

Introducing Ytterbium Acetate to Luminescent CsPbCl₃ Nanocrystals for Enhanced Sensitivity of Cu²⁺ Detection

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1. Experimental

1.1 Materials

Cs₂CO₃ (99.9%), PbCl₂ (99.99%), Pb(OAc)₂ (99%), octadecene (ODE, 90%), oleylamine (OLA, 80-90%) and octylamine (OctAm, 99%) were purchased from Macklin, oleic acid (OA, 90%) and octanoic acid (OctAc, 98%) were purchased from Alfa Aesar. All other chemical reagents including YbCl₃ (99%), Yb(OAc)₃·xH₂O (99.99%), ZnCl₂ (99%), cycloethane (90%), sodium oleate (99%), KCl (99%), FeCl₃·6H₂O (99%), MgSO₄·7H₂O (99%), NiCl₂·6H₂O (98%), CaCl₂·2H₂O (99%), Mn(OAc)₂·4H₂O (99%), CuCl₂·2H₂O (99%), sodium oleate (90%), AgNO₃ (99.5%), Al(NO₃)₃·9H₂O (99%), ErCl₃·6H₂O (99.9%), were purchased from Aladdin and used directly.

1.2 Synthesis of the Cs-oleate solution

0.4 g Cs₂CO₃, 1.2 mL OA, and 15 mL ODE were added into a 50 mL three-necked flask, then heated to 120 °C until the Cs source completely dissolved and the as-prepared solution sustained at 100 °C for subsequent experiments.

1.3 Synthesis of initial CsPbCl₃ NCs and series of CsPbCl₃ nanocrystals passivated by ytterbium acetate

For the synthesis of the initial CsPbCl₃ NCs, added PbCl₂ (0.056 g), OA (0.5 mL), OLA (0.8 mL), OctAc (0.5 mL), OctAm (0.5 mL) and ODE (5 mL) into a 50 ml 3-necked round-bottom flask under N₂ for 60 mins at 120 °C. Then, rapidly inject 0.7 mL of the prepared cesium oleate solution as the temperature increase to 140 °C. After 50 mins, cool the reaction mixture in an ice-water bath. The obtained product was separated by centrifugation for 10 mins at 9500 rpm, the precipitate was redispersed in 3 mL of cycloethane, centrifuged once again for 10 mins at 9500 rpm, and redispersed in 1 mL of cycloethane.

For the synthesis of CsPbCl₃ nanocrystals passivated by ytterbium acetate, diverse

amounts of $\text{Yb}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$ (0.03, 0.05 and 0.15 mmol) and PbCl_2 were added to the three-necked bottle together. And the CsPbCl_3 NWs were formed when the feeding amount is 0.05 mmol. The following steps are analogous to that during the synthesis of the initial CsPbCl_3 NCs.

For the synthesis of referenced samples R1 and R2, the 0.075 mmol $\text{Pb}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ and 0.05 mmol $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ were added into the reaction solution, respectively. The subsequent steps are similar to that in the production of the initial CsPbCl_3 NCs. And the corresponding product is defined as R1 and R2 for clarification, respectively.

1.4 Preparation of metal ions solution

Take Cu^{2+} ion solution as an example. 0.1 mmol CuCl_2 was dissolved by 0.5 mL H_2O to form a clear and transparent solution. Then put certain amounts of sodium oleate (molar ratio of Na : Cu, 2:1) into H_2O -ethanol mixture solution (ratio of volume, 1:1). The obtained copper oleate was centrifuged for 10 mins at 9500 rpm. The precipitate was dried overnight at 60 °C and dissolved in cyclohexane for storage. The other metal ions involved in this study were also prepared in the same way.

2. Characterizations

2.1 Morphology and structure characterization.

For the transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and elemental mapping measurements, the samples were imaged by a Titan transmission electron microscope (FEI Company) worked at 300 kV in EFTEM mode with a 20 KeV energy. And the Powder XRD characterization was performed by a Rigaku D/Max-Ra X-ray diffractometer. The inductively coupled plasma mass-spectrometry (ICP-MS) was measured on a Varian 720-ES ICP-optical emission spectrometer. X-ray photoelectron spectroscopy (XPS) patterns were obtained through a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operated at 150 W. The infrared Fourier spectroscopy was measured by a Fourier

transform infrared (FT-IR) spectrometer from Japan with a mercury cadmium telluride detector. The AFM images were obtained by conducting a DI Innova AFM (Bruker) in light tapping mode.

2.2 Optical and electrical characterization

Optical studies. The UV-vis absorption spectra were recorded by using a Shimadzu UV-3101PC UV-Vis scanning spectrophotometer in the range 300-900 nm. Photoluminescence spectra were recorded under ambient conditions by using an FLS365 spectrometer. The luminescence decay curves were acquired by an FLS920 spectrofluorometer. Absolute quantum yield was then calculated by using the Edinburgh L920 software package.

Defect density and conductivity measurement. The capacitor-like devices were fabricated by spinning. CsPbCl₃ perovskite active layers (20 mg mL⁻¹) at 1000 rpm for 40 s and depositing Ag by thermal evaporation in a vacuum deposition chamber. And the current-voltage (*I-V*) curves of the devices under diverse bias were measured by a Keithley 2400 sourcemeter.

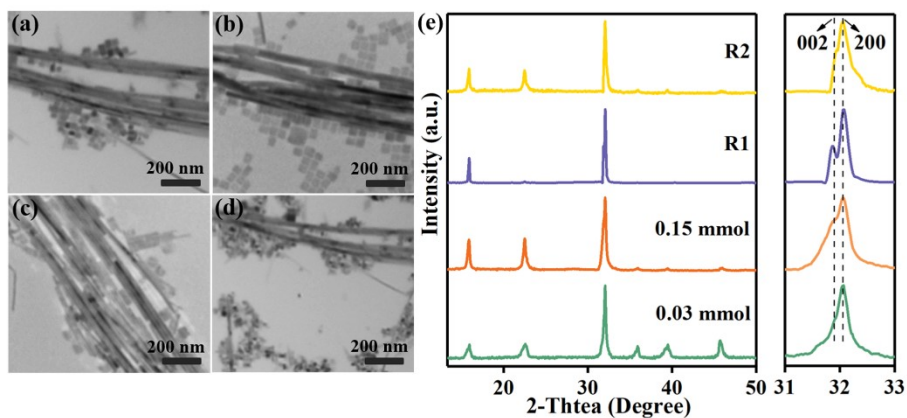


Fig. S1. TEM images of samples synthesized with adding different amounts of AcO⁻ (a) 0.03 mmol, (b) 0.15 mmol, (c) R1 and (d) R2; (e) XRD patterns of 0.03 mmol, 0.15 mmol AcO⁻ passivated CsPbCl₃ NCs, R1 and R2, with the selected zoom-in area centered at 31.8 and 32.1 degree.

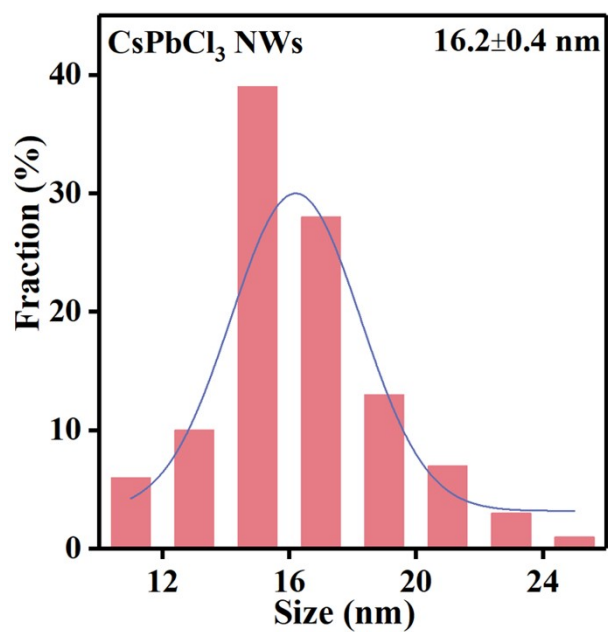


Fig. S2. Diameter size distribution of the final CsPbCl₃ NWs, calculated from TEM images.

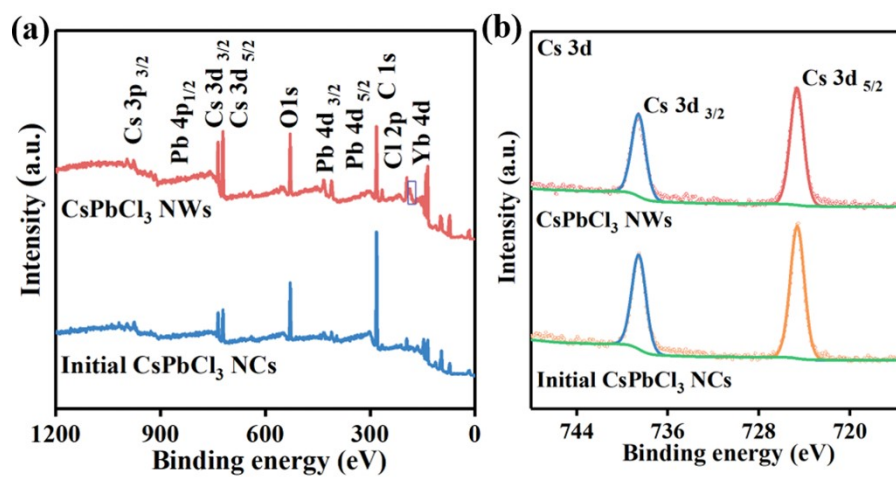


Fig. S3. High-resolution XPS analysis of initial CsPbCl₃ NCs and final CsPbCl₃ NWs corresponding to (a) survey spectra, (b) Cs 3d.

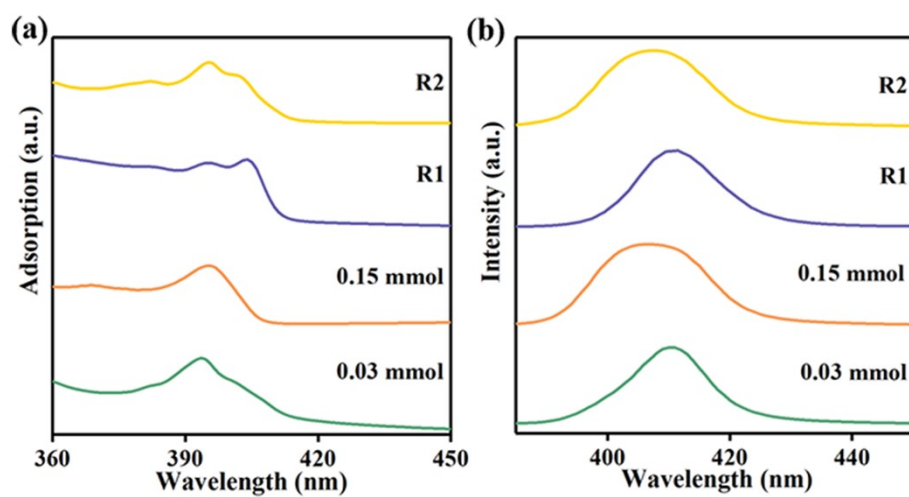


Fig. S4 (a) Absorption, (b) PL emission spectra for 0.03 mmol, 0.15 mmol AcO⁻ passivated CsPbCl₃ NCs and R1, R2.

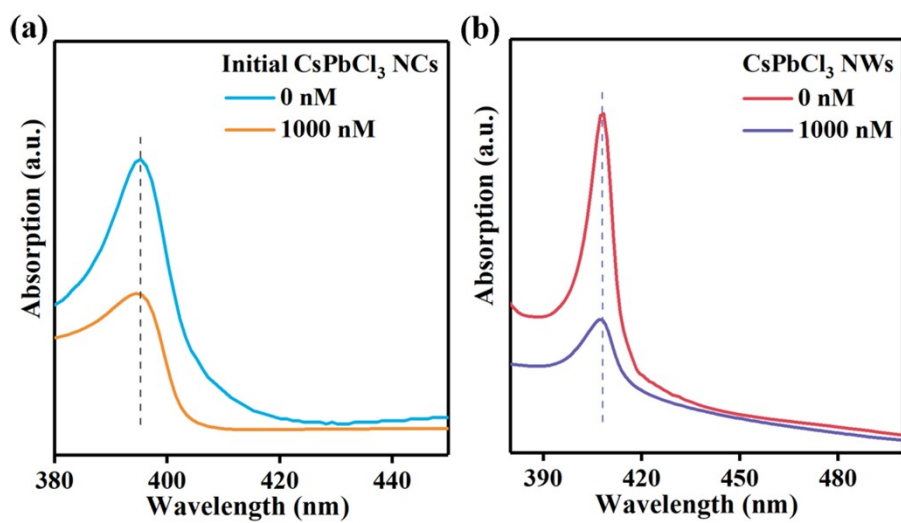


Fig. S5. (a) Absorption spectra of initial CsPbCl₃ NCs and (b) final CsPbCl₃ NWs after feeding certain concentration of Cu²⁺ ions.

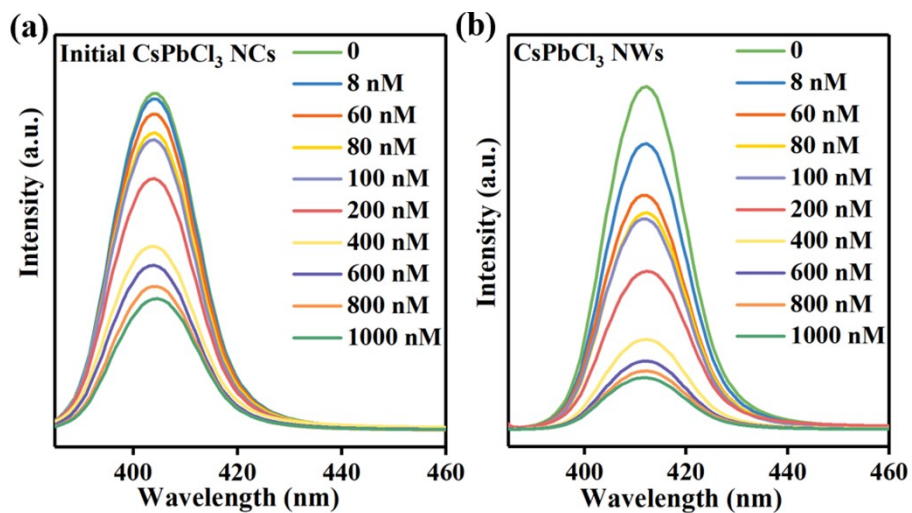


Fig. S6 The PL dependence of (a) initial CsPbCl₃ NCs and (b) final CsPbCl₃ NWs on Cu²⁺ concentration under 365 nm excitation.

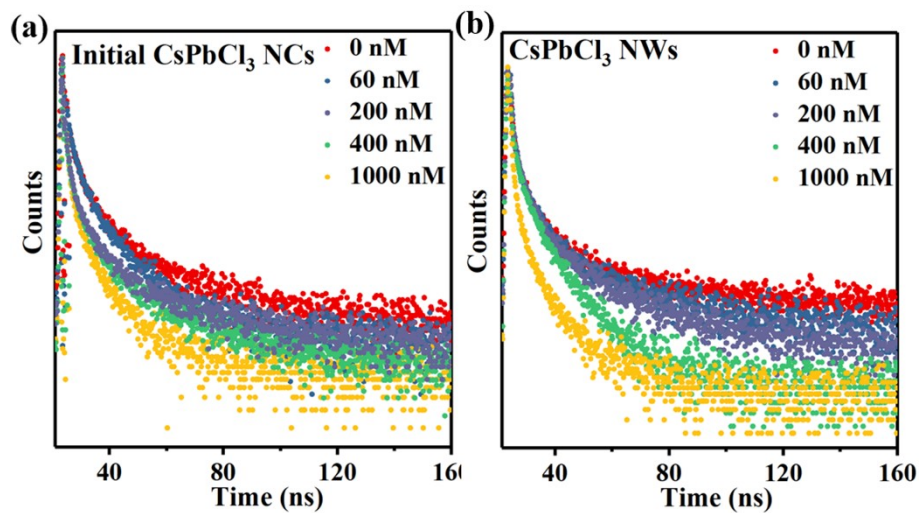


Fig. S7 The PL decay curves of (a) initial CsPbCl₃ NCs and (b) final CsPbCl₃ NWs vs. the Cu²⁺ concentration.

Table S1. ICP of mole ratio of Yb to Pb for the different amount of Yb(OAc)₃ passivated CsPbCl₃ NCs.

Yb(OAc) ₃ feeding amounts (mmol)	0	0.03	0.05	0.15
(ICP) mole ratio of Yb to (Yb+Pb) (%)	0	0.40	1.8	3.7

Table S2. Resistance, thickness and conductivity of the films deposited from initial CsPbCl₃ NCs and final CsPbCl₃ NWs. The resistances are determined from the slope of the *I-V* curves shown in Fig. 4b in the main text; thicknesses are obtained by AFM,

measurements and the conductivities are calculated from the formula: $\sigma = \frac{d}{AR}$

	Resistance (Ω)	Thickness (nm)	Conductivity (S/cm)
initial CsPbCl ₃ NCs	217.4	142	1.6×10^{-3}
CsPbCl ₃ NWs	26.0	165	15.8×10^{-3}

Table 3. Summary of perovskite-based fluorescent probes for Cu²⁺ in organic phase.

Probes	Solvent	Detection limit (nM)	Linear detection range	Ref
CsPbCl ₃ QDs	cyclohexane	20 nM	2×10 ⁻⁸ to 2×10 ⁻⁵ M	1
CsPbBr ₃ QDs	hexane	0.1 nM	0 to 1×10 ⁻⁷ M	2
CsPbCl ₃ NWs	cyclohexane	0.06 nM	0 to 1000 nM	This work

Table S4. The PL decay time of the initial CsPbCl₃ NCs after adding different amount of the Cu²⁺.

	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_{avg} (ns)
0 nM	1.22	0.47	10.23	0.53	9.37
60 nM	1.18	0.52	9.92	0.48	8.93
200 nM	1.12	0.47	9.40	0.53	8.61
400 nM	1.07	0.48	9.28	0.52	8.49
1000 nM	1.03	0.49	9.21	0.51	8.42

Table S5. The PL decay time of the final CsPbCl₃ NWs after adding different amount of the Cu²⁺.

	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_{avg} (ns)
0 nM	1.32	0.51	13.61	0.49	12.48
60 nM	1.21	0.52	12.52	0.48	11.41
200 nM	1.15	0.47	11.40	0.53	10.56
400 nM	1.04	0.45	9.13	0.55	8.43
1000 nM	0.89	0.66	8.35	0.34	7.48

Table S6. The PL decay time of the initial CsPbCl₃ NCs and final CsPbCl₃ NWs after adding the Cu²⁺.

	Initial CsPbCl ₃ NCs	Initial CsPbCl ₃ NCs (1000 nM)	CsPbCl ₃ NWs	CsPbCl ₃ NWs (1000 nM)
τ_1 (ns)	1.22	1.03	1.32	0.89
a_1	0.47	0.49	0.51	0.66
τ_2 (ns)	10.23	9.21	13.61	8.35
a_2	0.53	0.51	0.49	0.34
τ_{avg} (ns)	9.37	8.42	12.48	7.48

Reference

- 1 X. Sheng, Y. Liu, Y. Wang, Y. Li, X. Wang, X. Wang, Z. Dai, J. Bao and X. Xu, Cesium lead halide perovskite quantum dots as a photoluminescence probe for metal ions, *Adv. Mater.*, 2017, **29**, 1700150.
- 2 Y. Liu, X. Tang, T. o Zhu, M. Deng, I. P. Ikechukwu, W. Huang, G. Yin, Y. Bai, D. Qu, X. Huang and F. Qiu, All-inorganic CsPbBr₃ perovskite quantum dots as a photoluminescent probe for ultrasensitive Cu²⁺ detection, *J. Mater. Chem. C*, 2018, **6**, 4793-4799.