Electronic Supplementary Information

Phase transformation and size tuning in controlled-growth nanocrystals *via* self-seeded nucleation with preferential thermodynamic stability

Liwen Yang[1,2*], Yongchang Li[1], Suixi Yu[1], Jianhua Hao[2*], Jianxin Zhong[1], Paul K Chu[3]

[1]Laboratory for Quantum Engineering and Micro-Nano Energy Technology and Faculty of Materials and Optoelectronic Physics, Xiangtan University, Hunan 411105, China

[2]Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China

[3]Department of Physics and Materials Science, City University of Hong Kong , Tat Chee Avenue, Kowloon, Hong Kong, China

MATERIALS AND METHODS

Materials

The synthesis was carried out using commercially available reagents. The $Ln(NO_3)_3.6H_2O$ with purity of 99.99% were supplied by Sinopharm Chemical Reagent Company. All other chemicals were analytical grade and used as received without further purification.

Synthesis of $KGdF_4$ and $NaYF_4$ NCs

In a typical synthesis, 2 ml of the aqueous solution containing 8.75 mmol NaOH or KOH, 10 ml alcohol, and 20 ml oleic acid were added to a beaker sequentially under vigorous stirring to form a transparent homogeneous solution at room temperature. Then, 2.24 ml (1.12 mmol) 0.5 M of $Gd(NO_3)_3$ or $Y(NO3)_3$ with the designed Yb^{3+}, Er^{3+}, and Tm^{3+} doping contents was poured into the translucent solution under vigorous stirring and the

---

*Corresponding authors: ylwxtu@xtu.edu.cn; apjhhao@polyu.edu.hk

obtained mixture was aged for 10 min at room temperature. At last, 5 ml of 1.2 M NH_4F was added under vigorous stirring until a translucent solution was obtained. After agitating, the colloidal solution was transferred to a 50 ml stainless Teflon-lined autoclave. The reactions took place in an oven at 180~210 °C for 24 h. After the reaction, the products deposited on the bottom of the Teflon vessel were collected and washed with ethanol and deionized water for several times to remove other remnants, and then dried at 70 ^{o}C for 24 h.

Phase transformation between cubic $KGdF_4$ and hexagonal $NaGdF_4$ via Cation exchange of K^+ by Na^+

The aforementioned experimental procedures were first conducted for about 20 h. After the transparent reaction mixture was cooled to 100 ^{o}C, another semitransparent solution of accurately weighed NaOH and oleic acid was injected into the solution, rapidly heated to 180^{o}C, and maintained at this temperature for 2~20 h. After the reaction, the products deposited on the bottom of Teflon vessel were collected, washed with ethanol and deionized water several times to remove other remnants, and dried at 70 ^{o}C for 24 h.

In-situ phase transformation and size tuning of hexagonal $NaGdF_4$ NCs

In a typical preparation, 2 ml of the aqueous solution containing accurately weighed 8.75 mmol KOH, 10 ml alcohol, and 20 ml oleic acid were added to a beaker sequentially under vigorous stirring to form a transparent homogeneous solution at room temperature. Then, 2.24 ml (1.12 mmol) 0.5 M of $Ln(NO_3)_3$ with the designed Yb^{3+}, Er^{3+}, and Tm^{3+} doping contents was poured into the translucent solution under vigorous stirring and the obtained mixture was aged for 10 min at room temperature. Subsequently, 4 ml of the aqueous solution containing 6 mmol NH_4F was added under vigorous stirring until a translucent solution was obtained. The obtained mixture was aged for 30 min to form the amorphous precursor at room temperature. Before transferring to a Teflon-lined autoclave with an internal volume of 50 mL, the mixture was mixed with another transparent solution of accurately weighed NaOH and oleic acid. The reaction took place in an oven at 180~210 °C for 0~40 h. After the reaction, the products deposited on the bottom of Teflon vessel were collected, washed with ethanol and deionized water several times, and then dried at 70 ^{o}C for 24 h.

Synthesis of LnF_3 and M^{2+}doped LnF_3 NCs

The LnF_3 and M^{2+} doped LnF_3 NCs were prepared by a modified liquid solid solution solvothermal route, which is described in detail in Ref. 1. In a typical synthesis of LnF_3 NCs, an aqueous solution of cerium salt (0.5mol/L) was mixed with ethanol (20ml), oleic acid (20ml) and NaOA (5.0g) under thorough stirring. Then 4 ml of HF(1.0 mol/L) was added dropwise to the mixture. After vigorous stirring at room temperature for 30 min, the colloidal solution were transferred into a 100 mL Teflon-lined autoclave, sealed, and heated at 130 ^{o}C for 12 h. The final products were collected, washed several times with ethanol/cyclohexane, and purified by centrifugation. Introduction of M^{2+} ions and Ln^{3+} ions such as Eu^{3+}, Yb^{3+}, Er^{3+}, Tm^{3+} was achieved by adding the corresponding metal salts at predetermined concentrations.

Synthesis of ZrO_2 and Ln^{3+}doped ZrO_2 NCs

The ZrO_2 and Ln^{3+}doped ZrO_2 NCs were prepared by a modified liquid solid solution solvothermal route, which is described in detail in Ref. 2. In a typical synthesis, 10 ml aqueous solution of $ZrOCl_2$ (50 mol/L) was mixed with ethanol (10 mL), oleic acid (10 mL) and NaOA (0.8 g) under thorough stirring. Then, 1 mL ammonia (15 wt%) solution was added to the mixture. After vigorously stirring at room temperature for 10 min, the colloidal solution was transferred into a 25 mL Teflon-lined autoclave, sealed, and heated at 200 °C for 24 h. The final products were collected, washed several times with ethanol/cyclohexane, and purified by centrifugation. To introduce Gd^{3+} into the reaction system, $GdCl_3$with a predetermined concentration (mol%) was added.

Synthesis of CeO_2 and Ln^{3+}doped CeO_2 NCs

CeO_2 and Ln^{3+}doped CeO_2 NCs were synthesized via the following procedures as described in Ref. 3. In a typical synthesis procedure, 1 mmol $Ce(NH_4)_2(NO_3)_6$ was added into a three-necked flask (100 mL) with 20 mmol OA and 20 mmol ODE, followed by vacuum degassing at 100 °C for 30 min to remove water and oxygen. Then the solution was heated to 340 °C at a temperature rate of 5 K·min-1 under nitrogen. After maintaining at 340 °C for 60 min, the reaction was stopped and it was cooled down to room temperature. The CeO_2 NPs were precipitated by using an excess amount of ethanol, and then collected via centrifugation. Introduction of Ln^{3+} ions such as Yb^{3+}, Er^{3+}, Gd^{3+} was achieved by adding the corresponding metal salts at predetermined concentrations.

Characterization

The crystal structures of the synthesized samples were determined by X-ray diffraction (D/Max 8550) using a copper K_α radiation source (λ=0.154 nm) at 40 kV and 40 mA. The morphologies and microstructures were characterized by transmission electron microscopy (JEOL 2100) equipped with selected area electron diffraction (SAED) and an Oxford energy dispersive X-ray spectroscopy (EDS) system at an acceleration voltage of 200 KV. The TEM specimens were prepared by directly drying a drop of a dilute cyclohexane dispersion solution of the as-prepared products on the surface of a carbon-coated copper grid. The UC spectra were recorded on a spectrophotometer (R-500) under excitation by a 980 nm laser diode (LD) after the powder samples were compressed into smooth slices. The fluorescence spot of the parallel laser beam on the sample had a diameter of about 0.4 cm and the measurements were performed at room temperature. Upconversion photographic images of the samples were taken by a digital camera (Canon PowerShot A720, Japan) without adding any filter. Magnetization as a function of applied magnetic field ranging from -15 to 15 kOe was measured using a Lakeshore vibrating sample magnetometer at room temperature.

Table I Reactants, seed nucleus, final products, phase transformation, and size tuning during the growth of doped $NaYF_4$, LnF_3, CeO_2 and ZrO_2 NCs. "*c*", "*h*" and "*m*" represtent cubic phase, hexagonal phase, and monoclinic phase, respectively.

Reactant	Doping	Seed nucleus	Final Products	Phase transformation	Size tuning	Ref.
c-$NaYF_4$	Ln^{3+}	h-$NaLnF_4$	h-$NaY_{1-x}Ln_xF_4$	$c \rightarrow h$	↓	[4]
h-LnF_3	M^{2+}	c-MF_2	c-$Ln_{1-x}M_xF_{3-x}$	$h \rightarrow c$	↓	[1]
m-ZrO_2	Ln^{3+}	c-Ln_2O_3	c-$Zr_{1-x}Ln_xO_{4-x}$	$m \rightarrow c$	↓	[2]
c-Ln_2O_3	Ln^{3+}	c-CeO_2	c-$Ce_{1-x}Ln_xO_{4-x}$	$c \rightarrow c$	↑	[3]

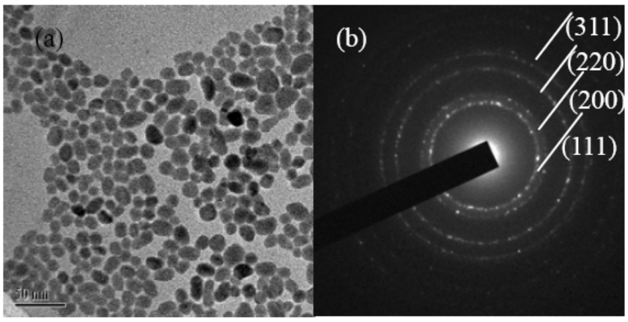

Figure S1 (a) and (b) Typical TEM image and selected electron diffraction (SEAD) pattern of the $KYb_{0.1}Gd_{0.9}F_4$ NCs. One can see that the $KYb_{0.1}Gd_{0.9}F_4$ NCs are nearly spherical in shape. All rings of the SAED pattern can be assigned to the (111), (200), (220) and (311) planes of the cubic structure $KGdF_4$.

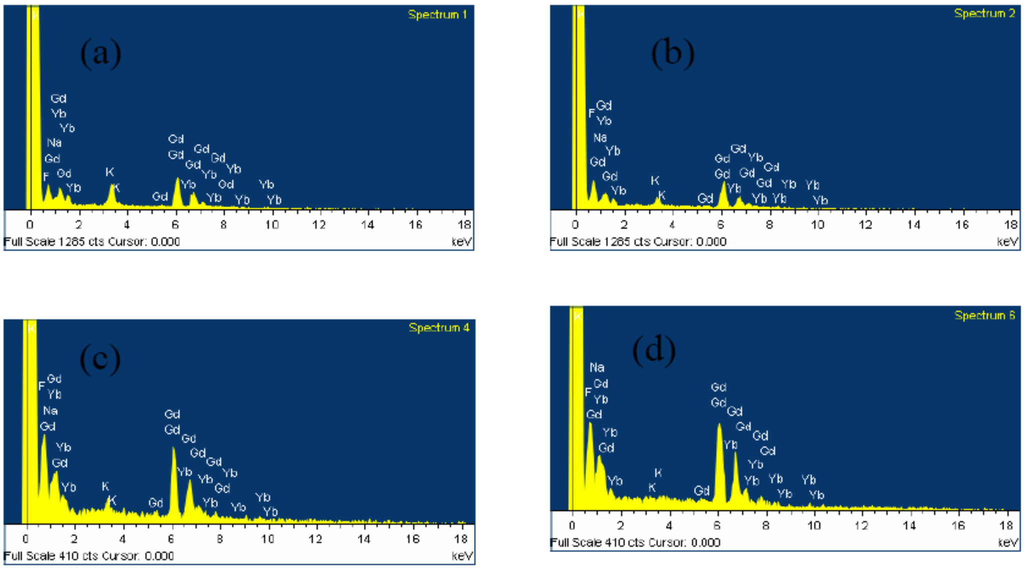

Figure S2 (a)-(d) EDS spectra taken from the oleate-capped cubic KYb$_{0.1}$Gd$_{0.9}$F$_4$ NCs reacted with 10mol% NaOA at 180°C for different time of 0 h, 2 h, 5 h, 20 h, respectively. The EDS results of the oleate-capped cubic KYb$_{0.1}$Gd$_{0.9}$F$_4$ NCs treated with NaOA for different periods of time at 180°C confirm that the major constituents of as prepared samples are K, Na, Yb, Gd, and F, which are consistent with their real elemental components. Furthermore, from the EDS results, one can see that as the reaction proceeds, the potassium content decreases gradually and disappears finally, implying the occurrence of cation exchange between potassium and sodium.

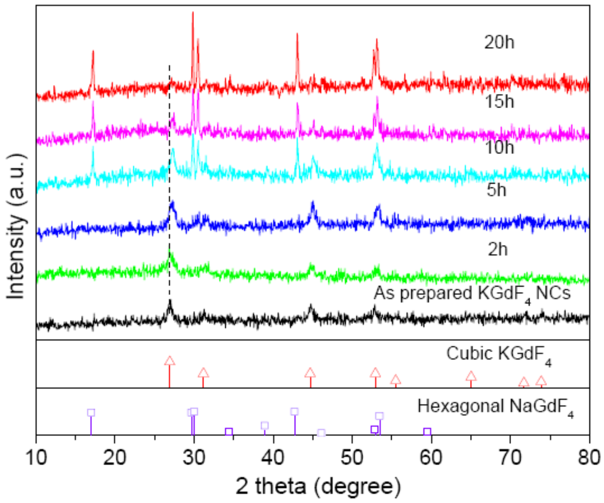

Figure S3 XRD patterns of the oleate-capped cubic $KYb_{0.1}Gd_{0.9}F_4$ NCs reacted with 10mol% NaOA at 180°C for different time. The data of cubic $KGdF_4$ and hexagonal $NaGdF_4$ are resourced from Ref. 5 and standard XRD card (JCPDS NO. 27-0699). One can see that in the initial stage (reaction time of 2 h), the XRD peak position of the cubic phase shifts to a high angle. The calculated cell constants become smaller, implying that cubic $KGdF_4$ NCs have partly transformed to cubic $NaGdF_4$ via cation exchange since the ionic radius of Na^+ is smaller than that of K^+. As the reaction proceeds further, the hexagonal phase $NaGdF_4$ emerges. When the reaction time is longer than 20 h, all the diffraction peaks belonging to the cubic phase disappear almost completely, and the pure hexagonal phase (β-$NaGdF_4$) is formed. Integrated with EDS results shown in Fig. S2, the XRD results reveal that the cubic $KGdF_4$ NCs are transformed to a hexagonal phase due to the cation-exchange between K^+ and Na^+.

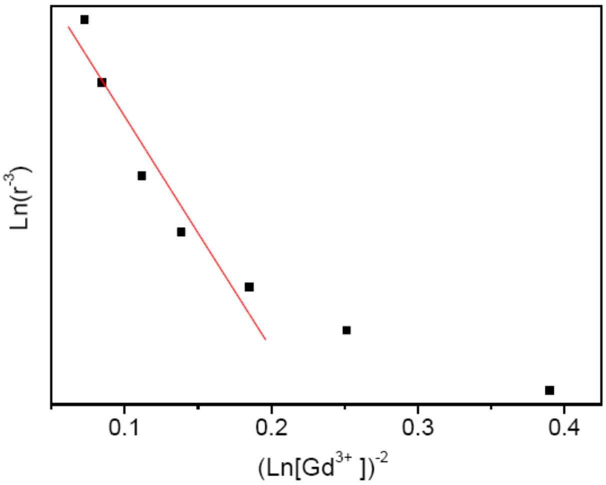

Fig. S4 Relationship between the amount of nominal Gd^{3+} doping concentration and the average size of the resulting ZrO_2 NCs, this is $\ln(r^{-3})$ versus $[\ln(Gd^{3+})]^{-2}$. The experimental data are resourced from Ref. 2.

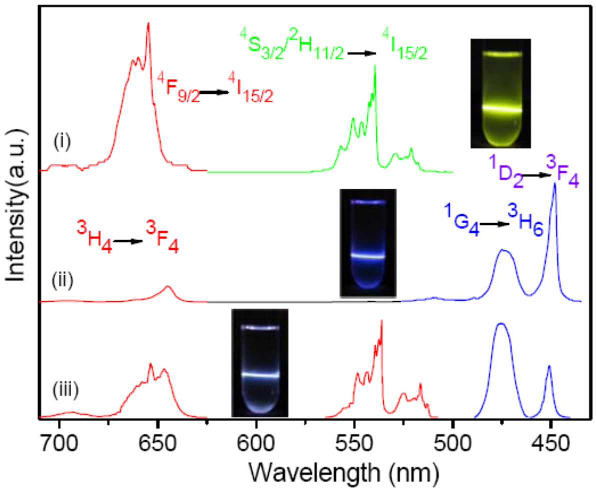

Figure S5 Room temperature UC emission spectra and digital photographs of $NaY_{0.55}Gd_{0.45}F_4$ nanostructures doped with (i) Yb^{3+}/Tm^{3+}, (ii) Yb^{3+}/Er^{3+} and (iii) $Yb^{3+}:Er^{3+}:Tm^{3+}$, respectively, under the excitation of a 980 nm LD. Strong green emissions centered at 540 nm and 525 nm and red UC one at 650 nm attributed to the $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+}, respectively, can be observed from the Yb^{3+}/Er^{3+} (25:0.2 mol%) co-doped sample, while intense blue emission bands at 451 and 478 nm corresponding to the $^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^3H_6$ transitions of Tm^{3+} ions, respectively, and red emissions at 650 nm assigned to $^3F_2/^3F_3 \rightarrow ^3H_6$ transitions of Tm^{3+} ions can be observed from the Yb^{3+}/Tm^{3+} (25:0.25 mol%) co-doped sample. Based on the generation of RGB light color from the different co-doped samples, elaborate designs of the Er^{3+}-Yb^{3+}-Tm^{3+} tri-doped $NaY_{0.55}Gd_{0.45}F_4$ sampes lead to adjustable balance of RGB intensities, allowing the tri-doped $NaY_{0.55}Gd_{0.45}F_4$ sample to display white UC emission.

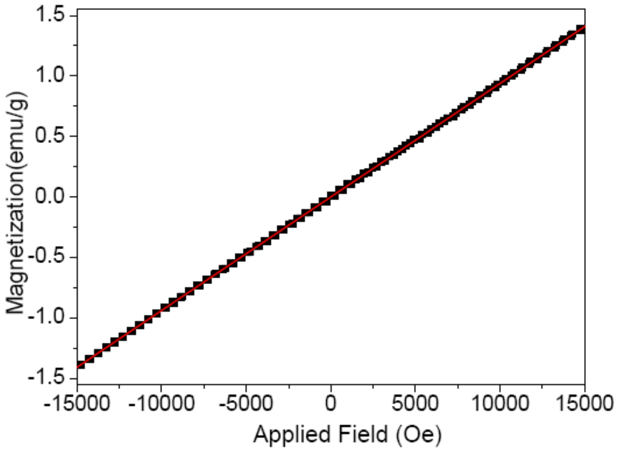

Figure S6 Typical magnetization vs magnetic field of the $NaYb_{0.1}Gd_{0.9}F_4$ NCs measured at room temperature. The NCs show paramagnetism ascribed to the fact that the magnetic moments associated with Gd^{3+} are all localized and noninteracting.

References

1. D. Chen, Y. Yu, F. Huang and Y. Wang, *Chem. Commun.*, 2011, **9**, 2601-2603.
2. F. Huang, D. Chen, J. Zhou and Y. Wang, *CrystEngComm*, 2011, **13**, 4500-4502.
3. H. Qiu, R. Fan, C. Cheng, S. Hao, D. Chen and C. Yang, *Chem. Commun.*, 2011, **47**, 9648-9650.
4. F. Wang, Y. Han, C. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong and X. Liu, *Nature*, 2010, **463**, 1061-1065.
5. L. W. Yang, Y. Y. Zhang, J. J. Li, Y. Li, J. X. Zhong and P. K. Chu, *Nanoscale*, 2010, **2**, 2805-2810.