Supporting Information

Crystalline Phase-dependent Cations Migration in Core-shell Lanthanide-doped Upconversion Nanoparticles

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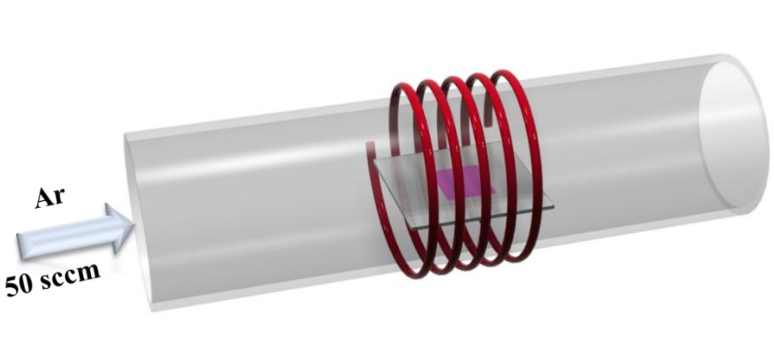

Figure S1. Schematic illustration of the UCNPs films annealing.

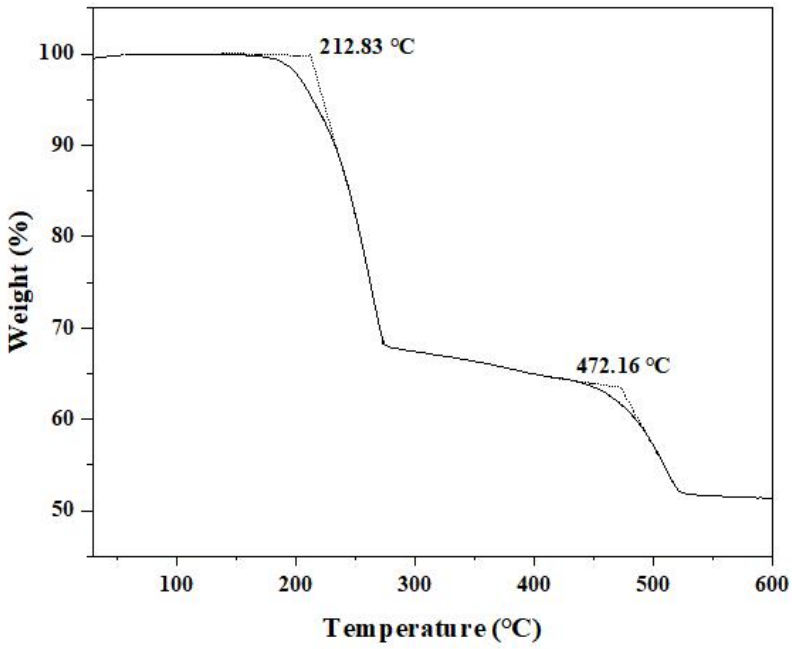

Figure S2. TG curve of $NaYF_4$:10%Er@$NaYbF_4$@$NaYF_4$

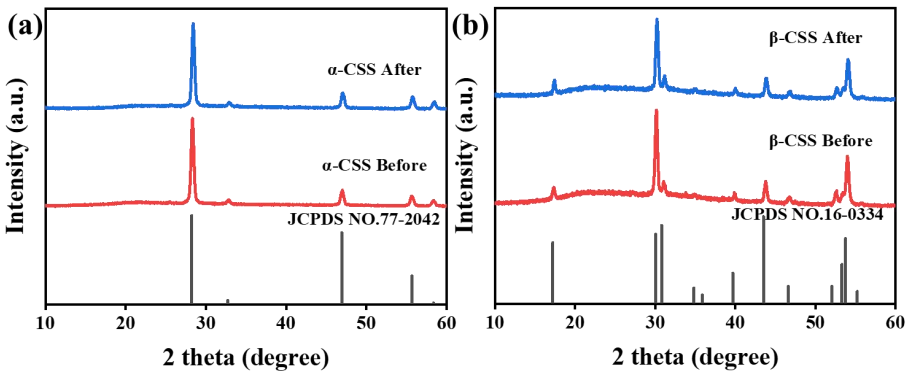

Figure S3. XRD patterns of α- (a) and β- (b) $NaYF_4$:10%Er@$NaYbF_4$@$NaYF_4$ UCNPs before and after annealing at 200 °C.

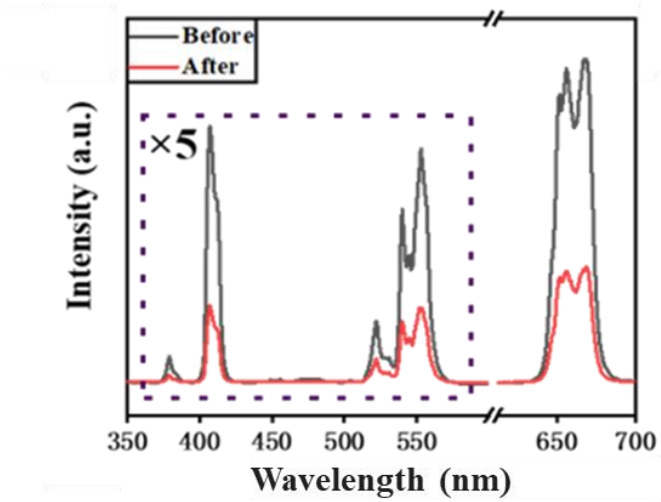

Figure S4. PL spectra of α-$NaYF_4$:10%Er@$NaYbF_4$@$NaYF_4$ UCNPs before and after annealing at 200 °C for 4 h.

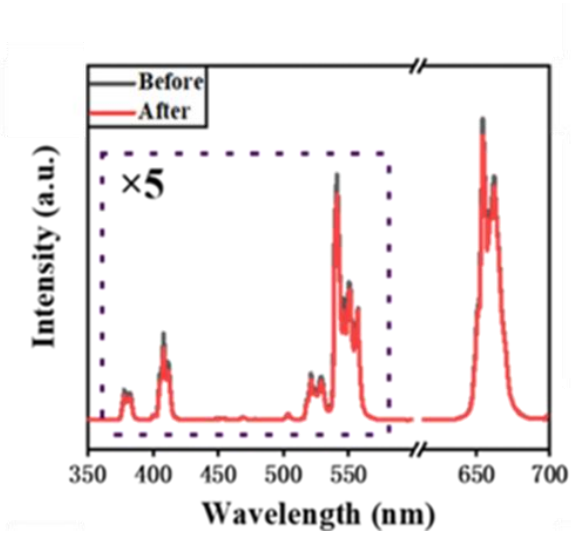

Figure S5. PL spectra for β- $NaYF_4$:10%Er@$NaYbF_4$@$NaYF_4$ UCNPs before and after annealing

at 200 °C for 4h.

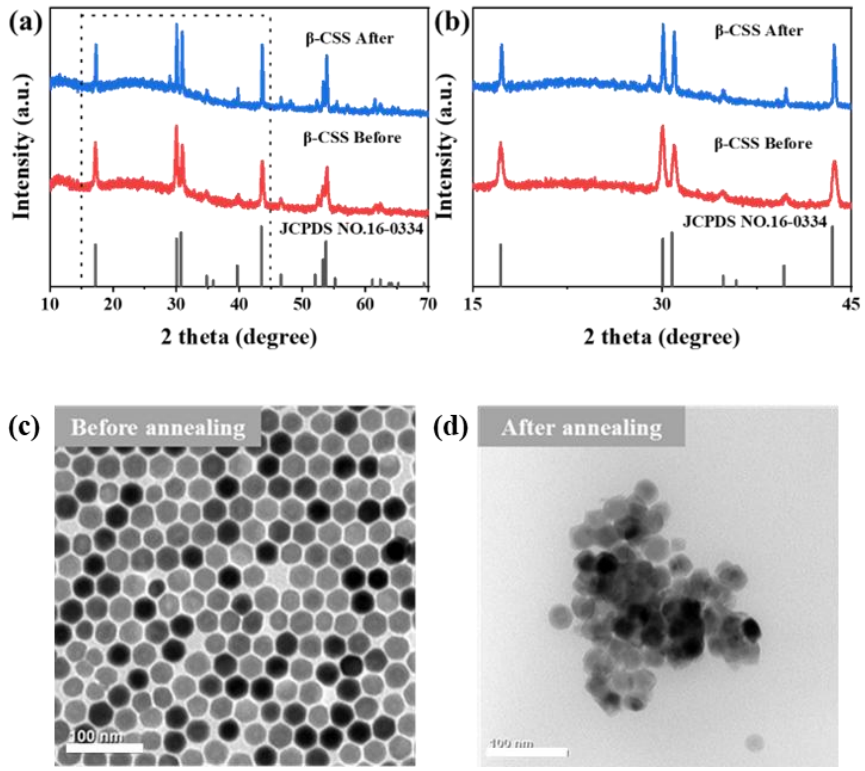

Figure S6. (**a-b**) XRD patterns (**c-d**) TEM images of β-$NaYF_4$:10%Er@$NaYbF_4$@$NaYF_4$ UCNPs film before and after annealing at 400 °C for 4 h.

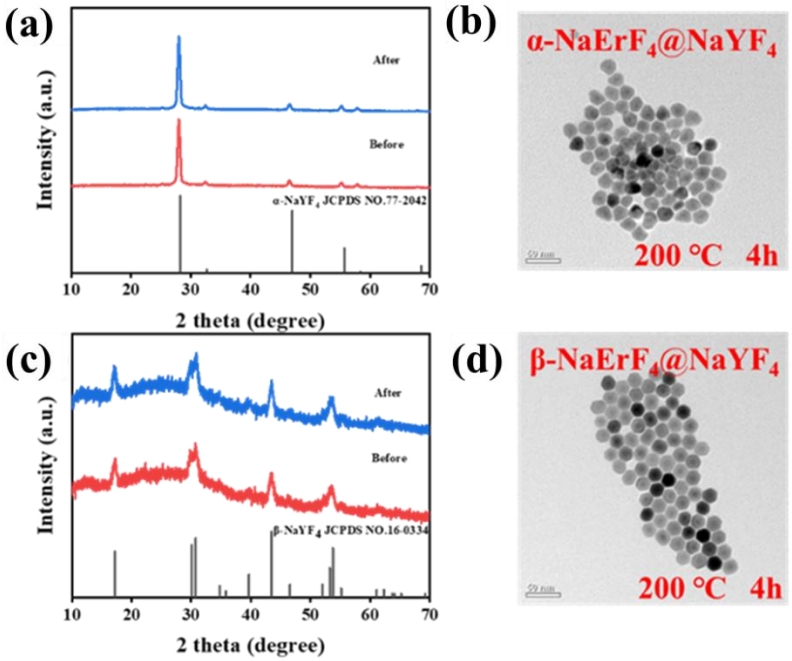

Figure S7. TEM images and XRD patterns of cubic (**a-b**) and hexagonal (**c-d**) core-shell $NaErF_4$@$NaYF_4$ UCNPs after annealing at 200 °C, respectively.

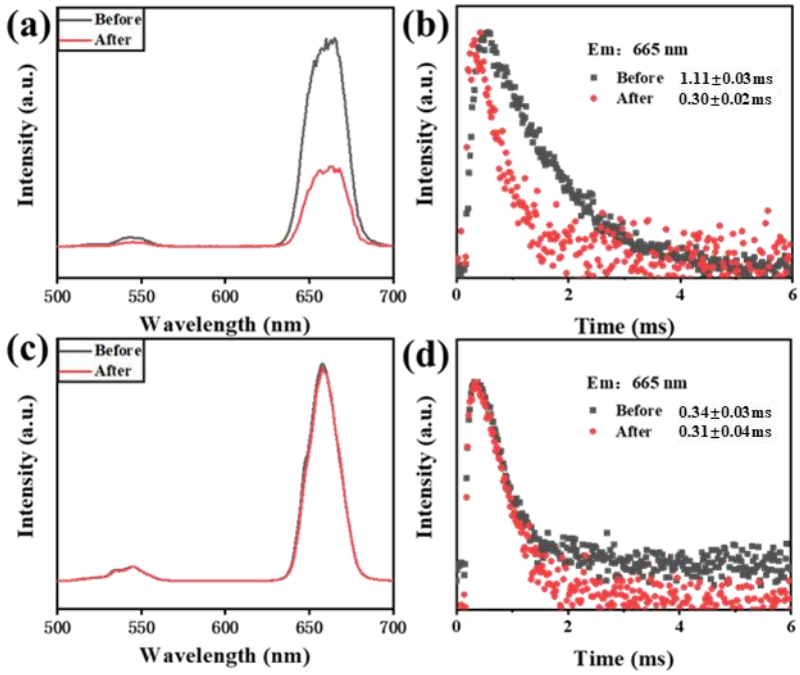

Figure S8. The PL spectra and decay curves of emission at 665 nm for α- (**a-b**) and β- (**c-d**) $NaErF_4$@$NaYF_4$ core-shell UCNPs before and after annealing at 200 °C for 4h.

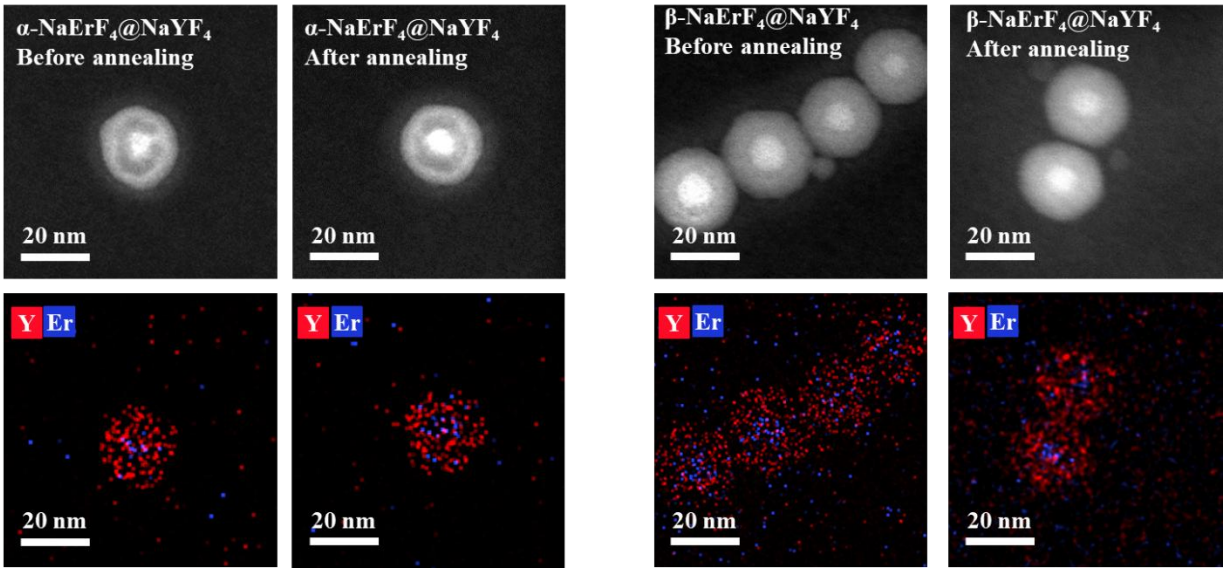

Figure S9. EDS mapping of α/β-$NaErF_4$@$NaYF_4$, before and after annealing at 200 °C for 4 h.

Table S1 Upconversion quantum yields of UCNPs before and after annealing at 200 °C for 4 h.

	$NaErF_4$@$NaYF_4$		$NaYF_4$:10%Er@$NaYbF_4$@$NaYF_4$	
Phase	α	β	α	β
Before annealing	-	0.17 %	5.42 %	6.82 %
After annealing	-	0.16 %	2.59%	6.81 %

The quantum yield of the upconversion emission was measured on the same spectrometer combined with an integration sphere. Before measurement, the above NPs dispersions were diluted to minimize scattering of the excitation light. An excitation power density of 4.5 $W \cdot cm^{-2}$ was used for all the measurements. The quantum yield (QY) was calculated by the following equation

$$QY=\frac{visible\ photons\ emitted}{980\ nm\ photons\ absorbed}=\frac{I_{em,sample}-I_{em,reference}}{I_{ex,reference}-I_{ex,sample}}$$

$I_{em,sample}$ and $I_{em,reference}$ are the integrated emission intensity in the range of 350-700 nm from the sample and the reference (~0), respectively. $I_{ex,reference}$ and $I_{ex,sample}$ are the integrated intensities of the excitation light in the presence of the reference and the sample, respectively. In the test, the cyclohexane was used as the reference.