

Supporting Information

**Opposite luminescence thermal behavior of upconversion
core/shell nanocrystals for anticounterfeiting**

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A. Nanocrystals synthesis

1. Materials

Holmium(III) acetate hydrate (99.9%), ytterbium(III) acetate tetrahydrate (99.9%), gadolinium(III) acetate hydrate (99.9%), sodium hydroxide (NaOH, $\geq 98\%$), ammonium fluoride (NH_4F , $\geq 98\%$), sodium trifluoroacetate (Na-TFA, 98%), 1-octadecene (ODE, 90%) and oleic acid (OA, 90%) were all purchased from Sigma-Aldrich and used as starting materials without further purification.

2. Synthesis of core nanocrystals

Hexagonal (β) phase $\text{NaGdF}_4\text{:Yb/Ho}$, or Tm core nanocrystals were synthesized using a coprecipitation method.^[1] In a typical synthesis, 1 mmol of lanthanide acetates ($\text{Gd/Yb/Ho}=78:20:2$, $\text{Gd/Yb/Tm}=79:20:1$, mol%) were added to a 100 mL round bottom flask containing 10 mL of OA and 15 mL of ODE. The mixed solution was heated slowly to 140 °C under vacuum with magnetic stirring and then kept for 30 min until it became clear. With the gentle flow of argon gas through the reaction flask, the solution was cooled slowly to room temperature. Subsequently, the methanol solution dissolved with 4 mmol of NH_4F and 2.5 mmol of NaOH was added and kept at 50 °C for 30 min with vigorous stirring. Then, the mixed solution was heated up to 70 °C to evaporate methanol and to 120 °C to evaporate the residual water. Finally, the solution was heated to 300 °C as quickly as possible in an argon atmosphere and kept at this temperature for 90 min for complete reaction and crystal formation. After reaction and cooling down to room temperature, the obtained nanoparticles were precipitated by addition of ethanol, collected by centrifugation, washed with ethanol three times, and finally dried in an oven at 60 °C for further characterization.

3. Synthesis of core/shell nanocrystals^[1]

Preparation of the inert-shell precursor Gd-OA

7.5 mmol of gadolinium(III) acetate hydrate, 10 mL of OA and 15 mL of ODE were added to a 100 mL flask, and then the mixed solution was heated at 140 °C under vacuum with vigorous stirring until a clear solution formed. After that, the solution was cooled down to room temperature and the colorless Gd-OA (0.3 mol/L) precursor solution was obtained.

Preparation of the active-shell precursor Gd/Yb-OA

7.5 mmol of lanthanide acetates (Gd/Yb =80:20, mol%), 10 mL of OA and 15 mL of ODE were added to a 100 mL flask. The mixed solution was heated at 140 °C under vacuum with vigorous stirring until a clear Gd/Yb-OA (0.3 mol/L) precursor solution was obtained.

Preparation of the Na-TFA-OA precursor

8 mmol of Na-TFA and 20 mL of OA was loaded in a 100 mL flask and heated at 50 °C for 60 min under vacuum with vigorous stirring, until a clear Na-TFA-OA precursor solution (0.4 mol/L) was obtained.

Synthesis of NaGdF₄:Yb/Ho@NaGdF₄:20%Yb active-shell nanocrystals and NaGdF₄:Yb/Tm@NaGdF₄ inert-shell nanocrystals

In a typical synthesis, 8 mL of OA and 12 mL of ODE was added to a 100 mL flask, followed by addition of 5 mL cyclohexane solution containing pre-prepared NaGdF₄:Yb/Ho, or Tm core nanospheres (0.5 mmol) under vigorous stirring with gentle flow of argon gas. Then the mixed solution was heated at 75 °C for 10 min under vacuum to evaporate cyclohexane. After the cyclohexane was completely removed under vacuum, the system was switched to an argon flow and the solution was quickly heated to 300 °C. Subsequently, 2 mL of the RE-OA (active shell: Gd/Yb-OA; inert shell: Gd-OA; 0.3 mol/L) precursor solution and 3 mL of Na-TFA-OA (0.4 mol/L)

precursor solution was alternately added into the flask at 300 °C. The injection cycle of shell precursors was performed for several times and the interval time between each injection was kept at 15 min. The resulting solution was then kept at 300 °C for 30 min. Finally, the solution was cooled down to room temperature and the obtained products were separated via centrifugation. The core/shell nanoparticles were then washed three times with ethanol and dried in an oven at 60 °C for further characterization. The shell thickness was controlled by adjusting the injection cycles of the shell precursors: one time for the 1.5 nm-thick shell, two times for 2.6 nm and three times for 3.5 nm.

B. Screen printing

The patterns were printed using a modification of a previously reported procedure.^[2] In a typical fabrication, 30 mg of the hybrids consisting of NaGdF₄:Yb/Ho@NaGdF₄:Yb active-shell nanocrystals and NaGdF₄:Yb/Tm@NaGdF₄ inert-shell nanocrystals (mass ratio = 700: 1) with certain weight ratios were dispersed into 100 μL terpineol. Subsequently, 24 mg of ethyl cellulose was mixed with the above solution. The mixture was sonicated for 5 min in the hot water bath. Then, the as-prepared upconversion fluorescent inks were printed on the paper through a 300 mesh counts screen to obtain various patterns.

C. Characterizations

Low-resolution and high-resolution transmission electron microscopy (TEM) images were taken with a Tecnai G2 microscope. Powder X-ray diffraction (XRD) data was collected by a Shimadzu XD-3A X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Upconversion luminescence (UCL) spectra were collected by a portable spectrometer (Maya2000Pro, Ocean Optics Co.) using a continuous 975 nm diode laser as the excitation source. The temperature-dependent UCL spectra of solid-state nanocrystals were measured in various atmospheres with the aid of a temperature-controlled heating cell. Temperature-dependent photoluminescence dynamics was investigated by a FLS1000 fluorescence spectrometer (Edinburgh Instruments) upon excitation with a pulsed 975 nm laser. Luminescent images of the printed patterns under the 975 nm laser irradiation were taken by a digital camera of iPhone 7 (Apple Inc.).

D. Data processing

1. Lifetime calculation

The average luminescent lifetimes were evaluated *via* the following equation:

$$\tau = \frac{1}{I_0} \int I(t) dt \quad (\text{S1})$$

where $I(t)$ is the time-dependent luminescence intensity and I_0 is the peak intensity.

2. color shift calculation

To quantitatively evaluate the color-tunable ability, the temperature-induced color change (Δc) is defined by the following equation:^[2]

$$\Delta c = \sqrt{(\mu'_t - \mu'_o)^2 + (v'_t - v'_o)^2 + (\omega'_t - \omega'_o)^2} \quad (\text{S2})$$

where $\mu' = 4x/(3-2x+12y)$, $v' = 9y/(3-2x+12y)$, and $\omega' = 1-\mu'-v'$. (μ' , v') and (x , y) represent the chromaticity coordinates in uniform color space and in CIE 1931 color space, respectively, while o and t refer to the chromaticity coordinates at 30 and 150 °C, respectively.

E. Supplementary figures

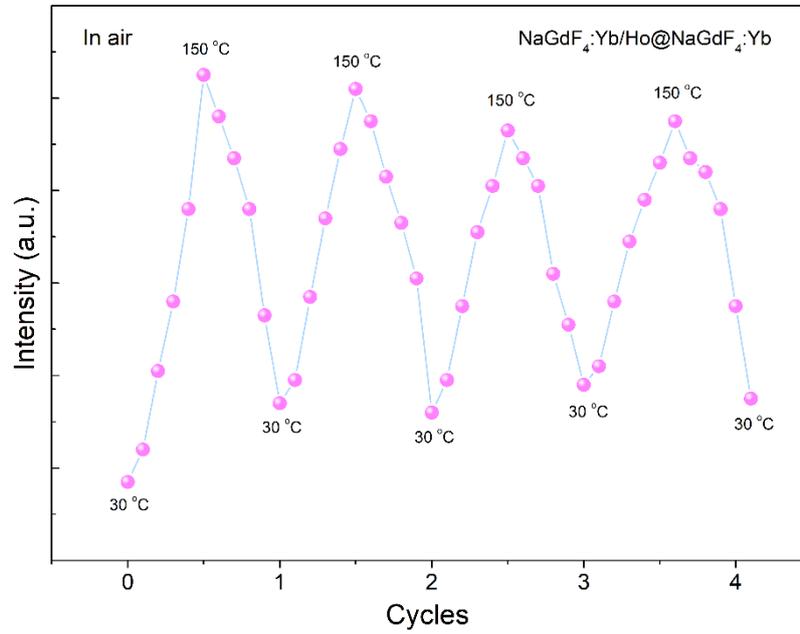


Figure S1. Integrated UCL intensity of NaGdF₄:20%Yb/2%Ho@NaGdF₄:20%Yb active-shell nanocrystals for four heating-cooling cycles in air.

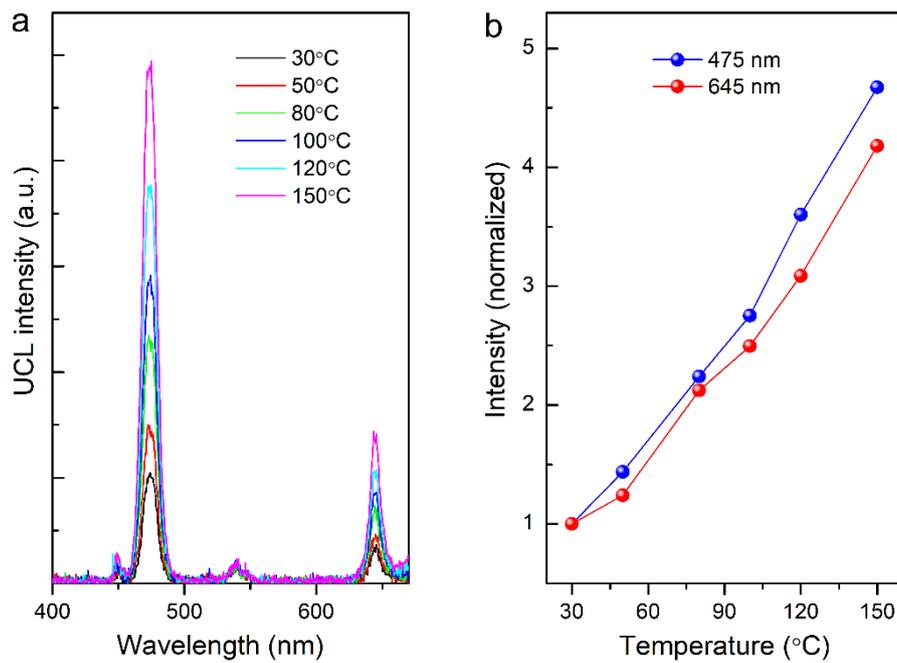


Figure S2. UCL spectra and integrated intensities of NaGdF₄:Yb/Tm core nanocrystals at elevated temperature from 30 °C to 150 °C in air.

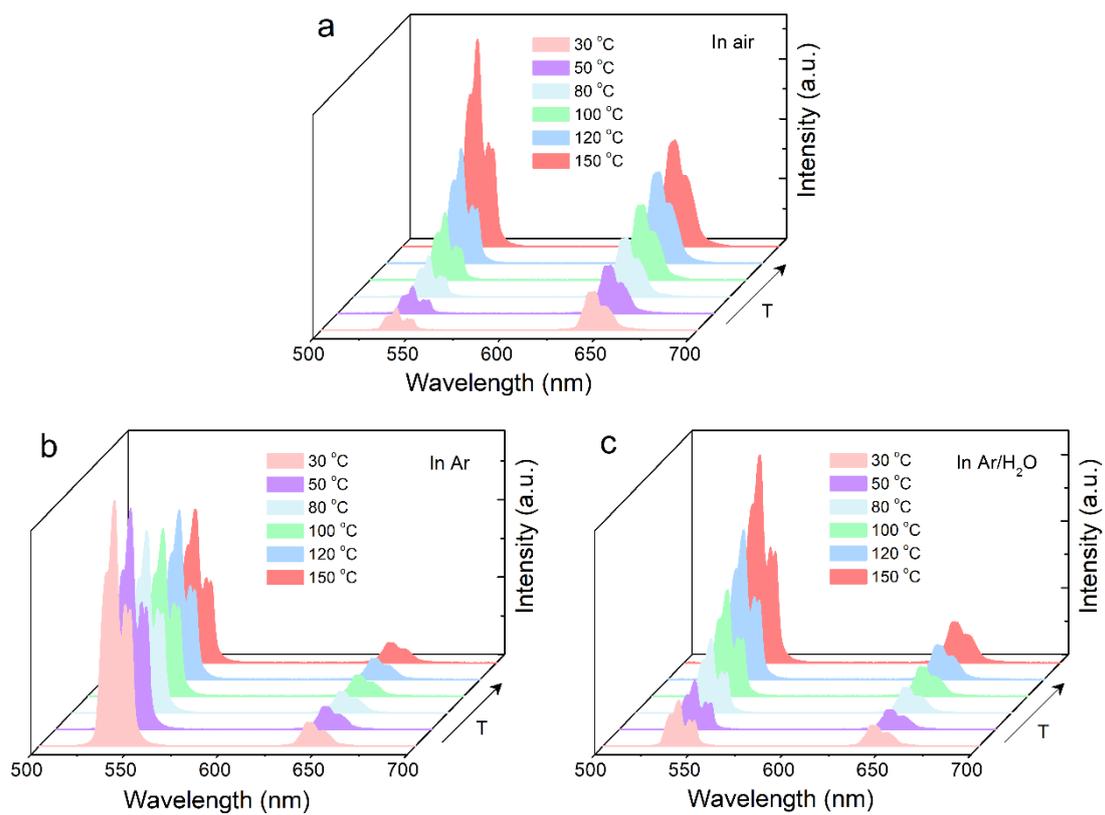


Figure S3. Temperature-dependent UCL spectra of NaGdF₄:Yb/Ho@NaGdF₄:20%Yb active-shell nanocrystals in (a) air, (b) Ar, and (c) Ar/H₂O atmospheres at elevated temperature from 30 °C to 150 °C.

F. References

- [1] Y. Hu, Q. Shao, P. Zhang, Y. Dong, F. Fang, J. Jiang, *J. Phys. Chem. C* **2018**, *122*, 26142–26152.
- [2] Y. Hu, Q. Shao, X. Deng, D. Song, S. Han, Y. Dong, J. Jiang, *J. Mater. Chem. C* **2019**, *7*, 11770–11775.