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A plasmonically enhanced charge generation layer for tandem organic light emitting device

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We studied silver nanoparticles (Ag NPs) as an n-type dopant in the charge generation connector of tandem organic light-emitting diodes. Due to the localized surface plasmonic resonance and quantum size effects, Ag NPs are more active and easy to lose electron comparing to bulk or film forms of Ag, and can work as excellent n-type dopant. For the tandem device with Ag NPs in the charge generation layer, the current efficiency is more than doubled and the driving voltage is less than twice compared to one single emission unit device. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4789979>]

Organic light-emitting diodes (OLEDs) are current-driven devices. Ideally, their luminance should linearly increase with the increase in current density. However, to achieve higher luminance in an actual application, an OLED has to operate at a relatively high current density, which induces severe bi-exciton formation,¹ polaron-exciton interaction,² and Joule heating,³ undesirably leading to a lower efficiency level and a shorter operational lifetime. By connecting two or more emissive units in series, the so-called tandem OLEDs offer the capability of higher current efficiency levels, longer operational lifetimes, and higher brightness compared to a single emissive unit OLEDs, while maintaining the same current density as the single unit OLEDs.^{4–10} In general, to make a low driving voltage and high efficiency tandem device, an excellent connector prone to generate charges is crucible, which will guarantee a low turn-on voltage of the resulting tandem device.

As demonstrated, the tandem device with charge generation connector (CGC) based on PN doped heterojunction architecture shows a high current efficiency and a low driving voltage.^{11,12} In the heterojunction, for p-type layer, molecules or transition metal oxides with high electron affinity are excellent dopants, such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ), molybdenum oxide (MoO₃), and tungsten oxide (WO₃).^{4–6} For n-type layer, chemicals with low ionization potential are required. So far, active metals (such as magnesium, cesium, and lithium), active metal-salt compounds (such as cesium carbonate, Cs₂CO₃), and some special organic molecule dopants are often used.^{5–10} We know cesium and lithium metal are difficult to use and store because of their activity. And their atoms are small in size and easy to diffuse into emission region, quenching the emission.¹³ Besides small atomic size, the chamber contamination is also a problem for magnesium evaporation. Although Cs₂CO₃ is a good n-type dopant for cathode ohmic contact in single emissive unit devices, it is not so in tandem devices.¹⁴ For organic n-type dopants,

besides their expensive price, we hardly know anything from their vendors.

Recently, localized surface plasmonic resonance (LSPR) of notable metal nanoparticles has attracted much attention in organic electronics due to its special characteristics on changing local electromagnetic field distribution, which enhances out-coupling efficiency for OLEDs^{15–17} and light absorption for organic photovoltaic devices (OPVs).^{15,18,19} So far, in most works, the applications of LSPR on organic electronic devices are limited to electrodes of the devices.^{15–19} We know that LSPR refers to that the valence electrons absorb incidence photons to be stimulated and oscillate, thus the energy of these electrons should be higher, i.e., the electron activity should be enhanced.²⁰ In this work, we designed and fabricated a tandem OLED based on CGC with silver nanoparticles (Ag NPs) as the n-type dopant. Additionally, the nanoparticle morphology can prevent such emission quenching existing in alkali metal doped devices.¹³

The organic materials used in this work are *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB), tris(8-hydroxyquinoline)aluminum(III) (Alq₃), 4,7-diphenyl-1,10-phenanthroline (Bphen), 4,4',4''-tris(*N*-3-methylphenyl-*N*-phenyl-amino)triphenylamine (m-MTDATA), and F4-TCNQ. Patterned ITO glasses (15 Ω/sq) were used as anode substrates. First, the ITO substrates were cleaned with de-ionized water, isopropanol, and acetone in sequence. Subsequently, they were oven-dried and treated in O₂ plasma. All thin films and LiF/Al electrodes were fabricated by thermal evaporation in a vacuum deposition system at a pressure of less than 4 × 10^{−4} Pa without breaking the vacuum. All the organics and metal compounds were evaporated at a rate of about 0.1–0.2 nm s^{−1}, and the metallic electrodes were evaporated at a rate of 0.8–1 nm s^{−1}. A shadow mask was used to define the cathode. The luminance-current density-voltage (L-J-V) characteristics and electroluminescence (EL) spectra were measured simultaneously with a Keithley 2400 power source meter and a Photo Research PR 650 spectrometer. The scanning electron microscopy (SEM) was performed using a LEO 1550 scanning electron micrograph. The absorption spectra were recorded using a PerkinElmer

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Lambda 950 UV/Vis/NIR spectrophotometer system. The time-resolved fluorescence spectroscopy (TRFS) measurements were performed using a fluorescence lifetime imaging microscopy system excited by a 375 nm pulsed laser. All measurements were carried out at room temperature in ambient atmosphere.

As shown in Fig. 1, three OLED devices with the following structures were fabricated and compared, device A: ITO/NPB(60 nm)/Alq₃(60 nm)/LiF(1 nm)/Al(100 nm), device B: ITO/NPB(60 nm)/Alq₃(60 nm)/Alq₃: Ag (1:1 mol, 20 nm)/Al(100 nm), and device C: ITO/NPB(60 nm)/Alq₃(60 nm)/Bphen: Ag (1:1 mol, 20 nm)/m-MTDATA: F4-TCNQ (1:1 mol, 20 nm)/NPB(60 nm)/Alq₃(60 nm)/LiF(1 nm)/Al(100 nm). Device A is a conventional single emissive unit device, device B is a single emissive unit device with Ag doped Alq₃ electron injection layer, and device C is the doped connector tandem device. Devices A, B, and C were fabricated in a single run without breaking the vacuum. The CGC contains a doped planar PN heterojunction. The n-type layer is a 20 nm Bphen layer doped with Ag with 1:1 mole ratio as mentioned above. For the p-type layer, a commonly used hole injection material m-MTDATA and p-type dopant F4-TCNQ were employed with 1:1 mole ratio, and the thickness of the film is also 20 nm.

As reported, a 1-2 nm Ag film deposited on ITO or SiO₂ substrate through thermal evaporation is not continuous, but present as nanoparticles.^{21,22} To understand the form of Ag in the case of co-evaporation of Ag with organic host, we deposited 5 nm thick Ag doped Bphen film with 1:1 mole ratio on an ITO substrate by thermal co-evaporation method. The inset of Fig. 2 shows the SEM of the co-evaporated film. It can be seen that the film is made of Ag NPs embedded in the host molecule matrix, which is similar to the ultrathin Ag film case. The mean size of the Ag NPs is about 20 nm. We further measured the absorption of the film as shown in Fig. 2, where a clear LSPR absorption of Ag NPs can be seen.²⁰⁻²⁴ Additionally, there is an overlap between the LSPR absorption spectrum of Ag NPs and the emission spectrum of Alq₃ (Fig. 2), which is used as the emitting layer for the tandem device studied in this paper. Under the irradiation of luminescence from Alq₃, the LSPR should occur,²⁰⁻²⁴ which are supported by our further TRFS measurement. Figure 3 shows the fluorescence decay of a single-layer film of Alq₃ (5 nm), a double-layer film of Bphen: Ag (1:1 mol, 20 nm)/Alq₃ (5 nm), and a triple-layer film of Bphen: Ag (1:1 mol, 20 nm)/Bphen (10 nm)/Alq₃ (5 nm). It can be seen from Fig. 3 that the

FIG. 1. The schematics of the three devices studied.

FIG. 2. The absorption spectra of a 20 nm m-MTDATA: F4-TCNQ film, a 20 nm Bphen: Ag film, and a 20 nm Bphen film deposited on quartz substrate. The absorption of Ag NPs was obtained by comparing the absorption spectra of Bphen: Ag and Bphen films. There is an overlap between LSPR absorption spectrum of Ag NPs and photoluminescence spectrum of Alq₃. The insertion is the scanning electron micrograph of 5 nm thick Bphen: Ag film on ITO substrate obtained by thermal co-evaporation.

intrinsic lifetime of Alq₃ fluorescence is about 13.8 ns. With a double layer configuration of Bphen: Ag and Alq₃, the lifetime of Alq₃ fluorescence decreases sharply to about 5.6 ns. Further inserting a 10 nm spacer (Bphen) between Bphen: Ag and Alq₃ layers, the lifetime of Alq₃ fluorescence increases to about 11.1 ns, which is very close to the intrinsic lifetime of Alq₃. This indicates that when the distance between Ag NP and Alq₃ is close (without spacer), the plasmonic interaction between them is strong. With the insertion of a 10 nm spacer, the plasmonic interaction becomes weaker.^{15,20-24} As LSPR is actually a resonant photon-induced collective oscillation of valence electrons after photon absorption, which establishes when the frequency of incident photons matches the natural frequency of surface electron oscillation against the restoring force of positive nuclei.²⁰ So, the surface valence electrons of Ag NPs are agitated, and hence are easier to be lost comparing with the bulk form of Ag.²⁰

Figure 4 shows the current density-driving voltage curves and current efficiency plots of all devices. We can see that in Fig. 4, the driving voltage of device B is a slightly

FIG. 3. The time-resolved fluorescence spectroscopy of Alq₃ (5 nm), Bphen: Ag (1:1 mol, 20 nm)/Alq₃ (5 nm), and Bphen: Ag (1:1 mol, 20 nm)/Bphen (10 nm)/Alq₃ (5 nm) films deposited on quartz, and the monitoring wavelength is 510 nm. The extracted values of lifetime were obtained by a single exponential fitting.

FIG. 4. Current density-driving voltage curves and current efficiency of reference device A (conventional device), device B with Ag doped electron injection layer, and device C with Ag doped connector. The inset is the electroluminescence spectra of all devices at 10 mA/cm².

higher than that of device A, while the current efficiency of device B is slightly lower than that of device A, which indicates that the Ag doped Alq₃ film can work as an electron injection buffer layer comparable to LiF. The Ag NPs doped Alq₃ can be used as an electron injection layer originates from the LSPR effect as mentioned above, i.e., Ag NP behaves as a n-type dopant, similar to cesium, magnesium, or lithium.^{5–8} Interestingly as shown in Fig. 4, comparing to both devices A and B, the current efficiency of tandem device C is more than doubled, and the driving voltage is less than twice. In device C, the Ag NPs is far away from both electrodes, so the possibility of lightning rod effect can be excluded.¹⁵ As discussed above, the LSPR should be the main reason for the device performance improvement. Because there is a spectral overlap between LSPR absorption of Ag NPs and Alq₃ emission, the Ag NPs can absorb a portion of photons radiated from Alq₃ forming LSPR.²⁰ And, when the Ag NPs size is less than 30 nm, the surface plasmon can decay through the formation of energetic charge carriers which can transfer to neighboring molecules.²⁰ So, the activity of the electrons should be enhanced and such electrons are easier to be lost comparing to normal case with no LSPR. We can consider a positive cycle as follows. Similar to normal tandem device, huge amounts of charges are spouted at the CGC interface by charge transfer process, and the generated charges inject into two recombination zones, form excitons and radiate through relaxation. Simultaneously, a portion of such photons are absorbed by Ag NPs to form localized surface plasmons, and then the energetic electrons can easily transfer to Bphen molecules as the case of alkali metal dopant,^{5–8} facilitating the charge generating at CGC interface. The relaxed Ag NPs can absorb the photons radiated from Alq₃ again. So, such architecture effectively utilizes the device inner radiation. As shown in the inset of Fig. 2, we note that the EL spectra of devices B and C are slightly narrower in their blue edges compared to device A, i.e., their peaks are slightly red-shifted. This is considered to be possibly caused by the absorption of Ag NPs.

Moreover, as reported by Liu and Nunzi that the photoluminescence (PL) of Alq₃ can be enhanced to about 1.4 folds

due to the LSPR of Ag NPs.¹⁵ Although the Ag NPs were dispersed in Bphen layer, not in Alq₃ layer, and their distance is large, the enhancement in PL probably exists in the zone close to Bphen: Ag/Alq₃ interface. Additionally, Wu demonstrated that as the Ag NPs size decreases to nanometer scale, the reduction activity of Ag particles is strengthened.²³ Combining such factors, the Ag NPs act as an effective n-type dopant enhancing the tandem devices optically and electrically, leading to more than doubled performance.

Under external electrical bias, the charges are generated through electron transfer process across the PN heterojunction interface formed by the p-type m-MTDATA: F4-TCNQ layer to n-type Bphen: Ag NPs layer. The generated charges would inject into two emissive units, respectively, and form excitons by recombining with the charges injected from the two outmost electrodes.

Additionally, in order to confirm the CGC based on LSPR indeed improves the tandem device performance, we fabricated a CGC device with structure ITO/Bphen: Ag (1:1 mol, 20 nm)/m-MTDATA: F4-TCNQ (1:1 mol, 20 nm)/Al (100 nm). As shown in Fig. 5, under the irradiation of a yellow light, we can clearly see that the driving voltage is lowered comparing to the case without irradiation. Because, as shown in Fig. 5, only Ag NPs has the absorption in yellow range, and m-MTDATA: F4-TCNQ layer and Bphen layer hardly have any absorption in this range. The phenomenon should be caused by LSPR of Ag NPs. Such results not only prove that the Ag NPs can work as n-type dopant in tandem

FIG. 5. (a) Current density-driving voltage curves of CGC device under irradiation and in dark. The inset is the transmittance spectrum of Bphen: Ag film. (b) The spectral overlap between the absorption spectrum of Bphen: Ag and the emission spectrum of the yellow exciting light got from white LED lamp with filter.

device but also can explain why the driving voltage of such tandem device C is lower than two times of single unit device A. Though the Ag NPs absorbed a portion of photons irradiated from Alq₃, which should lower down the overall efficiency of tandem device C, considering the low absorbance below 0.1 (Fig. 2) and high transmittance shown of Bphen: Ag film (Fig. 5), the loss caused by Ag NPs absorption is very small. So, the overall influence of introduction of Ag NPs is positive.

We investigated the tandem device with an Ag NPs incorporated CGC. Due to LSPR and enhanced reduction activity of Ag NPs, the tandem device presented much improved performance. The Ag NPs absorbed a very small portion of photons generated from the tandem OLED itself, however, with the help of LSPR, such absorption facilitated the charge generation in CGC layer through charge transfer process in the PN connector interface under external electrical bias.

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