Electronic Supplementary Information

Multicolor output and shape controlled synthesis of lanthanide-ion doped fluorides upconversion nanoparticles

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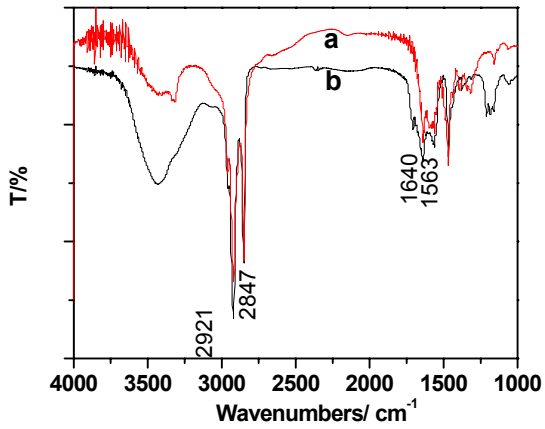

Fig. S1 FT-IR spectra of $NaYF_4$:20%Yb,2%Er UCNPs prepared in OM (a) and OA/OM (b, 5/50).

We characterized the obtained $NaYF_4$:20%Yb,2%Er UCNPs by FT-IR spectroscopy. The FT-IR spectra exhibited the bonding of the ligand molecules on the surface of nanoparticles. The peaks at 2847 and 2921 cm^{-1} were due to the symmetric and asymmetric $\upsilon(CH_2)$ stretching modes. A broad peak at 3350 cm^{-1} originated either from the υ(N-H) stretching of the NH_2 group of octadecylamine or the υ(O-H) stretching mode of adsorbed water. The peak at 1563 cm^{-1} arose from the υ(N–H) scissoring mode, which indicated that the N-H bonds were intact and that octadecylamine bound to the nanoparticles surface. Compared with $NaYF_4$:20%Yb,2%Er UCNPs prepared in OM, we can observe that the absorption band at 1640 cm^{-1} became stronger in the sample of UCNPs prepared with OA/OM of 5/50, which could be ascribed to the coordination of carbonyl group of OA molecules.[1,2]

Addition of an undoped shell ($NaYF_4$) upon the $NaYF_4$:20%Yb, 2%Er core could result in the increase of the final particle size, compared with $NaYF_4$:20%Yb,2%Er cores. So, the formation of a $NaYF_4$:20%Yb,2%Er/$NaYF_4$ core/shell structure is usually characterized by TEM images.[1,3]

Fig. S2 shows the TEM images of $NaYF_4$:20%Yb, 2%Er and $NaYF_4$:20%Yb,2%Er/$NaYF_4$ core/shell UCNPs prepared at 300 °C. It is shown that the mean size of core/shell UCNPs (~ 25 nm) was bigger than that of $NaYF_4$:20%Yb, 2%Er (~ 20 nm), implying the formation of core/shell structure.

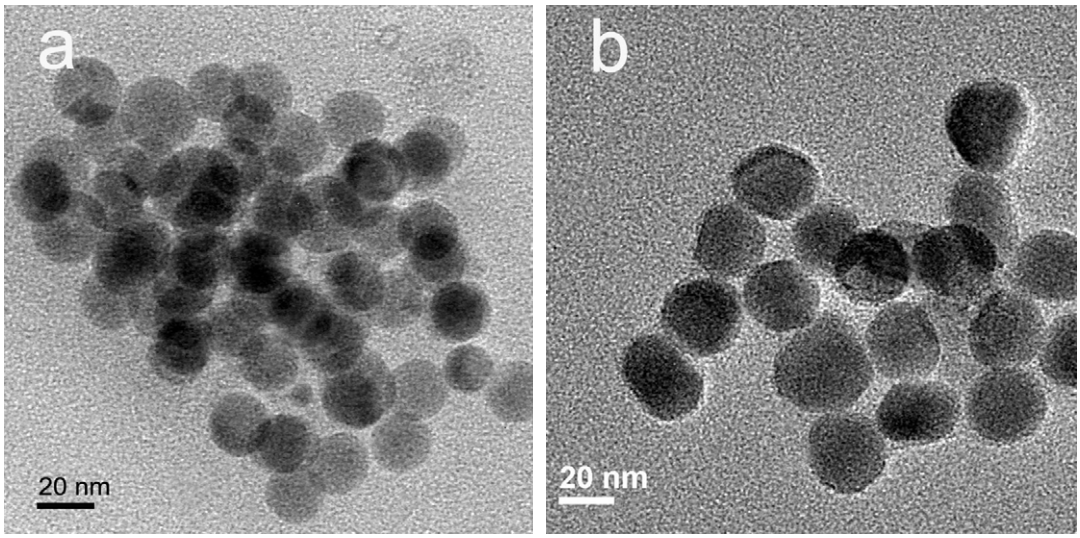

Fig. S2 TEM images of $NaYF_4$:20%Yb,2%Er (a) and $NaYF_4$:20%Yb,2%Er/$NaYF_4$ core/shell (b) UCNPs prepared at 300 °C.

We also estimated the micro-stress of Yb/Ho and Yb/Tm co-doped UCNPs, based on the Williamson-Hall methodology. Similar to the above results, the increase of reaction temperature decreased the micro-stress of UCNPs, and reduced the internal defects.

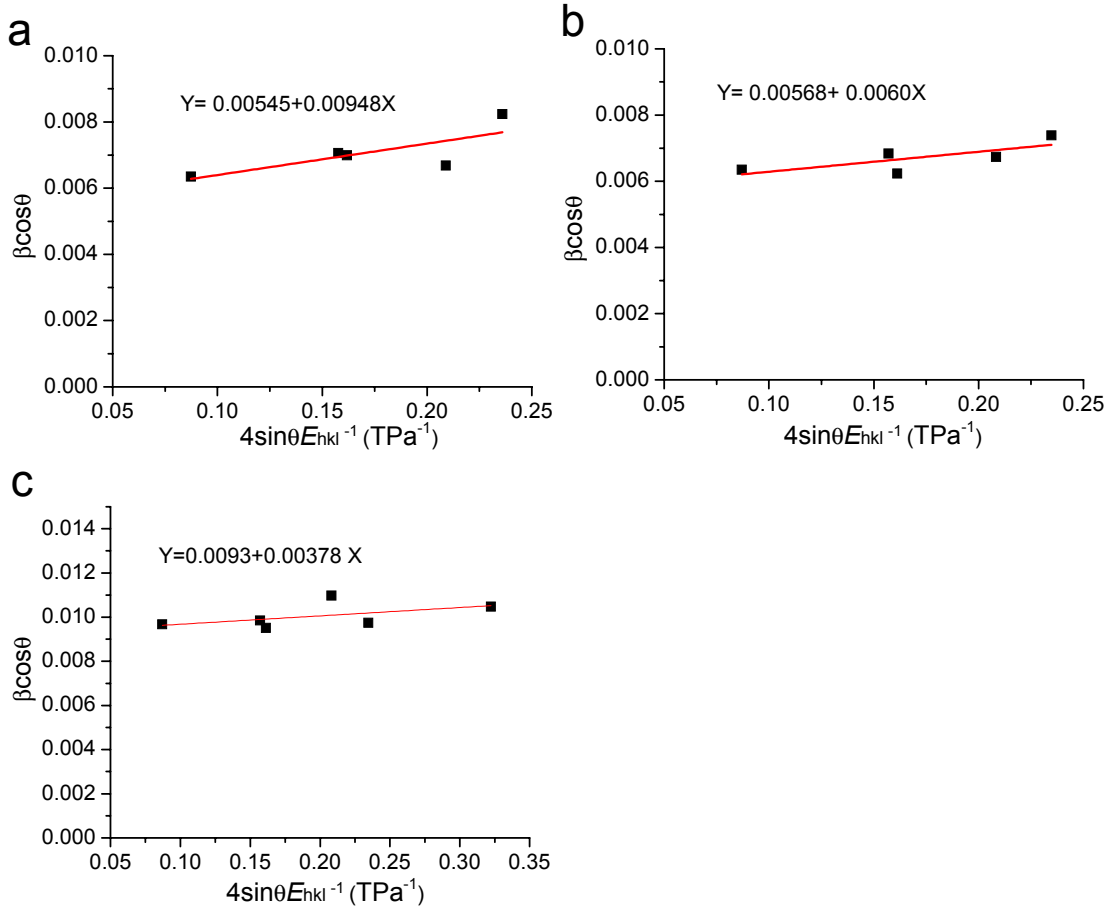

Fig. S3 Williamson–Hall plots of $NaYF_4$:20%Yb, 2%Ho UCNPs prepared at different temperatures for 1 h (a, 260 °C; b, 300°C ; c, 320°C).

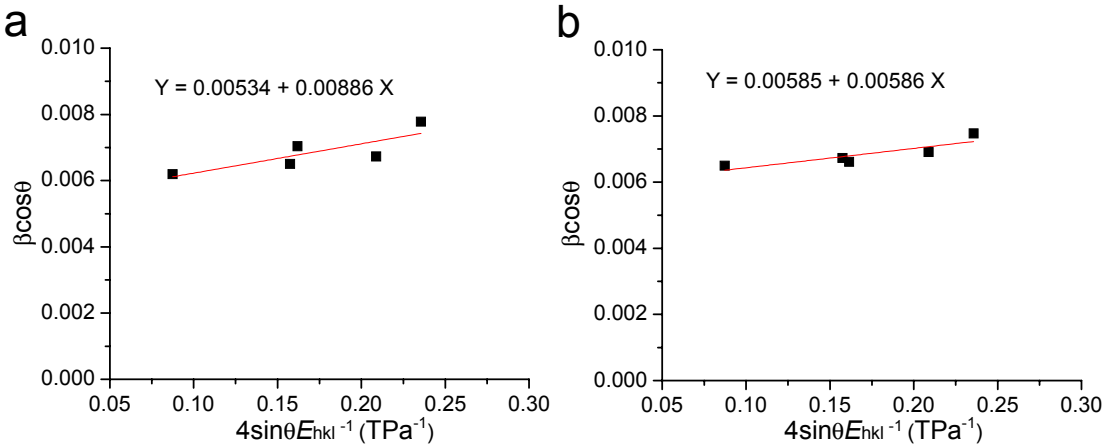

Fig. S4 Williamson–Hall plots of $NaYF_4$:20%Yb, 0.5%Tm UCNPs prepared at different temperatures for 1 h (a, 280 °C; b, 320°C).

Similarly, the micro-stress of the corresponding $NaYF_4$:20%Yb,2%Er UCNPs prepared at different time was also estimated by Williamson–Hall equation. It is observed that the estimated micro-stress of nanoparticles decreased as the reaction time prolonged (Fig. S5), indicating the decrease of internal defects of $NaYF_4$:20%Yb, 2%Er.

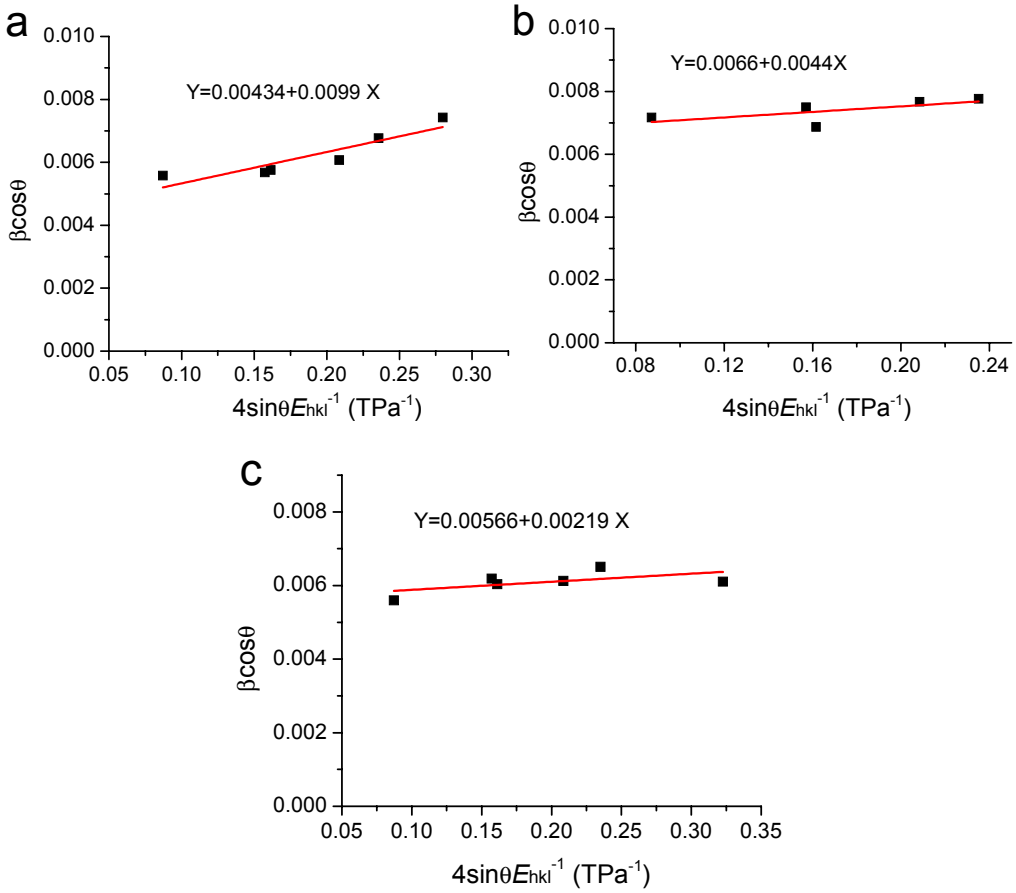

Fig. S5 Williamson–Hall plots of $NaYF_4$:20%Yb, 2%Er UCNPs prepared at 300 °C for different time (a, 40 min; b, 50 min; c, 1.5 h).

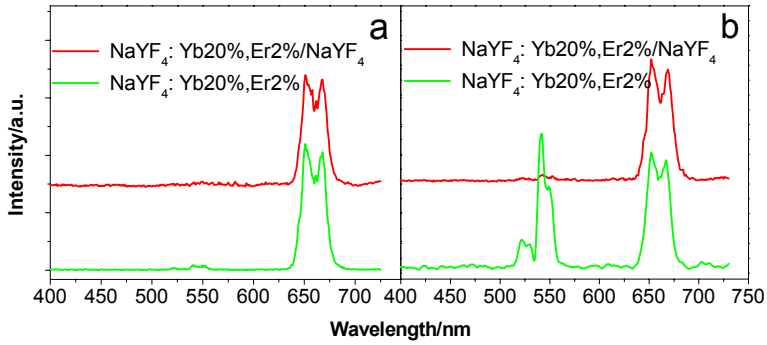

Fig. S6 Upconversion spectra of $NaYF_4$:20%Yb, 2%Er core UCNPs prepared at 300 °C for 40 min (a) and 1.5 h (b), and its corresponding $NaYF_4$:20%Yb,2%Er/$NaYF_4$ core/shell UCNPs (normalized to Er^{3+} 650 nm emisssion). All of nanoparticles were excited at 980 nm with a 175 mW diode laser.

We also found that $NaYF_4$:20%Yb, 2%Er/$NaYF_4$ core/shell UCNPs were nearly in red emission. Addition of $NaYF_4$ shell did not increase the intensities of green emissions and RGR of core/shell UCNPs, though the total intensities were enhanced, implying that surface defects did not take effect in the present work.

References:

1 H. X. Mai, Y. W. Zhang, L. D. Sun and C. H. Yan, *J. Phys. Chem. C*, 2007, **111**, 13721.
2 H. X. Mai, Y. W. Zhang, L. D. Sun and C. H. Yan, *J. Phys. Chem. C*, 2007, **111**, 13730.
3 G. S. Yi and G. M. Chow, *Chem. Mater.* 2007**, 19**, 341.