

Supplementary Information

Thermal enhanced NIR-NIR anti-Stokes emission in rare earth doped nanocrystals

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Materials and methods

$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), NH_4F (99.99%), NaOH (99.9%), KOH (99.9%), oleic acid (OA, 90%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich.

1. Synthesis of NaYF_4 : Yb^{3+} , Nd^{3+} nanocrystals

NaYF_4 : Yb^{3+} , Nd^{3+} nanocrystals were synthesized by the coprecipitation method. Taken NaYF_4 : 20% Yb^{3+} , 6% Nd^{3+} as an example, 1 mmol $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE} = \text{Y}, \text{Yb}, \text{Nd}$) with the molar ratio of 74:20:6 were added to a 50 ml flask containing 6 ml OA and 15 ml ODE. The mixture was heated to 180 °C under argon for 30 min to obtain a clear solution and then cooled down to room temperature, followed by the addition of 5 mL methanol solution of NH_4F (4 mmol) and NaOH (2.5 mmol). After stirring for 30 min, the temperature was set at 100 °C and the solution was heated under argon for 30 min to remove methanol, and then the solution was further heated to 300 °C for 90 min. Finally, the reaction solution was cooled down to room temperature, and nanoparticles were precipitated by ethanol and washed with cyclohexane, ethanol and methanol for 3 times to get the NaYF_4 : 20% Yb^{3+} , 6% Nd^{3+} nanoparticles.

2. Controlled synthesis of ~10 nm NaYF_4 : Yb^{3+} , Nd^{3+} nanocrystals

The family of ~10 nm NaYF_4 : Yb^{3+} , Nd^{3+} nanocrystals with different doping concentration was synthesized by a similar method. Same as above method, the mixture of $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE} = \text{Y}, \text{Yb}, \text{Nd}$), 6 ml OA and 15 ml ODE was heated to 180 °C under argon for 30 min and then cooled down to room temperature. Then 8 mL methanol solution of 4 mmol NaOH was added to the mixture followed by 15 min stirring. By heating the solution to 100 °C for 15 min, the methanol was removed under argon. Again the mixture was cooled down to room temperature. After that 10 mL methanol solution of 4 mmol NH_4F was added to the mixture followed by 30 min stirring. Then the temperature was set at 100 °C and the solution was heated for 30 min to remove methanol, next the solution was further heated to 300 °C for 40 min. Finally,

the reaction solution was cooled down to room temperature to get the ~10 nm nanocrystals.

3. Synthesis of ligand-free NaYF₄: Yb³⁺, Nd³⁺ nanoparticles.

The oleate ligand was removed by a simple acid treatment process. Firstly, 4 ml ethanol and 4 ml HCl (0.2M) were added to the as-prepared OA⁻-capped NaYF₄: Yb³⁺, Nd³⁺ precipitate, then the solution was sonicated for 30 min and collected by centrifugation. And the precipitate was further washed for 3 times with 4 ml ethanol and 4 ml deionized water to get the ligand-free nanoparticles.

4. Characterization techniques

The morphology of the formed materials was characterized *via* transmission electron microscopy (TEM) imaging (Philips CM10 TEM with Olympus Sis Megaview G2 Digital Camera) with an operating voltage of 100 kV. The samples were prepared by placing a drop of a dilute suspension of nanocrystals onto copper grids.

The morphology of the annealed nanocrystal was characterized via scanning electron microscope (SEM) imaging (Supra 55VP, Zeiss) operated at 20.00 kV.

Fourier transform infrared (FTIR) spectra of the OA⁻-capped and OA⁻-free nanocrystals were measured on a FTIR spectrometer (Nicolet 6700, Thermo Scientific).

5. Temperature dependent spectra measurement

The temperature dependent spectra were measured with a home-built photoluminescence spectroscopy system. A fiber-coupled 976.5 nm diode laser (BL976-PAG500, controller CLD1015, Thorlabs) with adjustable power up to 500 mW works as the pumping source. By using a temperature heating stage (thermocouple TH100PT, heater HT24S, controller TC200, Thorlabs), the spectra could be measured from room temperature to 453 K by a commercial spectrometer (Shamrock 193i, Andor) with an EMCCD (iXon Ultra 888, Andor) as the detector. For Ar atmosphere

measurement, an additional inclosed heating stage (HFS600E-P, Linkam) was used to block air. In addition, the emission signal was filtered by a short pass filter (SPF, FF01-842/SP-25, Semrock) to remove the scattered excitation laser.

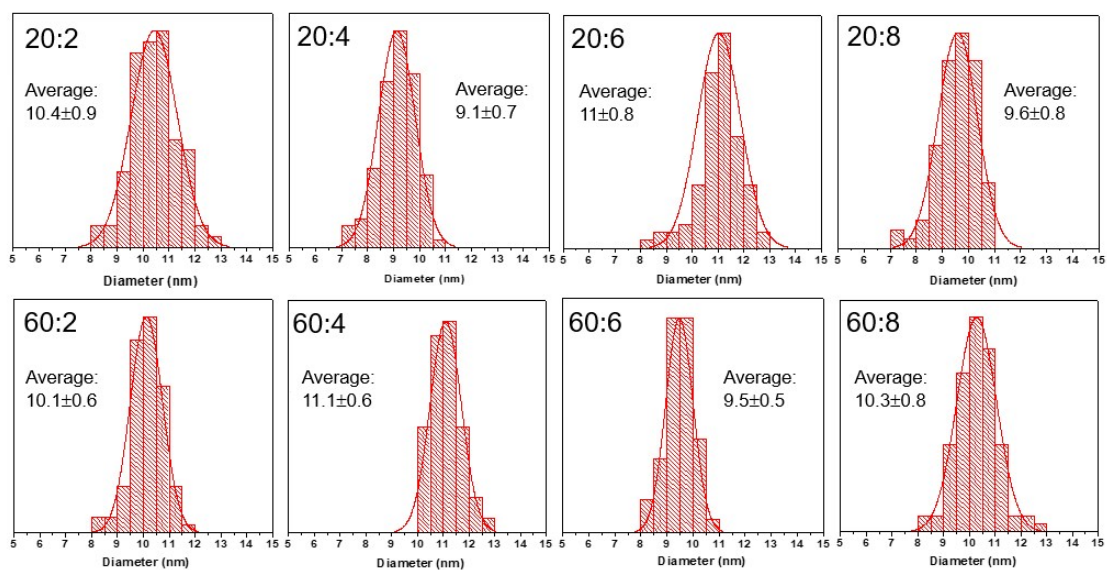


Figure S1. TEM images and size distributions of the ~10 nm NaYF₄: Yb³⁺, Nd³⁺ samples. The doping concentration ratio of Yb³⁺: Nd³⁺ (%) is labeled in each TEM image. Scale bar is 20 nm.

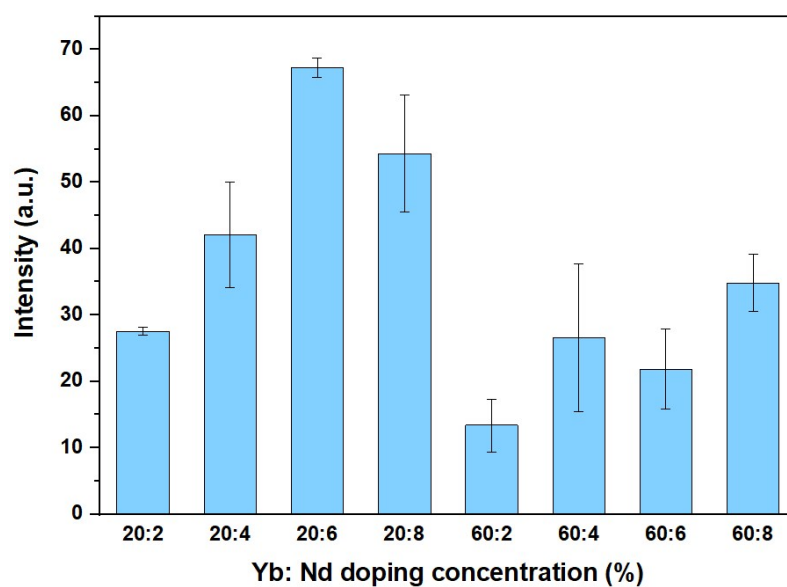


Figure S2. Comparison of 803 nm emission intensity of the ~10 nm NaYF₄: Yb³⁺, Nd³⁺ samples. By controlled synthesis of the different Yb³⁺, Nd³⁺doping samples with similar size, the emission intensities of the ~10 nm samples are comparable.

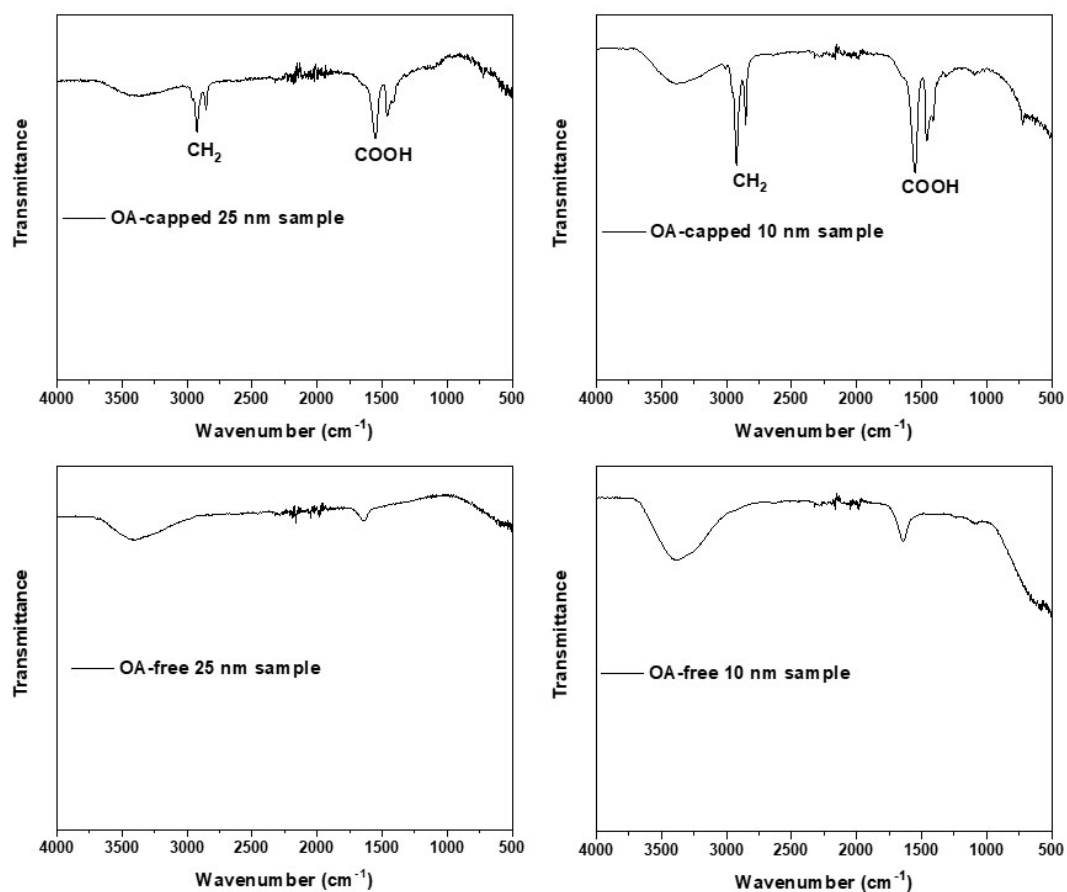


Figure S3. FTIR results of the as-prepared OA-capped and OA-free samples. After acid treatment, both CH₂ stretching and COOH stretching disappeared, which means surface OA has been removed from 25 nm NaYF₄: 20% Yb³⁺, 6% Nd³⁺ and 10 nm NaYF₄: 20% Yb³⁺, 6% Nd³⁺ nanoparticles.

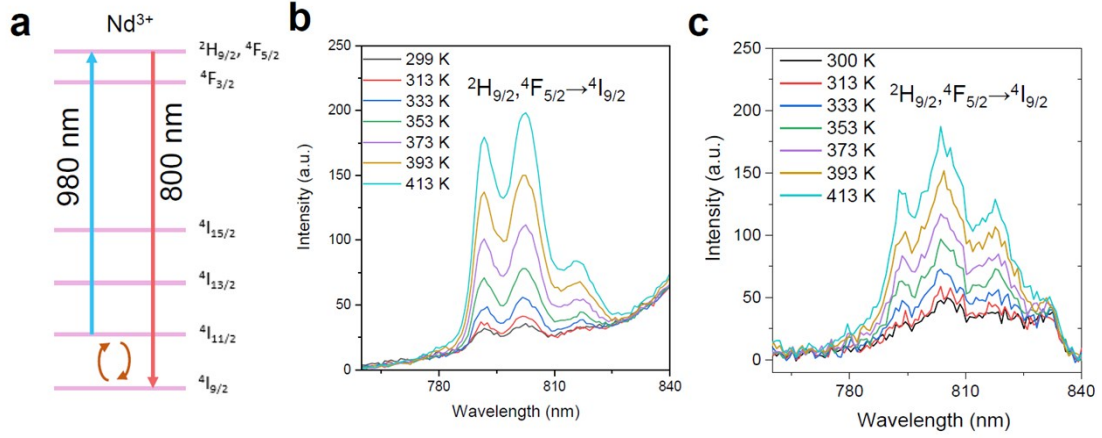


Figure S4. The thermal enhancement caused by the possible Boltzmann distribution. The Boltzmann distribution (a) is supposed to increase the population in $4I_{11/2}$ and lead to the stronger transition of $4I_{11/2} \rightarrow 2H_{9/2}, 4F_{5/2}$ under 980 nm excitation at elevated temperatures. From room temperature to 413 K, $\text{NaYF}_4: 6\% \text{Nd}^{3+}$ (b) and $\text{NaYF}_4: 20\% \text{Nd}^{3+}$ (c) show thermal enhanced 800 nm emission. However, both two samples only show limited enhancement, i.e., around five times for $\text{NaYF}_4: 6\% \text{Nd}^{3+}$ and three times for $\text{NaYF}_4: 20\% \text{Nd}^{3+}$. Such level of enhancement is almost neglectable compared to over two orders of magnitude enhancement in $\text{Yb}^{3+}\text{-Nd}^{3+}$ co-doped samples.

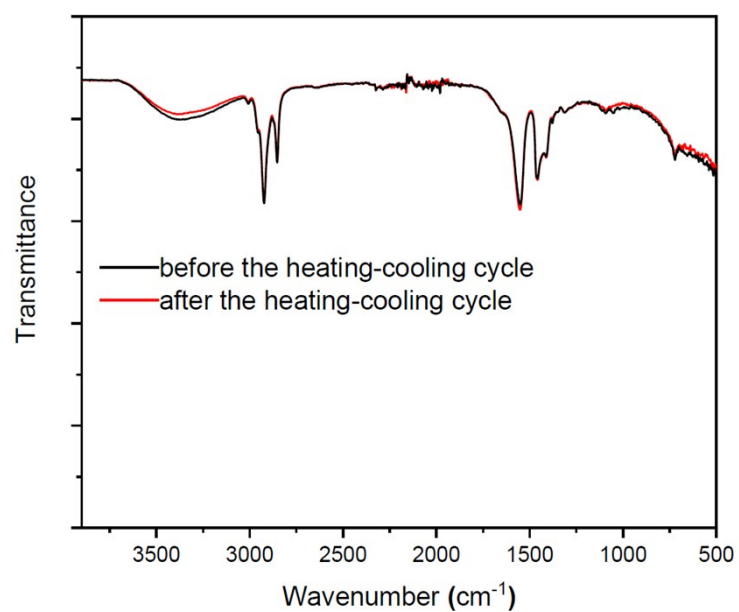


Figure S5. The FTIR spectrum of the 10 nm NaYF₄: 60% Yb³⁺, 8% Nd³⁺ samples before and after the heating-cooling test.

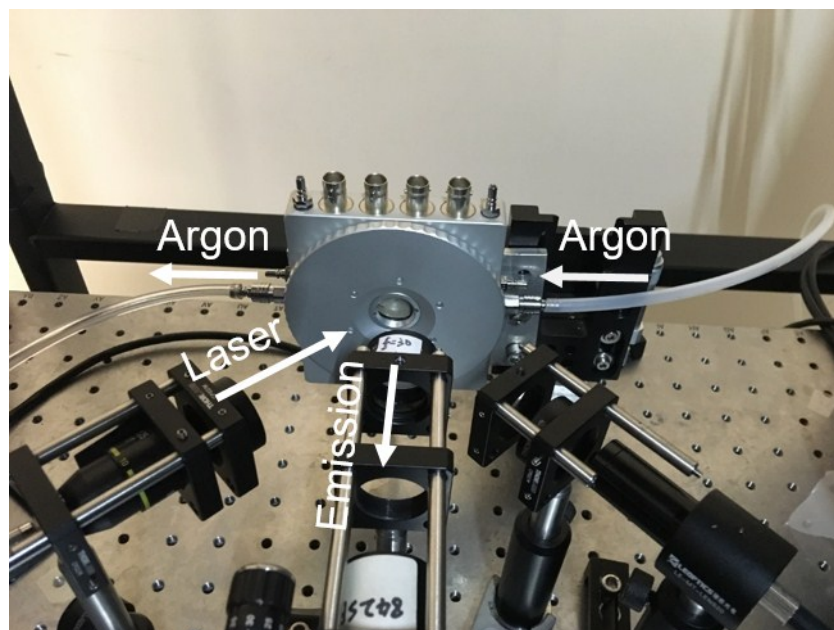


Figure S6. Test system used for Ar atmosphere measurement. By using an inclosed heating stage, the sample could be measured under Ar to avoid the influence caused by moisture in air.

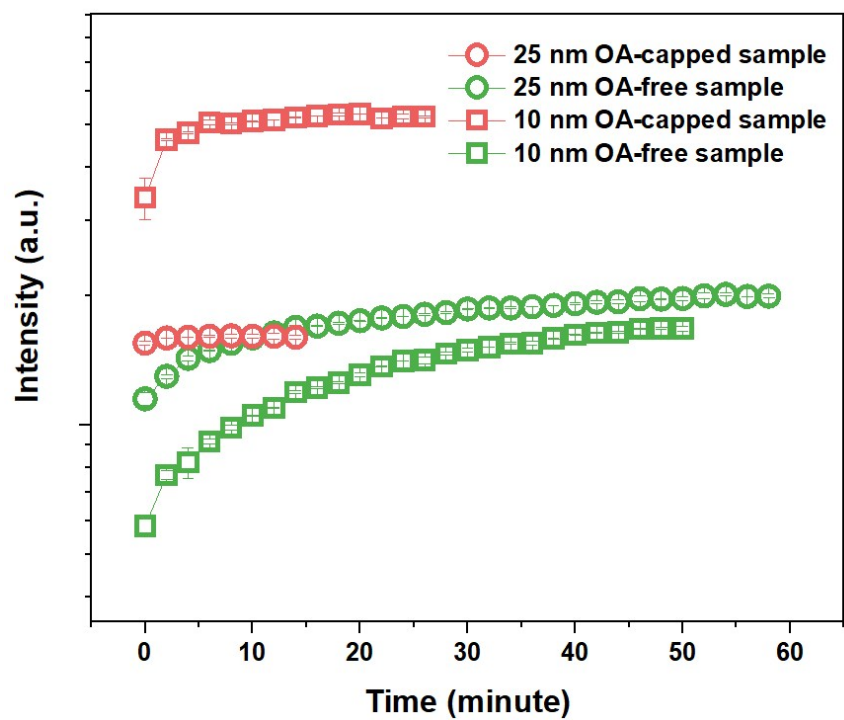


Figure S7. Moisture release process at 453 K. Time starts from the moment when the set temperature arrives at 453 K, the moisture has been totally removed from the samples until the intensity is stable.

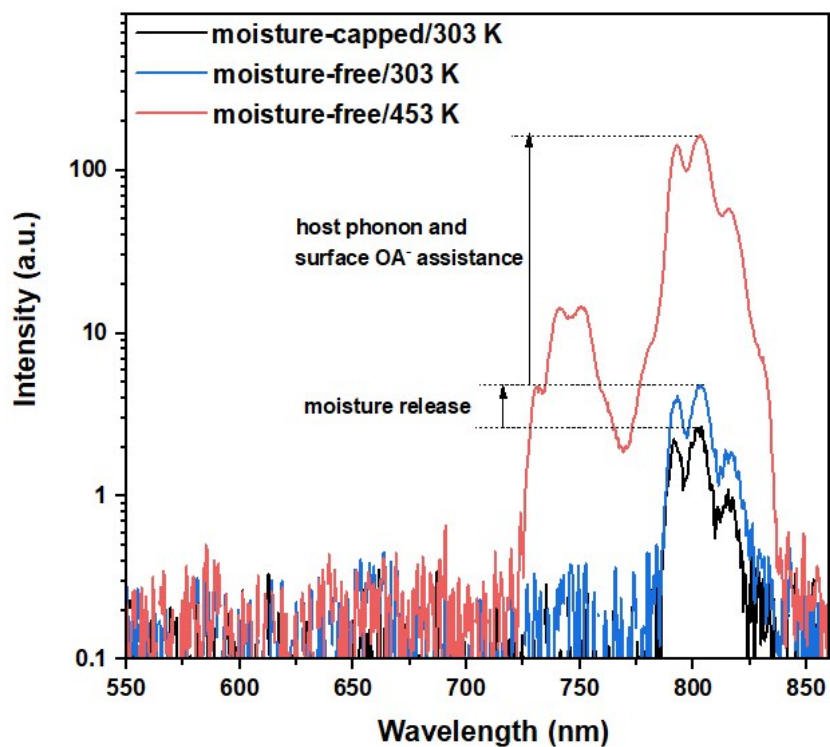


Figure S8. Enhancement factors calculation. Take the 25 nm OA-capped NaYF₄: Yb³⁺, Nd³⁺ sample in Figure 3e for example, the sample exhibits a higher intensity at 303 K after removing the moisture, thus the factor of moisture release equals to the intensity ratio of moisture-capped sample to moisture-free sample at 303 K. Due to the host phonon and surface OA assistance, the moisture-free sample realizes a dramatic emission enhancement at 453 K, thus the factor of host phonon and surface OA assistance is the ratio of the intensity at 453 K to it at 303 K, then by subtracting the factor of host phonon assistance for the 25 nm OA-free sample, the factor of surface OA assistance is also quantified.