Supporting information

Core-shell-shell heterostructures of α-NaLuF₄:Yb/Er@NaLuF₄:Yb@MF₂ (M = Ca, Sr, Ba) with remarkably enhanced upconversion luminescence

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Supplementary Experimental Section

Synthesis of cubic and hexagonal NaLuF$_4$:Yb/Er mixture

The mixture of cubic and hexagonal NaLuF$_4$:Yb/Er was employed as control groups. The synthesis process of these control groups is basically identical with that of pure cubic NaLuF$_4$:Yb/Er demonstrated in the manuscript, except the amount of NaOH and NH$_4$F were changed. Two control samples were made in this work, which were distinguished by the added amount of NaOH and NH$_4$F. The first sample was injected with an excess amount of NaOH and NH$_4$F (the molar ratio of NH$_4$F/NaOH was 4:2.5, NH$_4$F = 0.1851 g, NaOH = 0.125 g), the molar ratio of Na$^+$/RE$^{3+}$ was 3.125 (RE$^{3+}$ = Lu$^{3+}$ + Yb$^{3+}$ + Er$^{3+}$). This sample was named as CG1. The second sample was injected with a normal stoichiometric amount of NaOH and NH$_4$F (the molar ratio of NH$_4$F/NaOH was 4:2.5, NH$_4$F = 0.1481 g, NaOH = 0.1 g), the molar ratio of Na$^+$/RE$^{3+}$ was 2.5 (RE$^{3+}$ = Lu$^{3+}$ + Yb$^{3+}$ + Er$^{3+}$). This sample was named as CG2.
Fig. S1 XRD patterns of CG1 (Na⁺/RE³⁺ = 3.125), CG2 (Na⁺/RE³⁺ = 2.5), and S1 (Na⁺/RE³⁺ = 1.875) samples. The black vertical lines lay at the bottom are pure hexagonal phase NaLuF₄ card, and at the top are pure cubic phase NaLuF₄ card.
Fig. S2 TEM images of (a) S1 and (b) S2. The scale bars are 20 nm in (a) and (b).
Fig. S3 HAADF-STEM images of S3 (a), S4 (b), S5 (c). EDX element mapping images of Ca (d) and Lu (g) for S3, Sr (e) and Lu (h) for S4, Ba (f) and Lu (i) for S5, all the EDX element mapping images are in the same area with HAADF-STEM images. Quantitative EDX element distributions of Lu and Ca along the red line in (a) for S3 (j), Lu and Sr along the red line in (b) for S4 (k), Lu and Ba along the red line in (c) for S5 (l). The scale bars in (b), (e), (h) are 10 nm, while the rest are 20 nm.
Fig. S4  Size distributions of (a) S1, (b) S2, (c) S3, (d) S4, and (e) S5.
Fig. S5 UCL spectrum of $\alpha$-NaLuF$_4$:Yb/Er.