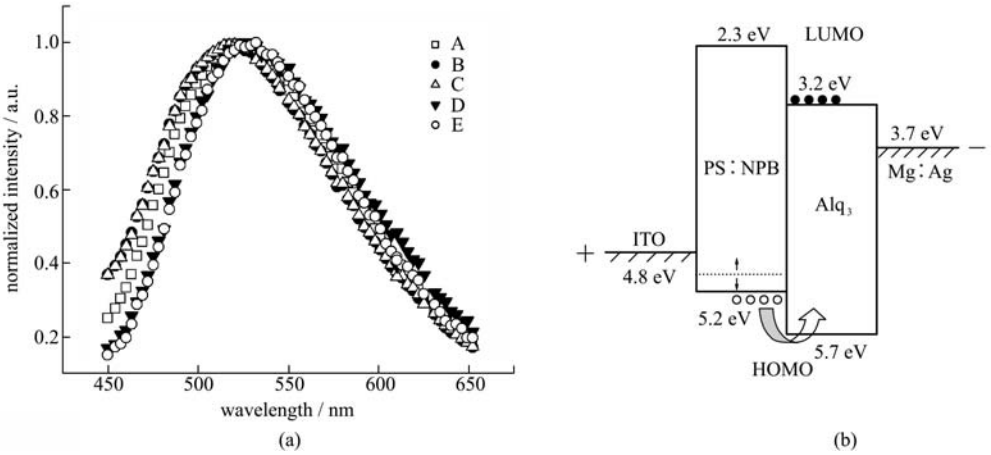

Fig. 2 Devices under bias voltage of 15 V. (a) EL spectra; (b) energy level diagram

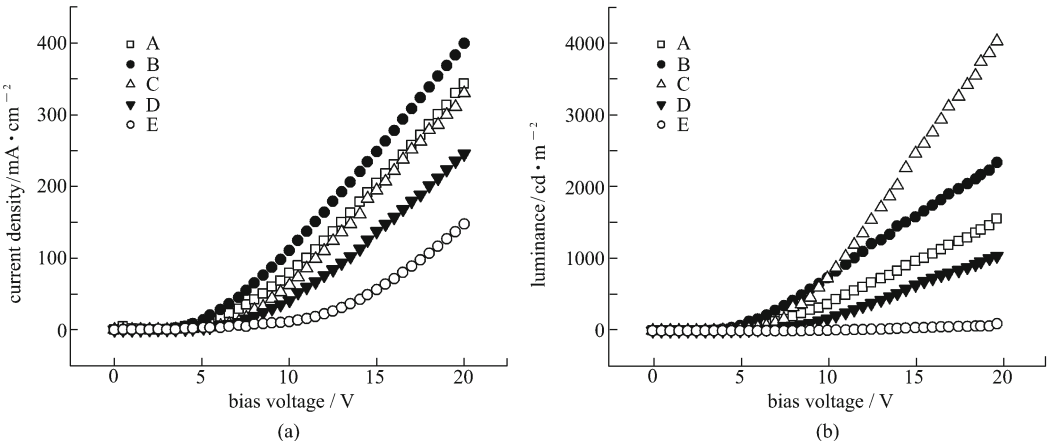

Fig. 3 Curves of the devices. (a) Current density-voltage (*J-V*); (b) luminance-voltage (*L-V*)

luminance characteristics at a bias voltage of 20 V are illustrated in Fig. 4. From Fig. 3(a), it can be seen that the current density of the five devices A–E increases with applied voltage and augments nonlinearly with voltage according to a power law in the region of high electric field intensity (>10 V), exhibiting a typical rectification characteristic of diodes. Meanwhile, from Fig. 4(a), we can see that the current density of device B is the highest (about 400 mA/cm^2), and that of device A, C, D and E decreases orderly. Assuming the other external conditions to be totally the same, there should be a close relationship between the current characteristics and the concentration proportion (x:y) of composite hole transporting layer. As is known, PS is a polymeric insulator, and its intrinsic insulating property will introduce series resistance, accordingly weakening the conductive capability of organic thin films. The mean hole drift mobility of PS:NPB film is continuously lowered with the increase of PS proportion in the doping system, and the carrier transportation ability of the hole transporting layer is decreased, leading to a lowered current device density. From Fig. 4(a), however, it can also be seen that the current density of device A (x:y = 1:9) is lower than that of device B (x:y = 3:7). We attribute this result to the non-ideal film morphology caused by the nonuniform distribution of NPB in the PS matrix where PS concentration is far too low. The rough interface between HTL and the emitting layer results in an incomplete transmission channel and increases the contact resistance of heterojunction interface, which causes a low current density.

As shown in Fig. 3(b), the luminance of the devices increases regularly with drive voltage, but their increasing magnitude is different. Device C has a larger magnitude and attains to a maximum luminance of 4025 cd/m^2 at 20 V. The *L-V* curve of device E seems to be horizontal in this coordinate scale, indicating that its luminance is far below that of other devices. From Fig. 4(a), we can see that the device luminance augments with the increase of PS proportion at first, attains to its maximum value at x:y = 1:1 (device C), and then decreases abruptly until it reaches its bottom value (95 cd/m^2) at x:y = 9:1 (device E). It can be concluded that from the point of view of luminance parameter, an optimum concentration proportion of PS and NPB (x:y = 1:1) is available in these devices. The mass fraction of insulating PS in doping system should not be too large or too small. If PS proportion is

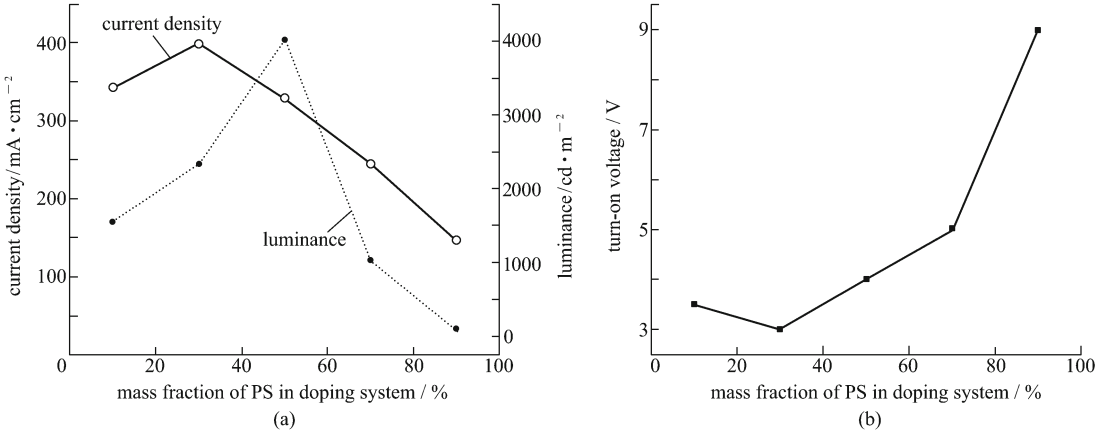

Fig. 4 Current density and luminance at 20 V (a) and turn-on voltage (b) versus mass fraction of PS

Table 1 Main parameters of device performance

device	PS:NPB (x:y)	V_T/V	J/mA·cm^{-2}	L_{max}/cd·m^{-2}	η_{lm}/lm·W^{-1}	CIE
A	1:9	3.5	344	1555	0.24	(0.34, 0.55)
B	3:7	3.0	400	2338	0.38	(0.33, 0.54)
C	1:1	4.0	330	4025	0.57	(0.33, 0.56)
D	7:3	5.0	245	1039	0.03	(0.34, 0.56)
E	9:1	9.0	147	95	0.02	(0.32, 0.55)

far too small, the distribution of dopant small molecules in composite layer is nonuniform, which is caused by the limited carrying capacity of the polymer matrix. This nonuniformity may lead to a problem of film quality, and eventually deteriorates the device performance. If the PS proportion is far too large, the excellent insulating property of PS makes it more difficult for holes to hop among NPB molecules, which seriously damages the hole transporting property of NPB. Especially, in the devices whose PS proportion exceeds 90%, the hole drift mobility of PS:NPB composite film is remarkably diminished, making it extremely hard for holes to transmit from anode to Alq_3 layer and greatly decreasing the probability of radiative recombination of holes and electrons, thus the device luminance is fairly low.

3.3 Turn-on voltage and efficiency

As demonstrated in Fig. 4(b), the turn-on voltages (V_T) (defined as the bias voltage at $L = 1$ cd/m^2) of devices A–E are 3.5, 3.0, 4.0, 5.0 and 9.0 V, respectively. It exhibits a regular variation of increase with PS proportion. V_T attains to 9.0 V at x:y = 9:1. This result may be attributed to the enhanced injection barrier of holes into the emitting layer, which is caused by the decreased charge transporting ability of HTL with the increase of PS proportion. According to Fowler-Nordheim tunneling theory [13]:

$$J_T = BF^2 \exp\left[-\frac{4(2m_{eff})^{1/2}\Delta^{3/2}}{3\hbar eF}\right], \quad (2)$$

where J_T is current density; F is electric field intensity, a function of voltage; Δ is barrier height; m_{eff} is the effective mass of carriers; $\hbar$ is Planck constant; B is a constant determined by material. Obviously, the injection current is inversely proportional to the barrier height. Given the current value definite, a higher barrier demands a more intensive electric field which is a function of voltage. Thus, due to the carrier tunneling effect, a high drive voltage is required to overcome a high energy barrier to obtain the same device current, which determines a relatively high turn-on voltage. In addition, the film of a doping system whose PS proportion is too small can be of low quality, which similarly increases the hole injection barrier of HTL, and this is the reason for the higher turn-on voltage of device A compared to that of device B.

Luminance efficiency of the devices were calculated according to the following equation:

$$\eta_{lm} = \frac{\pi I}{10 V_{bias} i} \text{ (lm/W)}, \quad (3)$$

where η_{lm} is luminance efficiency, I is luminance, and i is the current passed through the device. From Eq. (3), the maximum luminance efficiency of the devices after turn-on is 0.24, 0.38, 0.57, 0.03 and 0.02 lm/W, respectively. The variation of luminance efficiency of devices shows a similar tendency as the luminance does, reaches its maximum at x:y = 1:1 and falls to its minimum at x:y = 9:1. From the point of view of efficiency parameter, x:y = 1:1 is also the optimum doping concentration in PS:NPB devices.

Table 1 lists in detail the characteristic parameters of the five devices (J is at 20 V).

4 Conclusion

Double-layer green OLED with PS:NPB composite hole transporting layer of different doping concentration was fabricated by spin-coating method. The study of device electroluminescent characteristics demonstrated that the device current decreases and turn-on voltage increases simultaneously with the PS proportion increases, and the luminance as well as its efficiency showed a different variation tendency and reach their maximum values at PS:NPB = 1:1. It is concluded that in this kind of OLED device, an optimum PS:NPB concentration proportion is available for the purpose of reducing device cost and optimizing device performance. This work is a valuable reference and guide for the construction of composite hole transporting layer and the technique improvement used to fabricate novel OLED devices by spin-coating methods.

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