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Surface plasmon-enhanced electroluminescence in organic light-emitting diodes incorporating Au nanoparticles

Y. Xiao,¹ J. P. Yang,¹ P. P. Cheng,¹ J. J. Zhu,¹ Z. Q. Xu,¹ Y. H. Deng,¹ S. T. Lee,² Y. Q. Li,^{1,a)} and J. X. Tang^{1,a)}

¹*Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China*

²*Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China*

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Surface plasmon-enhanced electroluminescence (EL) in an organic light-emitting diode is demonstrated by incorporating the synthesized Au nanoparticles (NPs) in the hole injection layer of poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid. An increase of $\sim 25\%$ in the EL intensity and efficiency are achieved for devices with Au NPs, whereas the spectral and electrical properties remain almost identical to the control device. Time-resolved photoluminescence spectroscopy reveals that the EL enhancement is ascribed to the increase in spontaneous emission rate due to the plasmonic near-field effect induced by Au NPs. © 2012 American Institute of Physics. [doi:10.1063/1.3675970]

Organic light-emitting diodes (OLEDs) have shown the potential for lighting source and display applications due to their high brightness, low power consumption, and excellent color gamut.^{1–6} Significant progress has been made in the past decades for the development of high-performance OLEDs, and nearly 100% internal quantum efficiency has been achieved by using phosphorescent emitting materials and optimizing device architectures.^{4–6} However, the poor light extraction efficiency of $\sim 20\%$ in a conventional OLED limits the external quantum efficiency due to the total internal reflection (TIR) at the glass substrate/air and indium-tin-oxide (ITO)/substrate interfaces, the waveguide (WG) mode at the organic/ITO anode interface, and the surface plasmon (SP) losses at the metallic cathode/organic interface.^{7–10}

Various methods have been proposed to enhance light out-coupling in OLEDs, including surface microstructures on ITO anode to reduce the WG mode loss,^{11,12} photonic crystals or microlens arrays attached on the glass substrate for the reduction of TIR,^{13,14} corrugated cathode to reduce SP losses,^{15–18} optical microcavity structures,¹⁹ and so on. Recently, the localized SP effect excited by metallic nanostructures is becoming one of the most attractive approaches for light emission enhancement in OLEDs through the coupling with localized SP resonance and the emission energy.^{15–18,20,21} For example, Koo *et al.* have demonstrated the enhancement of light extraction efficiency in OLEDs by a quasi-periodic buckling structure without introducing spectral changes and directionality.¹⁵ The roughness on the cathode side induced by lithography process¹⁶ or template transform¹⁵ can match the momentum of SPs and radiated light, leading to the SP enhancement. However, the attempt of introducing SP effect into OLEDs by metallic nanostructures has been limited by the difficulty in applying nanoscale lithographic patterning technologies with large-area devices. In this Letter, the pre-synthesized Au nanoparticles

(NPs) with a diameter of 40 \sim 50 nm have been incorporated into a hole-injection layer (HIL) of poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) for OLEDs to induce localized SPs. An observable enhancement in electroluminescence (EL) is achieved without any influence on spectral and electrical properties due to the Au NPs-generated plasmonic near-field enhancement.

The devices were fabricated on ITO-coated glass substrate with a sheet resistance of 10 Ω /sq. The Au NPs were prepared through the standard sodium citrate reduction method as reported previously.²² Au NPs were dispersed into the aqueous solution of PEDOT:PSS in an optimized ratio as a HIL. The resulting solution was spin-coated onto UV-zone treated ITO glass substrate and subsequently annealed at 110 °C in air. Due to the low concentration of Au NPs in the mixed solution, the incorporation of Au NPs does not alter the film thickness of PEDOT:PSS, which was estimated to be ~ 40 nm by the alpha-SETM Spectroscopic Ellipsometer. Then, the samples were transferred to the evaporation chamber with a base pressure of 2×10^{-6} Torr, where the device fabrication was completed by thermal evaporation of an 150 nm-thick tris(8-quinolinolato) aluminum (Alq₃) layer as the emission/electron-transporting layer, and an 100 nm-thick Al as the cathode through shadow mask. To minimize experimental variation, each layer was simultaneously deposited for all samples in the same batch. The current density-voltage-brightness (J-V-B) characteristics and EL spectra of the corresponding devices were measured simultaneously with a programmable Keithley model 2400 power source and a PhotoResearch PR-655 spectrometer. Absorption spectra were recorded by an UV/vis spectrophotometer (PerkinElmer Lambda 750). Steady state photoluminescence (PL) spectra were recorded by Fluorescence spectrometer (Horiba Flworomax-4). For time-resolved PL measurements, the sample was excited by a 370 nm pulsed light source. A time-correlated single photon counting spectrometer was combined with the Fluorolog-3 spectrofluorometers (Horiba-FM-1515) to record the dynamic signal, which is synchronized to the pulse.

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: jxtang@suda.edu.cn and yqli@suda.edu.cn.

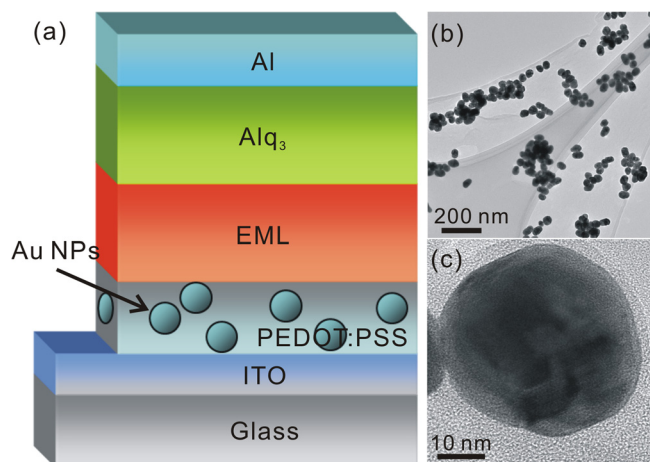


FIG. 1. (Color online) (a) Schematic device structure of an OLED incorporating Au NPs in the PEDOT:PSS layer. (b) TEM and (c) high-resolution TEM images of the synthesized Au NPs.

The schematic of the OLED structure incorporating chemically synthesized Au NPs in the PEDOT:PSS HIL is shown in Fig. 1(a). In order to avoid the interference with Al electrode that will cause SP losses, the distance between emitting layer and metal cathode in OLEDs is a crucial factor and should be large enough.^{23,24} In this study, the Alq₃ thickness of 150 nm was used, which almost totally drops off the influence of SP losses caused by Al electrode. Transmission electron microscopy (TEM) (FEI Tecnai G² F20 S-TWIN, at 200 kV) was used to characterize the topography of Au NPs, which were dipped onto the copper grid and dried for measurement. According to TEM and high resolution TEM images shown in Figs. 1(b) and 1(c), Au NPs are spherical in shape and highly dispersed with an average diameter of 40~50 nm.

Figure 2(a) plots the J-V characteristics of OLEDs with and without Au NPs in the PEDOT:PSS layer. As evident in Fig. 2(a), the electrical property of the corresponding devices remain almost identical, indicating that the hole injection efficiency is not significantly influenced by the presence of Au NPs in the PEDOT:PSS layer. Ultraviolet photoelectron spectroscopy (UPS) measurement was also performed to investigate the PEDOT:PSS layers with and without Au NPs (not shown here). The results demonstrated that there is no obvious difference in the hole injection barrier heights between these two HILs. In addition, there is negligible change of EL spectra as shown in the inset of Fig. 2(a), revealing the independence of spectral property on the incorporation of Au NPs.

However, Fig. 2(b) shows that the current efficiency of the device with Au NPs mixed PEDOT:PSS layer shows a significant increase compared with the control device without Au NPs. For instance, the efficiency increases from 1.04 cd/A compared to 1.28 cd/A at a current density of 40 mA/cm², in which the enhancement ratio is about 25%. The angular dependence of EL spectra for devices with and without Au NPs in PEDOT:PSS exhibits the almost identical characteristics with increasing the viewing angles (see supplemental Fig. 1),²⁵ which rules out the microcavity effect on the efficiency enhancement. According to the calculation results, SP penetration depth is approximately 30–40 nm in the environment near

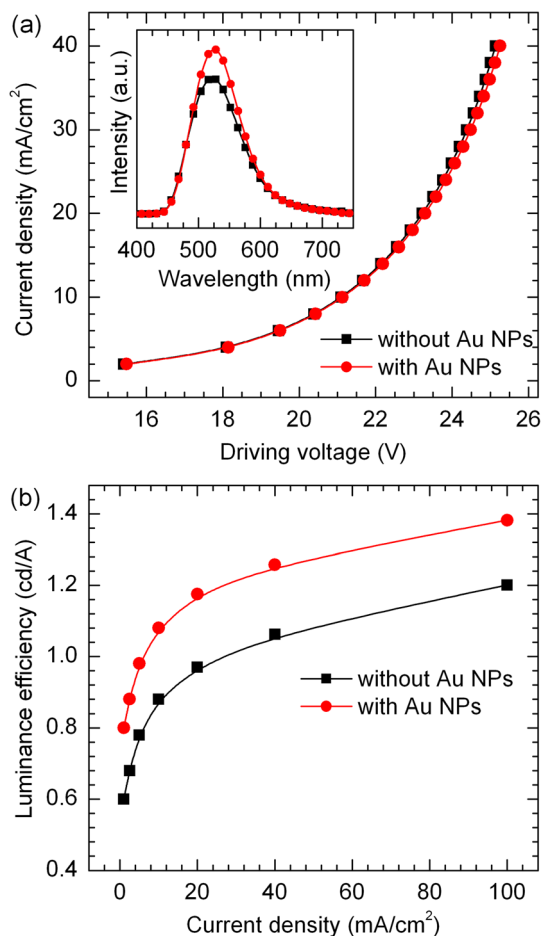


FIG. 2. (Color online) (a) Current density-voltage (J-V) and (b) efficiency-current density characteristics of OLEDs with and without Au NPs in the PEDOT:PSS layer. Inset of (a) is the corresponding EL spectra at the current density of 40 mA/cm².

the Alq₃/metal interface.²¹ Therefore, it is reasonable to infer that the EL enhancement as observed in Fig. 2 is associated with the SP effect, since the emission layer of Alq₃ can fall in the local near-field of SPs induced by Au NPs.

For more accurate proof of correlating the EL enhancement with SP resonance, the absorption of the PEDOT:PSS layers with and without Au NPs was measured as shown in the inset of Fig. 3. The PL spectrum of Alq₃ is also plotted for comparison. It is observed that the absorption in the region of 450 to 600 nm is enhanced with the incorporation of Au NPs into the PEDOT:PSS layer, which almost coincides with the PL peak of Alq₃. The overlap of two spectra indicates the possible resonance between radiated light generated in Alq₃ and localized SPs excited by Au NPs, which will result in an effective energy transfer and therefore the enhanced emission intensity.²⁶

It has been reported that the coupling process between SPs and radiated light is much faster than spontaneous recombination of excitons, and the exciton lifetime in SP-enhanced devices should be much decreased.^{17,27} Here, time-resolved PL spectra of a 50 nm-thick Alq₃ layer on PEDOT:PSS coated ITO glass substrates with and without Au NPs were measured as shown in Fig. 3. It is noted that the decay time of the PL emission (at 530 nm) of Alq₃ layer on PEDOT:PSS without Au NPs is 14.73 ns, whereas it is obviously decreased to 13.60 ns with the incorporation of Au NPs into the

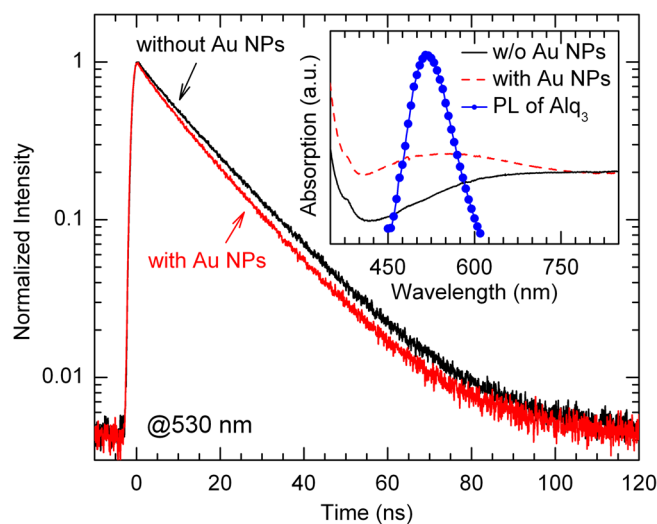


FIG. 3. (Color online) Time-resolved PL spectra detected at the wavelength of 530 nm via a 370 nm laser source. The inset shows the absorption spectra of the PEDOT:PSS mixed with (dashed line) and without (solid line) Au NPs on ITO-glass substrate and the PL spectrum of an Alq₃ layer (solid line with circles).

PEDOT:PSS layer. Therefore, time-resolved PL measurement provides the direct observation of the enhanced spontaneous emission rate of Alq₃ induced by localized SP resonance on Au NPs, which can be described as near-field enhancement.²⁸ In addition, the spherical shape of Au NPs could result in the high electromagnetic field distribution around Au NPs and the scattering of SPs of high momentum SPs (see supplemental Figure 2), which are beneficial to the extraction of the SP energy as light and therefore the EL enhancement.²⁵

To further clarify the effect of localized SP resonance on the EL enhancement, the OLEDs with various emitters were fabricated, in which 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1) benzopyrroprano(6,7,8-i,j) quinolizin-11-one (C545T) and 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyl julolidyl-9-enyl)-4H-pyran (DCJTB) were used as dopants for green and red emissions, respectively. Figure 4 shows the influence of Au NPs on the current efficiency of devices with C545T:Alq₃ (1 wt %, 20 nm) and DCJTB:Alq₃ (3 wt %, 20 nm) emission layers (EMLs), respectively. A 130 nm-thick Alq₃ layer was inserted between the EML and Al cathode to avoid the SP losses caused by metal electrode. As shown in Fig. 4(a), the current efficiency for the device without Au NPs is only 2.9 cd/A at a current density of 20 mA/cm², while it is ~20% improved to 3.5 cd/A with the incorporation of Au NPs into the PEDOT:PSS layer. Meanwhile, the inset of Fig. 4(a) shows a significant EL enhancement for green emission without any spectral change. This is because the resonance energy of the SP excitation mode matches with the excitons of C545T in OLEDs, leading to an effective SP enhancement by Au NPs. On the contrary, there is no observable EL enhancement of the OLED with red emission as shown in Fig. 4(b), where the current efficiency as well as EL spectra of two devices are almost the same. As the EL peak of DCJTB is located at 600 nm, there is lack of the overlap between the emission of DCJTB and the resonance energy of the SP excitation mode. Therefore, it is expected that the coupling between radiated red emission of DCJTB and SPs of Au NPs is blocked.

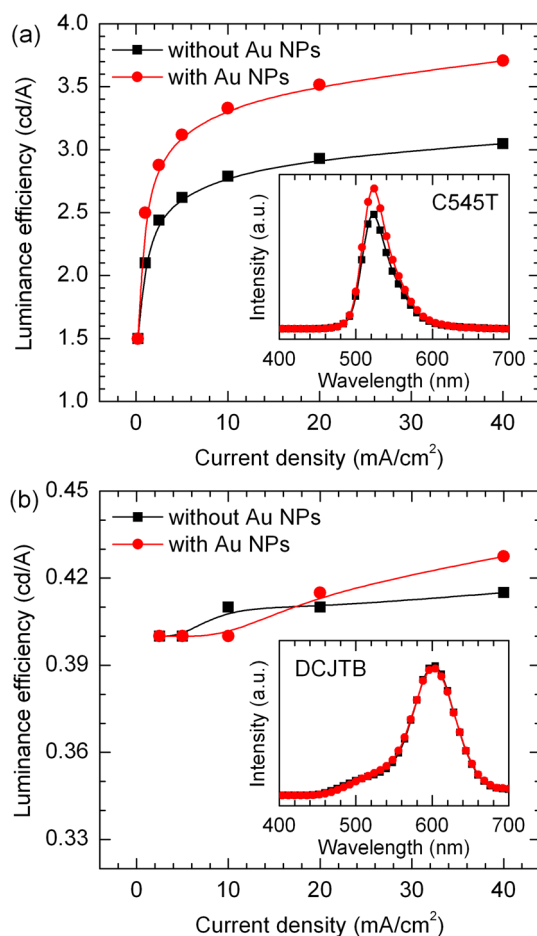


FIG. 4. (Color online) Comparison of current efficiency of (a) green emission and (b) red emission OLEDs with and without Au NPs in the PEDOT:PSS layer. Insets are the corresponding EL spectra at a current density of 20 mA/cm².

In summary, we have demonstrated the SP-enhanced EL in OLEDs by simply incorporating chemically synthesized Au NPs with a diameter of 40~50 nm into the spin-coated PEDOT:PSS film as a hole injection layer. The increase of EL intensity and current efficiency for green emission devices is achieved without affecting the spectral and electrical properties. The underlying mechanism is associated with the near-field enhancement via an effective coupling between light radiation and localized SPs around Au NPs. These results have shown that the plasmonic effect has great potential in the application of OLEDs.

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