

Supporting Information

Comparative investigation of optical spectroscopic and thermal effect in Nd³⁺-doped nanoparticles

Shuai Wang,^{‡a} Bin Shen,^{‡b} Han-Lin Wei,^a Zixiao Liu,^c Yong Zhang,^b Zhigang Chen,^c Yan Su,^d Jun-Zheng Zhang,^a Haifang Wang^{a,*} and Qianqian Su^{a,*}

^aInstitute of Nanochemistry and Nanobiology, Shanghai University, Shanghai 200444, China.

^bFaculty of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China.

^cState Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

^dGenome Institute of Singapore, Agency of Science Technology and Research, 138672, Singapore

*Corresponding authors: Q. Su, H. Wang, Email: chmsqq@shu.edu.cn; hwang@shu.edu.cn.

Experimental Section

Materials: Gd(CH₃CO₂)₃·xH₂O (99.9%), Y(CH₃CO₂)₃·xH₂O (99.9%), Nd(CH₃CO₂)₃·xH₂O (99.9%), Yb(CH₃CO₂)₃·xH₂O (99.9%), Tm(CH₃CO₂)₃·xH₂O (99.9%), Er(CH₃CO₂)₃·xH₂O (99.9%), Ho(CH₃CO₂)₃·xH₂O (99.9%), NaOH (>98%), NH₄F (>98%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) were all purchased from Sigma-Aldrich. Chloral hydrate (>99%), sodium oleate (>97.0%) was obtained from Aladdin. Ethanol (AR), cyclohexane (AR) and hydrochloric acid (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Physical Measurements: Low-resolution transmission electron microscopy (TEM) measurements were conducted on a HT7700 field emission transmission electron microscope operated at an acceleration voltage of 120 kV. High-resolution TEM images and the energy-dispersive X-ray (EDX) spectroscopic analysis were performed using a FEI Talos F200S transmission electron microscope operated at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) results were obtained on a Rigaku D/MAX-2200 equipped with a rotating anode and a Cu K α radiation source ($\lambda = 0.15418$ nm). Luminescence spectra and their decay curve were recorded at room temperature with a FS5 (Edinburgh), in conjunction with 808 nm and 980 nm diode lasers. The quantification of the excitation power density was measured by Laser power densitometer TS5 (Changchun New Industries Optoelectronics Technology Co., Ltd.) to keep the power density consistent when comparing the emission intensities. UV-vis absorption spectra were recorded

using a PerkinElmer Lambda 750 ultraviolet-visible-near infrared spectrometer. FTIR spectra were obtained using a PerkinElmer Spectrum Two. Unless otherwise specified, all spectra were recorded under identical experimental conditions.

Synthesis of NaGdF₄:Yb/Tm core nanoparticles: Yb/Tm, Yb/Er or Yb/Ho co-doped NaGdF₄ nanoparticles were prepared according to a modified literature procedure^[1]. Gd(CH₃CO₂)₃ (0.067 g; 0.2 mmol), Yb(CH₃CO₂)₃ (0.069 g; 0.196 mmol) and Tm(CH₃CO₂)₃ (0.001 g; 0.004 mmol) in a water stock solution (2 mL) were added in a 50 mL three-neck round-bottom flask charged with OA (5 mL) and ODE (5 mL) at room temperature. The mixture was heated to 150 °C and maintained this temperature for 1 h. After cooling down to 50 °C, NH₄F (0.05 g; 1.36 mmol) and NaOH (0.04 g; 1 mmol) in a methanol solution (4.4 mL) was subsequently added and stirred for 30 min. The resulting mixture was then heated to 100 °C within 15 min and *in vacuo* for another 15 min to remove the methanol. The resulting solution was heated to 300 °C and kept for 1.5 h with argon before cooling down to room temperature. The as-synthesized nanoparticles were precipitated by ethanol, collected by centrifugation at 7000 rpm for 5 min, and then washed with ethanol for three times. The core nanoparticles were dispersed in cyclohexane (4 mL) before shell coating experiments. The synthesis of NaYF₄:Yb/Tm core nanoparticles was identical to that for NaGdF₄:Yb/Tm core nanoparticles except for the use of a stock solution of Y³⁺ and OA (3 mL) and ODE (7 mL).

Synthesis of NaGdF₄:Yb/Tm@NaGdF₄:x%Yb core-shell nanoparticles: The synthesis of core-shell nanoparticles was developed via a similar literature procedure.^[1] The pre-obtained NaGdF₄:Yb/Tm core nanoparticles were served as seeds for shell coating. The precursor of shell was first prepared by the same procedure as mentioned above and then cooled down to 80 °C. A stock cyclohexane solution (4 mL) of NaGdF₄:Yb/Tm nanoparticle seeds were added and kept at this temperature for 30 min to remove the cyclohexane. NH₄F (0.05 g; 1.36 mmol) and NaOH (0.04 g; 1 mmol) in a methanol solution (4.4 mL) was then added and stirred at 50 °C for 30 min. The reaction was then heated to 300 °C under an argon atmosphere. After 1.5 h, the reaction was stopped. The synthesized core-shell nanoparticles were precipitated out by the addition of ethanol, collected by centrifugation, washed with ethanol, and finally dispersed in cyclohexane.

Synthesis of NaGdF₄:Yb/Tm@NaGdF₄:50%Nd@NaGdF₄ and NaGdF₄:Yb/Tm@NaGdF₄:20%Yb@NaGdF₄:10%Yb50%Nd@NaGdF₄ core-multishell nanoparticles: Multishelled core-shell nanoparticles were prepared using a procedure similar to the one for NaGdF₄:Yb/Tm@NaGdF₄:x%Yb core-shell nanoparticles mentioned above. The core-shell nanoparticles were used as seeds and then coated with a layer of NaGdF₄ with or without the

Yb³⁺ and Nd³⁺ dopants. The synthetic procedure for core-multishell nanoparticles using NaYF₄ as the host matrix was identical to that for NaGdF₄ core-multishell nanoparticles except for the use of a stock solution of Y³⁺ and OA (3 mL) and ODE (7 mL).

Synthesis of NaYF₄:Yb/Tm@NaYF₄:20%Yb@NaYF₄:10%Yb50%Nd@NaYF₄ (about 17–22 nm diameter) core-multishell nanoparticles: Yb/Tm, Yb/Er or Yb/Ho co-doped NaYF₄ nanoparticles were prepared according to a modified literature procedure^[2]. Y(CH₃CO₂)₃ (0.106 g; 0.4 mmol), Yb(CH₃CO₂)₃ (0.138 g; 0.392 mmol) and Tm(CH₃CO₂)₃ (0.002 g; 0.008 mmol) in a water stock solution (4 mL) were added in a 50 mL three-neck round-bottom flask charged with OA (10 mL) and ODE (10 mL) at room temperature. The mixture was heated to 150 °C and maintained this temperature for 1 h before cooling down to room temperature. A sodium oleate powder (6.4 mmol) was then added to the resulted solution. The obtained mixture was then heated to 100 °C and maintain at this temperature under vacuum for 1 h, followed by the addition of an ammonium fluoride solid (6.4 mmol). Subsequently, the resulting mixture was slowly heated to 160 °C and maintained at this temperature for 1 h, and then degassed for 10 min. The reaction mixture was then heated to 320 °C under a nitrogen atmosphere and kept for 30 min. After cooling down to room temperature, the obtained nanoparticles were precipitated by the addition of ethanol and collected by centrifugation. After washing with ethanol and cyclohexane for three times, the obtained products were finally dispersed in cyclohexane. The synthetic protocol of shell coating onto the NaYF₄:Yb/Tm core nanoparticles was identical to that for NaGdF₄:Yb/Tm@NaGdF₄:20%Yb@NaGdF₄:10%Yb50%Nd@NaGdF₄ core-multishell nanoparticles

Synthesis of NaGdF₄:Yb/Tm@NaGdF₄:20%Yb@ NaGdF₄:10%Yb50%Nd@NaGdF₄ core-multishell nanoparticles: Multishelled core-shell nanoparticles were prepared using a procedure similar to the one for NaGdF₄:Yb/Tm@NaGdF₄:x%Yb core-shell nanoparticles mentioned above. The core-shell nanoparticles were used as seeds and then coated with a layer of NaGdF₄ with or without the Yb³⁺ and Nd³⁺ dopants. The synthetic procedure for core-multishell nanoparticles using NaYF₄ as the host matrix was identical to that for NaGdF₄ core-multishell nanoparticles except for the use of a stock solution of Y³⁺ and OA (3 mL) and ODE (7 mL).

Synthesis of ligand-free nanoparticles: Ligand-free nanoparticles were prepared according to a reported literature procedure.^[3] The OA-capped nanoparticles were first mixed with ethanol (1 mL) and a hydrochloric acid solution (1 mL; 2 M). The nanoparticles were ultrasonicated for 10 min to remove the surface ligands and collected by centrifugation at 12000 rpm for 20 min, washed with ethanol for three times, and then dispersed in deionized water.

The thermal effect of Nd³⁺-doped nanoparticles upon excitation at 808 and 980 nm: Ligand-free nanoparticles with NaGdF₄ host matrix were dispersed in deionized water at a concentration of 20 mg mL⁻¹. Then 3 mL dispersion of nanoparticles was transferred into quartz cuvettes the temperature of the dispersion is monitored by a thermometer (CENTER-303 Type-K, Qunte Co. Ltd.). The 808 nm laser fiber outlet was immobilized 3.0 cm below the water-air interface and the power density was 2.0 W cm⁻². After the solution reached thermal equilibration at 25 °C, the laser light irradiation was applied and the temperature of the dispersions were recorded every 30 s. The heating effect test for deionized water without nanoparticles was carried out with the same protocol.

Animal experiments: The animal experiments were conducted in accordance with the guide for the animal care and use program guidelines of Shanghai University and were approved by Shanghai University. BALB/c nude male mice was used to examine the heating effect of Nd³⁺-doped nanoparticles *in vivo* upon excitation at 808 and 980 nm. The mice were supplied by Shanghai Slack Laboratory Animals Co., Ltd. The mice aged 8 weeks with a weight of 18–22 g. The mice were anesthetized by injecting chloral hydrate (5% aqueous solution, 100 μL) and then 100 μL of ligand-free nanoparticles in aqueous solution (20 mg mL⁻¹) was subcutaneously injected in the hind leg of the mice. The excitation power density for both lasers was set at 0.5 W cm⁻² and the irradiation spot was about 10 mm in diameter. Thermal images were captured with an infrared thermal imager FORTIC 225s (Shanghai Rexiang Electromechanical Technology Co., Ltd.) every 60 s.

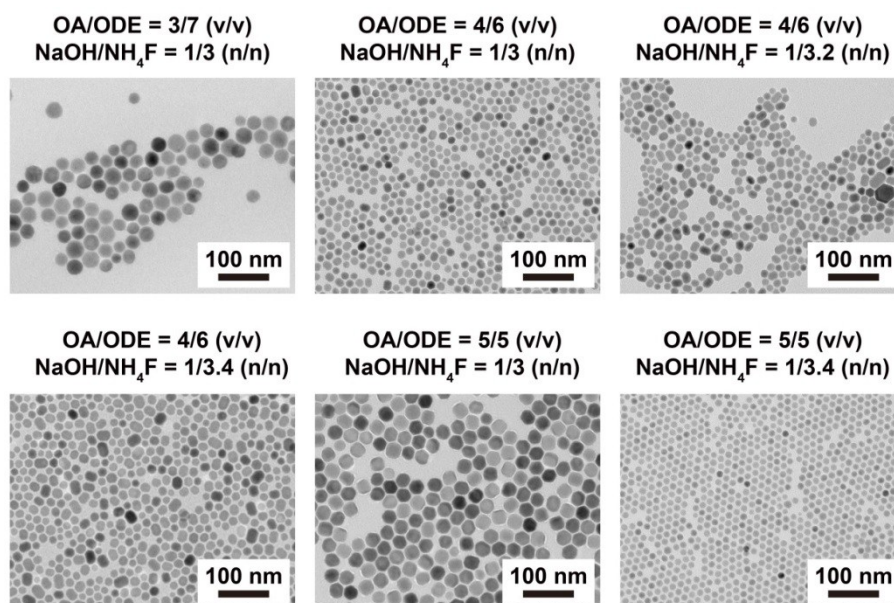


Figure S1. Control experiments investigating the morphology of $\text{NaGdF}_4\text{:Yb/Tm}$ as a function of the amounts of OA/ODE and $\text{NaOH/NH}_4\text{F}$.

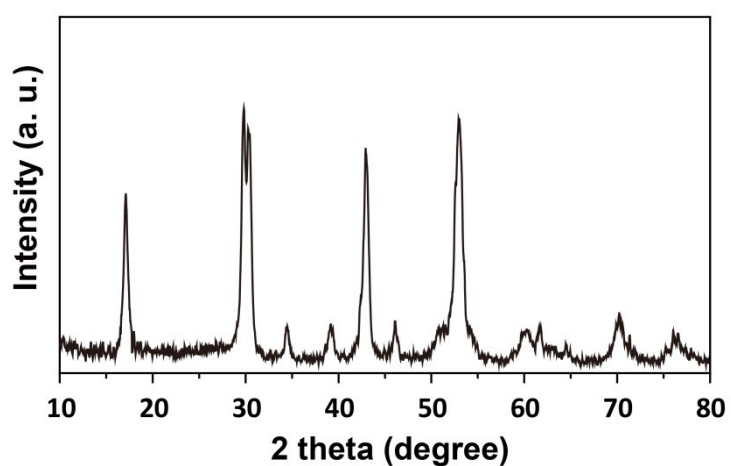


Figure S2. XRD pattern of Gd-Cm-SSS nanoparticles.

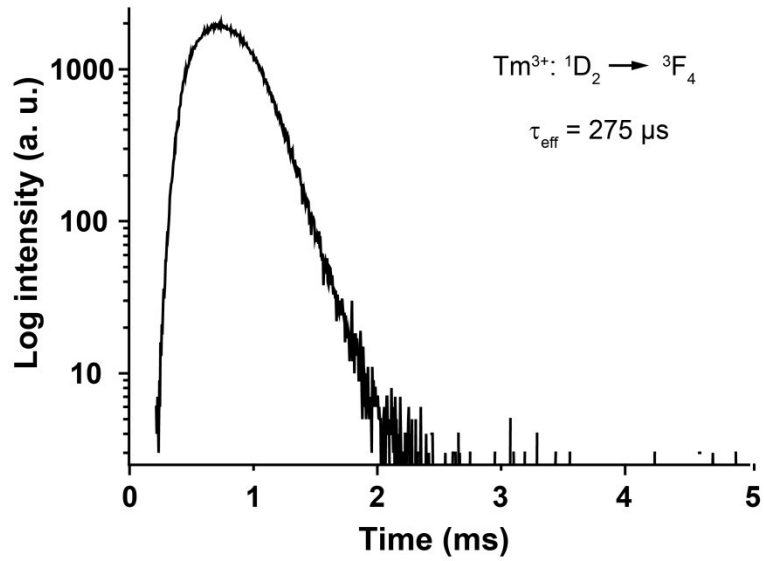


Figure S3. Upconversion luminescence decay curves of Tm^{3+} emission at 450 nm for $\text{Gd-C}_{\text{TmSSS}}$ nanoparticles.

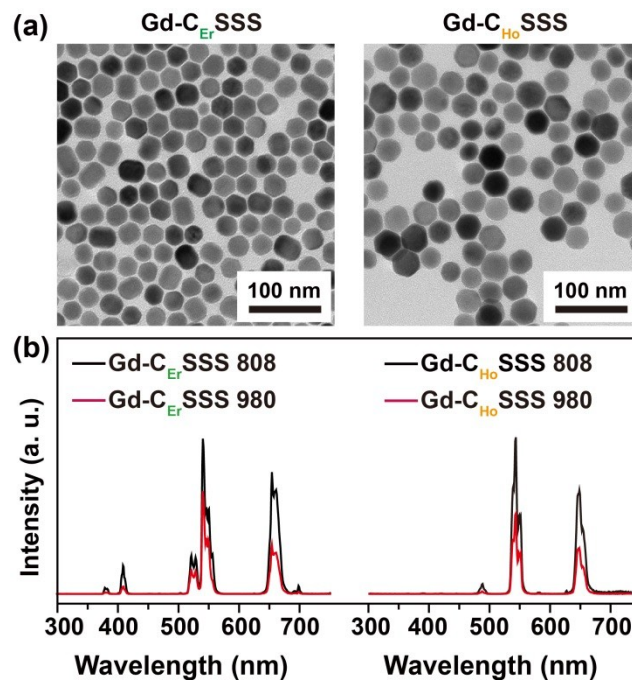


Figure S4. (a) TEM images of Gd-based core-multishell upconversion nanoparticles doped with Er^{3+} (left) and Ho^{3+} (right). (b) Upconversion emission spectra of the corresponding Er^{3+} and Ho^{3+} -doped nanoparticles under excitation of 808 and 980 nm lasers at a power of 2.0 W cm^{-2} (1.0 wt% in cyclohexane).

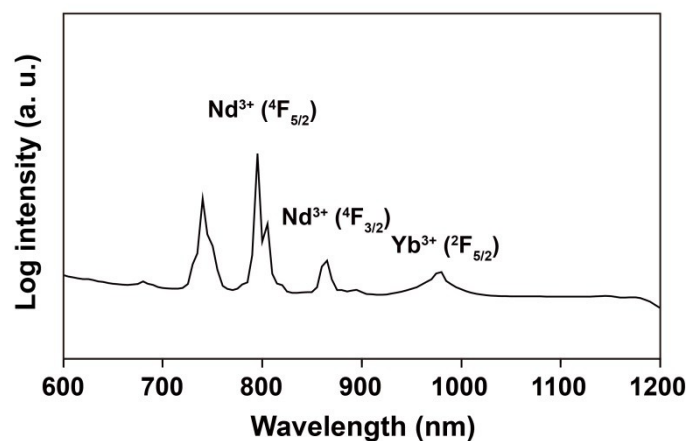


Figure S5. Absorption spectrum of Gd-C_{Tm}SSS nanoparticles.

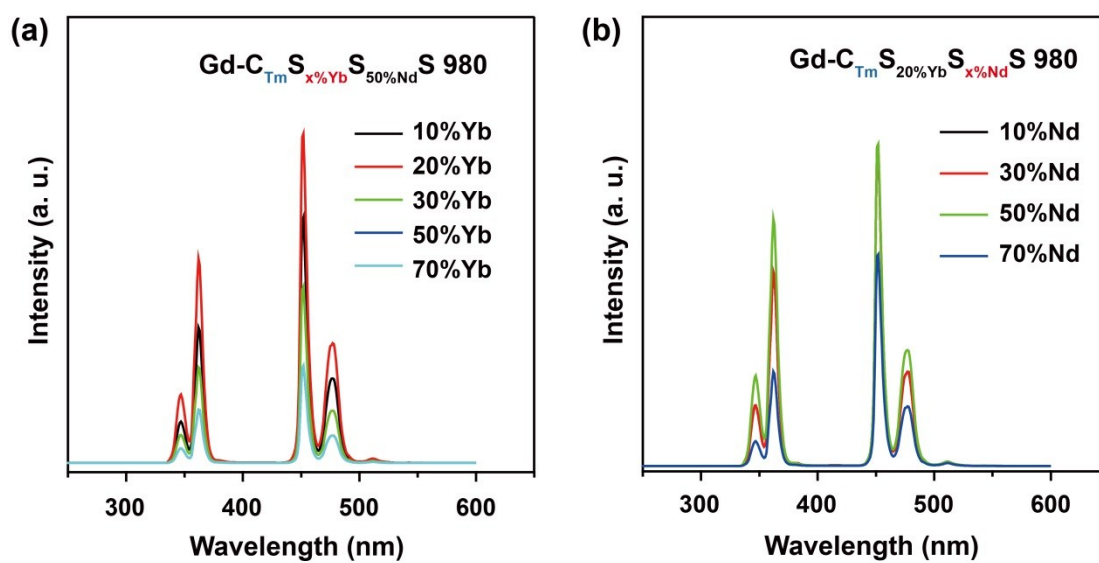


Figure S6. Upconversion emission spectra of the Nd³⁺-doped core-multishell nanoparticles as a function of Yb³⁺ (a) and Nd³⁺ (b) doping concentration. All spectra were measured under excitation of a 980 nm laser at a power of 1.0 W cm⁻² (1.0 wt% in cyclohexane).

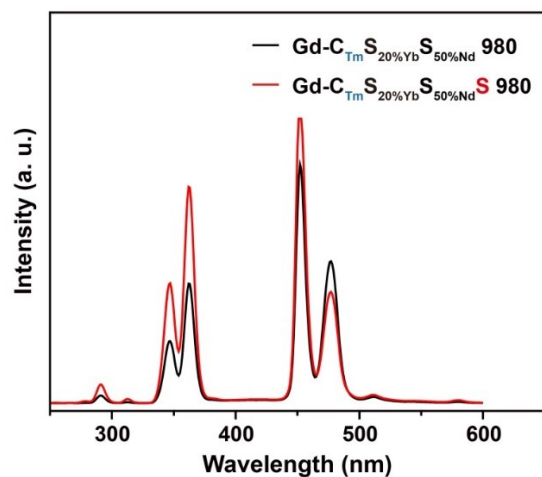


Figure S7. Upconversion emission spectra of the Nd^{3+} -doped core-multishell nanoparticles with and without the outermost shell of NaGdF_4 . All spectra were measured under excitation of a 980 nm laser at a power of 1.0 W cm^{-2} (1.0 wt% in cyclohexane).

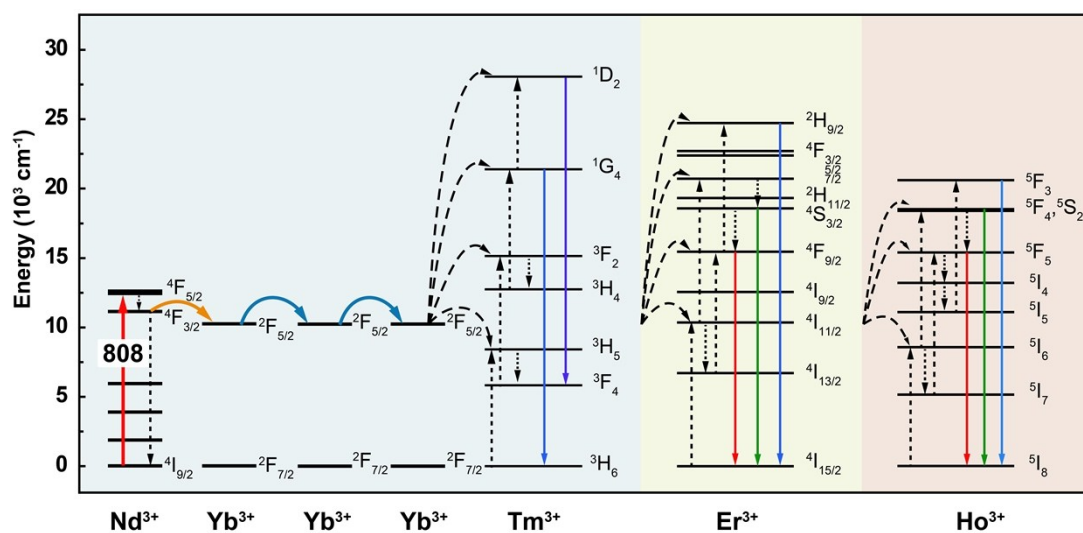


Figure S8. Schematic energy level diagram illustrating typical upconversion processes for Nd^{3+} , Yb^{3+} , Er^{3+} and Ho^{3+} . The full up, dotted, and full down arrows represent excitation, multiphonon relaxation and emission processes, respectively.

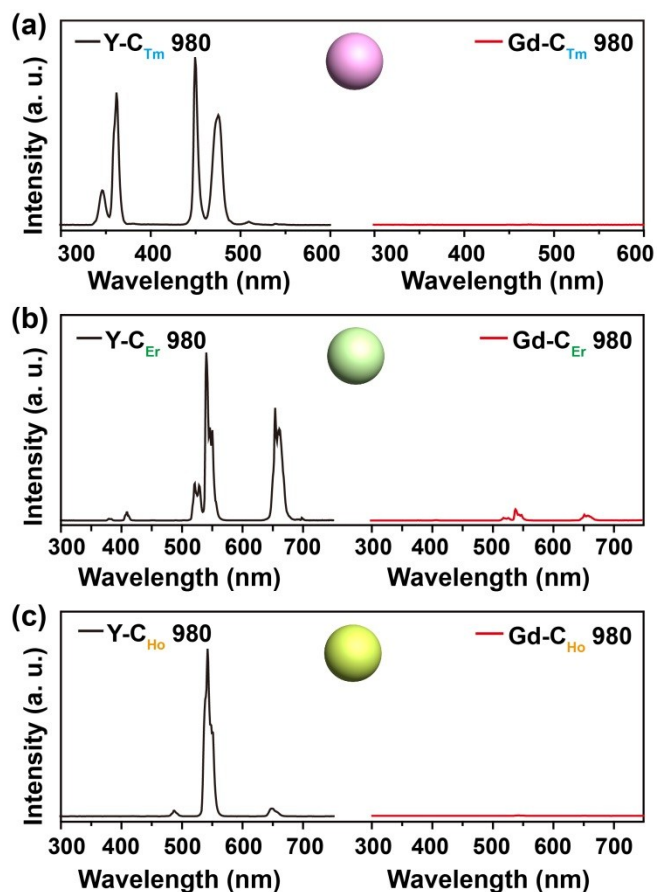


Figure S9. Photoluminescence investigations of Yb^{3+} -sensitized NaYF_4 (left) and NaGdF_4 (right) upconversion nanoparticles doped with 49%Yb/1%Tm (a), 18%Yb/2%Er (b), 18%Yb/2%Ho (c) in cyclohexane. The spectra were recorded under excitation of a 980 nm laser at a power density of 2.0 W cm^{-2} .

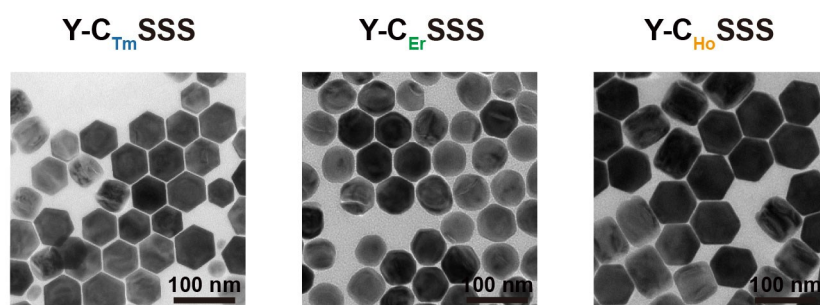


Figure S10. TEM images of the as-synthesized Nd^{3+} -doped upconversion nanoparticles (about 60–70 nm diameter) using NaYF_4 as the host matrix with Yb/Tm (left), Yb/Er (middle) and Yb/Ho (right) dopants.

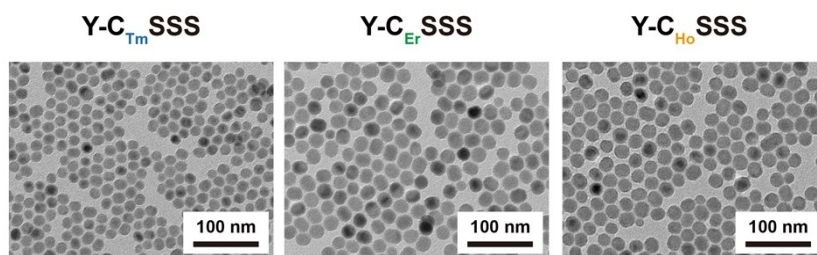


Figure S11. TEM images of the as-synthesized small Nd^{3+} -doped upconversion nanoparticles (about 17–22 nm diameter) using NaYF_4 as the host matrix with Yb/Tm (left), Yb/Er (middle) and Yb/Ho (right) dopants.

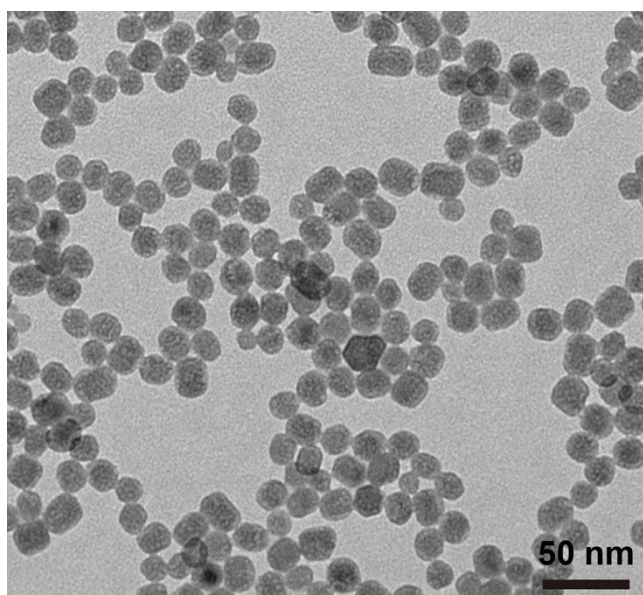


Figure S12. TEM images of ligand-free Nd^{3+} -doped upconversion nanoparticles.

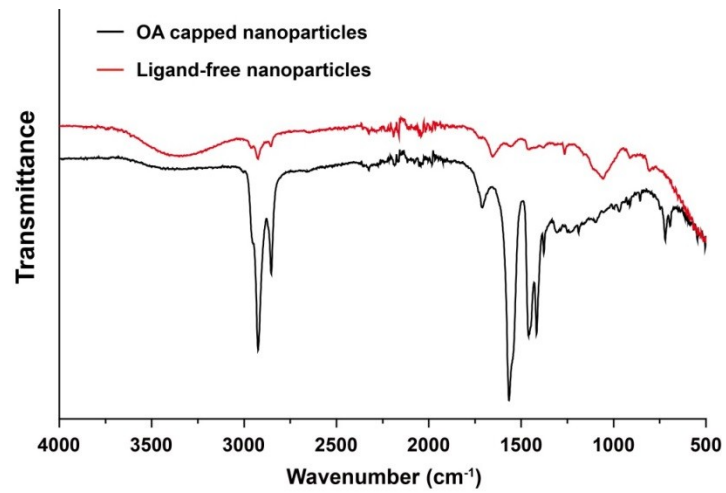


Figure S13. FTIR spectra of oleic acid (OA) capped and ligand-free Nd³⁺-doped nanoparticles revealing that the OA-related absorption bands disappeared after washing the nanoparticles with HCl solution.

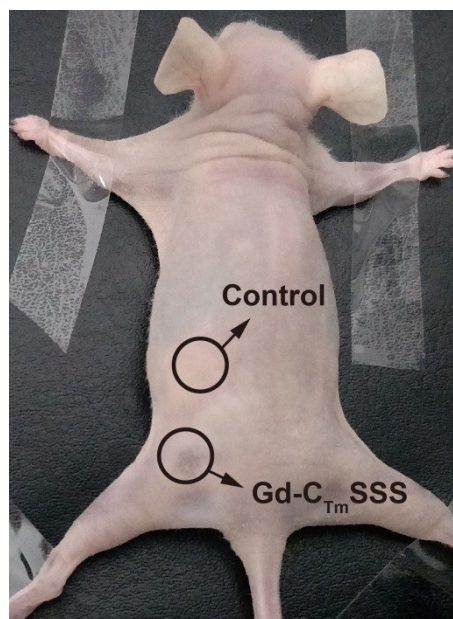


Figure S14. Photograph of a nude mouse injected with Gd-C_{Tm}SSS nanoparticles (100 μL) at a concentration of 20 mg mL⁻¹ for infrared thermal imaging experiments.

References

- [1] Q. Su, S. Han, X. Xie, H. Zhu, H. Chen, C. Chen, R. Liu, X. Chen, F. Wang and X. Liu, *J. Am. Chem. Soc.*, 2012, 134, 20849–20857.
- [2] R. Shi, X. Ling, X. Li, L. Zhang, M. Lu, X. Xie, L. Huang and W. Huang. *Nanoscale*, 2017, 9, 13739–13746.
- [3] N. Bogdan, F. Vetrone, G. A. Ozin and J. A. Capobianco, *Nano Lett.*, 2011, 11, 835–840.