**Electronic Supplementary Information** 

## Hexagonal β-Na(Y,Yb)F<sub>4</sub> Based Core/Shell Nanorods: Epitaxial Growth, Enhanced and Tailored Up-conversion Emission

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**Fig. S1** XRD patterns of  $\alpha$ -NaYbF<sub>4</sub>: 0.02Er<sup>3+</sup> with different reaction time under 180 °C. The  $\alpha$ -NaYbF<sub>4</sub> is the isostructure to  $\alpha$ -NaYF<sub>4</sub> (JCPDS 06-0342). The standard pattern (JCPDS 27-1427) of  $\beta$ -NaYbF<sub>4</sub> is shown at the top for comparison.



Fig. S2 XRD patterns of samples Q1-Q5 after epitaxial growth. The standard patterns of  $\beta$ -NaYF<sub>4</sub> (JCPDS 16-0334) and  $\alpha$ -NaYF<sub>4</sub> (JCPDS 06-0342) are shown for comparison.



**Fig. S3** (a) XRD pattern of  $\beta$ -NaYbF<sub>4</sub>: 0.02Er<sup>3+</sup>. The standard pattern of  $\beta$ -NaYbF<sub>4</sub> (JCPDS 27-1427) is shown for comparison. (b) TEM of  $\beta$ -NaYbF<sub>4</sub>: 0.02Er<sup>3+</sup>.



Fig. S4 (a) XRD pattern of  $\alpha$ -NaYF<sub>4</sub>. The standard pattern of  $\alpha$ -NaYF<sub>4</sub> (JCPDS 06-0342) is shown for comparison. (b) TEM of  $\alpha$ -NaYF<sub>4</sub>.



**Fig. S5** XRD patterns of P samples. P0 is  $\beta$ -NaYF<sub>4</sub>: 0.20Yb<sup>3+</sup>, 0.02Ho<sup>3+</sup> core. The standard pattern of  $\beta$ -NaYF<sub>4</sub> (JCPDS 16-0334) is shown for comparison.



**Fig. S6** XRD patterns of R samples. R0 is  $\beta$ -NaYbF<sub>4</sub>: 0.02Er<sup>3+</sup> core. The standard patterns of  $\beta$ -NaYbF<sub>4</sub> (JCPDS 27-1427) and  $\beta$ -NaYF<sub>4</sub> (JCPDS 16-0334) are shown for comparison.



**Fig. S7** (a) Typical STEM in HAADF, (b) Element mapping of Yb, (c) Y and (d) Yb+ Y in the rod of P5.



**Fig. S8** (a) Typical STEM in HAADF, (b) Element mapping of Yb, (c) Y and (d) Yb+ Y in the rod of R5.