Electronic Supplementary Information

Revealing the in-situ NaF generation balance for user-friendly control synthesis of sub-10 nm monodisperse low level Gd^{3+} doped β-$NaYbF_4$:Er

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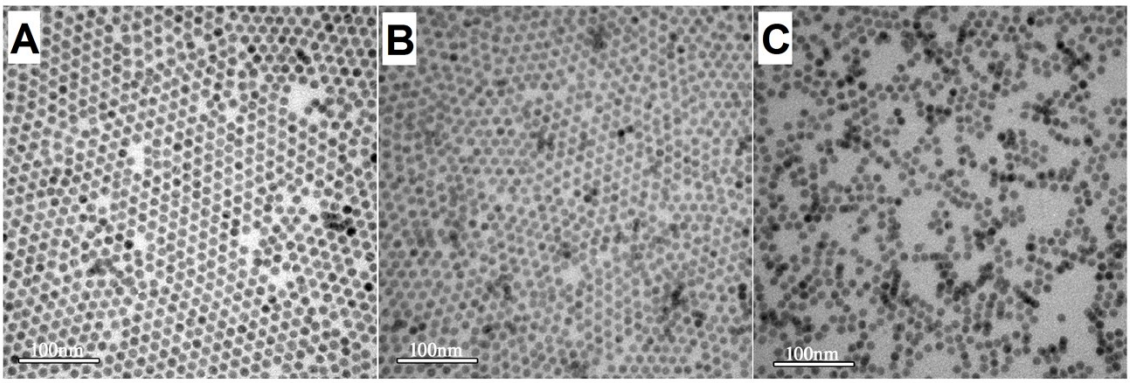

Figure S1. TEM images of β-$NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy with respective NH_4F/RE ratio of 4.25:1 (A), 4.75:1 (B) and 5:1 (C). All the NC growth reactions were performed at 300 °C for 20 min.

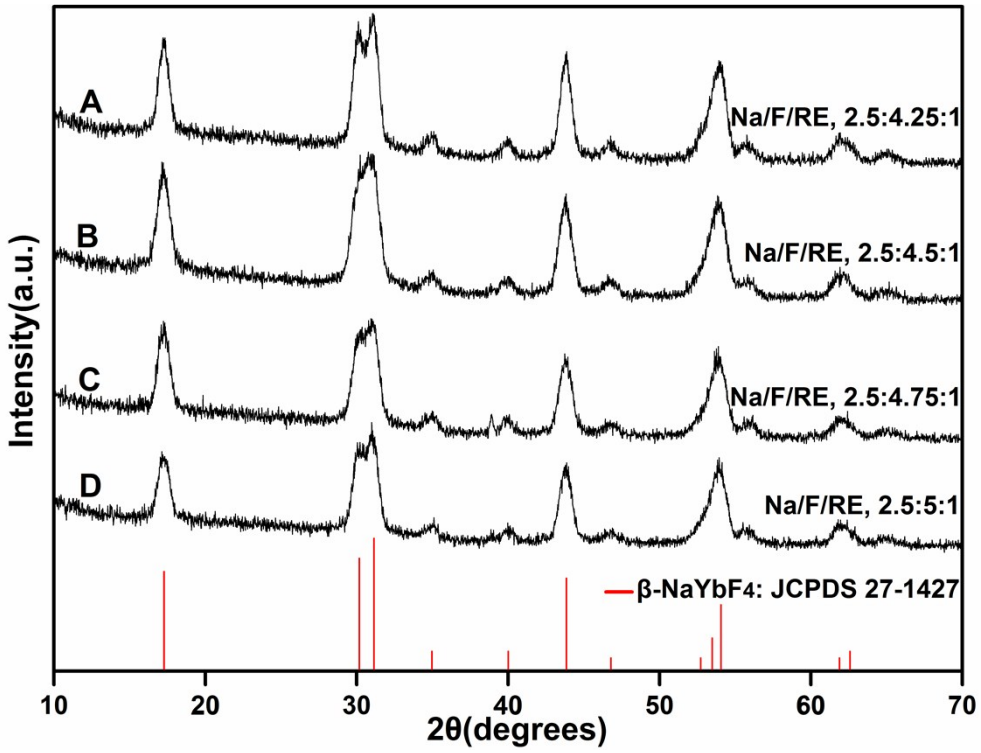

Figure S2. XRD patterns of $NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy but different Na/F/RE ratios. All the NC growth reactions were performed at 300 °C for 20 min.

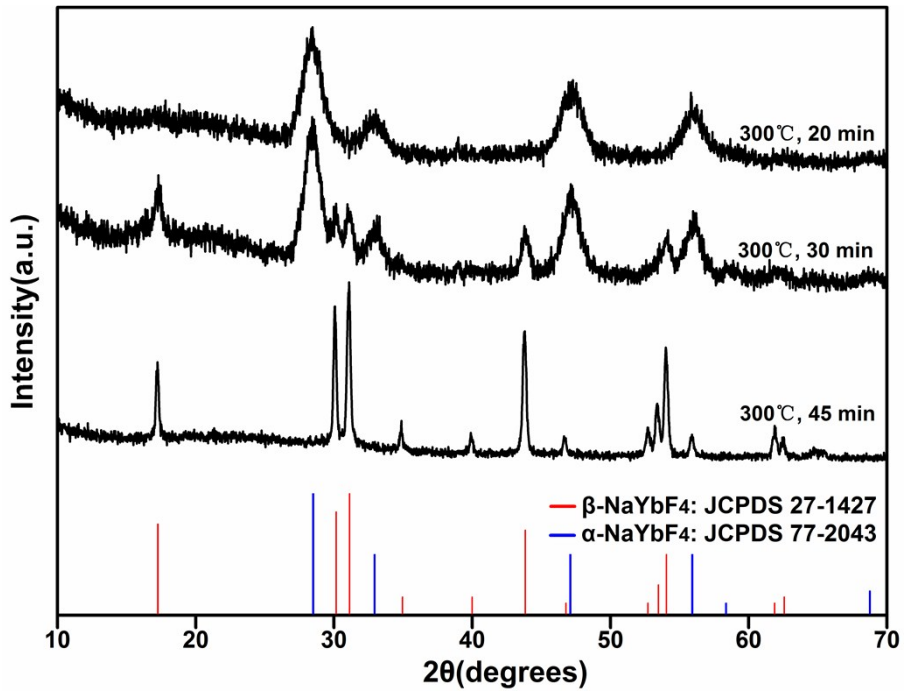

Figure S3. XRD patterns of $NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy at the NaOA/NH_4F/RE ratio of 2.5:6:1 and different reaction times.

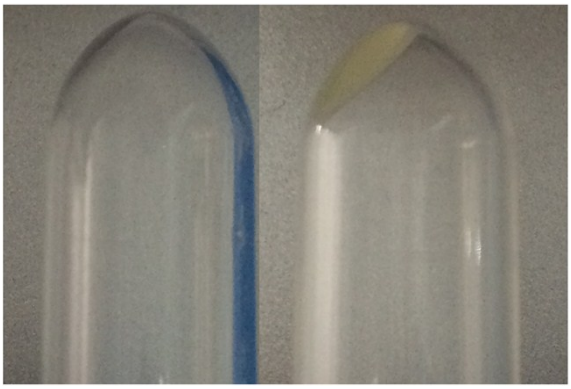

Figure S4. Digital photo of the collected precipitate *via* direct centrifugation for the optimized NH_4F/RE ratio (4.5:1)-based solvothermal system (left) and the high NH_4F/RE ratio (6:1)-based solvothermal system (right). Both reactions were performed according to NaOA-based solvothermal strategy and were stopped after reacting at 160 °C for 0 min.

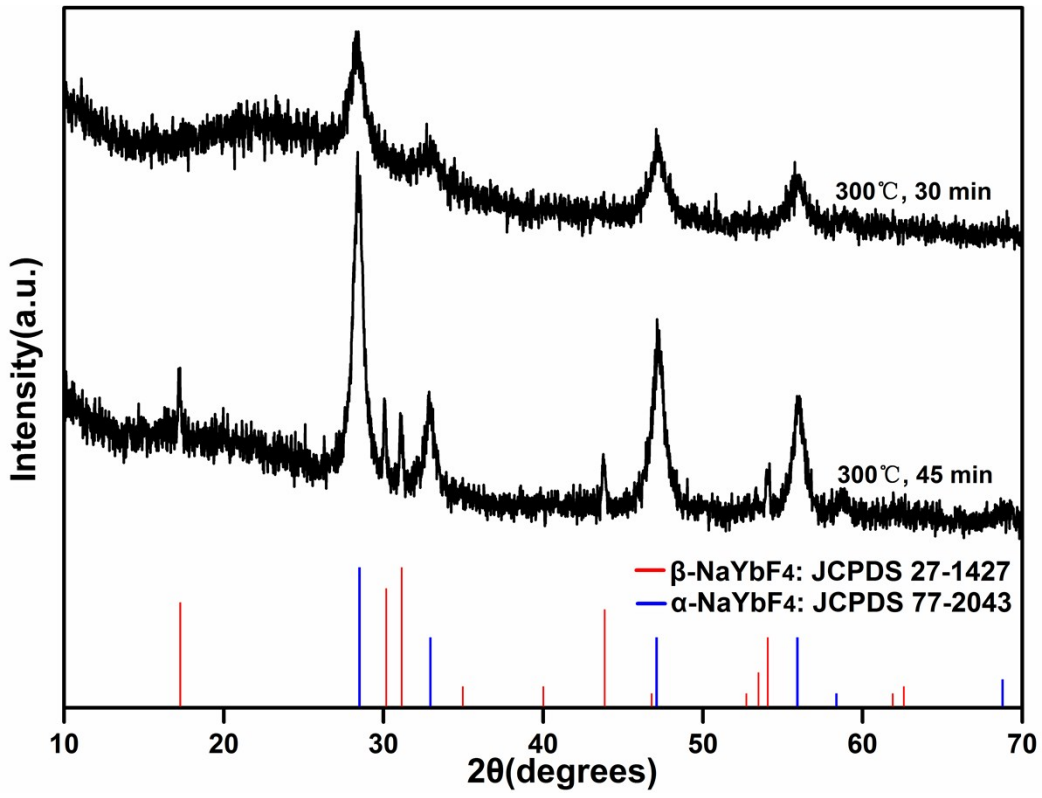

Figure S5. XRD patterns of $NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy at the NaOA/NH_4F/RE ratio of 2.5:3.5:1 and different reaction time. The results showed pure β-$NaYbF_4$:Er could not be achieved even after reacting at 300 °C for 45 min by using such fluoride-deficient solvothermal environment.

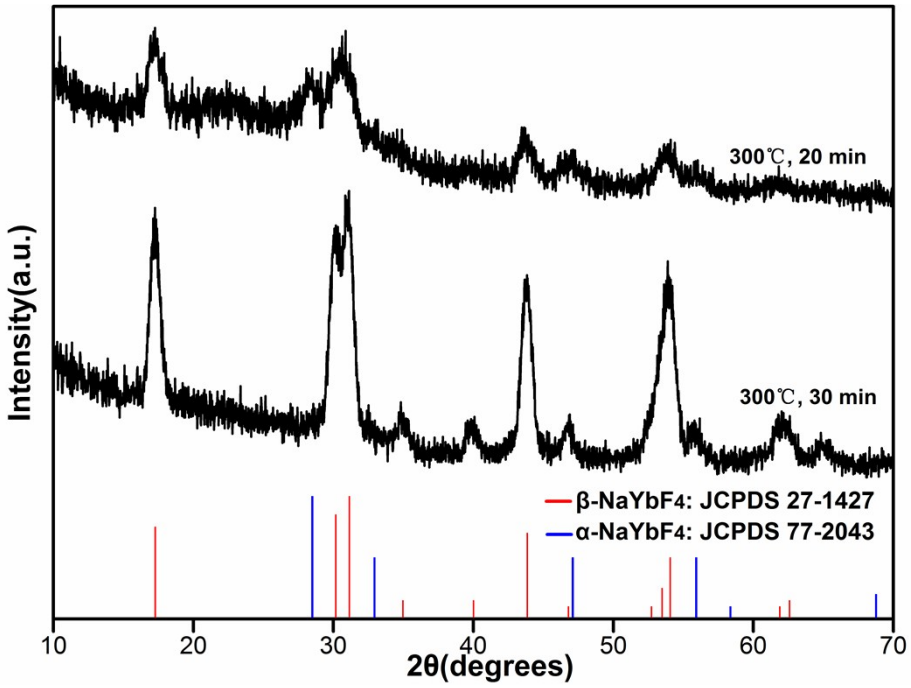

Figure S6. XRD patterns of $NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy at the NaOA/NH_4F/RE ratio of 1.9:4.5:1 and different reaction times.

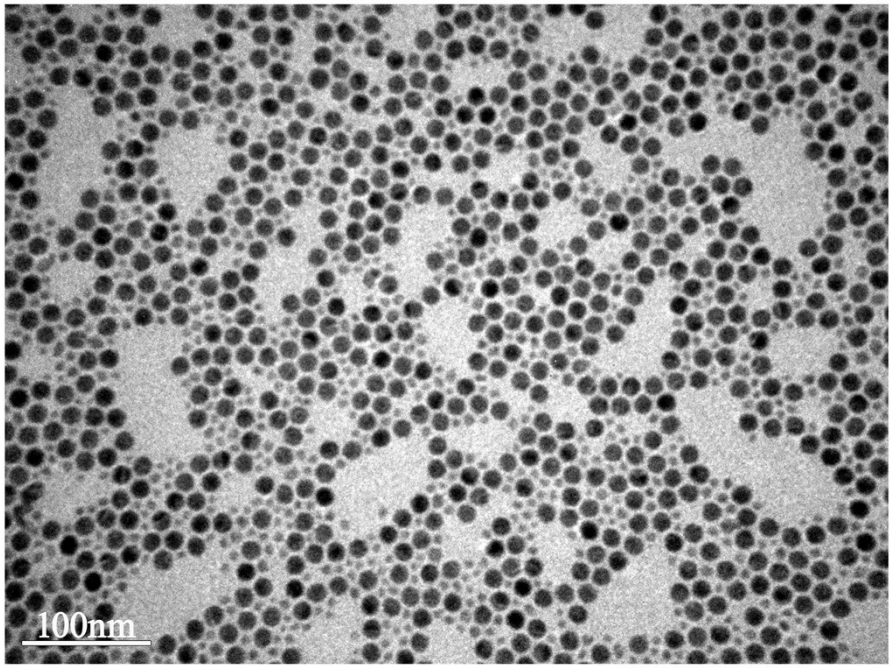

Figure S7. TEM image of $NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy at the NaOA/NH_4F/RE ratio of 1.5:4.5:1. The NC growth reaction were performed at 300 °C for 30 min. Narrowly size distributed β-$NaYbF_4$:Er can be observed in the TEM image, while there is also a large number of small-sized NCs, indicating the α-to-β transition is still not finished completely.

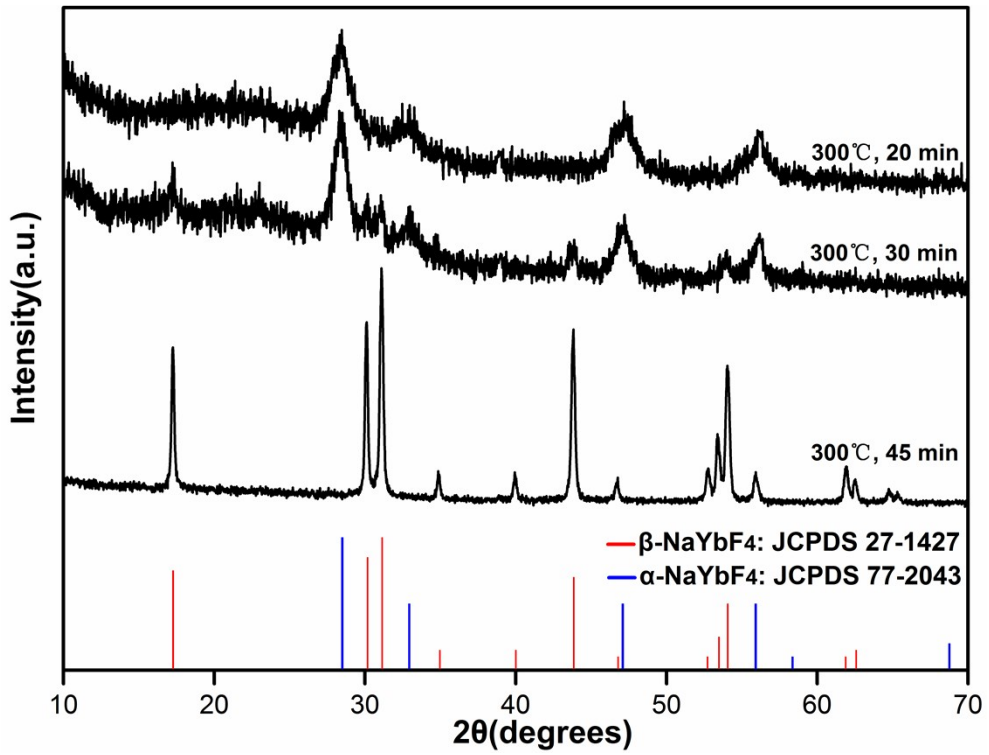

Figure S8. XRD patterns of $NaYbF_4$:Er prepared by using NaOA-based solvothermal strategy at the NaOA/NH_4F/RE ratio of 3:6:1 and different reaction times.

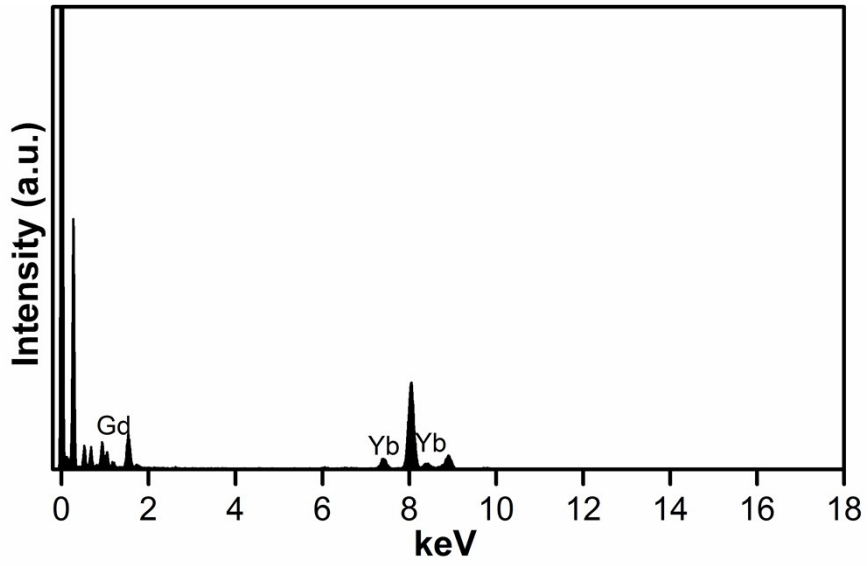

Figure S9. EDXA spectrum of the monodisperse 5.5 nm β-$NaYbF_4$:Gd/Er(10/2%) prepared by reacting at 300 °C for 15 min.

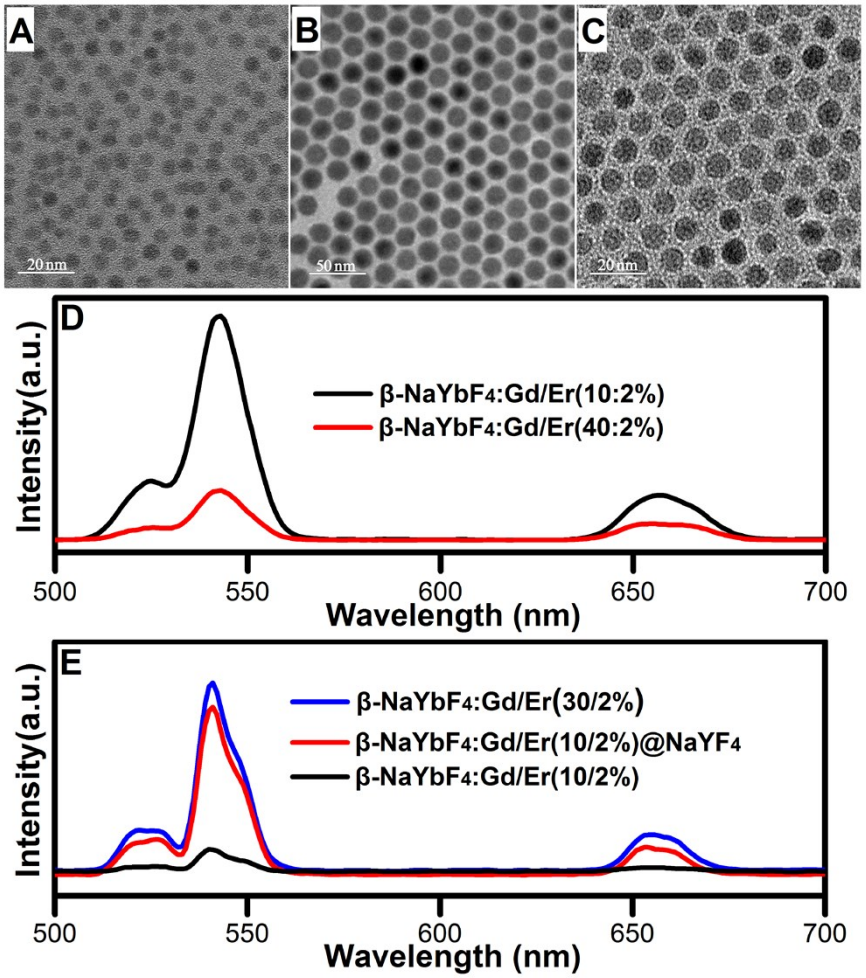

Figure S10. TEM images: (A) β-$NaYbF_4$:Gd/Er (40:2%) prepared by using the NaOA-based solvothermal strategy and the same synthesis procedures to those of the 5.5 nm β-$NaYbF_4$:Gd/Er (10/2%); (B) Large-sized β-$NaYbF_4$:Gd/Er(30:2%) prepared according to the literature; [1] (C) Core/shell-structured β-$NaYbF_4$:Gd/Er (10:2%)@$NaYF_4$. (D) Upconversion luminescence spectra of the β-$NaYbF_4$:Gd/Er (40/2%) sample shown in Figure S10A and 5.5 nm β-$NaYbF_4$:Gd/Er (10/2%) under 980 nm excitation (20 W cm^{-2}). (E) Upconversion luminescence spectra of the β-$NaYbF_4$:Gd/Er (30:2%) sample shown in Figure S10B, core/shell-structured β-$NaYbF_4$:Gd/Er (10:2%)@$NaYF_4$ sample shown in Figure S10C and the 5.5 nm β-$NaYbF_4$:Gd/Er (10/2%) under 980 nm excitation (10 W cm^{-2}). The samples used for upconversion luminescence spectra measurements were dispersed in cyclohexane.

References

1 Y. L. Liu, K. L. Ai, J. H. Liu, Q. H. Yuan, Y. Y. He and L. H. Lu, *Angew. Chem., Int. Ed.*, 2012, **51**, 1437−1442.