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Supporting Information

Highly thermostable fluoride nanocrystal-in-glass composite (NGC) for mid-infrared emission

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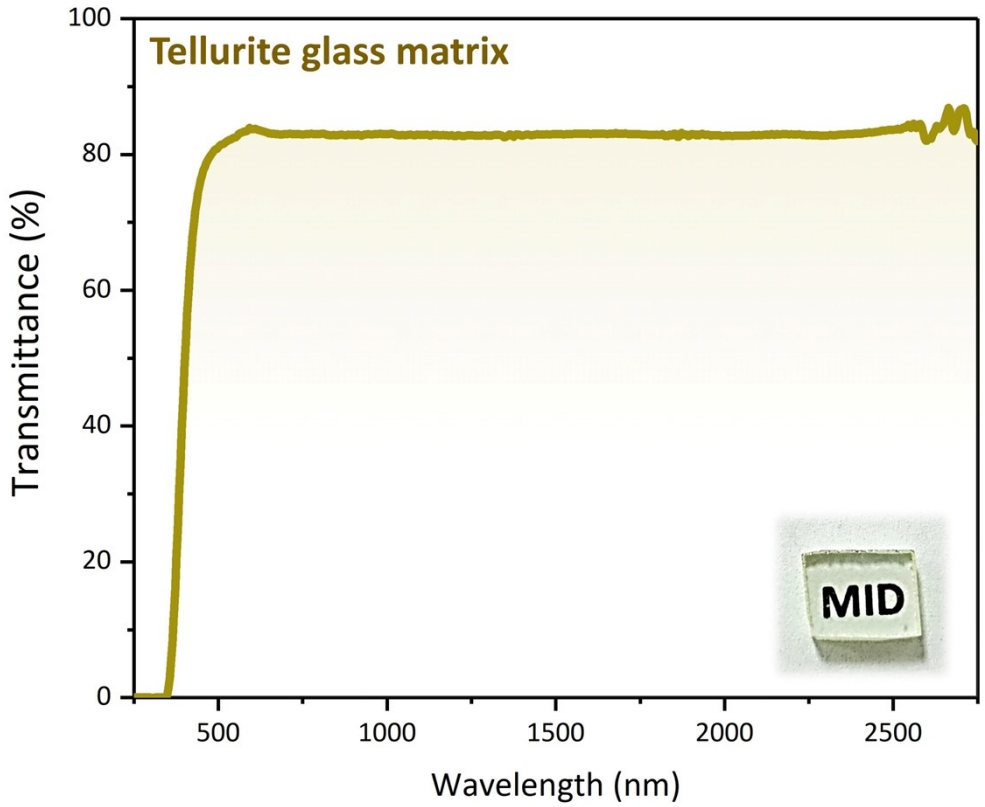

Fig. S1 Ultraviolet-visible-infrared transmission spectrum of the as-prepared tellurite glass matrix. The inset is the photograph of the as-prepared tellurite glass matrix.

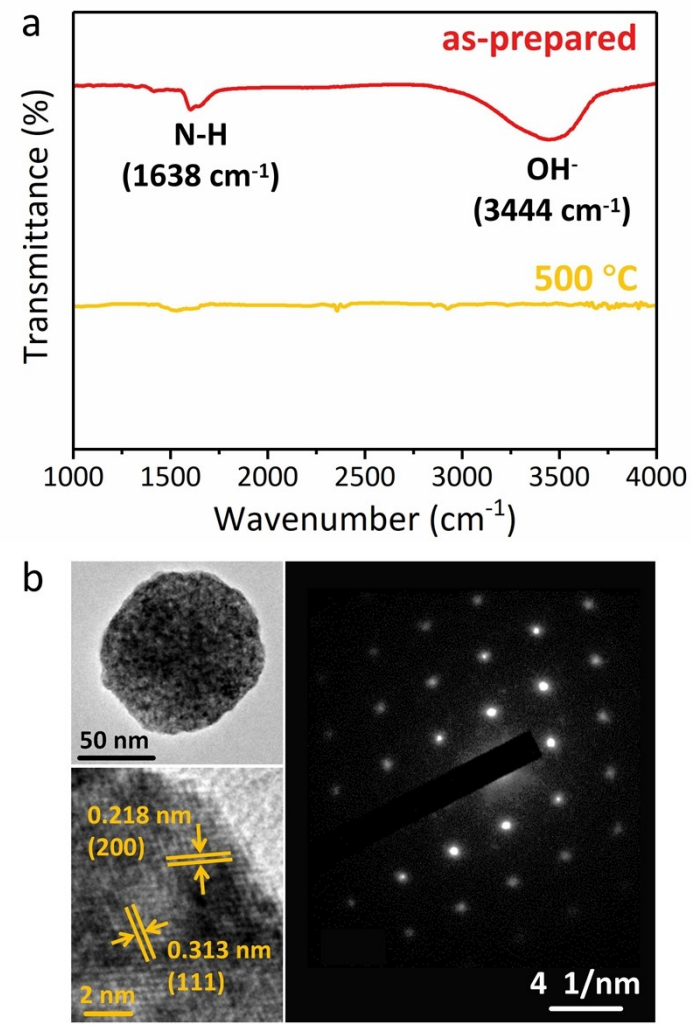

Fig. S2 (a) Fourier transform-infrared spectroscopy spectra of the as-prepared $NaYF_4:Er^{3+}$ nanocrystals (NCs) and their thermal annealing at 500 °C for 2 h. (b) Transmission electron microscopy (TEM) image (top left), high-resolution TEM image (bottom left), and selected area electron diffraction pattern (right) of a single as-prepared $NaYF_4:Er^{3+}$ NC.

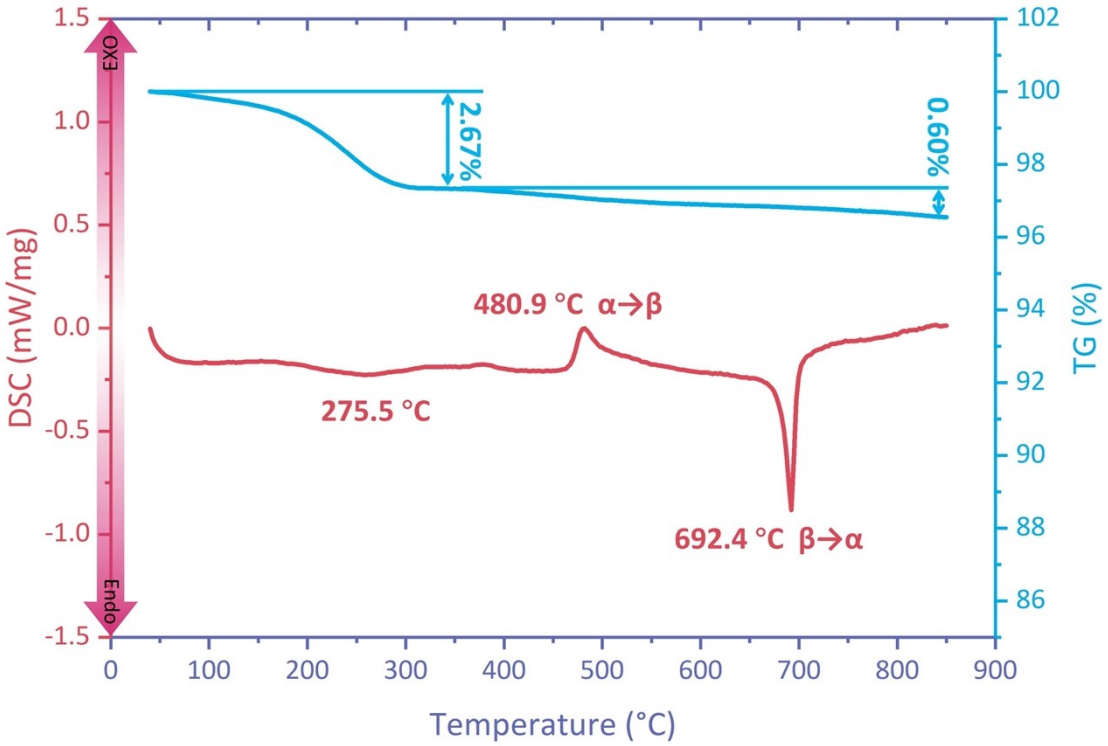

Fig. S3 Thermogravimetry-differential scanning calorimetry (TG-DSC) curves of the as-prepared $NaYF_4:Er^{3+}$ NCs in air atmosphere with a heating rate of 10 °C/min.

DSC curve exhibits two endothermic peaks and one exothermic peak. The first endothermic peak at 270.5 °C is due to the dehydration and combustion of the surface organic ligands, which results in a weight loss of 2.67%. The exothermic peak at 480.9 °C and the endothermic peak at 692.4 °C correspond to the phase transition between cubic (α) and hexagonal (β) $NaYF_4$. The vaporization of some residual organic ligands during this process leads to a weight loss of 0.6%.

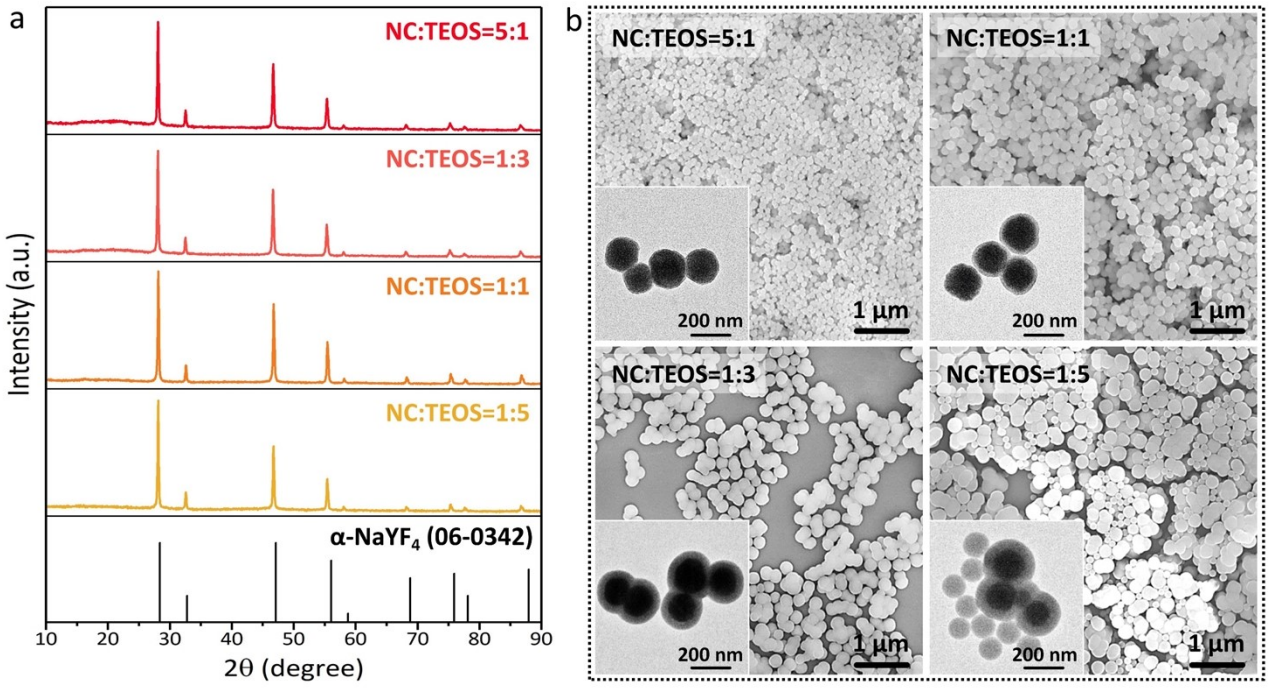

Fig. S4 (a) X-ray diffraction (XRD) patterns and (b) scanning electron microscopy (SEM) images of $NaYF_4:Er^{3+}@SiO_2$ NCs prepared at different mass ratios between $NaYF_4:Er^{3+}$ NCs and tetraethyl orthosilicate (TEOS). Insets in (b) are corresponding TEM images.

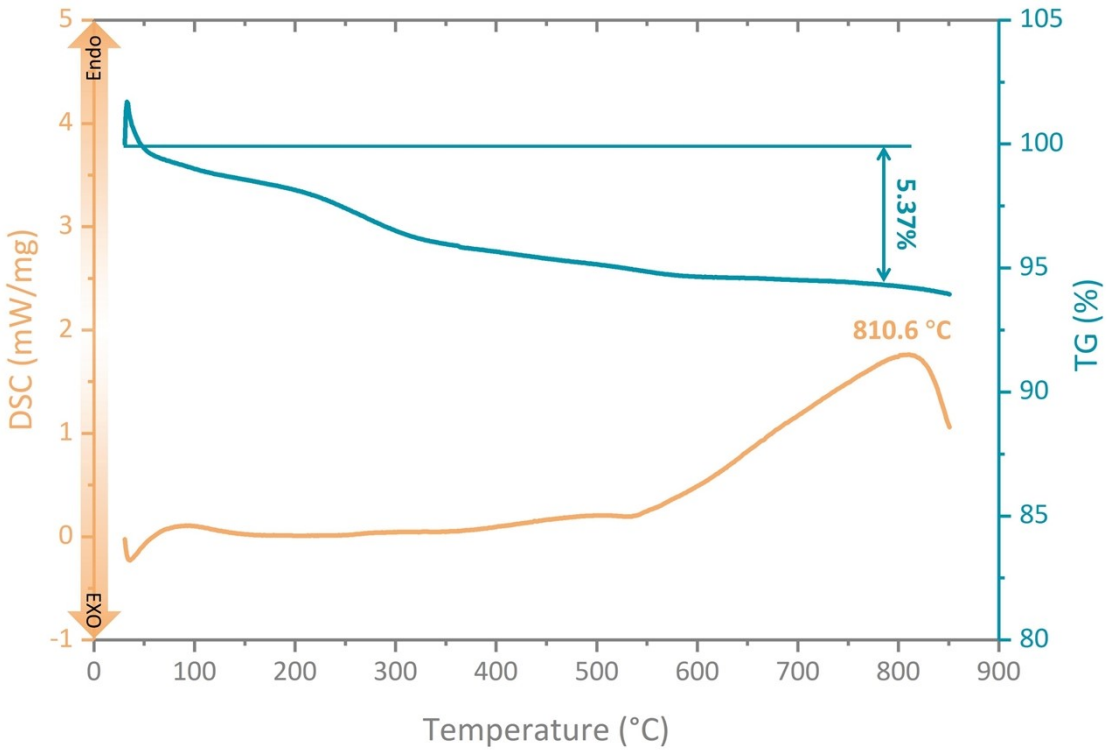

Fig. S5 (a) TG-DSC curves of the as-prepared $NaYF_4:Er^{3+}@SiO_2$ NCs in air atmosphere with a heating rate of 10 °C/min.

The DSC curve shows there are no endothermic or exothermic peaks below 800 °C, indicating as-prepared $NaYF_4:Er^{3+}@SiO_2$ NCs did not go through phase transition processes. But during this temperature range, there is a 5.37% weight loss. This can be attributed to the dehydration and combustion of surface organic ligands. Due to the protection of the SiO_2 shell, this is a very slow process, so that no endothermic peak was detected. When the temperature is above 800 °C, there is an endothermic process. According to the XRD pattern of α-$NaYF_4:Er^{3+}@SiO_2$ NCs annealed at 800 °C (**Fig. S9**), this endothermic process is a complex process, including the phase transformation between α- and β-$NaYF_4$ as well as the reaction between $NaYF_4$ and SiO_2.

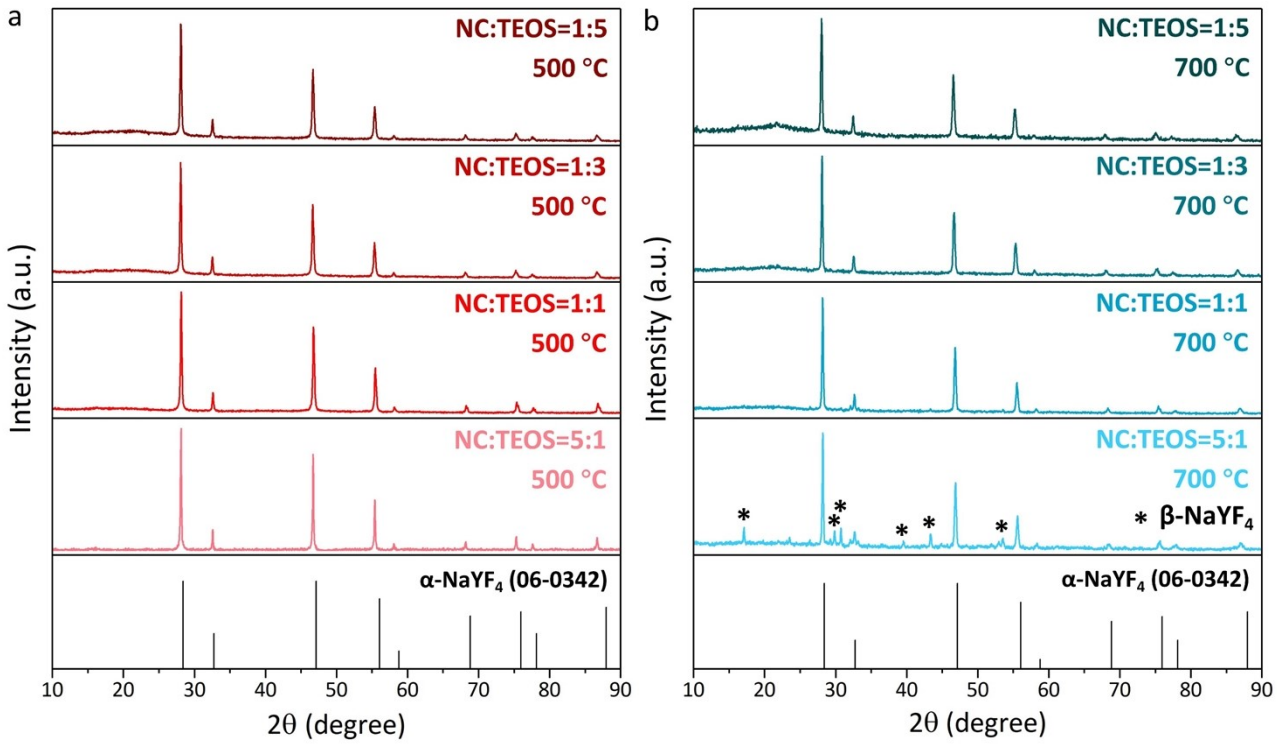

Fig. S6 XRD patterns of $NaYF_4:Er^{3+}@SiO_2$ NCs prepared at different mass ratios between $NaYF_4:Er^{3+}$ NCs and TEOS annealed at different temperatures for 2 h: (a) 500 °C, (b) 700 °C.

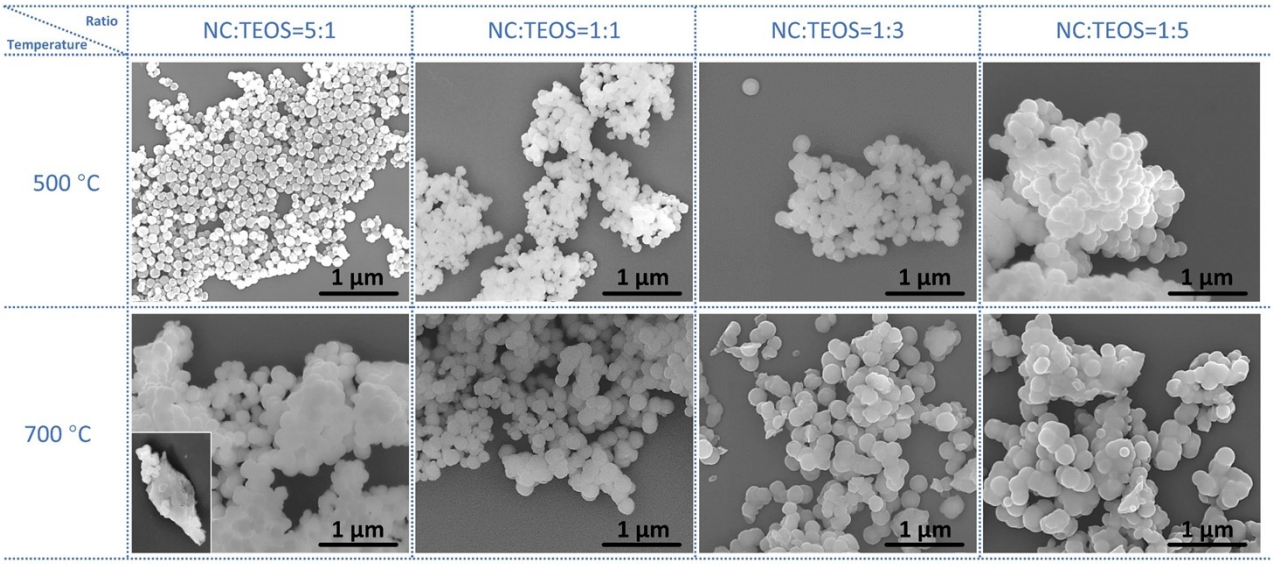

Fig. S7 SEM images of $NaYF_4:Er^{3+}@SiO_2$ NCs prepared at different mass ratios between $NaYF_4:Er^{3+}$ NCs and TEOS annealed at 500 °C and 700 °C for 2 h, respectively.

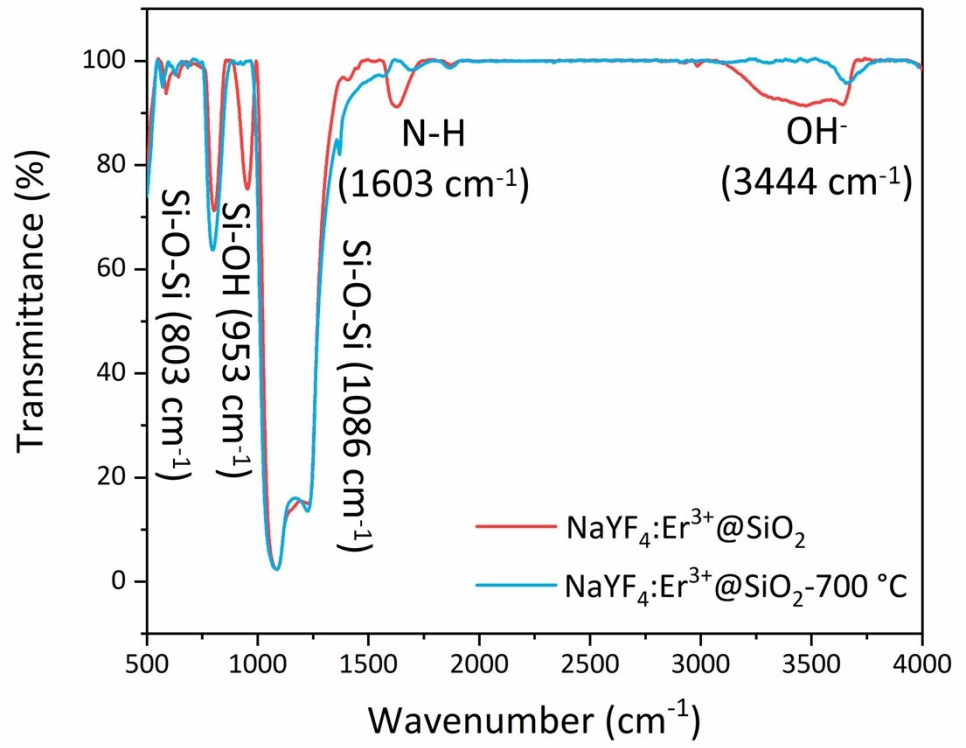

Fig. S8 FTIR spectra of the as-prepared $NaYF_4:Er^{3+}@SiO_2$ NCs and their thermal annealing at 700 °C for 2 h.

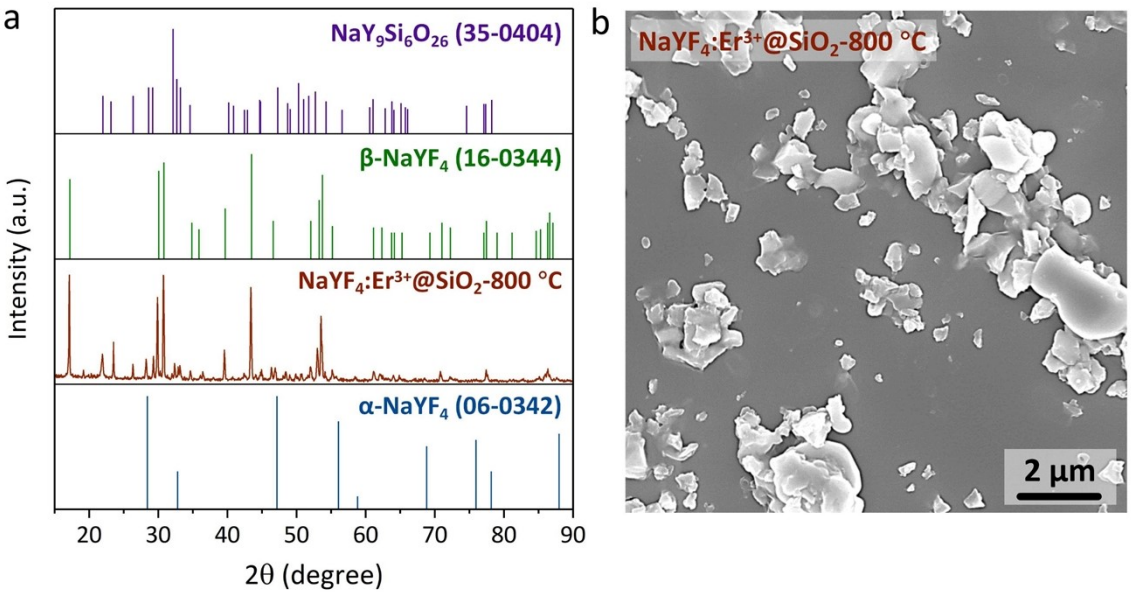

Fig. S9 (a) XRD patterns and (b) SEM image of the as-prepared $NaYF_4$:Er^{3+}@SiO_2 NCs annealed at 800 °C for 2 h.

As shown in this Figure, when increasing the annealing temperature to 800 °C, multiple crystalline phases appear in the samples, including α-$NaYF_4$, β-$NaYF_4$, and silicon oxides. This indicates that at higher temperature (≥ 800 °C), $NaYF_4$ would react with SiO_2 shell, and without protection of SiO_2 shell, most unreacted α-$NaYF_4$ would transform into β-$NaYF_4$. This series of transitions also led to a serious morphological collapse. Accordingly, the highest thermal stability temperature of the as-prepared $NaYF_4$:Er^{3+}@SiO_2 NCs is 700 °C.

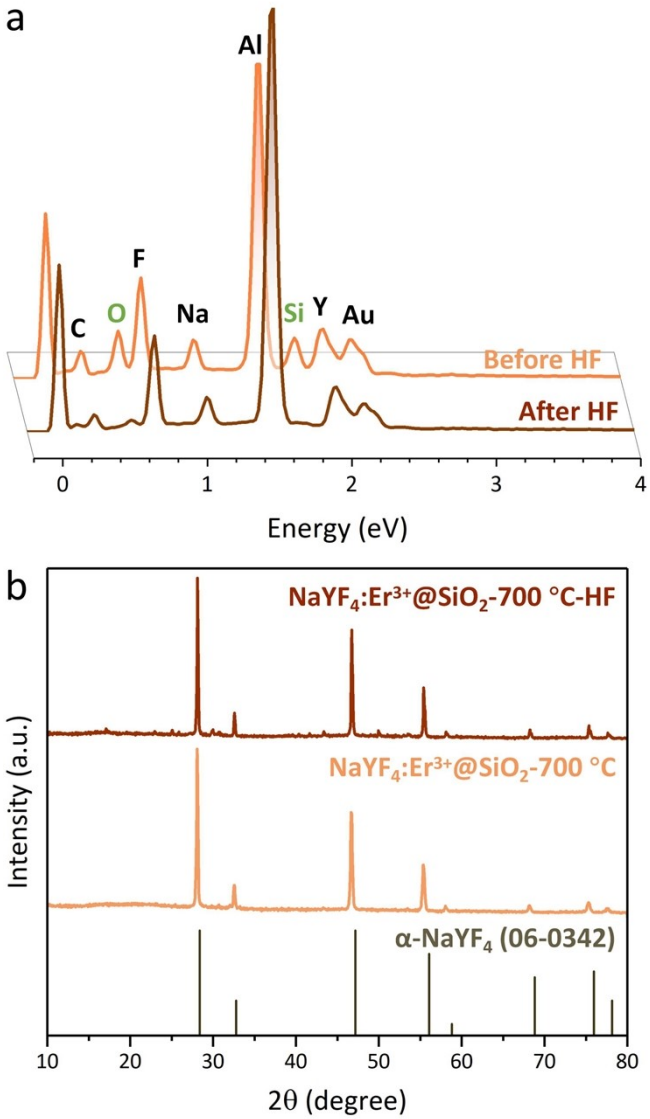

Fig. S10 (a) Compositional analysis and (b) XRD patterns of $NaYF_4:Er^{3+}@SiO_2$ NCs annealed at 700 °C for 2 h before and after hydrofluoric acid (HF) treatment.