Two-mode upconversion color-tuning of Er:NaYbF4 nanocrystals and

their high-efficiency photothermal conversion

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1. Experiments

1.1 Chemicals.

Lutetium (III) chloride (LuCl₃, 99.9%), ytterbium (III) chloride (YbCl₃, 99.9%), erbium (III) chloride (ErCl₃, 99.9%), yttrium (III) chloride (YCl₃, 99.9%), sodium hydroxide (NaOH, 95%), ammonium fluoride (NH₄F, 96%), oleic acid (OA, 90%), 1octadecene (ODE, 90%) were purchased from Macklin (Shanghai, China). All chemicals were used as received.

1.2 Synthesis of Er:NaYbF4 and 2Er18Yb:NaYF4 core-only nanoparticles.

OA capped 1 mol% Er³⁺ doped NaYbF₄ (1Er:NaYbF₄) nanocrystals were synthesized via a modified thermal decomposition method. In a typical experiment (Scheme 1a), totally 1 mmol of Ln chloride (Ln = Er/Yb) methanol solution (1 M), with pre-determined molar ratio, were mixed with 10 mL of OA and 15 mL of ODE in a 50 mL three-necked flask. Under the protection of argon atmosphere, after stir for 15 min at room temperature, the mixture was heated at 110 °C for 10 min to remove the residual methanol and water in the mixture. Then, the mixture was heated to 180 °C for 40 min to form a transparent solution. Stirring for 20 minutes after cooling down to room temperature, a methanol solution (13 mL) containing NH₄F (4 mmol) and NaOH (2.5 mmol) was added and stirred at 110 °C for 45 min. Next, the solution was rapidly heated to 300 °C, and maintained at this temperature for 1.5 h and then cooled down to room temperature. The resulting core-only nanocrystals were precipitated by the addition of ethanol, collected by centrifugation, washed with methanol and ethanol several times, and finally re-dispersed in 10 mL of cyclohexane. Nanocrystals with different sizes were obtained by altering the ratio of OA and ODE. 2 mol% Er³⁺ and 18 mol% Yb³⁺ doped NaYF₄ (2Er/18Yb:NaYF₄) nanocrystals were prepared following the same route.

1.3 Synthesis of Er:NaYbF4@NaLuF4 nanocrystals.

For the epitaxial growth, Lu³⁺ instead of the most popular Y³⁺ was selected for the inert layer encapsulation because the closer radius of Lu³⁺ compared to that of Yb³⁺ in the core. In a typical synthesis of core-shell nanocrystals (Scheme 1a), 0.5 mmol of Lu³⁺ (LuCl₃ methanol solution, 1 M) was added into a 50 mL flask containing 8 mL of OA and 12 mL of ODE. The core-shell nanocrystals were prepared following the same synthesis route of Er:NaYbF4. The only difference is that additional 5 mL of the as-synthesized core-only nanocrystals dispersion, containing 0.5 mmol of Er:NaYbF4 as the seeds for further epitaxial growth, was added together with the NH4F and NaOH. The final product was washed several times and redispersed in 5 mL of cyclohexane.

1.4 Application experiments

We customized a glass mold containing 21 grooves, 3 mm in length, 0.7 mm in width, and 0.5 mm in depth. These 21 grooves are arranged to form the shape of three numerals "8". We added different samples to these 21 grooves. For the "HEU" information hiding, as shown in Figure S18a, we added core-shell nanocrystal liquid to the red region and 2Er/18Yb:NaYF4 liquid to the green region. Both liquids are transparent and cannot be distinguished under sunlight. Consequently, the encrypted information, similarly as shown in Figure S18b, 8Er/2Yb:Y2O3 powder is added to the light red region and core-shell nanocrystal powder to the light green area. Both are white powders and cannot be distinguished under sunlight. So, the encrypted information is revealed by changing the pulse width.

1.5 Characterization

The crystal structures of the as-synthesized nanocrystals were identified by powder X-ray diffraction (XRD, LabX XRD-6100, Shimadzu). The diffraction patterns were recorded in the range of 2θ from 10° to 70° with a resolution of 0.02° per step. The particle morphologies were observed through transmission electron microscopy (TEM, Tecnai G2, EEI). Energy-dispersive X-ray (EDX) mapping measurements were also performed on a EEI Tecnai G2 TEM operated at 200 kV. UV-vis absorption spectra of the nanocrystals and transmittance of the nanocrystalpolymer composites were measured using a HITACHI UH5700 UV/vis-NIR scanning spectrophotometer. For the spectral measurements, a continuous wave (CW) 980 nm laser diode (LWIRL980-12W, Laser wave) was used as the pumping source. The UC spectra of the different samples were recorded by a customized spectrometer (QM8000, Horiba), a grating with 1200 grooves/mm and PMT detector were employed for the measurements within 200-900 nm, while a 600 grooves/mm grating and InGaAs detector were used for wavelength higher than 900 nm. All the obtained spectra were corrected by the build-in correction function. For the calculation of upconversion QYs (in the experiment, the samples were taken from the supernatant liquid), due to the switching of PMT and InGaAs detectors, the excitation and emission spectra of samples were corrected by dividing the measured emission intensity by the ratio of the observed spectrum of a halogen tungsten lamp to its black-body irradiation spectrum at 2832 K (Fig. S19). To avoid the signal saturation, an optical neutral density filter was applied to effectively reduce the laser power for InGaAs detector. The attenuation rate of the filter at the 980 nm wavelength is 0.64% (Fig. S20a-c). The long pulse excitation for color tuning and time-resolved spectra was achieved by modulating the CW laser into a square wave using a signal generator (DG1032Z, Rigol). The short pulse excitation for color tuning was provided by a tunable midband OPO laser as the pulse excitation source (410-2400 nm, Vibrant 355II, OPOTEK, Carlsbad, CA, USA). PL emission spectra under long and short pulse excitation were measured by highly sensitive CCD spectrometer: Horiba Lumetta, Canada.

2. Equation

This efficiency can be calculated through monitoring one heating/cooling cycle of sample cell, using the following equation:

$$\eta = \frac{hS(T_{\max} - T_0) - Q_b}{I(1 - 10^{-A})}$$
(1)

where T_{max} is the equilibrium temperature; T_0 is the initial ambient temperature; I = 950 mW is the incident laser power; Q_b , expressing heat dissipated from 980 nm light absorbed by the sample, measured to be 8.7 mW by using a quartz cuvette containing pure cyclohexane without Er:NaYbF₄ nanocrystals (Fig. S21); A is the absorbance of nanocrystals in the cuvette cell (Fig. S22). In order to calculate the heat transfer coefficient of hS from quartz cuvette to the surrounding environment, the time constant τ_s is introduced and obtained by linear fitting (Fig. S23).

3. Tables and supporting figures

Sample	T_{max} (°C)	T ₀ (°C)	А	τ (s)	hs (J/°C)
18.2 nm (C)	34.6	19.5	0.1	267.75	5.44
24.2 nm (CS)	30	19.5	0.053	338.7	4.3
24.3 nm (C)	24.2	18.9	0.009	545.55	2.67
35.2 nm (CS)	24.1	19.2	0.0135	479.4	3
66 nm (C)	26.1	19.2	0.043	392.8	3.7

 Table S1 Relevant calculation parameters of photothermal conversion efficiency

Table S2 Photothermal conversion efficiency of Er:NaYbF4 and Er:NaYbF4@NaLuF4

of different sizes.

Sample size	С	CS
18.2 nm	38%	33.5%
24.3 nm	28%	20.6%
66 nm	18.8%	/
00 1111	10.070	

a d J 100 mm b e 100 nm L f C _1 100 nm 100 nm L

Fig. S1 The TEM images of (a-c) different sizes Er:NaYbF4 core-only and (d-f) the corresponding Er:NaYbF4@NaLuF4 core-shell nanocrystals.



Fig. S2 Histogram of the core and core-shell sizes corresponding to small, medium and large nanocrystals.



Fig. S3 The TEM images of (a) 2Er:NaYbF4@NaLuF4 core-shell nanocrystals, the size is 31 nm. (b) 10Er:NaYbF4@NaLuF4 core-shell nanocrystals, the width is 31.5 nm and the length is 47.5 nm.



Fig. S4 The emission spectra of Er:NaYbF4@NaLuF4, 2Er:NaYbF4@NaLuF4 and 10Er:NaYbF4@NaLuF4 core-shell nanocrystals with different excitation power.



Fig. S5 The CIE coordinates of 1Er:NaYbF4@NaLuF4, 2Er:NaYbF4@NaLuF4 and 10Er:NaYbF4@NaLuF4 core-shell nanocrystals change with the excitation power.



Fig S6 The emission spectra (350-600 nm) of core-shell nanocrystals with the excitation power increasing (0.5 W-5 W). "*" is an emission peak of 557 nm.



Fig. S7 The luminescent intensity ratios of 407 nm to 557 nm with different power from 0.5 W to 5 W. Since the signal at 407 nm and 557 nm before 2W is very low, the data lack research value, so the data before 2W is shaded.



Fig. S8 (a) The variation of red-green emission intensity ratio of 18 nm, 24 nm and 66 nm core nanocrystals with the excitation power. (b) The corresponding CIE coordinates of 18 nm, 24 nm and 66 nm core nanocrystals change with the excitation power.



Fig. S9 (a) The variation of red-green emission intensity ratio of 24 nm, 35 nm and 79 nm core-shell nanocrystals with the excitation power. (b) The corresponding CIE coordinates of 24 nm, 35 nm and 79 nm core-shell nanocrystals change with the excitation power.



Fig. S10 Time-dependent Er^{3+} population profiles of the as-synthesized core-shell nanocrystals at 541 and 654 nm upon pulsed excitation at 980 nm.



Fig. S11 The CIE coordinate of core-shell nanocrystals under short (7 ns) and long (1.5 ms) pulse 980 nm excitation.



Fig. S12 Normalized 2Er/18Yb:NaYF₄ nanocrystals PL emission spectra (a) under short pulse (7 ns) and (b) long pulse (1.5 ms) 980 nm excitation. (c)The CIE coordinate of 2Er/18Yb:NaYF₄ nanocrystals under short (7 ns) and long (1.5 ms) pulse 980 nm excitation.



Fig. S13 The emission spectra and excitation spectra of 980nm of small core-shell nanocrystals (red) and cyclohexane (black) under (a) 1 W, (b) 1.25 W, (c) 1.5W, (d) 1.75 W, (e) 2 W, (f) 2.25 W, (g) 2.5 W, (h) 2.75 W, (i) 3 W, (j) 3.25 W excitation.



Fig. S14 The emission spectrum and excitation spectrum of 980nm of core (red), core-shell nanocrystals (green) and cyclohexane (black) under 82 W/cm² excitation.



Fig. S15 Downshifting QY of 1530 nm emissions of 24 nm core-shell nanocrystals under different excitation power densities.



Fig. S16 (a) Downshifting QY of core and core-shell nanocrystals with different sizes under 82 W/cm² excitation. (b) Total (upconversion and downshifting) QY of core and core-shell nanocrystals with different sizes under 82 W/cm² excitation.



Fig S17 The surface temperature distributions of pork under 35 second and 1.8 W (a) pulse excitation and (b) CW excitation.



Fig. S18 (a) The red region is filled with core-shell nanocrystals, the green region is filled with 2Er/18Yb:NaYF₄ in the "HEU" message encryption. (b) The light red region is filled with 8Er/2Yb:Y₂O₃ nanocrystals, the light green region is filled with core-shell nanocrystals in the "HEU" message encryption.



Fig. S19 The irradiance spectra in the visible region (red) and near infrared region (purple) were measured using a halogen lamp and the irradiance spectra of the Planck blackbody radiation of 2832 K(gray). The purple shaded area a represents part of the upconversion emission and the yellow shaded area represents a part of the near-infrared emission.



Fig. S20 (a) The decay rate of the optical attenuator at 980 nm by a microwatt power densitometer (150 ~ 750 μ W). (b) The decay rate of the optical attenuator at 980 nm by a milliwatt power densitometer (10 ~ 20 mW). (c) The transmission spectrum of the optical attenuator by the UV/vis-NIR scanning spectrophotometer.



Fig. S21 The absorption spectrum of cyclohexane (855 \sim 1150 nm). At 980nm, A $_{37}$ is 0.004.



Fig. S22 (a) The absorption spectrum of 18 nm, 24 nm and 66 nm core nanocrystals ($855 \sim 1150$ nm). (b) The absorption spectrum of 24 nm, 35 nm and 79 nm core-shell nanocrystals ($855 \sim 1150$ nm).



Fig S23 (a) Variation of time vs. T function of the 18 nm, 24 nm and 66 nm core nanocrystals, from which τ s constant can be calculated through the linear fitting. (b) Variation of time vs. T function of 24 nm, 35 nm and 79 nm core-shell nanocrystals.