

Supplementary Information

Near-Infrared-Excitable Perovskite Quantum Dots via Coupling with

Upconversion Nanoparticles for Dual-Model Anti-Counterfeiting

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I. Experimental section

1. Chemicals and Reagents

Yttrium(III) acetate hydrate ($\text{Y}(\text{CH}_3\text{CO}_2)_3$, 99.9%), ytterbium(III) acetate hydrate ($\text{Yb}(\text{CH}_3\text{CO}_2)_3$, 99.9%), thulium(III) acetate hydrate ($\text{Tm}(\text{CH}_3\text{CO}_2)_3$, 99.9%), erbium(III) acetate hydrate ($\text{Er}(\text{CH}_3\text{CO}_2)_3$, 99.9%), ammonium fluoride (NH_4F , >98%), sodium hydroxide (NaOH , >98%), cyclohexane, Cs_2CO_3 (99.9%), PbBr_2 (99.999%), PbI_2 (99.999%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) and oleylamine (OAm, 70%) were all purchased from Sigma-Aldrich. Unless otherwise noted, all the chemicals were used without further purification.

2. Characterization

UV-vis absorption spectra were conducted on a SHIMADZU UV-3600 spectrophotometer. Transmission electron microscopy (TEM) images were obtained on a JEOL-1400 transmission electron microscope (JEOL). The upconversion luminescence spectra were taken on Edinburgh FSP920 equipped with a photomultiplier in conjunction with 980 nm diode laser and a xenon arc lamp (Xe900). PL spectra of all-inorganic perovskite quantum dots (IPQDs) also were obtained on the Edinburgh FSP920 using the xenon arc lamp as the exciting light source ($\lambda_{\text{ex}} = 365$ nm). Digital photographs were taken by a Canon EOS 700D camera.

3. Synthesis of core-shell $\text{NaYF}_4:\text{Yb/Tm}$ (20/0.5 mol%)@ NaYF_4 nanoparticles

Core-shell nanoparticles $\text{NaYF}_4:\text{Yb/Tm}$ (20/0.5 mol%)@ NaYF_4 (Tm-UCNPs) adopted in this work were synthesized by coprecipitation method. The synthetic process followed a recipe from the literature with some slight modifications.¹ At first, $\text{NaYF}_4:\text{Yb/Tm}$ (20/0.5 %) core nanoparticles were synthesized. In the typical process, aqueous solutions of 1.59 mL $\text{Y}(\text{CH}_3\text{CO}_2)_3$ (0.20 mol L^{-1}), 0.40 mL $\text{Yb}(\text{CH}_3\text{CO}_2)_3$ (0.20 mol L^{-1}) and 0.10 mL $\text{Tm}(\text{CH}_3\text{CO}_2)_3$ (0.02 mol L^{-1}) were mixed with OA (3 mL) in a 50 mL two-neck flask. The mixture was heated at 150 °C and kept stirring for 30 min. Then, ODE (7 mL) was added into the mixture and kept at 150 °C for another 30 min. The heating mantle was removed and the reaction mixture was allowed to cool down to below 50 °C. A mixture of 2 mL NaOH methanol solution (0.50 mol L^{-1}) and

4 mL NH_4F methanol solution (0.40 mol L^{-1}) was quickly poured into the reaction flask. The solution temperature was heated up to $50 \text{ }^\circ\text{C}$ and kept at this temperature for 30 min. Then, the temperature was increased to $100 \text{ }^\circ\text{C}$ and the flask was connected to a Schlenk line. The mixture was kept reacting under vacuum for 15 min to remove the solvents with low boiling point and then heated to $290 \text{ }^\circ\text{C}$ under the protection of nitrogen. After 2 h, the reaction mixture was cooled down to room temperature. The mixture was transferred into centrifuge tube and added with ethanol. The resulted core nanoparticles were washed with cyclohexane and ethanol several times and re-dispersed in 4 mL cyclohexane.

The synthetic process of core-shell nanoparticles is similar to the process of core nanoparticles. An aqueous solution (2 mL) of $\text{Y}(\text{CH}_3\text{CO}_2)_3$ (0.20 mol L^{-1}) was added into OA (3 mL) in a 50 mL two-neck flask. The mixture was heated at $150 \text{ }^\circ\text{C}$ for 30 min. 7 mL ODE was followingly added into the mixture and kept at $150 \text{ }^\circ\text{C}$ for another 30 min. After the mixture was cooled down to $100 \text{ }^\circ\text{C}$, the as-synthesized $\text{NaYF}_4\text{:Yb/Tm}$ (20/0.5 %) core nanoparticles in 4 mL cyclohexane was added. After 30 min, the reaction mixture was cooled down to below $50 \text{ }^\circ\text{C}$ and a mixture of 2 mL NaOH methanol solution (0.50 mol L^{-1}) and 4 mL NH_4F methanol solution (0.40 mol L^{-1}) was quickly added into the reaction flask. The following steps were the same as the above. The resulted core-shell nanoparticles also were washed with cyclohexane and ethanol several times and re-dispersed in 4 mL cyclohexane.

4. Synthesis of core-shell $\text{NaYF}_4\text{:Yb/Er}$ (18/2 mol%)@ NaYF_4 nanoparticles

The synthetic process of core-shell nanoparticles $\text{NaYF}_4\text{:Yb/Er}$ (18/2 mol%)@ NaYF_4 (Er-UCNPs) was similar to that of Tm-UCNPs. During the core nanoparticle preparation, aqueous solutions of 1.60 mL $\text{Y}(\text{CH}_3\text{CO}_2)_3$ (0.20 mol L^{-1}), 0.36 mL $\text{Yb}(\text{CH}_3\text{CO}_2)_3$ (0.20 mol L^{-1}) and 0.04 mL $\text{Er}(\text{CH}_3\text{CO}_2)_3$ (0.20 mol L^{-1}) were mixed instead.

5. Synthesis of IPQDs

Hot injection method was utilized to synthesize IPQDs.² 0.40 g Cs_2CO_3 , 1.25 mL OA and 15 mL ODE were mixed in a 50 mL two-neck flask and kept heating at $100 \text{ }^\circ\text{C}$ under vacuum for 15 min. Then, the mixture was kept at $130 \text{ }^\circ\text{C}$ for 1 h under the

protection of nitrogen. After 1 h, the reaction temperature was increased to 150 °C for another 0.5 h until all the Cs_2CO_3 had reacted with OA to generate a clear Cs-precursor solution. 0.18 mmol PbX_2 such as PbCl_2 (0.052 g), PbBr_2 (0.069 g), PbI_2 (0.087 g) or their mixtures were mixed with 0.50 mL OA, 0.50 mL OAm and 5 mL ODE and degassed at 100 °C for 15 min. Then, the reaction mixture was kept at 130 °C for 1 h under nitrogen to dissolve all the PbX_2 salts. Subsequently, the temperature was raised up to 160 °C and kept for 10 min. Then, 0.50 mL previously prepared Cs-precursor solution was swiftly injected into the reaction mixture and the flask was immersed into ice bath after 5 s to stop the reaction. The nanocrystals were obtained through centrifuging at 6000 rpm for 8 min. The resulted products were redispersed in 4 mL cyclohexane for further use.

6. Synthesis of UCNPs/IPQDs composites

Tm-UCNPs were hybridized with IPQDs CsPbBr_3 , $\text{CsPbBr}_{1.8}\text{I}_{1.2}$, $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ and CsPbI_3 while Er-UCNPs were combined with IPQDs $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ and CsPbI_3 . The synthetic process was just a mixing step of the two kinds of nanomaterials. 1 mL the prepared IPQDs solution was diluted into 3 mL with cyclohexane, and then mixed with 200 μL UCNPs solution. The mixed solution emitted pure IPQDs luminescence instead of UCNPs emission under 980 nm laser and was further applied in anti-counterfeiting.

II. Excitation and emission spectra of IPQDs

In Fig. S1, excitation and emission spectra of IPQDs were detected to decide which kinds of IPQDs to be coupled with UCNPs. Emissions of IPQDs CsPbBr_3 , $\text{CsPbBr}_{1.8}\text{I}_{1.2}$, $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ and CsPbI_3 have no overlap of main emission peaks of Tm-UCNPs. As a result, these four kinds of IPQDs were mixed with Tm-UCNPs. Similarly, there is no cross section existing in emission spectra of IPQDs $\text{CsPbBr}_{1.2}\text{I}_{1.8}$, CsPbI_3 and Er-UCNPs. At last, IPQDs $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ and CsPbI_3 were coupled with Er-UCNPs. All the IPQDs have broad excitation spectra demonstrating all of them can be excited by the emissions of Tm-UCNPs and Er-UCNPs.

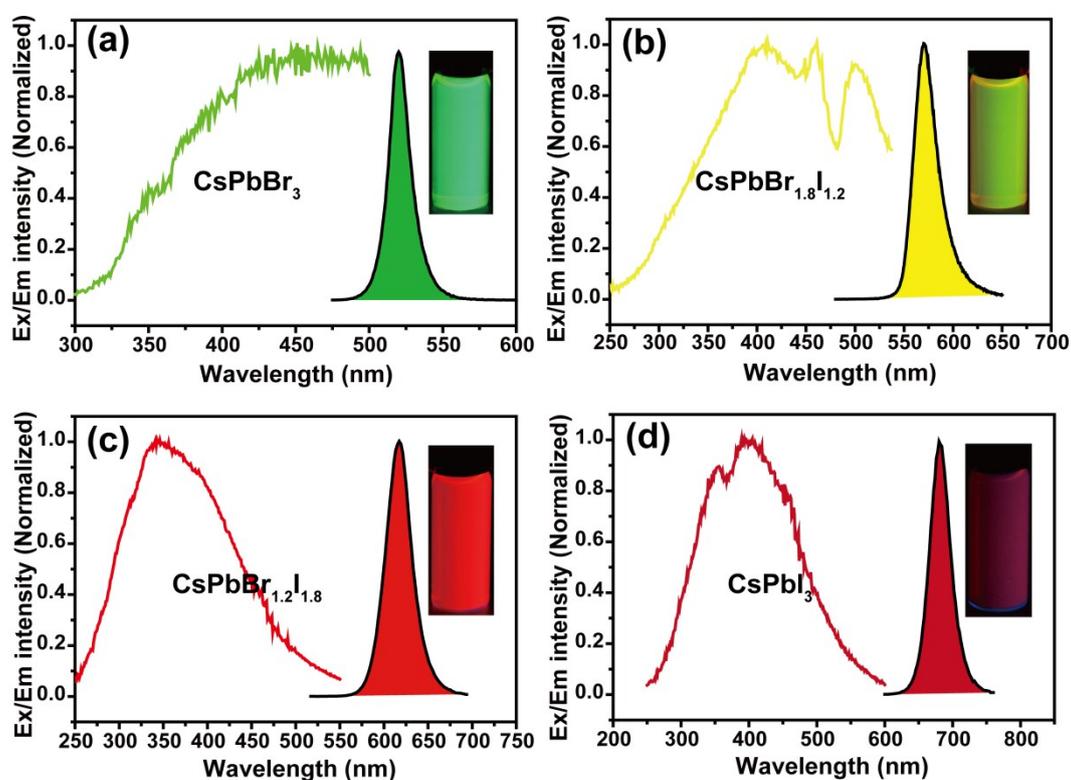


Fig. S1 The excitation and emission spectra of IPQDs CsPbBr_3 (a), $\text{CsPbBr}_{1.8}\text{I}_{1.2}$ (b), $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ (c) and CsPbI_3 (d).

III. Optimization of mixed volume of UCNPs in IPQDs solutions

Composites of Tm-UCNPs and two kinds of IPQDs (CsPbBr_3 and $\text{CsPbBr}_{1.2}\text{I}_{1.8}$) were taken as examples to optimize the mixed volume of UCNPs in IPQDs solutions. PL intensities of the mixtures exhibited obvious concentration-dependence (Fig. S2). Luminescent intensities of the mixtures increased with the increase of mixed volume of Tm-UCNPs. It was referred that more IPQDs were excited by UCNPs when UCNPs concentrations increased. At last, 200 μL UCNPs were selected to be coupled with IPQDs solutions.

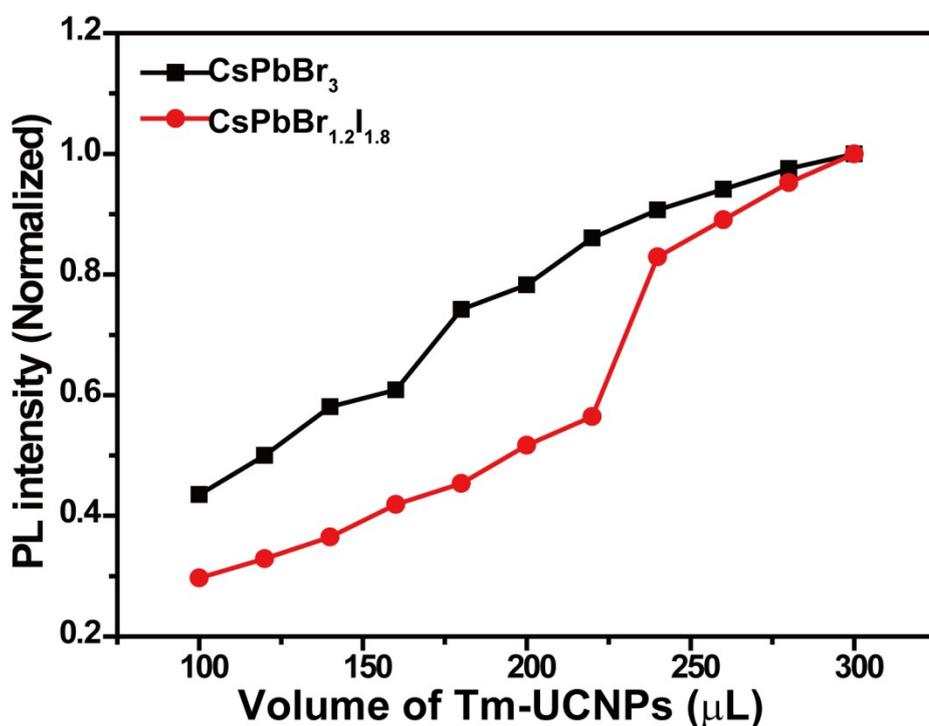


Fig. S2 Optimizing the mixed volume of Tm-UCNPs in CsPbBr_3 and $\text{CsPbBr}_{1.2}\text{I}_{1.8}$ solutions.

IV. TEM images of the UCNPs/IPQDs composites

Three kinds of composites (Tm-UCNPs/CsPbBr₃, Tm-UCNPs/CsPbI₃ and Er-UCNPs/CsPbI₃) were selected to be characterized by TEM. The TEM images clearly showed that some IPQDs were adjacent to UCNPs facilitating the energy transferring between the two kinds of materials (Fig. S3). Thus, IPQDs were successfully excited by UCNPs.

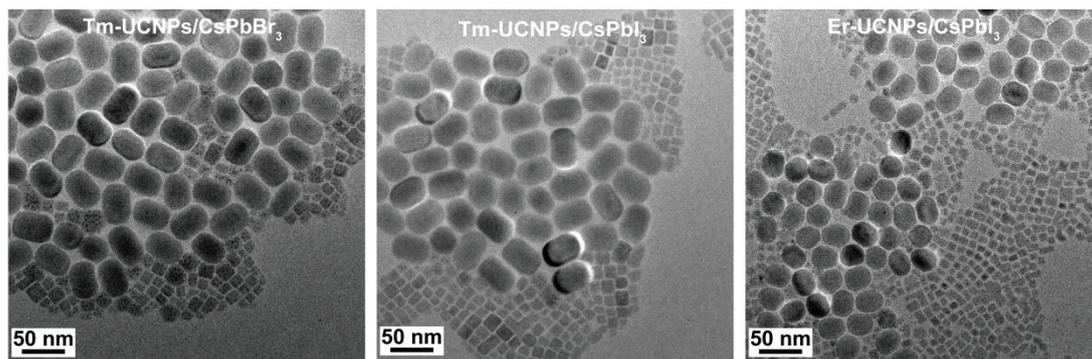


Fig. S3 TEM images of the composites of IPQDs and UCNPs.

V. Quantum yields

Although IPQDs possess a high fluorescence conversion efficiency, the fluorescence conversion efficiency of UCNP commonly is relatively low. Therefore, the quantum yields (QYs) of UCNP and UCNP/IPQDs composites are not high (Table S1). Fortunately, the excellent absorbing capability of IPQDs can mitigate this drawback in a certain degree. The UCNP/IPQDs composites give bright and pure emissions under NIR excitation.

Table S1. The QYs of the UCNP and UCNP/IPQDs composites.

Materials	Tm-UCNPs	Tm-UCNPs/CsPbBr ₃	Tm-UCNPs/CsPbBr _{1.2} I _{1.8}
QYs (%)	0.38	0.19	0.32

VI. Control experiments

Two control experiments were conducted to prove mixing was a necessary step in this work. Pure IPQDs displayed no luminescence while the composites of UCNP and IPQDs exhibited intense emissions under excitation of 980 nm laser (Fig. S4). IPQDs and UCNP were separately put in two cuvettes and excited by 980 nm laser. PL intensities of the separated IPQDs decreased sharply compared to that of the composited IPQDs (Fig. S5). The results demonstrated IPQDs were efficiently excited when they were mixed with UCNP.

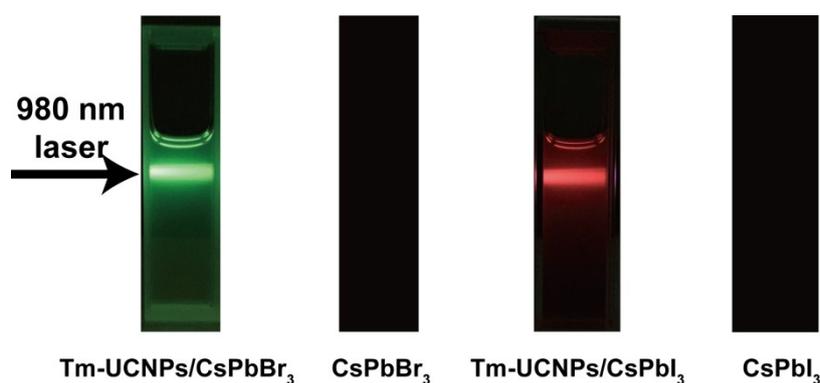


Fig. S4 PL images of the UCNP/IPQDs composites and pure IPQDs under NIR excitation.

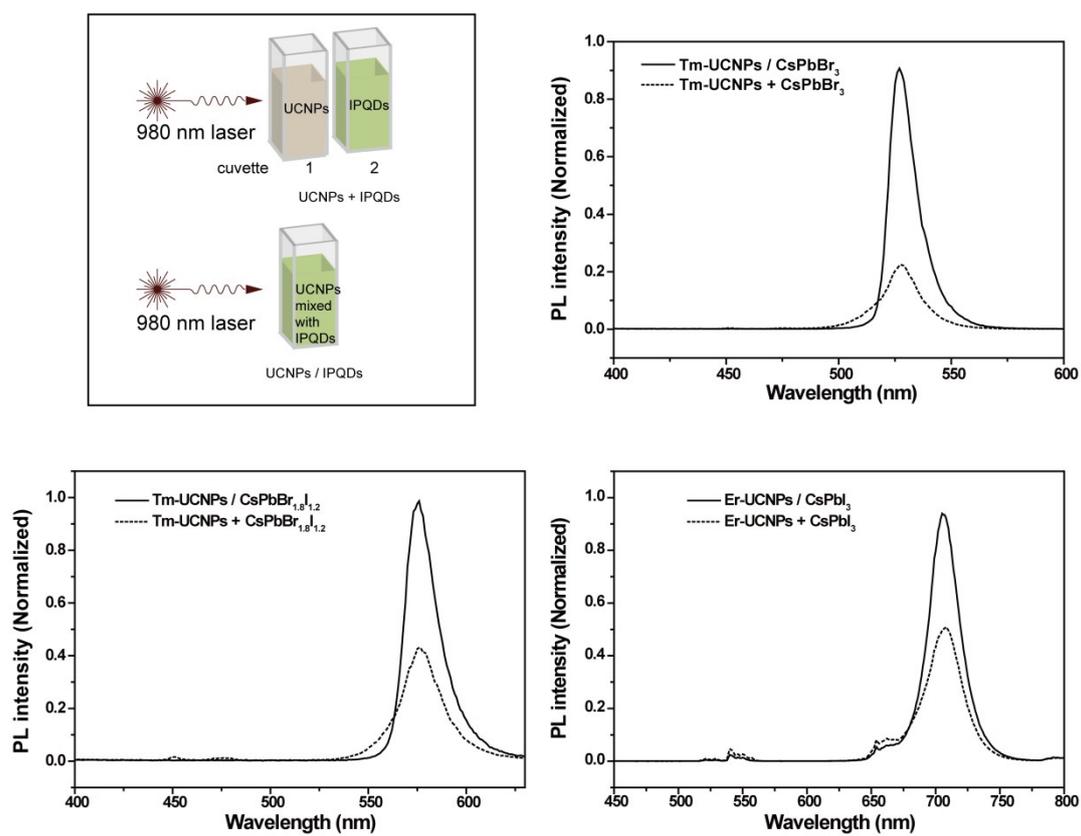


Fig. S5 The comparison of PL intensities of the composited and separated IPQDs.

References:

1. F. Wang, R. Deng and X. Liu, *Nat Protoc*, 2014, **9**, 1634.
2. Y. Wang, X. Li, J. Song, L. Xiao, H. Zeng and H. Sun, *Adv. Mater.*, 2015, **27**, 7101.