Supporting Information

Energy Loss Mechanism of Upconversion Core/Shell Nanocrystals

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A. Nanocrystal synthesis

1. Materials

Gadolinium(III) acetate hydrate (99.9%), ytterbium(III) acetate tetrahydrate (99.9%), erbium(III) acetate hydrate (99.9%), sodium hydroxide (NaOH, ≥98%), ammonium fluoride (NH_4F, ≥98%), sodium trifluoroacetate (Na-TFA, 98%), 1-octadecene (ODE, 90%), and oleic acid (OA, 90%) were all purchased from Sigma-Aldrich and used as starting materials without further purification. Cyclohexane, ethanol were purchased from Aladdin Chemistry Co., Ltd.

2. Synthesis of core nanocrystals

2.1 β-$NaGdF_4$:20%Yb/2%Er nanocrystals

Hexagonal (*β*) phase $NaGdF_4$:Yb/Er core nanocrystals were synthesized using a modification of a previously reported procedure.[1] First, 1 mmol of lanthanide acetates (Molar ratio: Gd/Yb/Er = 78:20:2) was added to a 100 mL round bottom flask containing 10 mL of OA and 15 mL of ODE. The mixed solution was heated slowly to 140 °C under vacuum with magnetic stirring and then kept for 30 min until it became clear. With the gentle flow of argon gas through the reaction flask, the solution was cooled slowly to room temperature. Subsequently, the methanol solution dissolved with 4 mmol of NH_4F and 2.5 mmol of NaOH was added and the mixed solution was kept at 50 °C for 30 min with vigorous stirring. Then, the resulting solution was heated up to 70 °C to evaporate methanol and to 120 °C to evaporate the residual water. Finally, the solution was heated to 300 °C as quickly as possible in an argon atmosphere and kept at this temperature for 90 min for complete reaction and crystal formation. After cooling down to room temperature, the obtained nanocrystals were precipitated by the addition of ethanol, collected by centrifugation, washed three times with ethanol, and finally dried in an oven at 60 °C for further characterization.

2.2 *β-Na91%YbF$_4$:9%Er nanocrystals*

Small-sized β-NaYbF$_4$:Er nanocrystals (~6 nm) were synthesized by a previously reported procedure.[2] 1 mmol of rare earth acetate (molar ratio: Yb/Er = 91:9) was added to a 100 mL round bottom flask containing 24 mL of OA and 24 mL of ODE. The mixture was heated slowly to 140 °C under vacuum with magnetic stirring and then kept for 30 min until it became clear. After the temperature dropped below 50 °C, 8 mmol sodium oleate were added to the solution. The mixed solution was degassed for 1 h at 100 °C under vacuum and vigorous stirring resulting in a clear solution. After closing vacuum and switching to argon flow, 11 mmol NH_4F were added to the solution at 100 °C. Subsequently, the solution was heated to 160 °C for 1 h under argon flow until NH_4F dissolved completely. Then, the solution was heated to 310 °C as quickly as possible in an argon atmosphere and kept at this temperature for 30 min. After colling to room temperature, the resulting suspension was centrifuged by the addition of ethanol and water, collected by centrifugation, washed three times with ethanol and water, and used to fabricate core/shell nanocrystals immediately.

3. Synthesis of core/shell nanocrystals[3]

3.1 Preparation of the inert-shell precursor Gd-OA

7.5 mmol of gadolinium(III) acetate hydrate, 10 mL of OA and 15 mL of ODE were added to a 100 mL flask, and then the mixed solution was heated at 140 °C under vacuum with vigorous stirring until a clear solution was formed. After that, the solution was cooled down to room temperature and the colorless Gd-OA precursor solution (0.3 mol/L) was obtained.

3.2 Preparation of the Na-TFA-OA precursor

8 mmol of Na-TFA and 20 mL of OA was loaded in a 100 mL flask and heated at 50 °C for 60 min under vacuum with vigorous stirring, until a clear Na-TFA-OA precursor solution (0.4 mol/L) was obtained.

3.3 Synthesis of active-core/inert-shell nanocrystals

In a typical synthesis, 8 mL of OA and 12 mL of ODE were added to a 100 mL flask, followed by the addition of 5 mL cyclohexane solution containing the pre-prepared nanocrystal seeds (Table S1) under vigorous stirring. Then the mixed solution was heated at 75 °C for 10 min under vacuum to evaporate cyclohexane. After the cyclohexane was completely removed, the system was switched to an argon flow and the solution was quickly heated to 290 °C. Subsequently, 2 mL of the Gd-OA precursor solution (0.3 mol/L) and 3 mL of Na-TFA-OA precursor solution (0.4 mol/L) were alternately added into the flask at 290 °C. The injection cycle of shell precursors was performed for various times corresponding to the shell thickness (Table S1) and the interval time between each injection was kept at 15 min. Finally, the solution was cooled down to room temperature and the obtained products were separated via centrifugation. The core/shell nanocrystals were then washed three times with ethanol and dried in an oven at 60 °C for further characterization.

Table S1. Shell thickness corresponding to the injection cycle times in the synthesis of core/shell nanocrystals

Core@shell(ST, nm)	Nanocrystal Seeds, (Ln^{3+} ions in core, mmol)	Injection cycle times
$NaGdF_4$:Yb/Er@$NaGdF_4$(1.1)	$NaGdF_4$:Yb/Er, 0.5	1
$NaGdF_4$:Yb/Er@$NaGdF_4$(3.0)	$NaGdF_4$:Yb/Er, 0.5	3
$NaGdF_4$:Yb/Er@$NaGdF_4$(5.4)	$NaGdF_4$:Yb/Er, 0.5	6
$NaGdF_4$:Yb/Er@$NaGdF_4$(6.9)	$NaGdF_4$:Yb/Er, 0.5	12
$NaGdF_4$:Yb/Er@$NaGdF_4$(11.3)	$NaGdF_4$:Yb/Er@$NaGdF_4$(6.9), 0.125	3

$NaGdF_4$:Yb/Er@$NaGdF_4$(13.2)	$NaGdF_4$:Yb/Er@$NaGdF_4$(11.3), 0.125	6
$NaGdF_4$:Yb/Er@$NaGdF_4$(17.7)	$NaGdF_4$:Yb/Er@$NaGdF_4$(13.2), 0.0625	3
$NaYbF_4$:Er@$NaGdF_4$(7.5)	$NaYbF_4$:Er, 0.5	12
$NaYbF_4$:Er@$NaGdF_4$(11.2)	$NaYbF_4$:Er@$NaGdF_4$(7.5), 0.125	3

B. Computational methods

1. Decay time

The average luminescent lifetimes were determined *via* the following equation:

$$\tau = \frac{1}{I_0}\int I(t)dt \qquad \text{(S1)}$$

where *I(t)* is the time-related luminescence intensity and I_0 is the maximum intensity.

2. Unit effective volume luminescence (UEVL) intensity

The active-core volume percentage of core/shell NCs is calculated first, and then the UEVL intensity is obtained *via* the following equation:

$$UEVL = \frac{Emission\ \ peak\ \ area}{Core\ \ volume\ \ percentage} \qquad \text{(S2)}$$

3. Unit effective volume absorption (UEVA) intensity

The active-core volume percentage of core/shell NCs is calculated first, and then the UEVA intensity is obtained *via* the following equation:

$$UEVA = \frac{Absorption\ \ peak\ \ area}{Core\ \ volume\ \ percentage} \qquad \text{(S3)}$$

C. Lifetime equation

Based on a long-range electronic-to-vibrational energy transfer model,[4] a decay time equation was deduced. A core/shell nanocrystal and a quencher are considered as a system. Changes of electron state in the system are described by Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi\left(\overrightarrow{r'},t\right) = \hat{H}\Psi\left(\overrightarrow{r'},t\right) \qquad \text{(S4)}$$

where $\Psi\left(\overrightarrow{r'},t\right)$ is the wave function, and the Hamiltonian can be written as

$$\hat{H} = \left|\Psi_I\right\rangle\hat{H}_I\left\langle\Psi_I\right| + \left|\Psi_F\right\rangle\hat{H}_F\left\langle\Psi_F\right| + \hat{V} \qquad \text{(S5)}$$

where Ψ_I (Ψ_F) is the initial (final) wave function, and $\hat{H}_I$ ($\hat{H}_F$) is the initial (final) Hamiltonian. The static energy $\hat{V}$ is the coupling strength, and can be approximated to lowest order by

$$V = \frac{1}{\varepsilon R^3}\mu_{el}\mu_{vib} \qquad \text{(S6)}$$

where μ_{el} is the core electronic dipole moment, and the μ_{vib} is the bond-mode vibrational transition dipole moment. *R* is the coupling distance, namely inert-shell thickness. $\varepsilon = n^2$ is the dielectric permittivity, and *n* is the refraction index.

According to the Fermi's golden rule, overtone vibrational energy transfer (OVET) rate to a single quencher can be written as

$$\Gamma_{nr} = \frac{2\pi\kappa^2|V|^2}{\hbar\gamma} \qquad \text{(S7)}$$

where κ^2 = 2/3 is a geometric factor, and γ^{-1} is the density of states.

In the system, the radius of core is *r*, and the effective radius of a quencher is r_0. The number of quenchers on the nanocrystal surface can be approximated as

$$N = \frac{4(r+R)^2}{r_0^2} \qquad \text{(S8)}$$

The OVET rate is given by

$$\Gamma_{OVET} = N\Gamma_{nr} = \frac{8\pi\kappa^2\left|\mu_{el}\right|^2\left|\mu_{vib}\right|^2}{\hbar\gamma r_0^2 n^4}\frac{(r+R)^2}{R^6} \quad \text{(S9)}$$

In the system, the measured Yb^{3+} $^2F_{2/5}$ decay time τ_m is a combination of the intrinsic lifetime τ_i and a nonradiative surface quenching decay time τ_q, which have the following relationship[5]

$$\frac{1}{\tau_m} = \frac{1}{\tau_i} + \frac{1}{\tau_q} = \frac{1}{\tau_i} + \Gamma_{OVET} \quad \text{(S10)}$$

$$\tau_m = \frac{1}{\frac{1}{\tau_i} + \Gamma_{OVET}} = \frac{\tau_i}{1 + \frac{8\pi\tau_i\kappa^2\left|\mu_{el}\right|^2\left|\mu_{vib}\right|^2}{\hbar\gamma r_0^2 n^4}\frac{(r+R)^2}{R^6}} \quad \text{(S11)}$$

D. Supporting figures

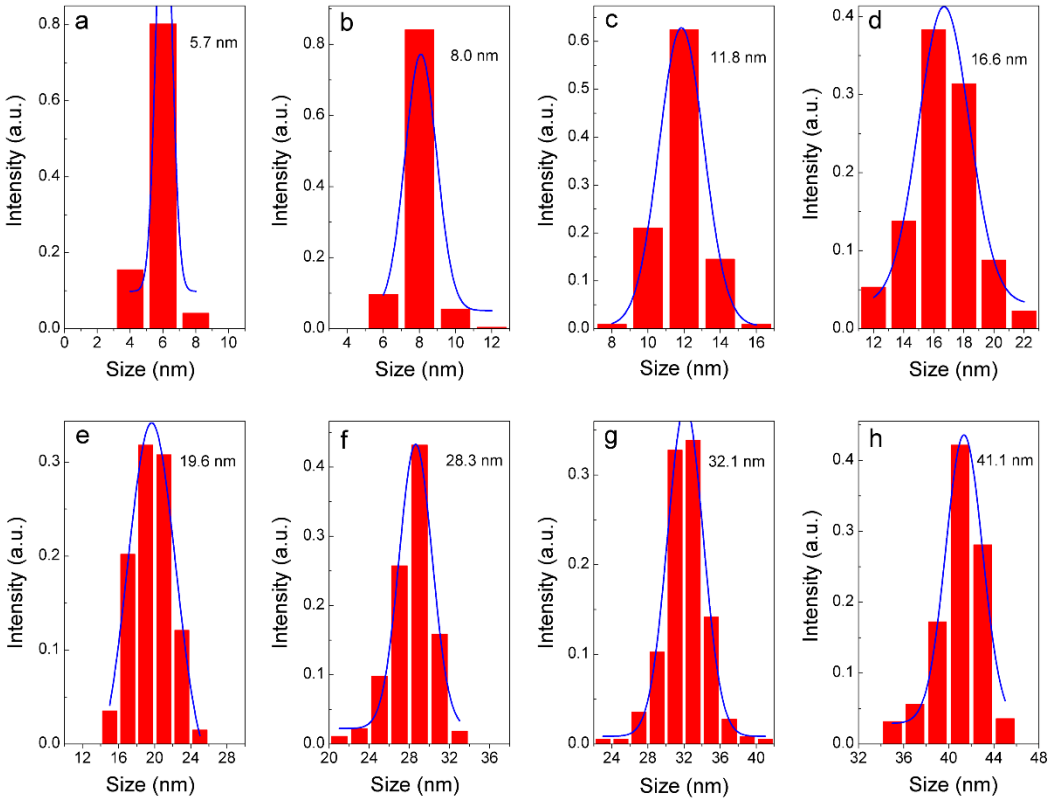

Figure S1. (a-h) Size histograms of the samples shown in Figure 1a-h, correspondingly.

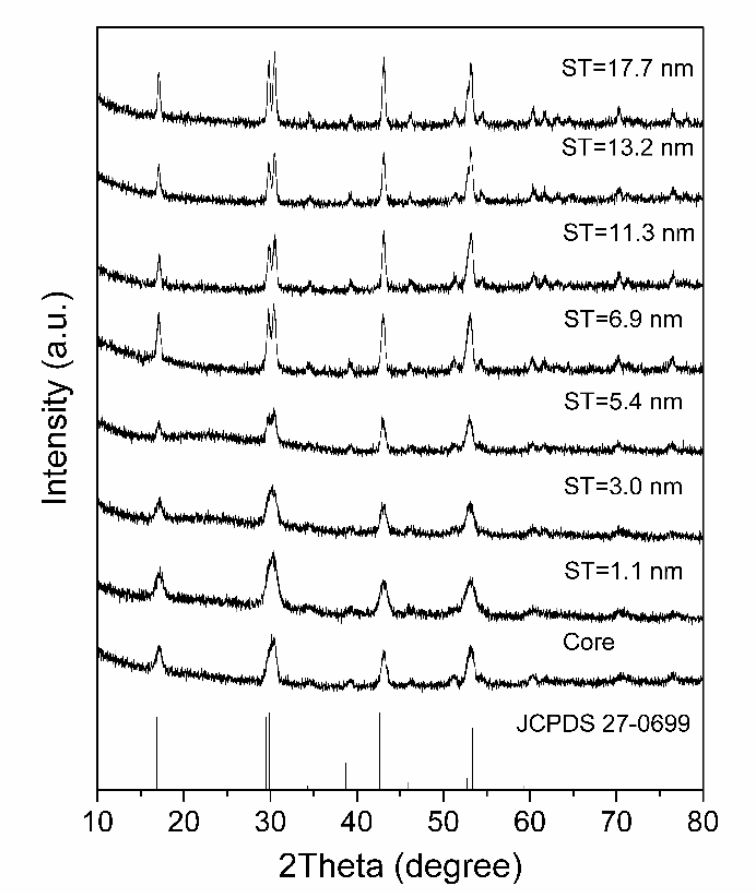

Figure S2. XRD patterns of core-only and all core/shell nanocrystals with the various inert-shell thickness.

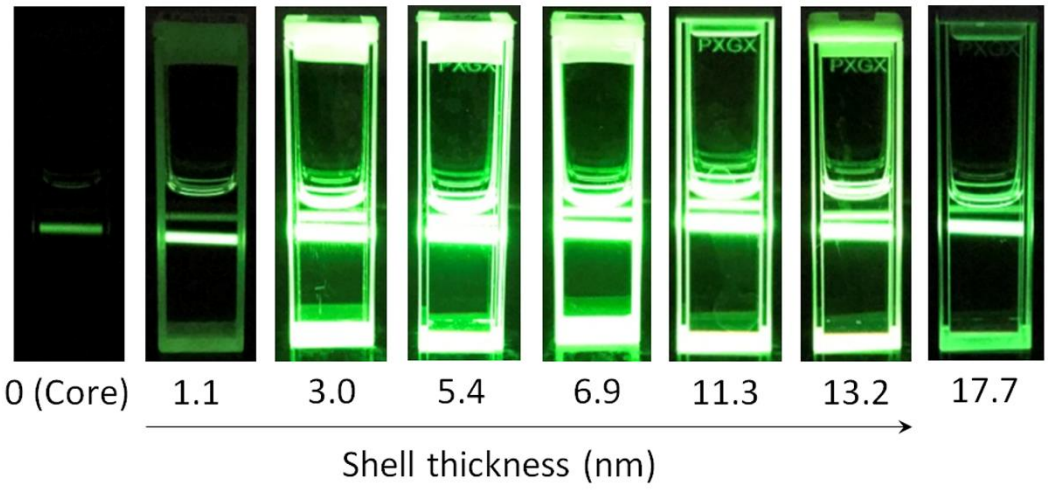

Figure S3. Photographs of the UCL for the all samples in toluene under 975 nm excitation at 20 W/cm^2 (colloid concentration: 10 mg/mL).

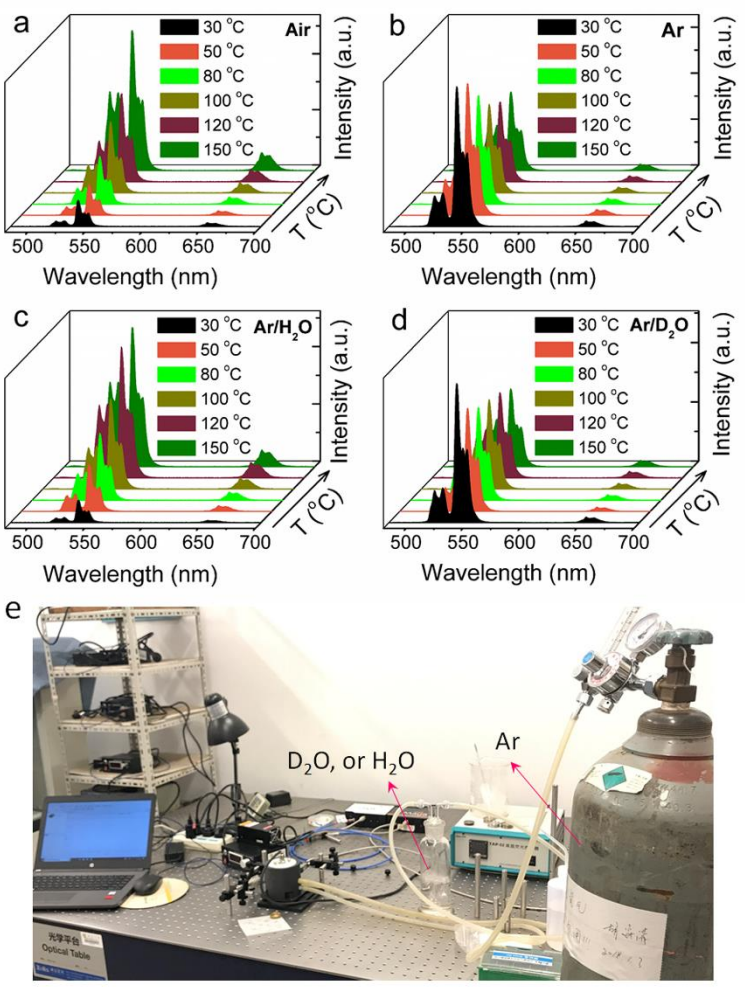

Figure S4. The UCL spectra of nanocrystals with the inert-shell thickness of 1.1 nm in (a) air, (b) Ar, (c) Ar/H_2O, and (d) Ar/D_2O atmospheres under 975 nm excitation (power density 1.6 W/cm^2). (e) Experimental setup for temperature-dependent spectral measurements in the Ar, Ar/D_2O or Ar/H_2O atmosphere.

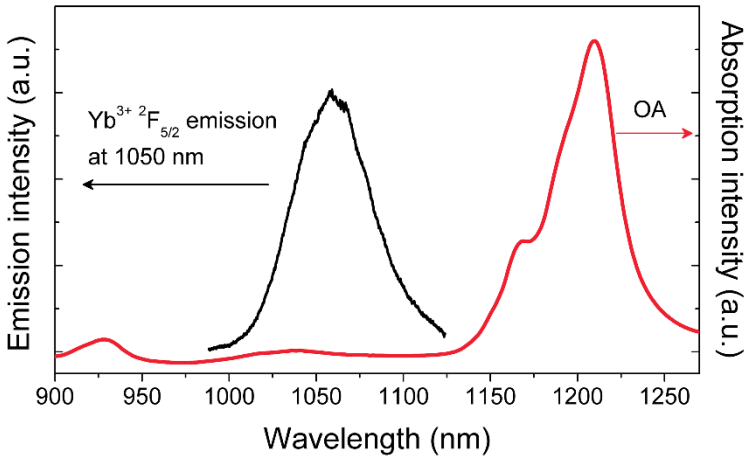

Figure S5. Yb^{3+} $^2F_{5/2}$ emission spectrum at 1050 nm as well as the absorption spectra of oleic acid (OA).

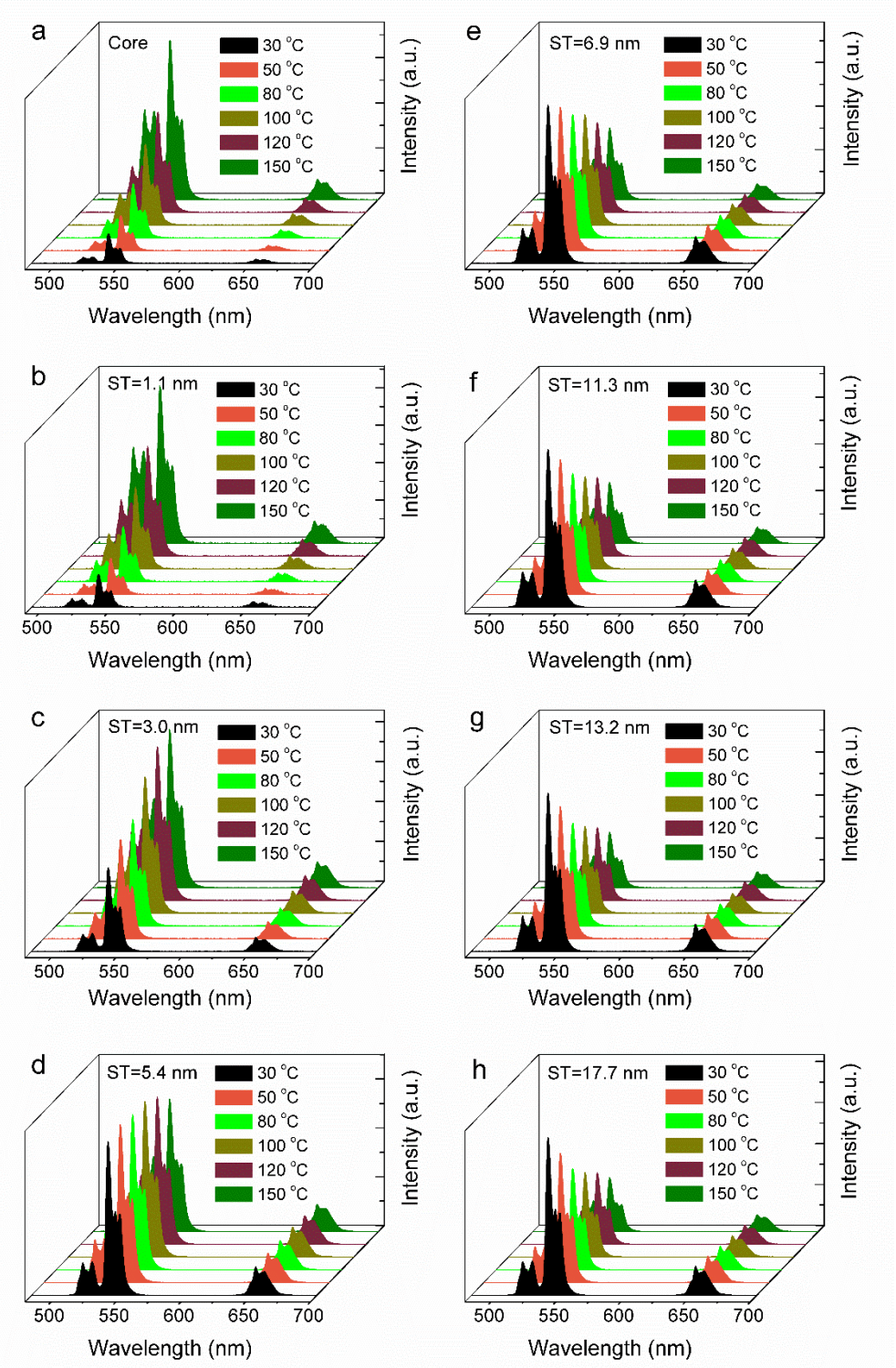

Figure S6. Temperature-dependent UCL spectra of core-only and all core/shell nanocrystals with the various inert-shell thickness in air (power density: 1.6 W/cm^2).

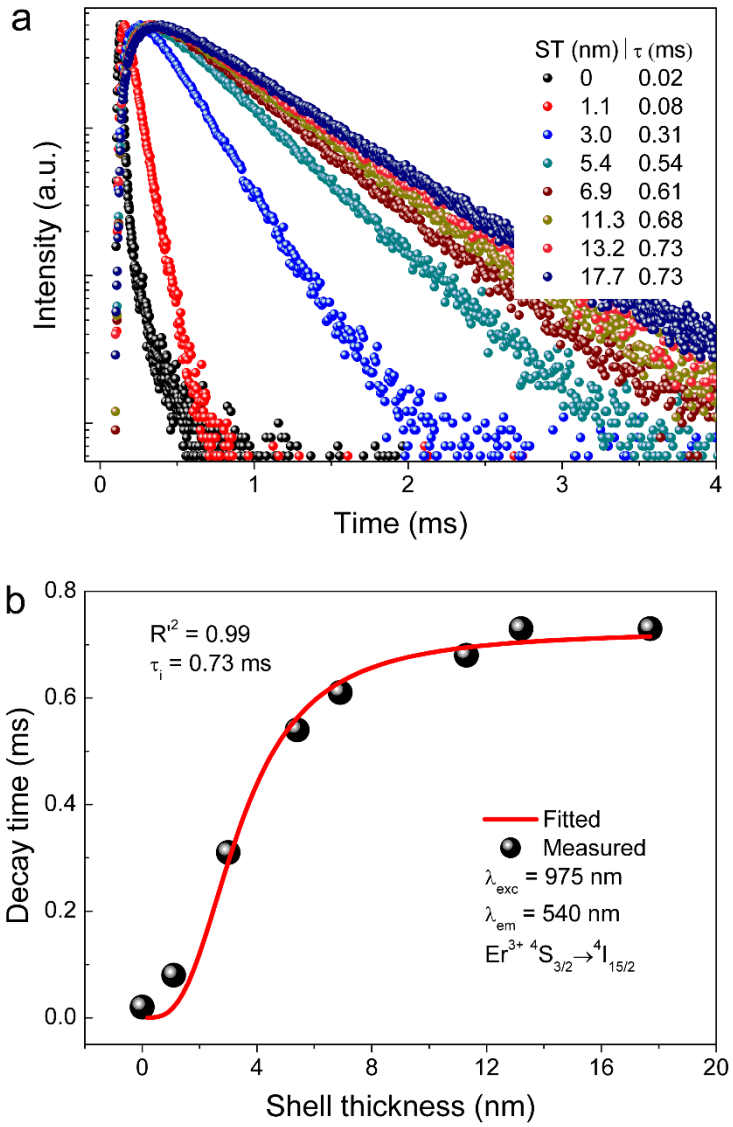

Figure S7. (a) Time-dependent Er^{3+} $^4S_{3/2}$ emissions of nanocrystals with various shell thickness after 975 nm excitation. (b) Er^{3+} $^4S_{3/2}$ lifetimes of nanocrystals are fitted with Equation 1. The coefficient of determination R'^2 is 0.99, and the fitting intrinsic lifetime τ_i is 0.73 ms.

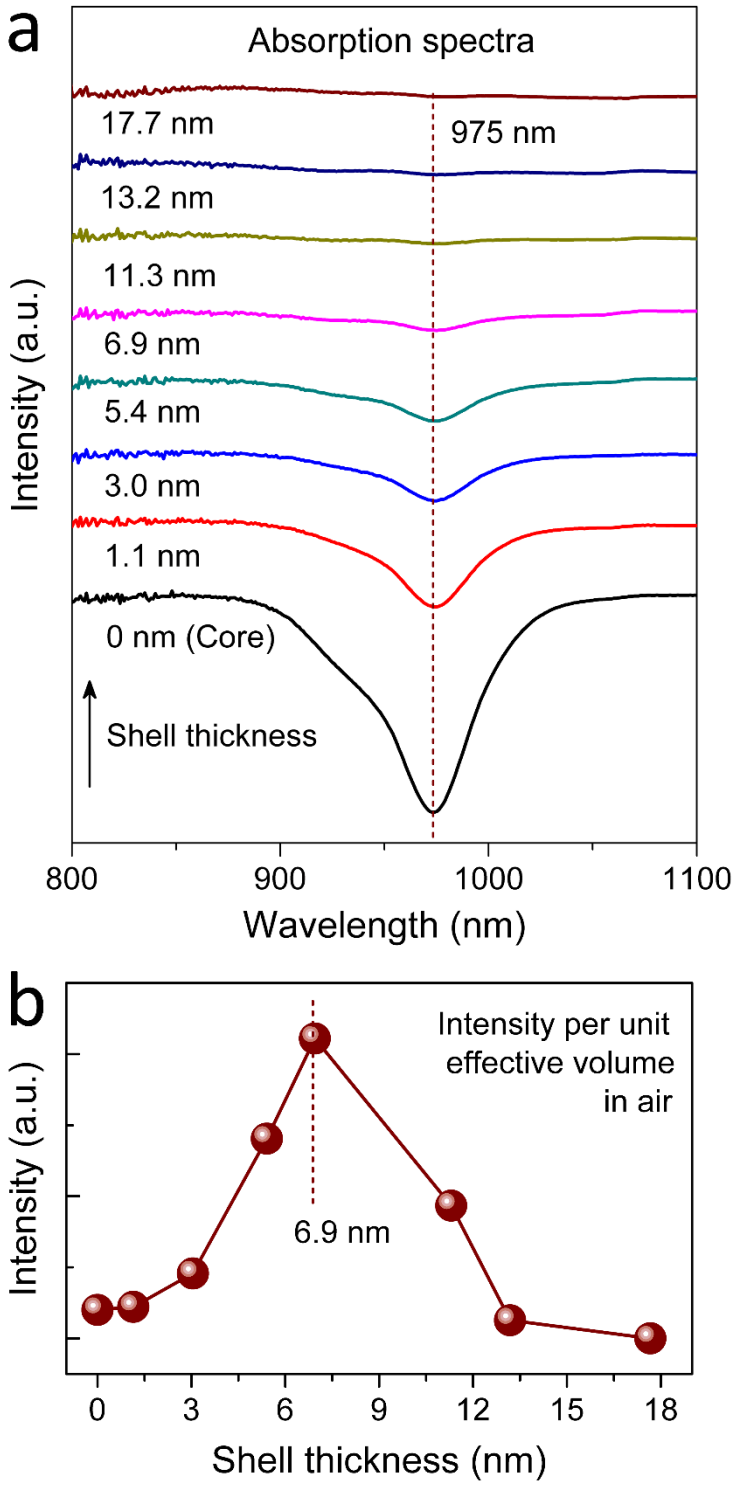

Figure S8. (a) Absorption intensities of all samples at 975 nm were obtained by a Cary 5000 UV-vis-NIR spectrophotometer. (b) The absorption intensity per unit effective

volume in air.

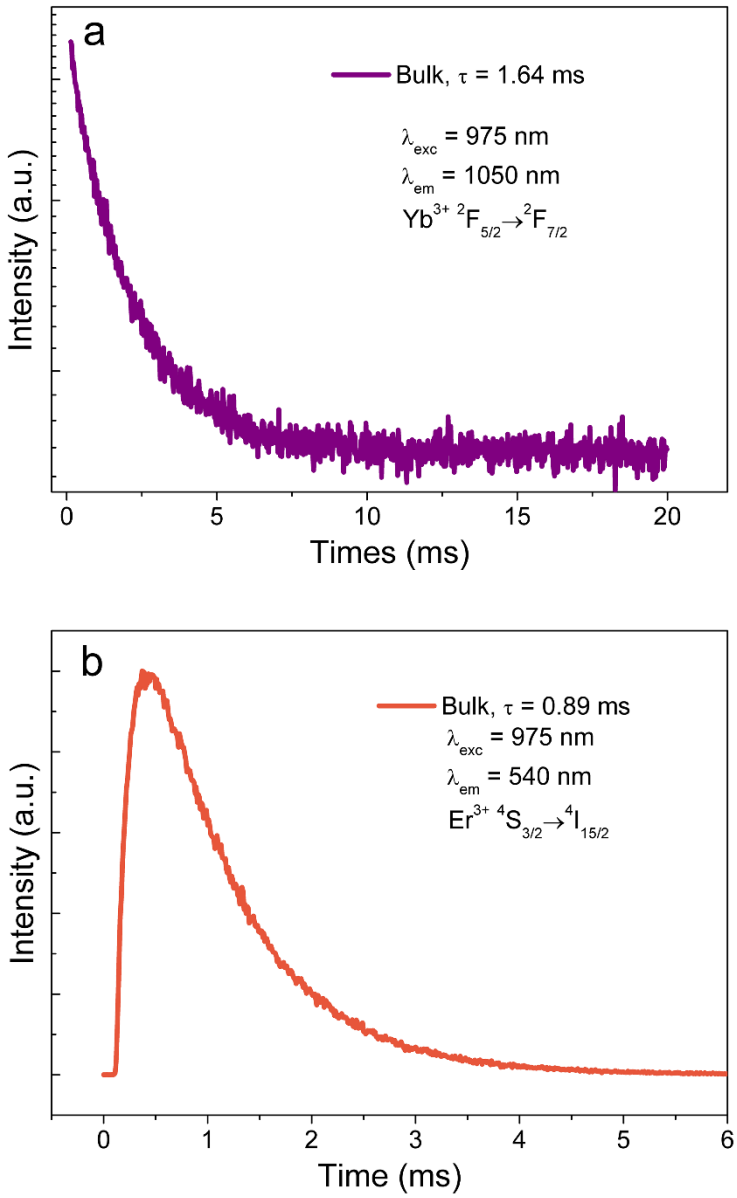

Figure S9. Decay times of bulk materials ($NaYF_4$:20%Yb/2%Er) for (a) Yb^{3+} $^2F_{5/2}$ emission at 1050 nm and (b) Er^{3+} $^4S_{3/2}$ emission at 540 nm, respectively.

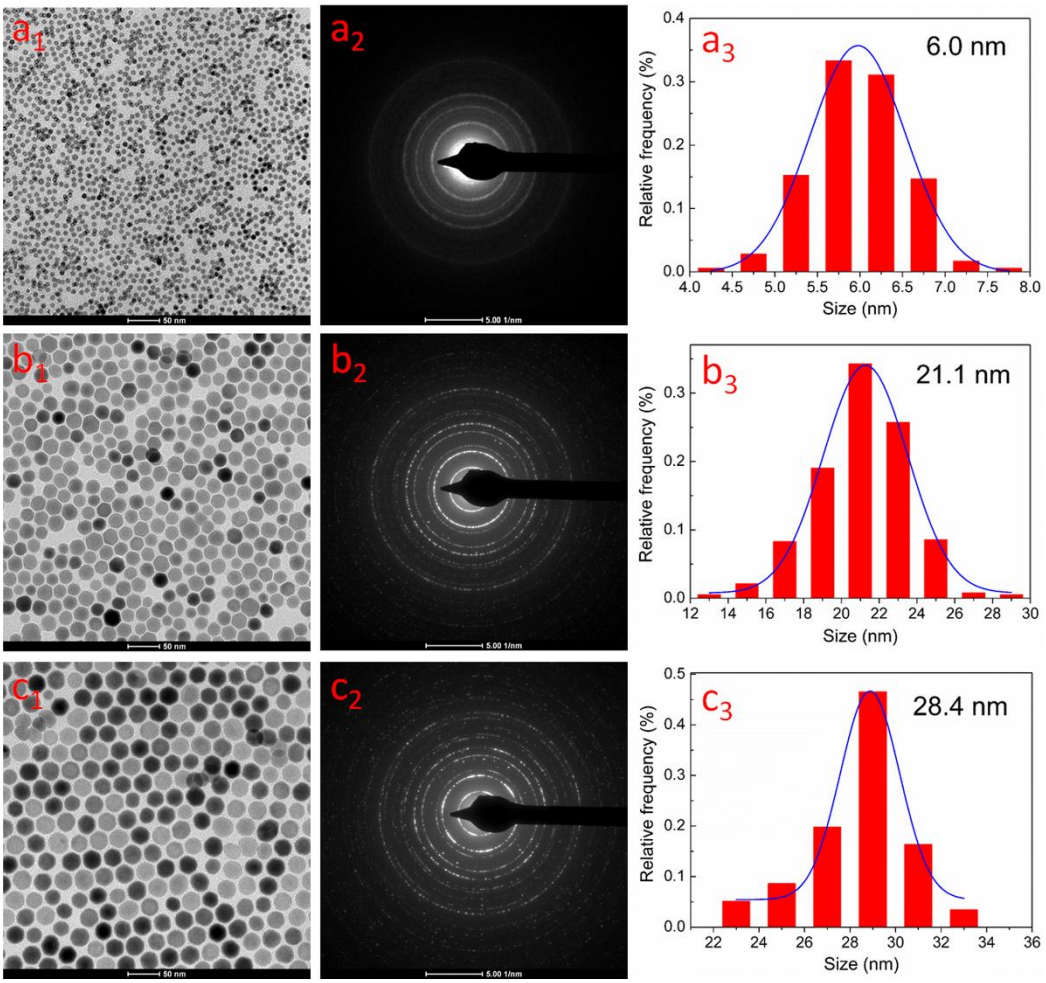

Figure S10. TEM images, selected area electron diffraction patterns, and size histograms of ($a_{1\text{-}3}$) Na91%YbF_4:9%Er core-only nanocrystals (~6.0 nm), ($b_{1\text{-}3}$) Na91%YbF_4:9%Er@$NaGdF_4$ core/shell nanocrystals (~21.1 nm), and ($c_{1\text{-}3}$) Na91%YbF_4:9%Er@$NaGdF_4$ core/shell nanocrystals (~28.4 nm), respectively. Noting that all samples have the same-sized Na91%YbF_4:9%Er core.

E. References

(1) Abel, K. A.; Boyer, J.-C.; Veggel, F. C. J. M. v. Hard Proof of the $NaYF_4/NaGdF_4$ Nanocrystal Core/Shell Structure. *J. Am. Chem. Soc.* **2009,** *131*, 14644–14645.

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