

## Supporting Information

### Enhanced upconversion luminescence and controllable phase/shape in NaYF<sub>4</sub>:Yb/Er crystals through Cu<sup>2+</sup> ions doping

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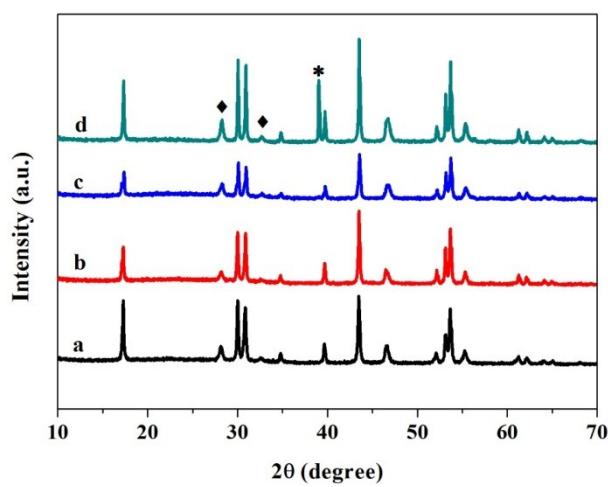
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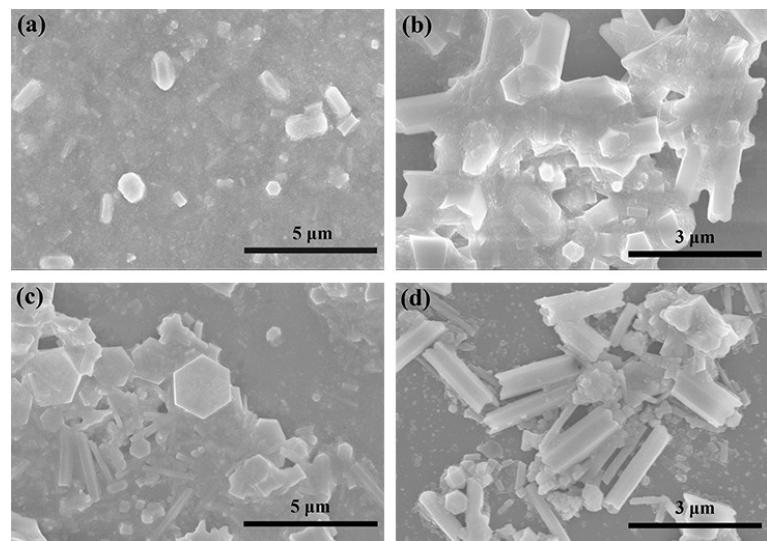
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**Table S1** Nominal ratio and ICP-OES results of cation mole ratios in the products

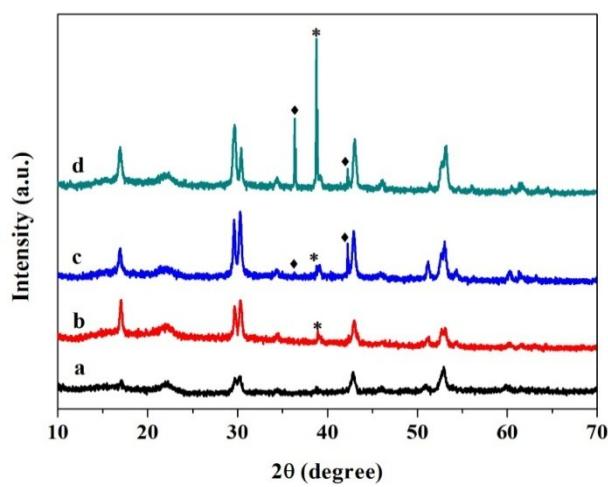
NaYF <sub>4</sub> :X%Cu/18%Yb/2%Er	Na: Y: Yb: Er: Cu	
	Nominal ratio	ICP-OES result
X=0	1.000: 0.800: 0.180: 0.020	0.876: 0.837: 0.146: 0.017
X=20	1.000: 0.600: 0.180: 0.020: 0.200	1.194: 0.766: 0.189: 0.025: 0.020
X=35	1.000: 0.450: 0.180: 0.020: 0.350	1.107: 0.638: 0.277: 0.035: 0.049
X=40	1.000: 0.400: 0.180: 0.020: 0.400	1.011: 0.711: 0.202: 0.025: 0.062
X=60	1.000: 0.200: 0.180: 0.020: 0.600	0.869: 0.671: 0.180: 0.022: 0.127



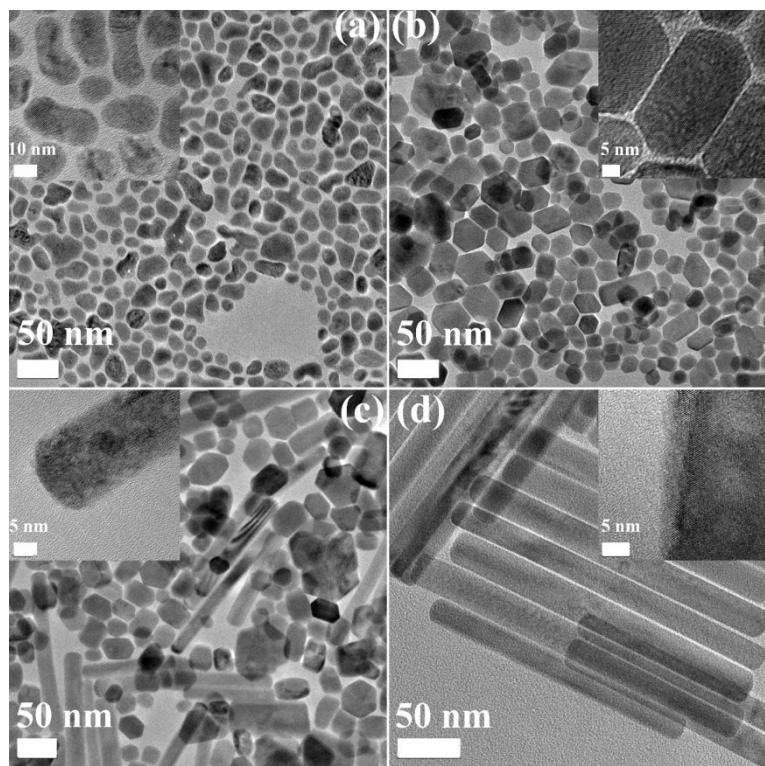
**Fig. S1** XRD patterns of  $\text{NaYF}_4:\text{Yb}/\text{Er}$  crystals with various  $\text{F}^-/\text{RE}^{3+}$  ratio of 4:1, 5:1, 6.67:1, 10:1 (curves a–d), some diffraction peaks of the cubic phase are marked with ◆; The peaks marked by an asterisk (\*) arise from excessive cubic  $\text{NaF}$ .



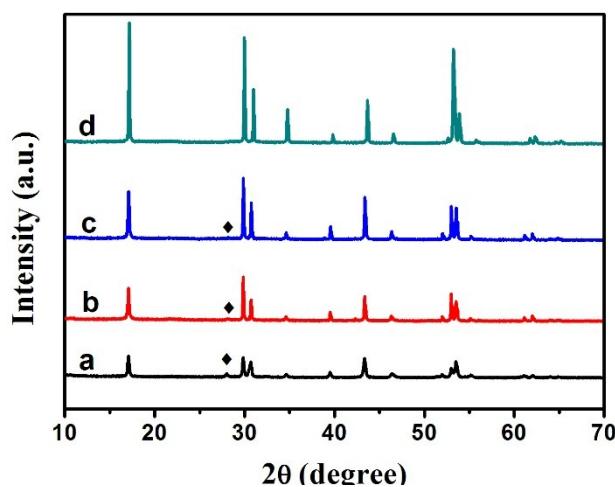
**Fig. S2** The typical SEM images of NaYF<sub>4</sub>:Yb/Er crystals with various F<sup>-</sup>/RE<sup>3+</sup> ratio of (a) 4:1, (b) 5:1, (c) 6.67:1, (d) 10:1.



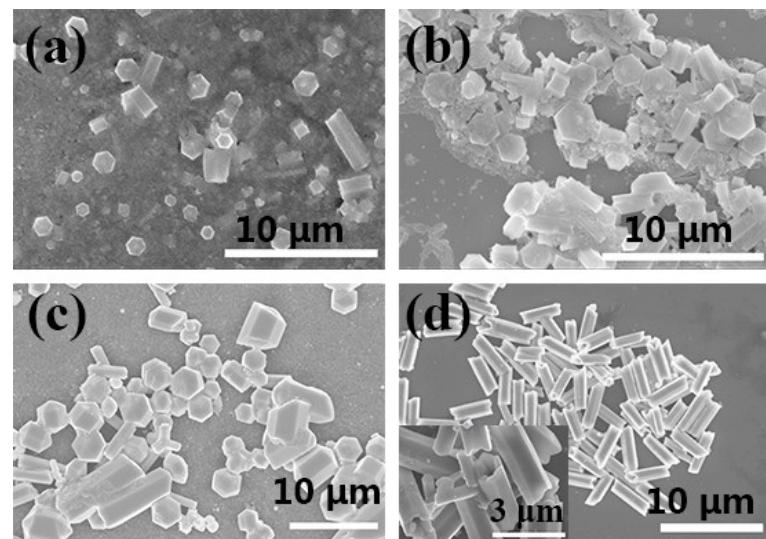
**Fig. S3** XRD patterns of  $\text{NaGdF}_4:\text{Yb}/\text{Er}$  crystals co-doped with  $\text{Cu}^{2+}$  ions at various concentrations of 0, 20, 40 and 60 mol% (curves a–d). The peaks marked by an asterisk (\*) arise from excessive cubic  $\text{NaF}$ .



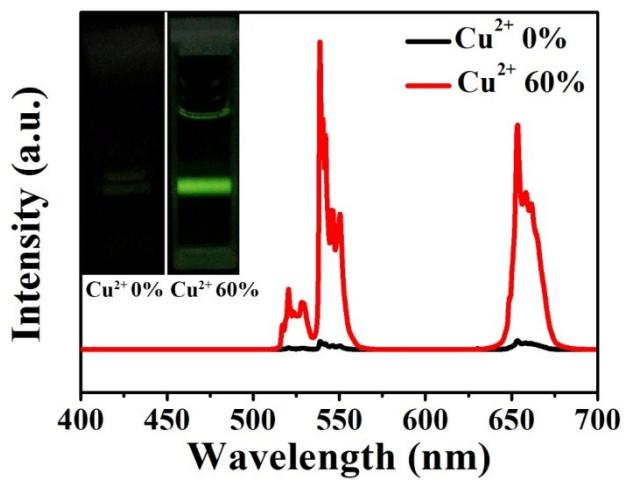
**Fig. S4** Typical TEM images of  $\text{NaGdF}_4\text{:Yb/Er/Cu}$  crystals. (a) 0 mol%  $\text{Cu}^{2+}$  ion, (b) 20 mol%  $\text{Cu}^{2+}$  ions, (c) 40 mol%  $\text{Cu}^{2+}$  ions, (d) 60 mol%  $\text{Cu}^{2+}$  ions, insets show the corresponding HRTEM images.



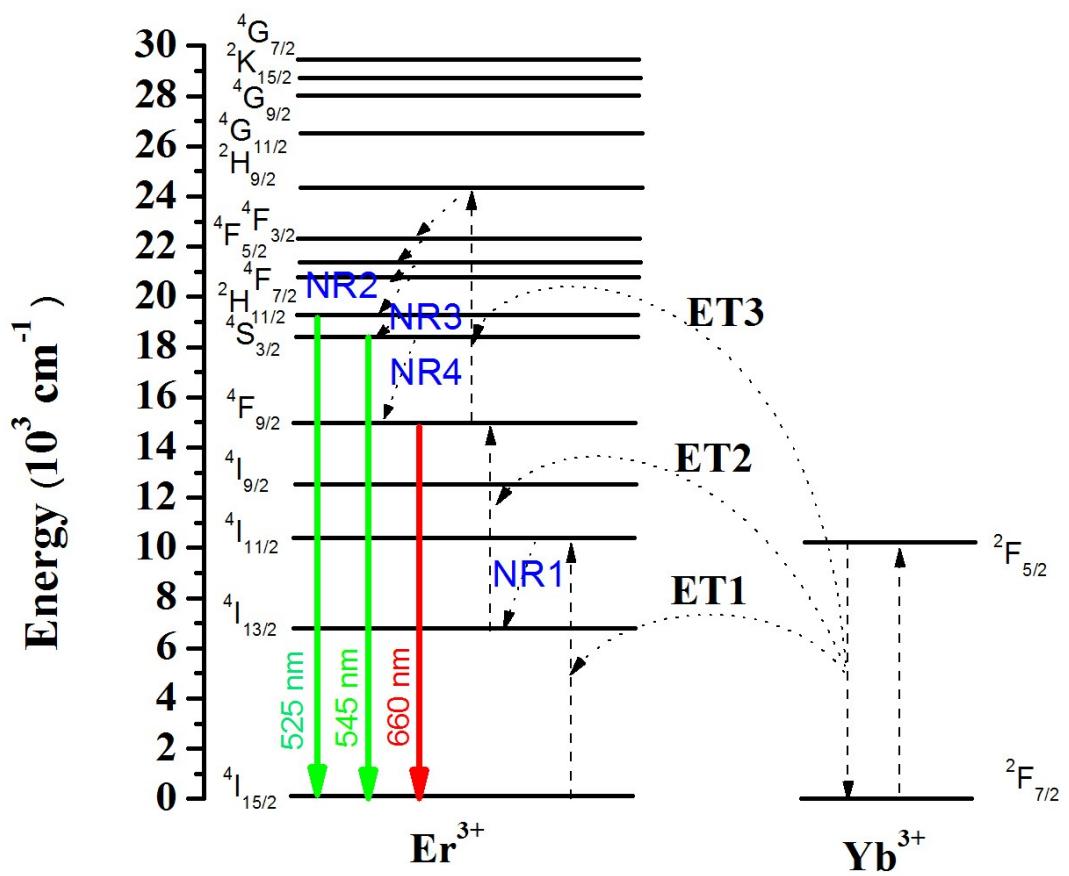
**Fig. S5** XRD patterns of  $\text{NaLuF}_4:\text{Yb}/\text{Er}$  crystals co-doped with  $\text{Cu}^{2+}$  ions at various concentrations of 0, 20, 40 and 60 mol% (curves a–d). Some diffraction peaks of the cubic phase are marked with ◆.



**Fig. S6** Typical SEM images of  $\text{NaLuF}_4\text{:Yb/Er/Cu}$  crystals. (a) 0 mol%  $\text{Cu}^{2+}$  ion, (b) 20 mol%  $\text{Cu}^{2+}$  ions, (c) 40 mol%  $\text{Cu}^{2+}$  ions, (d) 60 mol%  $\text{Cu}^{2+}$  ions, insets show the corresponding enlarged morphology of the crystal.



**Fig. S7** Room temperature upconversion emission spectra of  $\text{NaYF}_4:\text{Yb}/\text{Er}$  crystals with 0 and 60 mol%  $\text{Cu}^{2+}$  dopant ions ( $0.14 \text{ W/mm}^2$ ). Inset: luminescence photographs of the corresponding samples dispersed in cyclohexane (1 mg/mL,  $0.71 \text{ W/mm}^2$ ).



**Fig. S8** Energy level diagrams of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions, showing possible energy transfer mechanisms for red and green UC emissions of  $\text{Er}^{3+}$  activators in the host.