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Supporting Information

Aluminum chloride assisted synthesis of near-unity emitting Mn²⁺-doped CsPbCl₃ perovskite nanocrystals for bright white light-emitting diodes

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Experimental Section

Chemicals: Lead chloride (PbCl₂, Aladdin, 99.999%), manganese chloride anhydrous (MnCl₂, Aladdin, 99.99%), aluminum chloride anhydrous (AlCl₃, Macklin, 99%), cesium carbonate (Cs₂CO₃, Aladdin, 99.99%), 1-octadecene (ODE, Alfa Aesar, 90%), oleylamine (OLA, Alfa Aesar, 90%), oleic acid (OA, Alfa Aesar, 90%), trioctylphosphine (TOP, Macklin, 90%), n-hexane (Aladdin, anhydrous 99%), tetramethyl orthosilicate (TMOS, Macklin, 90%), 395 nm UV LED chip (Wocan Technology), blue-emitting and green-emitting CdSe/ZnS NCs (Suzhou Xingshuo Nanotech Co., Ltd), glass cement (Yongbang composite material). All chemicals were used directly without further purification.

Preparation of Cesium Oleate Solution: The Cs_2CO_3 (0.68 mmol) was mixed with ODE (10 mL), loaded into a 50 mL three neck round-bottom flask, and degassed under vacuum at 120 °C for 60 min. Then the mixed solution was injected with OA (1 mL) under nitrogen protection and heated up to 150 °C until a clear solution was obtained.

Synthesis of Mn²⁺:CsPbCl₃ NCs: In a typical synthesis of Mn²⁺:CsPbCl₃ NCs, 0.2 mmol of PbCl₂, various doses of MnCl₂, 5 mL of ODE, 1.5 mL of OA, 1.5 mL of OLA, and 1 mL of TOP were loaded into a 50 mL three-neck flask, and the solution was heated up to 190 °C after the conventional degassing and purging procedures. Subsequently, 1 mL of cesium oleic acid stock solution at 100°C was rapidly injected. The reaction solution was kept at 190 °C for 60 s. Then, the solution was cooled in an ice-water bath. The mixture solution was centrifuged for 10 min at 5000 rpm, and the obtained precipitate was re-dispersed into n-hexane, centrifuge again to take the supernatant for characterization store.

Synthesis of AlCl₃@Mn²⁺:CsPbCl₃ NCs: In a typical synthesis of AlCl₃@Mn²⁺:CsPbCl₃ NCs, 0.4 mmol of AlCl₃, 0.2 mmol of PbCl₂, 0.02 mmol of MnCl₂, 5 mL of ODE, 1.5 mL of OA, 1.5 mL of OLA, and 1 mL of TOP were loaded into a 50 mL three-neck flask, and the solution was heated up to 190 °C after the conventional degassing and purging procedures. After incubating at 190 °C for 10 min, 1 mL of cesium oleic acid stock solution at 100°C was rapidly injected (water droplets could be observed at the mouth of the three-necked bottle during the 10-minute incubation). The reaction solution was kept at 190 °C for 60 s. Then, the solution was cooled in an ice-water bath. The mixture solution was centrifuged for 10 min at 5000 rpm, and the obtained precipitate was re-dispersed into n-hexane, centrifuge again to take the supernatant for characterization store. AlCl₃@Mn²⁺:CsPbCl₃ NCs with various Mn²⁺ doping concentrations were obtained by changing the molar feed ratio of MnCl₂ and AlCl₃ precursor (with respect to PbCl₂), and keeping the molar amount of PbCl₂ unchanged.

Synthesis of AlCl₃@CsPbCl₃ NCs: The synthesis method is the same as the synthesis of Mn²⁺:CsPbCl₃ NCs, except that AlCl₃ replaces MnCl₂.

Preparation of the SiO₂ coated AlCl₃@Mn²⁺:CsPbCl₃ NCs: AlCl₃@Mn²⁺:CsPbCl₃ NCs colloid was re-dispersed into 3 mL n-hexane, centrifuged to take the supernatant. The 15 μ L TMOS precursor was injected into 1 mL n-hexane solution of AlCl₃@Mn²⁺:CsPbCl₃ NCs at 2/1 of the AlCl₃ precursor with 0.1/1 of Mn²⁺ (with respect to PbCl₂) and stirred vigorously for 30 min in ambient conditions. Subsequently, 5 μ L deionized water was added and stirred slowly for another 90 min. After that, the obtained NCs solution was centrifuged for 10 min at 5000 rpm and the supernatant was collected.

Fabrication of WLEDs: WLED was prepared with AlCl₃@Mn²⁺:CsPbCl₃ NCs coated with SiO₂ (AlCl₃@Mn²⁺:CsPbCl₃/SiO₂ NCs) and blue, green-emitting CdSe/ZnS NCs on a commercial GaN chip. The AlCl₃@Mn²⁺:CsPbCl₃/SiO₂ NCs n-hexane solution was mixed with glass cement, the same as the blue, green-emitting CdSe/ZnS NCs heptane solution. Then, the above three mixtures were covered on the 395 nm UV-LED chip in the order of orange/green/blue, and the interval between each covering was 10 min. Finally, it was cured in ambient conditions for 15 min to form the final WLED, and the performance of the WLED device was characterized.

Characterization

The UV–visible absorption spectra of NCs were recorded using a spectrophotometer (PerkinElmer, Lambda 750). The Horiba Jobin Yvon Fluorolog-3 spectrometer with a timecorrelated single-photon counting system was used to measure the PL spectrum, PL QY, and PL decay curves of NCs. The inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700s) was used to identify the compositions of NCs. The X-ray diffraction (XRD) spectra were performed on a SMARTLAB3KW X-ray diffractometer equipped with Cu-K α radiation (λ = 1.540 Å). A transmission electron microscope (TEM) was performed on an FEI TECNAI G2 F30 operating at an accelerating voltage of 300 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250XI+ X-ray photoelectron spectrometer. The energy-dispersive X-ray spectroscopy (EDS) characterizations were completed with a SU8020 scanning electron microscope. Fourier transform infrared spectroscopy (FTIR) data were obtained with a VERTEX 70 FTIR Spectrometer. Ocean optics Spectrum TEQ-PL was used to measure the optical properties of the as-obtained WLEDs.

Additional Data Analysis



Fig. S1. UV-visible absorption spectra of AlCl₃@Mn²⁺:CsPbCl₃ NCs under different AlCl₃ precursor.

| | Mn doping | PLQY | | Ref | |
|--|--------------|------|--|--------------|--|
| System | (Mn/Pb) | (%) | Note | | |
| $Mn:CsPb(Cl_yBr_{1-y})_3$ | 5 | 40 | Synthesis by ion exchange | 1 | |
| Mn:CsPbCl ₃ | 1.5 | 54 | Post-treatment with KCl | 2 | |
| Mn:CsPbCl ₃ | 2 | 55 | Coated with SiO ₂ | 3 | |
| Mn:CsPb(Cl _y Br _{1-y}) ₃ | 2 | 59 | Synthesis by ion exchange | 4 | |
| Mn:CsPbCl ₃ | 3 | 63 | Doped with Rb | 5 | |
| Mn:CsPbCl ₃ | 1 | 65 | Microwave-assisted synthesis | 6 | |
| Mn:CsPbCl ₃ | 0.2 | 68 | Doped with CuCl ₂ | 7 | |
| Mn:CsPbCl ₃ | 1 | 70 | Doped with NiCl ₂ | 8 | |
| Mn:CsPb(Cl _y Br _{1-y}) ₃ | 2 | 75 | Doped with CeCl ₃ | 9 | |
| Mn:CsPbCl ₃ | 2 | 97 | Post-treatment with CdBr ₂ | 10 | |
| Mn:CsPbCl ₃ | 3 | 99 | Post-treatment with CdCl ₂ | 11 | |
| Mn:CsPbCl ₃ | 0.1 | 87 | AlCl ₃ assisted synthesis | This work | |
| Mn:CsPbCl ₃ | 0.1 | 98 | AlCl ₃ assisted synthesis jointly with coated with SiO ₂ | This work | |

Table S1. Summary of the feed ratios and optical parameters of Mn^{2+} doped CsPbCl₃ NCs reported in previous works.



Fig. S2. PL decay curves of (a) exciton and (b) Mn^{2+} of $AlCl_3@Mn^{2+}:CsPbCl_3$ NCs under different $AlCl_3$ precursor. The excitation wavelength is 368 nm.

The PL decay curve was fitted using a bi-exponential decay function as:

$$I(t) = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}}$$
(1)

where *I* is the luminescence intensity, a_1 and a_2 are the amplitudes, and τ_1 and τ_2 are the decay time constants for the exponential components. And then the average lifetime can be calculated by using the following equation:

$$\tau = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2} \tag{2}$$

Table S2. Summary of the radiative recombination rates (κ_r), non-radiative recombination rates (κ_{nr}) and κ_r/κ_{nr} of the exciton and Mn²⁺ emissions respectively, for Mn²⁺:CsPbCl₃ NCs synthesized without and with AlCl₃.

| Sample (Different AlCl ₃ precursor with 0.1/1 of Mn/Pb) | κ_r^{eh} | κ^{Mn}_{r} | κ^{eh}_{nr} | κ_{nr}^{Mn} | $\frac{\kappa_r^{eh}}{\kappa_{nr}^{eh}}$ | $\frac{\kappa_r^{Mn}}{\kappa_{nr}^{Mn}}$ |
|---|---------------------|---------------------|---------------------|---------------------|--|--|
| | (ns ⁻¹) | (ns ⁻¹) | (ns ⁻¹) | (ns ⁻¹) | | |
| Mn ²⁺ :CsPbCl ₃ (0/1) AlCl ₃ @Mn ²⁺ :CsPbCl ₃ (2/1) | 0.003 | 0.337 | 0.243 | 112.333 | 0.012 | 0.003 |
| | 0.038 | 0.478 | 1.583 | 0.086 | 0.024 | 5.556 |

 $*\kappa_{r}^{eh}$ and κ_{r}^{Mn} are the radiative recombination rate of exciton and Mn²⁺, respectively.

 κ_{nr}^{eh} and κ_{nr}^{Mn} are the non- radiative recombination rate of exciton and Mn²⁺, respectively.



Fig. S3. PL decay curves of Mn^{2+} in Mn^{2+} :CsPbCl₃ NCs with different Mn^{2+} concentration. The excitation wavelength is 365 nm.



Fig. S4. PL QY of excitons in CsPbCl₃ NCs synthesized with different content of AlCl₃.



Fig. S5. PL decay curve of excitons in CsPbCl₃ NCs without AlCl₃ and Mn^{2+} . The excitation wavelength is 368 nm.



Fig. S6. Temperature-dependent PL spectra of $AlCl_3@Mn^{2+}:CsPbCl_3$ NCs ($AlCl_3/PbCl_2 = 2/1$). The excitation wavelength is 365 nm.



Fig. S7. Boltzmann analysis of Mn^{2+} PL intensity as a function of temperature. The black line is a linear fit of the plot from 140 to 240 K, yielding the activation energy (E_a) of 73.17 meV.

The Boltzmann analysis of the time-integrated Mn^{2+} PL intensity (I_{Mn}) as a function of temperature (T) can be expressed in¹²

$$I_{Mn}(T) = I_{Mn}(300 \ K) * e^{-\frac{E_a}{k_B T}}$$

where I_{Mn} (300 K) is the Mn²⁺ PL intensity at 300 K, E_a is the energy barrier of the energy transfer from the mediating trap states to Mn²⁺-dopant, and k_B is the Boltzmann constant.



Fig. S8. NC size distributions of $AlCl_3@Mn^{2+}:CsPbCl_3$ NCs with $AlCl_3/PbCl_2$ feed ratio of 0/1 (a), 1/1 (b), 2/1 (c) and 3/1 (d).



Fig. S9. XRD patterns of CsPbCl₃ NCs synthesized with different content of AlCl₃.



Fig. S10. The full XPS spectrum of AlCl₃@Mn²⁺:CsPbCl₃ NCs.



Fig. S11. Cs, Pb, Cl, Mn, and Al element mapping images of $AlCl_3@Mn^{2+}:CsPbCl_3$ NCs with $AlCl_3/PbCl_2$ ratio of 2/1.



Fig. S12. XPS profiles of (a) Pb 4f, (b) Cl 2p, and (c) Mn 2p of $AlCl_3@Mn^{2+}:CsPbCl_3 NCs$ without and with $AlCl_3(AlCl_3/PbCl_2 = 2/1)$.



Fig. S13. XRD patterns of AlCl₃@Mn²⁺:CsPbCl₃ NCs without and with coating SiO₂.



Fig. S14. (a) TEM and (b) HR-TEM images of $AlCl_3@Mn^{2+}:CsPbCl_3NCs$ ($AlCl_3/PbCl_2 = 2/1$) coated with SiO_2 .



Fig. S15. FTIR spectra of AlCl₃@Mn²⁺:CsPbCl₃ NCs coated with and without SiO₂.



Fig. S16. Typical test result of PLQY of AlCl₃@Mn²⁺:CsPbCl₃ NCs coated with SiO₂.



Fig. S17. PL decay curve of exciton of $AlCl_3@Mn^{2+}:CsPbCl_3/SiO_2$ NCs. The excitation wavelength is 368 nm.

The PL decay curve was fitted using a bi-exponential decay function as:

$$I(t) = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}}$$
(1)

and then the average lifetime can be calculated by using the following equation:

$$\tau = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2} \tag{2}$$

Finally, the energy transfer efficiency (η_{ET}) from exciton to Mn²⁺ is calculated according to the following equation is 0.9,

$$\eta_{ET} = 1 - \frac{\tau_{avg\,1}}{\tau_{avg\,2}} \tag{3}$$

where $\tau_{avg\,1}$ and $\tau_{avg\,2}$ are the exciton average lifetimes of CsPbCl₃ NCs and AlCl₃@Mn²⁺:CsPbCl₃/SiO₂ NCs, respectively.

Table S3. Summary of the radiative recombination rates (κ_r), non- radiative recombination rates (κ_{nr}) and κ_r/κ_{nr} of the exciton and Mn²⁺ emissions respectively for the AlCl₃@Mn²⁺:CsPbCl₃ NCs without and with coated with SiO₂.

| Sample (AlCl ₃ / PbCl ₂ = $2/1$ and Mn/Pb = $0.1/1$) | κ_r^{eh} | κ^{Mn}_{r} | κ^{eh}_{nr} | κ_{nr}^{Mn} | $\frac{\kappa_r^{eh}}{\kappa_{nr}^{eh}}$ | $\frac{\kappa_r^{Mn}}{\kappa_{nr}^{Mn}}$ |
|---|---------------------|---------------------|---------------------|---------------------|--|--|
| | (ns ⁻¹) | (ns ⁻¹) | (ns ⁻¹) | (ns ⁻¹) | | |
| AlCl ₃ @Mn ²⁺ :CsPbCl ₃ | 0.038 | 0.478 | 1.583 | 0.086 | 0.024 | 5.556 |
| AlCl ₃ @Mn ²⁺ :CsPbCl ₃ /SiO ₂ | 0.055 | 0.542 | 1.945 | 0.020 | 0.028 | 27.027 |

 $*\kappa_r^{eh}$ and κ_r^{Mn} are the radiative recombination rate of exciton and Mn²⁺, respectively.

 κ_{nr}^{eh} and κ_{nr}^{Mn} are the non- radiative recombination rate of exciton and Mn²⁺, respectively.



Fig. S18. Integrated PL intensity of Mn^{2+} ions in AlCl₃@ Mn^{2+} :CsPbCl₃/SiO₂ NCs as a function of temperature.

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