Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Orthogonal Optical Encoding via Excitation-Modulated Core-Shell Perovskite Nanocrystals

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I. Supplementary Methods

Materials

Octadecene (ODE; 90%, Sigma-Aldrich), Oleic acid (OA; 90%, Sigma-Aldrich), Oleylamine (OM; 80-90%, Sigma-Aldrich), Cesium fluoride (CsF, 99.9%, Macklin), Sodium acetate anhydrous (CH_3COONa, 99%, Tianjin Damao Chemical Reagent Factory), Yttrium(III) acetate tetrahydrate ($Y(CH_3COO)_3·4H_2O$, 99.9%, Aladdin) Erbium(III) acetate tetrahydrate ($Er(CH_3COO)_3·4H_2O$, 99.99%, Aladdin).

Methods

Synthesis of $Cs_2NaYF_6:Er^{3+}$: $Cs_2NaYF_6:Er^{3+}$ nanoparticles were synthesized by the high-temperature co-precipitation (two-step method). Briefly, 0.01~0.5 mmol $Er(CH_3COO)_3$, 0 ~ 0.49 mmol $Y(CH_3COO)_3$, and 0.5 mmol CH_3COONa were mixed with 8 mL OA, 4 mL OM, and 8 mL ODE in a 100 mL two-neck round-bottom flask. The mixture is heated to 130 ℃ and stirred continuously for 30 min to remove residual water and oxygen. After cooling to room temperature, 5 mL of methanol solution containing 3 mmol CsF was added, and the solution was stirred at 60 °C for 30 min, then heated to 140 ℃ under vacuum to remove methanol. Subsequently, the solution was heated to 320 ℃ under argon gas flow, and vigorously stirred for 60 min. After cooling to room temperature, the product was collected by centrifugation at 9,000 rpm for 5 min and washed three times with 15 mL ethanol to remove impurities. The final sample was redispersed in 5 mL of cyclohexane.

Synthesis of Cs_2NaYF_6:Er^{3+}@Cs_2NaYF_6: The synthesis method of Cs_2NaYF_6:Er^{3+}@Cs_2NaYF_6 core-shell nanoparticles is similar to that of the core. 0.5 mmol $Y(Ac)_3$ and 0.5 mmol CH_3COONa mixed with 8 mL OA, 4 mL OM, and 8 mL ODE, reacted at 130 ℃ for 30 min. Before adding CsF, 4 mL cyclohexane solution of the pre-synthesized core nanoparticles was introduced into the reaction mixture. The Core-shell nanoparticles were obtained by repeating the above reaction and washing steps.

Characterization

The morphologies of all samples are recorded by a JEM-2100 transmission electron microscope (TEM). The phase structures of all samples are characterized by the XRD-6000 X-ray diffractometer (XRD) and the KRATOS, Ultra DLD X-ray photoelectron spectrometer (XPS). The UCL spectra and decay curves are measured by a Jobin Yvon iHR550 monochromator equipped with R928 and H10220B-75 photomultiplier tubes from Hamamatsu Photonics using the light sources of laser diodes.

Note 1. UC Luminescence mechanism

The power-dependent luminescence intensity is measured to verify the UC luminescence mechanism of NPs under 980 nm and 1550 nm excitation, as shown in Fig. S4b and S5b. The numbers of pumping photons (*n*) required for specific UC transitions are determined using the relation:

$$I \propto P^n \qquad \text{(S1)}$$

where *I* and *P* represent UC luminescence intensity and pumping power density, respectively. The *n* values for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (541 nm) transition can be calculated as

1.9 for 980 nm excitation and 2.6 for 1550 nm excitation, while those for the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (654 nm) transition are calculated as 1.8 for 980 nm excitation and 2.3 for 1550 nm excitation (Fig. S4 a, b and S5 a, b). These results confirm that both the red and green emissions for 980 nm excitation follow a two-photon process, whereas these for 1550 nm excitation exhibit a three-photon process.

II. Supplementary Figures

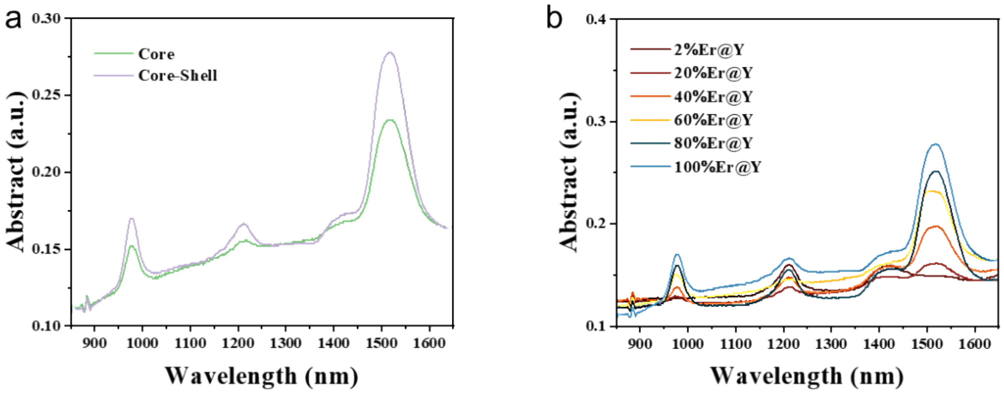

Fig. S1 (a-b) Absorption spectra of core and core-shell nanoparticles.

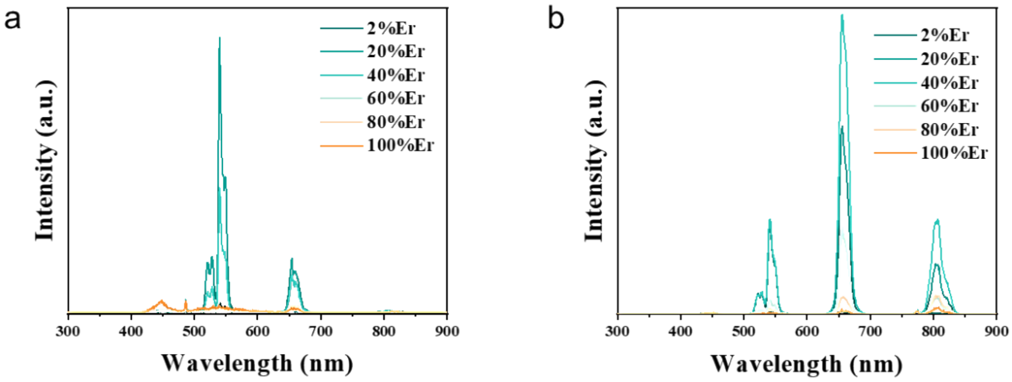

Fig. S2 Er^{3+} concentration-dependent UC luminescence spectra of Cs_2NaYF_6:xEr^{3+}@Cs_2NaYF_6 core-shell nanoparticles under 980 nm and 1550 nm excitation.

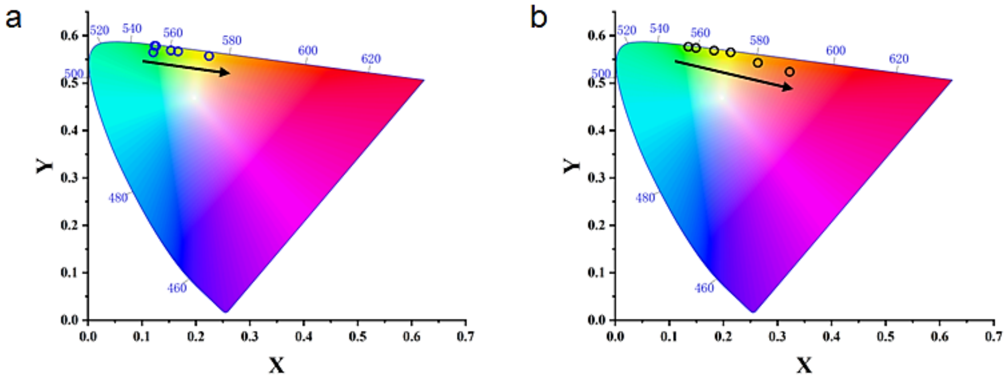

Fig. S3 (a-b) CIE coordinates of Cs_2NaYF_6:xEr^{3+}@Cs_2NaYF_6 core-shell nanoparticles under

980 and 1550 nm excitation.

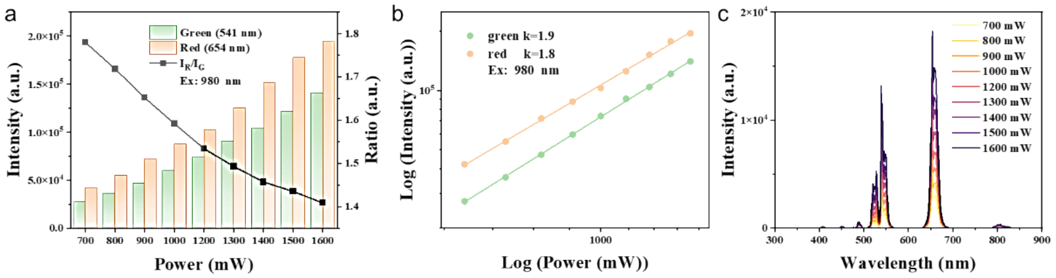

Fig. S4 (a) Power dependent integrated intensities and green (541 nm) to red emission (654 nm) ratios under 980 nm laser excitation. (b) Double logarithmic curve of luminescence intensity and versus excitation power. (c) Variable-power emission spectra excited by 980 nm laser.

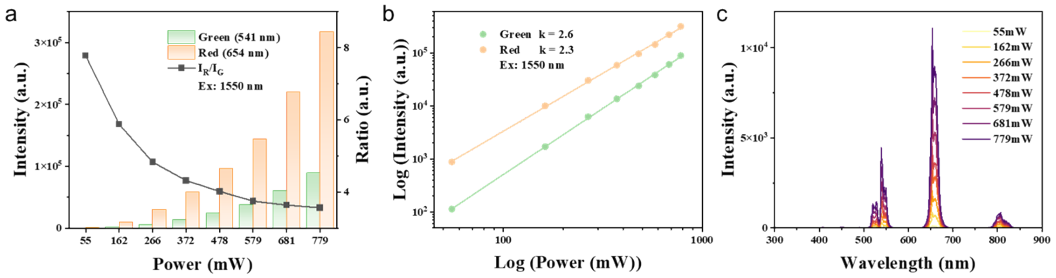

Fig. S5 (a) Power dependent integrated intensities and green (541 nm) to red emission (654 nm) ratios under 1550 nm excitation. (b) Double logarithmic curve of luminescence intensity and versus excitation power. (c) Variable-power emission spectra excited by 1550 nm laser.