Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Dual-mode excitation β-$NaGdF_4$:Yb/Er@β-$NaGdF_4$:Yb/Nd core shell nanoparticles with NIR-II emission and 5 nm core: controlled synthesis and growth mechanism by NaF/RE regulation

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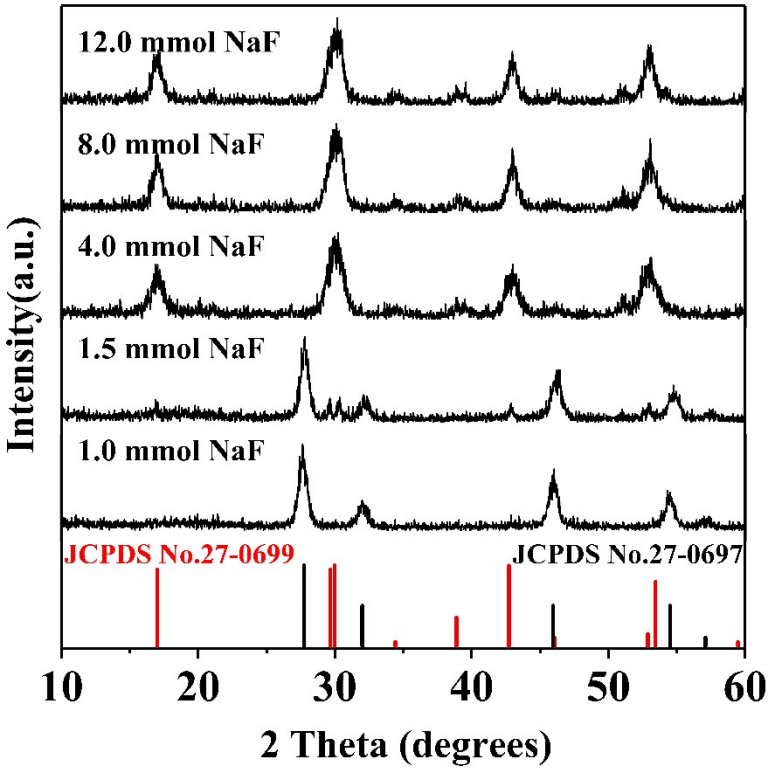


Figure. S1 XRD patterns of $NaGdF_4$:Yb/Er NPs synthesized under different molar ratio of NaF/RE, in 15 mL ODE, 15 mL OA, at 300 °C for 1 h.

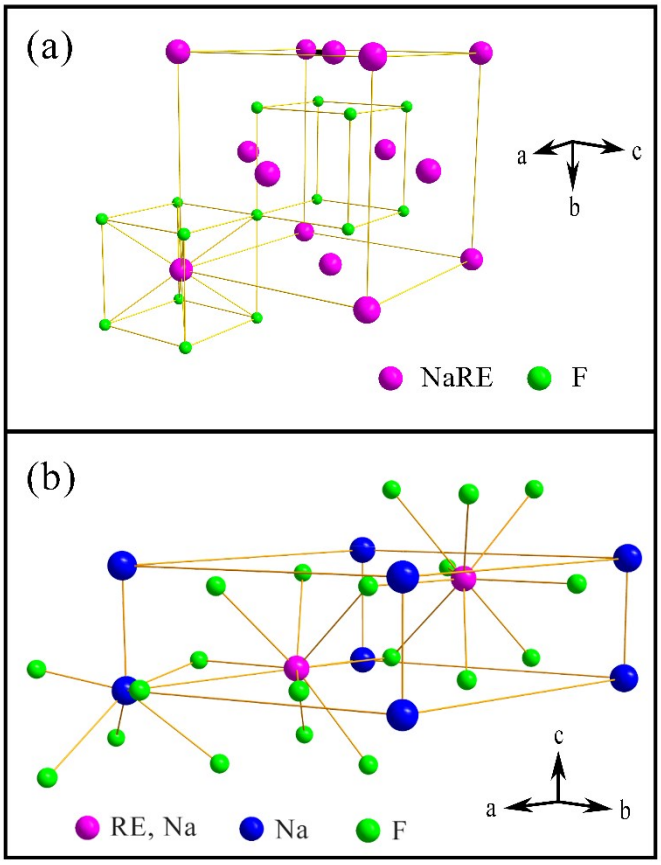


Figure. S2 Schematic presentation of (a) cubic phase and (b) hexagonal phase $NaREF_4$ structure. [S1]

Table S1 β-$NaGdF_4$ NPs synthesized under different reaction conditions and the corresponding particle size.

Samples	NaF/ RE	Reaction temperature	Reaction time	Particle size	Ref.
β-$NaGdF_4$:Yb/Er	4	290 °C	1 h	~ 5 nm	This work
β-$NaGdF_4$:Yb/Er	40.0	300 °C	1 h	~ 24 nm	[S2]
β-$NaGdF_4$:Yb/Tm	12.0	305 °C	1.5 h	~ 22 nm	[S3]
β-$NaGdF_4$:Yb/Tm	10.0	200 °C	12 h	＞100 nm	[S4]
β-$NaGdF_4$:Ce(Yb)/Ln	5.0	280 °C	10 h	20 ~ 25 nm	[S5]

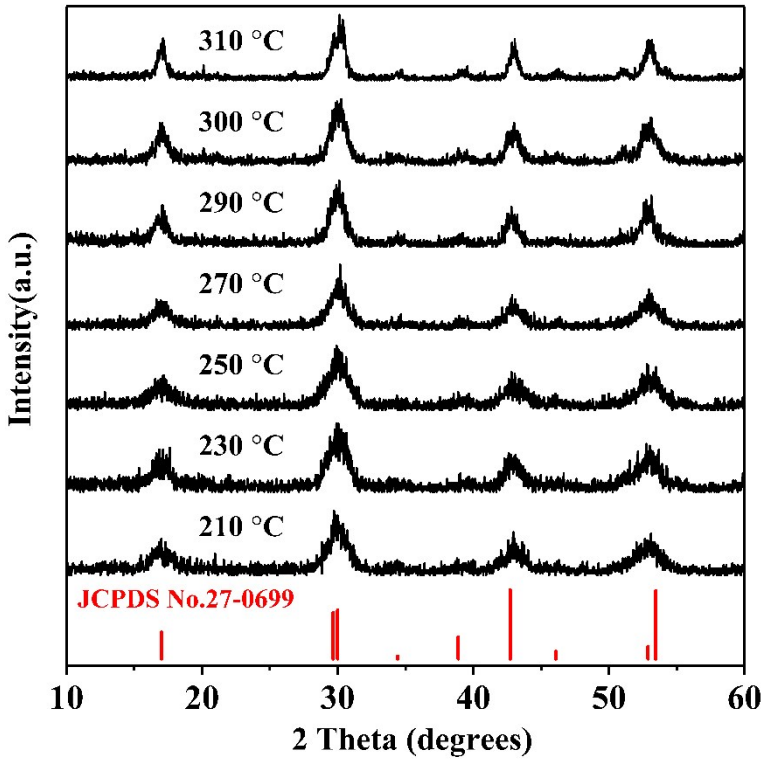


Figure. S3 XRD patterns of β-$NaGdF_4$:Yb/Er NPs synthesized under different reaction temperature with NaF/RE = 4, in 15 mL ODE, 15 mL OA, for 1 h.

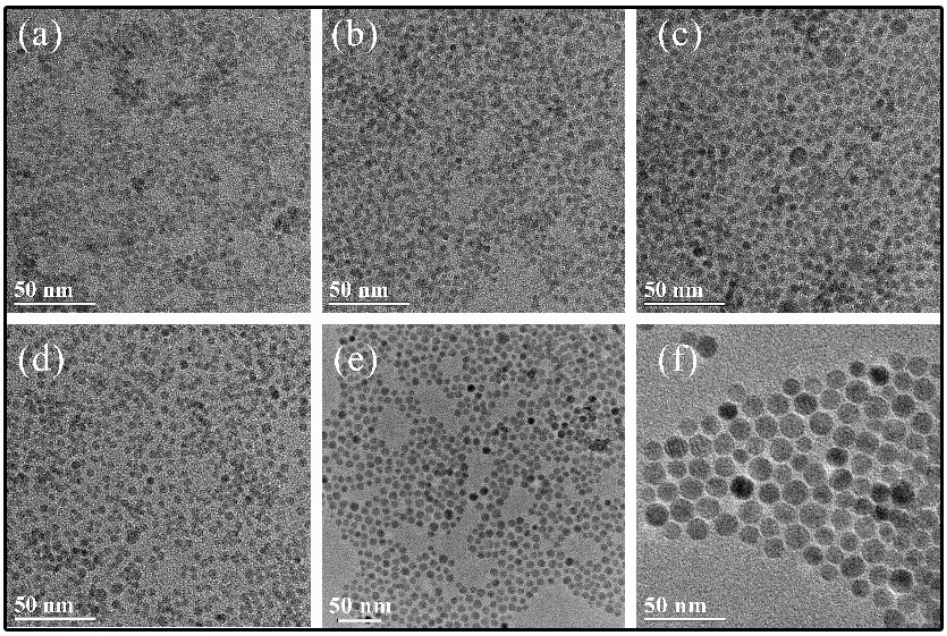


Figure. S4 TEM images of β-$NaGdF_4$: Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, for 1 h under different reaction temperature of (a) 210 °C, (b) 230 °C, (c) 250 °C, (d) 270 °C, (e) 300 °C; and (f) 310 °C for 20 min.

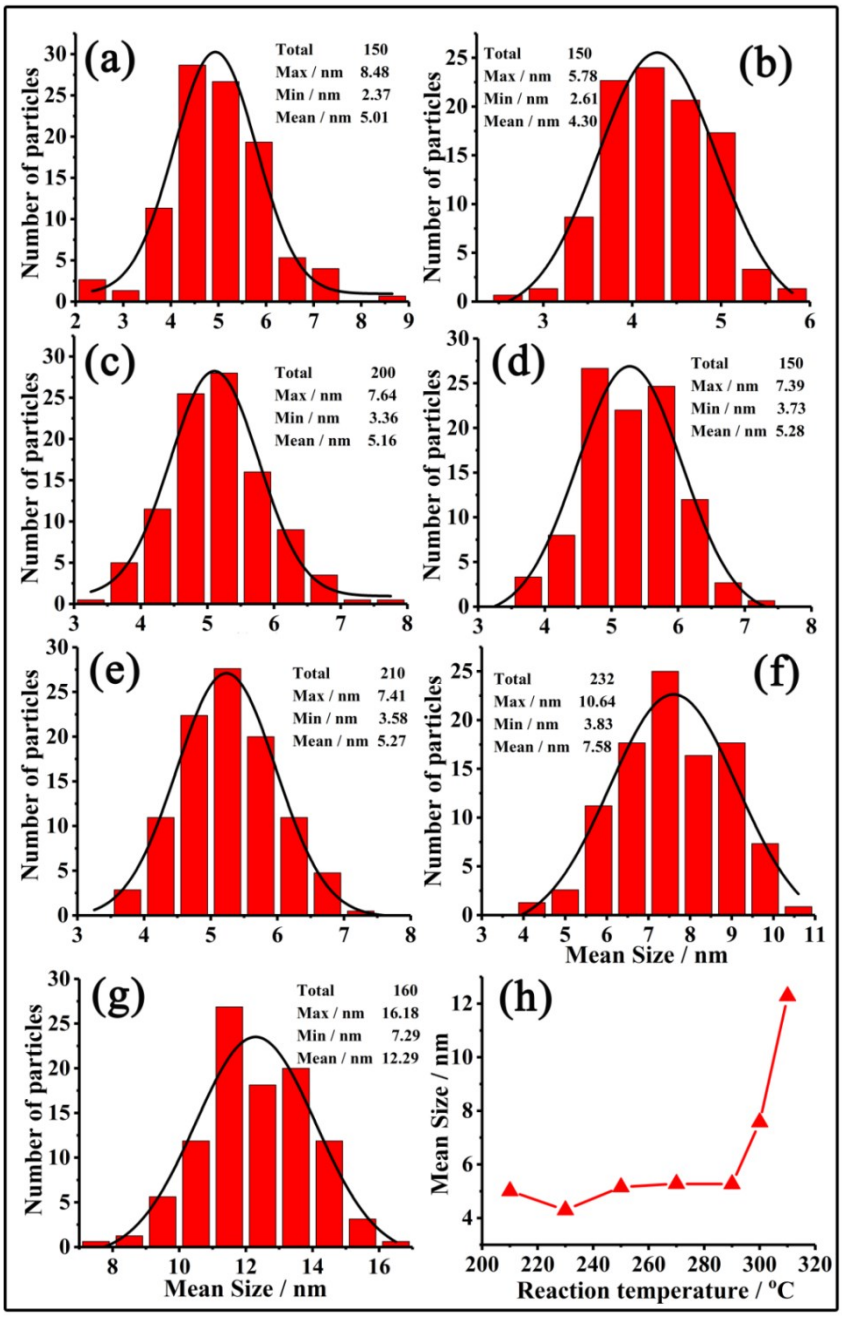


Figure. S5 Histogram of β-$NaGdF_4$:Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, for 1 h under different reaction temperature of (a) 210 °C, (b) 230 °C, (c) 250 °C, (d) 270 °C, (e) 290 °C, (f) 300 °C; (g) 310 °C for 20 min, and (h) the corresponding curve of the particle size changing with the reaction temperature.

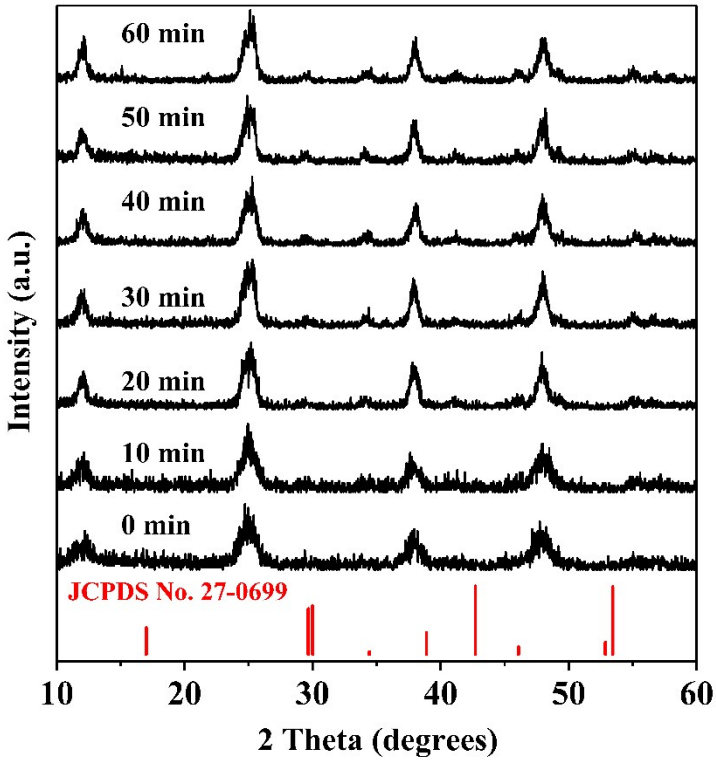


Figure. S6 XRD patterns of β-$NaGdF_4$:Yb/Er NPs synthesized under different reaction time with NaF/RE = 4, 15 mL ODE, 15 mL OA, at 310 °C.

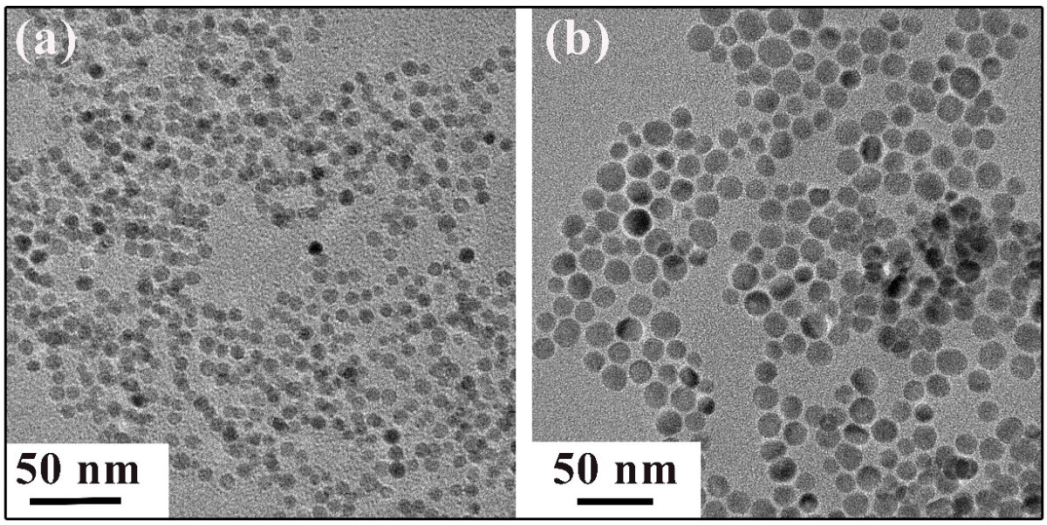


Figure. S7 TEM images of the β-$NaGdF_4$:Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, at 310 °C, for different reaction time of (a) 10 min, and (b) 30 min.

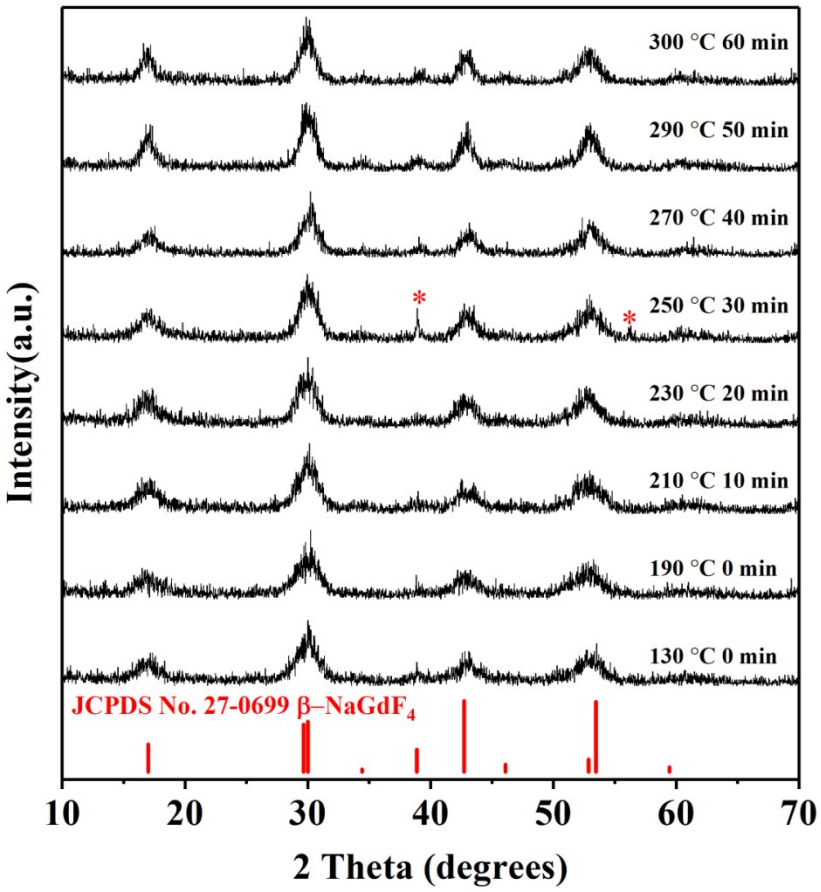


Figure. S8 XRD patterns of β-$NaGdF_4$:Yb/Er NPs synthesized under different reaction temperature and reaction temperature with NaF/RE = 4, in 15 mL ODE, 15 mL OA, at 300 °C for 1 h.

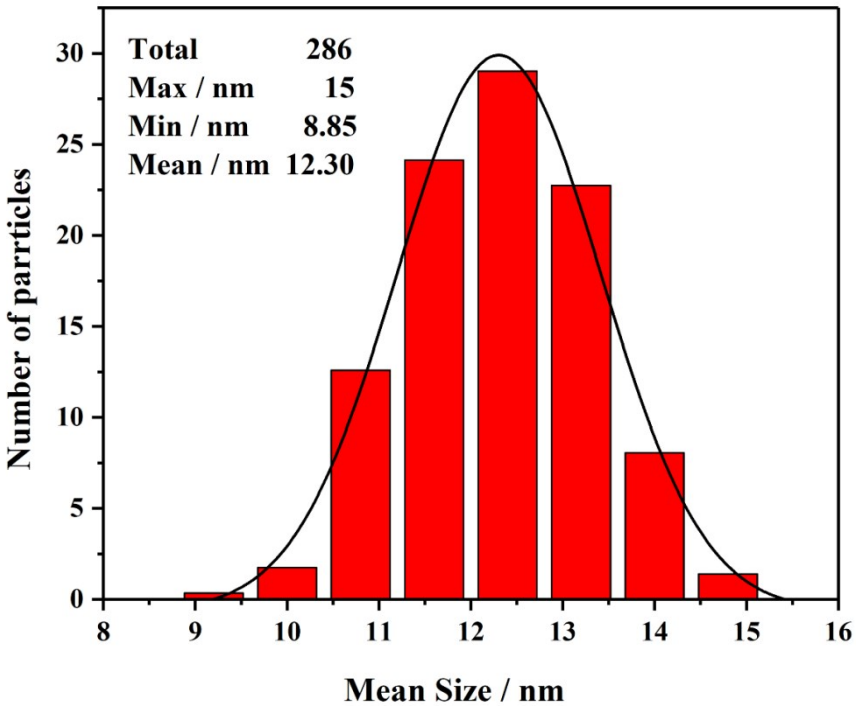


Figure. S9 Histogram of β-$NaGdF_4$:Yb/Er@β-$NaGdF_4$:Yb/Nd core shell NPs synthesized under 15 mL ODE, 15 mL OA at 310 °C for 30 min.

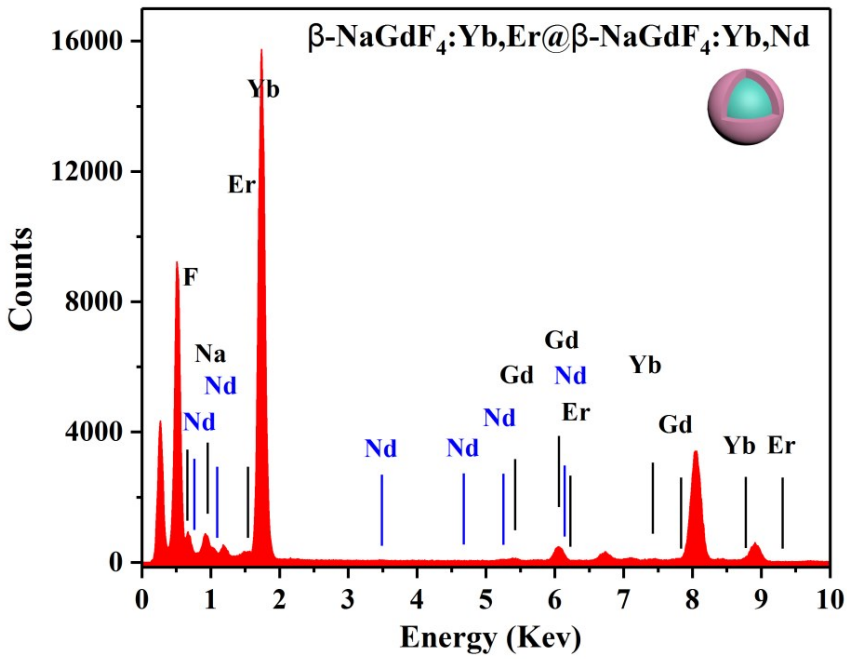


Figure. S10 EDS for the core shell NPs synthesized under 15 mL ODE, 15 mL OA, at 310 °C for 30 min (Inset: diagram of the core shell NPs).

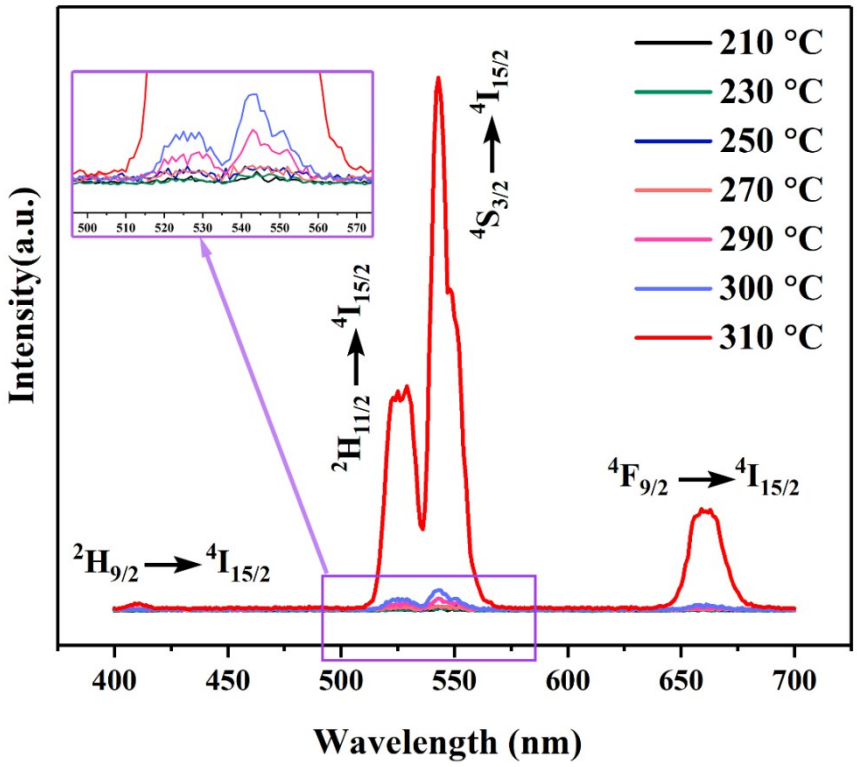


Figure. S11 Room-temperature emission spectra of β-$NaGdF_4$:Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, for 1 h, under different reaction temperature from 210 °C to 310 °C, at power density of 0.45 W cm^{-2}.

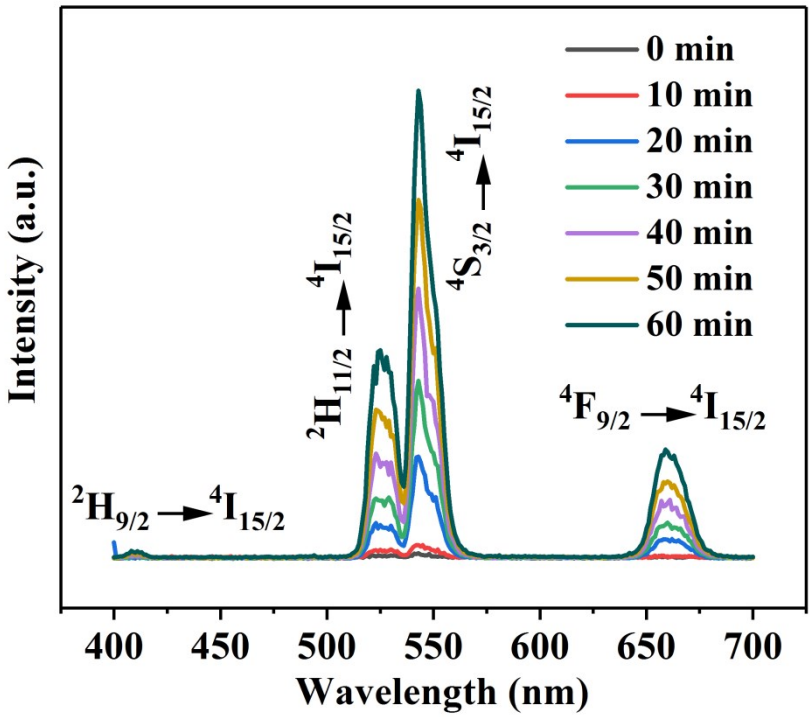


Figure. S12 Room-temperature emission spectra of β-$NaGdF_4$:Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, at 310 °C for different reaction time from 0 min to 60 min at power density of 0.45 W cm^{-2}.

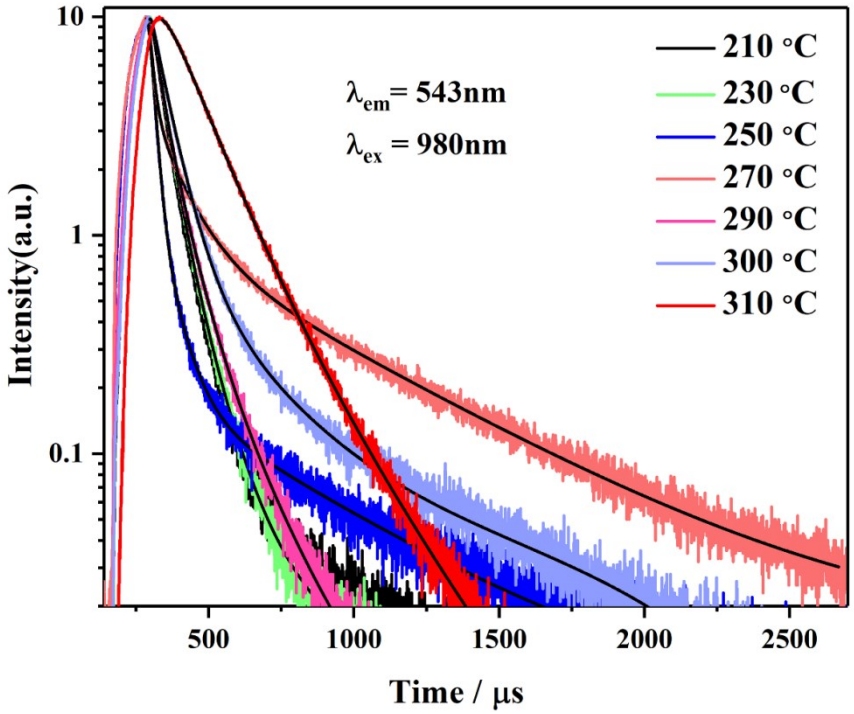


Figure. S13 Decay curve s at 543 nm ($^4S_{3/2}$ to $^4I_{15/2}$ transition of Er^{3+}) for β-$NaGdF_4$:Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, for 1 h, under different reaction temperature from 210 °C to 310 °C excited by 980 nm LD.

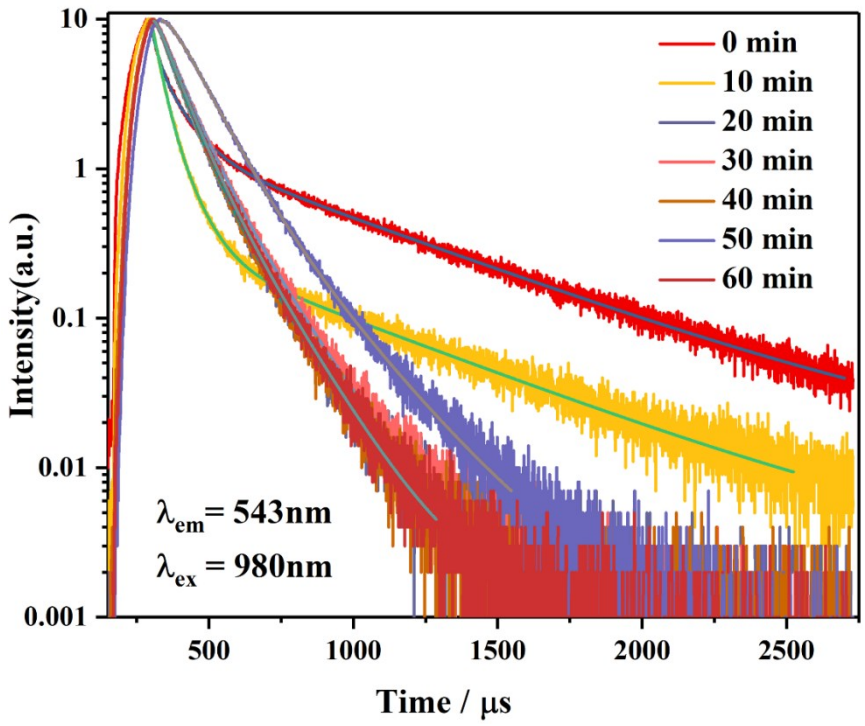


Figure. S14 Decay curves at 543 nm ($^4S_{3/2}$ to $^4I_{15/2}$ transition of Er^{3+}) for β-$NaGdF_4$:Yb/Er NPs synthesized under 15 mL ODE, 15 mL OA, NaF/RE = 4, at 310 °C for different reaction times from 0 min to 60 min excited by 980 nm LD.

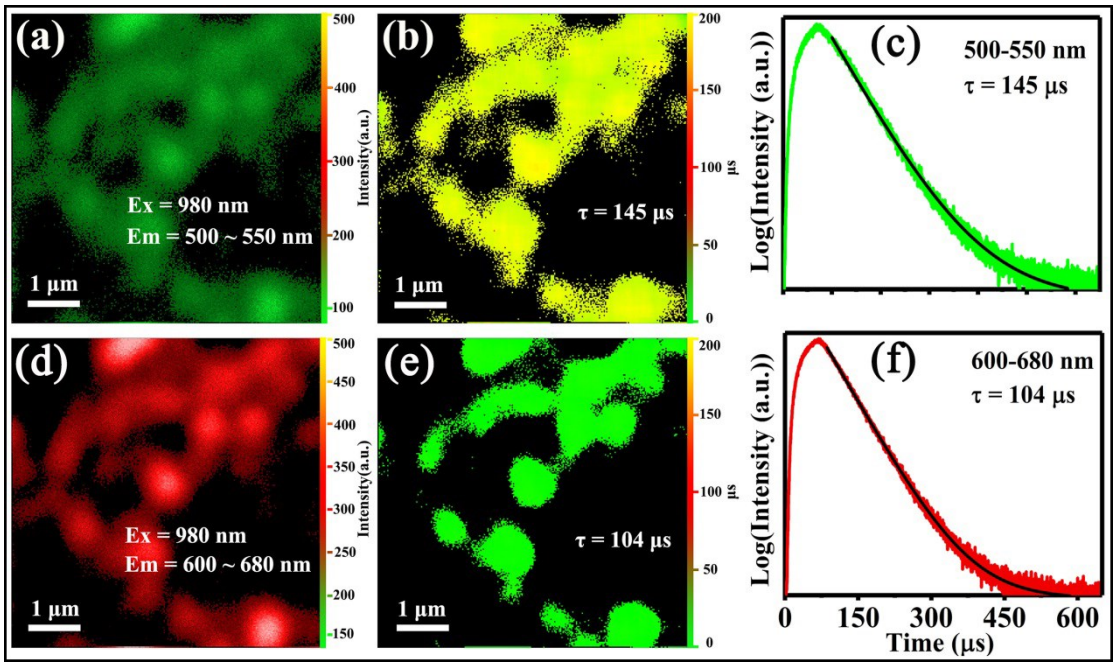


Figure. S15 (a, d) Emission intensity, (b, e) Lifetime imaging (c, f) luminescence decay curve of the core shell NPs at the green region (500-550 nm) and red region (600-680 nm) under 980 nm excitation.

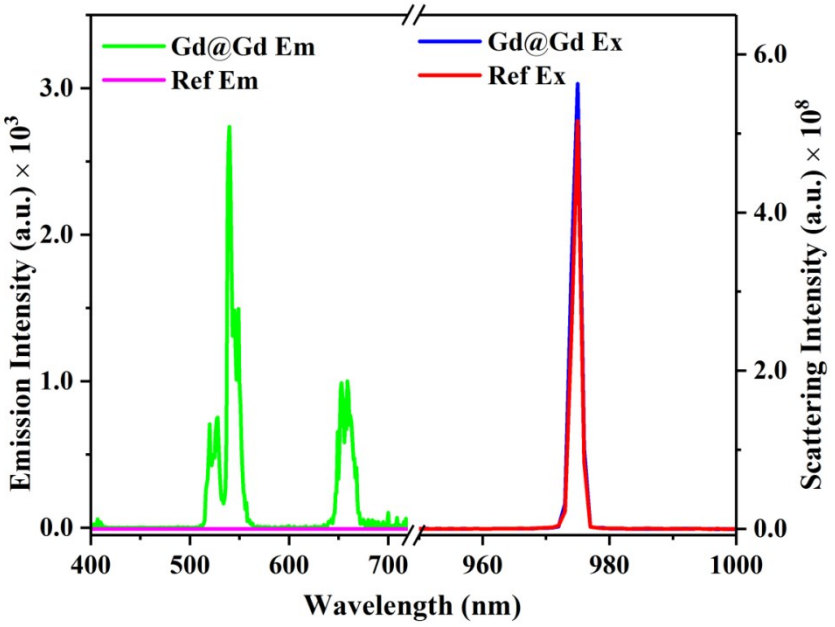


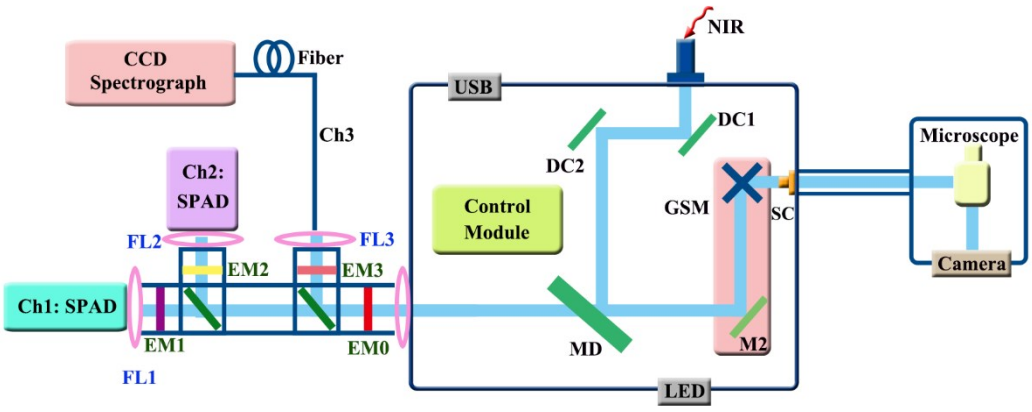
Figure. S16 UC emission (Em) and scattering (Ex) spectra of β-$NaGdF_4$:Yb/Er@β-$NaGdF_4$:Yb/Nd core shell NPs for illustration and reference (optically inert $NaGdF_4$) with a power density of 0.3 W cm^{-2}. Two optical attenuatuin filters (2.1 % and 0.9 % at 975 nm) were used to measure the scattering signal.

Table S2 Lifetime of different NPs with different particle size.

Samples	Particle size(nm)	Excitation wavelength(nm)	Lifetime(μs)	Ref.
Core shell	12.3	980 and 808	≈ 150	This work
β-$NaYF_4$:Yb/Er	50.0	808	140	[S6]
β-$NaYF_4$:Yb/Er	18.0	808	144	[S6]
β-$NaGdF_4$:Yb/Er@β-$NaGdF_4$	16.0	808	117	[S7]

Table S3 Absolute quantum yield of typical UCNPs.

Sample	Phase	Mean size (nm)	Power density (W/cm^2)	QY (%)	Ref.
$NaGdF_4$:Yb/Er@ $NaGdF_4$:Yb/Nd(powder)	Hexagonal	~ 13	0.3	0.03	This work
$NaGdF_4$:Yb/Er@ $NaGdF_4$(powder)	Hexagonal	16.0	25	2.6±1.4	[S7]
$NaGdF_4$:Yb/Er@ $NaGdF_4$(dispersion)	Hexagonal	16.0	25	0.11±0.02	[S7]



Scheme. S1 The ISS Q2 system for confocal microscopy imaging.

Scheme S1 shows the schematic diagram of the imaging system carried out on the ISS Q2 confocal laser scanning nanoscope. It was connected with a Nikon TiU microscope along with a Nikon water objective lens. The stage scanning (SC) is sufficient for many materials, and it is along with the piezo device to synchronize to the date acquisition unit of Fast FILM by ISS. In the Q2 system, near infrared ray (NIR) laser can enter through the laser input entry. When the 980 nm or the 808 nm lasers are used in the UC imaging, it was combined with the ISS laser launcher unit and was delivered to the Q2 system via the polarization maintain fiber optics. In Q2, the laser was combined by two dichroic mirrors (DC), DC1 and DC2 and then routed to the main dichroic mirror (MD). The MD reflects laser to the scanning mirrors to scan the sample and transmit the emission light to the detectors. In this study, 980 nm and 808 nm lasers were used for UC imaging, laser on or off can be modulated by TTL pulse train in frequency range of 1000 Hz, 5 % Duty Cycle. A 500-550 nm (green) and 600-680 nm (red) bandpass filter were used to collect date from the green and red spectral band. In this study, two detectors of SPCM-ARQH-14SPAD were used in channel 1 and channel 2, the third channel was used to measure the UC emission spectrum by attaching CCD spectrograph device via a 100 μm multimode fiber. Before each detector EM1, EM2, and EM3, an emission can be placed, emission filter before EM0 would work for all three detectors as shown in

Scheme S1. The samples were prepared as the following step: first prepare the UCNPs disperse in chloroform (0.1 mg/mL), then disperse one droplet of the UCNPs onto the cover-glass, then let it dry naturally. This characterization was performed in Analytical Instrumentation Center, at Peking University.

References

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