Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplemental Information

Compressed Energy Transfer Distance for Remarkable Enhancement of the Luminescence of Nd^{3+}-sensitized Upconversion Nanoparticles

Dan Wang, Bin Xue，Jun Song*, Junle Qu*

Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China
*Email - songjun@szu.edu.cn, songjun.opt@gmail.com

Part I. Supporting Data.

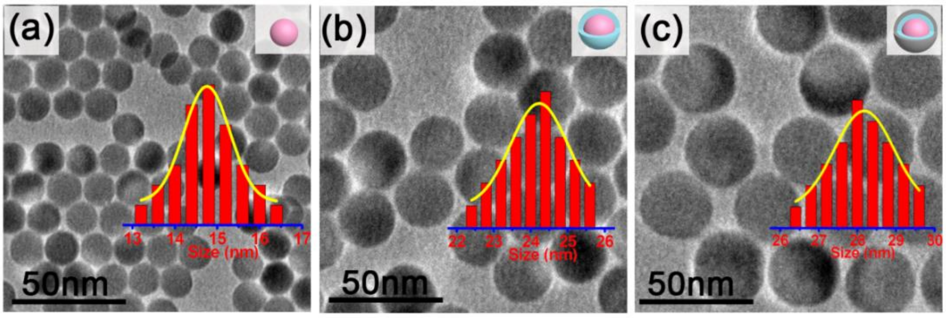

Fig. S1 TEM images of (a) 14.8 nm Yb/Ho core. (b) 24.4 nm Yb/Ho@Nd core-shell UCNPs. (c) 28.0 nm Yb/Ho @ Nd@Y core-shell-shell UCNPs.

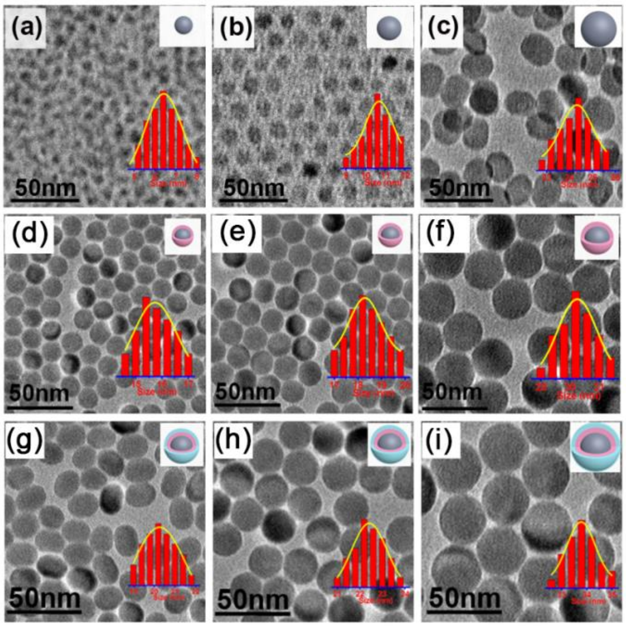

Fig. S2 TEM images of (a) 6.5 nm inert $NaYF_4$ nanoparticles. (b) 10.6 nm inert $NaYF_4$ nanoparticles. (c) 24.3 nm inert $NaYF_4$ nanoparticles. (d) 15.9 nm Y@ Yb/Ho core-shell UCNPs with 6.5 nm inert core. (e) 18.2 nm Y@ Yb/Ho core-shell UCNPs with 10.6 nm inert core. (f) 30.3 nm Y@Yb/Ho core-shell UCNPs with 24.3 nm inert core. (g) 20.1 nm Y@ Yb/Ho @Nd core-shell-shell UCNPs with 6.5 nm inert core. (h) 22.2 nm Y@Yb/Ho@Nd core-shell-shell UCNPs with 6.5 nm inert core. (i) 33.9 nm Y@Yb/Ho@Nd core-shell-shell UCNPs with 24.3 nm inert core.

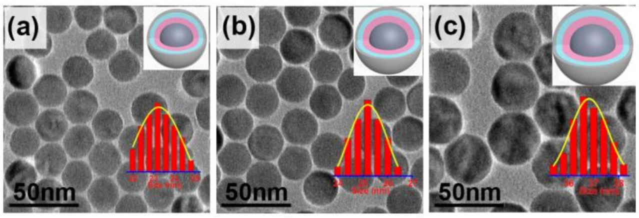

Fig. S3 TEM images of Y@Yb/Ho@Nd@Y core-shell-shell-shell UCNPs with different size of $NaYF_4$ core: (a) 23.2 nm with 6.5 nm inert core; (b) 25.2 nm with 10.6 nm inert core; (c) 36.7 nm with 24.3 nm inert core.

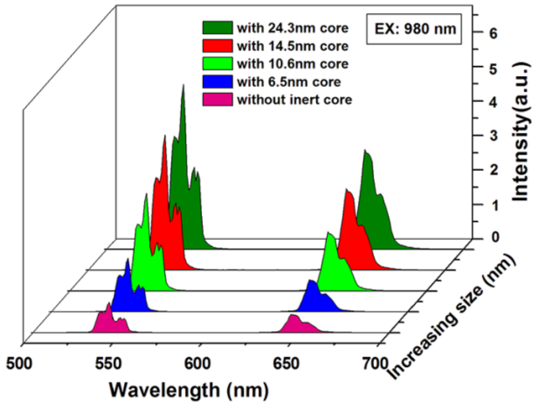

Fig. S4 UCL intensities of the Y@Yb/Ho UCNPs with increasing size of the inert cores upon 980 nm laser excitation.

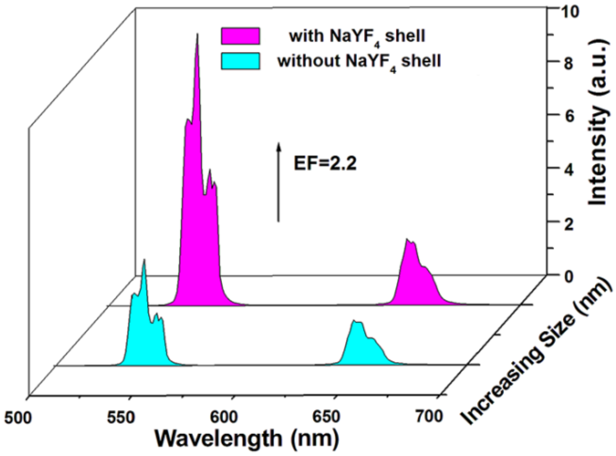

Fig. S5 UCL emission intensities of Y@Yb/Ho@Nd UCNPs and Y@Yb/Ho@Nd@Y UCNPs with core size of $NaYF_4$ upon 808 nm laser irradiation.

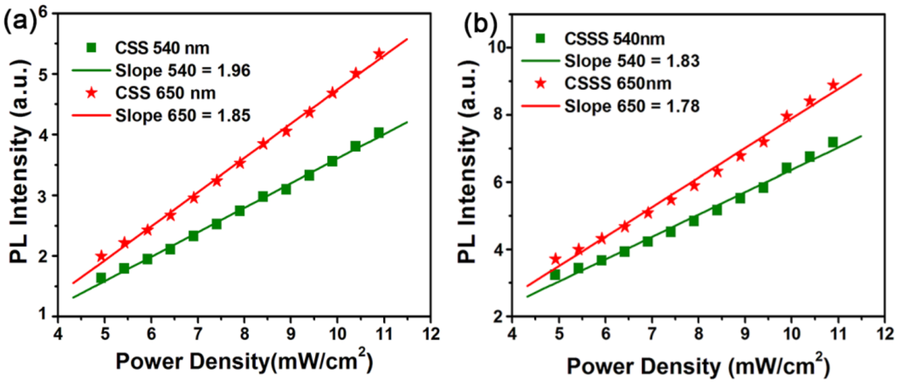

Fig. S6. (a) Power dependence of Yb/Ho@Nd@Y CSS UCNPs emissions at 540 and 650 nm. (b) Power dependence of Y@Yb/Ho@Nd@Y CSSS UCNPs emissions at 540 and 650 nm.

Part II. Calculation of the energy migration efficiency

Due to the Nd^{3+} ions and Yb^{3+} ions are doped in different region, the calculation of the average distance for co-doped system is not appropriate. Here, we define the average distance (R_{avr}) between Nd^{3+} and Yb^{3+} is the distance between the Nd-doped layer and the Yb-doped layer, which is the distance from the center of Nd-doped layer to the center of Yb-doped layer as (Fig. S7):

$$R_{avr} = \frac{d_1}{2} + \frac{d_2}{2} \tag{1}$$

Where, d_1 is the thickness of Nd-doped layer, d_2 is the thickness of Yb-doped layer.

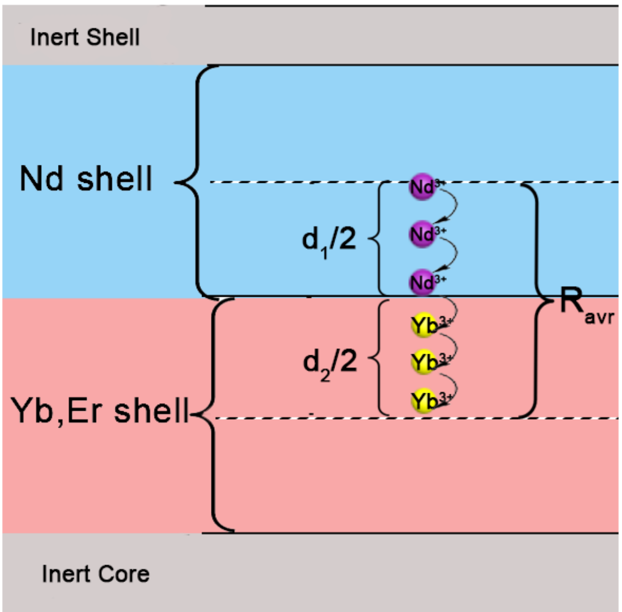

Fig. S7. Schematic graph of the average distance between the Nd^{3+}-doped layer and the Yb^{3+}-doped layer.

The energy migration efficiency (η) is defined as:

$$\eta = (\eta_1)^{n_1}\eta_T(\eta_2)^{n_2} \tag{2}$$

where, n_1 and n_2 are the migration step numbers in the Nd-doped layer and in the Yb-doped layer, respectively, η_1 is the energy migration efficiency at every migration step in the Nd-doped layer, η_2 is the energy migration efficiency at every migration step in the Yb-doped layer, η_T is the energy transfer efficiency from Nd^{3+} to Yb^{3+}. According the literature, η_1 is estimated about 20%,[1] η_2 is about 99.8%,[2] η_T is about 70%.[3]

For simplification, we assumed that excitation energy migrates vertically across from Nd-doped layer to Yb-doped layer, thus the average migration distance is the average distance (R_{avr}) between the Nd-doped layer and the Yb-doped layer, then:

$$R_{avr} \approx n_1 r_{\mathrm{step1}} + n_2 r_{\mathrm{step2}} \tag{3}$$

where r_{step1} and r_{step2} is the per migration step in the Nd-doped layer and in the Yb-doped, respectively.

According to eqn (1) and eqn (3), we obtain:

$$n_1 = \frac{d_1}{2}/r_{\mathrm{step1}} \tag{4}$$

and

$$n_2 = \frac{d_2}{2}/r_{\mathrm{step2}} \tag{5}$$

Similar to previous calculation,[2] for the 20% doping of Yb^{3+} in $NaYF_4$ and the 20% doping of Nd^{3+} in $NaYF_4$, the every migration step of Yb^{3+} r_{step2} is about 0.8 nm, the every migration step of Nd^{3+} r_{step1} is about 0.8 nm.

For the traditional sample without inert core (Fig. S1), d_1 is 4.7 nm, d_2 is 14.8 nm, according to eqn (4) and eqn (5), n_1 is calculated about 2.9375, n_2 is calculated about 9.25. According to eqn (2), energy migration efficiency η is:

$$\eta=(0.2)^{2.9375}\times(0.998)^{9.25}\times0.7=6.1\times10^{-3}$$

Whereas for the sample with inert core (Fig. 1), d_1 is 1.9 nm, d_2 is 3.3 nm, according to eqn (4) and eqn (5), n_1 is calculated about 1.1875, n_2 is calculated about 2.0625. According to eqn (2), energy migration efficiency η is:

$$\eta=(0.2)^{1.1875}\times(0.998)^{2.0625}\times0.7=0.103$$

Part III. References

1. 28. J. A. Caird, A. J. Ramponi and P. R. Staver, J. Opt. Soc. Am. B-Opt. Phys., 1991, 8, 1391-1403

2. J. Zuo, D. Sun, L. Tu, Y. Wu, Y. Cao, B. Xue, Y. Zhang, Y. Chang, X. Liu, X. Kong, W. J. Buma, E. J. Meijer and H. Zhang, Angew. Chem. Int. Ed., 2018, DOI: 10.1002/anie.201711606.

3. T. Kushida, J. Phys. Soc. Jpn., 1973, 34, 1318-1326.