Supporting Information

Direct imaging the upconversion nanocrystal core/shell structure at the sub-nanometer level: shell thickness dependence in upconverting optical properties

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Methods

Chemicals. Anhydrous YCl_3 (99.99 %), anhydrous $GdCl_3$ (99.99 %), anhydrous $YbCl_3$ (99.9 %), anhydrous $ErCl_3$ (99.9 %), NaOH (> 98 %), NH_4F (> 98 %), 1-octadecene (90 %), oleic acid (90 %) were purchased from Sigma-Aldrich. 1,2-Disteraroyl-sn-glycero-3-phosphoethanolamine-N-[carboxy (polyethylene glycol)-2000] (DSPE-PEG) was purchased from Avanti Polar Lipids. Unless otherwise noted, all chemicals were used as received without further purification.

Synthesis of $NaYF_4$: 20%Yb,2%Er core nanocrystals. In a typical method for the synthesis of $NaYF_4$: 20%Yb,2%Er nanocrystals, 0.78 mmol of anhydrous YCl_3, 0.20 mmol of $YbCl_3$ and 0.02 mmol of $ErCl_3$ were added to a 100-mL flask containing 10 mL of oleic acid and 15 mL of 1-octadecene. The mixture was heated at 150 ^oC for 30 min before cooling down to 50 ^oC to remove the water content from the solution. Shortly thereafter, 10 mL of methanol solution containing NH_4F (2.75 mmol) and NaOH (2.5 mmol) was added and the resultant solution was stirred for 30 min to remove the methanol. After the methanol was evaporated, the solution was heated to 300 ^oC under argon for 1 h and then cooled down to room temperature. The resulting nanoparticles were precipitated by addition of ethanol, collected by centrifugation at 6000 rpm for 5 min, washed with ethanol several times, and re-dispersed in 10 mL of cyclohexane.

Synthesis of $NaYF_4$: 20%Yb,2%Er@$NaGdF_4$ core-shell nanocrystals with 1 ML $NaGdF_4$ shell by SILAR procedure.

With the $NaYF_4$: 20%Yb, 2%Er@$NaGdF_4$ core/shell nanocrystal with 1 ML $NaGdF_4$ shell growth as an example, 0.139 mmol of $GdCl_3$ was added to a 100-mL flask containing 10 mL of oleic acid and 15 mL of 1-octadecene. The mixture was heated at 150 ^oC for 30 min before cooling down to 50 ^oC to remove the water content from the solution. Then the $NaYF_4$: 20%Yb,2%Er core nanocrystals in 10 mL of cyclohexane were added with a methanol solution (10 mL) containing NH_4F (0.38 mmol) and NaOH (0.348 mmol). The resultant solution was stirred for 30 min to remove the methanol. After the methanol was evaporated, the solution was heated to 300 ^oC under argon for 1 h and then cooled down to room temperature. The resultant nanoparticles were precipitated by addition of ethanol, collected by centrifugation at 6000 rpm for 5 min, washed with ethanol several times, and re-dispersed in 10 mL of cyclohexane. The above procedure was repeated to further deposition another monolayer. The dose per layer was listed in the Table S2 according to the calculation.

Synthesis of $NaYF_4$: 20%Yb,2%Er@$NaGdF_4$ core-shell nanocrystals with 6 ML $NaGdF_4$ shell by one-step coating procedure. 1.034 mmol of $GdCl_3$ (Calculated from Table S1) was added to a 100-mL flask containing 10 mL of oleic acid and 15 mL of 1-octadecene. The mixture was heated at 150 °C for 30 min before cooling down to 50 °C to remove water from the solution. Then the $NaYF_4$: 20%Yb,2%Er core nanocrystals (1 mmol) in 10 mL of cyclohexane were added along with a methanol solution (10 mL) of containing NH_4F (3.52 mmol) and NaOH (2.59 mmol). The resultant solution was stirred for 30 min to remove the methanol. After the methanol was evaporated, the solution was heated to 300 °C under argon for 1 h and then cooled down to room temperature. The resultant nanoparticles were precipitated by addition of ethanol, collected by centrifugation at 6000 rpm for 5 min, washed with ethanol several times, and re-dispersed in 10 mL of cyclohexane.

UC nanocrystals surface modification with lipid. DSPE-PEG and UC nanocrystals were mixed in a 5000 : 1 molar ratio in chloroform, after complete evaporation of the chloroform under a slight vacuum, the residue was heated at 80 °C and 1.0 mL of water was added to obtain an optically clear suspension containing DSPE-PEG micelles. Since this suspension contained both empty micelles and those containing UC nanocrystals, the empty micelles were removed with ultracentrifugation at 500,000 g for 2 h. The micelles containing UC nanocrystals formed a pellet while the empty micelles stayed suspended. The supernatant was discarded and the UC nanocrystals-micelles were resuspended in water.

Materials Characterization. Powder X-ray diffraction (XRD) data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochro-matized CuKα radiation (1.5406 Å). Upconverted

PL measurements were done on a home-made fluorescence spectrometer. Excitation light with wavelength 970 – 980 nm was generated by a continuous wave (CW) Ti: Sapphire laser (Spectra physics 3900S) pumped by an Ar^+-laser (Spectra physics BeamLock 2060). The near-infrared (NIR) laser output passed through a long wavelength-pass filter (Newport LP830) to remove visible and NIR fluorescence of the Ti: Sapphire crystal and neutral density filter wheel which was used to adjust the excitation beam power. The laser beam was focused on the sample by a lens with long focal distance of 15 cm. The upconverted fluorescence was collected at 45 ^{o} by a two-lens system and focused on the entrance slit of a spectrograph (Acton Research SpectraPro-500). NIR light scattered by the sample was blocked by short wavelength-pass filter (Newport KG3). The luminescence was dispersed by the spectrograph and detected by a TE-cooled CCD camera (Roper Scientific PIXIS-400). The power density of the 980 nm excitation was 10 W/cm^2.

Measurements for cryo-transmission electron microscopy (Cryo-TEM). An JEOL JEM-2100F (field-emission-gum) transmission electron microscope (TEM) equipped with a post-column Gatan imaging filter (GIF-tridium) was used for EELS measurements and TEM imaging. Acceleration voltage was 200 kV and point resolution *ca* could reach 0.20 nm. The energy resolution was 0.85 eV, determined by the full-width at half-maximum (FWHM) of the zero-loss peak. EELS spectra were recorded with a two-dimensional back-illuminated charge-coupled device camera (4000 × 2700 pixels) with a low read-out noise of three count r.m.s. and a negligible dark count noise. To avoid electron channeling effects, the selected grain was tilted slightly off the zone axis by 1 – 2 º. The convergence angle was about 0.7 mrad ($q \approx 0.04$ Å^{-1}) and the collection angle was ~ 3 mrad ($q \approx 0.17$ Å^{-1}). EELS data were acquired with a dispersion of 0.3 per channel for chemical analysis. The cooling stage used was Gatan 636 Model with double-tilting function. High angle annular dark field imaging (HAADF) was carried out using Gatan 777 package (detector and soft), and JEOL-STEM scanning system (ASID-2000). The spherical and chromatic aberration coefficients (Cs and Cc, respetcively) of the objective lens were 0.5 and 1.1 mm, respectively. The annular dark-field detector for ADF-STEM ranged from 42 to 65 mrad. A digital micrograph software (Gatan) was used for image recording/processing.

The spherical concentric shell model (CSM) was employed to calculate the amount of shell precursor necessary for the growth of each monolayer (ML)[1]. This model has been used extensively for the hexagonal CdS and ZnS shell deposition during the quantum dots core/shell nanocrystal synthesis process[1]. Because of the highly symmetric structure of the CdS, the ML was inferred to a thickness equal to half the *c*-lattice parameter. Although the $NaGdF_4$ shell adopted here has also hexagonal structure ($P6_3/m$, a = 6.02 Å, c = 3.60 Å) [2], the cation sites are of three types. A onefold site occupied by RE^{3+}, another site occupied randomly by $1/2Na^+$ and $1/2RE^{3+}$, and a twofold site occupied randomly by Na^+ and vacancies[2]. Therefore, referral to a $NaGdF_4$, the ML can be taken to mean a thickness equal to the *c*-lattice parameter of the bulk material, 0.36 nm in the case of the hexagonal $NaGdF_4$ (Figure S1). In order to realize these goals, we firstly synthesized hexagonal $NaYF_4$: 20%Yb, 2% Er core with the mean size of 15.70 nm. Next, the core was coated with the hexagonal $NaGdF_4$ shell layer adhering to the successive ion layer adsorption and reaction (SILAR) procedure[3].

The required $GdCl_3$ amount for every layer can be calculated by the following equations:

$$m_{layer(n)} = m_{particle(n)} - m_{particle(n-1)} = \rho(V_{particle(n)} - V_{particle(n-1)})$$

$$= \frac{3}{4}\pi\rho N * 10^{-21} * (r^3_{particle(n)} - r^3_{particle(n-1)}) \qquad (1)$$

Here $m_{layer(n)}$ represents the mass of layer n (n =1 – 10 in the present work), $m_{particle(n)}$, $V_{particle(n)}$ and $r_{particle(n)}$ represent the mass, volume and radius of the particle covered with n layers, respectively.

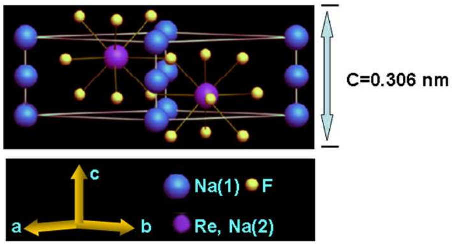
Attention should be paid to the “particle” we have used above, it doesn’t own the same composition of the particle we have synthesized, since the particle (n) consists of several kinds of materials. That can be expressed as $NaYF_4$: 20%Yb, 2%Er@$NaGdF_4$, while the ‘particle’ model here only owns a consistent value of ρ, so the value of $m_{particle(n)}$ don’t represent the true mass of the particle.

What we concern about is only the mass of each single layer of the shell, so if we use the true ρ (of the material of the layer) and *V* at the same time, we can get the true value of $m_{layer(n)}$.

Density of the $NaYF_4$ core and $NaGdF_4$ shell materials (ρ), particle number of one molar (N) are calculated as follows:

$$\rho = \frac{m}{v} = \frac{M * n}{c * \frac{\sqrt{3}}{2} a^2} = \frac{M * N'}{N_A * c * \frac{\sqrt{3}}{2} a^2} \tag{2}$$

Here *M* represents relative molecular mass of the material of the shell ($NaGdF_4$), *N´* means the number of $NaGdF_4$ units that one crystal cell contains and according to this following picture, *N´*=1.5



For $NaYF_4$, cell parameter is a = 5.96 Å, c = 3.53 Å, molecular weight (M) = 187.9, and ρ = 4.31 g/cm^3.

For $NaGdF_4$, the cell parameter is a = 6.02 Å, c = 3.60 Å, molecular weight (M) = 256.3, and ρ = 5.65 g/cm^3.

$$N = \frac{v_{per\ molar}}{v_{per\ particle}} = \frac{\frac{M_1}{\rho_1}}{\frac{4}{3}\pi r_0^3} = \frac{\frac{M_0}{\rho_0}}{\frac{4}{3}\pi r_0^3} = 2.15 \times 10^{19} \tag{3}$$

Here, r_0 = 7.85 nm, M_1, ρ_1 belong to the doped core ($NaYF_4$:Yb, Er) while M_0, ρ_0 belong to the undoped one ($NaGdF_4$), since there is no difference between the structures, their M_0/ρ value are equal.

According to equation (1), (2), (3), the expression of $m_{layer(n)}$ is demonstrated as follows:

For $NaYF_4$: 20%Yb, 2% Er: $m_{layer} = 0.509 * (r^3_{particle(n)} - r^3_{particle(n-1)})$

Table S1. Statistics obtained from analysis of the histograms corresponding to the particle sizes for samples 1-7 at various stages of $NaGdF_4$ shell grown

sample	$NaGdF_4$ ML	Measured d_m (nm)	Predicted d_p (nm)	d_m - d_p (nm)	σ (%)
1	0	15.70±2.00	□	□	12.1
2	2	17.42±2.10	17.14	+0.28	12.1
3	4	18.98±2.27	18.58	+0.40	12.0
4	6	20.58±2.43	20.02	+0.56	11.8
5	8	22.12±2.49	21.46	+0.66	11.3
6	10	23.83±2.56	22.90	+0.93	10.7
7	6	19.11±3.32	20.02	+1.19	17.4

TableS2. Calculation for the $NaGdF_4$ shell grown from 1st to 10th layer.

	Doses per layer/mmolar	Particle radius/nm	Volume ratio of shell/core
0	0	7.85	0
1	0.139	8.21	0.144
2	0.151	8.57	0.301
3	0.165	8.93	0.472
4	0.178	9.29	0.657
5	0.193	9.65	0.858
6	0.208	10.01	1.073
7	0.223	10.37	1.305
8	0.239	10.73	1.554
9	0.256	11.09	1.820
10	0.273	11.45	2.103

Table S3. Standard atomic spacings for different kinds of $NaReF_4$ with their respective *hkl* indexes from the PCPDFWIN database, and the lattice mismatches between the hexagonal $NaYF_4$ and $NaGdF_4$ crystals.

hkl	**100**	**110**	**101**	**111**	**201**	**102**
$NaGdF_4$	5.210	3.010	2.976	2.314	2.115	1.713
$NaYF_4$	5.170	2.980	2.900	2.270	2.080	1.661
Mismatch	0.77%	1.00%	2.55%	1.90%	1.65%	3.04%

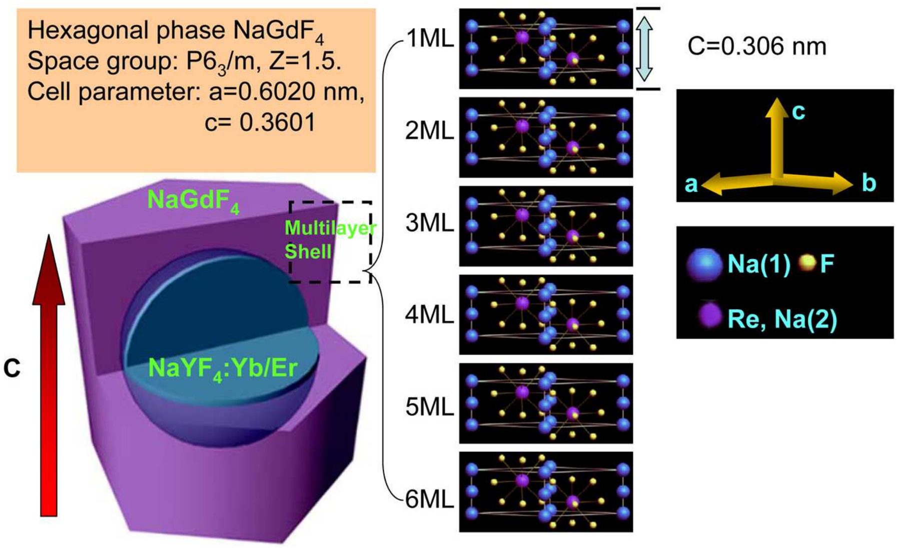


Figure S1. Schematic presentation and crystallographic data of the hexagonal-phase $NaYF_4$:Yb/Er@$NaGdF_4$ with 6 ML. A onefold site occupied by RE^{3+}, another site occupied randomly by $1/2Na^+$ and $1/2RE^{3+}$, and a twofold site occupied randomly by Na^+ and vacancies[2]. Referral to a $NaGdF_4$, ML can be taken to mean a thickness equal to the *c*-lattice parameter of the bulk material, 0.36 nm in the case of the hexagonal $NaGdF_4$. Throughout the growth process the nanocrystals maintain their initial quasi-spherical morphology except in the latter stages of shell growth for shell thickness larger than 4 MLs, where the nanocrystals begin to adopt a distinctly hexagonal shape.

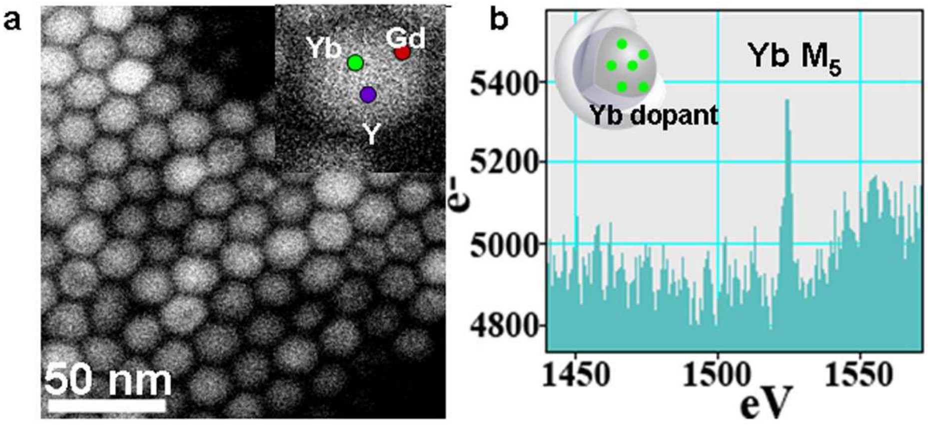


Figure S2. (a) HADDF-STEM image of the NaYF$_4$:Yb, Er@NaGdF$_4$ core/shell nanocrystals with 6 MLs. (b) EELS spectra of ytterbium M$_5$ edge taken from the probe location on the inferred NaYF$_4$:Yb, Er core (a) using the NaYF$_4$:Yb, Er@NaGdF$_4$ nanocrystal with 6 MLs NaGdF$_4$ shell. Yb M$_5$ edge signals (b) can be indicated when the EELS spectra taken from the probe location on the inferred NaYF$_4$:Yb, Er cores (a) (green colour).

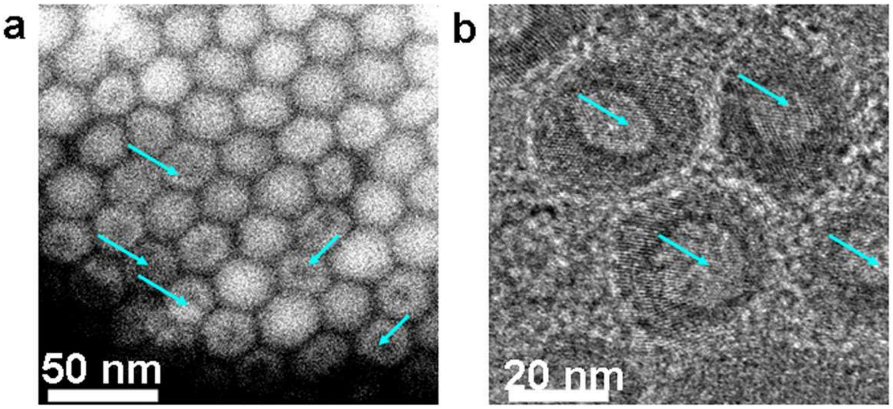


Figure S3. (a) HADDF-STEM image and Cryo-HRTEM images of the hexagonal NaYF$_4$:Yb, Er@NaGdF$_4$ core/shell nanocrystals with a 6ML shell taken at room temperature after 2 s irradiation. The hollow structure can be clearly observed under the electron-beam irradiation, therefore it's difficult to get the precise results because of the noticeable beam damage except the low temperature (96 K) is used.

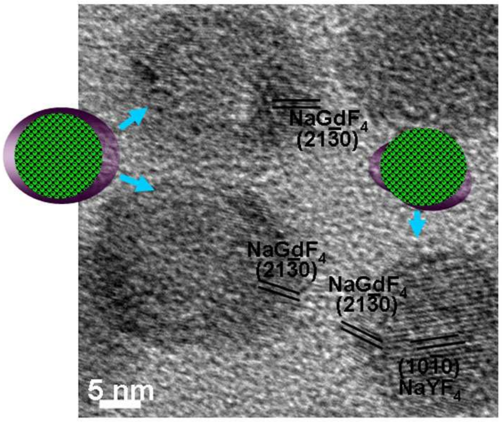


Figure S4. The Cryo-HRTEM image of the hexagonal $NaYF_4$:Yb, Er@$NaGdF_4$ core/shell nanocrystals with a 1 ML shell, revealing that the anisotropic shell growth always results in the voids at the initial ML deposition (uneven shell coating) (the lower right image in the figure). The lattice of the shell could be clearly observed which corresponds to the $(21\bar{3}0)$ plane of hexagonal $NaGdF_4$, and the lattice space of the inner core is 0.52 nm, corresponding to the $(10\bar{1}0)$ plane of the hexagonal $NaYF_4$.

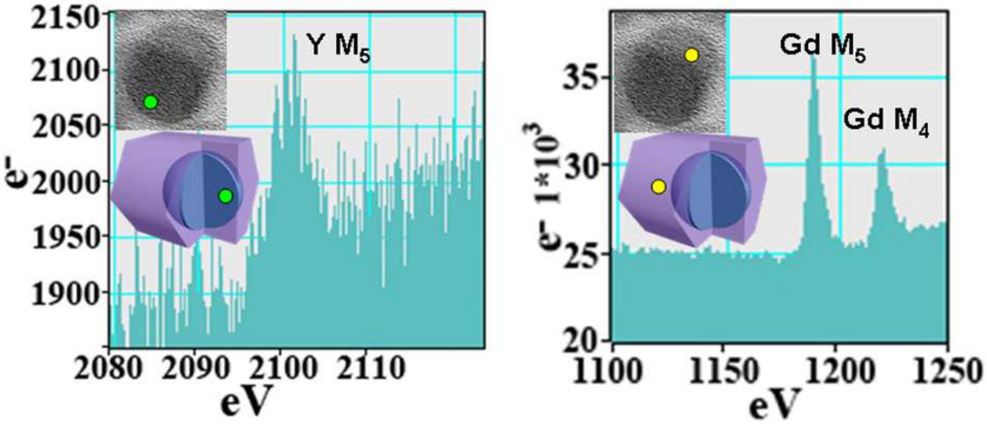


Figure S5. EELS spectra of ytterbium M_5 edge (a) and gadolinium M_4 edge (b) taken from the probe location on the periphery (inset in a) and central (inset in b) parts of the $NaYF_4$: 20% Yb, 2% Er@$NaGdF_4$ nanocrystals synthesized by the OSSC procedure. The uneven shell deposition also can be demonstrated by the EELS results. The Y signal can be detected at one end of the nanocrystal and the Gd signal can be detected at the center of the nanocrystal, further indicating the heterogeneous anisotropic growth.

References

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