Electronic Supplementary Information

Highly bright multicolour emission through energy migration in core/shell nanotubes

*Lu Liu,[a] Nannan Zhang,[a] Zhihua Leng,[a] Yimai Liang,[a] Ruiqing Li,[a] Lianchun Zou,[*b] Shucai Gan[*a]*

[a] College of Chemistry, Jilin University, Changchun 130026, P. R. China.

[b] Teaching Center of Basic Courses, Jilin University, Changchun 130062, PR China.

[*]Corresponding author: E-mail address: gansc@jlu.edu.cn (S. Gan).

Synthesis of $NaGdF_4$@$NaGdF_4$:5% Ce^{3+} core/shell NTs

For the growth of the $NaGdF_4$ shell on the ultrasmall $NaGdF_4$ cores, 0.2562 g of $NaGdF_4$ NTs prepared as above was redispersed into 20 ml deionized water by ultrasonic and vigorous stirring for 1 h, 0.475 mmol $Y(NO_3)_3$, 0.025 mmol $Ce(NO_3)_3$ was added into the above solution with stirring for 30 min, then 15 ml solution containing NaF (2.25 mmol) was added and the resulting mixture was stirred for another 30 min. Finally, the mixture solution was transferred into a stainless steel autoclave and heated at 130 ^oC for 12 h and then cooled down to room temperature. The precipitate was washed with deionized water and alcohol several times and dried at 80 ^oC for 6 h in a vacuum oven.

Synthesis of $NaGdF_4$@$NaYF_4$ core/shell NTs

For the growth of the $NaGdF_4$ shell on the ultrasmall $NaGdF_4$ cores, 0.2562 g of $NaGdF_4$ NTs prepared as above was redispersed into 20 ml deionized water by ultrasonic and vigorous stirring for 1 h, 0.5 mmol $Y(NO_3)_3$ was added into the above solution with stirring for 30 min, then 15 ml solution containing NaF (2.25 mmol) was added and the resulting mixture was stirred for another 30 min. Finally, the mixture solution was transferred into a stainless steel autoclave and heated at 130 ^oC for 12 h and then cooled down to room temperature. The precipitate was washed with deionized water and alcohol several times and dried at 80 ^oC for 6 h in a vacuum oven. $NaGdF_4$@$NaYF_4$:5% Ln^{3+} (Ln = Eu, Tb, Dy and Sm) NTs were prepared by the same procedure, except for adding additional 5% $Ln(NO_3)_3$ into the solution of $Y(NO_3)_3$ at the coating stage.

Figure S1. Powder XRD patterns of the $NaGdF_4$ doped with different rare earth ions (5%) and the standard reference pattern of $NaGdF_4$ (JCPDS#00-027-0699). Revealing the successful doping of Ln^{3+} (Ln = Eu, Tb, Dy and Sm) into $NaGdF_4$ host.

Figure S2. Powder XRD patterns of $Gd(OH)_3$ samples for different reaction time: 0 min (a), 10 min (b), 30 min (c), 1 h (d), 3 h (e) and 6 h (f). Other experimental conditions were the same: 130 ^{o}C, pH = 11.5.

Figure S3. SEM images of $Gd(OH)_3$ samples for different reaction time: 0 min (a), 10 min (b), 30 min (c), 1 h (d), 3 h (e) and 6 h (f). Other experimental conditions were the same: 130 ^{o}C, pH = 11.5. Scale bars represent 90 nm.

Figure S4. XRD results of the NCs obtained under different ratios of HF/Gd^{3+} (r): r=0 (a), r=1 (b), r=2 (c), r=4 (d), r=6 (e). Other experimental conditions were the same: 130 ^{o}C, 12 h.

Table 1. Dimension parameters of monodispersed $Gd(OH)_3$ (a), $NaGdF_4$ core only (b), $NaGdF_4@NaGdF_4$ core/shell (c), $NaGdF_4@NaGdF_4@NaGdF_4$ core/shell/shell (d) NCs.

Compound	Diameter /nm	Length /nm	Aspect Ratio
$Gd(OH)_3$	12.6	206.7	16.4
$NaGdF_4$	14.8	217.8	14.7
$NaGdF_4@NaGdF_4$	16.9	228.8	13.5
$NaGdF_4@NaGdF_4@NaGdF_4$	18.8	241.3	12.8

Figure S5. SEM images of NCs obtained under different ratios of HCl/Gd^{3+} (r): r=0 (A), r=1/2 (B), r=1/1 (C), r=3/1 (D), r=6/1 (E, F, G). Other experimental conditions were the same: 130 ^{o}C, pH = 11.5.

Figure S6. XRD results of the NCs obtained under different ratios of HCl/Gd^{3+} (r): r=0 (a), r=1/2 (b), r=1/1 (c), r=3/1 (d), r=6/1 (e). Other experimental conditions were the same: 130 ^{o}C, 12 h.

Figure S7. Element maps of Eu^{3+} (A), Tb^{3+} (B), Dy^{3+} (C) and Sm^{3+} (D) doped $NaGdF_4$@$NaYF_4$:5% Ln^{3+} core/shell samples.

Figure S8. Emission spectra of the NCs $NaGdF_4$@$NaGdF_4$:5 mol% Ce^{3+} and $NaGdF_4$ without Ce^{3+} dopant (Under the excitation of 251 nm). Exitation spectra of the as-prepared $NaGdF_4:Ln^{3+}$ (Ln = Eu, Tb, Dy and Sm). The dot lines denote two individual Gaussian components.

Table 2. Assignments of Eu^{3+}, Tb^{3+}, Dy^{3+} and Sm^{3+} emissions.

	Emissions /nm	Transitions
Eu^{3+}	525, 535, 555 582 (578), 591, 615 (627), 649, 689, 696	$^5D_1 \rightarrow {}^7F_{0,1,2}$ $^5D_0 \rightarrow {}^7F_{0,1,2,3,4,5}$
Tb^{3+}	381, 415, 438 489, 542, 585, 621	$^5D_3 \rightarrow {}^7F_{6,5,4}$ $^5D_4 \rightarrow {}^7F_{6,5,4,3}$
Sm^{3+}	560, 593, 640 (647), 699	$^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2,11/2}$
Dy^{3+}	478, 570	$^4F_{9/2} \rightarrow {}^6H_{15/2,13/2}$
Gd^{3+}	310	$^6P_J \rightarrow {}^8S_{7/2}$