Improving the efficiency and reducing efficiency roll-off in quantum dot light emitting devices by utilizing plasmonic Au nanoparticles†

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Studies on quantum dot light emitting devices (QD-LEDs) show that the lifetime of a QD exciton is modified by localized surface plasmon resonant (LSPR) coupling of Au nanoparticles (NPs). The efficiency roll-off of the device containing Au NPs was reduced by 15%. A significant enhancement of 116% for both luminance and current efficiency for the Au NP containing device was achieved under a high current density of 300 mA cm⁻². We evaluate that it takes about 10 ns for each QD to be injected by only one electron–hole from the electrodes, which is about the same length of time as the lifetime of a QD, ~10 ns. This result indicates that the enhanced radiative rate of QD emitters will decrease the concentration of excitons in the emission layer and reduce the nonradiative recombination caused by QD charging. Present findings demonstrate that the excellent performance of the devices is principally a result of LSPR coupling between Au NPs and QD emitters, which shortens the lifetime of the QD emitters and suppresses the Auger recombination in the QD-LEDs.

1 Introduction

Semiconductor quantum dots (QDs) have been extensively investigated for their potential applications in flat panel displays and solid-state lighting sources, due to their unique optoelectronic properties and high emission quantum yield, which are strongly dependent on their size and composition.¹⁻⁹ Moreover, semiconductor QDs can be prepared as stable colloidal dispersions in common solvents enabling a solution process, a standard scalable process that has been widely used in the development of a range of optoelectronic devices, the most notable for the present discussion being hybrid semiconductor QD light-emitting devices (QD-LEDs). Normal nanoparticle hybrid QD-LEDs consist of a thin QD layer or monolayer sandwiched between two or more organic/inorganic layers. Indium tin oxide (ITO) coated glass is usually used as a transparent conductive substrate, and Al, Ca, or Mg acts as a top electrode.¹⁰⁻¹³ To date, the efficiencies of QD-LEDs, especially for deep blue QD-LEDs, remain lower than those of organic light emitting devices (OLEDs). QD charging can lead to QD luminescence quenching via the nonradiative Auger recombination mechanism, which may be the dominant process limiting the efficiency of QD-LEDs.¹⁴ Auger recombination requires the presence of an exciton and an unpaired carrier (electron or hole) at a QD site, which can arise when the charge-carrier concentration is particularly high, especially when the concentration of one charge-carrier type is higher than that of the other charge-carrier type at the QD emission layer in a QD-LED. During Auger recombination, the energy released from the exciton recombination promotes an unpaired carrier to a higher energy level, from which it can thermally relax to its ground state.¹⁵ The probability of Auger recombination becomes larger as the current density increases, which leads to the QD-LEDs suffering from a dramatic decrease in efficiency at high current density, a behavior referred to as efficiency roll-off. Auger recombination occurs on the 100 ps time scale,¹⁶ much faster than the radiative recombination lifetime of QDs, which is on a time scale of the order of 10 ns,¹⁶,¹⁷ resulting in a rapid quenching of QD luminescence. In response to these concerns, we can suppress the Auger recombination or reduce the efficiency roll-off by two methods: (1) balancing the carrier injection in the devices, and (2) shortening the lifetime of the excitons in the QD emitting layer. We focus on the latter method to study the effect of the exciton lifetime on the device performance.

Thin metal films and nanostructures exhibit remarkable optical properties due to the plasmon modes they support. Au nanoparticles (NPs) have generated considerable interest in recent years due to their unique optical properties which are clearly different from those of the bulk.¹⁸ One of these properties is localized surface plasmon resonance (LSPR), which strongly affects the kinetic characteristics of nearby molecules.¹⁹ Compared with the approaches to fabricate
plasmonic-enhanced photovoltaic devices by nanoscale lithographic patterning technologies, the introduction of solution processable metallic NPs into the devices is an attractive way to generate the plasmonic effect in devices, and is more suitable for large-area and scalable fabrication. Au NPs induce a strong enhancement of the local electromagnetic pressure below 4 nm. This way to generate the plasmonic excited metallic NPs into the devices is an attractive solution processable method.

When a fluorescent emitter (e.g. QDs, dye) is placed within the proper range of the enhanced local electric field intensity, plasmonic interaction takes place, which can enhance the radiative decay rates of the fluorescent species.

In this study, Au NPs are introduced into QD-LEDs and the effect of LSPR triggered by the Au NPs on the device characteristics is theoretically and experimentally explored. The lifetime of the QD sample emission band matching the LSPR frequency is shortened, and the overall device performance is enhanced. We highlight the role of Au NPs and ascribe this enhancement to the suppression of Auger recombination of the QDs by the LSPR induced by the Au NPs.

2 Experimental

The Au NPs were chemically synthesized according to ref. 31, and were predominantly spherical with a diameter of \( \sim 10 \) nm. QD-LEDs containing the \( \sim 10 \) nm-diameter Au NPs were fabricated on glass substrates coated with ITO. The substrates were carefully cleaned by scrubbing and sonication. In order to achieve a trade-off between the strength of LSPR and the transparency of the substrate, a moderate density of Au NPs on the substrates was utilized for device fabrication. The Au NP layer was first deposited by spin-coating Au NPs on the substrate at 2000 rpm from a toluene solution (the optical density (OD) of the Au NPs solution was 20 at wavelength of 540 nm), and dried at 350 °C in a glove box (MBRAUN) for 30 min. Then a 5 nm thick hole-injection layer (HIL) of MoO\(_3\) was deposited by thermal evaporation at a deposition rate of 0.02 nm s\(^{-1}\) at a pressure below 4 \( \times 10^{-6} \) Torr. Subsequently the hole-transport layer (HTL), a poly-TPD layer, was spin-coated onto the HIL at 2500 rpm from a 0.5 wt% chlorobenzene solution and dried at 100 °C in a glove box (MBRAUN) for 30 min to give a high quality, homogeneous layer of approximately 20 nm. The QD layer was then deposited onto the HTL by spin-coating at a speed of 1200 rpm from toluene solutions of QDs (with emission peaks at 535 and 624 nm for the green and red QDs, respectively, and the QD was \( \sim 3 \) at the first excitonic peak), and the thickness of QD layer was \( \sim 3 \) monolayers (MLs). CdSe/CdS/ZnS QDs were synthesized following the procedure in ref. 32, and the details of the synthetic process and transmission electron microscopy (TEM) images (Fig. S1†) are shown in the ESL†. Following the deposition of the QD layer, the electron transport layer (ETL), 45 nm TPBI, was deposited by thermal evaporation at a pressure below 4 \( \times 10^{-6} \) Torr. The electron injection layer (EIL), LiF (1 nm), and the Al cathode (200 nm) were also deposited by thermal evaporation under the same conditions. The layer thickness and the deposition rate of the materials were monitored in situ using an oscillating quartz thickness monitor, and the deposition rates of TPBi and LiF were controlled to about 0.2 nm s\(^{-1}\) and 0.01 nm s\(^{-1}\), respectively. The deposition rate of metal Al film was controlled to about 0.5–1 nm s\(^{-1}\). For comparison, devices with the same structure but without Au NPs were also fabricated for green and red QDs. The current–voltage–luminance characteristics and electroluminescence (EL) spectra were measured with a programmable Keithley model 2400 power supply and a Photo-research PR655 spectrometer in air at room temperature. For all devices, no external package or encapsulation was applied after device fabrication. For the time-resolved PL measurements, the samples were fabricated on silicon glass substrates and all the films were fabricated using the same technique described above.

Device series for EL measurement:

- Device a: ITO/MoO\(_3\) (5 nm)/poly-TPD (20 nm)/green QD (\( \sim 3 \) MLs)/TPBi (45 nm)/LiF (1 nm)/Al (200 nm)
- Device b: ITO/Au NPs/MoO\(_3\) (5 nm)/poly-TPD (20 nm)/green QD (\( \sim 3 \) MLs)/TPBi (45 nm)/LiF (1 nm)/Al (200 nm)
- Device A: ITO/MoO\(_3\) (5 nm)/poly-TPD (20 nm)/red QD (\( \sim 3 \) MLs)/TPBi (45 nm)/LiF (1 nm)/Al (200 nm)
- Device B: ITO/Au NPs/MoO\(_3\) (5 nm)/poly-TPD (20 nm)/red QD (\( \sim 3 \) MLs)/TPBi (45 nm)/LiF (1 nm)/Al (200 nm)

Sample series for PL measurement:

- S-a: silicon substrate/green QD (\( \sim 3 \) MLs)
- S-b: silicon substrate/MoO\(_3\) (5 nm)/poly-TPD (\( \sim 20 \) nm)/green QD (\( \sim 3 \) MLs)
- S-c: silicon substrate/Au NPs/MoO\(_3\) (5 nm)/poly-TPD (\( \sim 20 \) nm)/green QD (\( \sim 3 \) MLs)
- S-A: silicon substrate/red QD (\( \sim 3 \) MLs)
- S-B: silicon substrate/MoO\(_3\) (5 nm)/poly-TPD (\( \sim 20 \) nm)/red QD (\( \sim 3 \) MLs)
- S-C: silicon substrate/Au NPs/MoO\(_3\) (5 nm)/poly-TPD (\( \sim 20 \) nm)/red QD (\( \sim 3 \) MLs)

Time-resolved photoluminescence (TRPL) measurements were carried out with an Edinburgh Instruments FL920 Spectrometer. The dynamic signal was collected at 535 and 624 nm for the green and red QDs, respectively, utilizing a 485 nm pulsed laser as an excitation source. The morphology of theAu NP films was characterized with a scanning electron microscope (SEM, Hitachi S4800). The transmission electron microscopy (TEM) images were recorded on a Philips TECNAI G2, operated at an accelerating voltage of 200 kV. The steady state photoluminescence (PL) was measured with a Hitachi F-4500 spectrophotometer.

3 Results and discussion

Fig. 1a shows the absorption of the Au NPs on the ITO substrate before and after the heating process. We can see that the absorption peak (\( \sim 540 \) nm) of the Au NPs changes little after undergoing the heating process, which is in agreement with the report by S. Link et al., that the localized surface plasmon energy of Au NPs is not sensitive to their sizes. The supplementary information shows the SEM images of the Au NP containing ITO substrates before (Fig. S2a†) and after heating (Fig. S2b†).
Separate Au nanoparticles with lower surface coverage are observed, and the Au NPs are hardly changed by the heating process. Fig. S1c† shows the SEM image of the bare ITO-coated glass substrate. For the investigation of the LSPR effect triggered by Au NPs on the QD-LEDs, two QD samples with emission peaks at 535 nm (green QDs, emission band matching the LSPR frequency) and 626 nm (red QDs, emission band mismatched with the LSPR frequency) were chosen. The PL and absorption spectra of the two QDs are shown in Fig. 1b.

Firstly, we modelled the distribution of the field intensity at the LSPR wavelength of 540 nm by finite difference time domain (FDTD) from Lumerical. All the dielectric constants are taken from the material database of the software. The transverse magnetic (TM) distributions around the Au NP were modelled for different distances between the centers of two NPs (see Fig. S3a–g†), because only TM illumination can induce LSPR. The electric field is located in close proximity to the Au NPs when the distance between the centers of two Au NPs is 10 nm. But the electric field is spread further away from the Au NPs as the distance between the Au NPs is increased. We find that almost the same electric field distribution is obtained for distances of 35 and 40 nm. Considering the optical characteristics (transmittance and reflectance) of the ITO substrates containing Au NPs, we chose a moderate concentration for the Au NPs solution (OD ∼20 at a wavelength of 540 nm) to deposit the Au NPs layer. As depicted in Fig. S2a,† the distance between the Au NPs is ∼33 nm. Fig. 2 shows the TM distribution. Here, z is defined as the light incident direction, and x is the polarization direction. The maximum field enhancement occurs parallel to both the polarization of the electric field and to the Au NPs layer. The light intensity around Au NPs with a particle size of 10 nm is enhanced more than 29-fold in comparison with the incident light. Although the near-field effect exponentially decreases with increasing distance from the Au NPs to the active layer, 14 the light intensity enhancement by the Au NPs is not less than 5-fold up to more than 20 nm away from the ITO surface (at z = 0). So a total thickness of ∼25 nm for the hole injection and transport layers was chosen for use as the spacer between the Au NPs and the QD layer (considering the roughness of the ITO substrates containing Au NPs, the actual distance between Au NPs and the QDs will be less than 25 nm).

The electric field distribution for transverse electric (TE) was also calculated and the data is shown in the ESI (Fig. S4†); the introduction of Au NPs has no influence on the electric field distribution of TE. In addition, the electric field distributions of TE and TM polarization for the sample without Au NPs were also modeled (Fig. S5a and b†) to further illustrate the effect of the Au NPs on the electric field distributions. As can be seen, the phenomenon of electric field enhancement disappeared for the sample without Au NPs.

In order to further examine the influence of LSPR on the radiative decay of excitons in QDs due to the presence of Au NPs, the TRPL spectra of the corresponding samples are presented in Fig. 3, according to the method reported in the literature. 25 In terms of the PL decay profiles of the QDs, when the green QDs are deposited on the poly-TPD film, the lifetime (τ_{exciton}) of the QD excitons is shortened from 6.06 ns to 3.78 ns, which is due to the charge separation from QD to poly-TPD as reported by our group previously. 26 The τ_{exciton} is further decreased to 2.49 ns with the introduction of the Au NPs, which is due to the LSPR induced by the Au NPs. The red QDs on the poly-TPD film show the same decrease in τ_{exciton} from 8.49 ns to 5.66 ns due to the charge separation as shown in Fig. 3b. However, no shortening in the red QD lifetime was observed.

![Fig. 1](image1.png) (a) The absorption spectra of the Au NPs before and after the heating process, and (b) the PL spectra of the green and red QDs excited at 485 nm.

![Fig. 2](image2.png) Simulated electric field profile of transverse magnetic (TM) illumination of a device with Au NPs at the wavelength 540 nm.
temperature $T$ and electric field $F$ dependent mobility, and $F(x)$ is the electric field in the OLED. Considering the similarity between OLEDs and QD-LEDs, except for the QD emission layer, it is reasonable to evaluate the current density for the QD-LED using this equation. In order to estimate the number of electrons injected into one QD per nanosecond, we consider the parameters in eqn (1) that are constant in our calculation. For simplicity of calculation we assume that the charge carriers are balanced. The electric field is about $10^5$ V cm$^{-1}$, a value often used in OLEDs,$^{48}$ and $\mu(F,T)$ is about $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. We find that the rate of electron–hole injection into the emission layer is nearly $10^{10}$ m$^{-2}$ ns$^{-1}$ under the current density of 100 mA cm$^{-2}$. In our QD-LED, the diameters of the QDs are about 4 and 7 nm, and consequently the QD area density in the emission area is about $10^{11}$ mm$^{-2}$. Thus, it perhaps takes about 10 ns for each QD to be injected by one electron–hole. It is valuable to note that the radiative lifetime ($\sim 12.3$ ns) of the QD in our device is of the same order as the time for an electron to be injected into the QD from the cathode. In addition, the current density required to excite every QD can also be calculated from eqn (2):$^{49}$

$$J_s = [M]qd/\tau_{\text{exciton}}$$

where $[M]$ is the total concentration of QDs, $q$ is the electronic charge, $d$ is the thickness of the exciton formation zone, and $\tau_{\text{exciton}}$ is QD lifetime. In our device, the $J_s$ is about $10^3$ mA cm$^{-2}$. This result also demonstrates the validity of the rate of electron–hole injection into the emission layer calculated above. As we know, a prerequisite for Auger recombination is one or more additional charges present in the QD core, i.e. QD charging. The introduction of Au NPs into the QD-LED shortens the radiative lifetime of the QDs to 2.49 ns, which must reduce the probability of QD charging. In other words, the Auger recombination must be suppressed by enhancing the radiative rate of the QD emitters in our QD-LED containing Au NPs.

Fig. 4a shows the current density–luminance characteristics of devices a and b. As can be seen, the luminance of device b is higher than that of device a. The luminance is 888 cd m$^{-2}$ and 1227 cd m$^{-2}$ under a current density of 100 mA cm$^{-2}$ for devices a and b, respectively. Under a current density of 300 mA cm$^{-2}$, the luminance reaches 1154 cd m$^{-2}$ and 2490 cd m$^{-2}$ for devices a and b, respectively. With the introduction of the Au NPs, enhancements of 38% and 116% were obtained under 100 and 300 mA cm$^{-2}$, respectively. The inset in Fig. 4a shows the EL spectra of the devices. The two devices have the same EL spectra, which indicates that the introduction of Au NPs does not change the emission features of device b, and the recombination range is still in the QD layer. Fig. 4b shows the current density–efficiency curves of devices a and b. Under the same operating current density, a higher efficiency is achieved for the Au NPs containing device. The current efficiency is 0.88 cd A$^{-1}$ and 1.24 cd A$^{-1}$ under the current density of 100 mA cm$^{-2}$ for device a and b, respectively. Under a current density of 300 mA cm$^{-2}$, the efficiency is 0.40 cd A$^{-1}$ and 0.86 cd A$^{-1}$ for device a and b, respectively. The corresponding enhancement factors are 41% and 115% under the operating current densities with the introduction of Au NPs due to the mismatch between the resonance frequency of LSPR and the emission band of the red QDs. As we know, direct contact between the emitters and Au NPs can quench the excitons and result in a decrease in the emitter lifetime. Here, we can exclude this possibility in our devices by comparing the lifetimes of S-B and S-C.

As discussed above, Auger recombination occurs on the 100 ps time scale, much faster than the radiative recombination lifetime of QDs, which is on a time scale of the order of 10 ns. To date, no reports have demonstrated a decrease of the radiative recombination lifetime of QDs to the 100 ps time scale. It seems to be impossible to shorten the radiative lifetime of QDs by LSPR in order to compete with the Auger recombination process. In other words, the QD charging process is too fast to be avoided. But this is not the case in QD-LEDs. For QD-LEDs, the QD charging is limited by many factors. One is the time of the charge-carrier injection into the QD layer from the electrodes. Here, we calculated this important parameter as follows:

In an OLED, the current density of the device is described by the following equation:$^{47}$

$$J(x) = ep(x)\mu(F,T)F(x)$$

where $J(x)$ is the current density of the OLED, $e$ is the electron charge, $\sim 1.6 \times 10^{-19}$ C, $p(x)$ is the carrier density, $\mu(F,T)$ is the
of 100 mA cm$^{-2}$ and 300 mA cm$^{-2}$, respectively. The efficiency roll-off up to 100 mA cm$^{-2}$ is 54% and 39% relative to the maximum efficiency for devices a and b, respectively.

In order to further understand why the device performance is enhanced by the introduction of Au NPs, we measured the PL spectra of samples S-c and S-b, as shown in Fig. 4c. We can see that the PL intensity of the sample with Au NPs was hardly enhanced relative to that without Au NPs. For the sample S-c excited by a Xe lamp in F-4500, the exciton was formed in the QD layer directly after the excitation light irradiated the QD layer, which is different to the case of electrical excitation in device b. We know that the Auger recombination occurs on the 100 ps time scale,$^{14}$ which is too fast to be affected by the LSPR generated by the Au NPs in the case of light excitation. The inset of Fig. 4b shows the efficiency difference between devices a and b under the same current density (the difference is obtained from the efficiency of device b minus that of device a). It is valuable to note that a higher enhancement factor is achieved under higher operating current density. As mentioned above, we ascribe this enhancement to the suppression of Auger recombination due to the LSPR induced by the Au NPs, which results in a higher enhancement under higher current density. High current density leads to a high probability of QD charging or Auger recombination. Consequently, the suppression of Auger recombination is more effective under higher current density in the Au NPs device.

Fig. 5a shows the current density–luminance characteristics of devices A and B based on red QDs. As can be seen, the luminance is almost the same under all operating current densities for devices A and B. This result further demonstrates

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**Fig. 4** (a) The current density–luminance curves for the green QD devices, inset is the EL spectra of devices a and b. (b) The current density–efficiency curves for the green QD devices, inset is the difference in the efficiency of devices a and b under different current densities. (c) The PL spectra with and without Au NPs by measuring samples S-c and S-b, respectively.

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**Fig. 5** (a) The current density–luminance curves for the red QD devices, inset is the EL spectra of devices A and B. (b) The current density–efficiency curves for the red QD devices.


the effect of LSPR on the red QD device. The enhancement is not observed for device B due to the mismatch between the resonance frequency of LSPR and the emission band of the red QDs. Inset is the EL spectra for devices A and B, in which no change is observed in the optical features of device B. Fig. 5b shows the current density–efficiency curves of devices A and B. The same trend as that of the luminance is observed for the efficiency, which further proves the operation mechanism of the LSPR generated by Au NPs. The active area of each device (~4 mm²) was measured under an optical microscope to reduce the possible device-to-device error caused by small variations in the device area. All the devices were repeated to eliminate any possible run-to-run differences as a result of subtle variations in the processing conditions. Similar phenomena were observed, which indicates the validity of our results.

Fig. 6 shows the voltage–current density characteristics of the four devices. As can be seen, the devices containing Au NPs have higher current density than devices without Au NPs under the same operating voltage. We attribute this to the more efficient hole injection from the Au material. As can be seen, the work function of Au (~5.2) is higher than that of ITO (~4.7), which facilitates hole injection into the MoO3/poly-TPD layer from the Au anode. In addition, the effective thickness of the devices with Au NPs are decreased due to the roughness induced by the Au NPs on the ITO substrates, which may be another factor resulting in the increase of the current density. The current density of the red devices was a little higher than that of the corresponding green devices, which is due to the higher valence band (VB) of the red QDs than the green QDs. A higher VB will lead to a lower injection barrier between poly-TPD and the QDs, and facilitates hole injection. We note here that these devices are not optimized, and more efficient QD-LEDs are expected after optimization of the device parameters and the QD sample, for example, the thickness of the QD layer, TPBi layer and MoO3/poly-TPD layer, the distance between the QDs and Au NPs, the density of the Au NPs, etc.

4 Conclusions

In summary, we have demonstrated a plasmonic-enhanced green QD-LED by incorporating solution processable Au NPs into the device. The QD samples with emission band matched (green QD) and mismatched (red QD) with the frequency of the LSPR generated by the Au NPs were used in the QD-LEDs to investigate the effect of LSPR. No obvious effect on the optical characteristics was observed for the red QD-based device. The green QD device containing Au NPs had a higher luminance–efficiency than the device without Au NPs under a higher current density. Experimental and theoretical results show that this improvement results from the suppressed Auger recombination due to the enhanced exciton radiative rate in the active layer as a result of the LSPR-induced near-field enhancement in the active layer. Despite the fast Auger recombination process, which is on the order of 100 ps, the effect of LSPR on the device performance is obvious due to the slow charge transfer process in the case of electrical excitation. The effect of LSPR on the Auger recombination behavior almost vanishes when the sample is excited by light due to the large difference between the exciton lifetime (~10 ns) and the comparatively fast Auger recombination process (~100 ps). The method proposed here shows great potential for combining the plasmonic effect with a conventional device structure for high-performance QD-LEDs.

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Notes and references