Supplementary Information for

Enhanced two-step two-frequency upconversion luminescence in core/shell/shell nanostructure

Dongcheng Han,[a,b,c] Shizhi Yang,[a,c,] Qiang Zhao,[d *] Liangliang Zhang,[e] Yan Deng,[d]*

[a]Key Laboratory of Atmospheric Optics, Anhui Institute of Optics and Fine Mechanics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China

[b]Science Island Branch of Graduate School, University of Science and Technology of China, Hefei, Anhui 230026, China

[c]Advanced Laser Technology Laboratory of Anhui Province, Hefei 230037, China

[d]School of Environment and Energy Engineering, Anhui Jianzhu University, Hefei 230601, China

[e]Anhui Easpeed Technology Co. Ltd, Hefei, Anhui 230088, China

*Corresponding Authors

Shizhi Yang: szyang@aiofm.ac.cn

Qiang Zhao: rommel99@163.com

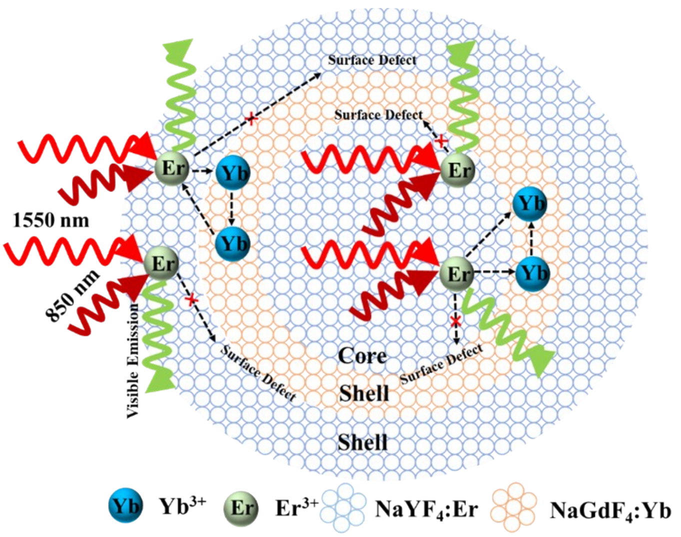


Figure S1. The designed core/shell/shell nanostructure to enhance the TSTF UCL.

A novel strategy of designed core/shell/shell nanostructure was first proposed to enhance the TSTF UCL intensity and contrast, as shown in Figure S1. Commonly, RE-doped UCNPs often suffer from low UC efficiency mainly caused by surface defects[1-3] and concentration quenching[4,5]. In order to get a stronger UCL, a core/shell/shell nanostructure was employed to reduce surface defects of UCNPs. In addition, doping

Er^{3+} ions separately in core and outer shell could not only decrease the concentration quenching of Ln^{3+} ions but also increase the absorption of 1550 nm. Yb^{3+} doped in inner shell could offer a new approach to improve 1550 nm absorption and UC emission.

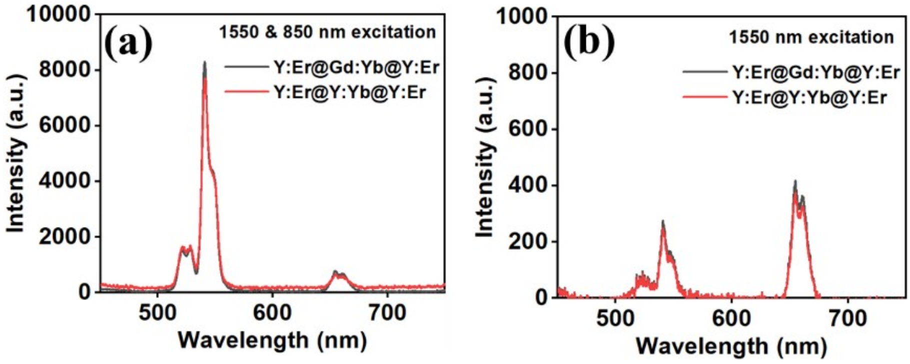


Figure S2. UC emission spectra of $NaYF_4$:Er@$NaGdF_4$:Yb@$NaYF_4$:Er (Y:Er@Gd:Yb@Y:Er) and $NaYF_4$:Er@$NaYF_4$:Yb@$NaYF_4$:Er (Y:Er@Y:Yb@Y:Er) UCNPs under (a) 850 & 1550 nm, (b) 1550 nm excitation.

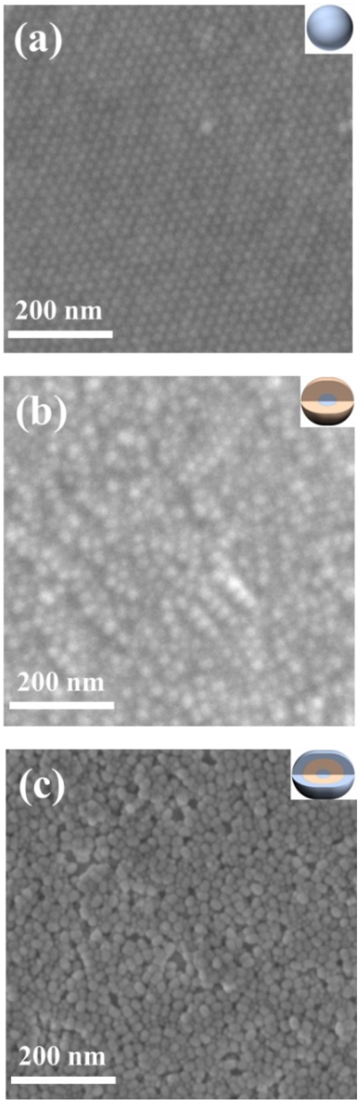
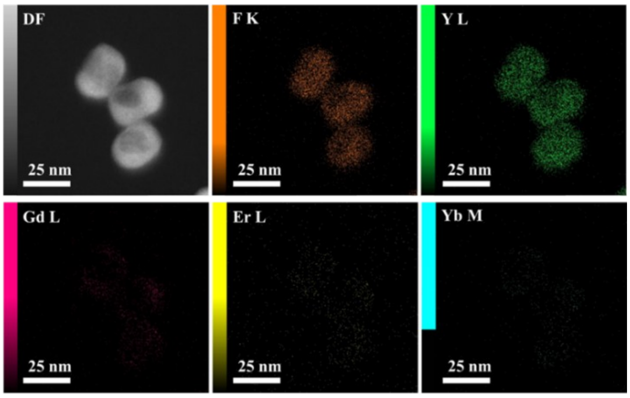


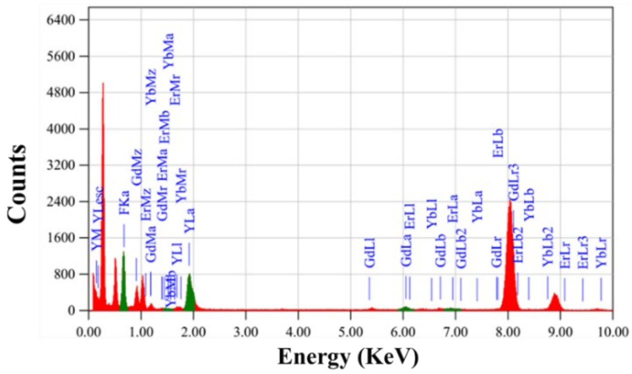
Figure S3. SEM images of (a) $NaYF_4$:0.5%Er, (b) $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb and (c) $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er UCNPs.

The shape of the $NaYF_4$:0.5%Er, $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb and $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er UCNPs could also be characterized by SEM (Figure S3). The morphology of above UCNPs changed gradually from quasi-sphere to rod-like with Yb^{3+}-doped $NaGdF_4$ and Er^{3+}-doped $NaYF_4$ layers covered respectively. The changed shape of as-prepared UCNPs demonstrates the successful synthesis of the core/shell/shell nanostructure. The similar results can also be gotten from Figure 4 and Figure 5.

(a)



(b)



(c)

Element	keV	Mass%	Counts	Sigma	Atom%	K
F K	0.677	23.14	7540.47	0.53	59.59	0.3534
Y L	1.922	69.07	7953.79	1.53	38.00	1.0000
Gd L	6.056	7.27	761.22	0.43	2.26	1.0992
Er L		ND			ND	
Yb M	1.521	0.53	83.90	0.18	0.15	0.7213

(d)

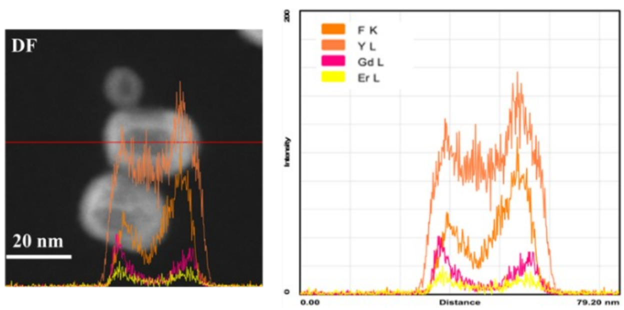


Figure S4. (a), (b) and (c) The energy dispersive spectrometer (EDS) data of $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er core/shell/shell UCNPs. (d) EELS line scan conducted with STEM imaging on a $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er core/shell/shell nanoparticle.

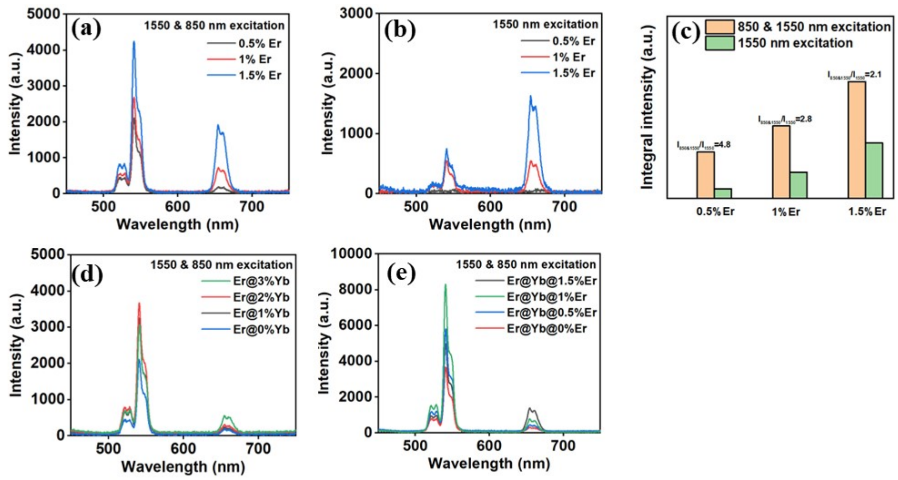


Figure S5. UC emission spectra of $NaYF_4$:x%Er (x = 0.5, 1, 1.5) UCNPs under (a) 850 & 1550 nm, (b) 1550 nm excitation. (c) The UCL integral intensity and contrast of the above as-prepared UCNPs. (d) UC emission spectra of (d) $NaYF_4$:0.5%Er@$NaGdF_4$:y%Yb (y = 0, 1, 2, 3) and (e) $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:z%Er (z = 0, 0.5, 1, 1.5) UCNPs under 850 & 1550 nm excitation.

In Figure S5, the UC emission spectra excited by 850 & 1550 nm or 1550 nm were measured for obtaining the UCL intensities and contrast of TSTF UCNPs. For $NaYF_4$:x%Er (x = 0.5, 1, 1.5) UCNPs (Figure S5a, b and c), when Er^{3+} ions doping concentrations raised from 0.5 to 1.5 mmol%, the TSTF UCL intensities gradually increased, however, the contrast decreased from 4.8 to 2.1. For a better application in 3-D display, the UCNPs with high contrast is more important than its UCL intensity. So, $NaYF_4$:0.5%Er UCNPs were selected as core. Then, a series of $NaGdF_4$:y%Yb (y = 0, 1, 2, 3) layers were covered on core UCNPs, As Figure S5d shown, when 2 mmol% Yb^{3+} doped in the inner shell, the $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb UCNPs exhibited a highest UCL intensity and contrast. Finally, by optimizing Er^{3+} ions doping concentrations in outer shell, the $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er UCNPs with highest UCL intensity and contrast were obtained (Figure S5e).

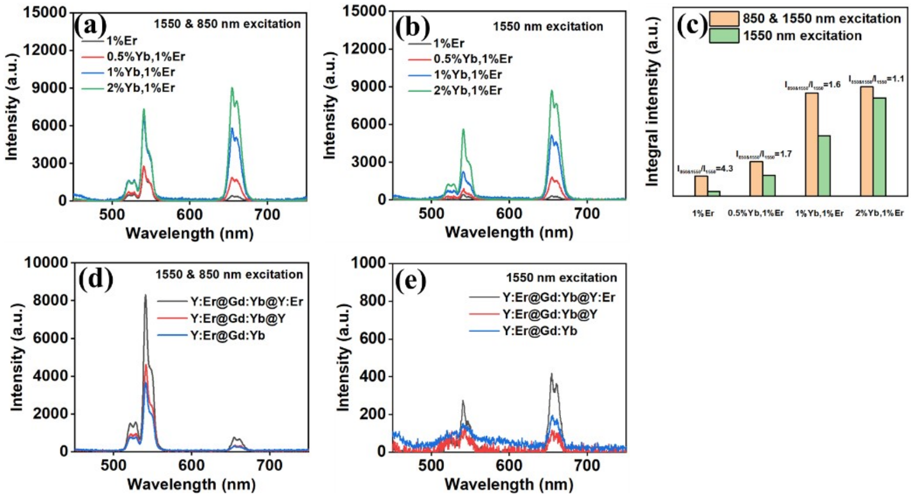


Figure S6. UC emission spectra of $NaYF_4$:x%Yb, 1%Er (x = 0, 0.5, 1, 2) UCNPs under (a) 850 & 1550 nm, (b) 1550 nm excitation. (c) The UCL integral intensities and contrast of the above as-prepared UCNPs. UC emission spectra of $NaYF_4$:Er@$NaGdF_4$:Yb@$NaYF_4$:Er (Y:Er@Gd:Yb@

Y:Er), $NaYF_4$:Er@$NaGdF_4$:Yb@$NaYF_4$ (Y:Er@Gd:Yb@Y) and $NaYF_4$:Er@$NaGdF_4$:Yb (Y:Er@Gd:Yb) UCNPs under (d) 850 & 1550 nm, (e) 1550 nm excitation.

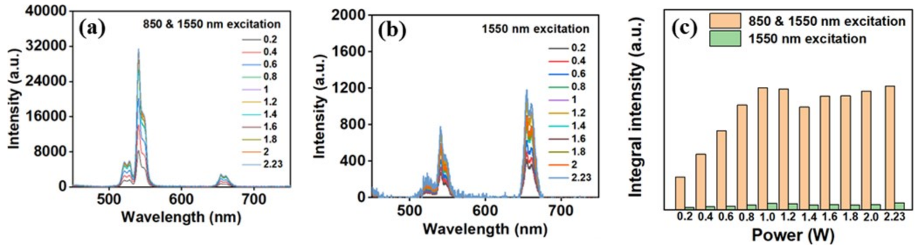


Figure S7. UC emission spectra of $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er UCNPs excited by (a) 850 & 1550 nm, (b) 1550 nm under different pump powers of 1550 nm. (c) The UCL integral intensity of as-prepared UCNPs under different pump powers of 1550 nm. The 850 nm laser power is kept at 0.2 W.

Under 850 nm excitation, no single-frequency UCL was observed in as-prepared UCNPs. Fixing the 850 nm excitation power at 0.2 W, the 1550 nm laser excitation power is gradually increased from 0.2 W to 2.23 W. The excitation power of the laser at 1550 nm increased was measured, as shown in Figure S7a, b. It could be seen that the UCL integral intensities of $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er UCNPs under 850 & 1550 nm excitation was enhanced with increasing pump power (0.2 ~ 1 W) (Figure S7c).

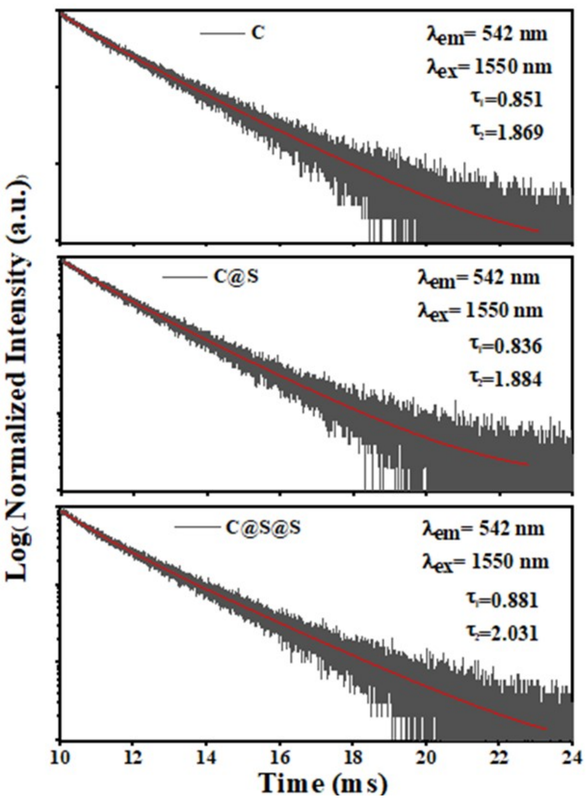


Figure S8. Time–decay curves of 542 nm UC emission for the $NaYF_4$:0.5%Er (C), $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb (C@S) and $NaYF_4$:0.5%Er@$NaGdF_4$:2%Yb@$NaYF_4$:1%Er (C@S@S) nanoparticles.

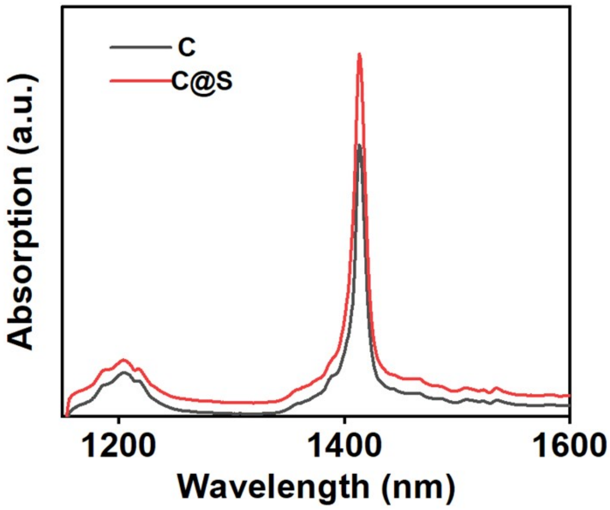


Figure S9. The absorption spectrum of C (black) and C@S (red) UCNPs around 1550 nm.

With the Yb^{3+}-doped $NaGdF_4$ shell covered, the absorption intensity of C@S UCNPs increased, which means that the doped-Yb^{3+} ions improved the absorption of 1550 nm excitation.

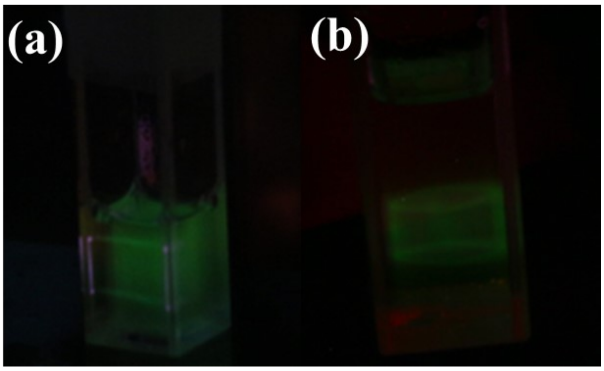


Figure S10. 3-D cube images of (a) Er@Er@Yb and (b) Er@Yb@Er UCNPs excited at 850 & 1550 nm.

Under the same experimental conditions, a clear green 3-D cube could be easily observed in Er@Yb@Er UCNPs (Figure S10b), while Er@Er@Yb UCNPs with low contrast is vague (Figure S10a), which shows that the high-contrast TSTF UCNPs plays a significant role in improving the display effect of 3-D display.

References

1. W. Bian, Y. Lin, T. Wang, X. Yu, J. Qiu, M. Zhou, H. Luo, S. Yu and X. Xu, *ACS Nano*, 2018, **12**, 3623-3628.

2. G. Tessitore, G. A. Mandl, M. G. Brik, W. Park and J. A. Capobianco, *Nanoscale*, 2019, **11**, 12015-12029.

3. D. Zhao, X. Li, R. Wang and F. zhang, *Nano Lett.*, 2014, **14**, 3634-3639.

4. X. Zheng, S. Swati and Y. Zhang, *Nanoscale*, 2018, **10**, 16447-16454.

5. M. Feng, R. Lv, L. Xiao，B. Hu, S. Zhu, F. He, P. Yang and J. Tian, *Inorg. Chem.*, 2018, **57**, 14594-14602.