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Electronic Supplementary Information

Efficient modulation of upconversion luminescence in NaErF₄-based

core-shell nanocrystals

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Experiments

1.1 Materials

Rare-earth oxides Lu_2O_3 (99.99%), Yb_2O_3 (99.99%), Er_2O_3 (99.99%), were purchased from Foshan Lansu Chemical Industry Company. NH₄F (98%) and NaOH (98.5%) were purchased from J&K Chemical. Oleic acid (OA) (>90%), and octadecane (ODE) (>90%) were purchased from Alfa Aesar. Cyclohexane and ethanol were supplied from Beijing Chemical Plants as well as were of analytical grade. The materials mentioned above were used directly without further purification. The rare-earth chlorides (LuCl₃.6H₂O, YbCl₃.6H₂O, ErCl₃.6H₂O) were prepared by the transformation of their respective rare-earth oxides (Lu₂O₃, Yb₂O₃, Er₂O₃).

1.2 Characterization

The morphologies of all nanoparticles were determined at 200 kV with JEOL JEM-2010 transmission electron microscope (TEM). The prepared samples were dispersed in cyclohexane and dropped onto the surface of a copper grid for TEM analysis. The size distribution histograms derived from the corresponding TEM images of 200 nanocrystals. Shimadzu XRD-7000 X-ray diffractometer was observed to characterize the crystal structure of the powder materials at a scanning rate of 2 °/min in the 20 range from 10 ° to 70 ° with Cu K_a radiation ($\lambda = 1.54$ Å). The reference data were taken from the Joint Committee on Powder Diffraction Standards (JCPDS). All the nanocrystals were dispersed in cyclohexane (2 mg/mL) for further spectroscopic measurements. The steady-state UCL spectra were measured by fluorescence spectrophotometer (FLS980, Edinburgh Instruments), excited by an external continuous-wave (CW) 980-nm diode laser (Changchun New Industries Optoelectronics Tech Co., MDL-H-980-5W), scanning from 500 nm to 700 nm with 190 W/cm² excitation power density. All the luminescence spectra were recorded at room temperature.

1.3 Synthesis^{1.2}

Synthesis of (RE = 1 mmol) NaErF₄ core nanoparticles. NaErF₄ core was synthesized via the solvothermal method. NaErF₄ core nanocrystals were prepared

following this process: the 1 mmol $\text{ErCl}_3.6\text{H}_2\text{O}$ mixed with 6 ml oleic acid (OA) and 15 ml octadecene (ODE), were added into a 250 ml flask under magnetic stirring. The mixture solution was stirred and heated to 130 °C under vacuum to form a homogeneous solution and then cooled down to room temperature. Then, NaOH (2.5 mmol) and NH₄F (4 mmol) were poured into the solution. The temperature of mixed solution was quickly increased to 290-300 °C for 1.5 hour under argon atmosphere. The solution was cooled down naturally under argon. The NaErF₄ nanocrystals solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 50 °C before being used for shell coating and further characterization.

Synthesis of (RE = 1 mmol) NaErF₄@NaLuF_{4:}xYb³⁺ (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanoparticles.

The core-shell nanoparticles were prepared according to a literature procedure. The NaErF₄ nanoparticles used seeds core were as for shell coating. NaErF₄@NaLuF₄·xYb³⁺ (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanocrystals were prepared following this process: the 1 mmol solid power including YbCl₃.6H₂O (x=0%, 5%, 9%, 20%, molar ratio), LuCl₃.6H₂O (1-x, molar ratio) mixed with 6 ml oleic acid (OA) and 15 ml octadecene (ODE), were added into a 250 ml flask under magnetic stirring. The mixture solution was stirred and heated to 130 °C under vacuum to form a homogeneous solution and then cooled down to room temperature. After that, NaErF₄ core nanoparticle (40mg) seeds were added into the mixture solution under vacuum for 30 min. Then, NaOH (2.5 mmol) and NH₄F (4 mmol) were poured into the solution. The temperature of mixed solution was quickly increased to 290-300 °C for 1.5 hour under argon atmosphere and then the solution was cooled down naturally under argon. The NaErF₄@NaLuF₄:xYb³⁺ (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanocrystal solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 50 °C before further characterization.

Synthesis of (RE = 0.72 mmol) NaErF₄ core nanoparticles.

The synthetic procedure was similar to above synthesis of (RE = 1 mmol) NaErF₄

core nanoparticles. Dosages of solid power $ErCl_3.6H_2O$ was (RE = 0.72 mmol). But the temperature of mixed solution was quickly increased to 290-300 °C for 50 min under argon atmosphere and then the solution was cooled down naturally under argon. The NaErF₄ nanocrystals solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 50 °C before being used for shell coating and further characterization.

Synthesis of (RE =0.72 mmol) NaErF₄@NaLuF_{4:}xYb³⁺ (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanoparticles

The synthetic procedure was similar to above synthesis of (RE = 1 mmol) NaErF₄@NaLuF₄:xYb³⁺ (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanoparticles. the 0.72 mmol solid power including YbCl₃.6H₂O (x= 0%, 5%, 9%, 20%, molar ratio), LuCl₃.6H₂O ((1-x), molar ratio) mixed with 6 ml oleic acid (OA) and 15 ml octadecene (ODE). But the temperature of mixed solution was quickly increased to 290-300 °C for 50 min under argon atmosphere and then the solution was cooled down naturally under argon. The NaErF₄@NaLuF₄:xYb³⁺ (x= 0%, 5%, 9%, 20%, molar ratio) nanocrystals solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 50 °C before being used for shell coating and further characterization.



Fig. S1 Size-distribution histograms of the (a) NaErF₄ core-only and (b-e) NaErF₄@NaLuF₄: xYb^{3+} (x= 0%, 5%, 9%, 20%) core-shell nanoparticles at lower [F]/[RE] ratio ([F]/[RE] = 4). Size-distribution histograms of (f) NaErF₄ core-only and (g-j) NaErF₄@NaLuF₄: xYb^{3+} (x= 0%, 5%, 9%, 20%) core-shell nanoparticles at higher [F]/[RE] ratio ([F]/[RE] = 5.6).



Fig. S2 TEM images of (a-c) NaErF₄@NaLuF₄ core-shell nanoparticles at different [F]/[RE] ratio ([F]/[RE] = 4, 4.8, 5.6). TEM images of (d-f) NaErF₄@NaLuF₄: $9\%Yb^{3+}$ core-shell nanoparticles at different [F]/[RE] ratio ([F]/[RE] = 4, 4.8, 5.6).



Fig. S3 TEM images of (a) NaErF₄ core-only and (b-e) NaErF₄@NaLuF₄: xYb^{3+} (x= 0%, 5%, 9%, 20%) core-shell nanoparticles at [F]/[RE] = 4.8.

As shown in Fig. S3, when the [F]/[RE] ratio was 4.8, the prepared core-only and their corresponding core-shell nanoparticles exhibited nearly rod-like shape and uniform size. The average size of these NaErF₄ core-only nanoparticles was 15.0×26.0 nm, and it increased to 40.0×55.0 nm, 38.0×53.8 nm, 36.5×51.5 nm, 36×50.4 nm respectively after NaLuF₄:xYb³⁺ (x=0%, 5%, 9%, 20%) shell coating.



Fig. S4 Selected XRD patterns of core (NaErF₄) with different [F]/[RE] ratio during synthesis process.



Fig. S5 Steady-state UCL spectra of NaErF₄@NaLuF₄: xYb^{3+} (x=0%, 5%, 9%, 20%) core-shell nanocrystals with [F]/[RE] ratio = 4.8 under 980 nm CW laser irradiation.



Fig. S6 Green-to-red ratios (G/R ratios) of NaErF4@NaLuF4: xYb3+ (x= 0%, 5%,9%, 20%) core-shell nanoparticles with different [F]/[RE] ratios.

As shown in Fig. S7, the core-shell nanocrystals (NaLuF₄: x Er³⁺@NaLuF₄ x= 25%, 50%, 100%) exhibited typical green emissions peaked at 520 nm and 540 nm, and red emission centered at 654 nm of Er³⁺. With the increase of Er³⁺ concentration in coreshell nanocrystals, we found that the green emissions gradually weakened while the

red emission gradually increased, leading to increasing R/G ratios. These results demonstrated the increasing cross-relaxation in Er^{3+} -highly doped system.



Fig. S7 (a) Steady-state UCL spectra of NaLuF₄: x Er^{3+} @NaLuF₄ (x=25%, 50%, 100%) core-shell nanocrystals with [F]/[RE] ratio =4 under 980 nm CW laser irradiation and (b) their corresponding G/R ratios.



Fig. S8 Power-dependent UCL intensity of (a) 540nm and (b) 654nm emissions of NaErF₄@NaLuF₄: xYb^{3+} (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanoparticles at lower [F]/[RE] ratio ([F]/[RE]=4). Power-dependent UCL intensity of (c) 540nm and (d) 654nm emissions of NaErF₄@NaLuF₄: xYb^{3+} (x= 0%, 5%, 9%, 20%, molar ratio) core-shell nanoparticles at higher [F]/[RE] ratio ([F]/[RE]=5.6).



Fig. S9 Energy transfer mechanism in NaErF₄@NaLuF₄ system. ³⁻⁶ Notes: ETU= energy transfer upconversion, CR= cross relaxation, A: Activator, S: Sensitizer.



Fig. S10 Energy transfer mechanisms in NaErF₄@NaLuF₄: Yb³⁺ system⁷⁻¹² at (a) low doping and (b) high doping Yb³⁺ respectively. Notes: ETU=energy transfer upconversion, CR= cross relaxation.

Reference

- 1. L. Sun, L. Li, R. Gao, K. Tang, L. Fu, X. C. Ai and J. P. Zhang, *Phys. Chem. Chem. Phys.*, 2018, 20, 17141-17147.
- X. Zhai, Y. Wang, X. Liu, S. Liu, P. Lei, S. Yao, S. Song, L. Zhou, J. Feng and H. Zhang, ChemPhotoChem, 2017, 1, 369-375.
- L. Yan, B. Zhou, N. Song, X. Liu, J. Huang, T. Wang, L. Tao and Q. Zhang, *Nanoscale*, 2018, 10, 17949-17957.
- 4. Q. Chen, X. Xie, B. Huang, L. Liang, S. Han, Z. Yi, Y. Wang, Y. Li, D. Fan, L. Huang and X. Liu, *Angew Chem. Int .Ed.*, 2017, **56**, 7605-7609.
- J. Zuo, Q. Li, B. Xue, C. Li, Y. Chang, Y. Zhang, X. Liu, L. Tu, H. Zhang and X. Kong, Nanoscale, 2017, 9, 7941-7946.
- Y. Shang, S. Hao, W. Lv, T. Chen, L. Tian, Z. Lei and C. Yang, J. Mater. Chem. C, 2018, 6, 3869-3875.

- 7. M. Wu, L. Yan, T. Wang, B. Zhou and Q. Zhang, Adv. Funct. Mater., 2019, 29, 1804160.
- 8. Y. Li, P. Zhang, H. Ning, J. Zeng, Y. Hou, L. Jing, C. Liu and M. Gao, Small, 2019, 15, 1905344.
- B. Huang, M. Sun, A. W. Dougherty, H. Dong, Y. J. Xu, L. D. Sun and C. H. Yan, *Nanoscale*, 2017, 9, 18490-18497.
- 10. X. Zheng, S. Shikha and Y. Zhang, Nanoscale, 2018, 10, 16447-16454.
- Q. Su, S. Han, X. Xie, H. Zhu, H. Chen, C. K. Chen, R. S. Liu, X. Chen, F. Wang and X. Liu, J .Am. Chem. Soc., 2012, 134, 20849-20857.
- 12. N. J. Johnson, S. He, S. Diao, E. M. Chan, H. Dai and A. Almutairi, *J. Am. Chem. Soc.*, 2017, **139**, 3275-3282.