Supplementary Material

Remarkable Photoluminescence Enhancement of $CsPbBr_3$ Perovskite Quantum Dots Assisted by Metallic Thin Films

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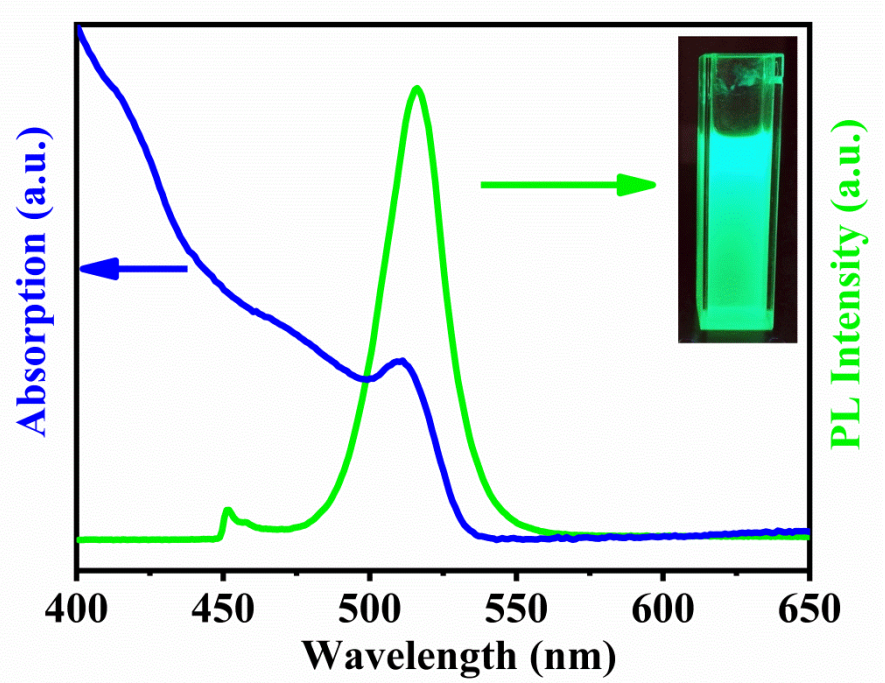

Figure S1: UV-vis absorbance (blue line) and PL (green line) spectra of $CsPbBr_3$ perovskite QDs. Inset: optical images of $CsPbBr_3$ QDs under a 365 nm UV lamp.

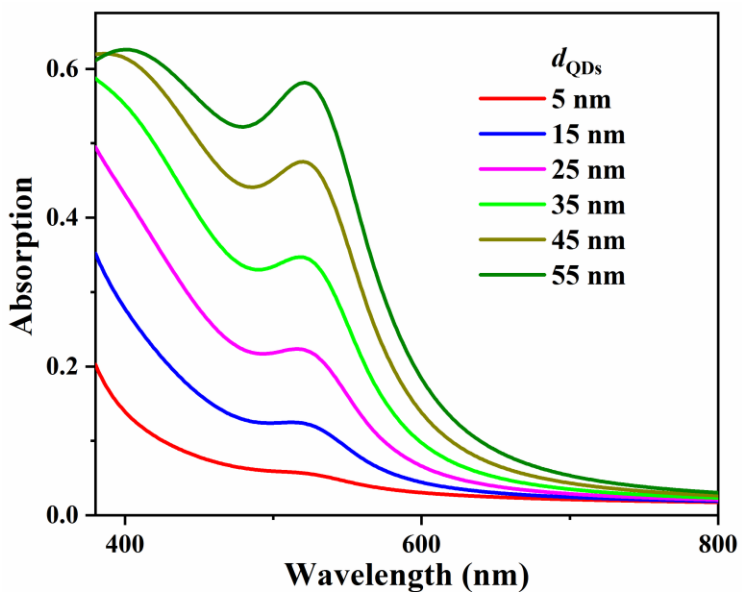

Figure S2: Calculated optical absorption spectra for six different thickness of CPB QDs thin films (d_{QDs} = 5, 15, 25, 35, 45 and 55 nm) on a 60 nm thickness Ag NP film separated by a 10 nm thick SiO_2 spacer. It is noted that there exists a critical thickness about d_{QDs} = 35 nm for the absorption enhancement effect.

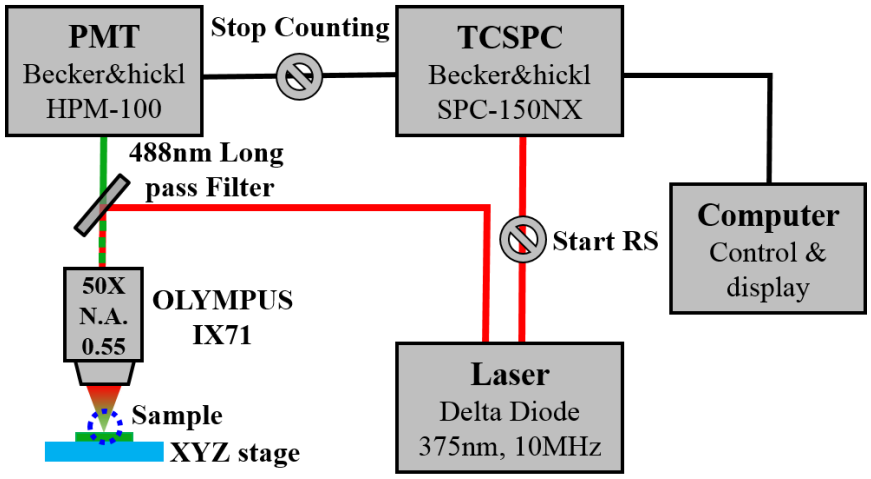

Figure S3: Experimental setup for lifetime measurements. PMT, Photomultiplier tube. TCSPC, Time-Correlated Single Photon Counting. RS, Reference Signal.

Note 1: Synthesis process of $CsPbBr_3$ QDs

The $CsPbBr_3$ quantum dots used in this experiment are prepared by ourselves, and the process is as follows. Typically, 40 mL of octadecene (ODE), 3 mL of oleic acid (OA) and 1 g of Cs_2CO_3 were in turn added into a 100 ml of three-neck flask under stirring. Subsequently, the container was degassed under argon flow at 130 ^oC for 30 min. Then the mixture solution was heated to 150 ^oC for another 45 min until all Cs_2CO_3 dissolved in OA and ODE. The solution was labeled as A. In another three neck-flask, 0.4 mmol of $PbBr_2$, 1 mL of OA, 1 mL of oleylamine (OAm) and 10 mL of ODE were in turn added into the flask under stirring and degassed under argon flow at 130 ^oC for 30 min until $PbBr_2$ dissolved in OA, OAm and ODE (Solution B). Then the temperature was raised to 160 ^oC and kept for another 10 min. Moreover, 1 mL of solution A was swiftly injected into the solution B. The reaction was terminated with an ice bath after 10 s. The as-prepared quantum dots solution was precipitated by adding 40 ml excess acetone and centrifuged at 8000 rpm for 3 min. The $CsPbBr_3$ QDs were collected and re-dispersed in 10 mL of n-hexane to form a stable QDs solution.

Note 2: The calculations of enhancement factor

To give a physical insight in the enhancement mechanisms, we theoretically estimate the enhancement factor with a semi-analytic dyadic Green's function model. Two main parts were considered, one was the normalized rate of energy dissipation on the emission wavelength of QDs and the other was the absorption enhancement at the excitation wavelength of pumped lasers. Therefore, the intensity enhancement factor can be obtained[S1,S2].

$$EF = \frac{Q}{Q_0} \cdot \frac{A}{A_0} \tag{1}$$

Firstly, we calculate the normalized rate of energy dissipation and assume a radiative dipole on top of the structure surface. The dyadic Green's function $\overleftrightarrow{\mathbf{G}}_0(\mathbf{r},\mathbf{r}_0)$ defines the electric field **E(r)** of an electric dipole **μ** located at $\mathbf{r_0=(x_0, y_0, z_0)}$ according to [S3-S5]:

$$\boldsymbol{E}(\boldsymbol{r}) = \omega^2 \mu_0 \mu_1 \overleftrightarrow{\mathbf{G}}_0(\mathbf{r},\mathbf{r}_0)\boldsymbol{\mu} \tag{2}$$

Utilizing angular spectrum representation of the dyadic Green's functions allowed us to analyze the contribution of each spatial frequency mode. For a single dipole emitter with in-plane orientation placed at a distance z_0 above a multilayer planar structure, the corresponding normalized rate of energy dissipation can be calculated using the following formulas:

$$\frac{P}{P_0}\Big|_{\parallel} = 1 + \frac{3}{4}\int_0^{\infty} \mathrm{Re}\left\{\frac{s}{s_z}\left[r^s - s_z^2 r^p\right]e^{2ik_0 z_0 s_z}\right\} ds \tag{3}$$

On the other hand, when the single dipole emitter placed with perpendicular orientation, we can get:

$$\frac{P}{P_0}\Big|_{\perp} = 1 + \frac{3}{2}\int_0^{\infty} \mathrm{Re}\left\{\frac{s^3}{s_z} r^p e^{2ik_0 z_0 s_z}\right\} ds \tag{4}$$

Then, the value of energy dissipation rate P/P_0 for the statistically averaged dipole orientation is given by:

$$\begin{aligned}\frac{P}{P_0}\Big|_{ave} &= \frac{2}{3}\frac{P}{P_0}\Big|_{\parallel} + \frac{1}{3}\frac{P}{P}\Big|_{\perp} \\ &= 1 + \frac{1}{2}\int_0^{\infty} \mathrm{Re}\left\{\frac{s}{s_z}\left[r^s - s_z^2 r^p\right] e^{2ik_0 z\, \delta_z}\right\} ds + \frac{1}{2}\int_0^{\infty} \mathrm{Re}\left\{\frac{s^3}{s_z} r^p e^{2ik\, z_0 s_{z0}}\right\} ds\end{aligned} \tag{5}$$

In equations (3)-(5), for convenience, $s = k_{\parallel}/k_0$, $s_z = \sqrt{1-s^2} = k_{\perp}/k_0$, $k_0 = \omega/c$. The reflection coefficients r^s and r^p for s- and p-polarized waves can be obtained by the transfer matrix method [S6]. The integrals are numerically evaluated by using an adaptive Gauss–Kronrod quadrature method [S7].

In addition, for an incoherently decaying quantum system with intrinsic quantum yield Q_0, the normalized spontaneous decay rate equals to[S8]

$$\frac{\Gamma}{\Gamma_0} = 1\text{-}Q_0 + Q_0 \frac{P}{P_0} \tag{6}$$

Where, $\Gamma_0 = \Gamma_r + k_{nr}$ and $\Gamma = \Gamma_r + \Gamma_m + k_{nr}$ (7)

On the other hand, $Q_0 = \dfrac{\Gamma_r}{\Gamma_r + k_{nr}}$ and $Q = \dfrac{\Gamma_r + \Gamma_m}{\Gamma_r + \Gamma_m + k_{nr}}$ (8)

Finally, combining equations (5)-(8), the radiative rate and quantum efficiency at the emission wavelength Q/Q_0 can be obtained.

Next step, we calculate the absorption enhancement factor due to the presence of the metallic layer through full-wave numerical simulations using the commercial package Lumerical FDTD Solutions, based on FDTD method. Transmission and reflection were respectively collected with power monitors behind the incident wave and the structure. Two-dimensional field profile monitors were utilized to record electromagnetic field distributions. The absorption of QDs on bare quartz substrate substrates Q_0 and on real samples Q can be obtained through numerical simulations. Finally, the absorption enhancement at the excitation wavelength A/A_0 can thus be obtained.

References

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