Supporting Information

Room-temperature Doping of Ytterbium into Efficient Near-infrared Emission $CsPbBr_{1.5}Cl_{1.5}$ Perovskite Quantum Dots

Shuangyi Zhao, [a] Yubo Zhang [b] and Zhigang Zang *[a]

[a] *Key Laboratory of Optoelectronic Technology & Systems (Minster of Education), Chongqing University, Chongqing, China*

[b] *Department of Physics, Southern University of Science and Technology, Shenzhen, China*

zangzg@cqu.edu.cn

Experimental Section

1. Materials

Cesium carbonate (Cs_2CO_3, 99.9%), lead bromide ($PbBr_2$, 99.9%) and Lead chloride ($PbCl_2$, 99.9%) were purchased from Xi'an polymer Light Technology Corp. Oleic acid (OA, >90%), Oleylamine (OAm, >90%) and Octadecene (ODE, >90%) were purchased from Adamas. Ytterbium nitrate pentahydrate ($Yb(NO_3)_3 \cdot 5H_2O$, 99.9%) was purchased from Alfa Aesar. All these reagents were used without further purification.

2. Synthesis of intrinsic $CsPbBr_3$ QDs

81.5 mg Cs_2CO_3, 4 mL ODE, and 0.5 mL OA were loaded into 100 mL three-neck flask to prepare the Cs-precursor. 138 mg $PbBr_2$ and 5 mL ODE were loaded into another 100 mL three-neck flask. The two flasks were degassed for 10 min. Then the flasks were heated to 120 °C under nitrogen flow for 1 h. After 1 h, 0.5 mL OAm and 0.5 mL OA were quickly injected into the Pb-flask at 120 °C, and then the temperature was increased to 150 °C. After 2 min, 0.8 mL Cs-precursor was injected quickly into the Pb-flask and the mixture was cooled in the ice-water bath to room temperature after 5 ~ 10 s.

3. Preparation of $PbCl_2$ anion source

55.62 mg $PbCl_2$, 10 mL ODE and 0.5 mL OA and 0.5 mL OAm were loaded into 100 mL three-neck flask to prepare the $PbCl_2$ anion source. The flask was degassed for 20 min and then heated 120 °C under nitrogen flow for 30 min. After 30 min, 1 mL OA and 1 mL OAm were added into the flask and the temperature was raised to 170 °C. After 5 min, the flask was cooled to the room-temperature and the golden yellow solution of $PbCl_2$ solution was obtained.

4. Preparation of Yb-precursor

17.97 mg $Yb(NO_3)_3 \cdot 5H_2O$ was dissolved in a mixture of methyl acetate : toluene with volume ratio of 1 : 3. The $Yb(NO_3)_3 \cdot 5H_2O$ solution was stirred for 30 min and the 0.01 mmol/mL transparent Yb-precursor solution was obtained.

5. Anion exchange of Cl^- ions and doping of Yb^{3+}ions

The 2 mL as-synthesized $CsPbBr_3$ QDs were centrifuged for 5 min at 10000 rpm and the supernatant was discarded. The pellet was resuspended in the toluene. The 1.44 mL $PbCl_2$ solution was added into the $CsPbBr_3$ QDs toluene solution and then stirred for 30 s to form the $CsPbBr_{1.5}Cl_{1.5}$ QDs.

The different amounts of Yb precursor were added into the $CsPbBr_{1.5}Cl_{1.5}$ QDs dispersion under continuous stirring for 10 min to achieve different Yb-dopant concentrations. Then the Yb doped $CsPbBr_{1.5}Cl_{1.5}$ QDs centrifuged for 5 min at 10000 rpm and the supernatant was discarded. The obtained pellet was resuspended in the toluene.

6. Characterization

The crystal phases of the samples was characterized byXRD with Cu Ka radiation (XRD-6100, SHIMADZU, Japan). The TEM was measured by an electron microscope (Libra 200 FE, Zeiss, Germany). Absorption spectrum was recorded ranging from 300 to 800 nm by a UV–vis spectrophotometer (UV-2100, SHIMADZU, Japan) under room temperature. The XPS results were performed on an Escalab 250 Xi. The

photoluminescence (PL) spectroscopy and the data of PL QY were measured by a PL system. The PL system (FLS920, Edinburgh Instruments) that was capable of measuring PL and PLQYs with an integration sphere was employed in this work. Moreover, the PL system consists of a Vis and a NIR photomultiplier, which can detect the light in the visible and NIR regions, respectively. Each sample of Yb-doped $CsPbBr_{1.5}Cl_{1.5}$ toluene solution was loaded into a clear quartz cuvette and was excited by a xenon lamp with the wavelength of 350 nm. The emission signals were collected and the corresponding emission spectra integrated area could be regarded as the photon energy of emission light (E_{em}). In addition, the scattering intensity of a blank (solvent only) (E_{bg})and the samples (E_{sa}) could be obtained from the integrated PL spectra of solvent and samples under the 350 nm excitation. The PLQY can be calculated by:

$$QY = E_{em} \ / (E_{bg} - E_{sa})$$

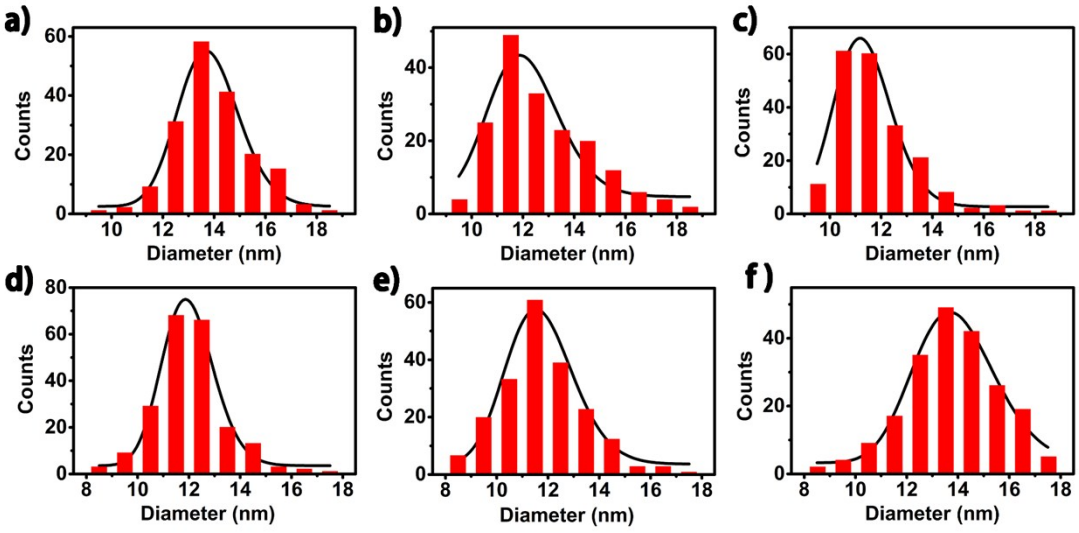
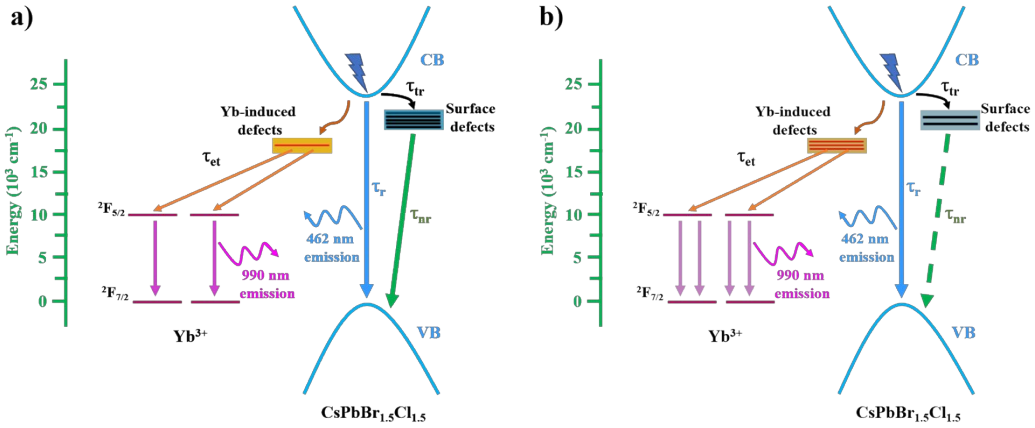


Figure S1. Size distribution of a) undoped $CsPbBr_{1.5}Cl_{1.5}$ QDs, b) 5% Yb, c) 8% Yb, d) 10% Yb, e) 20% Yb, f) 30% Yb doped $CsPbBr_{1.5}Cl_{1.5}$ QDs



Scheme 1. Schematic diagram of the energy transfer process of $CsPbBr_{1.5}Cl_{1.5}$ QDs doped with a) low amount of Yb and b) high amount of Yb.

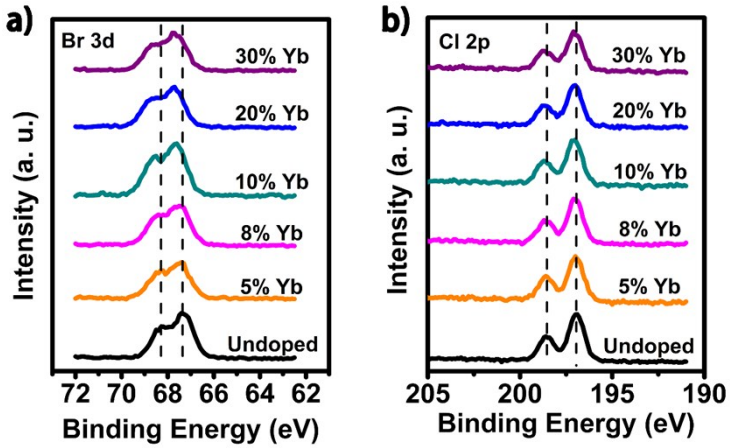


Figure S2. High-resolution X-ray photoelectron spectroscopy (XPS) spectra of a) Br 3d and b) Cl 2p for undoped and Yb-doped $CsPbBr_{1.5}Cl_{1.5}$ QDs.

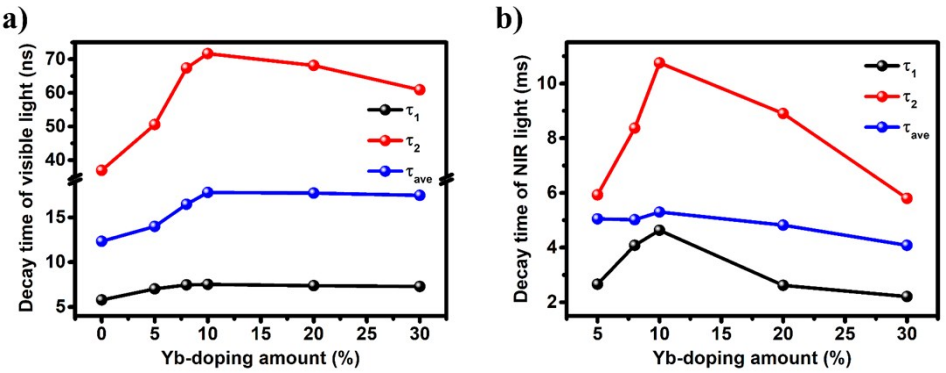


Figure S3. Dependence of a) visible PL and b) NIR PL decay lifetime, including fast decay time (τ_1), slow decay time (τ_2) and average decay time (τ_{ave}), on the Yb incorporation amount.

PL decay curves can be fitted with a bi-exponential decay function consisting of a fast decay time (τ_1) and a slow decay time (τ_2). The average decay time (τ_{ave}) can be calculated as following:

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

τ_1 is speculated to be the trap-assisted recombination, while τ_2 is speculated to be the free-charge carrier radiative recombination.[1] The increase of With the increase of Yb-doping amount, the decay time changes. The increase of decay time is attributed to the reduction of surface traps and suppression of exciton quenching.[2] Therefore, the incorporation of optimal amount of Yb^{3+} ions is proved to enhance the quality of QDs and improve their optical performance.

Table S1. Summary of visible photoluminescent decay time of Yb-doped $CsPbBr_{1.5}Cl_{1.5}$ QDs

	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_{ave} (ns)
Undoped	5.79	0.79	36.94	0.21	12.33
5% Yb	7.02	0.84	50.59	0.16	13.99
8% Yb	7.47	0.85	67.41	0.15	16.46
10% Yb	7.52	0.84	71.70	0.16	17.79
20% Yb	7.39	0.83	68.13	0.17	17.71
30% Yb	7.29	0.81	60.91	0.19	17.47

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2. H. Cho, S. H. Jeong, M. H. Park, Y. H. Kim, C. Wolf, C. L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T. W. Lee, *Science* 2015, 350, 1222.