Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Emission color tuning of core/shell upconversion nanoparticles by modulating the laser power or temperature

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A. Supplementary synthetic procedures of core/shell nanoparticles

1. Synthesis of $NaGdF_4$:0.2Yb/0.01Ho@$NaGdF_4$:0.2Yb/0.01Tm core/shell nanoparticles

Preparation of the Gd/Yb/Tm-OA shell precursor. 7.5 mmol of lanthanide acetates (Gd/Yb/Tm=79:20:1), 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 ^{o}C under vacuum with vigorous stirring until a clear solution formed. After that, the solution was cooled down to room temperature and the colorless Gd/Yb/Tm-OA (0.3 M) precursor solution was obtained.

Preparation of the Na-TFA-OA shell precursor. 8 mmol of Na-TFA and 20 mL of OA was loaded in a 100 mL flask and heated at 50 ^{o}C for 60 min under vacuum with vigorous stirring, until a clear Na-TFA-OA solution (0.4 M) was obtained.

Synthesis of core/shell nanoparticles. 8 mL of OA and 12 mL of ODE was added to a 100 mL flask and then heated at 140 ^{o}C under vacuum to remove residual water and oxygen. After the solution was cooled down to 50 ^{o}C, 5 mL cyclohexane solution containing pre-prepared $NaGdF_4$:Yb/Ho core nanoparticles (0.5 mmol) was quickly added under an argon flow. Then the mixed solution was heated at 70 ^{o}C for 15 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 295 ^{o}C. Subsequently, 2 mL of the Gd/Yb/Tm-OA (0.3 M) precursor solution and 3 mL of Na-TFA-OA (0.4 M) precursor solution was alternately added into the flask at 295 ^{o}C. The injection cycle of shell precursors was performed for three times and the interval time between each injection was kept at 15 min. Finally, the solution was cooled down to room temperature and the obtained core/shell nanoparticles were isolated via centrifugation. The $NaGdF_4$:Yb/Ho@$NaGdF_4$:Yb/Tm core/shell nanoparticles were then washed several times with ethanol and dried in air at 65 °C overnight for further characterization.

2. Synthesis of $NaGdF_4$:0.2Yb/0.01Tm@$NaGdF_4$:0.2Yb/0.3Ce/0.01Ho core/shell nanoparticles

Preparation of the Gd/Yb/Ce/Ho-OA shell precursor. 7.5 mmol of lanthanide acetates (Gd/Yb/Ce/Ho=49:20:30:1), 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 ^{o}C under vacuum with vigorous stirring until a clear solution formed. After that, the solution was cooled down to room temperature and the colorless Gd/Yb/Ce/Ho-OA (0.3 M) precursor solution was obtained.

Preparation of the Na-TFA-OA shell precursor. 8 mmol of Na-TFA and 20 mL of OA was loaded in a 100 mL flask and heated at 50 ºC for 60 min under vacuum with vigorous stirring, until a clear Na-TFA-OA solution (0.4 M) was obtained.

Synthesis of core/shell nanoparticles. 8 mL of OA and 12 mL of ODE was added to a 100 mL flask and then heated at 140 ºC under vacuum to remove residual water and oxygen. After the solution was cooled down to 50 ºC, 5 mL of cyclohexane solution containing pre-prepared $NaGdF_4$:Yb/Tm core nanoparticles (0.5 mmol) was quickly added under an argon flow. Then the mixed solution was heated at 70 ºC for 15 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 295 ºC. Subsequently, 2 mL of the Gd/Yb/Ce/Ho-OA (0.3 M) precursor solution and 3 mL of Na-TFA-OA (0.4 M) precursor solution was alternately added into the flask at 295 ºC. The injection cycle of shell precursors was performed for three times and the interval time between each injection was kept at 15 min. Finally, the solution was cooled down to room temperature and the nanoparticles were isolated and purified as given above. The obtained $NaGdF_4$:Yb/Tm@$NaGdF_4$:Yb/Ce/Ho core/shell nanoparticles were then dried in air at 65 °C overnight for further characterization.

3. Synthesis of $NaGdF_4$:0.2Yb/0.01Tm@$NaGdF_4$@$NaGdF_4$:0.2Yb/0.01Ho @$NaGdF_4$:0.2Yb core/shell/shell/shell nanoparticles

Preparation of $NaGdF_4$:0.2Yb/0.01Tm core nanoparticles (size ~7.3 nm). In order to obtain $NaGdF_4$:Yb/Tm core nanoparticles with smaller size, the synthesis temperature was decreased to 290 ºC. First, 1 mmol of lanthanide acetates (Gd/Yb/Tm=79:20:1) was added to a 100 mL three-necked flask containing OA (10 mL) and ODE (15 mL). The mixture was then heated to 140 ºC for 30 min with vigorous stirring to form a clear solution. After cooling down to 50 ºC, a methanol solution (10 mL) containing NH_4F (4 mmol) and NaOH (2.5 mmol) was added, and the resulting solution was stirred for 30 min under an argon flow. The solution was then heated to 70 ºC to remove excessive methanol. Subsequently, the solution was heated at 290 °C under an argon atmosphere for 90 min and then cooled down to room temperature. The as-prepared core nanoparticles were then isolated, washed and re-dispersed in cyclohexane.

Preparation of the Gd/Yb/Ho-OA shell precursor. 7.5 mmol of lanthanide acetates (Gd/Yb/Ho=79:20:1), 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 formed. After that, the solution was cooled down to room temperature and the colorless Gd/Yb/Ho-OA (0.3 M) precursor solution was obtained.

Preparation of Na-TFA-OA, Gd-OA and Gd/Yb-OA shell precursors. The Na-TFA-OA (0.4 M) precursor solution was prepared in the same procedure as given above. The synthetic procedures of Gd-OA (0.3 M) and Gd/Yb-OA (0.3 M) shell precursors were the same as those of Gd/Yb/Ho-OA, except that lanthanide acetates were adjusted accordingly.

Synthesis of core/shell/shell/shell nanoparticles. 4 mL of OA and 6 mL of ODE was added to a 100 mL flask and then heated at 140 °C under vacuum to remove residual water and oxygen. After the solution was cooled down to 50 °C, 1 mL cyclohexane solution of pre-prepared $NaGdF_4$:Yb/Tm (~7.3 nm) core nanoparticles (0.1 mmol) was quickly added under an argon flow. The mixed solution was then heated at 70 °C for 15 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 (0.3 M) precursor solution and 3 mL of Na-TFA-OA (0.4 M) precursor solution was alternately added into the flask at 290 °C. The injection cycle of Gd-OA and Na-TFA-OA shell precursors was performed twice to synthesize the $NaGdF_4$ layer, and the interval time between each injection was kept at 15 min. After the growth of the $NaGdF_4$ layer, 2 mL of Gd/Yb/Ho-OA (0.3 M) and 3 mL of Na-TFA-OA (0.4 M) precursor solution were alternately injected for five times to synthesize the $NaGdF_4$:Yb/Ho layer. And then 2 mL of Gd/Yb-OA and 3 mL of Na-TFA-OA were alternately injected twice for the synthesis of the outmost $NaGdF_4$:Yb shell. Finally, the solution was cooled down to room temperature and the obtained core/shell/shell/shell nanoparticles were isolated, washed and dried in air at 65 °C for further characterization.

B. Supporting figures

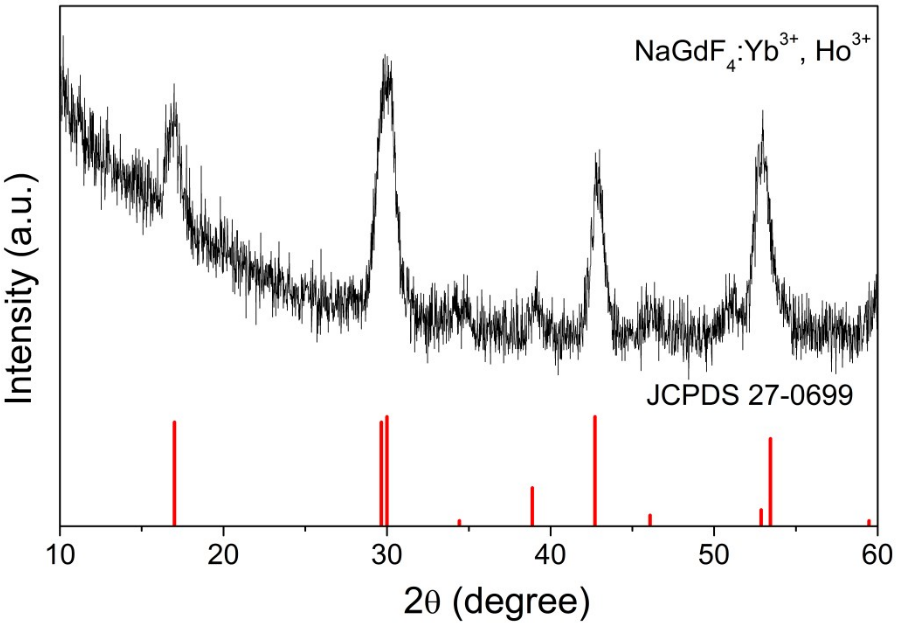

Fig. S1 XRD patterns of β-$NaGdF_4$:Yb/Ho nanoparticles.

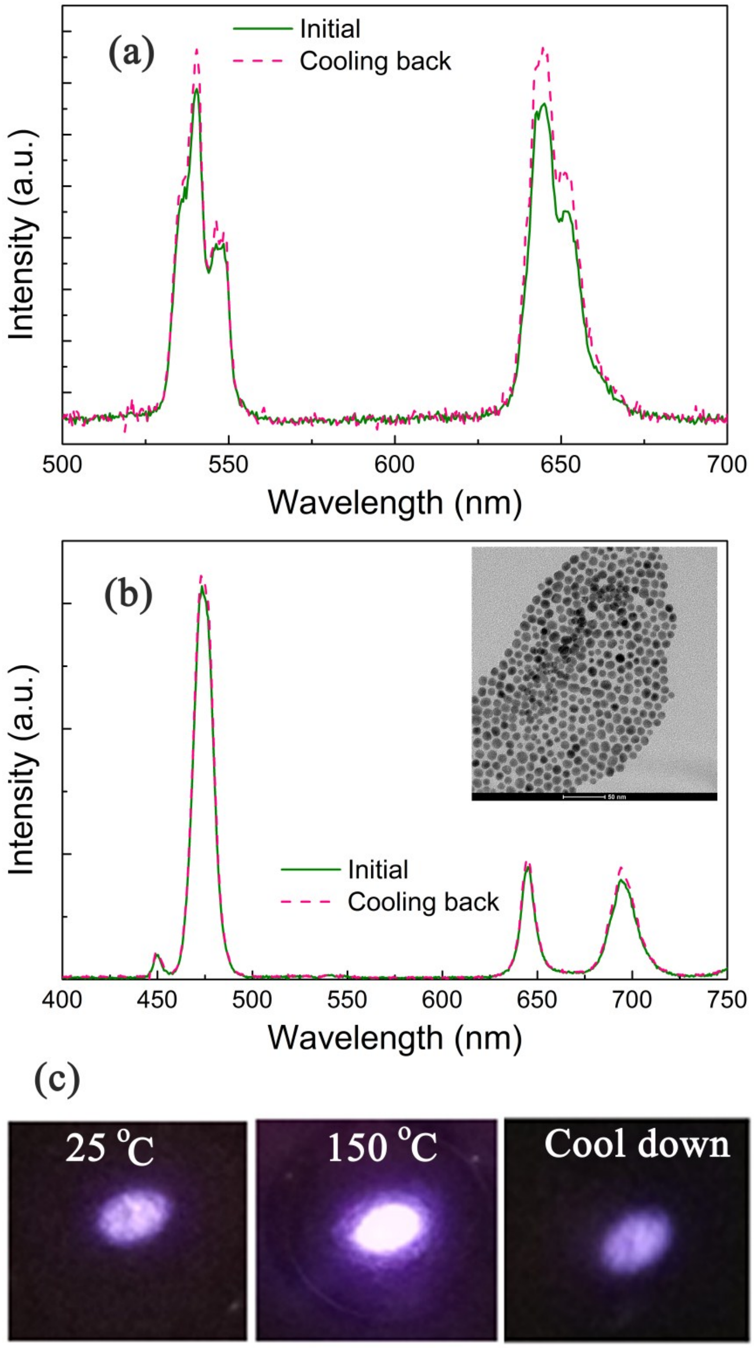

Fig. S2 UCL spectra of (a) $NaGdF_4$:0.2Yb/0.01Ho and (b) $NaGdF_4$:0.2Yb/0.01Tm nanoparticles before and after a heating–cooling cycle; (c) Photographs of $NaGdF_4$:0.2Yb/0.01Tm solid powers under the 970 nm laser excitation at various temperatures. The inset of (b) showed the TEM image of $NaGdF_4$:0.2Yb/0.01Tm UCNPs after a heating-cooling cycle.

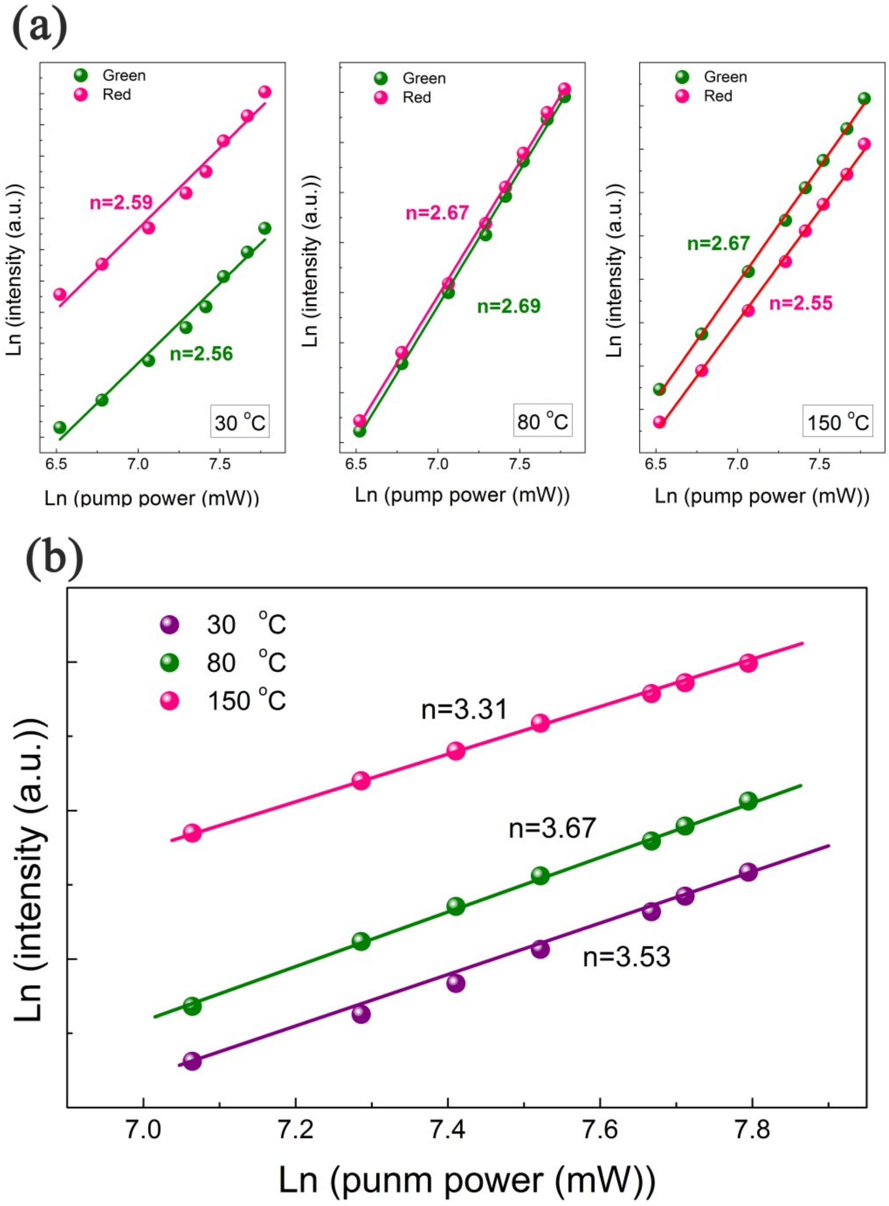

Fig. S3 Double logarithmic plots of the laser power dependent emission intensities: (a) green (~540 nm) and red (~645 nm) bands of $NaGdF_4$:Yb/Ho UCNPs; (b) blue (~475 nm) band of $NaGdF_4$:Yb/Tm UCNPs. The *n* values were obtained by fitting the power law of upconversion $I \propto P^n$. *I*: the visible output intensity; *P*: the infrared excitation power; *n*: the number of IR photons absorbed per visible photon emitted.

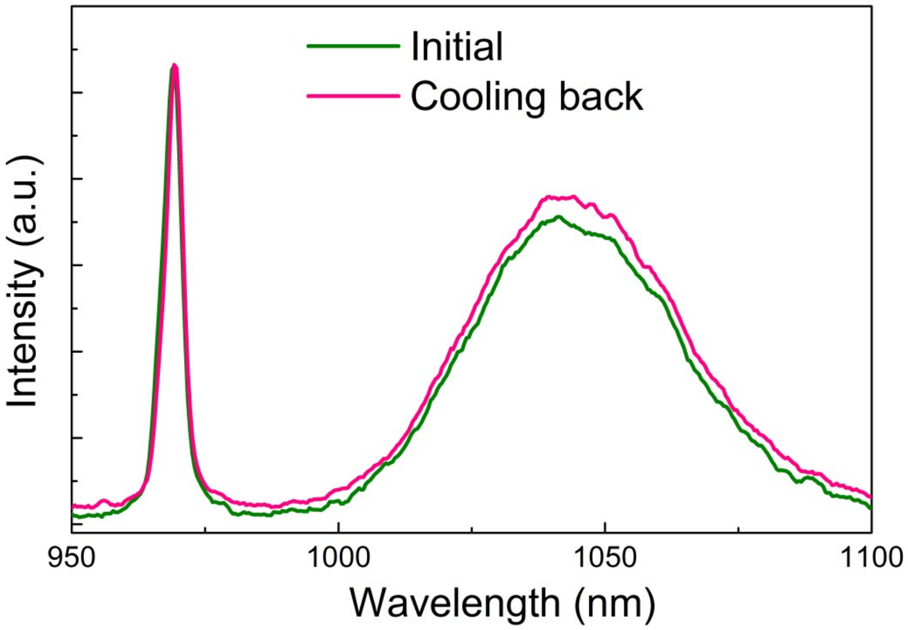

Fig. S4 Downconversion luminescence spectra of NaGdF$_4$:Yb/Ho UCNPs before and after a heating–cooling cycle (λ_{ex}=970 nm).

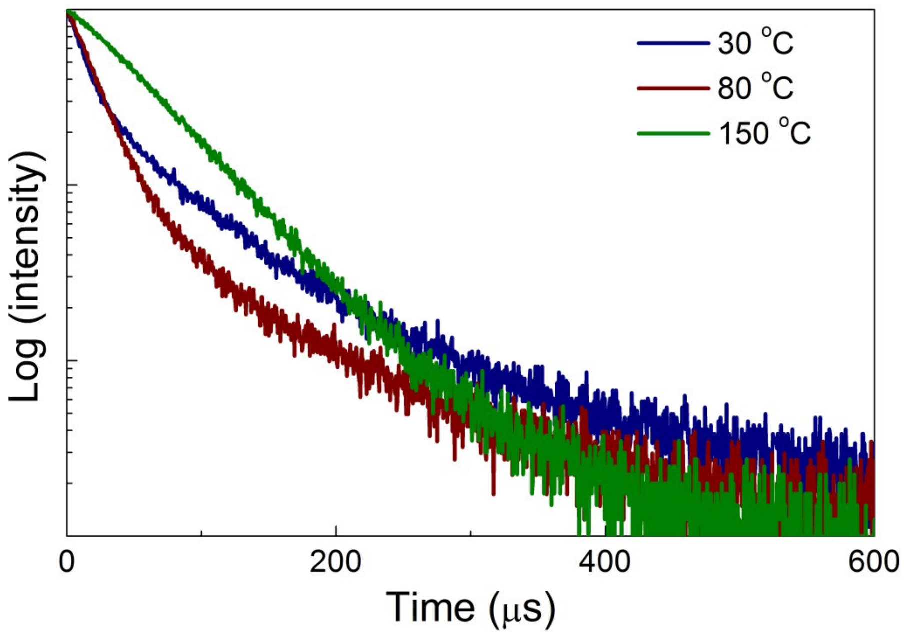

Fig. S5 Luminescence decay curves of Ho^{3+} emission at 540 nm in $NaGdF_4$:Yb/Ho UCNPs (λ_{ex}=980 nm) at various temperatures.

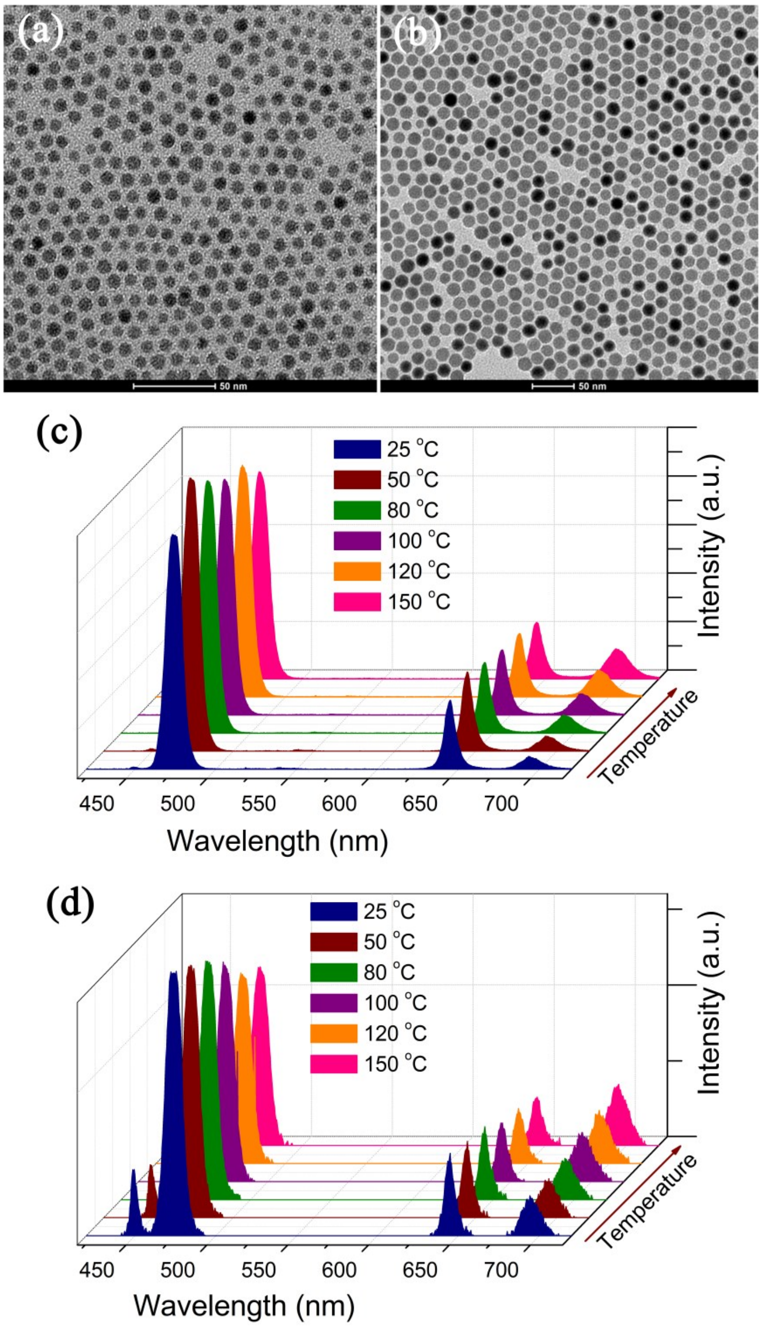

Fig. S6 TEM images of (a) $NaGdF_4$:Yb/Tm core-only (size ~ 8 nm) and (b) $NaGdF_4$:Yb/Tm@$NaGdF_4$ core/shell (~15 nm) UCNPs; (c) Temperature-dependent UCL spectra of $NaGdF_4$:Yb/Tm@$NaGdF_4$ core/shell UCNPs in the ambient atmosphere; (d) Temperature-dependent UCL spectra of $NaGdF_4$:Yb/Tm core-only UCNPs in the high-purity argon atmosphere.

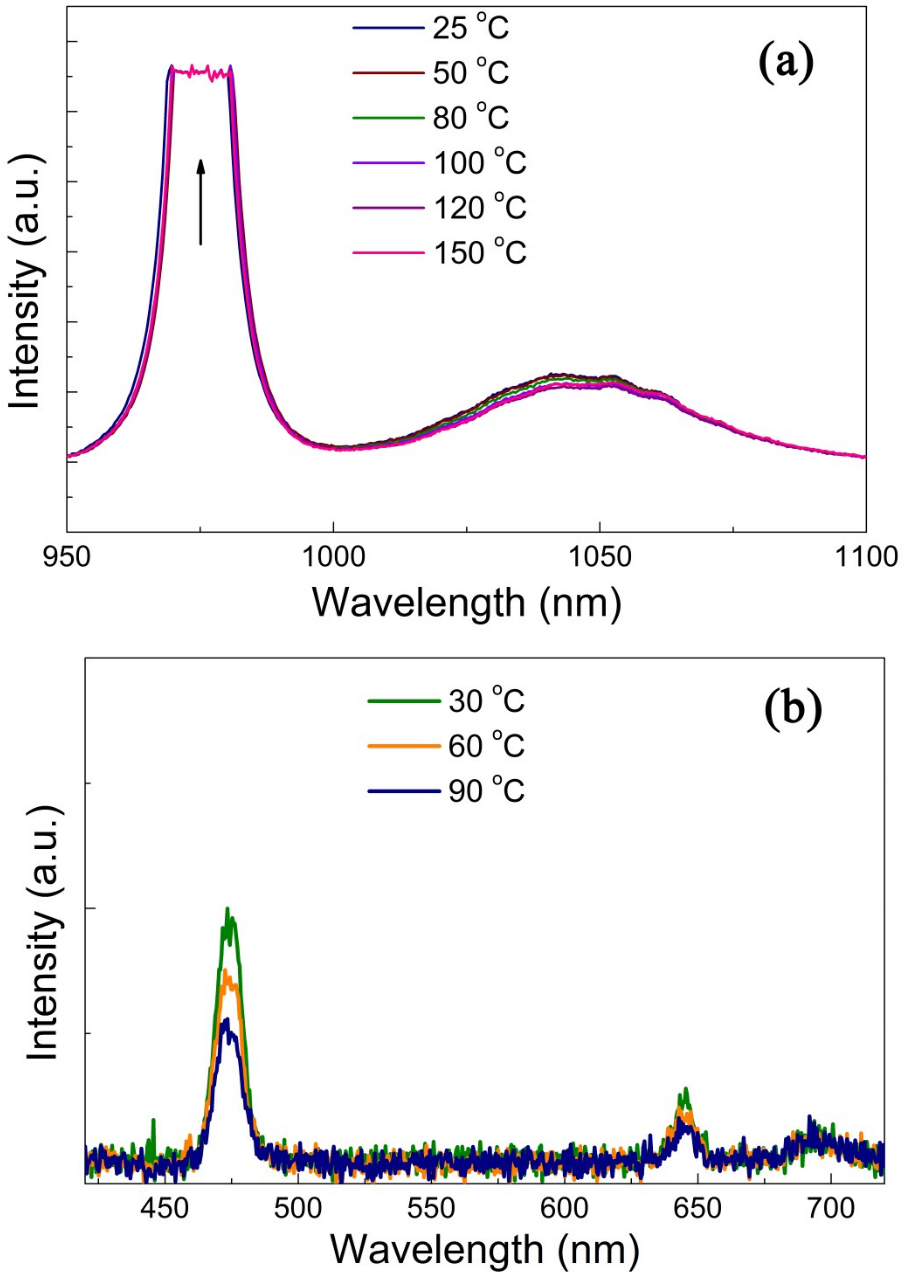

Fig. S7 (a) DCL spectra of NaGdF$_4$:Yb/Tm core-only UCNPs (λ_{ex}=970 nm) at various temperatures in the high-purity argon atmosphere, and the arrow represents the scattered signal from the excitation light source; (b) Temperature-dependent UCL spectra of NaGdF$_4$:Yb/Tm core-only UCNPs dispersed in the ODE solution.

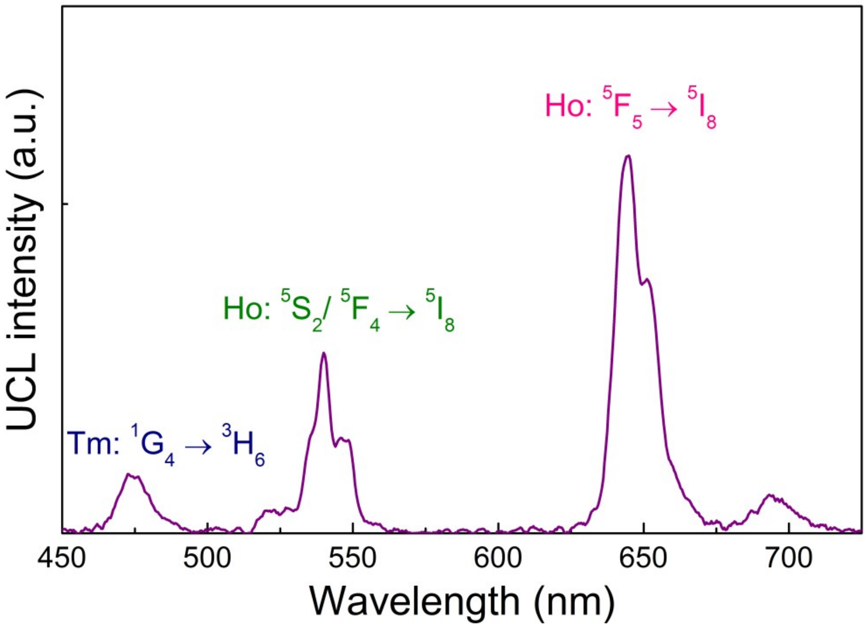

Fig. S8 UCL spectra of $NaGdF_4$:0.2Yb/0.01Ho/0.01Tm UCNPs at room temperature.

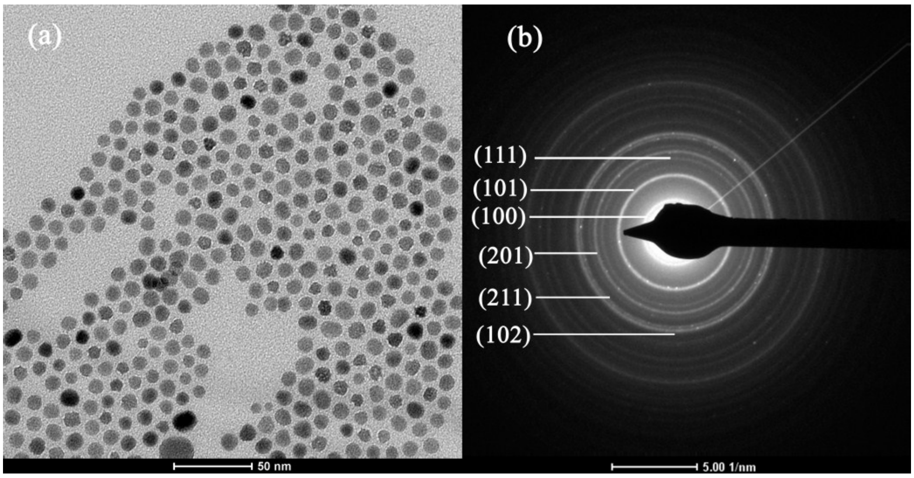

Fig. S9 The TEM image and SAED pattern of NaGdF$_4$:0.2Yb/0.005Ho/0.015Tm nanoparticles.

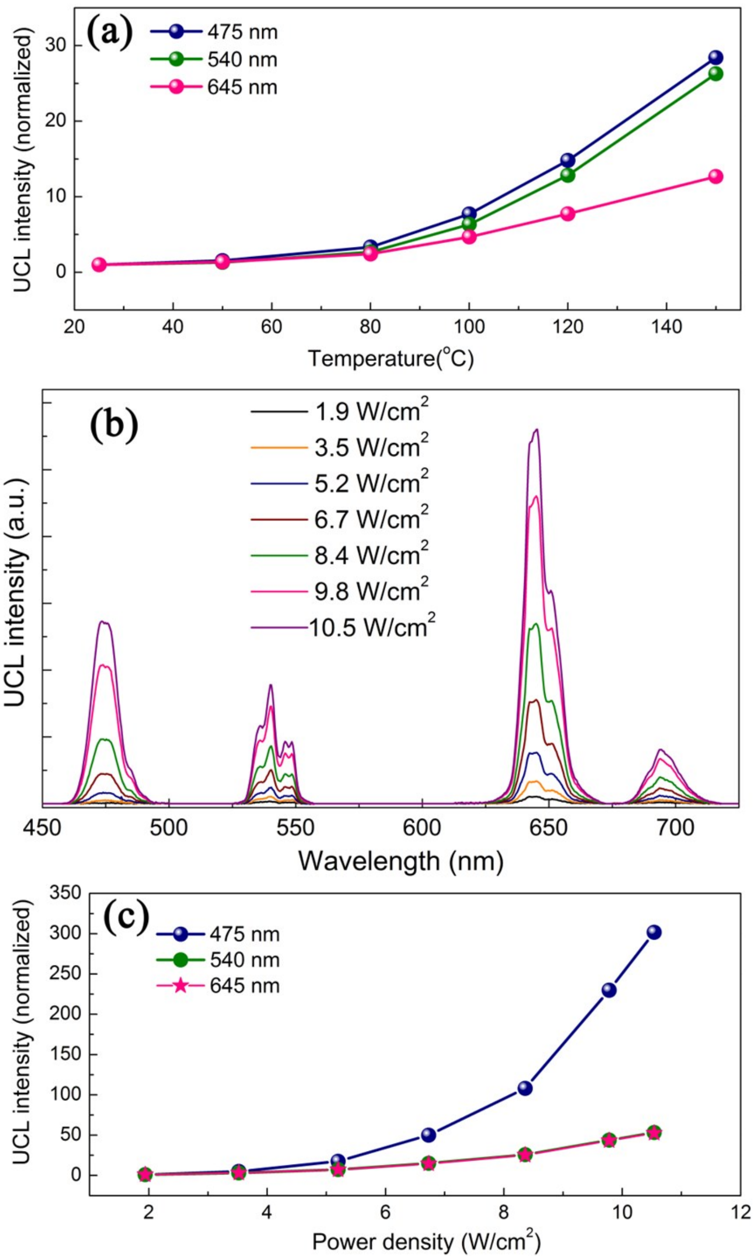

Fig. S10 (a) UCL intensities of blue (~475 nm), green (~540 nm) and red (~645 nm) emissions as a function of temperature for $NaGdF_4$:0.2Yb/0.005Ho/0.015TmUCNPs, and intensities were normalized to that at 25 °C for each emission band. (b) UCL spectra at various excitation power densities. (c) UCL intensities of blue (475 nm), green (540 nm) and red (645 nm) emission as a function of power density, and intensities were normalized to that at 1.9 W/cm^2 for each emission band.

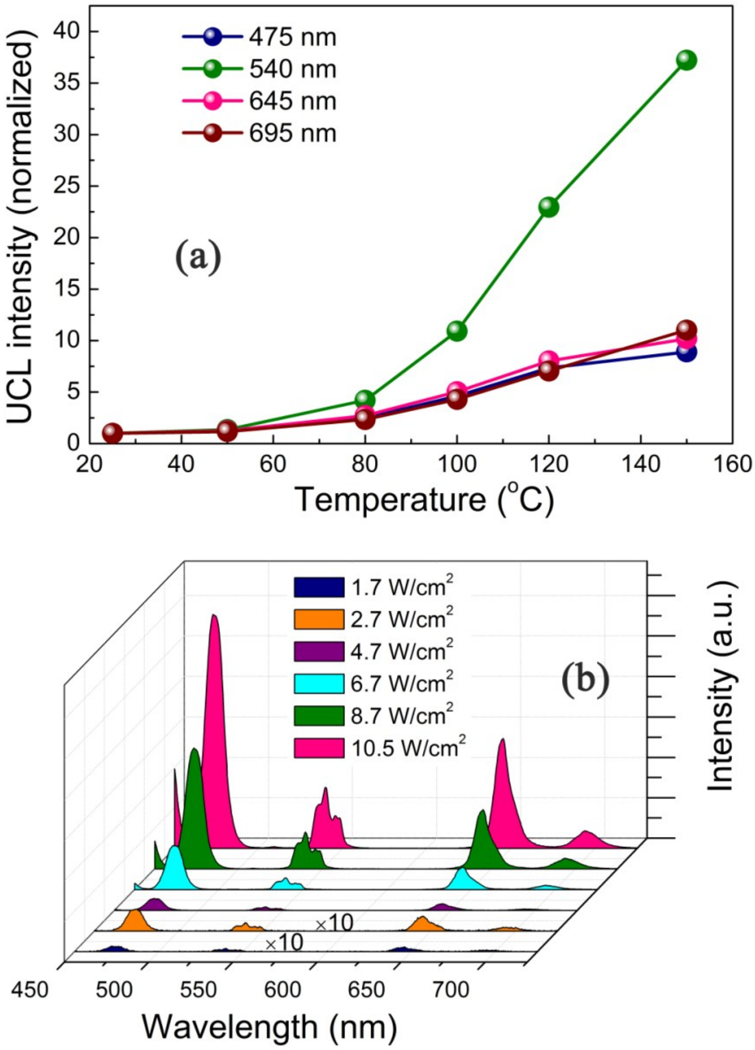

Fig. S11 (a) UCL intensities of blue, green and red emissions as a function of temperature for $NaGdF_4$:0.2Yb/0.01Tm@$NaGdF_4$:0.2Yb/0.01Ho core/shell UCNPs, and intensities were normalized to that at 25 °C for each emission band. (b) UCL spectra of $NaGdF_4$:0.2Yb/0.01Tm@$NaGdF_4$:0.2Yb/0.01Ho core/shell UCNPs at various excitation power densities. The UCL intensities at 1.7 and 2.7 W/cm^2 were magnified ten times for clarity.

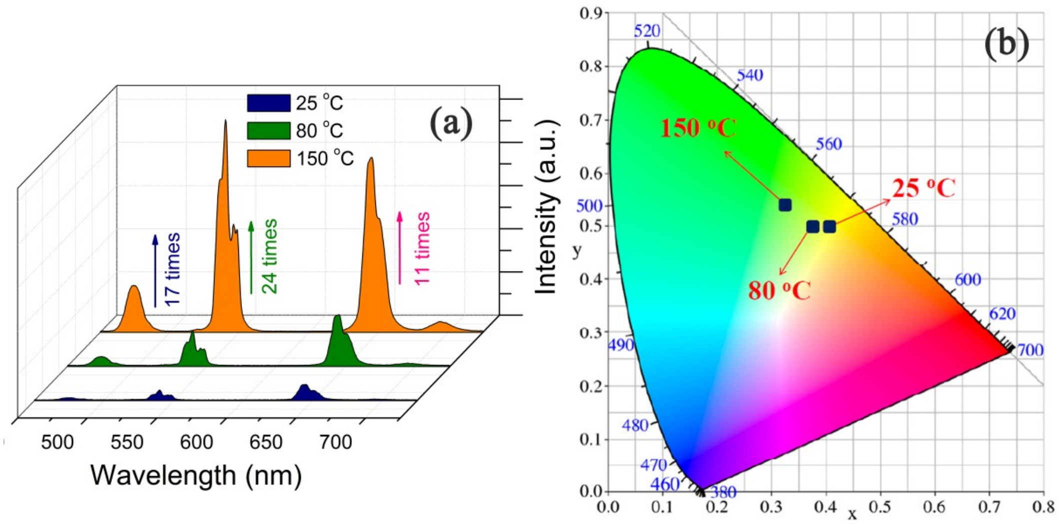

Fig. S12 (a) UCL spectra at various temperatures and (b) the corresponding chromaticity coordinates of $NaGdF_4$:0.2Yb/0.01Ho@$NaGdF_4$:0.2Yb/0.01Tm core/shell UCNPs.

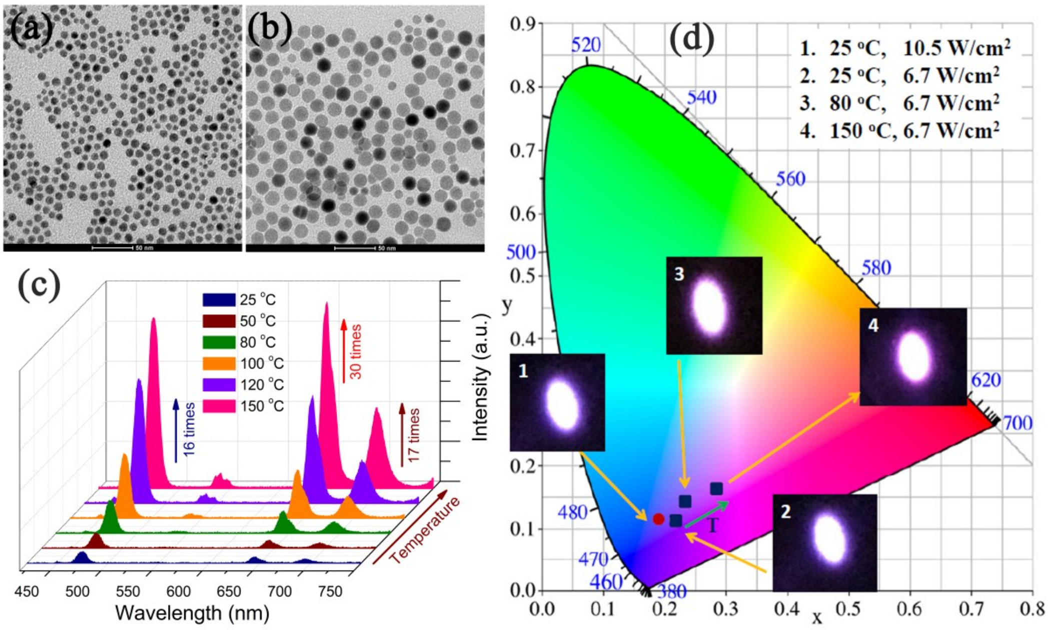

Fig. S13 TEM images of (a) $NaGdF_4$:Yb/Tm core-only (size ~ 9.5 nm) and (b) $NaGdF_4$:Yb/Tm@$NaGdF_4$:Yb/Ce/Ho core/shell (size ~16.5 nm) UCNPs; (c) UCL spectra and (d) the corresponding chromaticity coordinates of $NaGdF_4$:Yb/Tm@ $NaGdF_4$:Yb/Ce/Ho core/shell UCNPs at various temperatures. The insets of (d) showed photographs of core/shell UCNPs at various temperatures and excitation power densities.

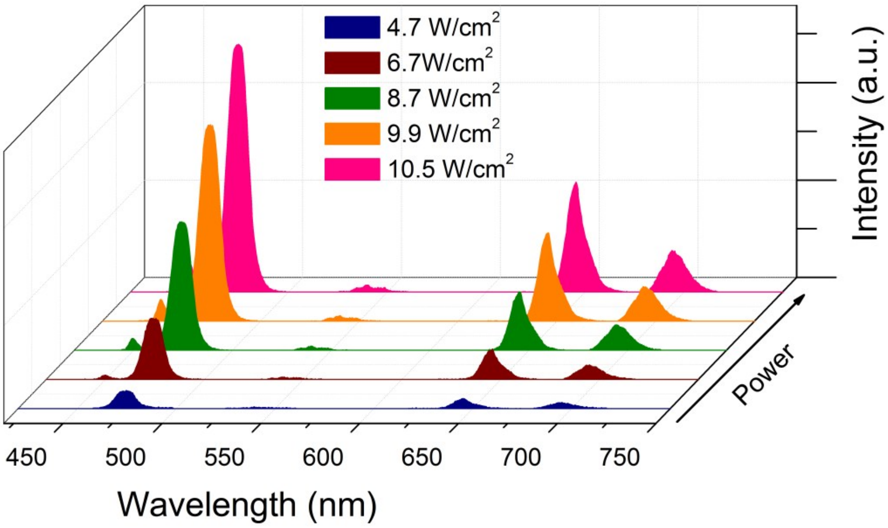

Fig. S14 Power-dependent UCL spectra of $NaGdF_4$:Yb/Tm@$NaGdF_4$:Yb/Ce/Ho core/shell nanoparticles.

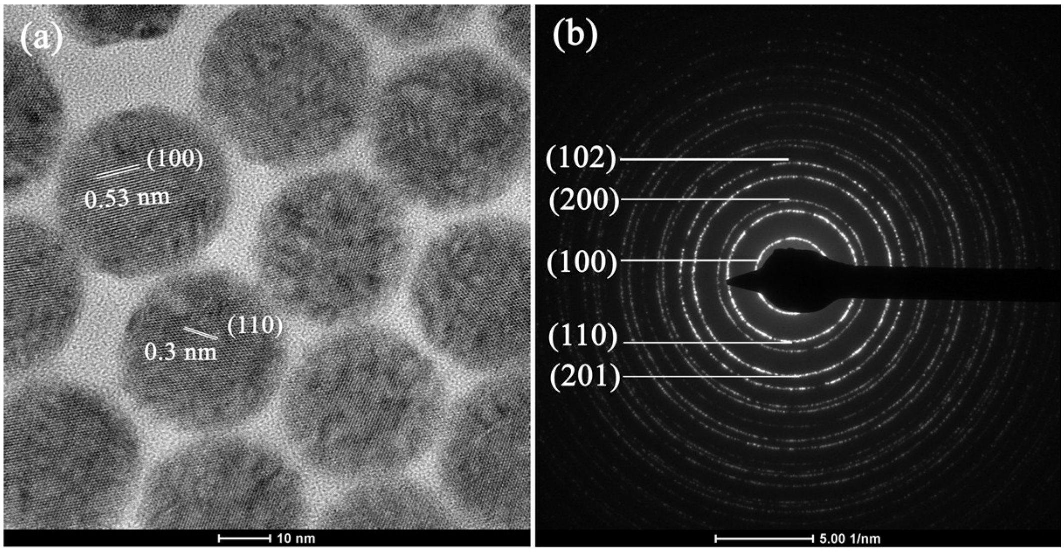

Fig. S15 (a) High-resolution TEM image and (b) selected area electron diffraction of $NaGdF_4$:0.2Yb/0.01Tm@$NaGdF_4$@$NaGdF_4$:0.2Yb/0.01Ho@$NaGdF_4$:0.2Yb core/shell/shell/shell nanoparticles, which exhibited a pure hexagonal phase.

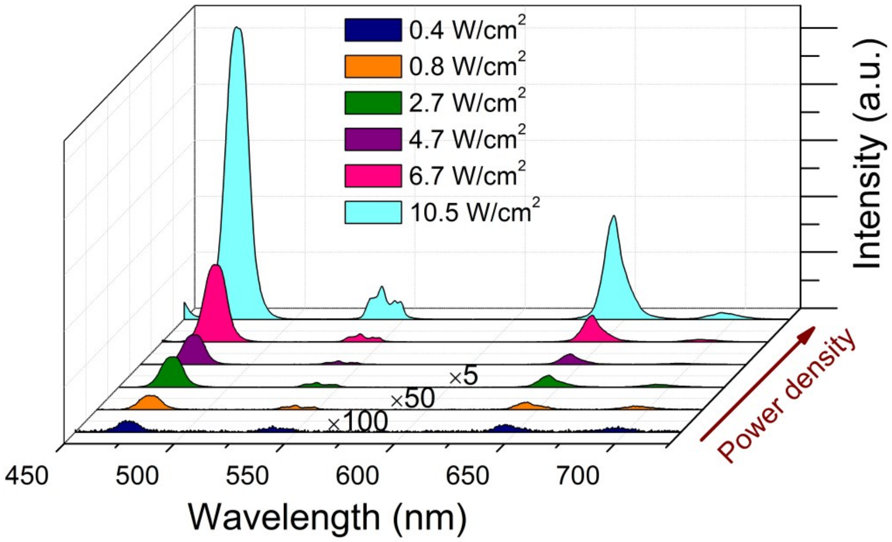

Fig. S16 Power-dependent UCL spectra of $NaGdF_4$:0.2Yb/0.01Tm@$NaGdF_4$ @$NaGdF_4$:0.2Yb/0.01Ho@$NaGdF_4$:0.2Yb core/shell/shell/shell nanoparticles.