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Supporting Information

Controlled synthesis of ultrasmall hexagonal $NaTm_{0.02}Lu_{0.98-x}Yb_xF_4$ nanocrystals with enhanced upconversion luminescence

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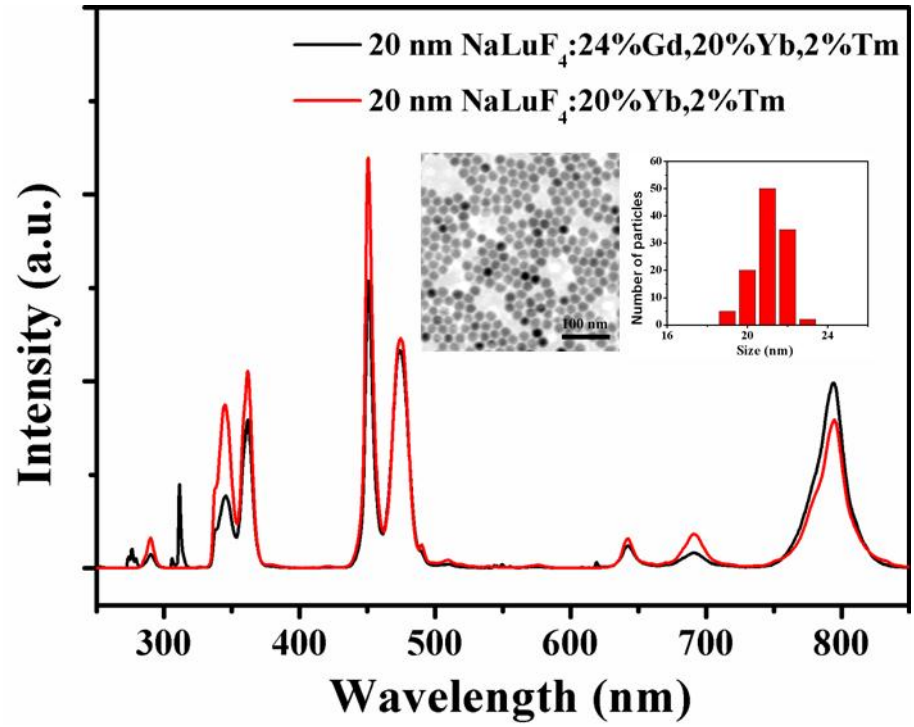

Fig. S1 UC luminescence spectra of $NaLuF_4$:20%Yb^{3+},2%Tm^{3+} and $NaLuF_4$:24%Gd^{3+},20%Yb^{3+},2%Tm^{3+} nanocrystals in cyclohexane solutions under the diode laser excitation at 980 nm (0.4 W). (Inset) TEM image and histogram of $NaLuF_4$:24%Gd^{3+},20%Yb^{3+},2%Tm^{3+} nanocrystals are inseted in (Particle size ~ 21 nm). TEM image and histogram of $NaLuF_4$:20%Yb^{3+},2%Tm^{3+} nanocrystals (Particle size ~ 20 nm) are shown in Fig. 1c and S2c, respectively. The $NaLuF_4$:24%Gd^{3+},20%Yb^{3+},2%Tm^{3+} nanocrystals were synthesized using pyrolysis of lanthanum trifluoroacetic precursors.[1]

In Gd^{3+} and Tm^{3+} codoped system, Gd^{3+} ions can be used to harvest pump photons and subsequently promote a neighboring accumulator ion (Tm^{3+}) to excited states. Moreover, the lowest excited level ($^6P_{7/2}$) of Gd^{3+} is situated in the UV region. The deleterious energy transfer between Gd^{3+} and Tm^{3+} will inevitablely result in energy loss. Thus, Gd^{3+} can quench the upconversion emission in the UV region.

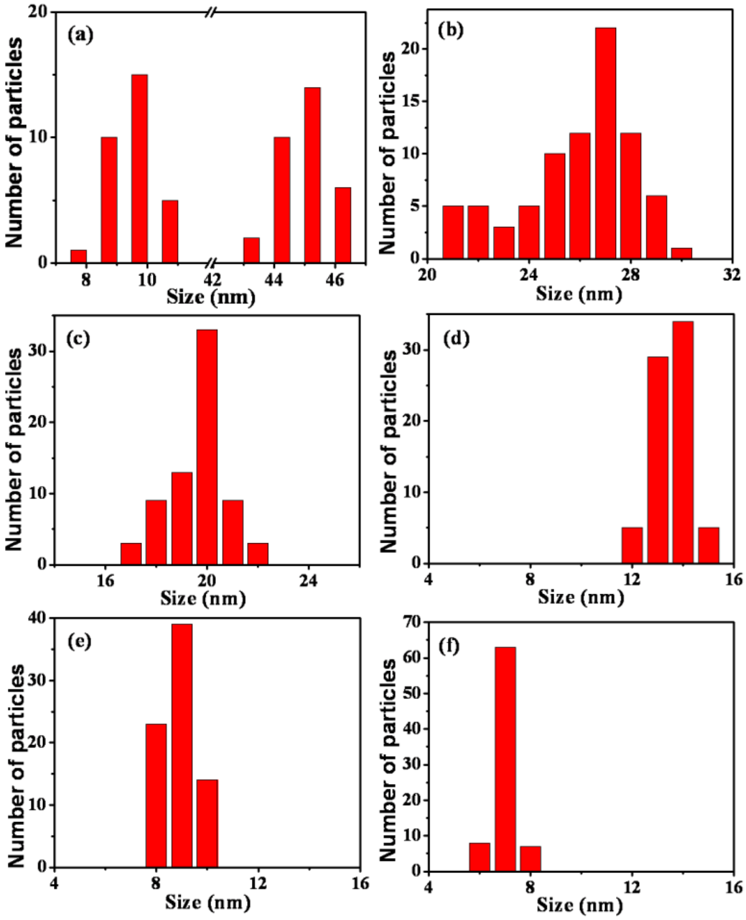

Fig. S2 Histograms of as-prepared $NaLuF_4$ samples prepared at different OM concentrations of (a) 0, (b) 1.5 mL, (c) 3mL, (d) 4.5 mL, (e) 6 mL, and (f) 7.5 mL.

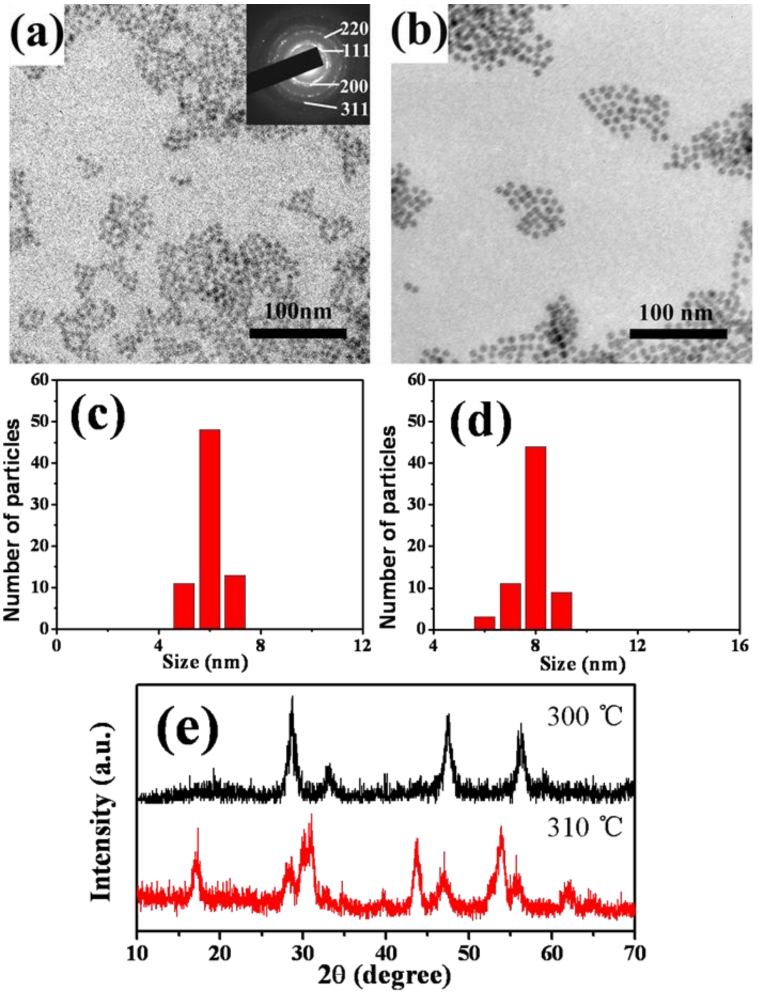

Fig. S3 Dependence of $NaLuF_4$ nanoparticle size and phase on the reaction temperature. Increasing the reaction temperature from 300 °C (a and c) to 310 °C (b and d) led to a significant increase in the hexagonal phase (e) but only a small increase in the nanocrystal diameter. Other synthesis conditions: 6 mL OA/6 mL OM/2.5 mmol NaOA; reaction time: 1 h.

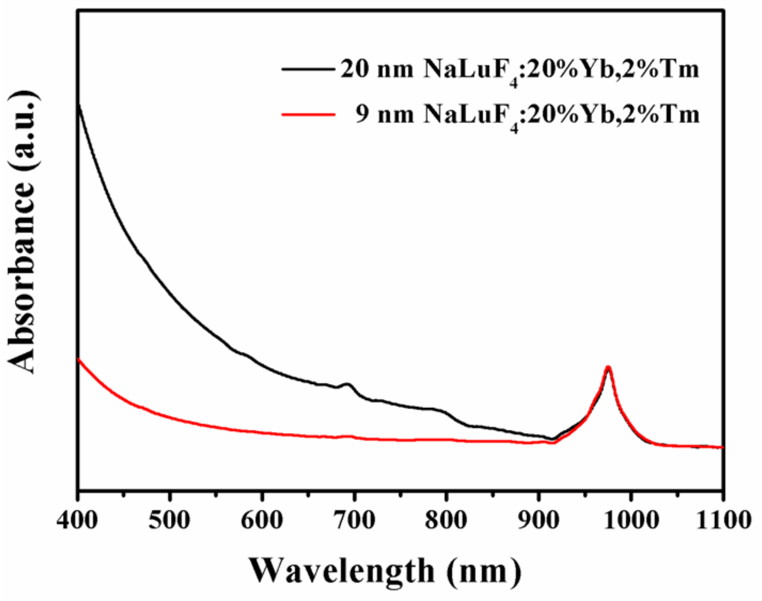

Fig. S4 Absorption of the two colloidal suspensions was matched at 975 nm for the $^2F_{7/2} \rightarrow 2F_{7/2}$ transition of Yb^{3+} ions. The concentrations of the nanoparticles are similar.

Table S1 Elemental analysis of ~9 nm and 20 nm nanoparticles of $NaLuF_4$:20%Yb^{3+},2%Tm^{3+} as determined by inductively coupled plasma (ICP) measurement.

Particle size (nm)	$Lu^{3+}/Yb^{3+}/Tm^{3+}$ feed ratio	$Lu^{3+}/Yb^{3+}/Tm^{3+}$ ratio in UCNPs
~ 9 nm	78/20/2	77.61/19.95/2.44
~20 nm	78/20/2	77.55/19.96/2.49

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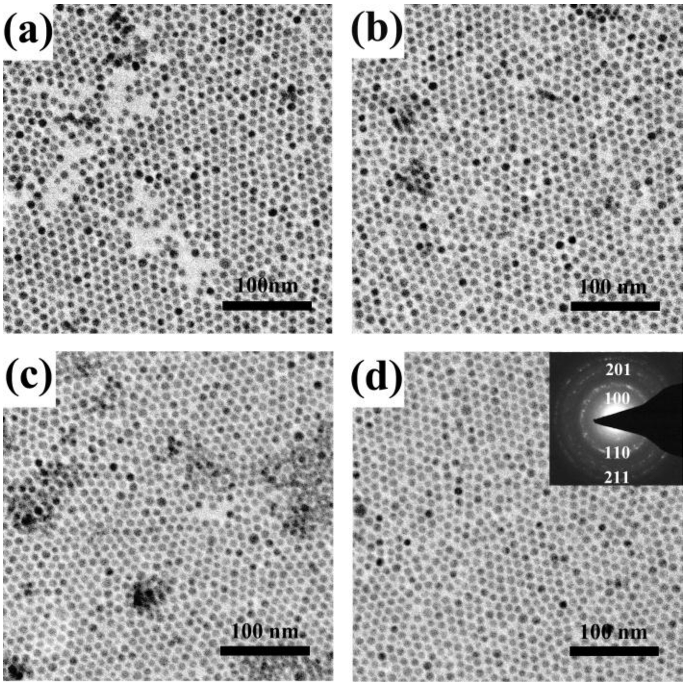

Fig. S5 TEM images of as-prepared $NaTm_{0.02}Lu_{0.98-x}Yb_xF_4$ nanoparticles doped with (a) 40% Yb^{3+}, (b) 60% Yb^{3+}, (c) 80% Yb^{3+}, and (d) 98% Yb^{3+} ions. The inset shows the selected area electron diffraction (SAED) pattern, indicating the hexagonal structure.

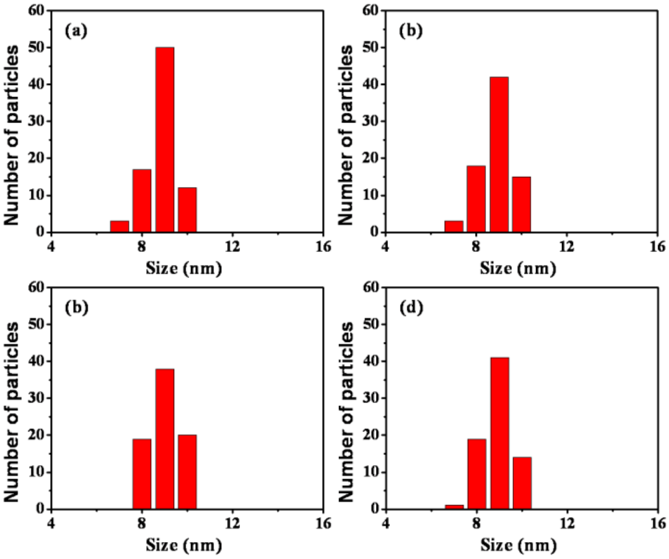

Fig. S6 Histograms of as-prepared $NaTm_{0.02}Lu_{0.98-x}Yb_xF_4$ nanoparticles doped with (a) 40% Yb^{3+}, (b) 60% Yb^{3+}, (c) 80% Yb^{3+}, and (d) 98% Yb^{3+} ions. All the nanoparticles of the $NaLuF_4$:Yb^{3+},Tm^{3+} are of hexagonal structure and monodispersed with the average diameter of around 9 nm.

The average sizes for nanoparticles with relative content of Yb^{3+} ions of 20%, 40%, 60%, and 100% were no obvious change because of the similar radius and electron charge density characteristics between Lu^{3+} and Yb^{3+} ions.

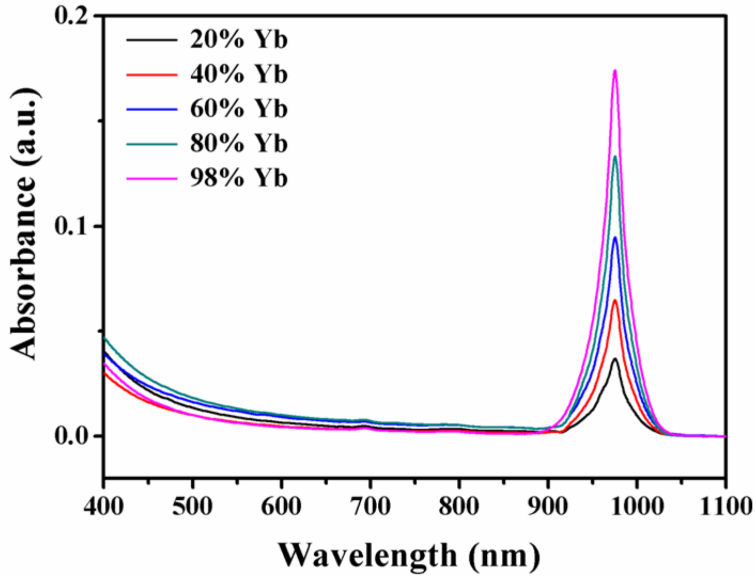

Fig. S7 Absorption of the as-prepared $NaTm_{0.02}Lu_{0.98-x}Yb_xF_4$ colloidal suspensions (0.1 M) doped with different Yb^{3+} ions.

Table S2 The feed ratio and actual ratio of various elements in the as-prepared $NaTm_{0.02}Lu_{0.98-x}Yb_xF_4$ nanocrystal. The data are obtained from ICP measurement.

Particle size (nm)	$Lu^{3+}/Yb^{3+}/Tm^{3+}$ feed ratio	$Lu^{3+}/Yb^{3+}/Tm^{3+}$ ratio in UCNPs
~ 9 nm	78/20/2	77.61/19.95/2.44
~ 9 nm	58/40/2	58.33/39.35/2.32
~ 9 nm	38/60/2	38.15/59.52/2.33
~ 9 nm	18/80/2	18.83/78.67/2.50
~ 9 nm	0/98/2	0/97.54/2.46

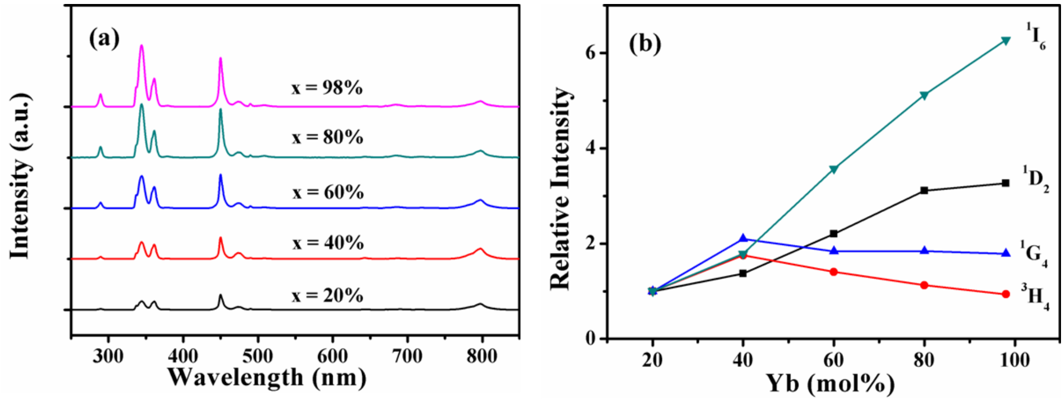

Fig. S8 Yb^{3+} dependent UC luminescence of $NaTm_{0.02}Lu_{0.98-x}Yb_xF_4$, which are calculated by Fig. S7 (Normalized at 975 nm for the $^2F_{7/2} \rightarrow {}^2F_{5/2}$transition of Yb^{3+} ions).

Obviously, the luminescent intensities of UV and blue emissions increase with the increasing Yb^{3+} ratio. For the NIR emission, its intensity increases at the beginning and then decreases gradually. In general, their luminescence intensity can be enhanced remarkably although the emissive ion will decrease via changing the solution concentration. The luminescence enhancement should be attributed to due to the increased rate of energy transfer between Yb^{3+} and Tm^{3+} ions.

References for supporting information

1. Q. Liu, Y. Sun, T. Yang, W. Feng, C. Li and F. Li, *J. Am. Chem. Soc.*, 2011, **133**, 17122.