Supporting information for

Dual-defect Passivation Role of Lithium Bromide Doping in Reducing Nonradiative Loss in $CsPbX_3$ (X = Br, I) Quantum dots

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Experimental section

Chemicals

All chemicals are purchased from Aladdin and used without purification unless otherwise noted. Cesium carbonate (Cs_2CO_3, 99.99%, metal basis), lithium carbonate (Li_2CO_3, 99.99%, metal basis), lithium bromide (LiBr, 99.99%, metal basis), lead bromide ($PbBr_2$, 99.999%, metal basis),

lead iodide (PbI_2, 99.99%, metal basis), oleic acid (OA, analytically pure, chemical reagent), oleylamine (OAm, 80–90%), 1-octadecene (ODE, >90.0%, GC), and n-hexane (GC, 98.0%, chemical reagent), hydrobromic acid (HBr), ethyl alcohol absolute (EtOH), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), deionized water.

Synthesis of LiBr as the lithium precursor

Li precursor is formed by the reaction of lithium carbonate with hydrobromic acid.

$$Li_2CO_3 + 2HBr = 2LiBr + H_2O + CO_2 \uparrow$$

Li_2CO_3 solid particles can react with HBr quickly, leaving a transparent and clear solution, which is the aqueous solution of LiBr. Precursor solutions with different concentrations were prepared by means of LiBr crystallization while adding deionized water, EtOH, DMF or DMSO.

Synthesis of Cs-OA as the Cesium precursor (Cs-Pre)

Cs-oleate was prepared according to the method described in the previous report.[1] Octadecene (20 ml ODE), oleic acid (1.25 ml OA) and 1.25 mmol Cs_2CO_3 (0.407g) were added into a 50 ml three-necked flask with magnetic stirring to make them mix adequately in a magnetic stirring heating sleeve. Subsequently, the temperature of the reaction system was kept at 120 ℃ for 1 h. Then the system temperature was increased up to 150 ℃ and kept at this temperature until the solution becomes clear and transparent. All processes were carried out under a nitrogen atmosphere.

Synthesis of $CsPbX_3$:xLi QDs with the hot-injection method

$CsPbBr_3$: xLi QDs were synthesized with the hot-injection (HI) method reported by Protesescu et al.[1] with just some modifications. 5 ml ODE were injected into a 50 ml three-necked flask, and then 0.188 mol $PbBr_2$ (0.087 g) were loaded into the flask. The flask was heated to 120 ℃ slowly with stirring via the magnetic stirring heating sleeve, and kept at this temperature for 1 h under the

N_2 atmosphere. Then 0.5 ml OA and 0.5 ml OAm were injected into the flask. When $PbBr_2$ and oleic acid react fully, lithium precursor solution is added. After the solution becomes clear and transparent again, the temperature was increased up to 160 ℃, and then 0.4 ml Cs-pre solution were injected into the system rapidly. After 10 s, the reaction mixture was cooled in an ice-water bath. The $CsPbBr_3$: xLi QDs were collected by adding 20 ml toluene and centrifuging at 5000 rpm for 10 min. The precipitated QDs were dispersed by 10 ml toluene.

$CsPbI_3$: xLi QDs were synthesized as the same as the above-mentioned process except the lead precursor.

Measurement and characterization

Ultraviolet–visible (UV–Vis) absorption spectra for colloidal solutions were collected in the 300–800 nm region. Photoluminescence (PL) was measured using a Hitachi F-7000 fluorescence spectrophotometer. Powder X-ray diffraction (XRD) data were recorded using a Rigaku D/max 2200 X-ray diffractometer with a Hi-Star 2D area detector using Cu Kα radiation (1.54 Å) at 40 kV and 30 mA. Transmission electron microscopy (TEM) studies were carried out using a JEM-2100 at 200 kV. Luminescence lifetime was test using Edinburgh FLS980 fluorescence spectrometer that using hydrogen lamp at 7.02kV and 40MHz. Photoexcited PLQY was test vie using the Integrating sphere in Edinburgh FLS1000 fluorescence spectrometer. The temperature-dependent PL spectra was test using Edinburgh FLS980 fluorescence spectrometer that using polystyrene to make samples gel. X-ray photoelectron spectroscopy (XPS) was test using the K-Alpha+ of Thermo fisher Scientific with vacuum degree of ~ 2×10^{-7}mba, the energy of mono al K α source is 1486.6ev, 6mA × 12kV.

DFT Calculation

DFT calculation were performed by the Vienna Ab-initio Simulation Package (VASP).[2,3] The effective core potential was described by the General Gradient Approximation (GGA) method. The Perdew-Burke-Ernzerhof was used to describe the exchange correlation energy. The cut-off energy was set to be 400 eV. The 3x3x4 k-point mesh is employed for density of states and

electron density difference calculations to obtain accurate electronic structure and distribution. $CsPbBr_3$ supercell (2×2×1) was constructed as the control sample based on the optimized lattice with PM-3M space group constant of 5.874Å×5.874Å×5.874Å. Compared with the control sample, a few Li ions were arranged at different positions in the Li-doped sample. Considering the actual size of the atoms in the crystal and without considering the bonding between Li^+ and other atoms, only the octahedral interstitial can be added Li^+, so the doping interstitial position of Li^+ is tentatively located in the center of octahedral interstitial.

Supporting date

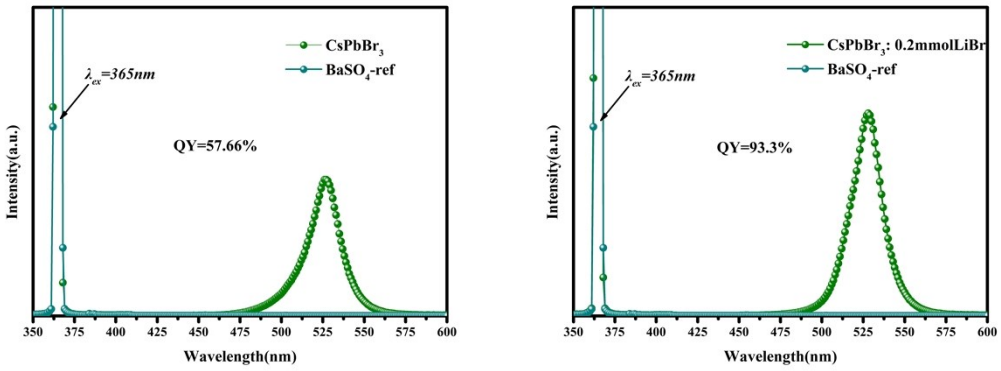

Figure S1 (a)PL spectra and internal PLQY of pure $CsPbBr_3$ excited by 365nm; (b)of pure $CsPbBr_3$: 0.2mmolLiBr.

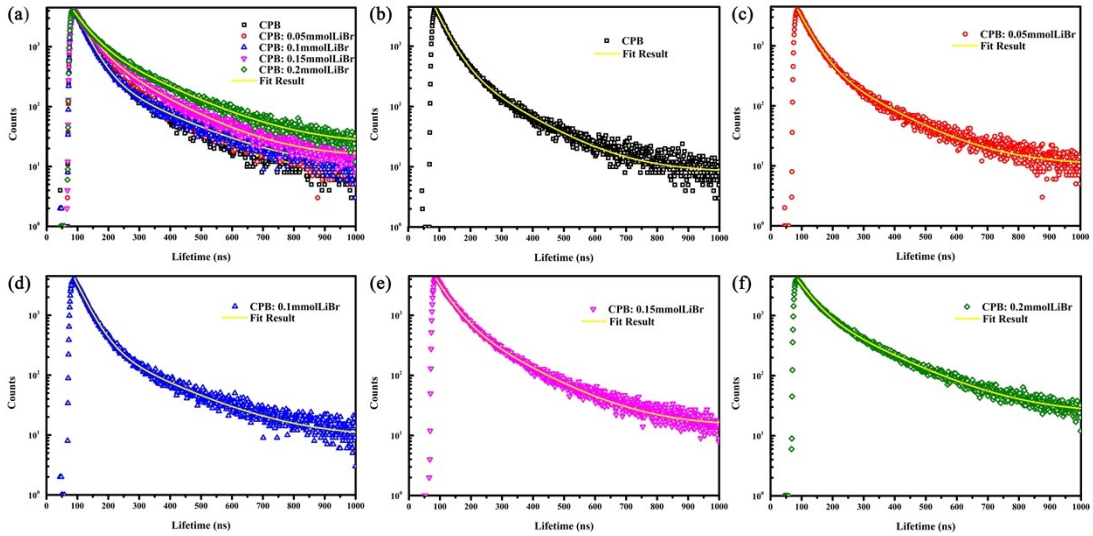

Figure S2 (a) The photoluminescence lifetime and and the corresponding fitting curve of $CsPbBr_3$ QDs with different LiBr concentrations; (b) of $CsPbBr_3$ QDs; (c) of $CsPbBr_3$: 0.05mmolLiBr QDs; (d) of $CsPbBr_3$: 0.1mmolLiBr QDs; (e) of $CsPbBr_3$: 0.15mmolLiBr QDs; (f) of $CsPbBr_3$: 0.2mmolLiBr QDs.

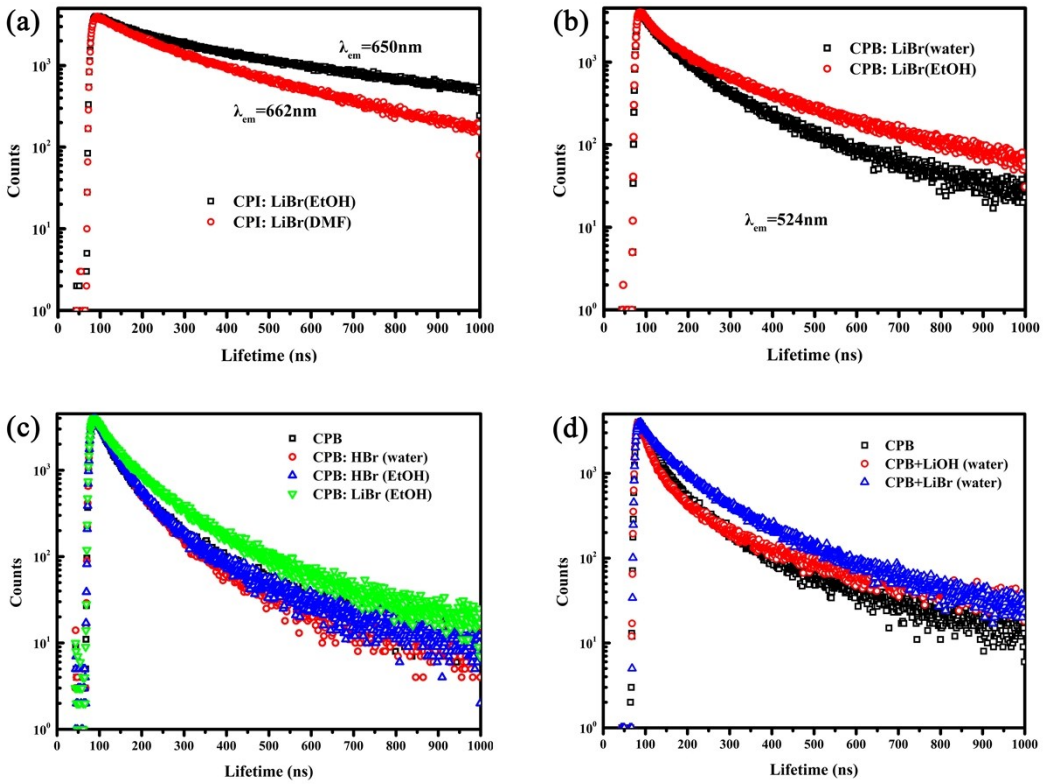

Figure S3 (a)Lifetime curves of LiBr doped CsPbI3 with different solvents; (b)Lifetime curves of LiBr doped CsPbBr3 with different solvents; (c)Lifetime curves of different Br dopants;(d) Lifetime curver of different Li dopants.

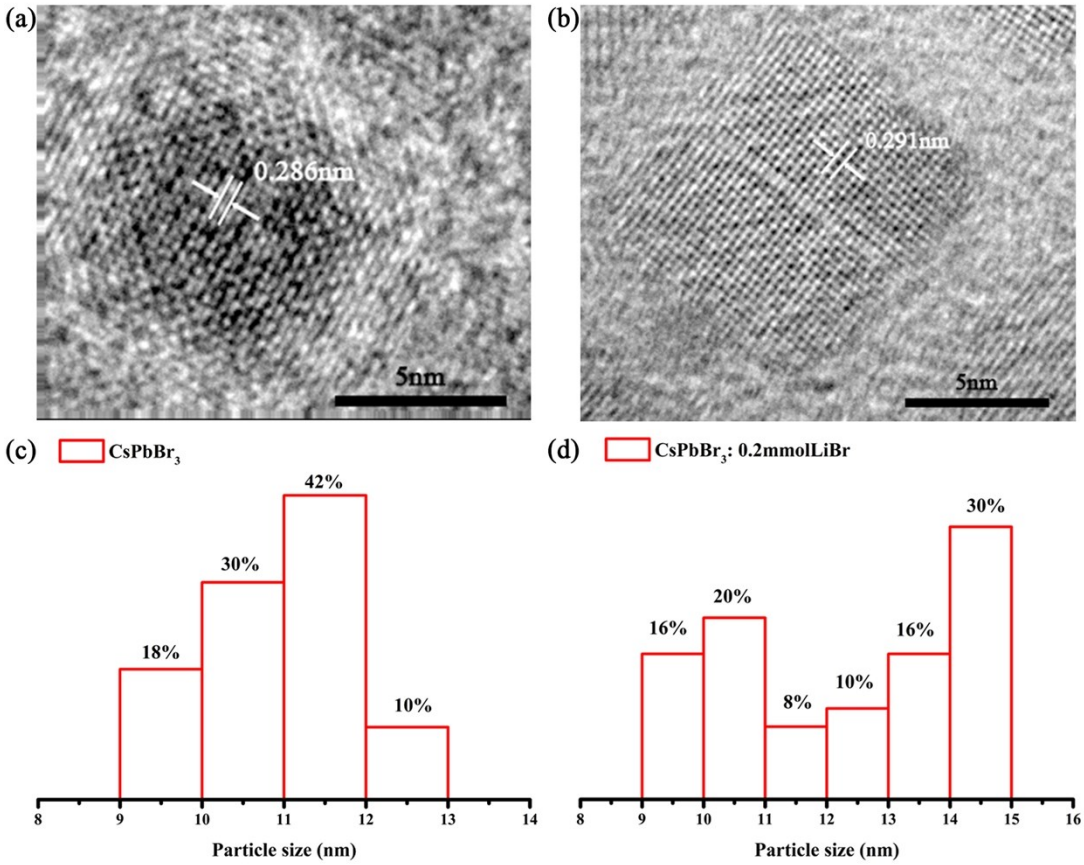

Figure S4 (a) High resolution transmission electron microscopy of $CsPbBr_3$ QDs; (b) of $CsPbBr_3$: 0.2mmolLiBr QDs; (c) Particle size distribution of CsPbBr3 QDs; (d) of $CsPbBr_3$: 0.2mmolLiBr QDs.

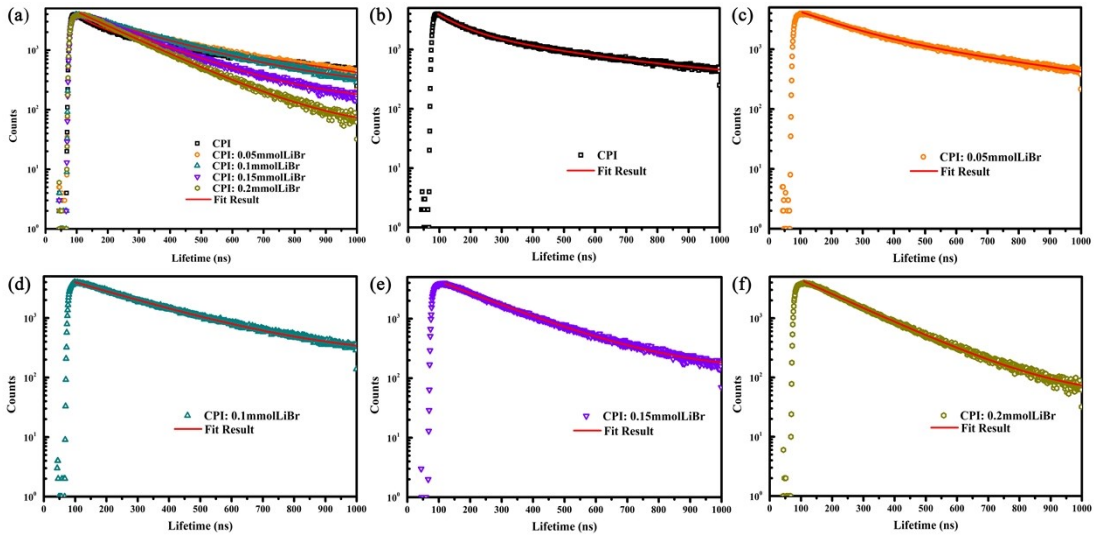

Figure S5 (a) The photoluminescence lifetime and the corresponding fitting curve of $CsPbI_3$ QDs with different LiBr concentrations; (b) of $CsPbI_3$ QDs; (c) of $CsPbI_3$: 0.05mmolLiBr QDs; (d) of $CsPbI_3$: 0.1mmolLiBr QDs; (e) of $CsPbI_3$: 0.15mmolLiBr QDs; (f)of $CsPbI_3$: 0.2mmolLiBr QDs.

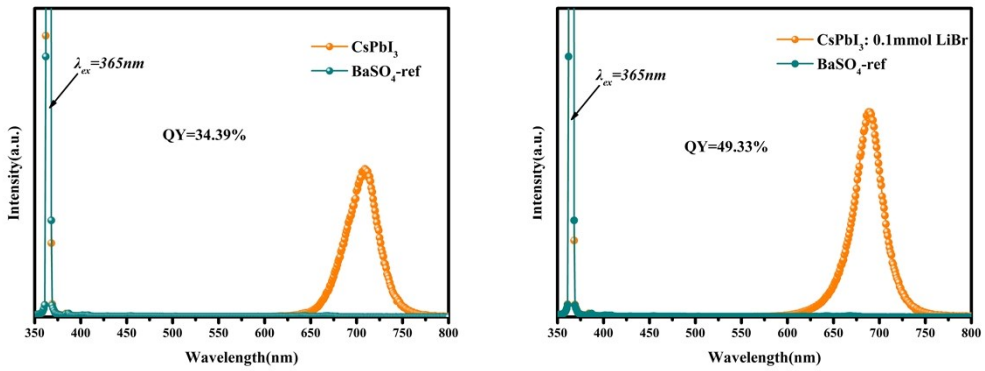

Figure S6 (a)PL spectra and internal PLQY of pure $CsPbI_3$ excited by 365nm; (b)of pure $CsPbBr_3$: 0.1mmolLiBr.

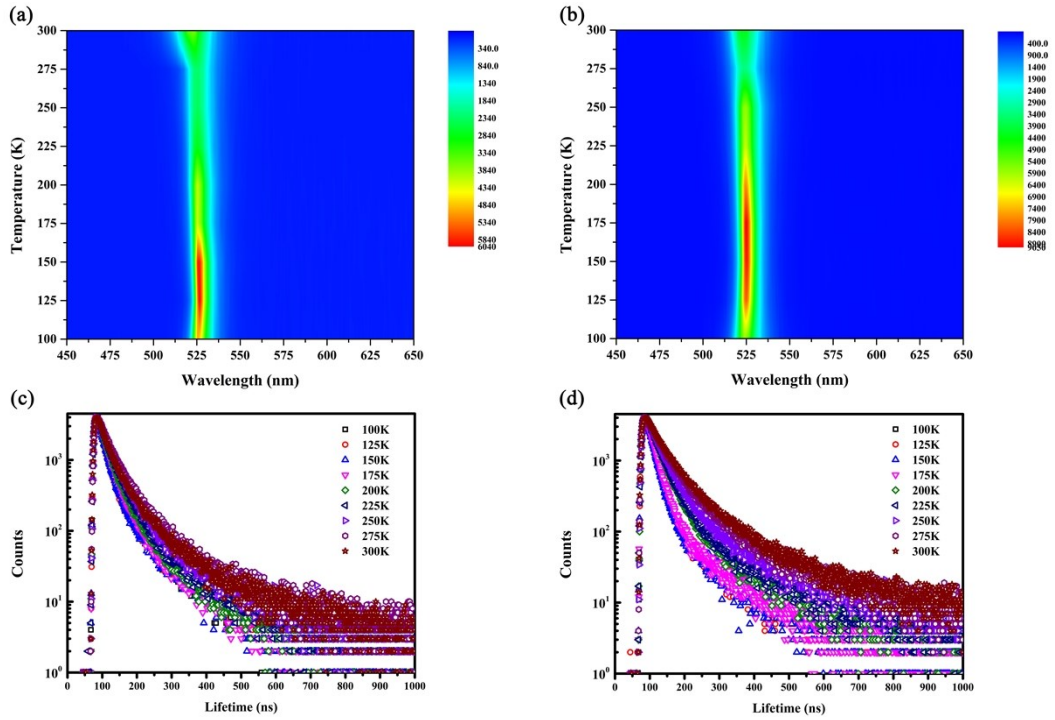

Figure S7 (a) The temperature-dependent PL spectra of CsPbBr3; (b) of CsPbBr3: 0.2mmolLiBr; (c) Lifetime curves of CsPbBr3; (d) of CsPbBr3: 0.2mmolLiBr.

Reference

1. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, Nanocrystals of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut, *Nano Letters*, 2015, **15**, 3692-3696.

2. Kresse and Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical review. B, Condensed matter*, 1996, **54**, 11169-11186.

3. Kresse and Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, *Physical review. B, Condensed matter*, 1994, **49**, 14251-14269.