Supporting Information

Facile and mass production synthesis of β-NaYF₄:Yb³⁺,Er³⁺/Tm³⁺ 1D microstructures with multicolor up-conversion luminescence

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Experimental details

All of the chemical reagents used in this experiment are analytical grade and were received without further purification. $Y(NO_3)_3$, NaF, NaNO₃ and KNO₃ were purchased from Sinopharm Chemical Reagent Co., Ltd (China). $Yb(NO_3)_3$, Er(NO₃)₃ and Tm(NO₃)₃ were prepared by dissolving the corresponding Yb_2O_3 , Er₂O₃, and Tm₂O₃ (99.99%, purchased from Changchun Applied Chemistry Science and Technology Limited, China.) in HNO₃ solution at elevated temperature followed by evaporating superfluous HNO₃ and the under vacuum.

In a typical process for the synthesis of hexagonal NaYF₄, stoichiometric Y(NO₃)₃, NaF, NaNO₃, KNO₃ with molar ratio of 1:4:50:25 were thoroughly mixed with an appropriate amount of ethanol in an agate mort and ground for 30 min. This mixture was then transferred into an alumina crucible and heated at 350 °C for different reaction time. After cooled down to the room temperature, the as-annealed samples were washed with deionized water, and subsequently dried at 100 °C overnight. Hexagonal NaYF₄:Yb³⁺/Er³⁺, NaYF₄:Yb³⁺/Tm³⁺ products were prepared in a similar procedure by adding corresponding Yb(NO₃)₃, Er(NO₃)₃, Tm(NO₃)₃ into the precursor mixture. Notably, we can easily and routinely scale up this process to produce large amount of NaYF₄ product.

Characterization. X-ray powder diffraction (XRD) measurements were performed on a Rigaku TTR III diffractometer at a scanning rate of 10°/min in the 20 range from 10° to 80°, with graphite monochromatic Cu Ka radiation ($\lambda = 0.15405$ nm). SEM micrographs and energy-dispersive X-ray (EDX) spectra were obtained using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi) equipped with an energy-dispersive X-ray spectrum (EDS, JEOL JXA-840). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) patterns were recorded on a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gatan multiple CCD camera. Up-conversion emission spectra were obtained using 980 nm LD Module (K98D08M-30W, China) as the excitation source and detected by R955 (HAMAMATSU) from 400–900 nm. All the measurements were performed at room-temperature (RT).



Fig. S1 FE-SEM images with low magnification (A), high magnification (B), single microrod (C, D), TEM image (E), HRTEM image (F) of the NaYF₄ microrods obtained at 2 h.



Fig. S2 SEM image of $NaYF_4$ prepared at 350 °C for 10 min. The inset is the corresponding XRD pattern.



Fig. S3 SEM images of NaYF₄ products prepared at 350 °C for 30 min (A), 1 h (B), 2 h (C), and 4 h (D). The insets are their corresponding high-magnification FE-SEM images.



Fig. S4 XRD patterns of the as-prepared NaYF₄ nanostructures obtained at 30 min (A), 1 h (B), 2 h (C) and 4 h (D), respectively. The standard data for β -NaYF₄ (JCPDS No. 16–0334) are shown as references.



Fig. S5 Schematic energy-level diagrams of the Er³⁺, Tm³⁺, and Yb³⁺ dopant ions and the UC mechanism excited by 980 nm laser diode. The solid, dotted, and curly arrows indicate radiative, non-radiative energy transfer and multi-photon relaxation processes, respectively.