Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Enhancing upconversion of manganese through spatial control of energy migration for multi-level anti-counterfeiting

Long Yan, Xixi Wang, Zhengce An, Zhiyong Hu, Huiming Liu, Shanhui Xu, and Bo Zhou*

State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Fiber Laser Materials and Applied Techniques, and Institute of Optical Communication Materials, South China University of Technology, Guangzhou, 510641, China.

E-mail: zhoubo@scut.edu.cn

Experimental section

Reagents

Gd_2O_3 (99.99%), Y_2O_3 (99.99%), Yb_2O_3 (99.99%), Tm_2O_3 (99.99%), Lu_2O_3 (99.99%), $CaCO_3$ (99%), $Mn(CH_3COO)_2{\cdot}4H_2O$ (99%), CF_3COONa (98%), oleylamine (80-90%), absolute ethanol, and cyclohexane were purchased from Aladdin. Oleic acid (90%), 1-octadecene (90%), CF_3COONa (98%) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich. All the reagents were used without any further purification. $RE(CF_3COO)_3$ were prepared by dissolving the lanthanide oxides in CF_3COOH.

Sample synthesis

Synthesis of $Ln(CF_3COO)_3$ In a typical synthesis, a lanthanide oxide was added into a solution containing slightly excessive trifluoroacetic acid with continuous stirring and refluxing until an optically transparent solution was formed. The resulting solution was filtered and the following solution was dried in an oven at 105 ^oC for 12 h to obtain $Ln(CF_3COO)_3$ powders.

Synthesis of α-$NaGdF_4$:Yb/Tm(49/1 mol%) nanoparticles A given amount of $Ln(CF_3COO)_3$ (1 mmol; 0.49 mmol $Yb(CF_3COO)_3$, 0.50 mmol $Gd(CF_3COO)_3$ and 0.01 mmol $Tm(CF_3COO)_3$) and CF_3COONa (1 mmol) were added to a 100-mL flask containing oleic acid (3.5 mL), oleylamine(3.5 mL) and 1-octadecene (7 mL). The resulting mixture was heated to 110 ^oC for 15 min with vigorous magnetic stirring under vacuum and then heated at 300 ^oC under an argon flow for 30 min before cooling down to room temperature. The resulting core nanoparticles were collected by centrifugation, washed with ethanol, and finally dispersed in 10 ml cyclohexane.

Synthesis of α-$NaGdF_4$:Yb/Tm(49/1 mol%)@$NaGdF_4$ nanoparticles A given amount of 0.20 mmol $Gd(CF_3COO)_3$, 0.20 mmol CF_3COONa and 2 mL as-prepared core were added to a 50-mL flask containing oleic acid (5 mL) and 1-octadecene (5 mL). The resulting mixture was heated to 110 ^oC for 15 min with vigorous magnetic stirring under vacuum and then heated at 300 ^oC under an argon flow for 30 min before cooling down to room temperature. The resulting core-shell nanoparticles were collected by centrifugation, washed with ethanol, and finally dispersed in 2 mL cyclohexane. The core-shell nanoparticles with adjustable thickness of $NaGdF_4$ layer were prepared through a fine tuning of the shell layer precursor content.

Synthesis of α-$NaGdF_4$:Yb/Tm(49/1 mol%)@$NaGdF_4$@$NaGdF_4$:Mn nanoparticles A given amount of 0.20 mmol $Gd(CF_3COO)_3$, 0.20 mmol CF_3COONa and 1 ml as-prepared core were added to a 50-mL flask containing oleic acid (5 mL) and 1-octadecene (5 mL). The resulting

mixture was heated to 110 ^{o}C for 15 min with vigorous magnetic stirring under vacuum. Then 0.24 mmol $Mn(CH_3COO)_2$ (Gd:Mn=1:1.2) were add and stirred at 110 ^{o}C for 10 min under vacuum. The solution was heated to 300 ^{o}C and kept for 30 min under argon atmosphere. The resulting core-shell-shell nanoparticles were collected by centrifugation, washed with ethanol, and finally dispersed in 1 mL cyclohexane. The method with epitaxial growth of $NaLuF_4$, $NaLuF_4$ and CaF_2 shell is using a similar procedure except for the use of different precursors.

Characterization

The upconversion emission spectra were measured by a Zolix OmniFluo-FLS-133P-HGU spectrofluorometer equipped with 980 nm laser diodes. The decay curves were measured using the same spectrofluorometer through the use of the pulsed lasers as excitation sources. The concentrations of various UCNPs during the emission spectra measurement were fixed to 0.1 mmol/mL according to the amount of core. Low- and high-resolution transmission electron microscopy (TEM) measurements together with energy-dispersive X-ray spectroscopy (EDS) were performed on a JEM 2100F with an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) data were recorded on a Philips Model PW1830 X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). The Mn concentration was measured by the inductively coupled plasma-atomic emission spectrometry (ICP-AES). The upconversion emission photographs were taken by a digital camera.

Figures S1-S6

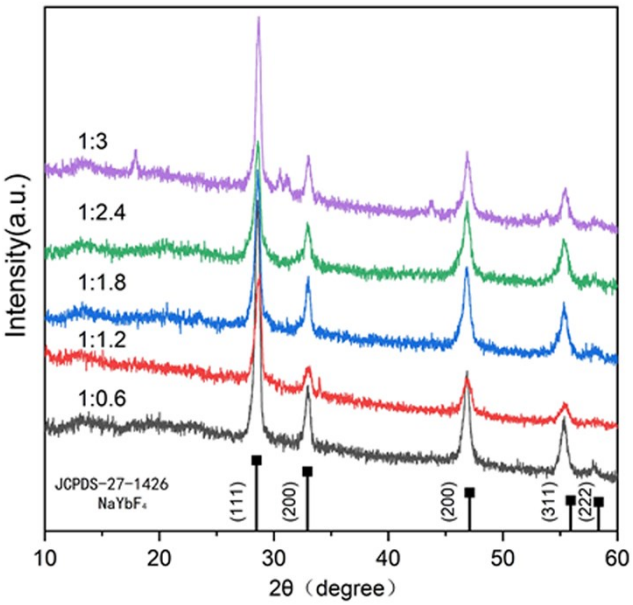

Fig. S1 XRD patterns of $NaGdF_4$:Yb/Tm@$NaGdF_4$@$NaGdF_4$:Mn core-shell-shell nanoparticles with different namely molar ratio of Gd^{3+} to Mn^{2+}. The card JCPDS-27-1426 is from cubic phase $NaYbF_4$.

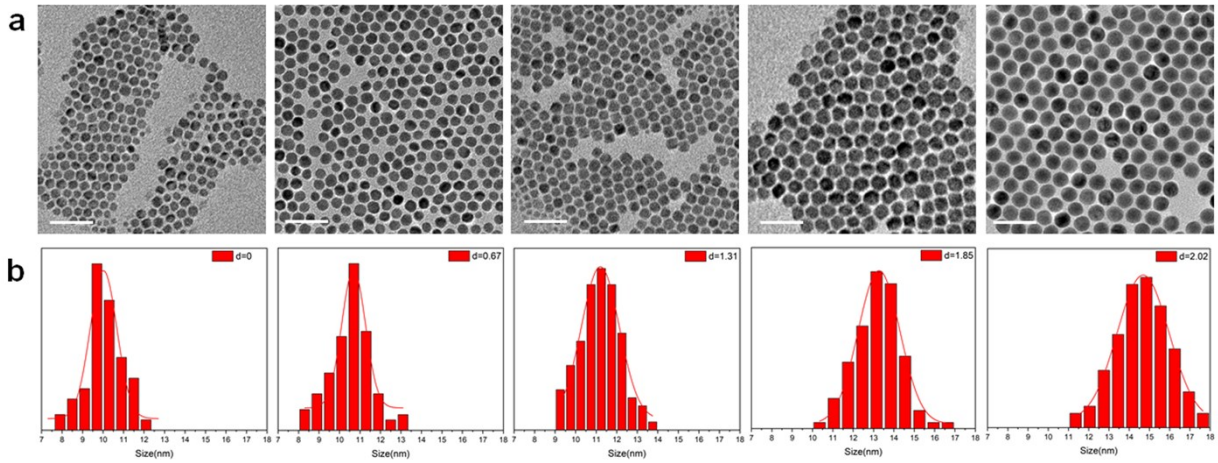

Fig. S2 (a) TEM images and (b) size distribution characteristic of $NaGdF_4$:Yb/Tm core seeds coating with different $NaGdF_4$ interlayer thicknesses (0-2.02 nm) related to sample $NaGdF_4$:Yb/Tm@$NaGdF_4$@$NaGdF_4$:Mn nanoparticles. Scale bars, 50 nm.

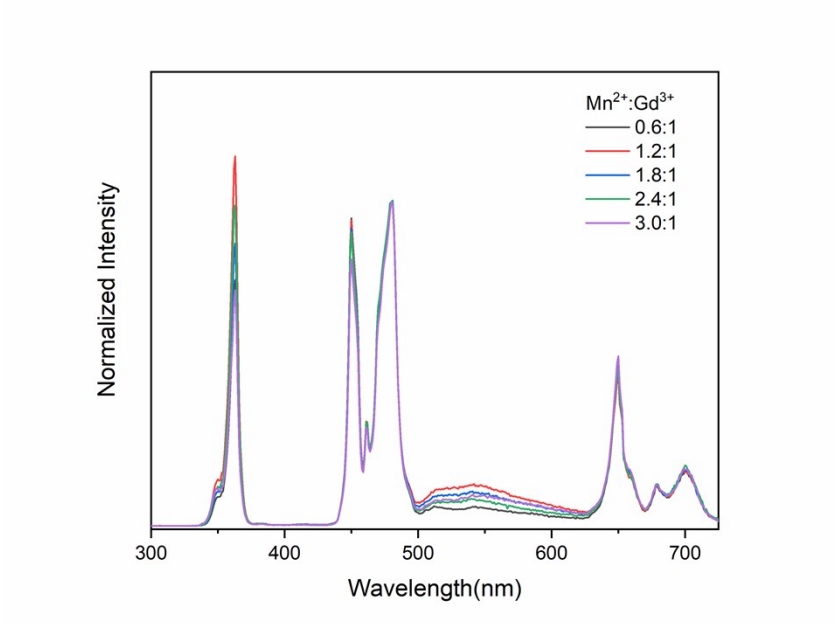

Fig. S3 The upconversion emission spectra of the $NaGdF_4$:Yb/Tm@$NaGdF_4$@$NaGdF_4$:Mn nanoparticles by optimizing the concentration of $Mn(CH_3COO)_2$ under 980 nm excitation. The spectra is normalized at 480 nm.

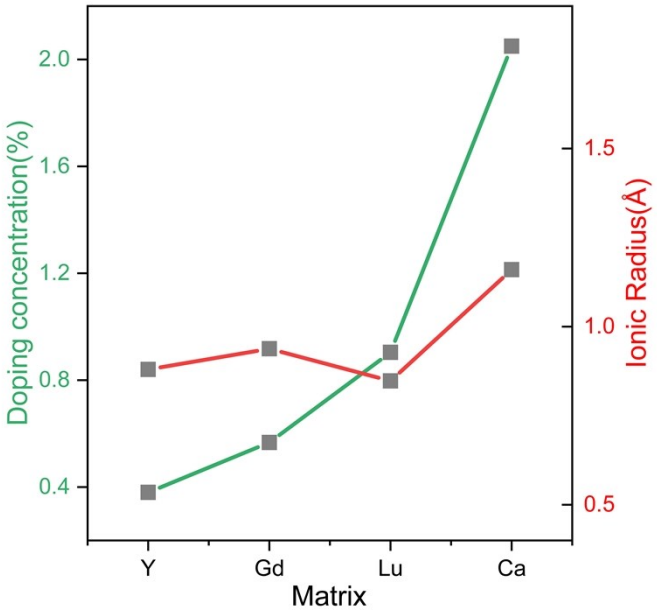

Fig. S4 The relationship between the radius of matrix ions and the actual doping concentration.

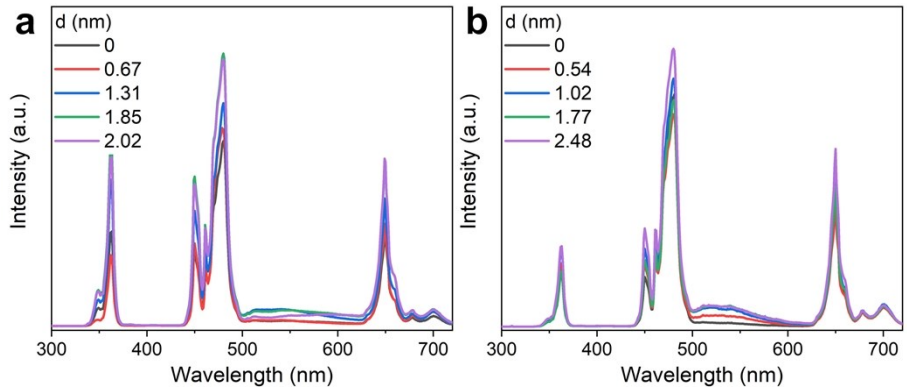

Fig. S5 (a,b) Upconversion emission spectra of (a) $NaGdF_4$:Yb/Tm@$NaGdF_4$ @$NaGdF_4$:Mn and (b) $NaGdF_4$:Yb/Tm@$NaGdF_4$@$NaYF_4$:Mn core-shell-shell nanoparticles with different thicknesses of migratory $NaGdF_4$ interlayer under 980 nm excitation.

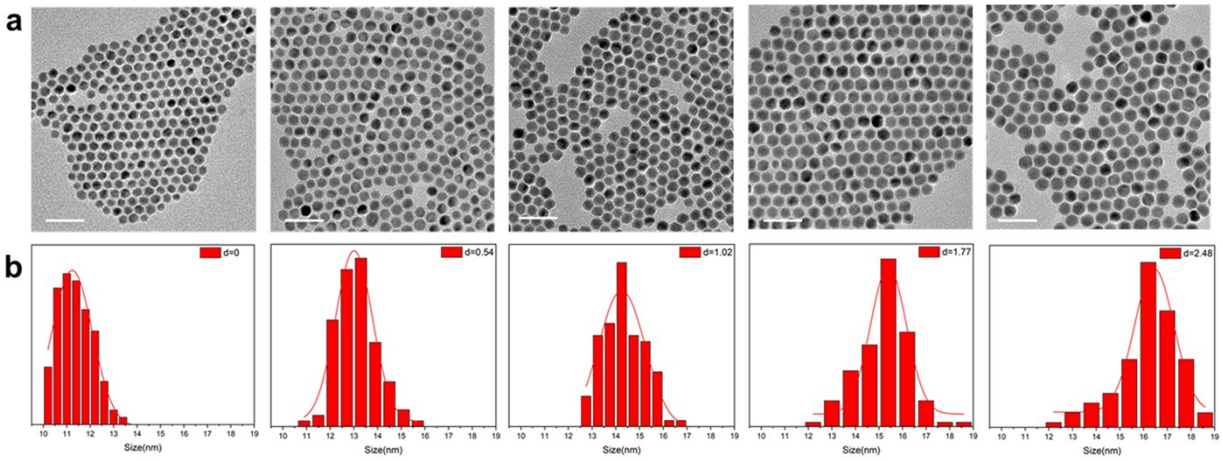

Fig. S6 (a)TEM images and (b) size distribution characteristic of $NaGdF_4$:Yb/Tm core seeds coating with different $NaGdF_4$ interlayer thicknesses (0-2.48 nm) related to sample $NaGdF_4$:Yb/Tm@$NaGdF_4$@$NaYF_4$:Mn nanoparticles. Scale bars, 50 nm.

Table S1

Table S1. Measured lifetime (τ) of $NaGdF_4$:Yb/Tm@$NaGdF_4$@$NaGdF_4$:Mn^{2+} nanoparticles with tuning the thickness (d) of inner $NaGdF_4$ layer from 0 to 2.02 nm.

d (nm)	$\tau_{362\ nm}$ (ms)	$\tau_{450\ nm}$ (ms)	$\tau_{480\ nm}$ (ms)	$\tau_{650\ nm}$ (ms)	$\tau_{800\ nm}$ (ms)
0	0.217	0.225	0.393	0.370	0.386
0.67	0.257	0.281	0.424	0.494	0.701
1.31	0.305	0.289	0.453	0.496	0.714
1.85	0.321	0.304	0.595	0.506	0.882
2.02	0.342	0.327	0.644	0.631	0.992