Electronic Supplementary Information

Facile ex-situ NaF size/morphology tuning strategy for highly monodisperse sub-5 nm β-$NaGdF_4$:Yb/Er

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Materials and Chemicals

$Gd(CH_3COO)_3{\cdot}xH_2O$ (99.9%), $Yb(CH_3COO)_3{\cdot}4H_2O$ (99.9%), $Er(CH_3COO)_3{\cdot}xH_2O$ (99.9%), Oleic acid (HOA, technical grade, 90%), 1-octadecene (ODE, technical grade, 90%) and sodium oleate (NaOA) were obtained from Sigma-Aldrich (St. Louis, MO, USA). $GdCl_3{\cdot}6H_2O$ (99.9%), $YbCl_3{\cdot}6H_2O$ (99.9%) and $ErCl_3$ (99.9%) were obtained from Aladdin Reagent (Shanghai, China). All the other reagents were of analytical reagent grade.

Instrumentation and Characterization

Transmission electron microscopy (TEM) and high-resolution TEM images, high-angle annular dark-field (HAADF) images, element maps and Energy-dispersive X-ray analysis (EDXA) were achieved on a Tecnai G^2 F20 microscopy (FEI, USA). X-ray powder diffraction (XRD) pattern collections were performed on a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.15418 nm). RF-5301 spectrofluorometer (Shimadzu, Japan) equipped with an external 980 nm laser source was used to measure upconversion luminescence spectra of UCNCs.

Small-sized NaF preparation and size/morphology regulation.

Small-sized NaF was prepared by the *ex-situ* sodium/fluoride-to-NaF conversion strategies, which were realized by dissolving corresponding sodium/fluoride sources in methanol and performing ultrasonic-assisted dissolution for 8 min. Three combinations of $NaOH/NH_4F$, $NaOA/NH_4F$ and $(NaOH+NaOA)/NH_4F$ were used to produce small-sized NaF.

Nano-sized NaF/MSNaF based solvothermal synthesis of $NaGdF_4$:Yb/Er(30/2 mol%).

The synthesis procedures were actually performed according to NaOH based solvothermal strategy for the preparation of UCNCs in literature.[1,2] Firstly, rare-earth acetates (total amount, 0.6 mmol), HOA (6 mL) and ODE (9 mL) were added sequentially to a 50 mL flask to construct a solvothermal system. And then, the system was heated at 160 °C for 30 min to realize the

conversion from rare-earth acetates to rare-earth oleates. After cooling down to 35 °C, a methanolic nano-sized NaF solution, which was formed by the reaction between NaOH (1.5 mmol) and NH_4F (2.4 mmol) in methanol (6 mL), was added. After stirring at 35 °C for 30 min to achieve low temperature nucleation, the system was heated to 100 °C to remove methanol, and then to predetermined nanocrystal growth temperature (~13 °C/min). On finishing nanocrystal growth, the system was cooled down naturally. Purified product was dispersed in cyclohexane, and the insoluble component was removed by centrifugation before further characterizations.

The synthesis procedures for MSNaF based solvothermal synthesis of UCNCs were the same as those in nano-sized NaF based solvothermal synthesis of UCNCs except that NaOA (1.5 mmol), instead of NaOH, was used.

Solvothermal synthesis of $NaGdF_4$:Yb/Er(30/2 mol%) according to a mixed mode of (NaOH+NaOA)-to-NaF conversion strategy.

The mixed mode of (NaOH+NaOA)-to-NaF conversion was realized by adding 0.75 mmol of NaOH, 0.75 mmol of NaOA and 2.4 mmol of NH_4F into methanol (6 mL), followed by ultrasonic-assisted reaction. The $NaGdF_4$:Yb/Er synthesis procedures were the same as those in nano-sized NaF based solvothermal synthesis except that such (NaOH+NaOA)/NH_4F solution, instead of NaOH-NH_4F solution, was used.

NaOA based solvothermal synthesis of $NaGdF_4$:Yb/Er(30/2 mol%).

Rare-earth oleates were formed by using the same procedures in NaOH based solvothermal synthesis of UCNCs. And then, NaOA (1.5 mmol) was added to the reaction system, followed by stirring at this temperature for 10 min. Methanolic NH_4F (2.4 mmol) was then added. The following steps were similar to those in nano-sized NaF based solvothermal synthesis.

NaF level monitoring in solvothermal synthesis system.

The solvothermal system was cooled down to room temperature quickly by using cool air flow after the predetermined synthesis procedures were completed. Precipitate was collected from reaction system *via* direct centrifugation. The as-obtained precipitate was then washed with cyclohexane. XRD analysis to the as-obtained precipitates indicated most of them were NaF. The mass of the as-obtained precipitate was used to reflect the amount of unconsumed NaF in system.

Rare-earth chlorides/nano-sized NaF based solvothermal synthesis of $NaGdF_4$:Yb/Er(30/2 mol%) by using a low nanocrystal growth temperature of 280 °C

The $NaGdF_4$:Yb/Er(30/2 mol%) was prepared according to the literature without modification.[3] Notably, rare-earth chlorides, instead of rare-earth acetates, were used in the synthesis. In addition, the nanocrystal growth was performed at 280 °C for 20 min.

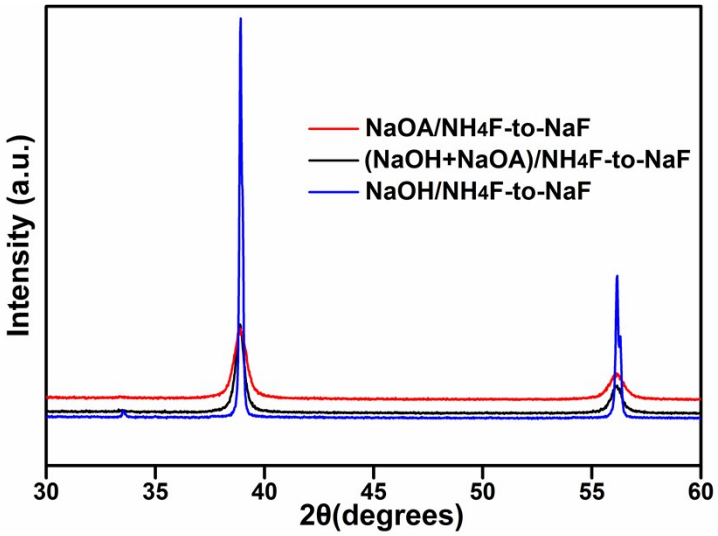

Fig. S1 XRD patterns of small-sized NaF achieved by using the NaOH/NH_4F-to-NaF, NaOA/NH_4F-to-NaF and mixed mode of (NaOH+NaOA)/NH_4F-to-NaF conversion strategies. All XRD patterns agree with the standard XRD pattern of NaF (JCPDS 36-1455), suggesting the formation of NaF. XRD peak width comparisons showed smaller NaF was formed according to both NaOA/NH_4F-to-NaF and (NaOH+NaOA)/NH_4F-to-NaF conversion strategies, whereas larger NaF was formed according to the NaOH/NH_4F-to-NaF conversion strategy.

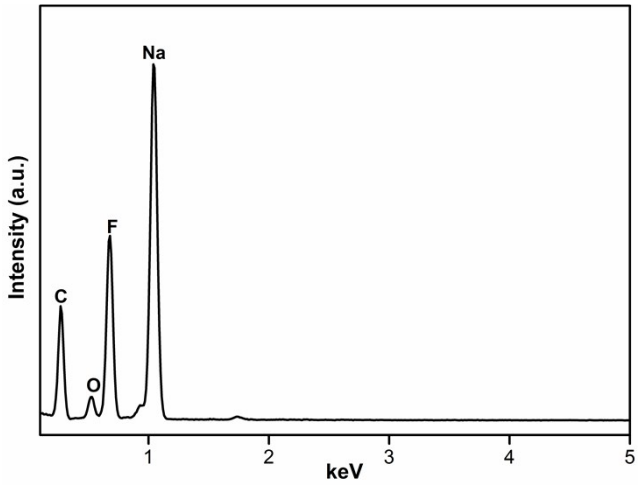

Fig. S2 EDXA spectrum of the MSNaF shown in Fig. 1C. The Na/F ratio in the MSNaF was ~1.2:1, which was slightly higher than that in NaF (1:1), demonstrating the reactivity of the NaOA/NH_4F-to-NaF conversion in methanol was moderate. There seemingly was a small amount of unconverted NaOA absorbed on the MSNaF.

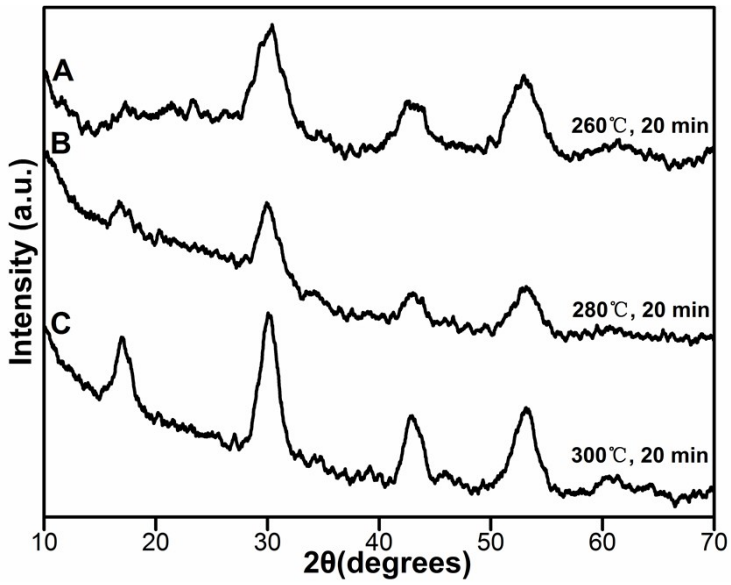

Fig. S3 XRD patterns: $NaGdF_4$:Yb/Er prepared by using MSNaF based solvothermal strategy at different nanocrystal growth temperatures. All XRD patterns agree with the standard XRD pattern of β-$NaGdF_4$ (JCPDS 27-0699), suggesting the formation of β-$NaGdF_4$:Yb/Er.

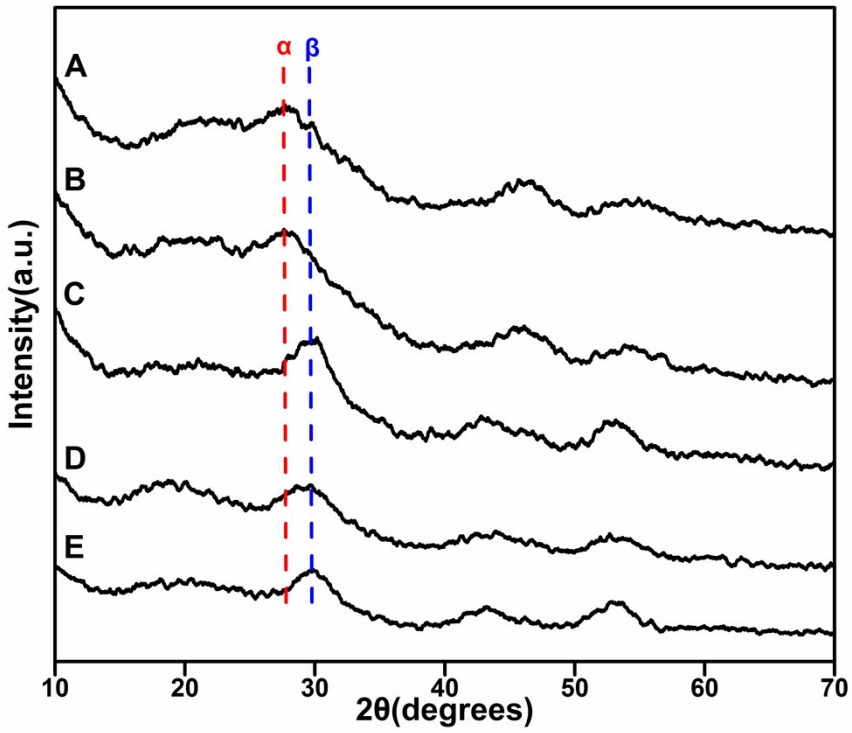

Figure S4. XRD patterns: $NaGdF_4$:Yb/Er prepared by using nano-sized NaF based solvothermal strategy and reacting at 240 °C for (A) 0 min, (B) 10 min and (C) 20 min; $NaGdF_4$:Yb/Er prepared by using MSNaF based solvothermal strategy and reacting at 240 °C for (D) 0 min and (E) 10 min.

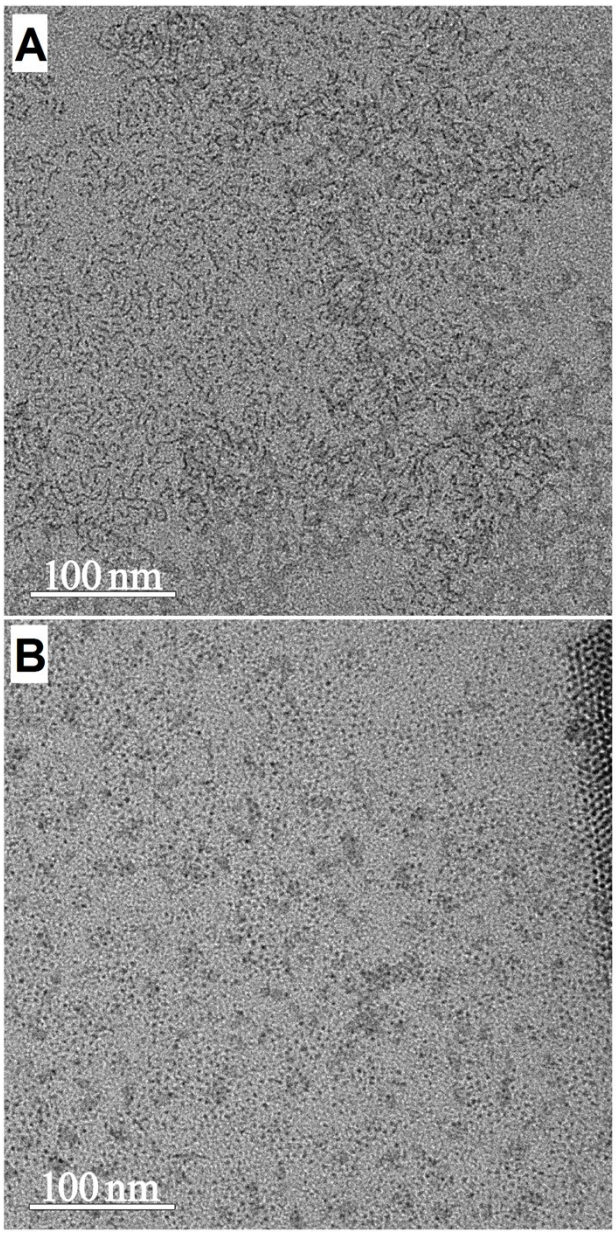

Figure S5. TEM images of β-$NaGdF_4$:Yb/Er prepared by using the MSNaF based solvothermal strategy. The nanocrystal growth reactions were performed at 240 °C for 5 min (A) and 300 °C for 5 min (B), respectively.

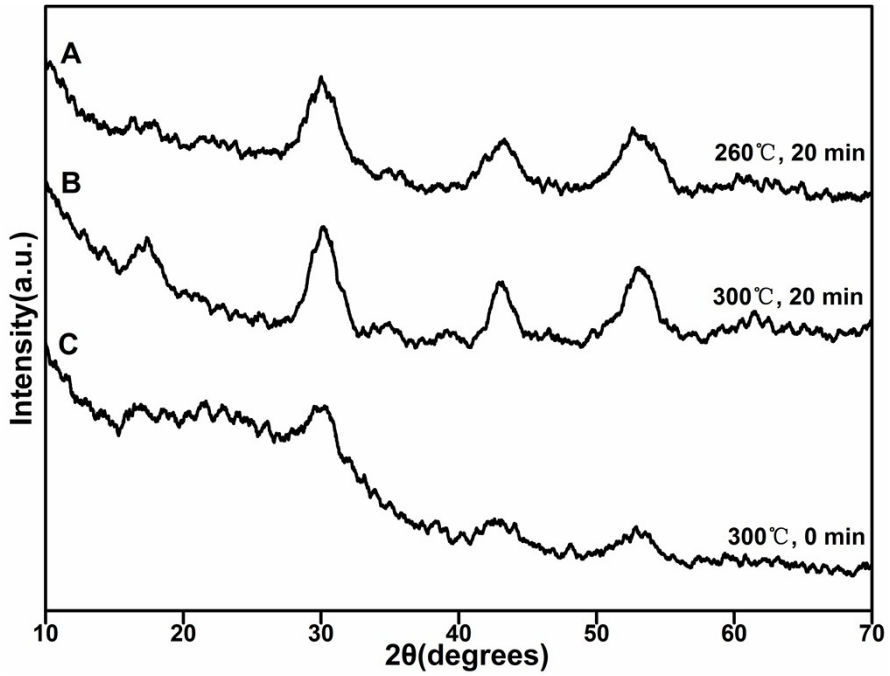

Figure S6. XRD patterns: $NaGdF_4$:Yb/Er prepared by using NaOA based solvothermal strategy.

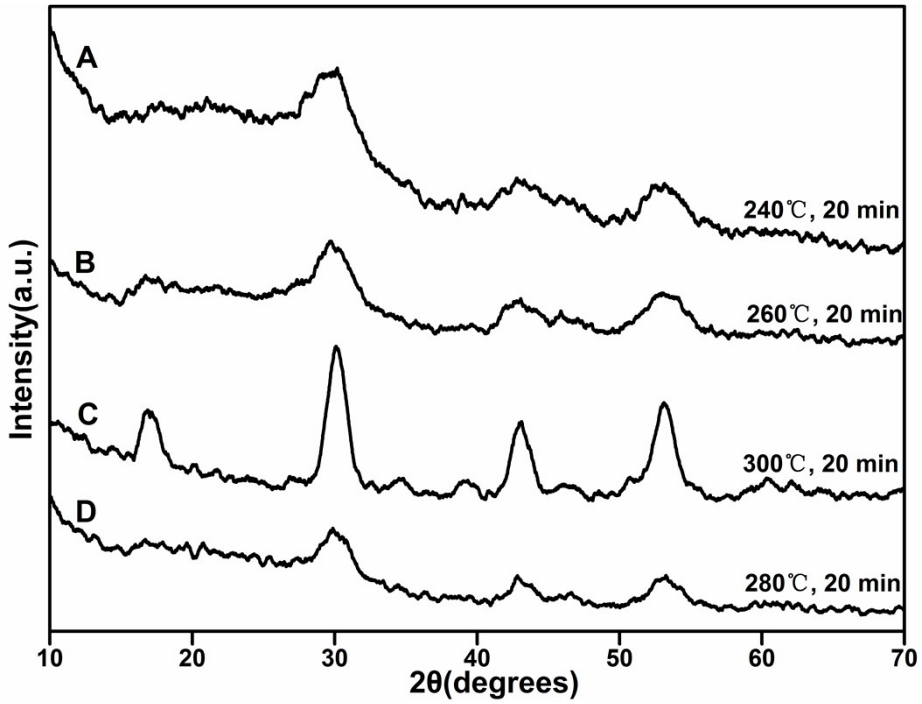

Figure S7. XRD patterns: $NaGdF_4$:Yb/Er prepared by using nano-sized NaF based solvothermal strategy and reacting at different conditions. Particularly, the sample used in (D) was prepared by using rare-earth chlorides, instead of rare-earth acetates.

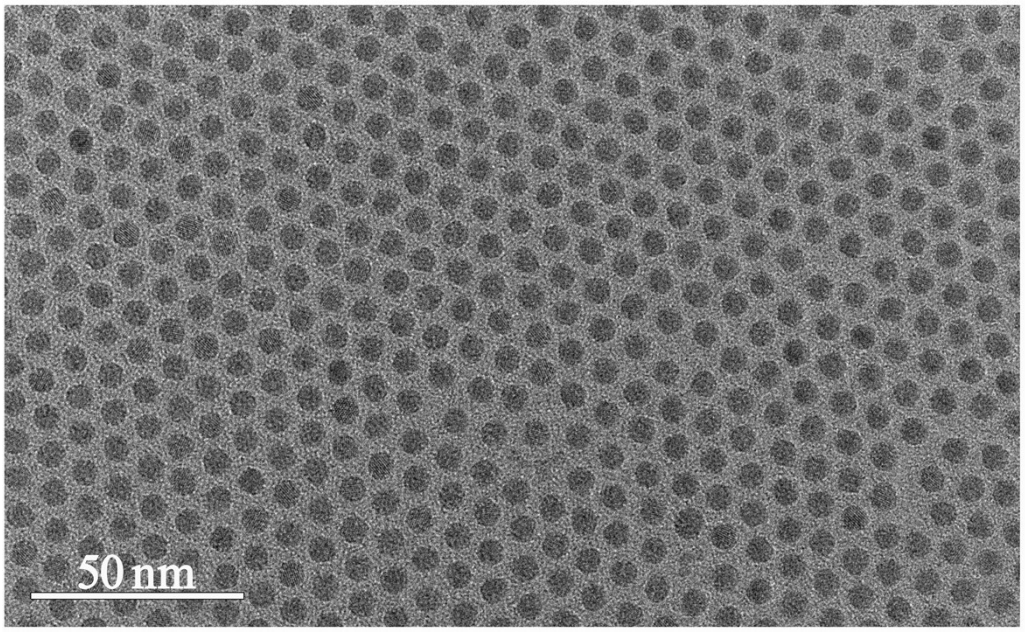

Figure S8. Large scale TEM image of β-$NaGdF_4$:Yb/Er prepared by using nano-sized NaF based solvothermal strategy and reacting at 300 °C for 20 min. The as-obtained β-$NaGdF_4$:Yb/Er was highly monodisperse.

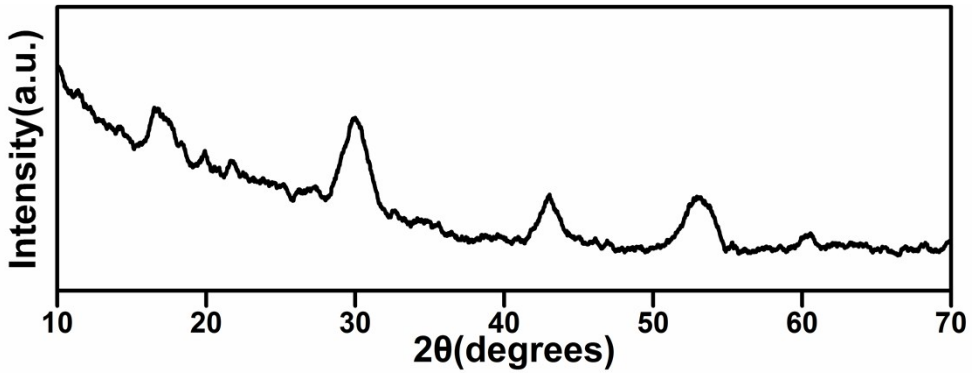

Figure S9. XRD pattern: $NaGdF_4$:Yb/Er prepared by using the mixed mode of (NaOH+NaOA)-to-NaF strategy and reacting solvothermally at 300 °C for 10 min.

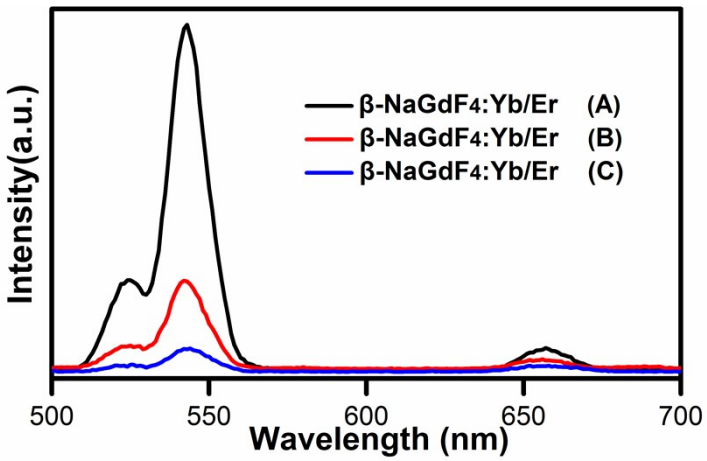

Figure S10. Upconversion luminescence spectra of β-$NaGdF_4$:Yb/Er dispersed in cyclohexane under 980 nm excitation (10 W cm^{-2}). (A) 6.3 nm β-$NaGdF_4$:Yb/Er prepared by using the rare-earth acetates/nano-sized NaF based solvothermal strategy (Fig. 3C); (B) 4.6 nm β-$NaGdF_4$:Yb/Er prepared by using rare-earth acetates/mixed mode of (NaOH+NaOA)-to-NaF conversion strategy (Fig. 4B); (C) β-$NaGdF_4$:Yb/Er prepared by using the rare-earth chlorides/nano-sized NaF based solvothermal strategy (nanocrystal growth was performed at 280 °C for 20 min) according to literature.

References

1 N. J. J. Johnson, W. Oakden, G. J. Stanisz, R. S. Prosser and F. C. J. M. van Veggel, *Chem. Mater*., 2011, **23**, 3714−3722.

2 Z. Q. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606.

3 J. Liu, G. Y. Chen, S. W. Hao and C. H. Yang, *Nanoscale* 2017, **9**, 91−98.