Electronic Supplementary Information

# Energy Transfer Mechanism Dominated by the Doping Location of Activators in Rare-Earth Upconversion Nanoparticles

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## Experiment Section

### Synthesis of $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb core-shell nanoparticles.

The $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb core-shell nanoparticles were synthesized using a procedure similar to $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb-Eu core-shell nanoparticles. The $NaGdF_4$:Yb-Er core nanoparticles were used as seeds for shell coating. The $NaGdF_4$:Yb-Er@NaGdF4:Yb core-shell nanocrystals were prepared following this process: the 1 mmol solid powder, totally consisted of $GdCl_3$ (0.80 mmol) and $YbCl_3$ (0.20 mmol), mixed with 15 ml oleic acid and 15 ml octadecene, were added into a 250 ml flask under magnetic stirring. The mixture solution was stirred and heated to 130 ℃ under vacuum to form a homogeneous solution and then cooled down to room temperature. After that, $NaGdF_4$:Yb-Er core nanoparticle seeds were added into the mixture solution. Then, NaOH (2.5 mmol) and $NH_4F$ (4 mmol) were poured into the solution. The temperature of mixed solution was quickly increased to 290-300 ℃ for 1 hour under argon atmosphere and then the solution was cooled down naturally under argon. The $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb core-shell nanocrystal solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 90 ℃ before further characterization.

### Synthesis of $NaGdF_4$:Yb core nanoparticles.

$NaGdF_4$:Yb core nanocrystals were prepared following this process: the 1 mmol solid powder, totally consisted of $GdCl_3$ (0.80 mmol) and $YbCl_3$ (0.20 mmol), mixed with 15 ml oleic acid and 15 ml octadecene, were added into a 250 ml flask under magnetic stirring. The mixture solution was stirred and heated to 130 ℃ under vacuum to form a homogeneous solution and then cooled down to room temperature. Then, NaOH (2.5 mmol) and $NH_4F$ (4 mmol) were poured into the solution. The temperature of mixed solution was quickly increased to 290-300 ℃ for 1 hour under argon atmosphere. The solution was cooled down naturally under argon. The $NaGdF_4$:Yb nanocrystals solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 90 ℃ before being used for shell coating and further characterization.

## The Synthesis of $NaGdF_4$:Yb@$NaGdF_4$:Yb-Er-Eu (15mol%) core-shell nanoparticles.

The $NaGdF_4$:Yb core nanoparticles were used as seeds for shell coating. $NaGdF_4$:Yb@$NaGdF_4$:Yb-Er-Eu core-shell nanocrystals were prepared following this process: the 1 mmol solid powder, totally consisted of $GdCl_3$ (0.635 mmol), $YbCl_3$ (0.20 mmol), $ErCl_3$ (0.015 mmol) and $EuCl_3$ (0.15 mmol), mixed with 15 ml oleic acid and 15 ml octadecene, were added into a 250 ml flask under magnetic stirring. The mixture solution was stirred and heated to 130 ℃ under vacuum to form a homogeneous solution and then cooled down to room temperature. After that, $NaGdF_4$:Yb core nanoparticle seeds were added into the mixture solution. Then, NaOH (2.5 mmol) and $NH_4F$ (4 mmol) were poured into the solution. The temperature of mixed solution was quickly increased to 290-300 ℃ for 1 hour under argon atmosphere and then the solution was cooled down naturally under argon. The $NaGdF_4$:Yb@$NaGdF_4$:Yb-Er-Eu core-shell nanocrystal solution was precipitated by centrifugation with ethanol and cyclohexane for three times, and then dried in air at 90 ℃ before further characterization.

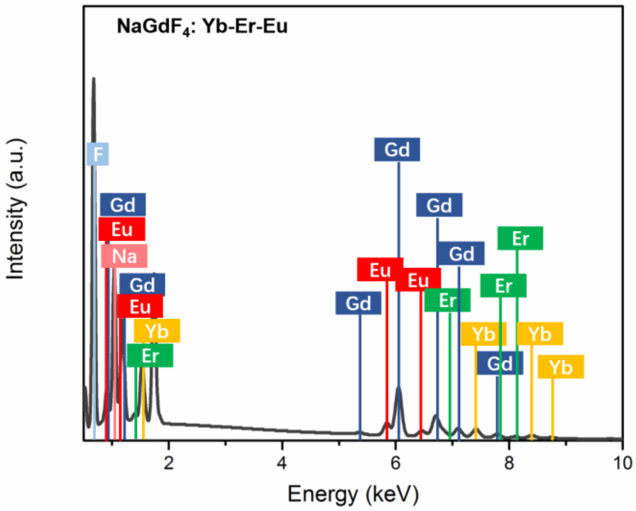

**Figure S1**. EDX pattern of $NaGdF_4$:Yb-Er-Eu core-only nanocrystals.

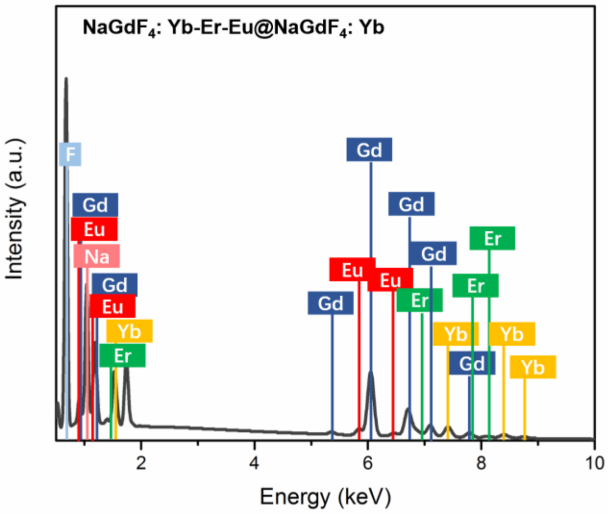

**Figure S2.** EDX pattern of $NaGdF_4$:Yb-Er-Eu@$NaGdF_4$:Yb core-shell nanocrystals.

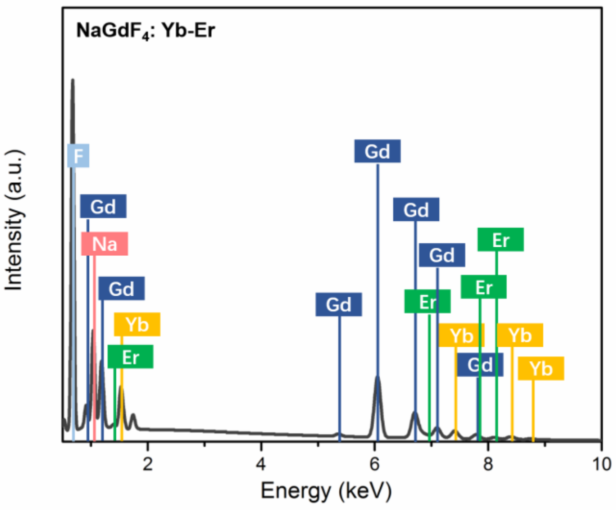

**Figure S3.** EDX pattern of $NaGdF_4$:Yb-Er core-only nanocrystals.

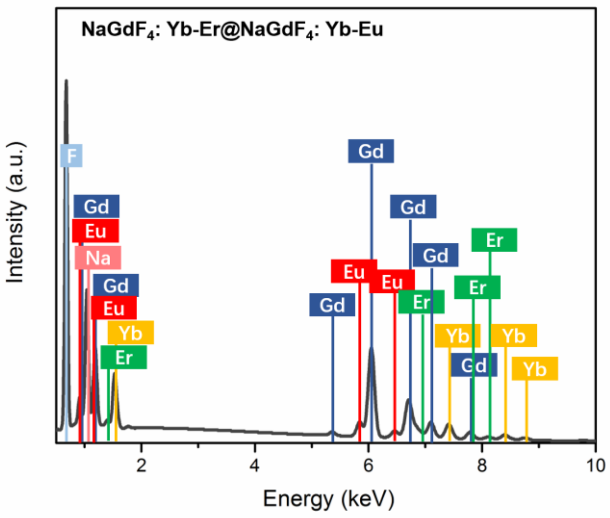

**Figure S4.** EDX pattern of $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb-Eu core-shell nanocrystals.

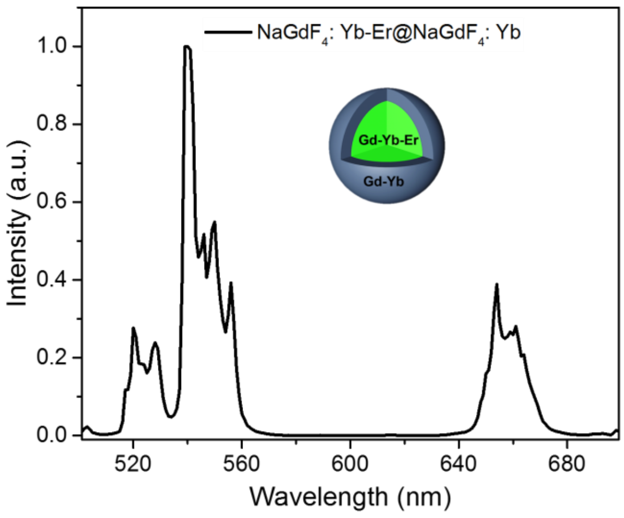

**Figure S5.** The UCL spectra of $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb core-shell nanoparticles.

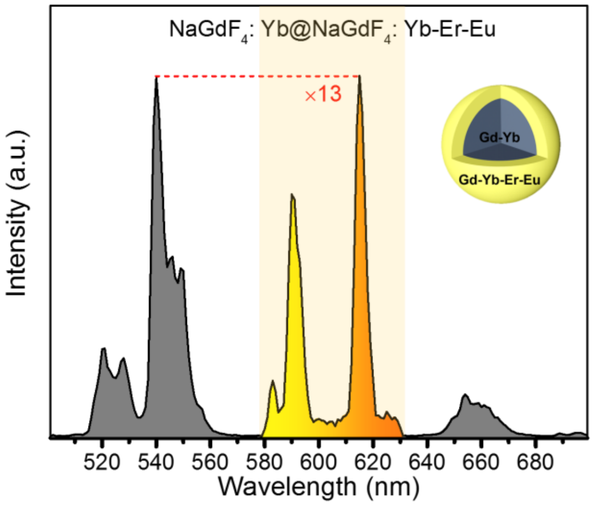

**Figure S6.** The UCL spectra of $NaGdF_4$:Yb@$NaGdF_4$:Yb-Er-Eu core-shell nanoparticles.

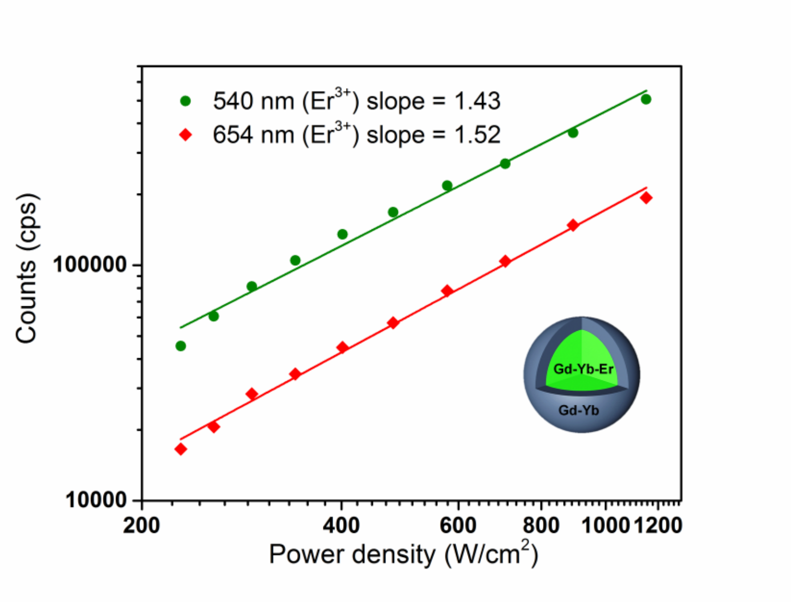

**Figure S7.** The UCL intensity of 540 nm (green) and 654 nm (red) emissions of $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb core-shell nanoparticles as a function of the excitation power density.

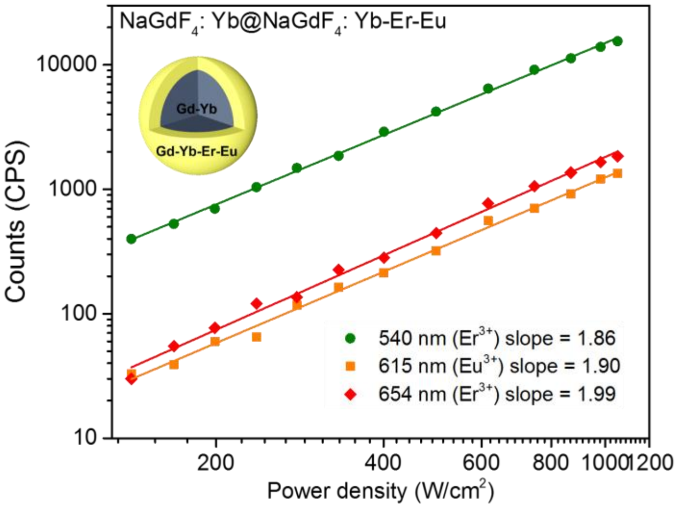

**Figure S8.** The UCL intensity of 540 nm (green), 615 nm (orange) and 654 nm (red) emissions of $NaGdF_4$:Yb@$NaGdF_4$:Yb-Er-Eu core-shell nanoparticles as a function of the excitation power density.

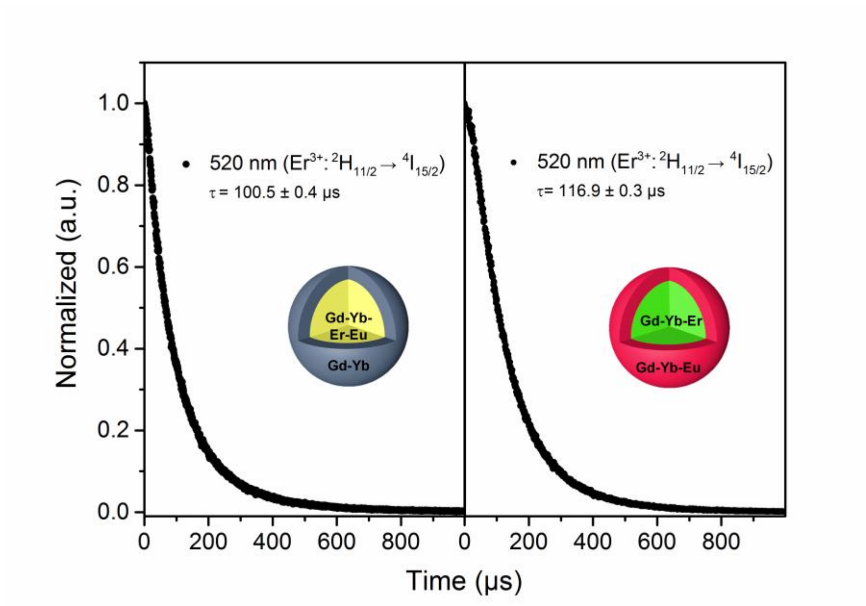

**Figure S9.** Upconversion luminescence decay curves of $Er^{3+}$ emission at 520 nm of $NaGdF_4$:Yb-Er-Eu@$NaGdF_4$:Yb core-shell (left) and $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb-Eu core-shell (right) nanoparticles.

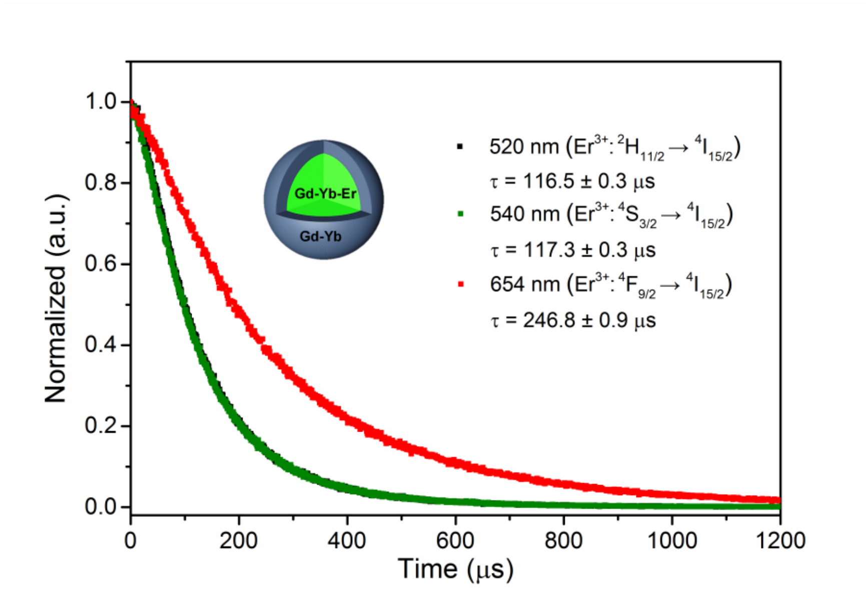

**Figure S10.** Upconversion luminescence decay curves of $Er^{3+}$ emission at 520 nm, 540 nm and 654 nm of $NaGdF_4$:Yb-Er@$NaGdF_4$:Yb core-shell nanoparticles.

The concentration of dopants also influenced its optical properties. We prepared four Eu doping concentration, 1%, 5%, 10% and 20%, with different doping location to investigate the effect of doping concentration on energy transfer efficiency. As were shown in Figure 3 and Figure S11-S12, in both different core-shell nanoparticles, the relative UCL intensity of Eu increased with the increasing Eu doping concentration when the doping concentration of Eu was less than 15%. When the Eu doping concentration increased to 20%, the relative UCL intensity of Eu decreased. The results indicated that increasing Eu doping concentration could reduce average energy transfer distance, leading to efficient energy transfer process. However, reduced energy transfer distance may also result in cross relaxation, leading to large energy loss.

Time-resolved luminescence were investigated in Figure S13-S16. When the Eu doping concentration was 20%, both lifetimes of Yb-Er-Eu@Yb and Yb-Er@Yb-Eu at 540 nm emission decreased compared to 15% doping concentration. Decreased lifetimes of Er emitting indicated more efficient energy transfer process because of the shorter average ion distance dominated by the increased doping concentration.

In Yb-Er-Eu@Yb nanoparticles, the fast decay($\tau_1$) and the slow decay($\tau_2$) of Eu emitting was respectively estimated to be 944.45 ± 87.09 μs and 3108.68 ± 65.87 μs, the computational lifetime decreased to 2545.98 s. This reduction may attribute to concentration quenching. In Yb-Er@Yb-Eu nanoparticles, the fast decay($\tau_1$) and the slow decay($\tau_2$) of Eu emitting was respectively estimated to be 120.24 ± 8.66 μs and 3054.12 ± 19.81 μs, the computational lifetime was 1499.16 s and the ratio of the slow decay increased to 0.47 because of the shortening average distance between Er and Eu.

In conclusion, the concentration of dopants influenced optical properties in Rare-Earth upconversion nanoparticles. Large doping concentration could reduce average energy transfer distance, leading to efficient energy transfer process. However, reduced energy transfer distance may also result in cross relaxation, leading to large energy loss. In a word, energy transfer distance and concentration quenching should be balanced in material design.

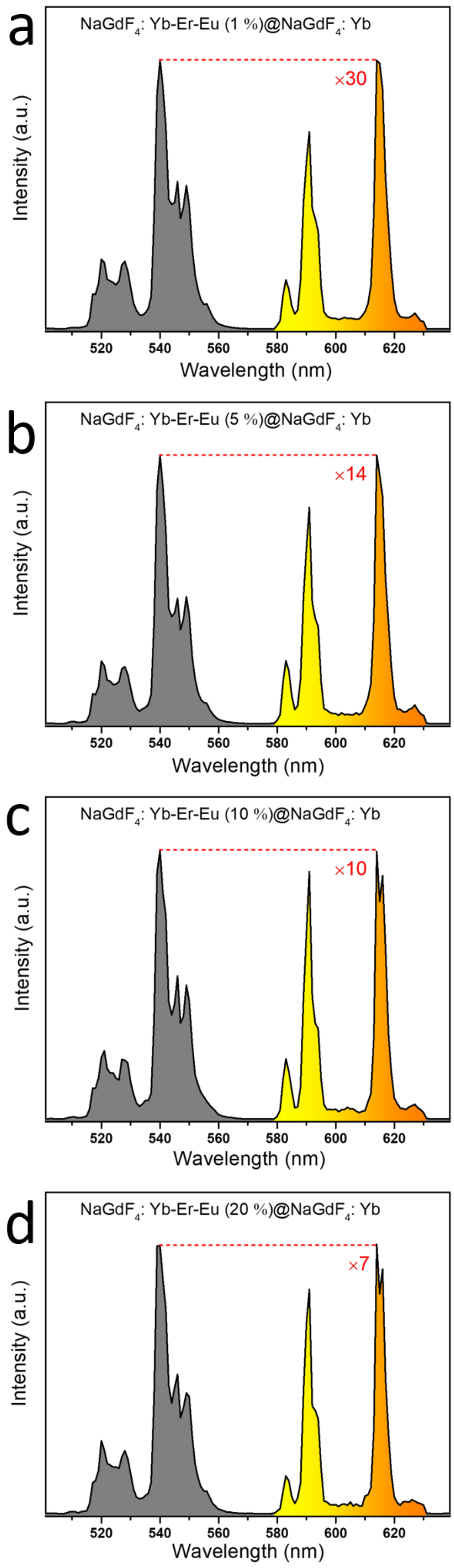

**Figure S11.** The UCL spectra of Yb-Er-Eu@Yb core-shell nanoparticles with different Eu doping concentration.

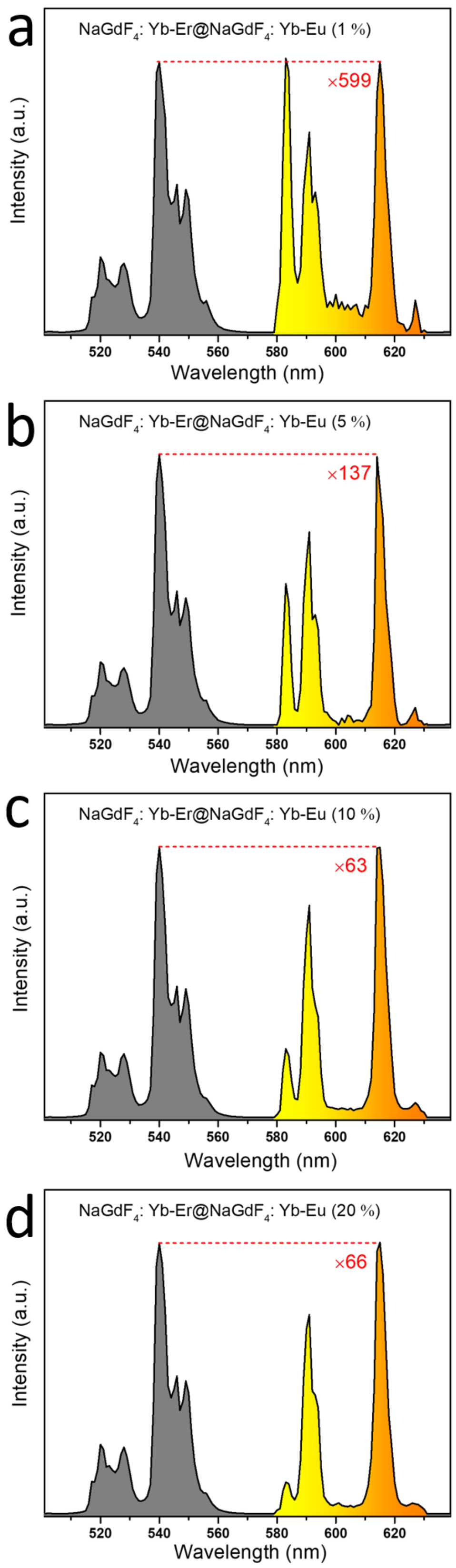
a
NaGdF$_4$: Yb-Er@NaGdF$_4$: Yb-Eu (1 %)
×599
Intensity (a.u.)
520
540
560
580
600
620
Wavelength (nm)
b
NaGdF$_4$: Yb-Er@NaGdF$_4$: Yb-Eu (5 %)
×137
Intensity (a.u.)
520
540
560
580
600
620
Wavelength (nm)
c
NaGdF$_4$: Yb-Er@NaGdF$_4$: Yb-Eu (10 %)
×63
Intensity (a.u.)
520
540
560
580
600
620
Wavelength (nm)
d
NaGdF$_4$: Yb-Er@NaGdF$_4$: Yb-Eu (20 %)
×66
Intensity (a.u.)
520
540
560
580
600
620
Wavelength (nm)

**Figure S12**. The UCL spectra of Yb-Er@Yb-Eu core-shell nanoparticles with different Eu doping concentration.

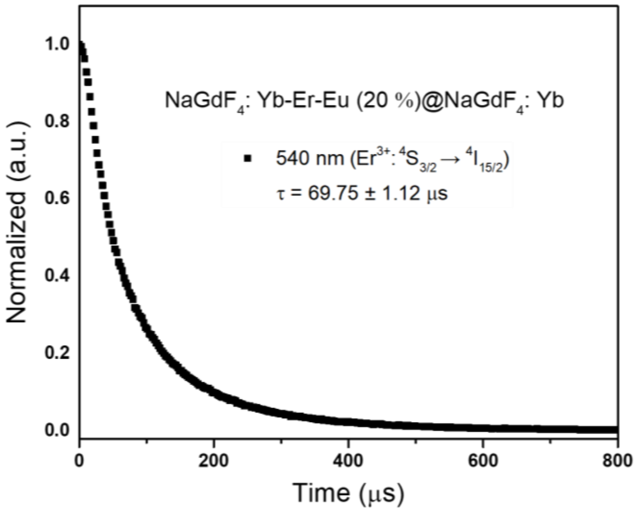

**Figure S13.** UCL decay curve of Er emission at 540 nm of Yb-Er-Eu (20%)@Yb core-shell nanoparticles.

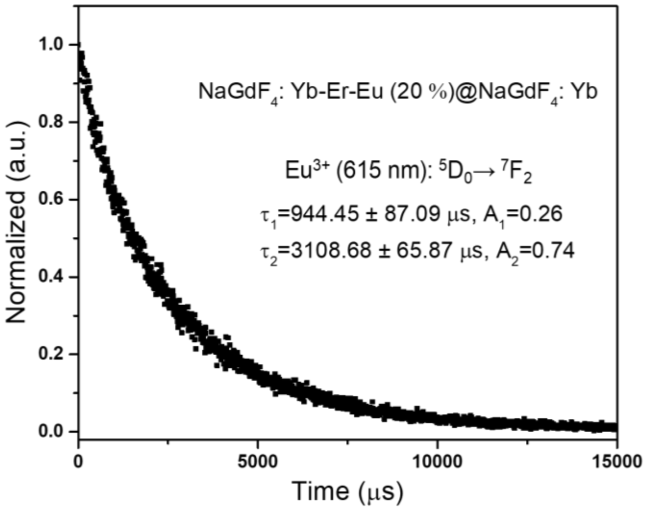

**Figure S14.** UCL decay curve of Eu emission at 615 nm of Yb-Er-Eu (20%)@Yb core-shell nanoparticles.

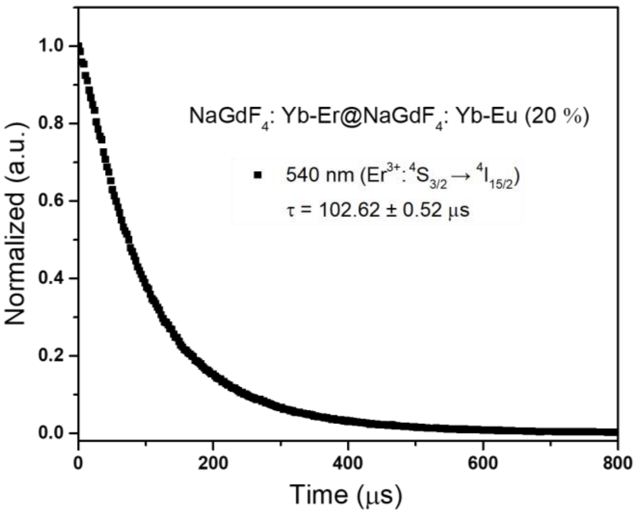

**Figure S15.** UCL decay curve of Er emission at 540 nm of Yb-Er@Yb-Eu (20%) core-shell nanoparticles.

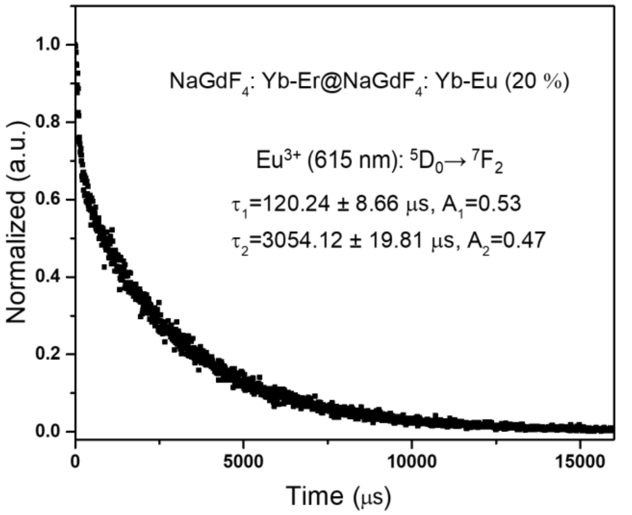

**Figure S16.** UCL decay curve of Eu emission at 615 nm of Yb-Er@Yb-Eu (20%) core-shell nanoparticles.

Two core-shell nanoparticles without Gd, $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb and $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu, were prepared to explore the UCL behavior. As was shown in Figure S17-S18, the UCL behavior of these core-shell were different. In $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb nanoparticles, the UCL intensity of Eu were 31 times weaker than Er. However，In $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu nanoparticles, this factor changed to 250. This difference indicated that Eu cannot populate efficiently without Gd when Er and Eu were spatial separated. Besides, $NaGdF_4$ was a better host matrix for Eu emitting than $NaYF_4$.

In order to further analyze the UCL properties, power dependent graph was shown to further illustrate the energy transfer process. Under 980 nm excitation, the slopes of 540 nm, 654 nm and 615 nm emission curves of $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb nanoparticles were 1.45, 1.69 and 1.22, respectively (Figure S19). The results indicated that Er and Eu emitting were all two-photon process. In $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu nanoparticles, the slopes of 540 nm, 654 nm and 615 nm emission curves nanoparticles were 1.68, 1.76 and 1.53, respectively. Particularly, the n value of Eu emitting was different from Gd nanoparticles. The results indicated that the Eu emitting was two-photon process similar to Er emitting. The lifetimes of Er emitting were also evaluated in Figure S21-S22. The green emitting lifetime of $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb nanoparticles was 166.72 ± 0.98 μs while it was 213.81 ± 1.43 μs in $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu nanoparticles. The result indicated more efficient energy transfer process.

The data proved that the Eu was populated directly by Er in both different core-shell nanoparticles. In $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb nanoparticles, Er and Eu were both in the core, the ion distance was short, Eu could be populated by Er directly. In the interface of $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu nanoparticles, the ion distance between Er and Eu was also short, the Eu could be populated by Er directly, however, most Eu could not be populated due to lack of Gd.

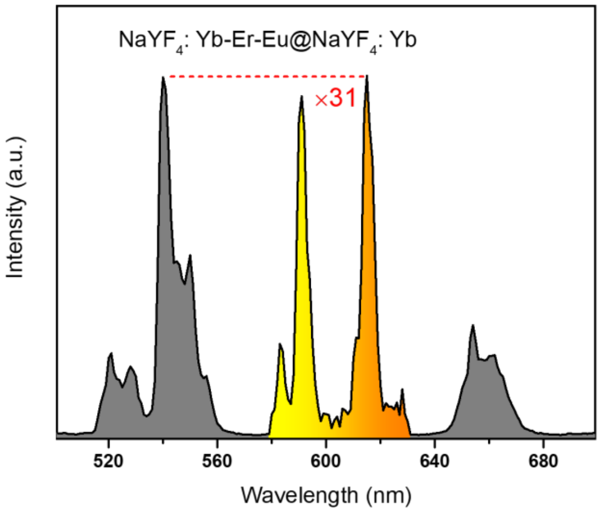

**Figure S17.** The UCL spectra of $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb core-shell nanoparticles.

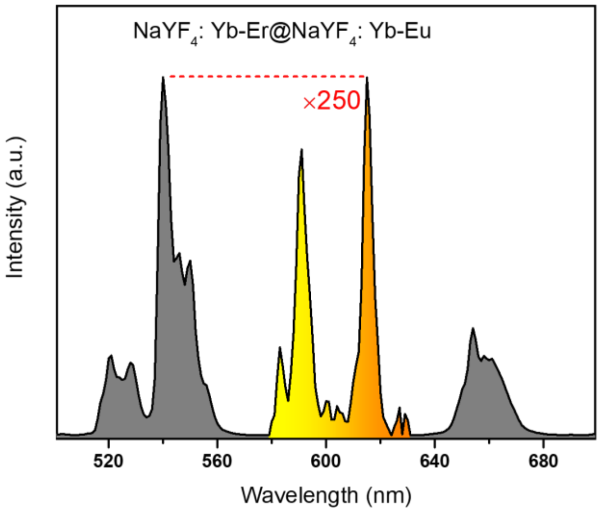

**Figure S18.** The UCL spectra of $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu core-shell nanoparticles.

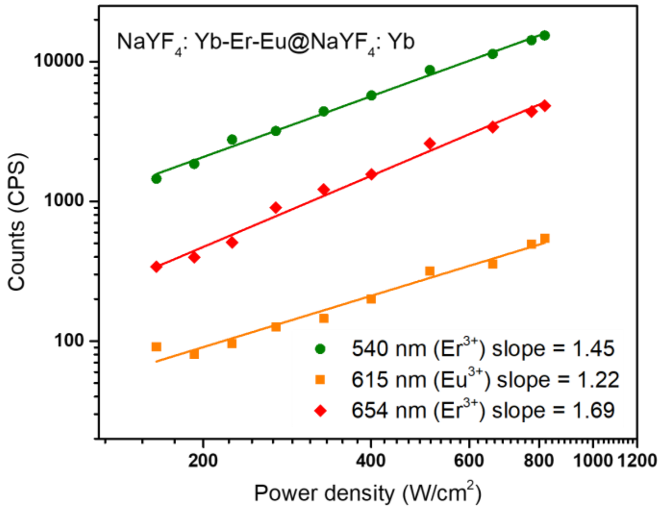

**Figure S19.** The UCL intensity of 540 nm (green), 615 nm (orange) and 654 nm (red) emissions of $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb core-shell nanoparticles as a function of the excitation power density.

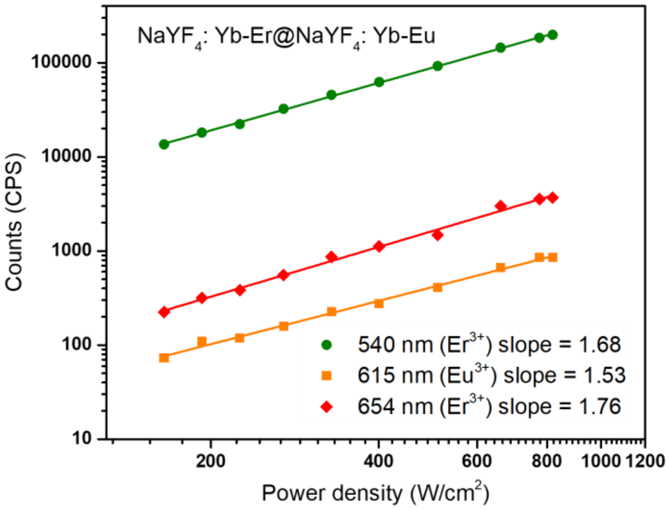

**Figure S20.** The UCL intensity of 540 nm (green), 615 nm (orange) and 654 nm (red) emissions of $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu core-shell nanoparticles as a function of the excitation power density.

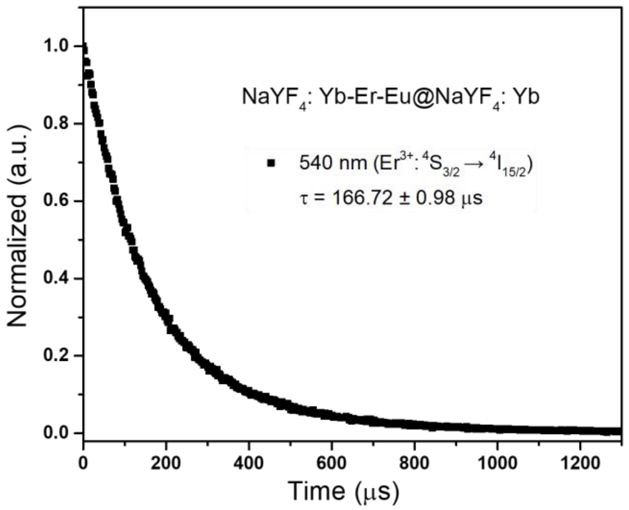

**Figure S21.** UCL decay curve of Er emission at 540 nm of $NaYF_4$:Yb-Er-Eu@$NaYF_4$:Yb core-shell nanoparticles.

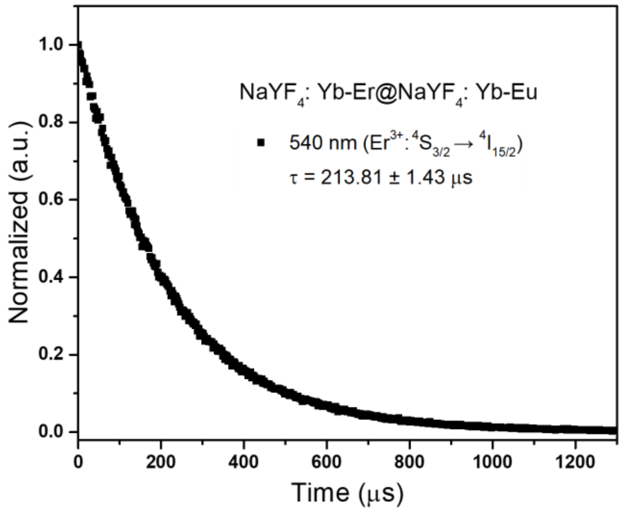

**Figure S22.** UCL decay curve of Er emission at 540 nm of $NaYF_4$:Yb-Er@$NaYF_4$:Yb-Eu core-shell nanoparticles.