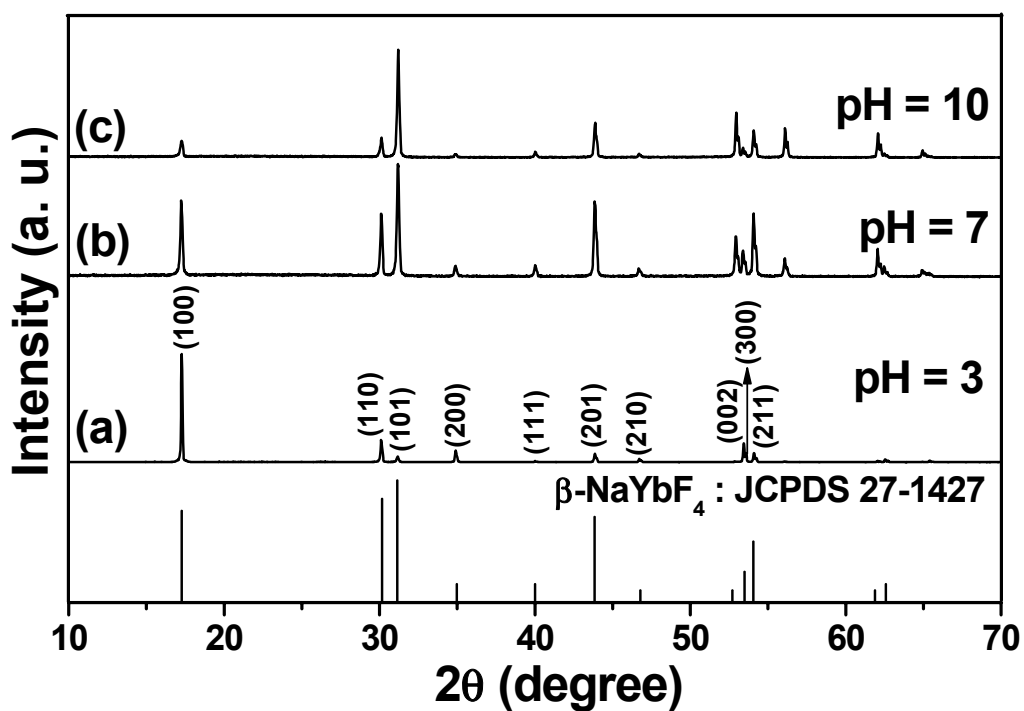


## Supporting Information

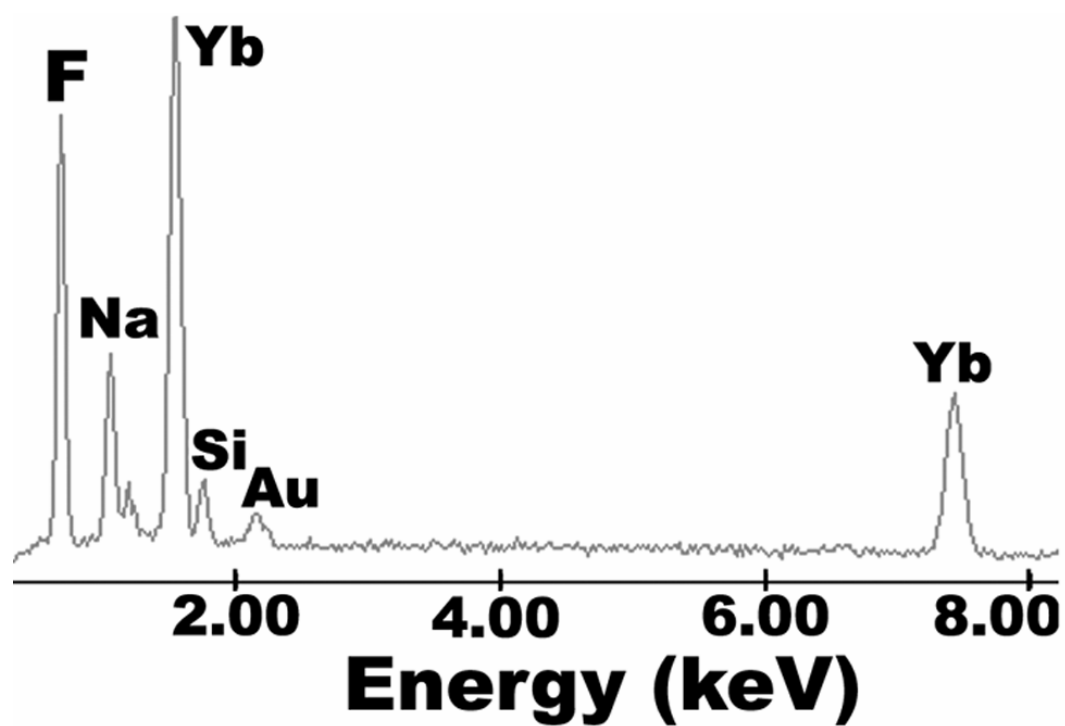
### Shape Controllable Synthesis and Upconversion Properties of $\text{NaYbF}_4/\text{NaYbF}_4:\text{Er}^{3+}$ and $\text{YbF}_3/\text{YbF}_3:\text{Er}^{3+}$ Microstructures

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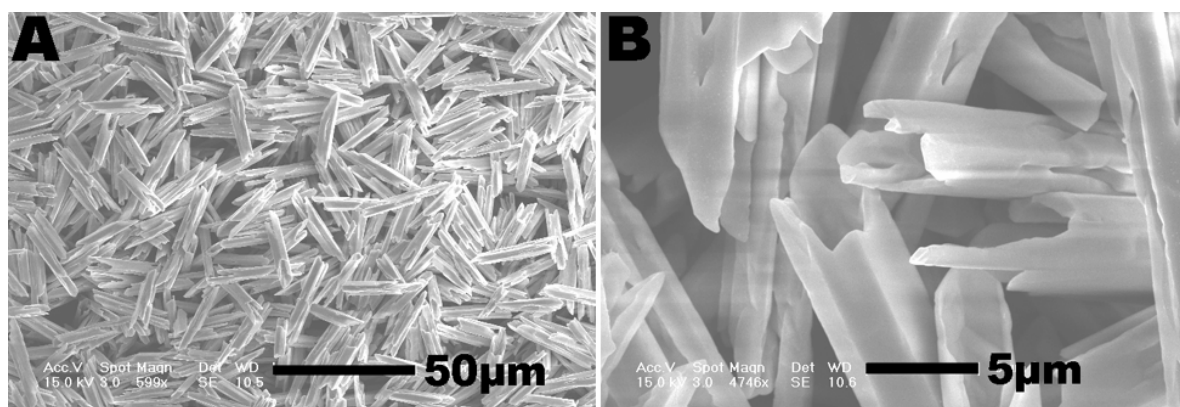
State Key Laboratory of Application of Rare Earth Resources, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022; and Graduate University of the Chinese Academy of Sciences, Beijing 100049, P. R. China



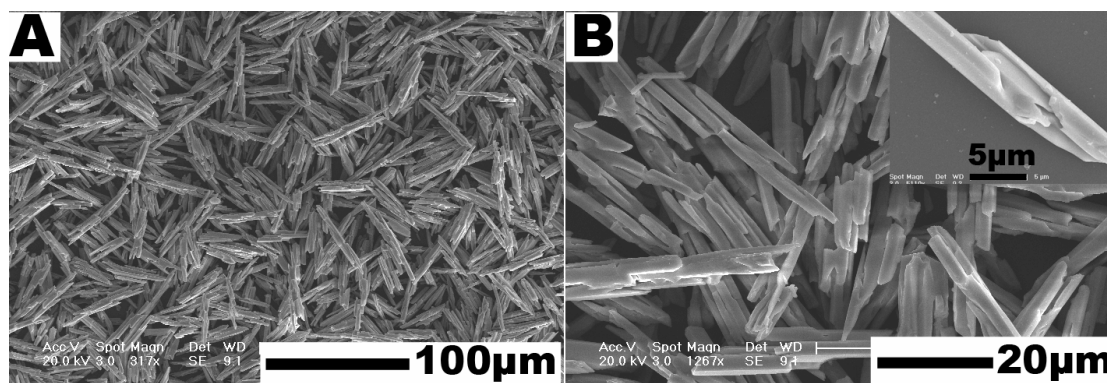
**Fig. S1** The XRD patterns of the as-prepared  $\beta\text{-NaYbF}_4$  products using  $\text{NH}_4\text{F}$  as fluoride source at 180 °C for 24 h at different pH values of (a) 3; (b) 7; (c) 10 and the standard data of  $\beta\text{-NaYbF}_4$  (JCPDS card no. 27-1427).



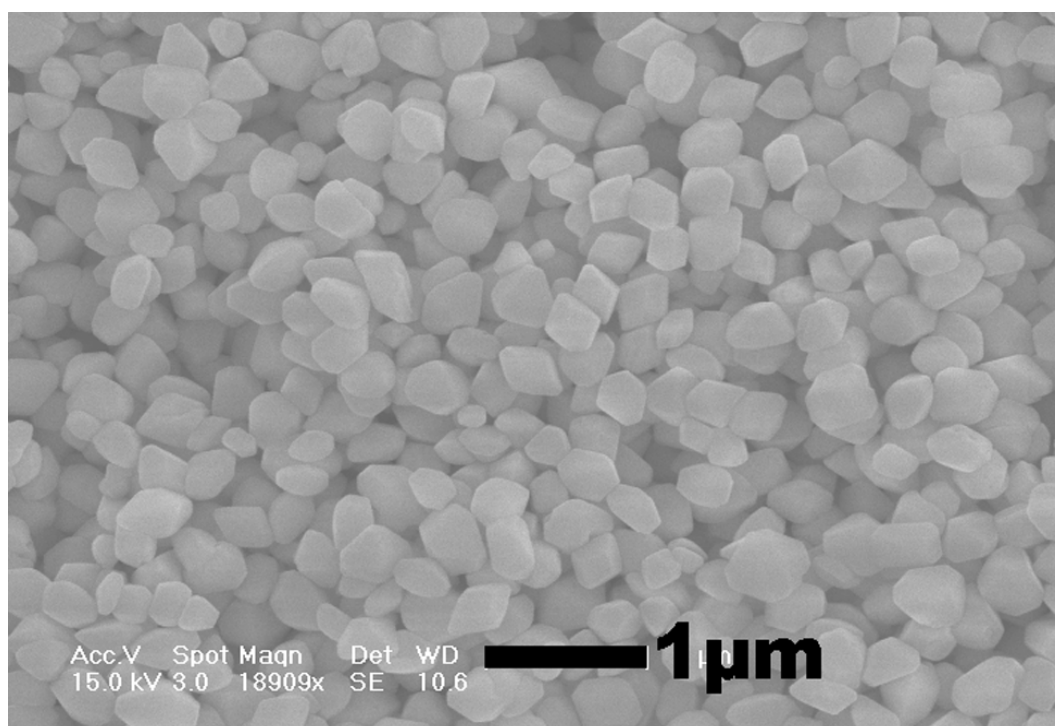
**Fig. S2** EDX spectrum of  $\beta$ -NaYbF<sub>4</sub> irregular microprisms (P1), revealing the presence of Na, Yb and F.



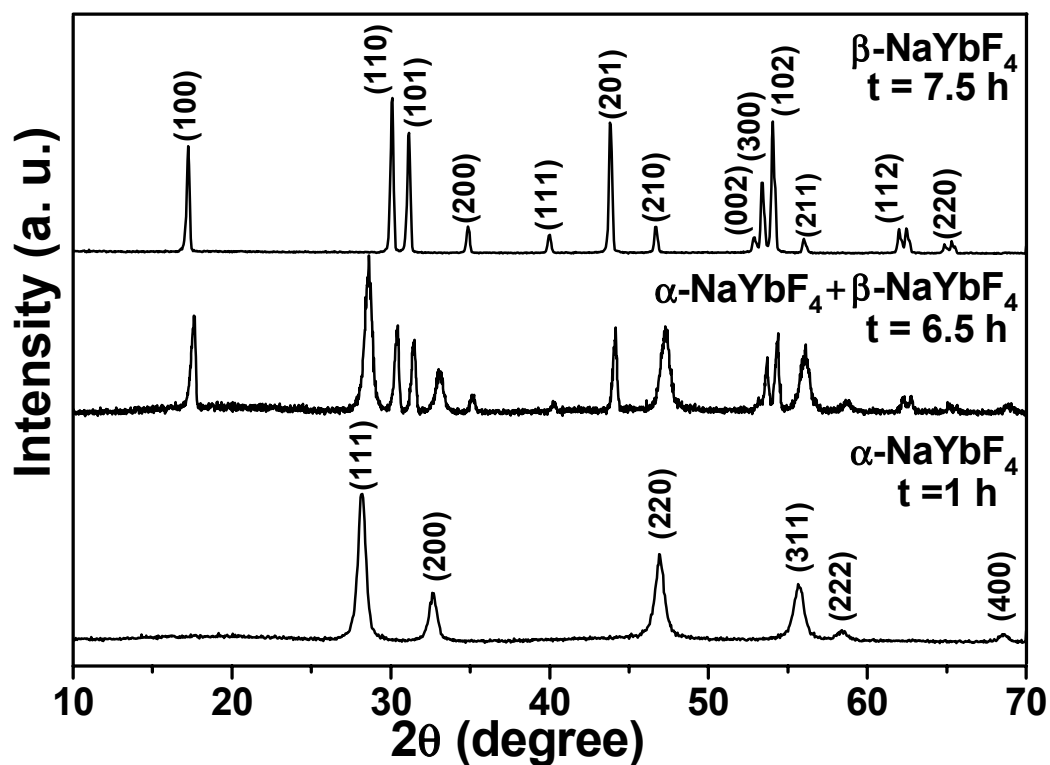
**Fig. S3** SEM images of  $\beta$ -NaYbF<sub>4</sub> microtubes using NaBF<sub>4</sub> as fluoride source (pH = 10).



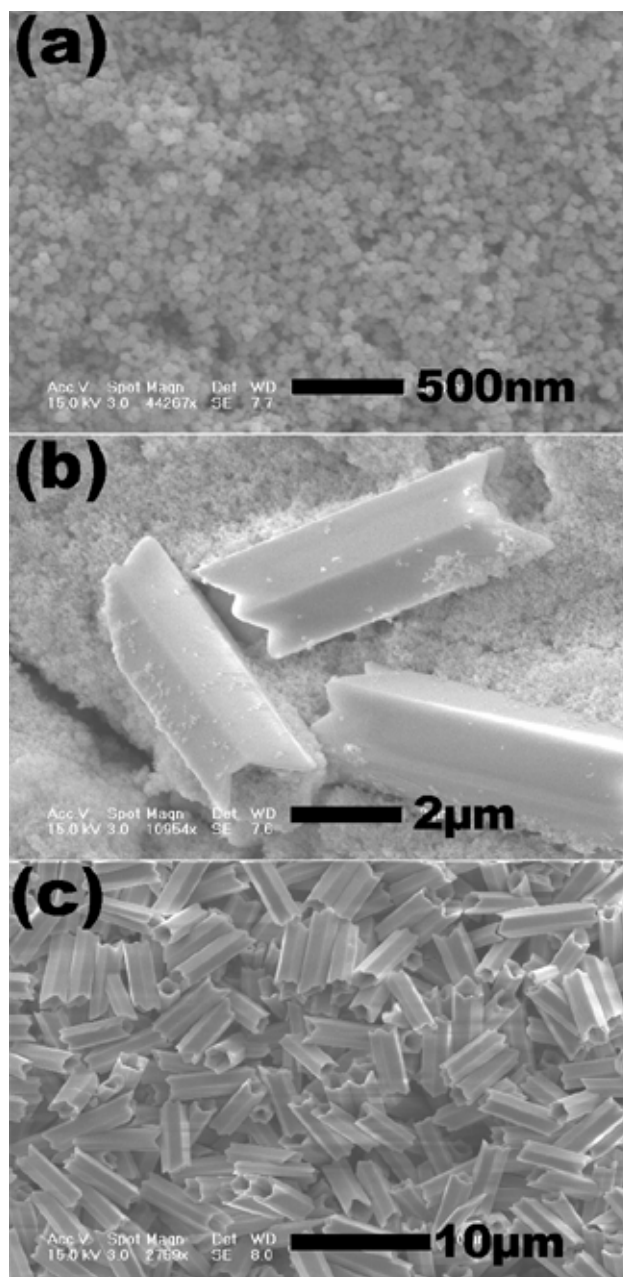
**Fig. S4** SEM images of  $\beta$ -NaYbF<sub>4</sub> in the absence of Cit<sup>3-</sup> and other conditions are similar to those preparing **P2**.



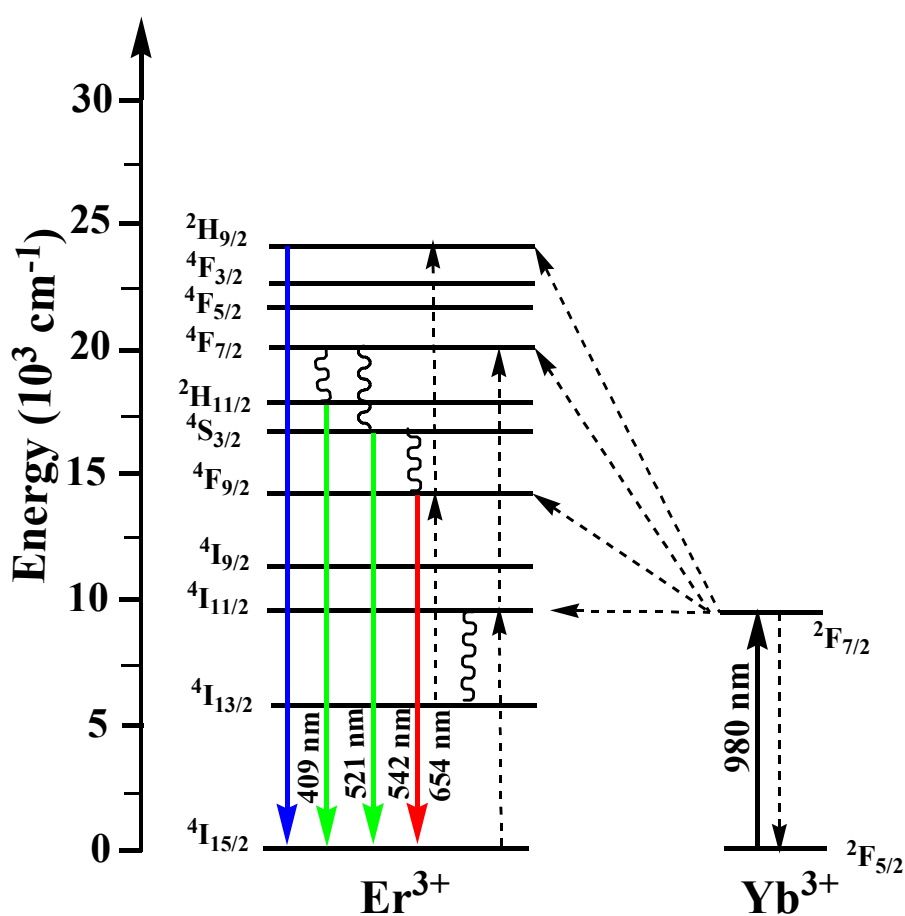
**Fig. S5** SEM images of  $\text{YbF}_3$  in the absence of  $\text{Cit}^{3-}$  and other conditions are similar to those preparing **P7**.



**Fig. S6** XRD patterns of the as-prepared NaYbF<sub>4</sub> samples at 180 °C for different periods of the reaction time of (a) 1 h; (b) 6.5 h; (c) 7.5 h using NaBF<sub>4</sub> as fluoride source. These samples were prepared under the similar conditions for synthesizing P9.



**Fig. S7** SEM images of the as-prepared samples using NaBF<sub>4</sub> as fluoride source at 180 °C for different periods of the reaction time of (a) 1 h; (b) 6.5 h; (c) 7.5 h, revealing the morphological evolution process of the  $\beta$ -NaYbF<sub>4</sub> microtubes. These samples were prepared under the similar conditions for synthesizing **P9**.



**Fig. S8** A scheme showing the energy-level and up-conversion luminescence process for  $\text{Er}^{3+}$  doped yttrium fluoride compounds. The full, dotted arrows, and curly lines represent emission, energy transfer, and multiphonon relaxation processes, respectively.