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Substantial Performance Improvement in Inverted Polymer Light-Emitting Diodes via Surface Plasmon Resonance Induced Electrode Quenching Control

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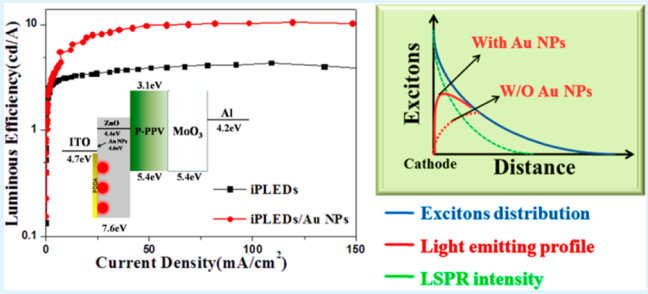
Supporting Information

ABSTRACT: Inverted-type polymer light-emitting diodes with Au nanoparticles modified ITO cathode has exhibited improved brightness from 5900 to 15 000 cd m^{-2} (1.5-fold enhancement) and enhanced luminous efficiency from 4.4 to 10.5 cd A^{-1} (1.4-fold enhancement), when greenish emissive polymer-P-PPV was applied as active layer. Both the experimental and theoretical results show that it is mainly attributed to effective overlapping between local surface plasmon resonance induced by Au nanopartices and excitons quenching region at ZnO/P-PPV interface, which makes originally electrode-quenched excitons emissive and increases excitons efficiency.



KEYWORDS: *Au NPs, PLEDs, p-type semiconducting polymer, excitons, electrode quenching*

Organic light-emitting diodes (OLEDs) have achieved great commercial success with OLED-based televisions entering the global market, but the high cost for the production of large-size OLED flat-panel monitors remains an obstacle to the widespread use of this technique. Though solution-processed polymer materials may be a choice to reduce costs, their efficiency roll-off is often rather large. In the past few years, the inverted-type polymer light-emitting diodes (iPLEDs) have been developed to enhance the stability and rectification ratio, which are important for the applications in flat-panel displays.[1−4]

Electrode quenching is one of the main problems in single carrier transport materials based PLEDs. Because most conjugated electroluminescence (EL) polymers are p-type semiconductors, in which electron mobility is usually 1−2 order of magnitudes lower than hole mobility.[5] The unbalanced carrier transport makes the formation of excitons take place near cathode, where the exciton is easily quenched by the electrode.[6−8] This type of quenching substantially results from the diffusing of excitons to electrode, which depends on the excitons lifetime.[5] Because EL efficiency is proportional to the yield of the emissive excitons, electrode quenching plays a negative role in devices performance. This issue is more serious in iPLEDs than in conventional PLEDs (cPLEDs), because of the additional unbalanced charge carrier injection between cathode and emissive layer.[1,6,7] The preponderant hole injection and transport in iPLEDs makes the formation of excitons near cathode, which suffering from the corresponding electrode quenching.[6−8] The recent methods to improve the efficiency include interfacial modification for energy level matching and emissive-layer engineering for transport balance,[1,2,4] which strongly depend on the natural properties of interface layer and emissive materials. Metal-enhanced fluorescence has been reported to decrease excitons lifetime and improve quantum efficiency in photoluminescence (PL) of fluorophore nearby, which results from the interaction between excited states of the fluorophore and local surface plasma resonance (LSPR) on metal nanoparticles (NPs) surface.[9−22] The enhancement based on LSPR is near-field, with a distance of maximum enhancement located between 1 and 10 nm.[9,17,19] Theoretically the distance can well overlap the interface between electrode and active layer, when the cathode is modified by metal NPs. Therefore, metal-enhanced fluorescence based on LSPR would show great potential in performance improvement of iPLEDs, where the LSPR working distance and the electrode quenching area are well-matching. However, to the best of our knowledge, there are few

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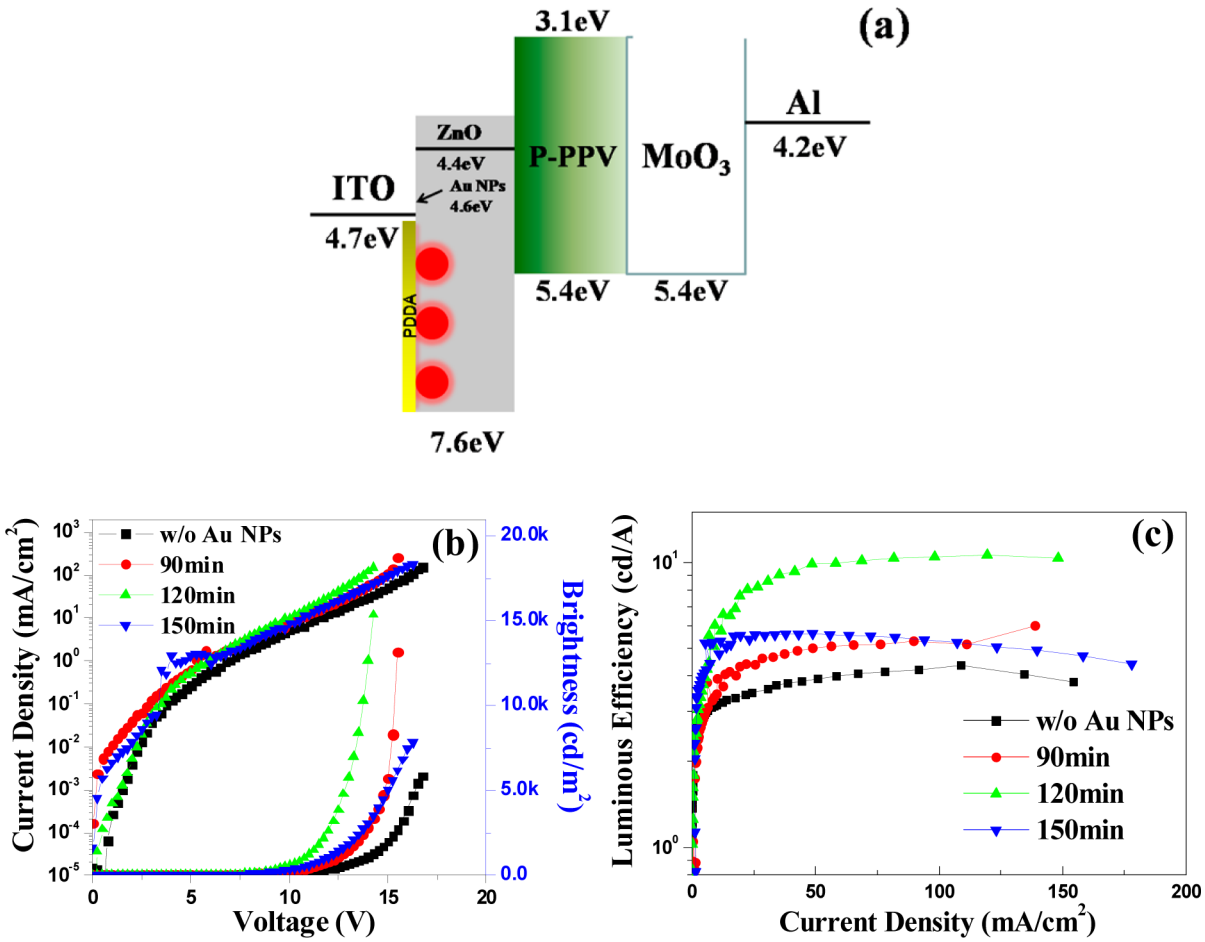

Figure 1. (a) Device structure and the energy level of iPLEDs/Au NPs. (b) iPLEDs/Au NPs (ITO/PDDA/Au NPs(x min)/ZnO(23 ± 2 nm)/P-PPV(80 nm)/MoO_3(10 nm)/Al(120 nm)) characteristics of current density vs applied voltage (I−V) and brightness vs applied voltage (B−V), and (c) luminous efficiency vs current density (LE−I) curves as a function of different electrostatic adsorption time of Au NPs.

literature reports on the LSPR effect of metal NPs in iPLEDs,[23] although excellent improvements have already been achieved in cPLEDs with 1.2−1.3-fold enhancement by SPR, light scattering, and/or electric effect induced by metal nanostructure.[15,22]

In this paper, ITO modified by gold (Au) NPs has been introduced into iPLEDs as the cathode. The device structure is optimized to make the electrode quenching region well overlapped with LSPR field range of Au NPs, which can control excitons lifetime and electrode quenching. As a result, when greenish emitting polymer-poly(2-(4-(3′,7′-dimethyloctyloxyphenyl)-1,4-phenylene-vinylene) (P-PPV) was applied as the active layer, the maximum brightness of iPLEDs/Au NPs is improved from 5900 to 15 000 cd m^{-2}, showing a 1.5-fold enhancement compared with iPLEDs. The maximum luminous efficiency (LE) of iPLEDs/Au NPs is enhanced from 4.4 to 10.5 cd A^{-1} and 1.4-fold enhancement of that in iPLEDs, which is excellent among the reported results of similar structures. Both the experimental and theoretical results reveal that the enhancement effect is mainly due to the effective overlap between the LSPR field and the excitons quenching region at ZnO/P-PPV interface, which makes full use of originally electrode-quenched excitons and increases excitons efficiency.

Figure 1a illustrates the device structure and the corresponding energy level of iPLEDs/Au NPs. The experimental methods are presented in the Supporting Information. Au NPs with 20 nm diameter are introduced onto ITO substrates by electrostatic adsorption process as our previous report (see Figure S1 in the Supporting Information).[14] In this work, the optimized device performance is observed from the Au NPs adsorbed from 0.12 nM solution by 120 min (SEM image as shown in Figure S3a, b in the Supporting Information). The work functions of pristine ITO, ITO substrates with only poly-(diallydimethylammonium chloride) PDDA and PDDA/Au NPs are measured of 4.7, 4.8, and 4.6 eV by Kelvin probe measurement, respectively (shown in Figure 1a). Different from evaporated gold thin film (5.2 eV), the work function of ITO/PDDA/Au NPs is 4.6 eV, which may be contributed to the nanosize effect and the surface modification of Au NPs by citrate.[24] It makes the energy level of cathode well match with ZnO buffer layer. Solution-processed ZnO thin films (23 ± 2 nm) as fabricated by sol−gel method on ITO substrate with and without Au NPs show the work function at 4.4 and 4.6 eV, respectively. ZnO as a buffer layer should be total coverage of Au NPs surface, because the direct contact with Au NPs will quench the fluorescence.[12] The emissive layer is P-PPV, which is a classic high-luminescent p-type semiconducting polymer with 5.4 eV HOMO and 3.1 eV LUMO.[4,5,14] The fluorescence and excitons radiative transition enhancement of P-PPV depend on the coupling of LSPR field and the excited state of P-PPV. The emission of P-PPV at 518 nm is well overlap with the LSPR extinction of Au NPs at 520 nm (see Figure S3e

in the Supporting Information), which is in favor of the effective enhancement of fluorescence emission.[10,13] Au NPs as a carrier of LSPR is introduced onto ITO in order to control of electrode quenching by decreasing excitons lifetime.

The devices performances of iPLEDs with the configuration of ITO/PDDA/Au NPs(x min)/ZnO(23 ± 2 nm)/P-PPV(80 nm)/MoO_3(10 nm)/Al(120 nm) (iPLEDs/Au NPs) as a function of Au NPs density are shown in Figure 1b, c and Figure S4 in the Supporting Information and the detailed characteristics are summarized in Table 1. In order to demonstrate the role of Au NPs, a control device with configuration of ITO/PDDA/ZnO(23 ± 2 nm)/P-PPV(80 nm)/MoO_3(10 nm)/Al(120 nm) (iPLEDs) was also fabricated. The monolayer of PDDA as a conducting polymer has been testified to make little disturbing in devices performance (see Figure S5 in the Supporting Information). In iPLEDs, the maximum brightness, LE, and power efficiency are about 5900 cd m^{-2} at 16.75 V, 4.4 cd A^{-1} at 16.25 V, and 1.1 lm W^{-1} at 8.25 V, respectively, and the turn-on voltage is 4.25 V. After the ITO cathode is modified with Au NPs (120 min), the maximum brightness of iPLEDs/Au NPs is more than 15000 cd m^{-2} at 14.25 V, showing a 1.5-fold enhancement compared with iPLEDs. The LE of iPLEDs/Au NPs is 10.5 cd A^{-1}, which is observed at 14 V and 1.4-fold improvement of that in iPLEDs. The power efficiency is 2.6 lm W^{-1} at 12.75 V which is 1.4-fold enhancement compare with iPLEDs, and the turn-on voltage is 3.75 V. When the electrostatic adsorption time lasted more than 120 min, the brightness and efficiency decreased quickly with an obvious leakage current of current density vs applied voltage curves, which is due to the nanoparticles aggregate at the high Au NPs coverage density. With the same emissive layer, the optimized device performance of cPLEDs (ITO/PEDOT:PSS(35 nm)/P-PPV(80 nm)/CsF(1.5 nm)/Al(120 nm)) is about 10000 cd m^{-2} brightness at 9.25 V and the 12.3 cd A^{-1} LE at 4.5 V with the turn-on voltage at 2.75 V (see Figure S6 in the Supporting Information). It indicates that the brightness and LE in iPLEDs/Au NPs can achieve similar level compared with cPLEDs, and especially it can obtain the higher brightness and the better stability than cPLEDs.

Table 1. Device Performance of iPLEDs

Au NP adsorption time (min)	maximum brightness ($\times 10^3$ cd m^{-2})	maximum luminous efficiency (cd A^{-1})	maximum power efficiency (lm W^{-1})	V_{on}[a] (V)
0	5.9	4.4 ± 0.1	1.1 ± 0.1	4.25
90	13	5.9 ± 0.2	1.3 ± 0.3	4.00
120	15	10.5 ± 0.3	2.6 ± 0.2	3.75
150	7.8	5.6 ± 0.1	1.5 ± 0.2	4.00

[a]The turn-on voltage at which brightness reach 1 cd m^{-2}

To the best of our knowledge, it is one of the best results in which brightness and efficiency are enhanced synchronously when coupling with Au NPs. As the literatures reported before, most of the results only achieve 40−60% enhancement. Kim and Tang have reported ∼1.2-fold performance enhancements in different types of metal NPs and devices structures, which originates from optic/electric dual function.[15,22] They have verified that NP-induced electric effect and light scattering enhancement can improve devices performance effectively. LSPR is an effective method for fluorescence enhancement. However, the limited working distance (1−10 nm) based on near-field effect makes it difficult to apply in EL devices.[13,14,17] As displayed below, we have shown by theoretical simulation and experimental that the excellent improvement of device performance in this work is mainly attributed to electrode quenching control. It profits from the effective coupling between LSPR field and exciton formation area.

The thickness of ZnO layer is one of the key factors to improving performance. Experimentally, the best performance is obtained at ZnO thickness of 23 ± 2 nm as shown above, which just covers Au NPs with 20 nm diameter (cross-section SEM as shown in Figure S3c, d in the Supporting Information). The devices performances of iPLEDs/Au NPs with the ZnO thickness of 40 nm are presented in Figure S7 and Table S1 in the Supporting Information as a comparison. In this case, the enhancement effect nearly disappear in total that only 18 and 22% enhancement in brightness and luminous efficiency has been obtained, respectively. Assuming Au NPs are excited by the fluorescence of P-PPV. The LSPR field induced by Au NPs is simulated by finite-different time-domain (FDTD) under devices environment (the thickness and dielectric constant for each layer) with the profile of LSPR intensity at axis line (x = 0) (Figure 2a). The intensity of LSPR field decreases very

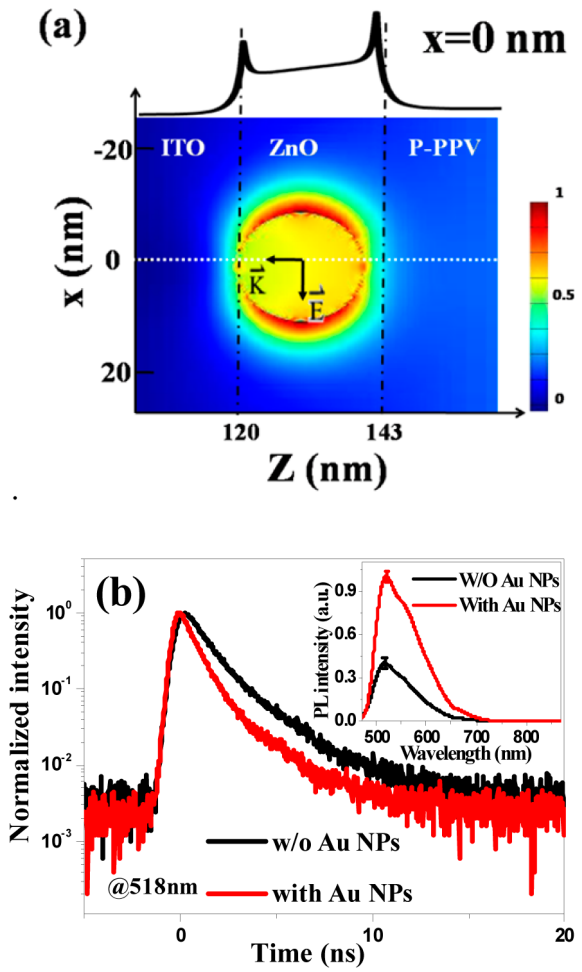

Figure 2. (a) Theoretical electric field profile in the ITO/Au NPs:ZnO/P-PPV structure by FDTD. (b) Time-resolved PL spectra detected at the wavelength of 518 nm excited by a 405 nm laser source. Inset: PL spectra of P-PPV layer with and without Au NPs. The data represent average values and standard deviations calculated from 10 devices. Structure: ITO/PDDA/Au NPs(120 min)/ZnO(23 ± 2 nm)/P-PPV(80 nm).

quickly as a function of distance, which is nearly disappeared after 10 nm. Thus, the thickness of ZnO buffer layer should be as thin as possible in order to put more emissive layer into the scope of Au NPs LSPR field. This is why the thickness of ZnO 23 ± 2 nm shows the best performance, and the thickness of ZnO 40 nm is too thick where LSPR field is out of emissive layer. The performance difference between different ZnO thickness supplies a direct evidence of near-field in device improvement.

The time-resolved PL spectra and steady PL measurements provide the direct evidence of lifetime decrease and fluorescence enhancement of P-PPV in the presence of Au NPs. The time-resolved PL spectra of P-PPV layer on ZnO film in Figure 2b shows that the exciton lifetime is 1.53 ns without Au NPs, and decreases to 1.20 ns with Au NPs (exciton lifetime calculated in the Supporting Information). The corresponding PL intensity is enhanced comparing with that without Au NPs (inset Figure 2b), which indicates that the decreased lifetime by Au NPs is from the increase in radiative velocity. In EL, the light emission process is similar to that in PL, where the decreased exciton lifetime and the increased radiative velocity are positive for effective EL emission, especially electrode quenching control.

The excitons distribution is different between PL and EL process in emissive layer. In PL process exciton can form in the whole light path. In EL process; however, the exciton is formed from electron/hole recombination, which depends on the corresponding energy level and electron/hole mobility of each layer. In this work, P-PPV is a p-type semiconducting polymer; it has electron injection barrier of ~1.5 eV compare with ZnO cathode without Au NPs, but an ohmic contact with the evaporated MoO_3/Al anode (Figure 1a). Because of the mismatch energy level and the unbalanced charge transport, the excitons come from hole/electron recombination that is mainly formed near the ZnO/P-PPV interface. As shown in Figure 3a, b and the blue line in Figure 3c, d, the excitons distribution shows maximum at interface and decreases quickly as a function of active layer thickness.[28] The damping curve is consistent with distance dependence of LSPR field (profile at $x = 0$ in Figure 2a, dash line in Figure 3d), which indicates an effective emission enhancement by LSPR. The excitons formed in emissive layer can be divided into two parts: emit photons or be quenched[29] (green and black spheres in Figure 3a, b). The excitons diffuse to electrode and can be quenched by electrode, where the electrode quenching would also a damping curve decreased from electrode interface to active layer. Thus, the light emitting profile (distribution of emitting photons) is shown as the red line in Figure 3c.[25] In the presence of Au NPs, part of originally electrode-quenched excitons can transfer to emit, because of the decreased excitons lifetime can limit the diffusion process. It can induce the shift of light emission profile (from the red dash line to the red full line in Figure 3d). The evolution of EL spectral shape gives experimental evidence for the light emission profile shift. Figure 3e shows the normalized EL spectra of iPLEDs with and without Au NPs operating at 10.0 V.[30] The relative intensity of 0−0 peak increases in the presence of Au NPs, which indicates the new light emission profile lowers the effect of reabsorption. The reabsorption comes from the overlap between absorption and EL emission of P-PPV (see Figure S8 in the Supporting Information), where the decreasing of reabsorption corresponds to the shorten of light path.[25] It indicates that the light emitting profile shift to ZnO electrode and achieve more efficient out-coupling.[25,26]

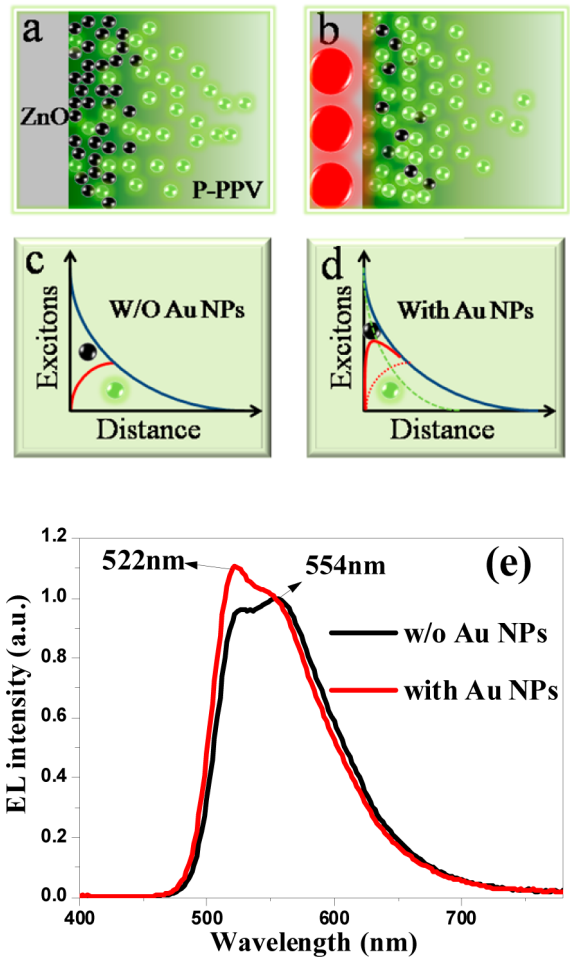

Figure 3. (a−d) Schematic diagram of excitons and emission distribution variation with and without Au NPs. Black and green sphere represent quenched excitons and emit photons, respectively. Blue line: Excitons distribution near cathode. Green line: The intensity of LSPR field from Au NPs. Red line: Light emitting profile in emissive layer. (e) Normalized EL intensity vs wavelength with and without Au NPs at 10 V.

The absolute intensity of EL spectra also has been enhanced after the modification of Au NPs at 10 V (see Figure S9 in the Supporting Information), which corresponds to part of efficiency enhancement.[16] In general, the cathode modification of Au NPs effectively decreases the excitons lifetime, which restrain the electrode quenching and transfer the quenched excitons to emit. It causes the substantial enhancement of excitons utilization and electric-photonic transformation.

The role of Au NPs in formation of "total" excitons (emissive excitons + quenched excitons) is determined by electrical parameters, because the optical detecting can only record the emissive parts.[27] The current density is increased and turn-on voltage is decreased in the presence of Au NPs, especially the combination cathodes of Au NPs/ZnO layer by interfacial modification decreases the work function of ZnO from 4.6 to 4.4 eV, which is in accordance with the work function of Au NPs mentioned above and would all play positive role for more "total" excitons formation. But 0.5 V decrease of turn-on voltage and 0.2 eV decrease of work function (1.5 eV electron injection barrier) are too small to increase "total" excitons obviously; and the improvement of devices performance mainly comes from the quenched excitons transferring to emit.

In conclusion, Au NPs are introduced to modify ITO cathode in inverted PLEDs and obtained 1.5-fold enhancement brightness and 1.4-fold enhancement luminous efficiency of the control device, which is one of the best results in Au NP-based devices performance enhancements. Both the experimental and theoretical results show it is mainly originated from effective overlapping between LSPR field and excitons quenching region at ZnO/P-PPV interface, which makes full use of electrode-quenched excitons and increases excitons efficiency. The unbalanced hole/electron injection/transportation is the basis of this type of enhancement, which is common in organic semiconducting polymers and molecules. Thus, we believe this is of great significance of plasmon applied in organic optoelectronics and the results promise Au NP-modified ITO cathode for using in the development of high-performance organic optoelectronic devices.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, the synthesis and characterizations of Au NPs, the fabrication of the electrostatic self-assembled layer of Au NPs, the AFM of the ZnO thin film, SEM images of electrostatic adsorption Au NPs on the ITO, cross-section SEM of structure ITO/(Au NPs)/ZnO, photoluminescence spectra of P-PPV film, characteristics of power efficiency vs current density curves as a function of different electrostatic adsorption time of Au NPs in iPLEDs, the effect of PDDA to the devices performance, device performance of cPLEDs, device performance of iPLEDs (the thickness of ZnO 40 nm), exciton lifetime calculatations, absorption spectrum and electroluminescence spectrum of P-PPV film, and iPLEDs of EL intensity at 10 V. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(28) The role of Au NPs in excitons distribution is characterized by the work function change of ZnO surface by Kelvin probe measurement, which is decreased from 4.6 to 4.4 eV after Au NPs. For a 0.2 eV decrease in work function would make a minor contribution to reduce electron injection barrier (1.5 eV), the excitons distribution with/without Au NPs are regarded as the same.

(29) To hint the exciton fortune clearly and simply, only electrode quenching is considered in this scheme without the classic nonradiative transition.

(30) In the ideal situation, the EL spectral shape should be compared with the same voltage and current density. However, the $I-V$ curve with and without Au NPs is not coincide with each other as shown in Figure 1b, thus it is impossible to keep the same voltage and current density coinstantaneously. For the EL spectra for one device (iPLEDs or iPLEDs/Au NPs) at different voltage and current density is similar in our device system, the change of EL spectra is compared between devices with and without Au NPs at the same voltage.