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Electronic Supplementary Information

Lanthanide-doped $NaGdF_4$ core-shell nanoparticles for non-contact self-referencing temperature sensors

Shuhong Zheng,[a] Weibo Chen,[a] Dezhi Tan,[a] Jiajia Zhou,[b] Qiangbing Guo,[a] Wei Jiang,[a] Cheng Xu,[a] Xiaofeng Liu*[a] and Jianrong Qiu*[a, c]

[a] State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang, 310027, P. R. China. E-mail:qjr@zju.edu.cn; Fax: +86 57188925079; Tel: +86 57188925079.

[b] College of Materials Science and Engineering, China Jiliang University, Hangzhou, Zhejiang, 310018, P. R. China.

[c] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, Guangdong, 510640, P. R. China.

Experimental Section

Chemicals. Gadolinium(III) acetate hydrate (99.99%), ytterbium(III) acetate hydrate (99.99%), thulium acetate hydrate (99.99%), terbium(III) acetate hydrate (99.99%), europium acetate hydrate (99.99%), sodium hydroxide (NaOH, >98%), 1-octadecene (90%), oleic acid (90%) were purchased from Sigma-Aldrich. Ammonium fluoride (NH_4F, >98%), and cyclohexane were purchased from Wako Pure Chemical Industries, Ltd. All of the chemicals were used without any further purification process.

Synthesis of β-$NaGdF_4$:Yb/Tm core Nanoparticles The lanthanide-doped $NaGdF_4$ core and core-shell nanoparticles were synthesized by a thermal-decomposition method as described in refs.[1, 2] with slight modification. In a typical procedure, 0.4 mmol of $Gd(CH_3COO)_3\cdot 4H_2O$, 0.392 mmol of $Yb(CH_3COO)_3\cdot 4H_2O$ and 0.008 mmol of $Tm(CH_3COO)_3\cdot 4H_2O$ were mixed with 8 mL of oleic acid (OA) and 12 mL of 1-octadecene in a 50 mL three-neck round-bottom flask. The mixture was then heated to 150 °C and kept there for 60 min in the presence of continuous N_2 flow and magnetic stirring, resulting in a clear yellowish-brown solution. After cooling the solution to room temperature, 10 mL of methanol solution containing 2.72 mmol NH_4F and 2 mmol NaOH was added, and the solution was stirred again at 50 °C for 30 min to remove methanol. Thereafter, the solution was heated to 290 °C and stayed for 90 min. Finally, after cooling down to room temperature, the nanocrystals were precipitated by addition of ethanol, and collected by centrifugation. They were washed with ethanol several times, and finally redispersed in cyclohexane.

Synthesis of β-$NaGdF_4$:Yb/Tm@β-$NaGdF_4$:A (A=1.5%mol Eu, 15%mol Tb , 15%/1.5%mol Tb/Eu) Core–Shell Nanoparticles. For shell growth (β-NaGdF4:Eu as an example), 0.788 mmol of $Gd(CH_3COO)_3{\cdot}4H_2O$ and 0.012 mmol of $Eu(CH_3COO)_3{\cdot}4H_2O$ were added to a 50 mL three-neck round-bottom flask containing 8 mL of OA and 12 mL of 1-octadecene and heated to 150 °C under N_2 flow and magnetic stirring for 60 min; likewise a clear yellowish-brown solution was developed. After cooling down to 80 °C, 0.4 mmol β-$NaGdF_4$:Yb/Tm nanocrystal seeds (core) in 6 mL of cyclohexane was added to the above solution. After complete evaporation of cyclohexane, 10 mL methanol solution containing 2.72 mmol NH_4F and 2 mmol NaOH was added and the mixture was stirred at 50 °C for 30 min. In a similar fashion, after the evaporation of methanol the solution temperature was raised to 290 °C and maintained for 90 min under N_2 flow with vigorous stirring. The core–shell nanocrystals were obtained finally at room temperature with the same method as described above.

References

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2 W. Zheng, S. Y. Zhou, Z. Chen, P. Hu, Y. S. Liu, D. T. Tu, H. M. Zhu, R. F. Li, M. D. Huang and X. Y. Chen, Angew. Chem. Int. Ed., 2013, 52, 6671.

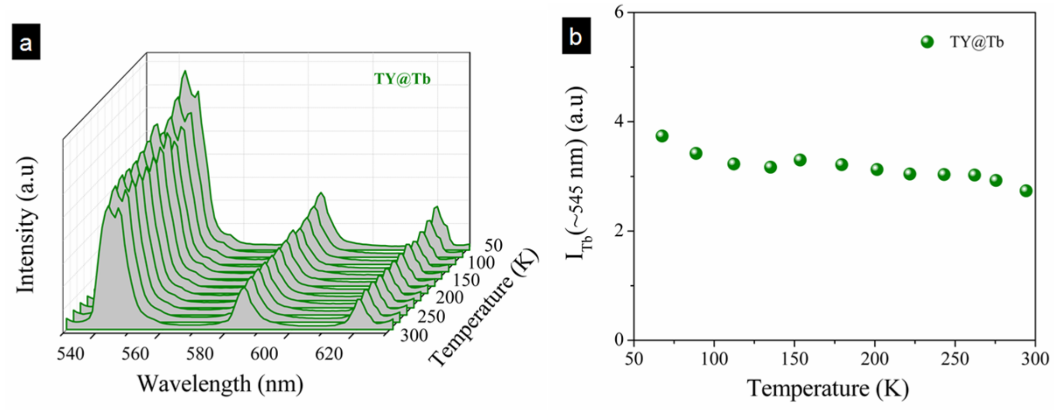

Fig. S1 (a) Upconversion emission spectra of singly Tb^{3+} doped core-shell nanoparticles ($NaGdF_4$:0.01Tm^{3+}/0.49Yb^{3+}@$NaGdF_4$:0.15Tb^{3+}) recorded between 50 and 300 K. (b) Temperature-dependence of the integrated emission intensity centered at 545 nm of Tb^{3+} ions.

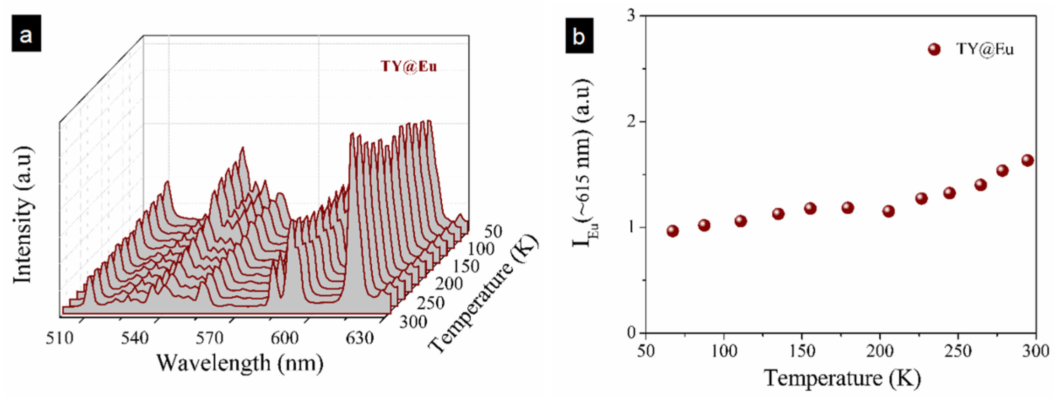

Fig.S2 (a) Upconversion emission spectra of singly Eu^{3+} doped core-shell nanoparticles ($NaGdF_4$:0.01Tm^{3+}/0.49Yb^{3+}@$NaGdF_4$:0.015Eu^{3+}) recorded between 50 and 300 K. (b) Temperature-dependence of the integrated emission intensity centered at 615 nm of Eu^{3+}ions.