Supporting information

Efficient Energy Transfer and Environmentally Stable Mn-doped $CsPbX_3$@$CsPb_2X_5$ Core-shell Materials

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Experimental Section

1.1. Materials

The cesium carbonate (Cs_2CO_3, 99.99%), manganese(II) chloride ($MnCl_2$, 99.99%), lead(II) bromide ($PbBr_2$, 99.99%), lead(II) iodide (PbI_2, 99.99%), oleic acid (OA, 85%), oleylamine (OAm, 80~90%), 1-octadecene (ODE, 90%), and toluene (>99.7%) were purchased from Aladdin. Poly(styrene) (PS) were purchased from Macklin. 365 nm blue light chips (5 W) were purchased from CREE company. All the reagents were used without further purification.

1.2 Synthesis of Mn-doped $CsPb(Cl/Br)_3$@$CsPb_2(Cl/Br)_5$ core-shell materials (MCC).

2.5 mmol Cs_2CO_3 was placed in solution consisting of 2.5 mL OA and 10 mL ODE and transferred to 100 mL three-neck flask. The solution was heated to 120 °C under vacuum and reacted for 1 h. After that, the Cs-OA precursor was obtained by heating to 140 °C and reacting for 1 h under N_2 environment. Note that the Cs-OA precursor needs to be held at 100 °C before use.

0.3 mmol $MnCl_2$/$PbBr_2$ (e.g. Mn/Pb=1.0, 0.15 mmol $MnCl_2$ and 0.15 mmol $PbBr_2$) was placed in solution consisting of 10 mL ODE, 0.5 mL OA and 0.5 mL OAm and transferred to another 100 mL three-neck flask. The temperature was increased to 120 °C under N_2 and held for 1 h. After that, the temperature was again increased to 170 °C for 10 min and 0.375 mL Cs-OA was injected into the solution. After 1h of reaction, the three-neck flask was immersed in ice water to terminate the reaction. The precipitates were obtained by centrifugation of the crude solution at 1000 rpm/min for 5 min and washed 2~3 times with toluene. Finally, the precipitation was dispersed into 15 mL toluene to obtain Mn-doped $CsPb(Cl/Br)_3$@$CsPb_2(Cl/Br)_5$ colloids.

1.3 Preparation of white light-emitting diodes (M-WLED).

15 mL Mn-doped $CsPb(Cl/Br)_3$@$CsPb_2(Cl/Br)_5$ colloids (Mn/Pb=2.0) and 0.5 g PS particles

were stirred at 60 ℃ for 3 h. Then, the solution was poured into the prefabricated molds and the polymer films were deposited at room temperature. Finally, the two films, MCC and $CsPbBr_3$@$CsPb_2Br_5$, were covered on a 365 nm UV chip to obtain P-WLEDs.

Characterization Methods

The microstructure and EDS spectra of samples were analyzed by HRTEM (JEOL JEM-F200) with energy dispersive spectrometer (EDS). The morphology of the samples were investigated by field emission scanning electron microscopy (FESEM, FEI Quatan FEG 250). Photoluminescence (PL) spectra and time-resolved PL (TRPL) decay curves of samples were recorded on Edinburgh Instruments FLS1000 spectrometer. The ultraviolet-visible (UV-Vis) absorption spectra were recorded with Jasco V-570 UV/VIS/NIR spectrophotometer. X-ray diffraction (XRD) patterns of samples were obtained with DB-ADVANCE X-Ray diffractometer. The electroluminescence (EL) spectra, luminous efficiency, color rendering index (CRI) and chromaticity coordinate of WLED were obtained with Keithley 2400 light meter and Photo Research 670 spectrometer. The CSs-WLED surface temperature was detected and recorded using thermal infrared imager (FOTRIC, USA).

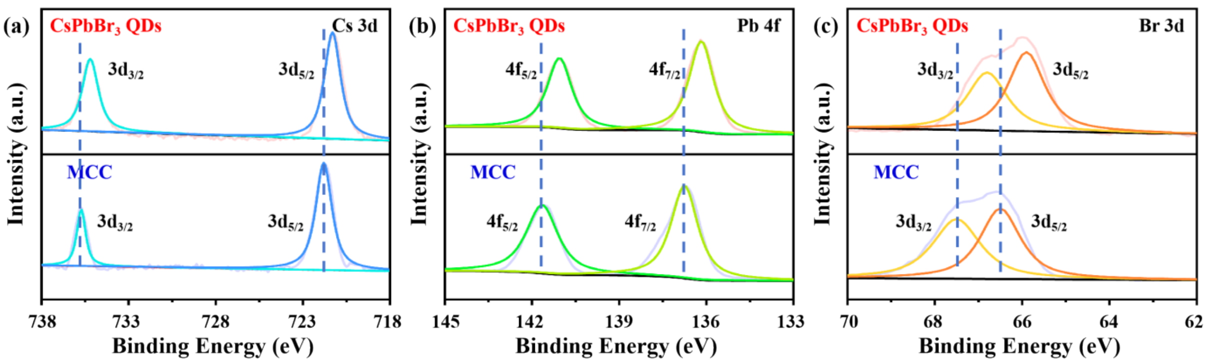

Fig. S1 Comparison of high-resolution XPS spectra of Cs 3d, Pb 4f and Br 3d.

Table S1. ICP-OES results and calculations.

Mn/Pb feeding ratio (mol/mol)	Mn^{2+} (g)	Mn^{2+} (mol)	Pb^{2+} (g)	Pb^{2+} (mol)	Mn/Pb doping ratio (mol/mol)
33%/67% (0.5/1.0)	0.000007	1.27412E-07	0.000076	3.66795E-07	26%/74%
50%/50% (1.0/1.0)	0.000012	2.18420E-07	0.000073	3.52317E-07	38%/62%
60%/40% (1.5/1.0)	0.000013	2.36622E-07	0.000062	2.99228E-07	44%/56%
67%/33% (2.0/1.0)	0.000013	2.36622E-07	0.000057	2.75097E-07	46%/54%
71%/29% (2.5/1.0)	0.000019	3.45832E-07	0.000069	3.33012E-07	51%/49%

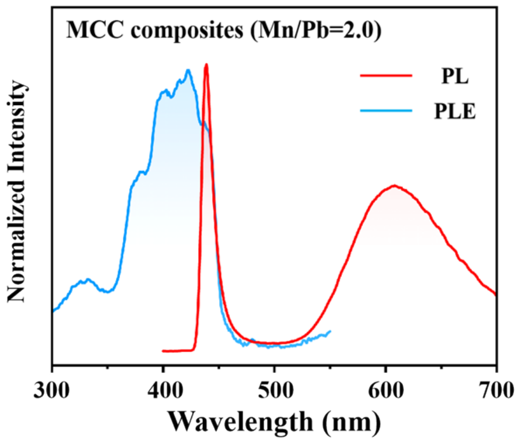

Fig. S2 PL excitation spectra of MCC composites (Mn/Pb=2.0) for emission at 600 nm.

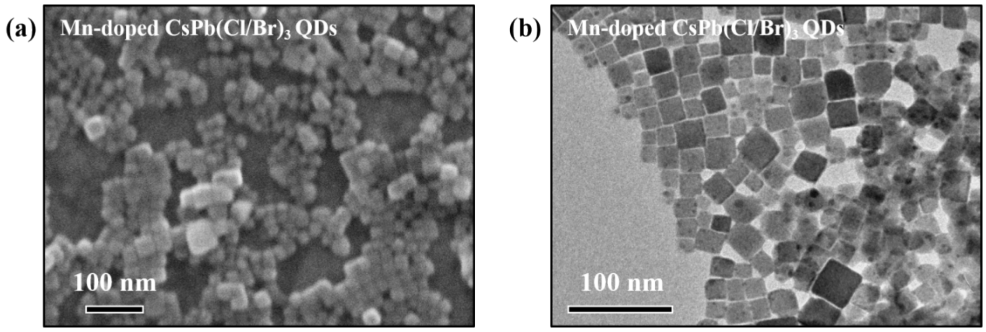

Fig. S3 (a) SEM and (b) TEM image of Mn-doped CsPb(Cl/Br)$_3$ QDs (Mn/Pb=2.0).

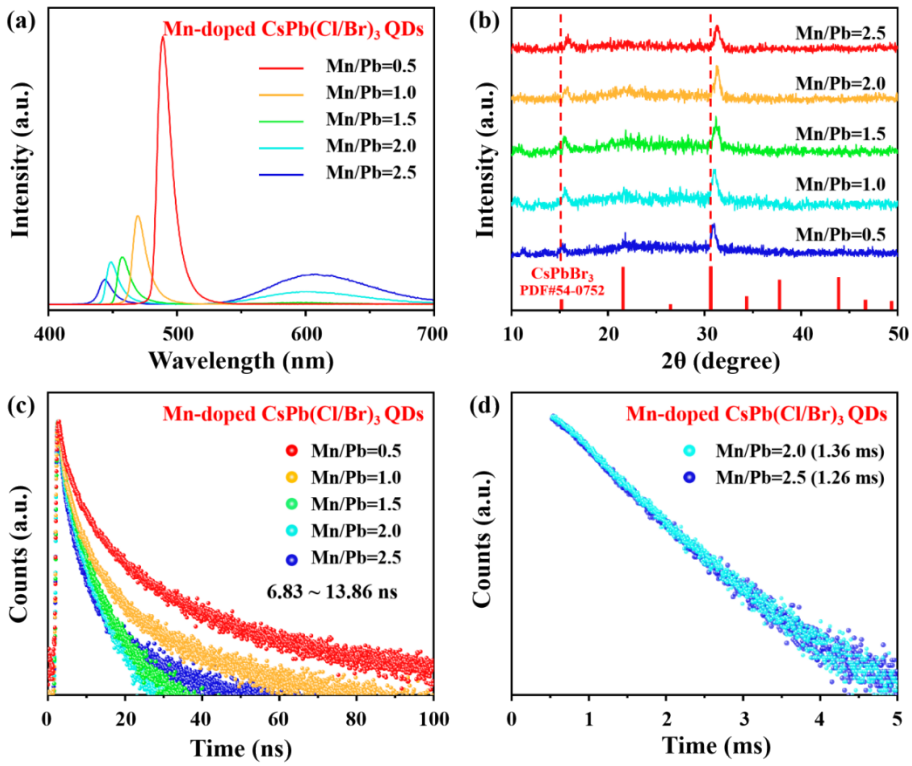

Fig. S4 PL spectra (λ=365 nm) and XRD patterns of $CsPb(Cl/Br)_3$ QDs with different Mn^{2+} doping amounts. Time-resolved fluorescence spectra of (c) excitons and (d) Mn^{2+} ions of $CsPb(Cl/Br)_3$ QDs with different Mn^{2+} doping amounts.

Table S2. Comparison of fluorescence lifetimes of MCC composites and Mn-doped $CsPb(Cl/Br)_3$ QDs.

MCC composites	Mn/Pb=0.5	Mn/Pb=1.0	Mn/Pb=1.5	Mn/Pb=2.0	Mn/Pb=2.5
τ_{ave} (exciton)	21.87 ns	17.19 ns	13.67 ns	11.91 ns	10.74 ns
τ_{ave} (Mn^{2+})	2.13 ms	2.20 ms	2.26 ms	2.33 ms	2.30 ms
Mn-doped $CsPb(Cl/Br)_3$ QDs	Mn/Pb=0.5	Mn/Pb=1.0	Mn/Pb=1.5	Mn/Pb=2.0	Mn/Pb=2.5
τ_{ave} (exciton)	13.86 ns	9.42 ns	8.34 ns	7.66 ns	6.83 ns
τ_{ave} (Mn^{2+})	-	-	-	1.36 ms	1.26 ms

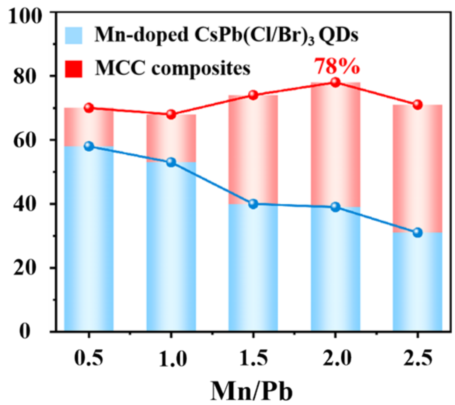

Fig. S5 Comparison of PLQY of MCC composites with different Mn^{2+} doping concentrations.

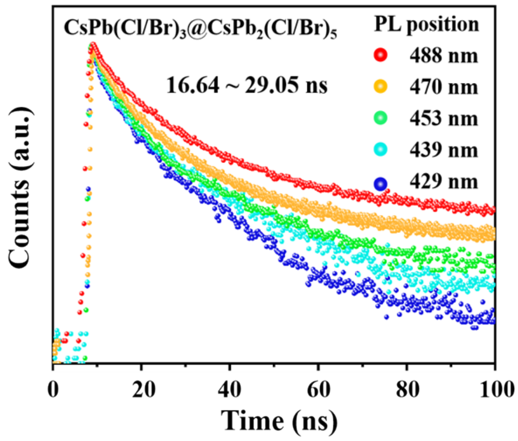

Fig S6. The time-resolved PL decays of $CsPb(Cl/Br)_3@CsPb_2(Cl/Br)_5$ composites.

Table S3. The exciton-to-Mn^{2+} energy transfer efficiency (η_{ET}) in MCC composites.

PL position (nm)	τ_0 (ns)	τ_1 (ns)	η_{ET}
488	29.05	21.87	24.7%
470	24.22	17.19	29.0%
453	21.53	13.67	36.5%
439	20.55	11.91	42.0%
429	16.64	10.74	35.5%

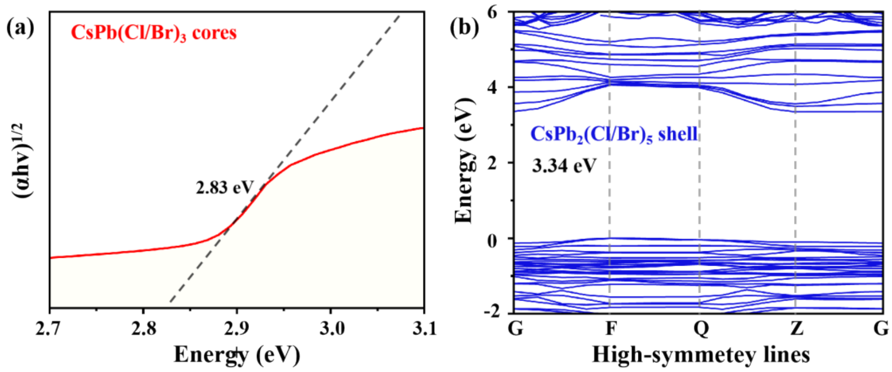

Fig. S7 (a) Optical band gap of $CsPb(Cl/Br)_3$ cores. (b) The electronic structures of tetragonal $CsPb_2(Cl/Br)_5$ shell.

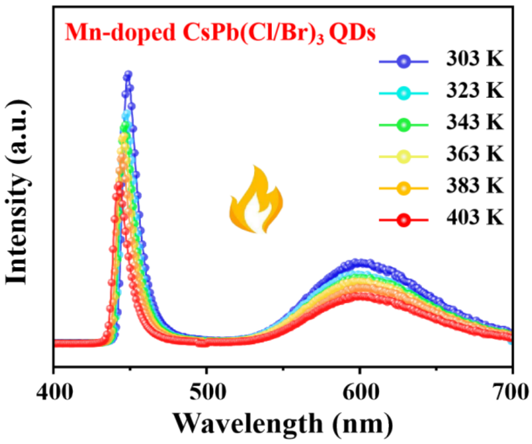

Fig. S8 Temperature-dependent PL spectra of Mn-doped $CsPb(Cl/Br)_3$ QDs (Mn/Pb=2.0) at 303~403 K.

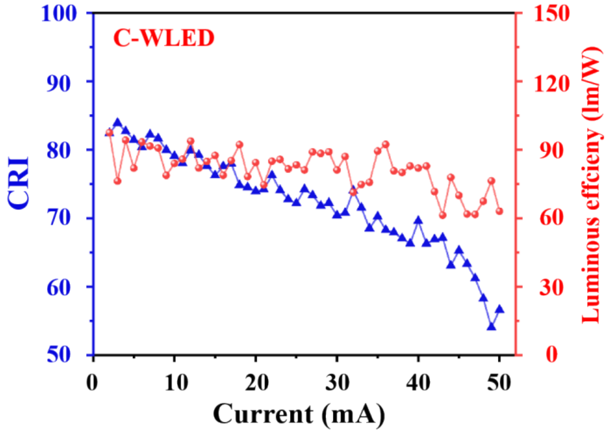

Fig. S9 Luminous efficiency and color rendering index of C-WLEDs at 2~50 mA driving current.