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Supplementary Information

Promote the threshold of Tm^{3+} concentration by an inert-core/active-shell structure

Ruozhen Wu, Lei Lei*, Shengjun Zhang, Junjie Zhang, Shiqing Xu*

College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, China

Corresponding author: leilei@cjlu.edu.cn and shiqingxu@cjlu.edu.cn.

1. Experimental section

1.1 Materials.

Gadolinium(III) acetate ($Gd(CH_3COO)_3$, 99.99%), ytterbium(III) acetate ($Yb(CH_3COO)_3$, 99.9%), thulium(III) acetate ($Tm(CH_3COO)_3$, 99.9%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%) and anhydrous methanol were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 99%), cyclohexane were obtained from Sinopharm Chemical Reagent Co., Ltd. Ammonium fluoride (NH_4F, 99%) from Aladdin and anhydrous ethanol from Hangzhou Gaojing Fine Chemical Co., Ltd were used. All chemicals were of analytical grade and used without further purification.

1.2 Synthesis of β-Yb/Tm: $NaGdF_4$ nanocrystals.

The monodisperse 20Yb/xTm: $NaGdF_4$ (x=0.5, 1, 3) nanocrystals were fabricated by a co-precipitation method. Taking 20Yb/0.5Tm: $NaGdF_4$ NCs as an example, 0.318 mmol of $Gd(CH_3COO)_3$, 0.08 mmol of $Yb(CH_3COO)_3$ and 0.002 mmol of $Tm(CH_3COO)_3$ were mixed in 4 mL of oleic acid and 6 mL of 1-octadecene in a 50 mL flask followed by heating at 150 °C for 30 min before cooling down to room temperature. A solution of 0.8 mmol of NH_4F and 1.32 mmol of NaOH in 6mL of methanol was added before the mixture was kept at 50 °C for 30 min. After methanol was evaporated, the resulting solution was heated to 280 °C under Ar flow with vigorous stirring for 90 min, and then cooled down to room temperature (RT). The products were

precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for three times, and finally re-dispersed in 4mL of cyclohexane.

1.3 Synthesis of β-$NaGdF_4$ core nanocrystals.

The synthetic procedure of β-$NaGdF_4$ core nanocrystals was similar as Yb/Tm: $NaGdF_4$, except that the content of lanthanides were replaced by 1.6 mmol of $Gd(CH_3COO)_3$, the content of oleic acid, 1-octadecene, NH_4F and NaOH are changed to 16 mL, 24 mL, 3.2 mmol and 5.28 mmol, respectively, and the reaction vessel was alternative to 100 mL flask. The nanocrystals were dispersed in 8 mL of cyclohexane and equally divided into four parts.

1.4 Synthesis of β-$NaGdF_4$@Yb/Tm: $NaGdF_4$ core/shell nanocrystals.

In a typical procedure for the synthesis of β-$NaGdF_4$@20Yb/3Tm: $NaGdF_4$ nanocrystals, 0.308 mmol of $Gd(CH_3COO)_3$, 0.08 mmol of $Yb(CH_3COO)_3$, 0.012 mmol of $Tm(CH_3COO)_3$, 4 mL of oleic acid and 6 mL of 1-octadecene were mixed in a 50 mL flask followed by heating at 150 ^oC for 30 min before cooling down to room temperature. One part of β-$NaGdF_4$ core NCs was added to the above solution and maintained at 80 °C for 40 min to remove cyclohexane. After the removal of cyclohexane, 6 mL of methanol solution containing 0.8 mmol of NH_4F and 1.32 mmol of NaOH were added and stirred at 50 °C for another 30 min. After methanol was evaporated, the solution was heated to 280 ^oC under Ar flow with vigorous stirring for 90 min, and then cooled down to RT. The products were precipitated by addition of ethanol, collected by centrifugation, washed with methanol and ethanol for three times, and finally re-dispersed in 4mL of cyclohexane.

1.5 Characterizations.

XRD analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu-K_a radiation (λ=0.154 nm). The size, shape and uniformity of the products were studied using a transmission electron microscope (TEM, FEI Tecnai G^2 F20 S-WTINE) equipped with an energy dispersive X-ray spectroscope (EDS). TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the products on the surface of a carbon coated copper grid. The actual chemical compositions were determined by inductively coupled plasma

(ICP) technique using a Perkin-Elmer Optima 3300DV spectrometer. UC emission spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with an adjustable laser diode (980 nm) as the excitation sources. To enable comparison of the UC emission intensities among different samples, the emission spectra were measured with the same instrumental parameters (for example: same mass of samples, same excitation wavelength and power, same excitation and emission slits, and so on). All the measurements were carried out at room temperature.

2. Table S1 and Figure S1-S4

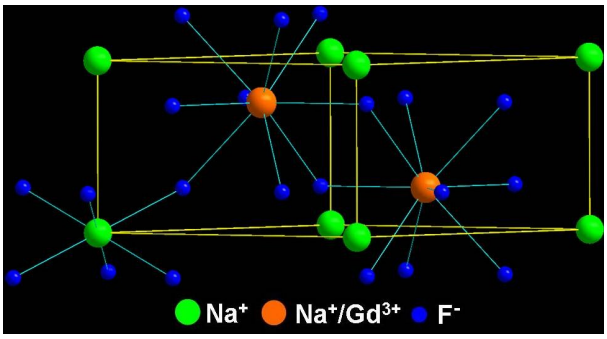

Figure S1. Schematic illustration of the crystal structure for β-$NaGdF_4$.

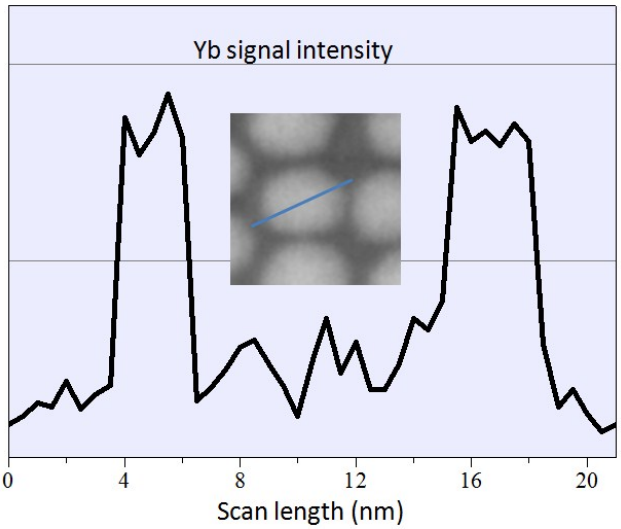

Figure S2 EDS line scan of a single $NaGdF_4$/Yb/Tm: $NaGdF_4$ core/shell NC.

Table S1 Nominal and ICP-AES measured results of the Yb/Tm ratio using Yb content as reference in the core/shell NCs.

$NaGdF_4$@20Yb/xTm:$NaGdF_4$	Yb : Tm	
	Nominal ratio	ICP-AES result
X=0.5	20: 0.5	20: 0.482
X=1.0	20: 1.0	20: 0.976
X=3.0	20: 3.0	20: 3.071
X=5.0	20: 5.0	20: 4.895

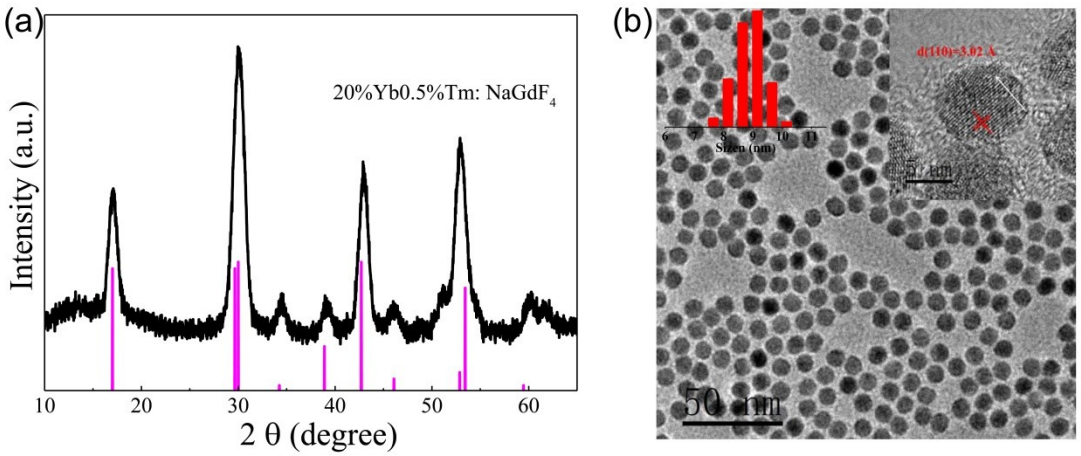

Figure S3. (a) X-ray diffraction data of 20Yb/3Tm: $NaGdF_4$ NCs, bars represent standard hexagonal $NaGdF_4$ crystal (JCPDS 27-0699) data; (b) Transmission electron microscopy images of 20Yb/0.5Tm: $NaGdF_4$ NCs. Insets display histograms of the size distribution (top-left) and high resolution TEM image of an individual NC (top-right).

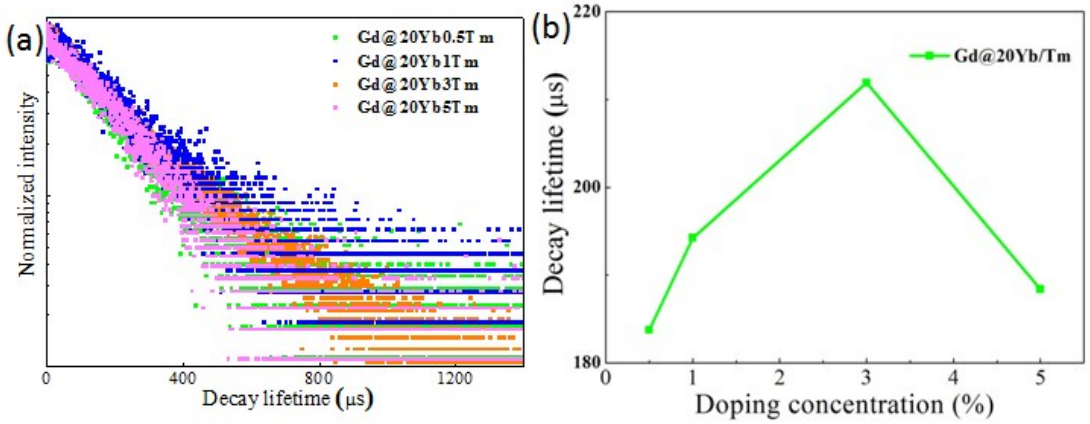

Figure S4. (a) The $^3H_4 \rightarrow {}^3H_6$ decay curves of Tm^{3+} ions in $NaGdF_4$@Yb/xTm: $NaGdF_4$ core-shell NCs (x = 0.5, 1, 3, 5) NCs under 980nm laser excitation; (b) The fitting lifetime value as a function of doping concentration in $NaGdF_4$@Yb/xTm: $NaGdF_4$ core-shell NCs.