

Supplemental Information for

Efficient sub-15 nm cubic-phase core/shell upconversion nanoparticles as reporters for ensemble and single particle studies

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Materials: Rare-earth oxides Er_2O_3 , Y_2O_3 , and Yb_2O_3 , sodium trifluoroacetate (NaTFA), and trifluoroacetic acid (TFA) were purchased from Aladdin Chemistry Co. Ltd. Oleic acid (OA, >90%), oleylamine (OM, >70%), and 1-octadecene (ODE, >90%), were obtained from Sigma-Aldrich Co. LLC and hexane and ethanol from Beijing Chemical Reagents, China. All materials were used as received without further purification.

Synthesis of $\alpha\text{-NaYbF}_4$: $x\%$ Er^{3+} cores ($x=5, 7, 12, 25$): 1 mmol RE_2O_3 (RE= Yb, Er) with a Yb/Er molar ratio of (100-x):x were added to a 250 ml flask containing 5 ml deionized water and 5 ml TFA. The reaction mixture was heated to 95 °C for one hour. Then the clear solution was evaporated to yield $\text{RE}(\text{TFA})_3$ as a dry powder. Next, 8 ml OA, 8 ml OM, 12 ml ODE, and 2 mmol NaTFA were added to the flask. The reaction mixture was heated to 120 °C for 30 min to remove water and oxygen under argon gas atmosphere, yielding a transparent solution, which was then heated to 300 °C at a heating rate of 12 °C/min and maintained under argon atmosphere for 30 min. Subsequently, the solution was cooled to room temperature and excess ethanol was added to precipitate the nanoparticles, which were removed by centrifugation and then redispersed in hexane.

Synthesis of $\alpha\text{-NaYbF}_4$: x mmol % Er^{3+} @ CaF_2 nanoparticles ($x=5, 7, 12, 25$): 2 mmol CaO were added to 5 ml deionized water and 5 ml TFA to obtain $\text{Ca}(\text{TFA})_2$. Then 0.5 mmol $\alpha\text{-NaYbF}_4$, 7 ml OA and 7 ml ODE were added to the flask. The reaction mixture was heated to 120 °C for 30 min to remove hexane, water, and oxygen under argon gas purge. Subsequently, the reaction mixture was heated to 300 °C at a heating rate of 12 °C/min and maintained 60 min under argon atmosphere. The solution was cooled to room temperature and ethanol was added. The resulting nanoparticles were purified by several precipitation-redispersion-washing cycles.

Characterizations: Transmission electron microscopic (TEM) measurements to determine the size and morphology of the UCNPs were done with a Tecnai G2 Spirit Twin 12 microscope using an as-prepared

UCNP dispersion dropped onto the surface of a copper grid and dried. Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/max- γ B diffractometer with a scanning rate of 1° min^{-1} in the 2θ range of $10\text{--}80^\circ$.

Determination of the quantum yield of the upconversion luminescence (Φ_{UC}): The P -dependent Φ_{UC} of the dispersed UCNP was determined with the calibrated integrating sphere setup from the ratio of the number of emitted photons in the wavelength region of 400-860 nm and the number of absorbed photons in the wavelength region of 962-982 nm, where the samples were excited. Both numbers were derived from spectrally corrected integrated intensities / photon fluxes. The design of the integrating sphere setup was previously reported¹.

Single particle widefield imaging: Single-particle measurements were done with a custom-made microscopic setup system. The 980 nm laser used for UCNP excitation was coupled into the optical path of a microscope through a multimode fiber (200 m) and passed through an 800 nm long-pass filter and a 500 mm focal length B-coated lens, followed by a A-coated 7:3 (reflexion (R): transmission (T)) beamsplitter and a 100X 1.4NA Oil objective onto the sample. The measurements were done with 100 ng/ml UCNPs dispersed in hexane that were spin-coated onto a coverslip. The widefield fluorescence images shown were corrected for the laser illumination profile.

Atomic force microscopy: A scanning AFM (Nanowizard III, JPK Instruments) was used for the measurements, which was operated in the AC mode to acquire the distribution and size of the UCNPs on the coverslip. The measurements were done with diluted UCNP dispersions spin-coated onto a cover slip.

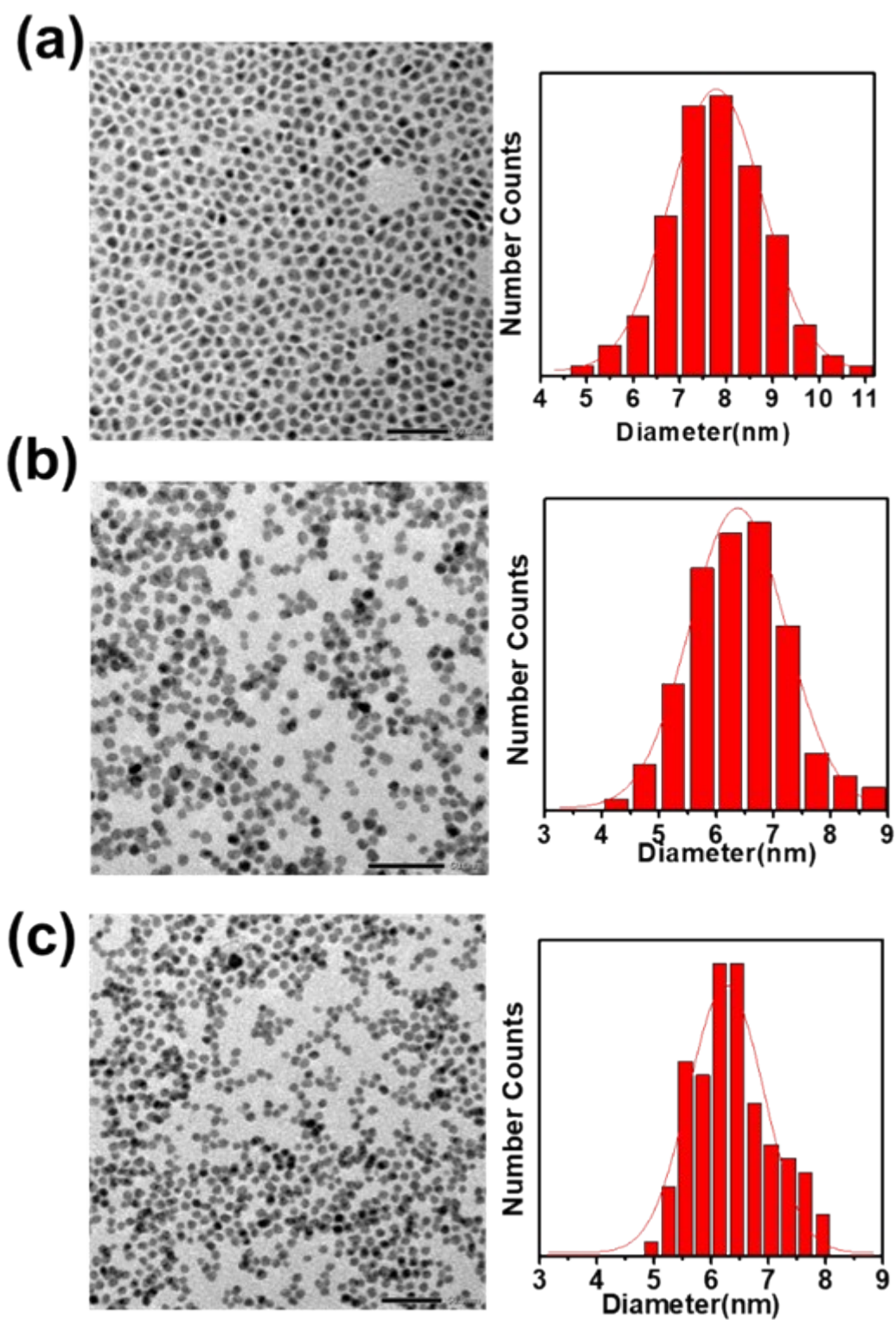


Figure S1. TEM images and histograms of size distribution of the $\text{NaYbF}_4: x\% \text{Er}^{3+}$ ($x = 7, 12, 25$) upconversion nanoparticles (UCNPs). All synthesized core NPs have almost identical shape and size, indicating the dopant concentration of Er^{3+} has a negligible effect on the particle morphology.

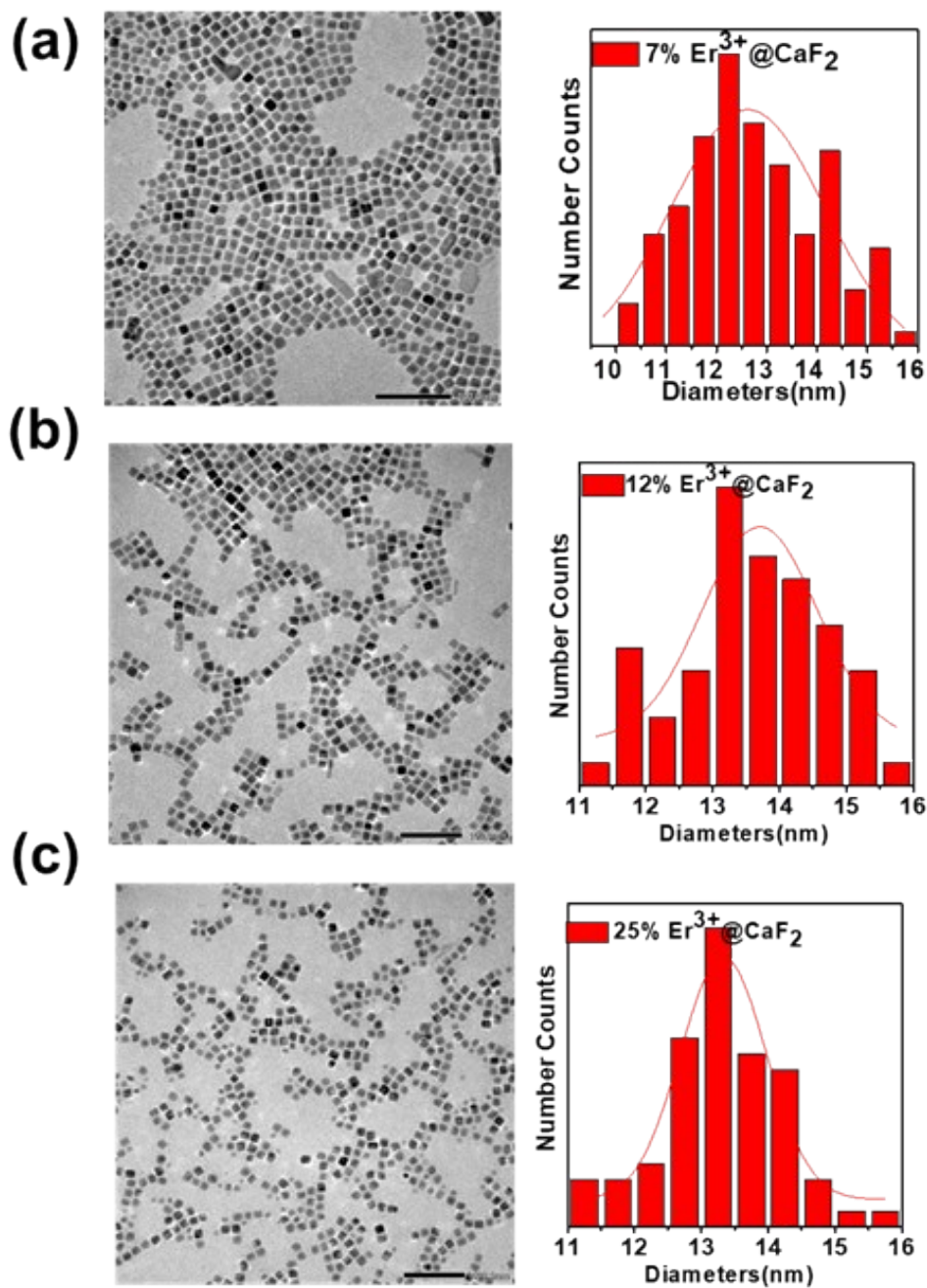


Figure S2. TEM images and histograms of size distribution of the NaYbF₄: x% Er³⁺ @CaF₂ (x=7, 12, 25) core/shell UCNPs. After coating with a CaF₂ shell, the size of the core/shell NPs is 11.75 nm, 12.6 nm, 13.3 nm, and 13.5 nm.

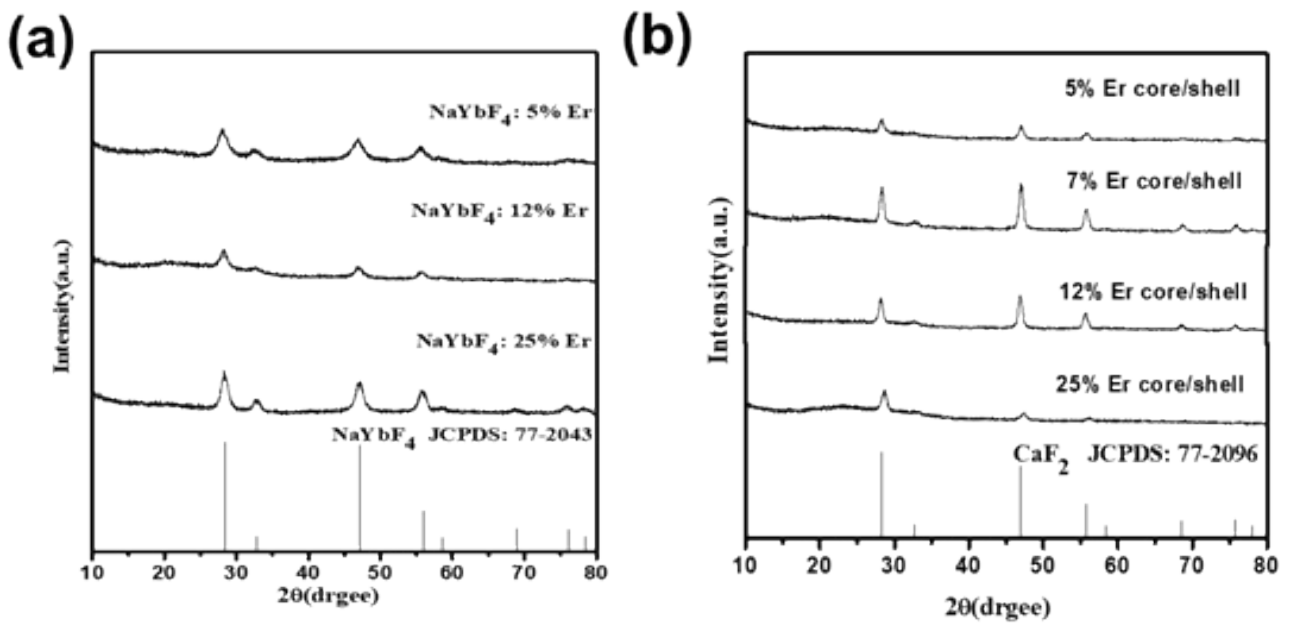


Figure S3. (a) XRD patterns of NaYbF₄: x% Er³⁺ and NaYbF₄: x% Er³⁺@CaF₂ (x=5.0, 7.4, 12.4, 25.2) UCNPs and the standard NaYbF₄ (JCPDS No. 77-2043) and CaF₂ (JCPDS No. 77-2096) are included.

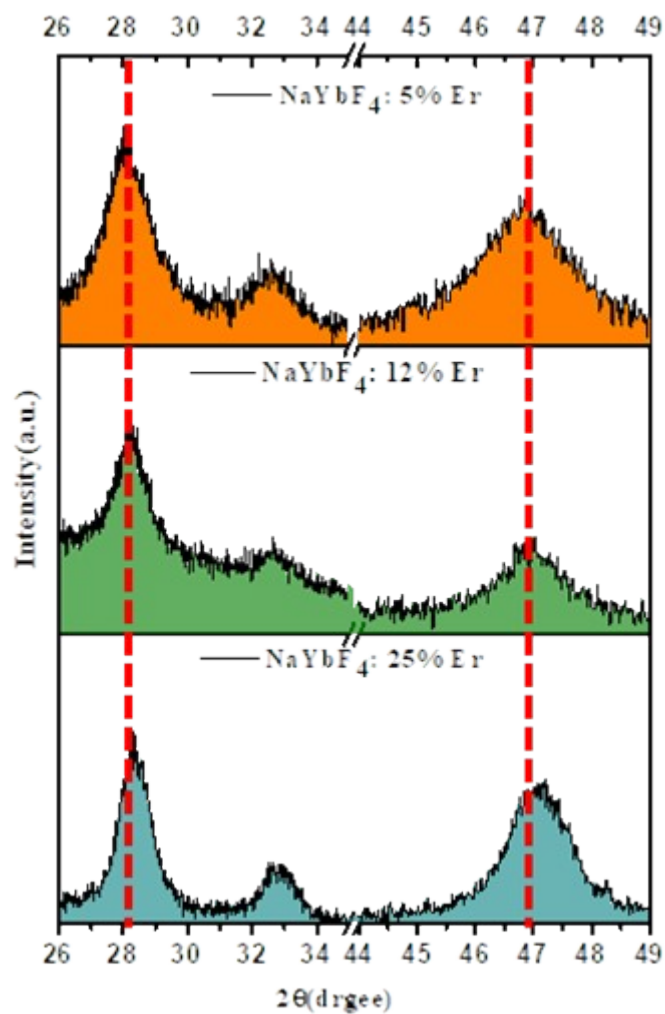


Figure S4. XRD reflex (220) in the reflection angle range of 26 ° - 49 ° of the core $\text{NaYbF}_4:x\% \text{Er}^{3+}$ - series ($x = 5, 12, 25$); reference 46.9 ° reflection of JCPDS:77-2043. With increasing of Er^{3+} ions doping concentration, the reflection angle range between 26° and 49° begins shifting to higher angles.

**here we chose 220 instead of 111 due to background/scatter signals towards angles < 28 ° (@ sample 5%)*

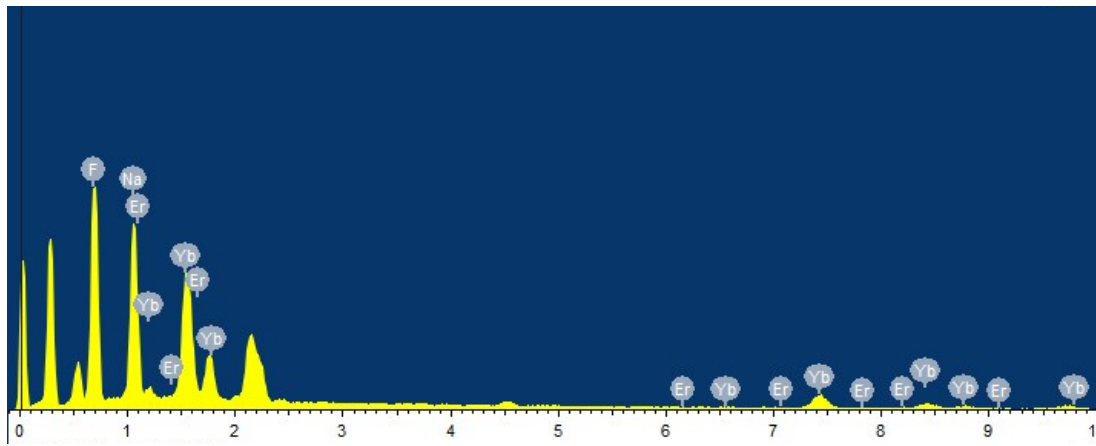


Figure S5 Energy dispersive spectrum (EDS) of core-only NaYbF₄: 5% Er³⁺ UCNPs. The presence of Na, F, Yb and Er in the UCNPs was confirmed.

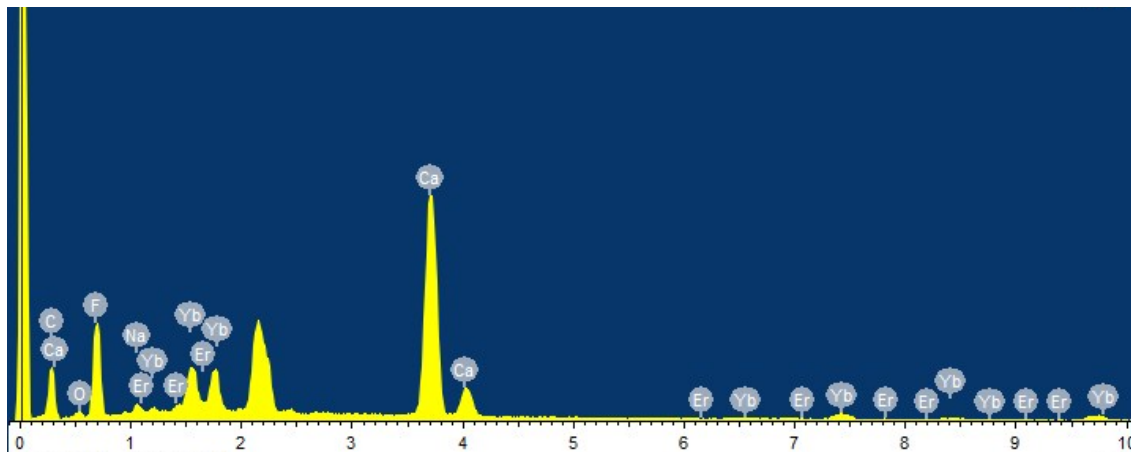


Figure S6 Energy dispersive spectrum (EDS) of NaYbF₄: 5% Er³⁺ @ CaF₂ nanoparticles. The presence of Na, F, Yb and Er in the UCNPs was confirmed, thereby demonstrating the formation of core/shell UCNPs.

Table S1 Determination of the Yb(ppm), Er(ppm), Ca(ppm) and Na(ppm) content of the differently doped NaYbF₄:X%Er³⁺@CaF₂ UCNPs and the calculated Yb and Er molar concentrations in the core/shell NPs doped with different Er³⁺ concentration.

sample	measured concentration via ICP-AES				Calc. RE mol fraction			
	X%Er ³⁺	Ca (ppm)	Na (ppm)	Er (ppm)	Yb (ppm)	Yb (mmol%)		X _{Er} (mmol%)
5		9.311	2.291	0.444	8.598	95%	5.0%	5
7		14.49	2.606	0.754	9.729	92.6%	7.4%	7
12		14.33	2.346	0.898	6.556	87.6%	12.4%	12
25		10.66	2.077	2.129	6.532	74.8%	25.2%	25

Table S2 Calculated number of unit cells in the core-only UCNPs and the shelling layer. Calculated core size and shell thickness using results from Figure S2 / TEM data Figure 1, NaYbF₄-unit cell size and ICP-AES results (assuming a perfect sphere)

Sample	Diameter (TEM)	N _{unit}	core amount	Shell amount	N _{unit,core}	N _{unit,shell}	Core diameter (calc)	Shell thickness (calc)
X _{Er}	[nm]		χ _{core}	χ _{shell}			[nm]	[nm]
5	11.75	5210	0.40	0.60	2064	3146	7.1	2.3
7	12.6	6272	0.33	0.67	2042	4231	7.7	2.4
12	13.3	9791	0.29	0.71	2840	6951	6.5	3.4
25	13.5	8812	0.33	0.67	2873	5939	6.3	3.7

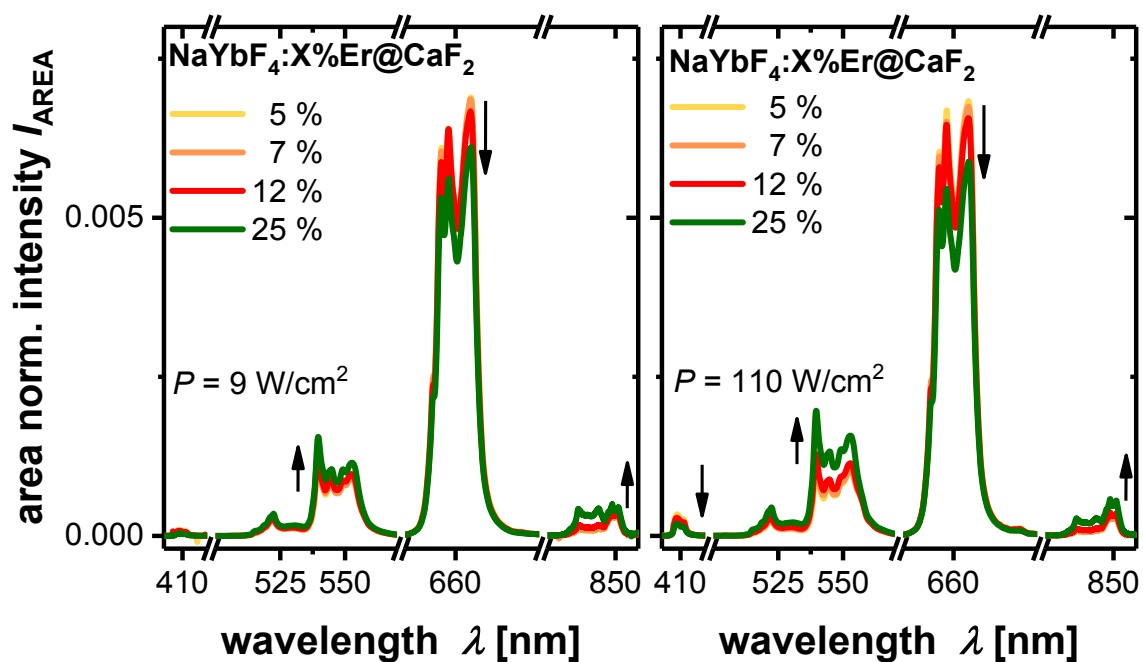


Figure S7. Area-normalized upconversion luminescence (UCL) spectra of $\text{NaYbF}_4: X\% \text{Er}^{3+} @\text{CaF}_2$ (left) measured at excitation power densities (P) of 9 Wcm^{-2} ($P_{\text{semi-nsat}}$) and (right) at 110 Wcm^{-2} (P_{sat}); excitation was at 980 nm . All samples with different Er^{3+} doping concentrations showed a stronger red emission. At a high Er^{3+} concentration, the emission intensity decreases due to the cross relaxation.

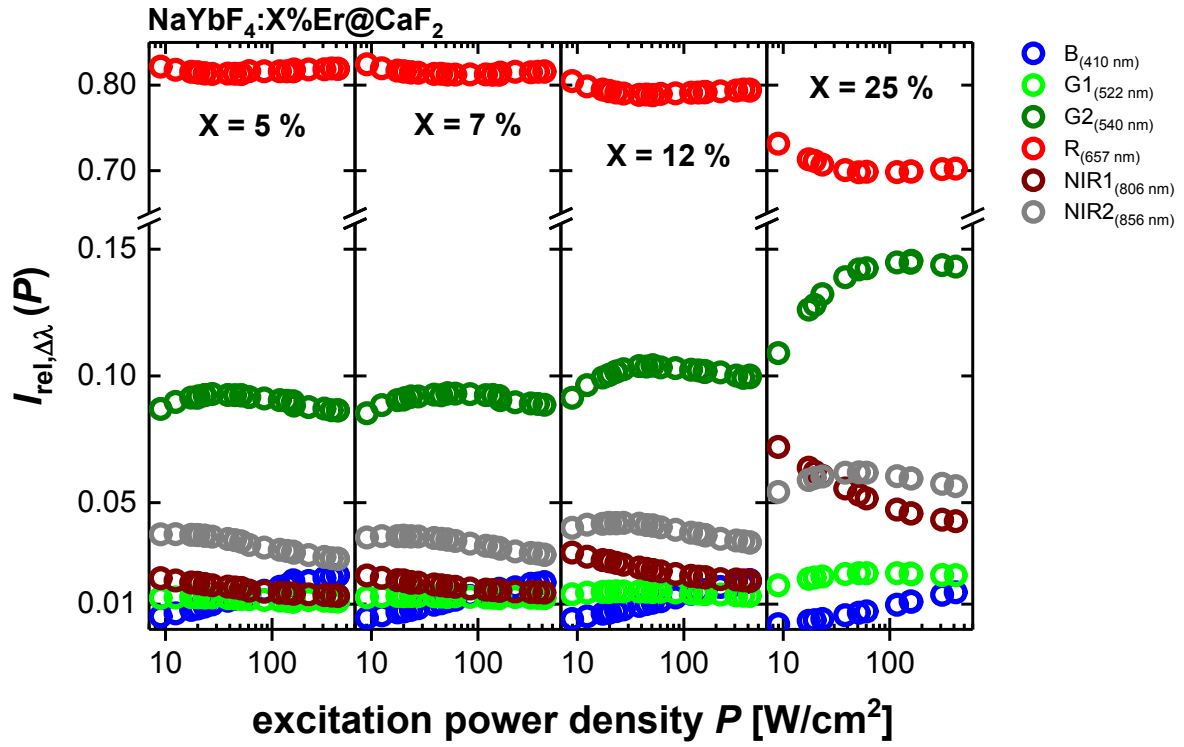


Figure S8. Relative spectral distribution of the UCL emission bands for Er³⁺ doping concentrations $x = 5, 7, 12,$ and 25% ; excitation was at 980 nm . The relative spectral distribute of red emission($R_{657\text{nm}}$) decreased with increasing Er³⁺ concentrations, while the green ($G2_{540\text{ nm}}$) and NIR emission (NIR1_{806nm} NIR2_{856nm}) increased, which has been reported before for quenched upconversion nanoparticles^{S1}.

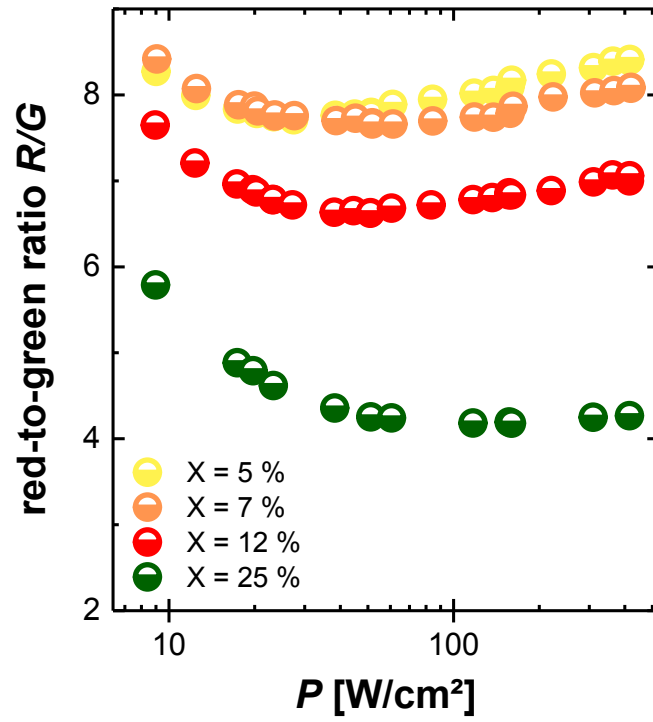


Figure S9. P -dependent red-to-green ratio for Er³⁺ doping concentrations $x = 5, 7, 12,$ and 25% ; excitation was at 980 nm. The red-to-green ratio of NPs gradually decreased with the increasing of Er³⁺ concentration.

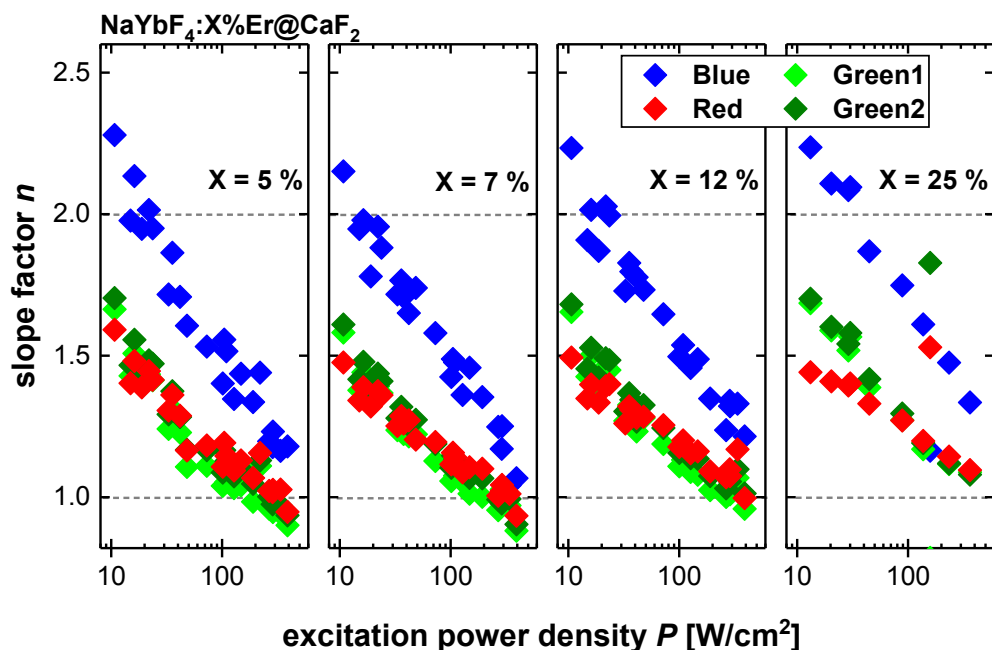


Figure S10. P -dependent slope factors of the core/shell NPs for Er^{3+} doping concentrations $x = 5, 7, 12,$ and 25% . At low P value, the slope values of the red and green emission of all UCNPs are between 1 and 2. While, at high P the slope values of NPs with a doping concentration of 5% and 7% are below 1, which indicates that a saturation occurs easier at low Er^{3+} concentration. At low P , the slope values of red and green values for a doping concentration of 5% and 7% are almost identical, while at higher Er^{3+} concentrations, the slope value of the green emission exceeds than that of the red emission, which corresponds to the increased green emission.

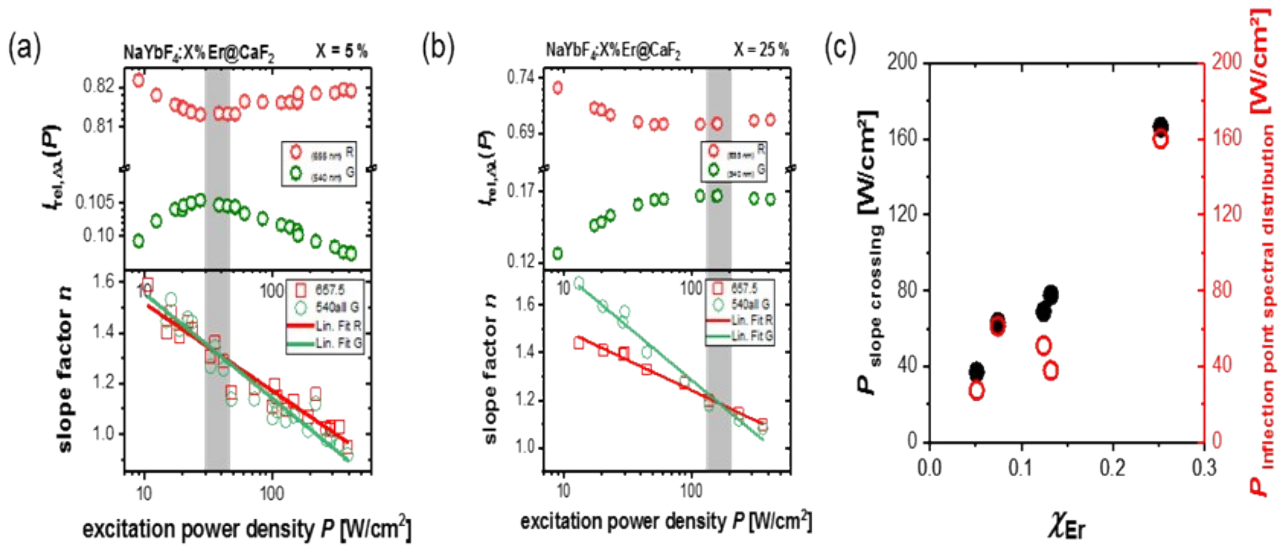


Figure S11. Correlation of the slope factors of the green and red UCL and the relative spectral distribution of both emission bands. (a-b) Relative spectral distribution of the green and red emission bands (top) and their corresponding slope factors (bottom) (a) $x = 5\%$, (b) $x = 25\%$, (c) red-green crossing points derived from the slopes (black) and the inflection points of the spectral distribution of the red and green emission (red) for Er^{3+} doping concentrations $x = 5, 7, 12, \text{ and } 25\%$ determined from the data shown in panels (a) and (b).

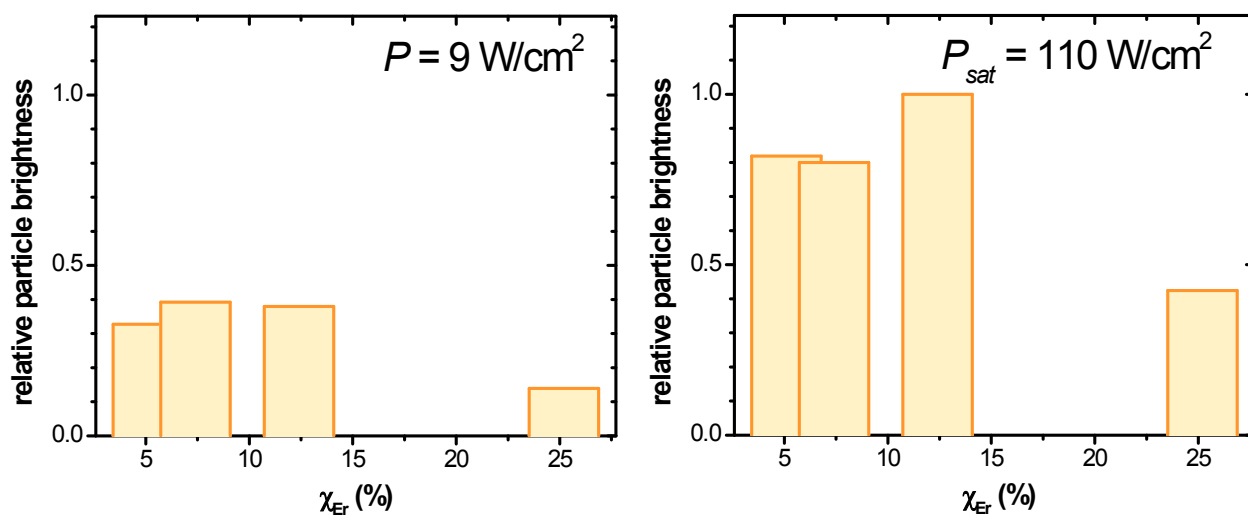


Figure S12 Relative brightness of NaYbF₄: x% Er³⁺ @CaF₂ particles (Er³⁺ doping concentrations x= 5, 7, 12, and 25 %) determined at $P = 9 \text{ W/cm}^2$ (left) and at a saturation power density $P = 110 \text{ W/cm}^2$ (right). The values were calculated considering the particle sizes and doping concentrations determined by us. All results are presented relative to the maximum value (x = 15) at $P = 110 \text{ W/cm}^2$.

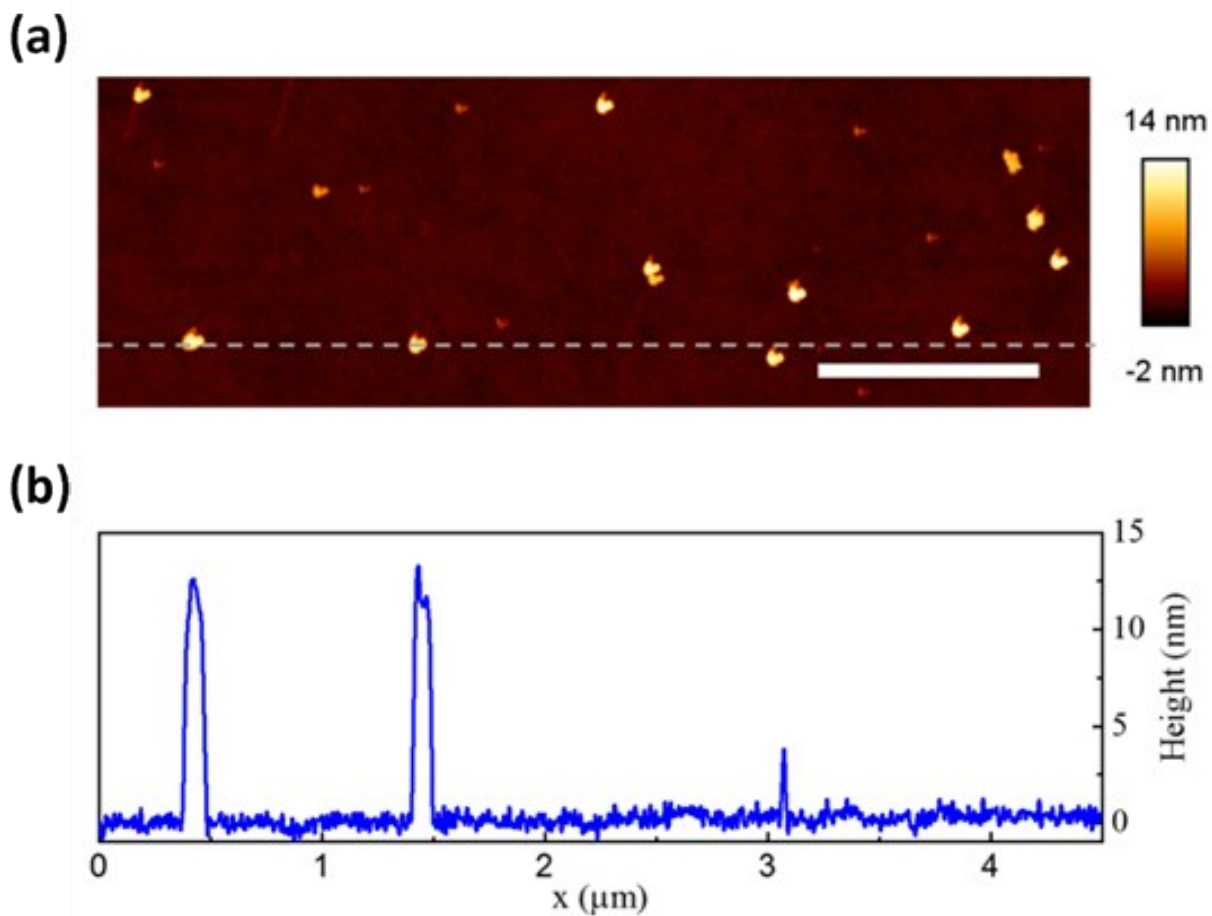


Figure S13 (a) AFM measurements of the core/shell structure UCNPs. Scale bar, 1 μm . (b) The height representation of the white dot line in (a).

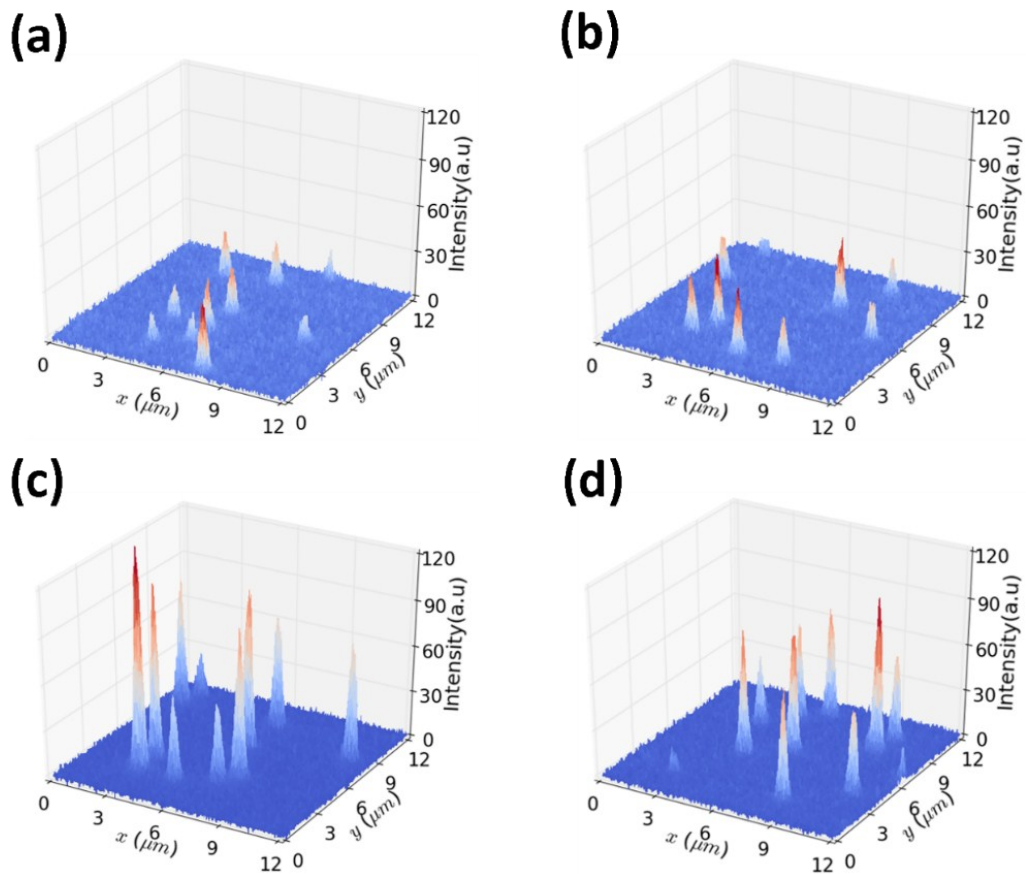


Figure S14 Three-dimensional representation of the widefield UCL images determined at $P = 10 \text{ kW/cm}^2$ of $\text{NaYbF}_4: x\% \text{Er}^{3+} @ \text{CaF}_2$ ($x = 5\%$ (a), 7% (b), 12% (c), 25% (d)) for excitation with a 980 nm laser. For each fluorescent image, the color shade scale linearly between the minimum and maximum intensities.

S1. C. Würth, M. Kaiser, S. Wilhelm, B. Grauel, T. Hirsch and U. Resch-Genger, *Nanoscale*, 2017, **9**, 4283-4294.