

Supporting Information

Thermally induced multicolor emissions of upconversion hybrids with large color shifts for anticounterfeiting

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A. Nanocrystal synthesis

1. Synthesis of β -NaYF₄:Yb/Ln microrods (MRs)

Hexagonal (β) phase NaYF₄:Yb/Ln (Ln = Er, Ho/Ce, or Tm) MRs were synthesized *via* a solvothermal method.¹⁻³ In a typical synthesis, NaOH (0.75 g, 18.75 mmol) was first dissolved in 3.75 mL of DI water, followed by addition of 12.5 mL of OA and 12.5 mL of ethanol under vigorous stirring. Thereafter, an aqueous solution of NH₄F (2 mol/L, 2.5 mL) was added to form a turbid mixture. Subsequently, a 5-mL aqueous solution of lanthanide acetates (Y/Yb/Er = 78:20:2, Y/Yb/Ce/Ho = 48:20:30:2, Y/Yb/Tm = 79.8:20:0.2, mol%; 0.2 mol/L) was added and the solution was kept stirring for 20 min. The resulting mixture was transferred into a 50-mL Teflon-lined autoclave and heated to 220 °C for 12 h. After cooling down to room temperature, the obtained MRs were isolated by centrifugation, washed with water and ethanol three times, and finally dried in an oven at 60 °C for further characterization.

2. Synthesis of β -NaGdF₄:Yb/Ln core nanocrystals (NCs)

β -NaGdF₄:Yb/Ln (Ln = Er, Ho/Ce, or Tm) core NCs were synthesized using a modification of a previously reported procedure.⁴ In a typical synthesis, 1 mmol of lanthanide acetates (Gd/Yb/Er = 78:20:2, Gd/Yb/Ce/Ho = 48:20:30:2, 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 NH₄F 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 NaGdF₄:Yb/Ln@NaGdF₄:xYb (x = 5%, 20%, 100%) core/active-shell nanocrystals *via* a layer-by-layer method⁵

Preparation of the active shell precursor 100%Yb-OA

7.5 mmol of ytterbium(III) acetate tetrahydrate, 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 Yb-OA (0.3 mol/L) precursor solution was obtained.

Preparation of the active shell precursor 80%Gd/20%Yb-OA

The active shell precursor 80%Gd/20%Yb-OA were prepared in an identical procedure as that of Yb-OA, except for that a mole ratio of Gd/Yb = 80:20 was used in the synthesis.

Preparation of the active shell precursor 95%Gd/5%Yb-OA

The active shell precursor 95%Gd/5%Yb-OA were prepared in an identical procedure as that of Yb-OA, except for that a mole ratio of Gd/Yb = 95:5 was used in the synthesis.

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/Ln@NaYbF₄ core/shell NCs

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/Ln core nanocrystals (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 Yb-OA precursor solution was added into the flask. After 10 min, 3 mL of Na-TFA-OA (0.4 mol/L) precursor solution was added into the flask at 300 °C, and the resulting solution was then kept at 300 °C for 15 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.

Synthesis of NaGdF₄:Yb/Ln@NaGdF₄:20%Yb core/shell NCs

NaGdF₄:Yb/Ln@NaGdF₄:20%Yb core/shell NCs were synthesized in an identical procedure as that of NaGdF₄:Yb/Ln@NaYbF₄ NCs, except for that 80%Gd/20%Yb-OA precursor was used in the synthesis.

Synthesis of NaGdF₄:Yb/Ln@NaGdF₄:5%Yb core/shell NCs

NaGdF₄:Yb/Ln@NaGdF₄:5%Yb core/shell NCs were synthesized in an identical procedure as that of NaGdF₄:Yb/Ln@NaYbF₄ NCs, except for that 95%Gd/5%Yb-OA precursor was used in the synthesis.

B. Method for lifetime determination

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.

C. Screen printing

The patterns were printed using a modification of a previously reported procedure.⁶ In a typical fabrication, 30 mg of the hybrids consisting of NaYF₄:Yb/Ln microrods and NaGdF₄:Yb/Ln@NaYbF₄ nanocrystals with certain weight ratios were dispersed into 100 μL terpineol (Ln = Er, Ho/Ce, or Tm). 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.

D. Supplementary figures

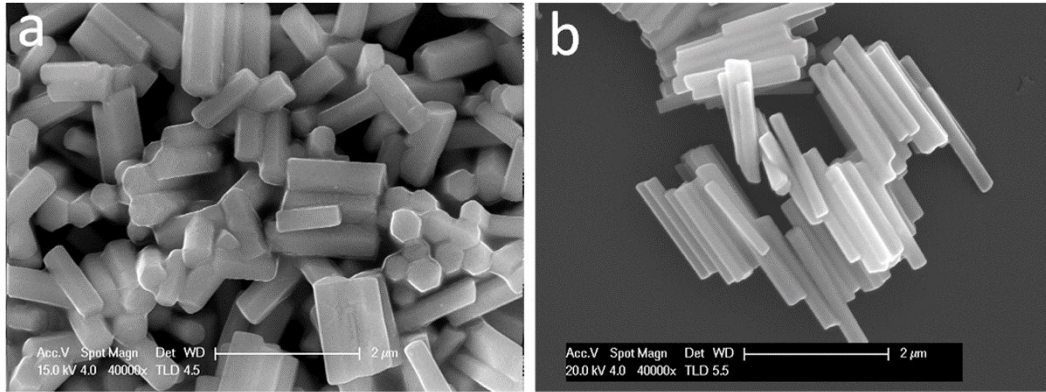


Figure S1. SEM images of (a) $\text{NaYF}_4:20\%\text{Yb}/30\%\text{Ce}/2\%\text{Ho}$ ($\sim 1180 \times 420$ nm) and (b) $\text{NaYF}_4:20\%\text{Yb}/0.2\%\text{Tm}$ ($\sim 1470 \times 180$ nm) microrods. Noting that the sectional dimension of $\text{Ho}^{3+}/\text{Ce}^{3+}$ doped microrods is larger than that of Er^{3+} or Tm^{3+} doped ones due to the incorporation of 30% Ce^{3+} ions.

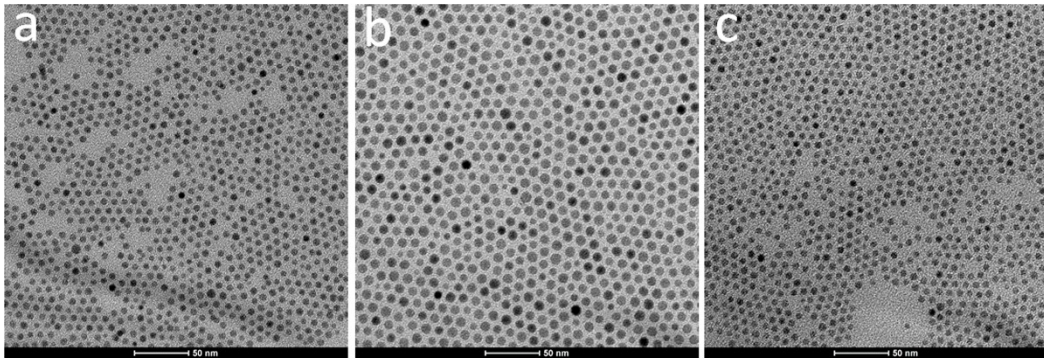


Figure S2. TEM images of (a) NaGdF₄:20%Yb/2%Er (~5.3 nm), (b) NaGdF₄:20%Yb/30%Ce/2%Ho (~8.7 nm) and (c) NaGdF₄:20%Yb/1%Tm (~5.4 nm) core-only nanocrystals.

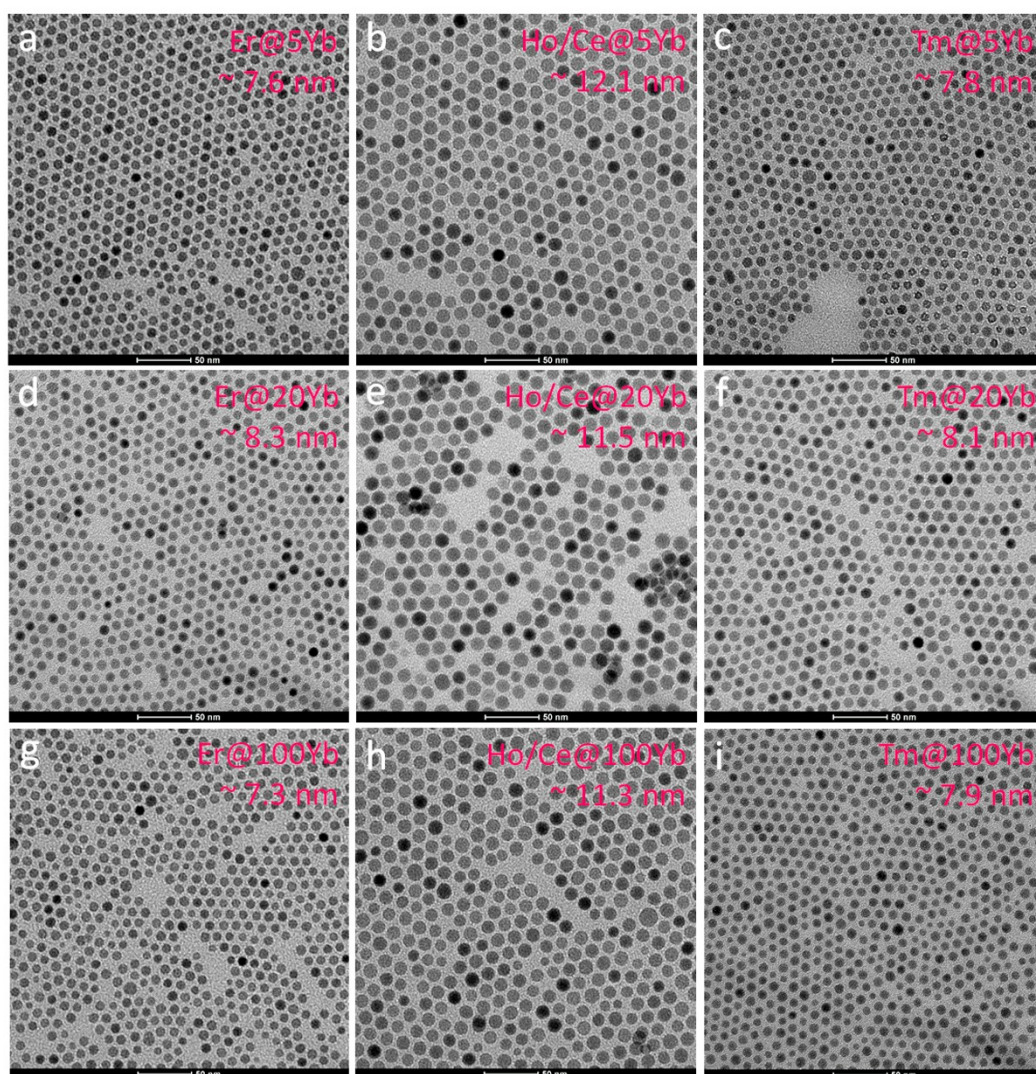


Figure S3. TEM images of (a-c) $\text{NaGdF}_4:20\%\text{Yb}/\text{Ln}@ \text{NaGdF}_4:5\%\text{Yb}$ ($\text{Ln}@5\text{Yb}$), (d-f) $\text{NaGdF}_4:20\%\text{Yb}/\text{Ln}@ \text{NaGdF}_4:20\%\text{Yb}$ ($\text{Ln}@20\text{Yb}$), and (g-i) $\text{NaGdF}_4:20\%\text{Yb}/\text{Ln}@ \text{NaYbF}_4$ ($\text{Ln}@100\text{Yb}$) NCs ($\text{Ln} = 2\%\text{Er}, 30\%\text{Ce}/2\%\text{Ho}$, or $1\%\text{Tm}$).

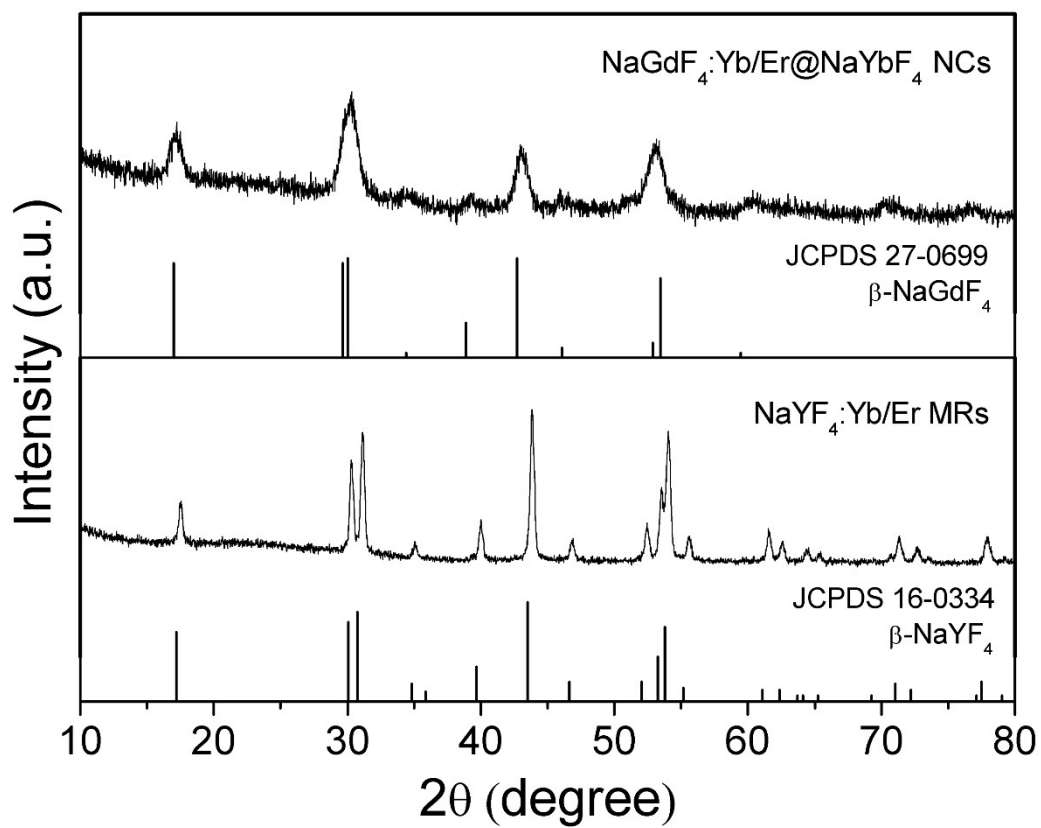


Figure S4. XRD patterns of $\text{NaGdF}_4:20\%\text{Yb}/2\%\text{Er}@ \text{NaYbF}_4$ nanocrystals (NCs) and $\text{NaYF}_4:20\%\text{Yb}/2\%\text{Er}$ microrods (MRs).

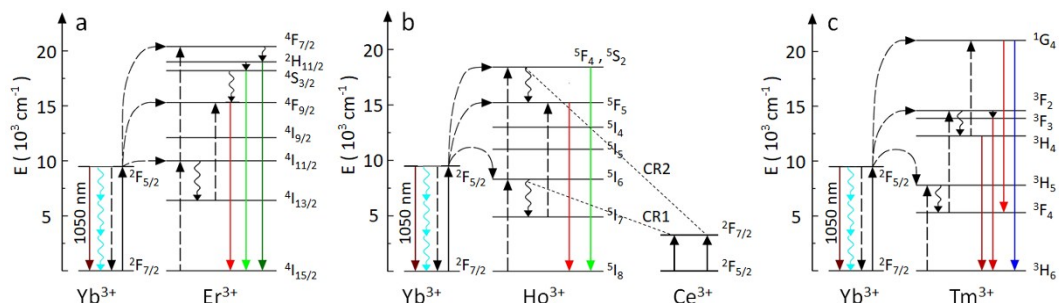


Figure S5. Simplified energy level diagrams of (a) Yb/Er, (b) Yb/Ho/Ce and (c) Yb/Tm UC systems. The blue wave arrows denote the multiphonon relaxation of $^2F_{5/2}$ state of Yb^{3+} caused by the quenching of surface-adsorbed water molecules. In the Yb/Er system, Er^{3+} ions show the dominant green emission around 540 nm ($^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$) as well as the relative weak red emission at 655 nm ($^4F_{9/2} \rightarrow ^4I_{15/2}$). Thus, Yb/Er doped UC materials mainly provide green emissions in the UC hybrids. In the Yb/Ho/Ce system, Ce^{3+} ions would quench the green emission of Ho^{3+} by cross-relaxation, leading to the dominant red emission of Ho^{3+} at ~ 650 nm ($^5F_5 \rightarrow ^5I_8$). In the Yb/Tm system, Tm^{3+} ions exhibit the dominant blue emission around 475 nm ($^1G_4 \rightarrow ^3H_6$), as well as the emissions at 655 nm ($^1G_4 \rightarrow ^3F_4$) and 700 nm ($^3F_3 \rightarrow ^3H_6$). The Yb/Ho/Ce and Yb/Tm doped UC materials mainly provides red and blue emissions in the UC hybrids, respectively.

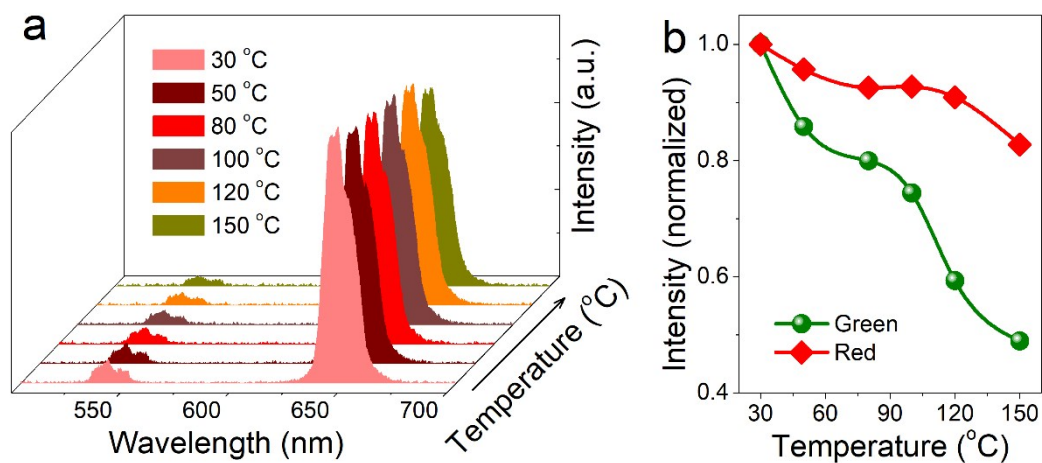


Figure S6. (a) Temperature-dependent UCL spectra and (b) integrated emission intensities of NaYF₄:20%Yb/30%Ce/2%Ho microrods. Noting that the integrated intensities are normalized to that at 30 °C for each emission band (975 nm laser power density: 1.2 W/cm²).

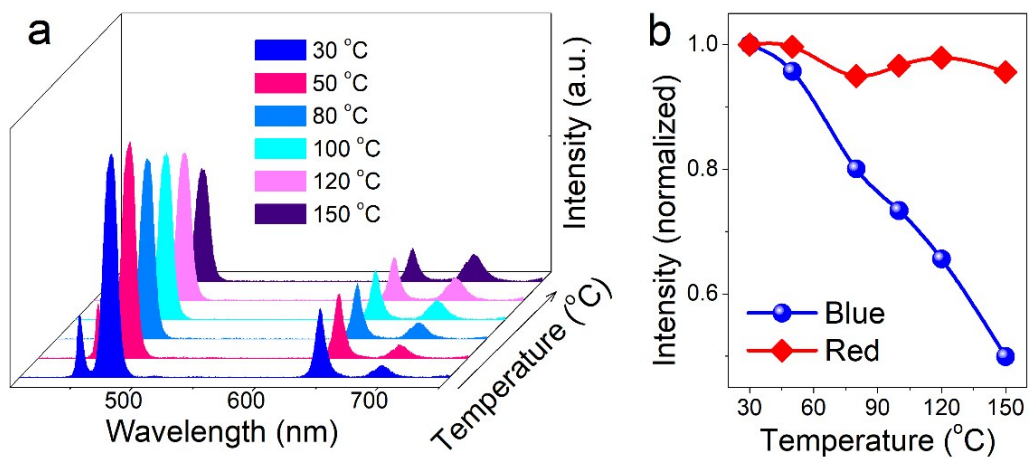


Figure S7. (a) Temperature-dependent UCL spectra and (b) integrated emission intensities of NaYF₄:20%Yb/0.2%Tm microrods. Noting that the integrated intensities are normalized to that at 30 °C for each emission band (975 nm laser power density: 1.2 W/cm²).

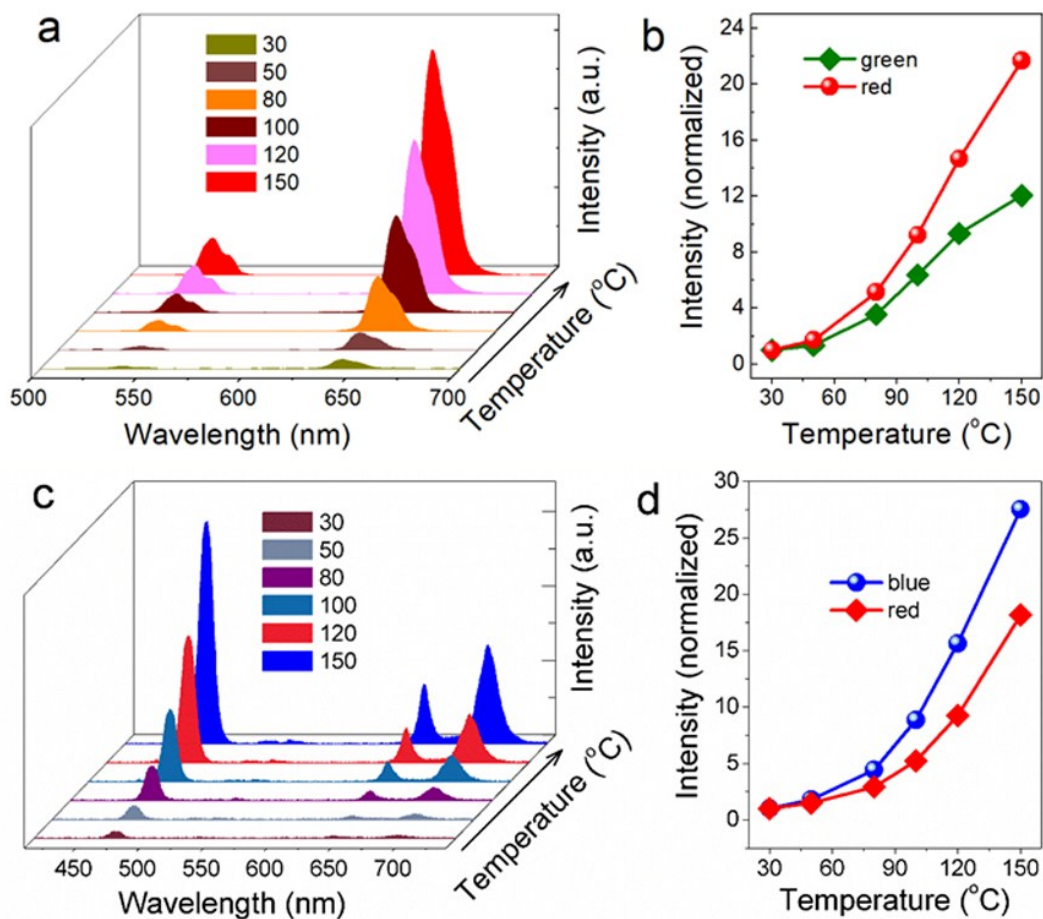


Figure S8. Temperature-dependent UCL spectra and integrated intensities of (a-b) NaGdF₄:20%Yb/30%Ce/2%Ho@NaYbF₄ and (c-d) NaGdF₄:20%Yb/1%Tm@NaYbF₄ nanocrystals, respectively. Noting that the integrated intensities are normalized to that at 30 °C for each emission band (975 nm laser power density: 1.2 W/cm²).

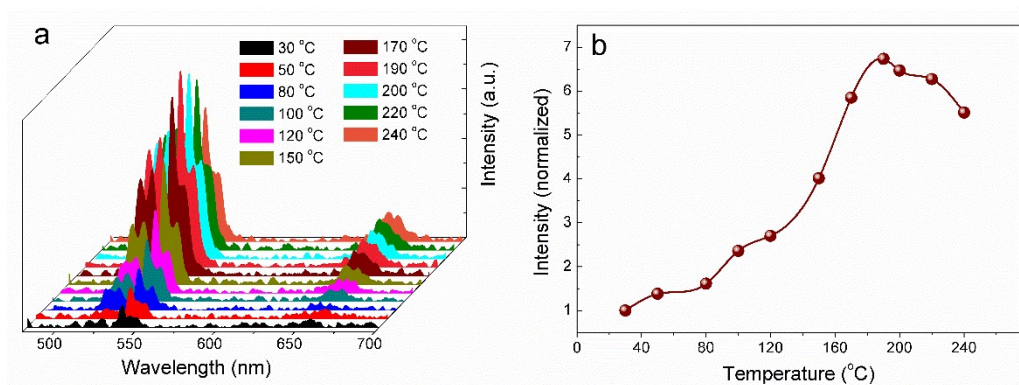


Figure S9. (a) Temperature-dependent UCL spectra and (b) integrated intensities of NaGdF₄:20%Yb/2%Er@NaYbF₄ core/shell NCs (power density: 1.2 W/cm²).

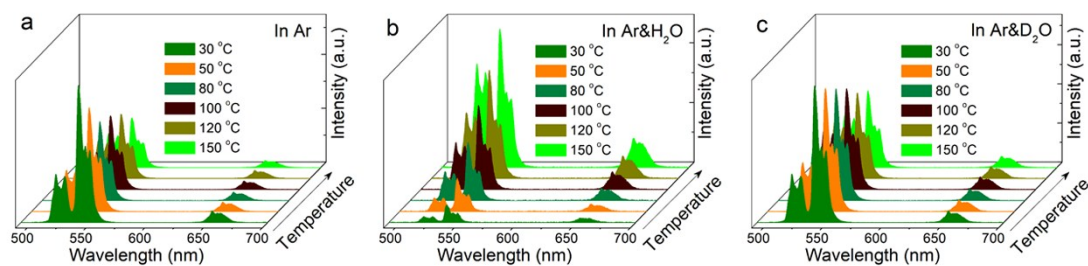


Figure S10. Temperature-dependent UCL spectra of NaGdF₄:20%Yb/2%Er@NaYbF₄ nanocrystals (a) in Ar, (b) in Ar/H₂O and (c) in Ar/D₂O (laser power density: 1.2 W/cm²).

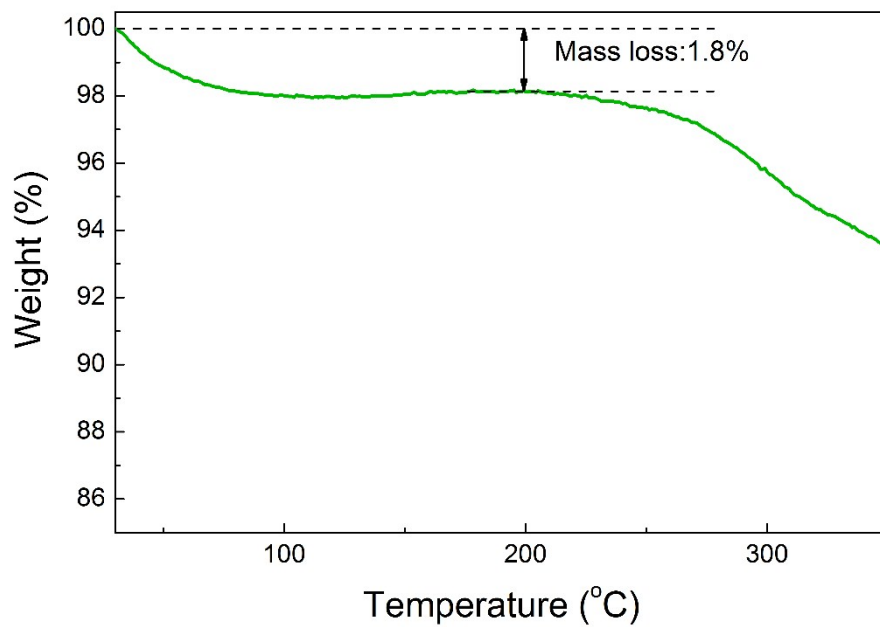


Figure S11. Thermogravimetric analysis of NaGdF₄:20%Yb/2%Er@NaYbF₄ NCs (30–350 °C, 5 °C/min).

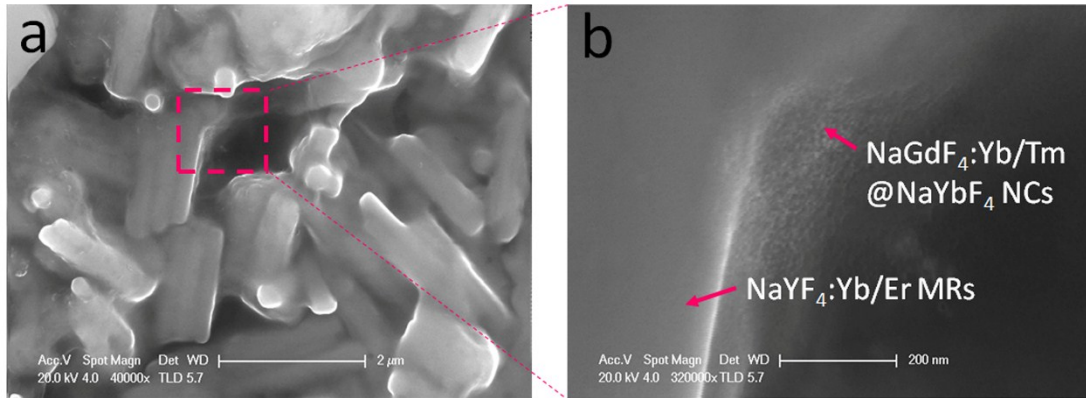


Figure S12. (a) SEM image and (b) partial enlarged detail of the hybrid by mixing NaYF₄:20%Yb/2%Er microrods (MRs) and NaGdF₄:20%Yb/1%Tm@NaYbF₄ nanocrystals (NCs).

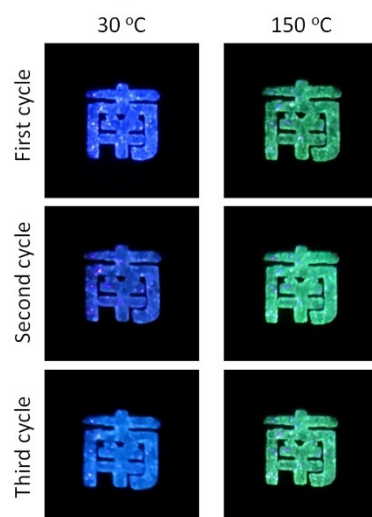


Figure S13. Color changes of the printed pattern by the H-BG ink under three heating-cooling cycles (power density: 1.2 W/cm²).

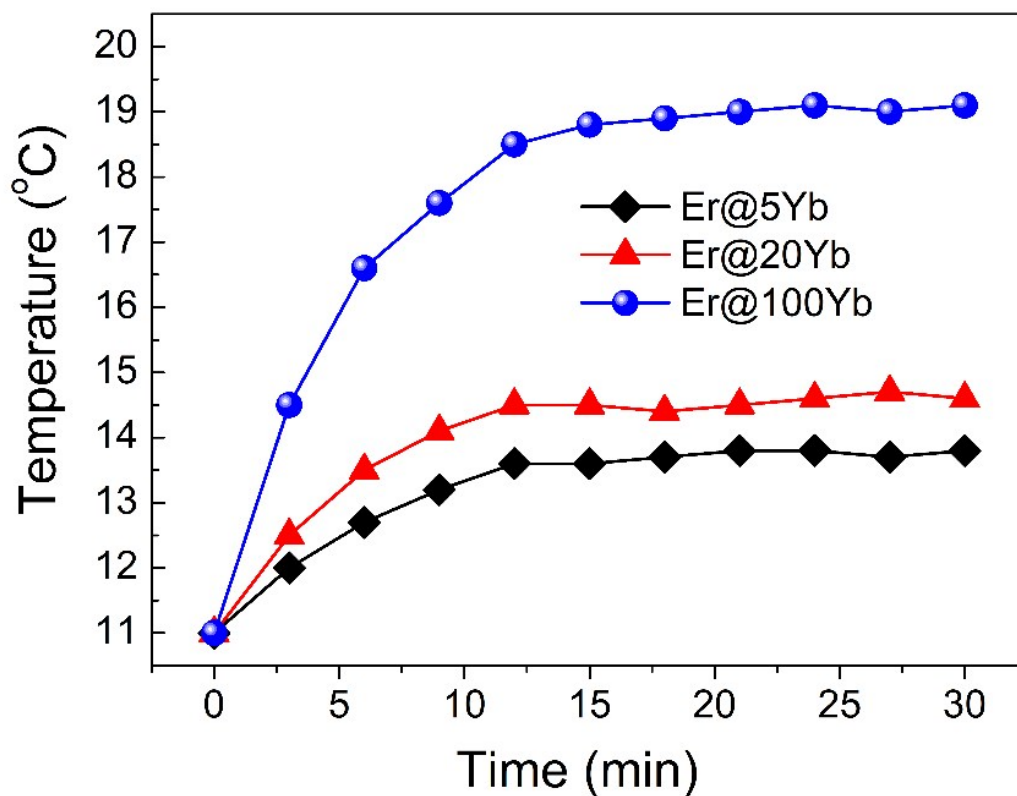


Figure S14. The temperatures changes of the colloidal solution of $\text{NaGdF}_4:\text{Yb,Er@NaGdF}_4:5\%\text{Yb}$ (Er@5Yb), $\text{NaGdF}_4:\text{Yb,Er@NaGdF}_4:20\%\text{Yb}$ (Er@20Yb) and $\text{NaGdF}_4:\text{Yb,Er@NaYbF}_4$ (Er@100Yb) nanocrystals in toluene. Noting that the laser power density is 3.6 W/cm^2 and the colloidal concentration is 10 mg/mL for measurements.

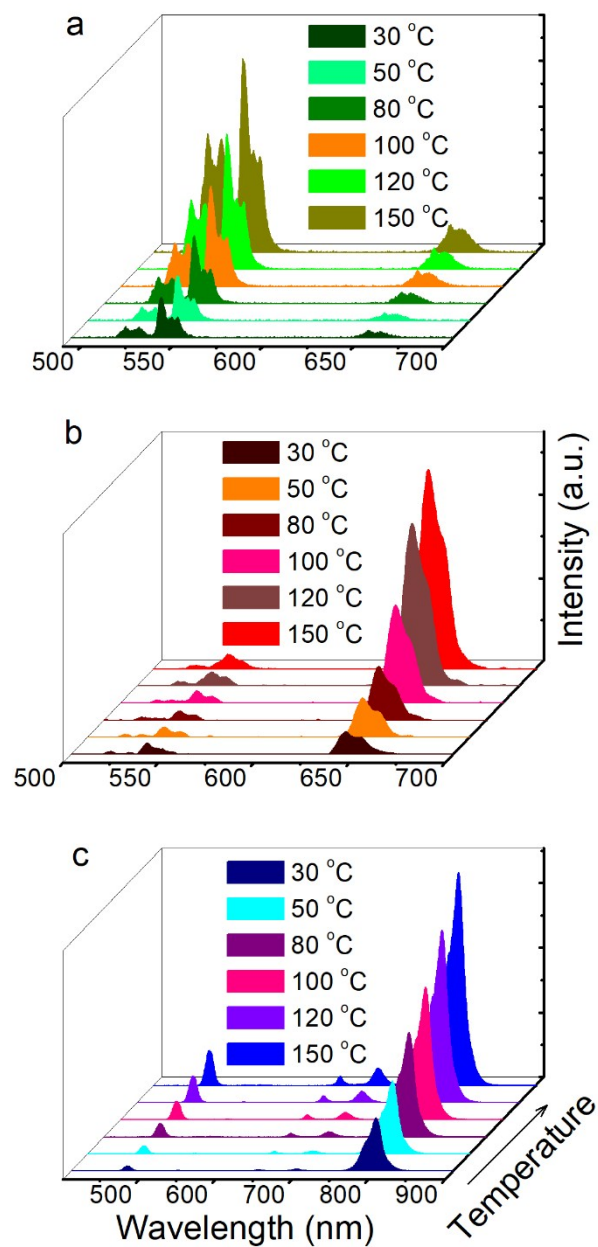


Figure S15. Temperature-dependent UCL spectra of (a) NaGdF₄:Yb/Er@NaGdF₄:20%Yb, (b) NaGdF₄:Yb/Ho/Ce@NaGdF₄:20%Yb, and (c) NaGdF₄:Yb/Tm@NaGdF₄:20%Yb nanocrystals (laser power density: 1.2 W/cm²).

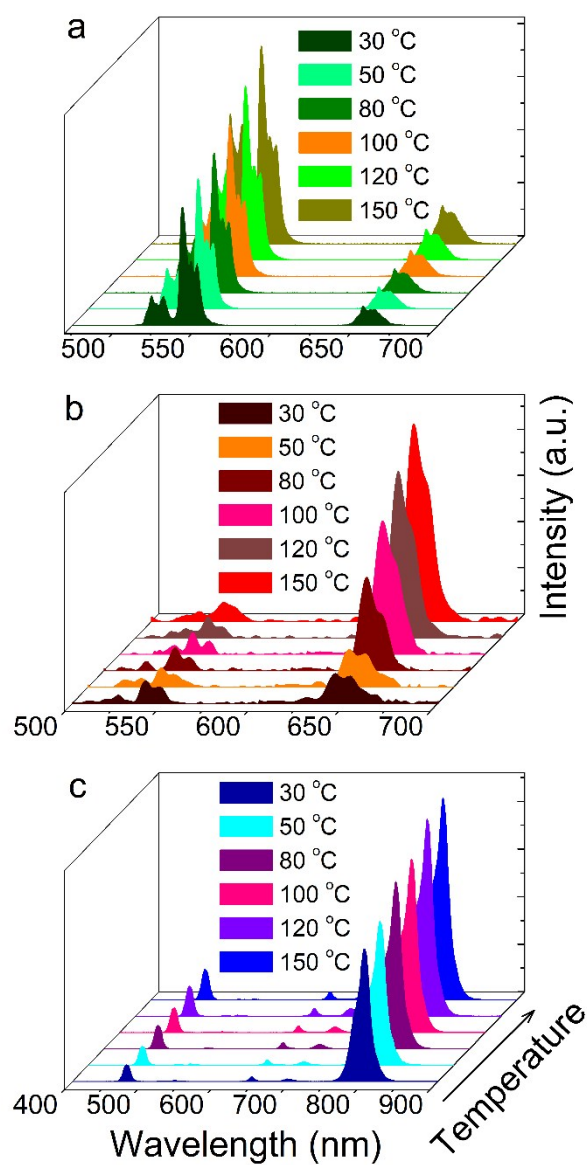


Figure S16. Temperature-dependent UCL spectra of (a) NaGdF₄:Yb/Er@NaGdF₄:5%Yb, (b) NaGdF₄:Yb/Ho/Ce@NaGdF₄:5%Yb, and (c) NaGdF₄:Yb/Tm@NaGdF₄:5%Yb nanocrystals (laser power density: 1.2 W/cm²).

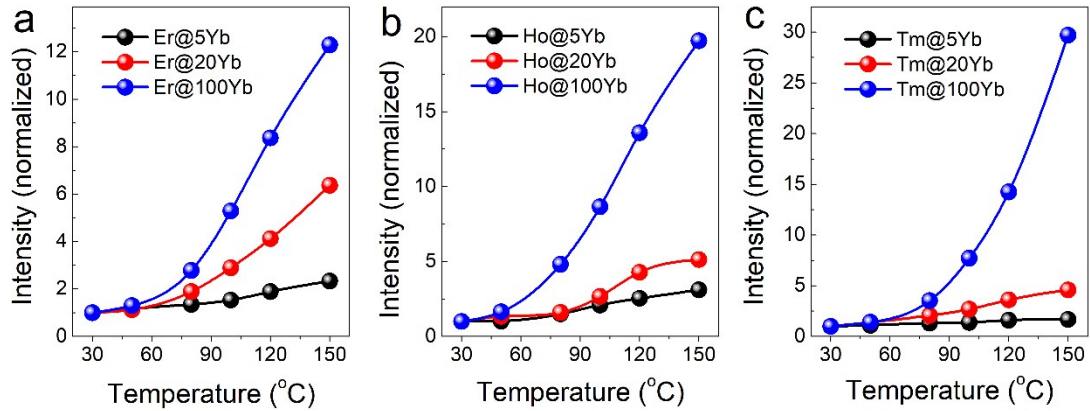


Figure S17. Temperature-dependent integrated intensities of core/active-shell nanocrystals (laser power density: 1.2 W/cm²): (a) NaGdF₄:20%Yb/2%Er@NaGdF₄:5%Yb (Er@5Yb), NaGdF₄:20%Yb/2%Er@NaGdF₄:20%Yb (Er@20Yb) and NaGdF₄:20%Yb/2%Er@NaYbF₄ (Er@100Yb); (b) NaGdF₄:20%Yb/2%Ho/30%Ce@NaGdF₄:5%Yb (Ho@5Yb), NaGdF₄:20%Yb/2%Ho/30%Ce@NaGdF₄:20%Yb (Ho@20Yb) and NaGdF₄:20%Yb/2%Ho/30%Ce@NaYbF₄ (Ho@100Yb); (c) NaGdF₄:20%Yb/1%Tm@NaGdF₄:5%Yb (Tm@5Yb), NaGdF₄:20%Yb/1%Tm@NaGdF₄:20%Yb (Tm@20Yb) and NaGdF₄:20%Yb/1%Tm@NaYbF₄ (Tm@100Yb).

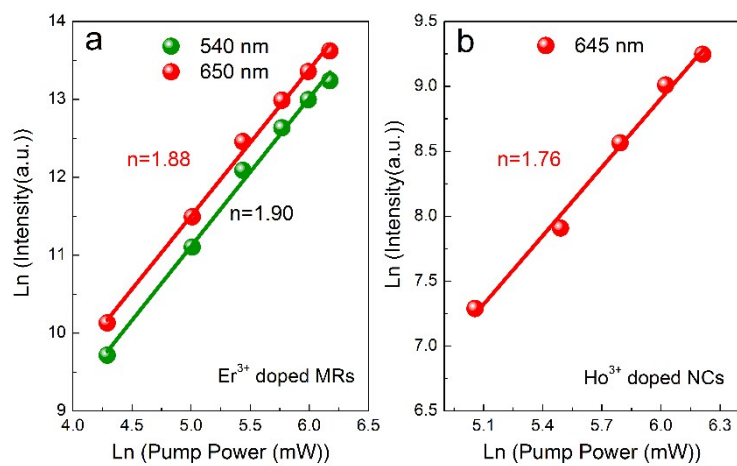


Figure S18. Double logarithmic plots of emission intensities vs laser powers: (a) Green and red emissions of Er^{3+} in $\text{NaYF}_4:\text{Yb}/\text{Er}$ microrods; (b) Red emission of Ho^{3+} in $\text{NaGdF}_4:\text{Yb}/\text{Ce}/\text{Ho}@/\text{NaYbF}_4$ nanocrystals.

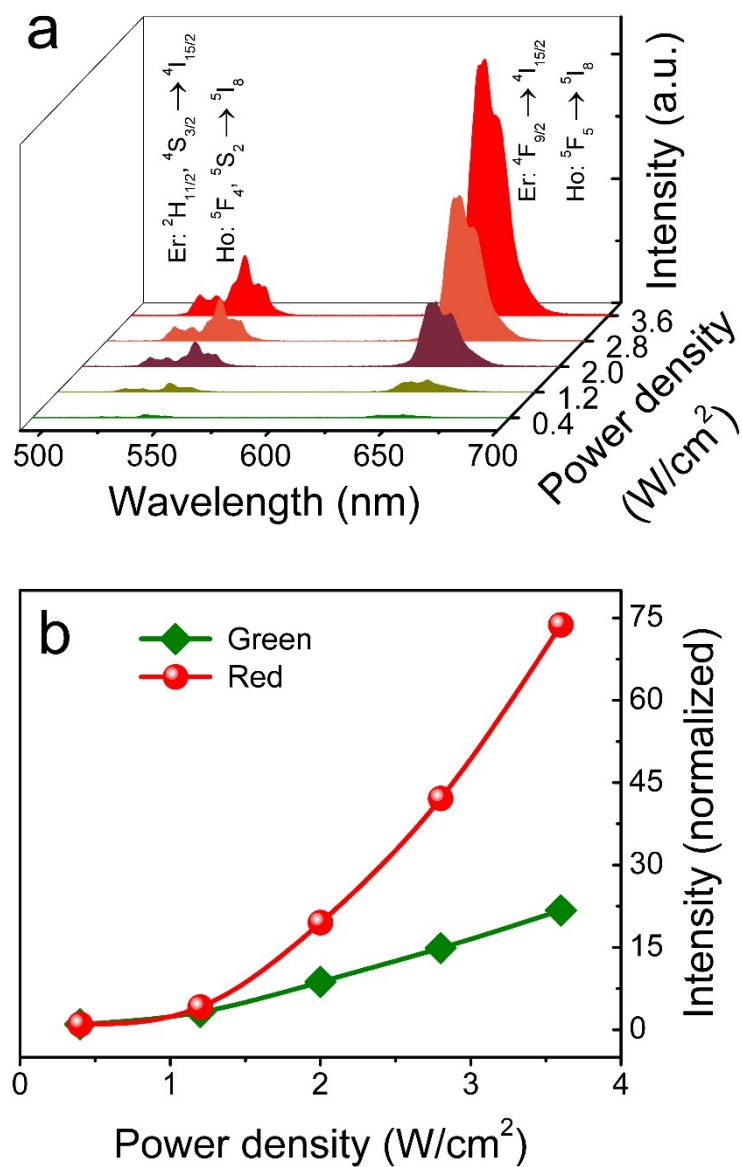


Figure S19. (a) Power-dependent UCL spectra and (b) integrated intensities of the H-GR hybrid consisting of NaYF₄:Yb/Er microrods and NaGdF₄:Yb/Ce/Ho@NaYbF₄ core/shell nanocrystals, and the integrated intensities of each emission band are normalized to that at 0.4 W/cm².

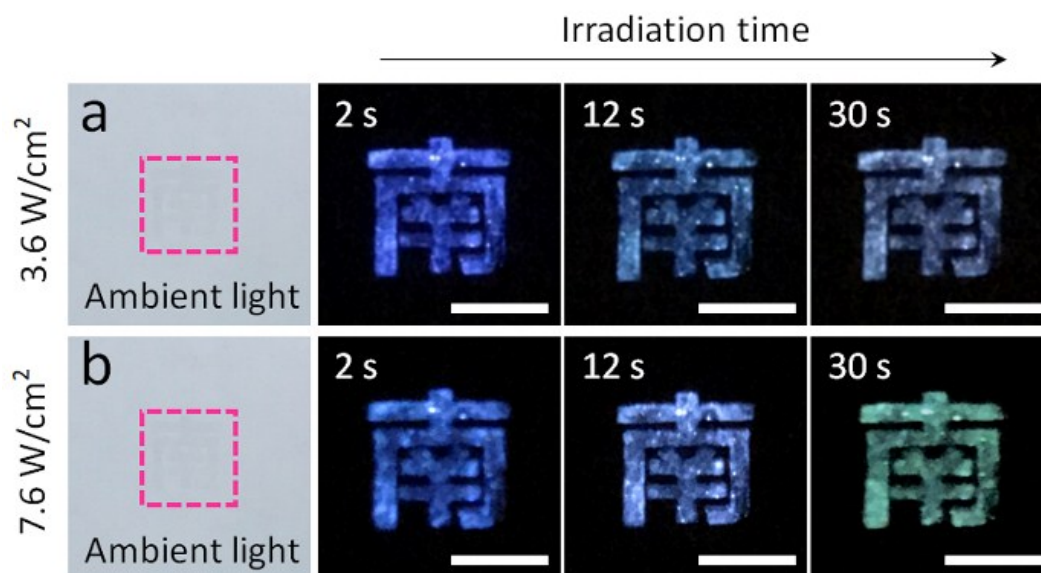


Figure S20. Color changes of the pattern printed with the ink that consists of NaGdF₄:20%Yb/2%Er@NaGdF₄:20%Yb nanocrystals and NaYF₄:20%Yb/2%Er microrods upon prolonging the irradiation time at the laser power density of (a) 3.6 W/cm² and (b) 7.6 W/cm². Scale bar: 5 mm.

E. References

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