

## Supplementary information

### One-pot reprecipitation strategy to synthesize CsPbX<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> composite nanocrystals

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## **Experimental**

### **Materials**

All chemicals were used as received without any further purification. Cesium bromide (CsBr, 99.999%), lead bromide (PbBr<sub>2</sub>, 99.999%), oleic acid (OA, 90%), oleylamine (OAm, 80-90%), octylamine (C<sub>8</sub>H<sub>19</sub>N, 99%), phosphoric acid (H<sub>3</sub>O<sub>4</sub>P, 85%) were purchased from Alfa Aesar. N, N-Dimethylformamide (DMF, 99.5%), zinc bromide (ZnBr<sub>2</sub>, 99.999%) were provided by Sigma-Aldrich. Didodecylammonium bromide (DDAB, 98%) was obtained from Macklin. Toluene (99.95%) was purchased from Fisher.

### **Synthesis of CsPbBr<sub>3</sub> NCs**

Reprecipitation method was employed for the synthesis of CsPbBr<sub>3</sub> NCs.<sup>1</sup> Typically, 0.1468 g PbBr<sub>2</sub>, 0.0851 g CsBr, 0.5 mL OAm, and 1.0 mL OA was added into 10 mL DMF, then the mixture was stirred at 120 °C for 2 h to obtain a clear solution. After cooling down to room temperature, 0.2 mL of the precursor solution was added into 10 mL toluene under vigorous stirring. After 10 seconds, the reaction was stopped, and as-obtained precipitate was purified by concentration.

### **Synthesis of octylammonium phosphate ((C<sub>8</sub>H<sub>17</sub>NH<sub>3</sub>)<sub>3</sub>PO<sub>4</sub>)**

Octylamine (10 mmol) and phosphoric acid (31 mmol) were mixed at 0 °C. After 30 min, white precipitate was extracted through vacuum filtration to remove the solvent. The precipitate was washed by hexane twice and dried overnight in an oven.

### **Synthesis of CsPbBr<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> NCs**

0.4 mmol octylammonium phosphate was dissolved in 10 mL toluene/isopropanol (v/v 5:1) mixed solution. 0.2 mL of above-mentioned precursor solution was rapidly added into the mixed solution. After stirring for 10 second, the final product was obtained by centrifugation.

#### **Post-treatment of CsPbBr<sub>3</sub> NCs**

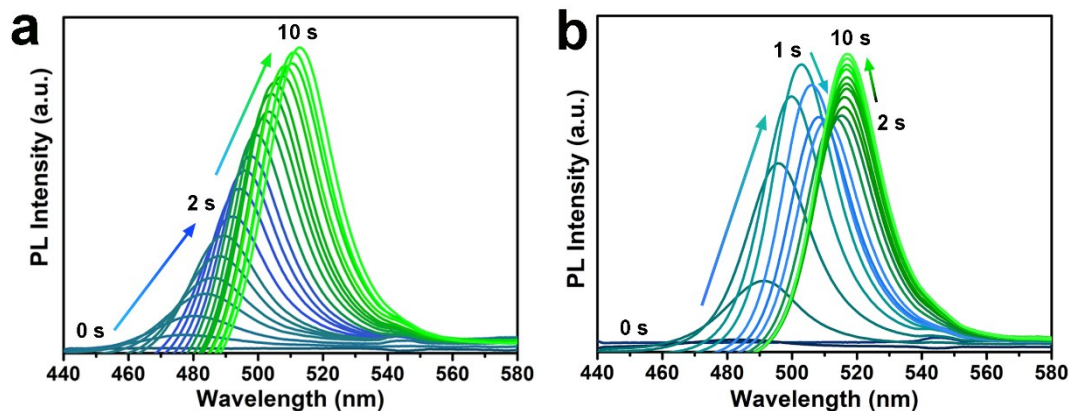
In ambient condition, 0.4 mL ZnBr<sub>2</sub> (or PbBr<sub>2</sub> or DDAB, 0.1 M, in toluene) was dropwise added into CsPbBr<sub>3</sub> solution and kept mild stirring for 30 minutes. The obtained sample was centrifuged at 9000 rpm for 5 min.

#### **Characterization Methods**

Powder X-ray diffraction (XRD) pattern was collected using an Empyrean diffractometer (monochrome Cu K $\alpha$ ,  $\lambda = 1.54056 \text{ \AA}$ ). UV-vis absorption spectra were acquired using an Evolution 220 spectrophotometer. PL spectra and PLQY values were obtained by a FLUOROMAX-4 spectrofluorometer equipped with a xenon lamp. PL lifetime was recorded by HORTB-FM-2015 fluorescence spectrophotometer. Transmission electron microscope (TEM) images were collected by a transmission electron microscopy (FEI Talos F200X, Thermo Fisher). Fourier transform infrared (FTIR) spectroscopy was performed on a Vertex 70 spectrometer in the range of 4000 to 600 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were carried out through a Shimadzu Ultra DLD with an Al K $\alpha$  source (1486.7 eV). TGA measurement was performed on a Mettler Toledo Switzerland thermogravimetric analyzer.

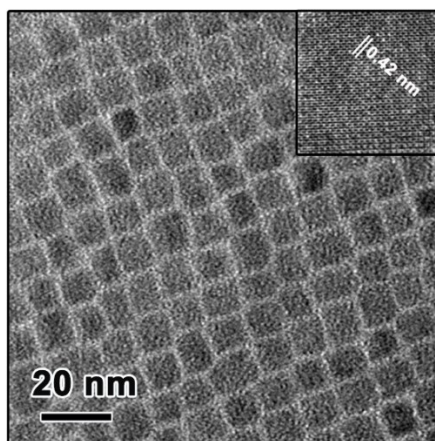


**Fig. S1** Photographs of CsPbBr<sub>3</sub> NCs dispersed in toluene under daylight (left) and UV light (right,  $\lambda = 365$  nm).

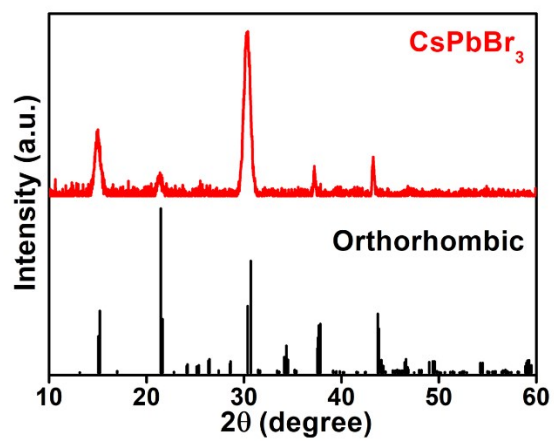


**Fig. S2** *In-situ* PL spectra of (a) CsPbBr<sub>3</sub> and (b) CsPbBr<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Interval is 0.2 s (0~2 s), 0.8 s (2~10 s).

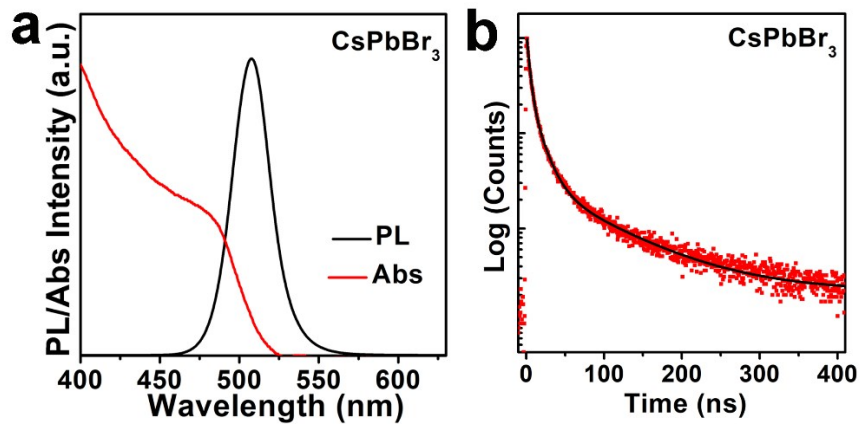
It should be mentioned that the final PL emission wavelength in this figure is different from the results in the manuscript, because the *in-situ* PL spectra represent the growth behavior in the raw solution, which was then centrifugated to obtain NCs with narrow size distribution.



**Fig. S3** TEM image of CsPbBr<sub>3</sub> NCs. Inset shows the corresponding HRTEM image.



**Fig. S4** XRD pattern of CsPbBr<sub>3</sub> NCs and the standard pattern of orthorhombic CsPbBr<sub>3</sub>.



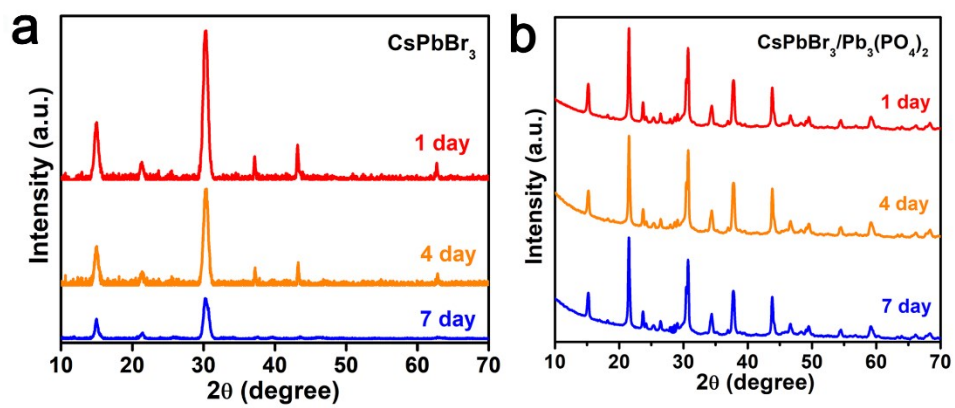
**Fig. S5** (a) Absorbance and PL spectra of  $\text{CsPbBr}_3$  NCs. (b) Time-resolved PL lifetime

of

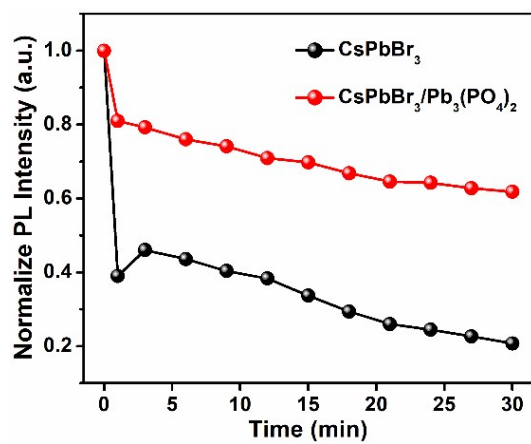
$\text{CsPbBr}_3$

NCs.

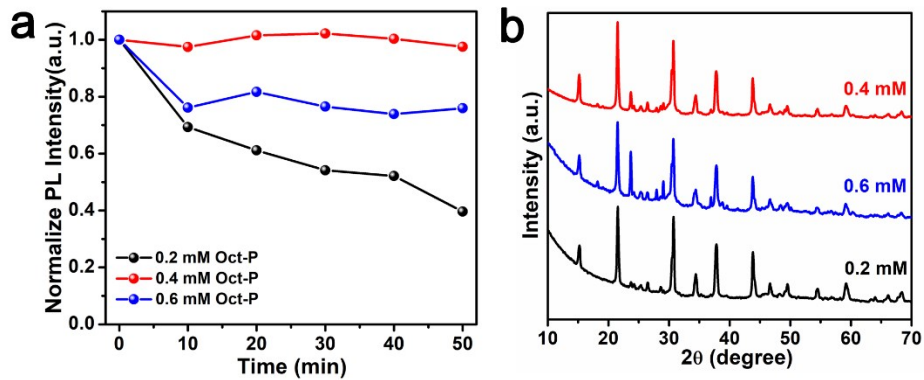




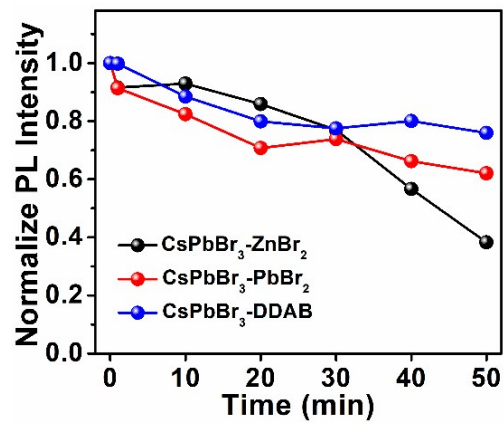
**Fig. S6** XRD patterns of (a) pristine CsPbBr<sub>3</sub> NCs and (b) CsPbBr<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> stored under ambient condition for a week.



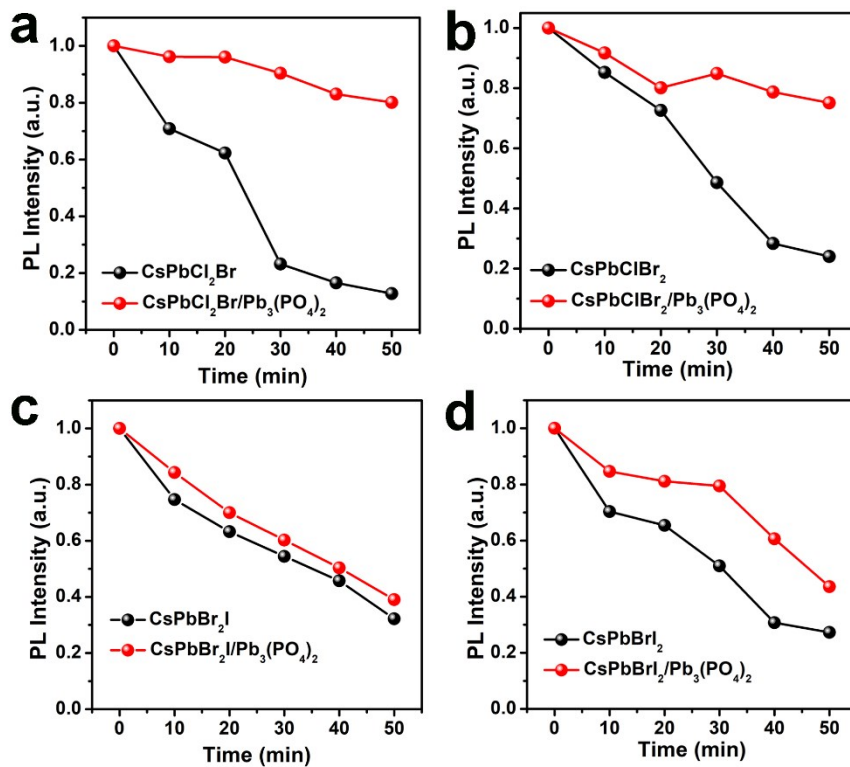
**Fig. S7** The resistance of CsPbBr<sub>3</sub> NCs and CsPbBr<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> NCs against acetone (25%, v/v).



**Fig. S8** (a) Comparison of water resistance of CsPbBr<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> obtained from different concentrations of phosphate, and (b) their corresponding XRD patterns.



**Fig. S9** The water resistance of CsPbBr<sub>3</sub> NCs treated by ZnBr<sub>2</sub>, PbBr<sub>2</sub> and DDAB, respectively.



**Fig. S10** PL intensity change showing the water resistance of CsPbX<sub>3</sub> NCs and CsPbX<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> NCs. X<sub>3</sub> = (a) Cl<sub>2</sub>Br, (b) ClBr<sub>2</sub>, (c) Br<sub>2</sub>I, (d) BrI<sub>2</sub>.

**Table S1** Detailed XPS and EDX results of different samples.

|     | <b>CsPbBr<sub>3</sub></b> |      |      | <b>CsPbBr<sub>3</sub>/Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></b> |      |      |      |
|-----|---------------------------|------|------|--|------|------|------|
|     | Cs                        | Pb   | Br   | Cs   | Pb   | Br   | P    |
| XPS | 1.00                      | 0.86 | 3.51 | 1.00   | 1.34 | 4.42 | 0.41 |
| EDS | 1.00                      | 1.01 | 3.72 | 1.00   | 1.47 | 4.56 | 0.44 |

**Table S2** Detailed synthesis information of the samples prepared by the reprecipitation method.

|                        | CsCl   | CsBr   | CsI    | PbCl <sub>2</sub> | PbBr <sub>2</sub> | PbI <sub>2</sub> | Oct-P |
|------------------------|--------|--------|--------|-------------------|-------------------|------------------|-------|
|                        | (mmol) | (mmol) | (mmol) | (mmol)            | (mmol)            | (mmol)           | (mM)  |
| CsPbCl <sub>2</sub> Br |        | 0.4    |        | 0.4               |                   |                  | 0.4   |
| CsPbClBr <sub>2</sub>  | 0.4    |        |        |                   | 0.4               |                  | 0.4   |
| CsPbBr <sub>3</sub>    |        | 0.4    |        |                   | 0.4               |                  | 0.4   |
| CsPbBr <sub>2</sub> I  |        |        | 0.4    |                   | 0.4               |                  | 0.4   |
| CsPbBrI <sub>2</sub>   |        | 0.4    |        |                   |                   | 0.4              | 0.4   |

#### References

1. X. Li, Y. Wu, S. Zhang, B. Cai, Y. Gu, J. Song and H. Zeng, *Adv. Funct. Mater.*, 2016, **26**, 2435-2445.