Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Sharpening upconversion nanoparticles to reduce surface quenching

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1. Materials

Yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$, 99.9%), Erbium chloride hexahydrate ($ErCl_3 \cdot 6H_2O$, 99.9%), ytterbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$, 99.9%), ammonium fluoride (NH_4F, 99.99%), sodium hydroxide (NaOH, 99%), 1-octadecene (ODE), oleic acid (OA), Ethanol, Methanol, and Cyclohexane were purchased from Sigma-Aldrich. All reagents are used as received without further purification.

2. Upconversion nanocrystals synthesis.

NaYF4:20%Yb,2%Er has been synthesized according to previously reported method.[1] In a typical experiment, 0.4 mmol $RECl_3$ (RE = Y, Yb, Er) was added to a flask containing 6 ml OA and 15 ml ODE. The mixture was heated to 160 ^{O}C under argon for 30 min to obtain a clear solution and then cooled down to room temperature, followed by the addition of 2 mL methanol solution of NH_4F (1.6 mmol) and NaOH (1 mmol). After stirring for 30 min, the solution was heated to 100 ^{O}C under argon for 20 min to remove methanol, and then the solution was further heated to 300 ^{O}C for different reaction times. Finally, the reaction solution was cooled down to room temperature. After centrifugation, the precipitate was purified by re-dispersion in cyclohexane, followed by precipitation with ethanol and separation by centrifugation. After 3 to 4 washing cycles, the nanocrystals were dispersed in cyclohexane.

For the synthesis of core-shell structure,[2] $YCl_3 \cdot 6H_2O$ (0.15 mmol) in 0.5 ml methanol solution was mixed with OA (6 ml) and ODE (6 ml). The mixture was degassed under Ar flow and heated to 160 ^{O}C for 30 min to form a clear solution, and then cooled to room temperature. Then, 2 ml methanol solution containing NaOH (0.375 mmol) and NH_4F (0.6 mmol) was added. Followed, 0.15 mmol of the core nanocrystals in cyclohexane solution was added and stirred for 20 min. The solution was slowly heated to 110 ^{O}C and kept for 20 min to completely remove the methanol. After that, the reaction mixture was quickly heated to 300 ^{O}C and held at that temperature for 60 min.

3. Characterization

Transmission electron microscopy (TEM) images were obtained on a JEOL 2010F transmission electron microscope. Powder X-ray diffraction (XRD) data were recorded from a Bruker D8 Advance diffractometer using graphitemonochromatized CuKα radiation (λ= 1.5406 Å) with 2θ range from 10° to 70° at a scanning rate of 2° per minute. The concentration of RE^{3+} in the reaction solution was tested by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Leeman Prodigy). The samples were centrifuged first, then the supernatant was digested and diluted with water before quantification by ICP-OES. Fluorescence spectra were recorded on a Hitachi F-500 fluorescence spectrophotometer equipped with a 980 nm continuous-wave laser excitation source. To measure luminescence lifetimes, the laser was operated in an “on−off’’ cycle using a function generator. The emission was collected by a single-photon avalanche photodiode (SAPD). The laser-on time and SPAD-on time are 500 us and 2500 us, respectively. The excitation power density is 1 W/cm^2. The sampling rate is 200 kHz.

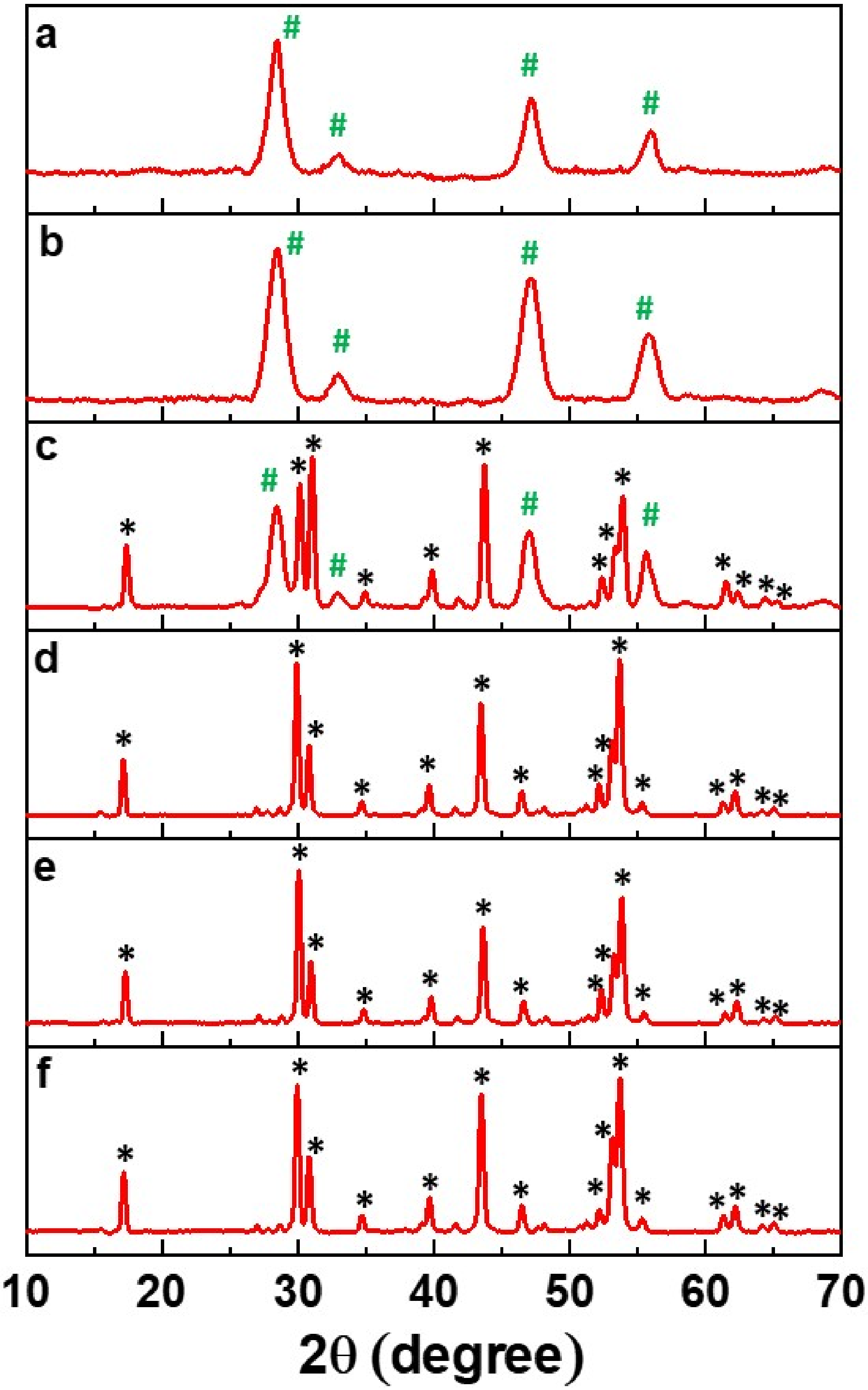
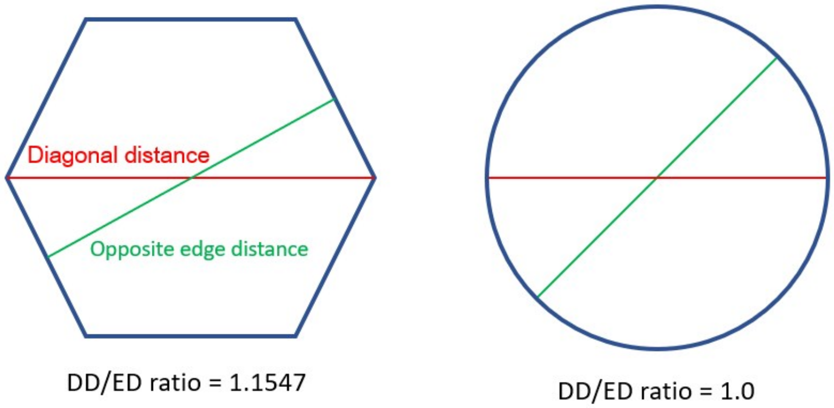


Figure S1. The XRD patterns of $NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals formed in the reaction solution at different reaction time (a, 2 min; b, 16 min; c, 30 min; d, 45 min; e, 60 min; and f, 90 min). # and * represent the standard peaks of α-$NaYF_4$ (JCPDS-06-0342) and β-$NaYF_4$ (JCPDS-016-0334). At the temperature of 300 °C, pure small α-$NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals are formed at first (as shown in a,b) and then β-$NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals are formed with the reaction time of 30 min. At this time point, the formed nanocrystals are a mixture of α-$NaYF_4$:20%Yb^{3+},2%Er^{3+} and β-$NaYF_4$:20%Yb^{3+},2%Er^{3+} nanocrystals as shown in c. At the reaction temperature of 300 °C for 45 min, pure β-NaYF4 nanocrystals are formed as show in d. This means the β-phase particles are formed in a consequential process via α-phase particles as a mediate at relatively high temperature. With prolonged reaction time, the phase of nanocrystals does not change as shown in e and f, which indicates the surface changes of nanocrystals could not be identified by XRD analysis.



$$\text{DD/ED ratio} = \frac{\text{Diagonal distance (DD)}}{\text{Opposite edge distance (ED)}}$$

Figure S2. Schematic illustration of the DD/ED ratio used to quantify the surface sharpness of formed hexagonal nanocrystals. The values of DD/ED ratio can theoretically range from 1.1547 (when nanocrystals have the sharpest surface) to 1.0 (when nanocrystals have the least sharp surface).

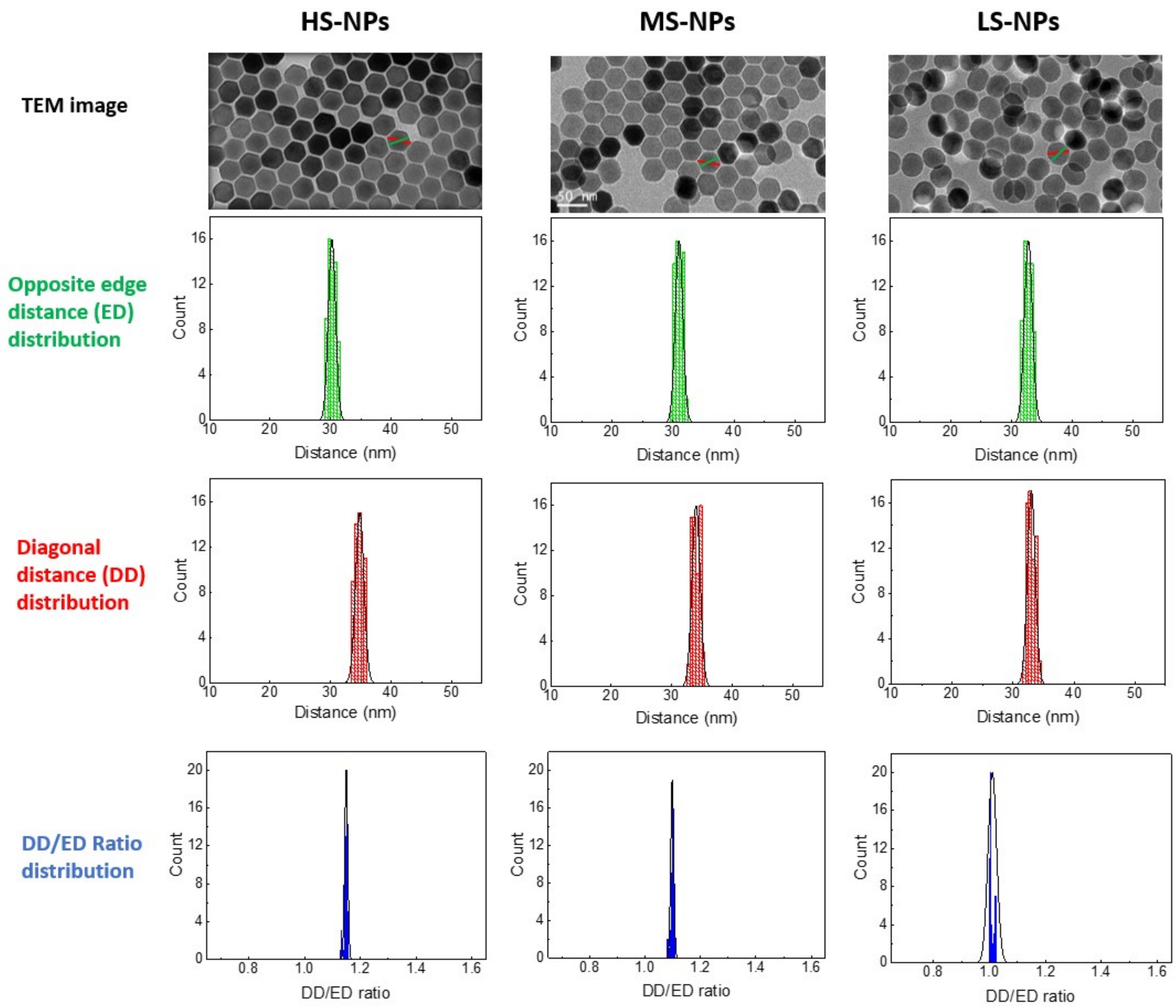


Figure S3. TEM images, opposite edge distance distribution histograms, diagonal distance distribution histograms, and the DD/ED ratio distribution histograms of the formed HS-NPs, MS-NPs, and LS-NPs. The average opposite edge distances of HS-NPs, MS-NPs, and LS-NPs are 30.3, 31.0, and 32.5 nm, respectively. The average diagonal distances of HS-NPs, MS-NPs, and LS-NPs are 34.8, 34.0, and 32.7 nm, respectively. The average DD/ED ratios of HS-NPs, MS-NPs, and LS-NPs are 1.15, 1.10, and 1.01, respectively.

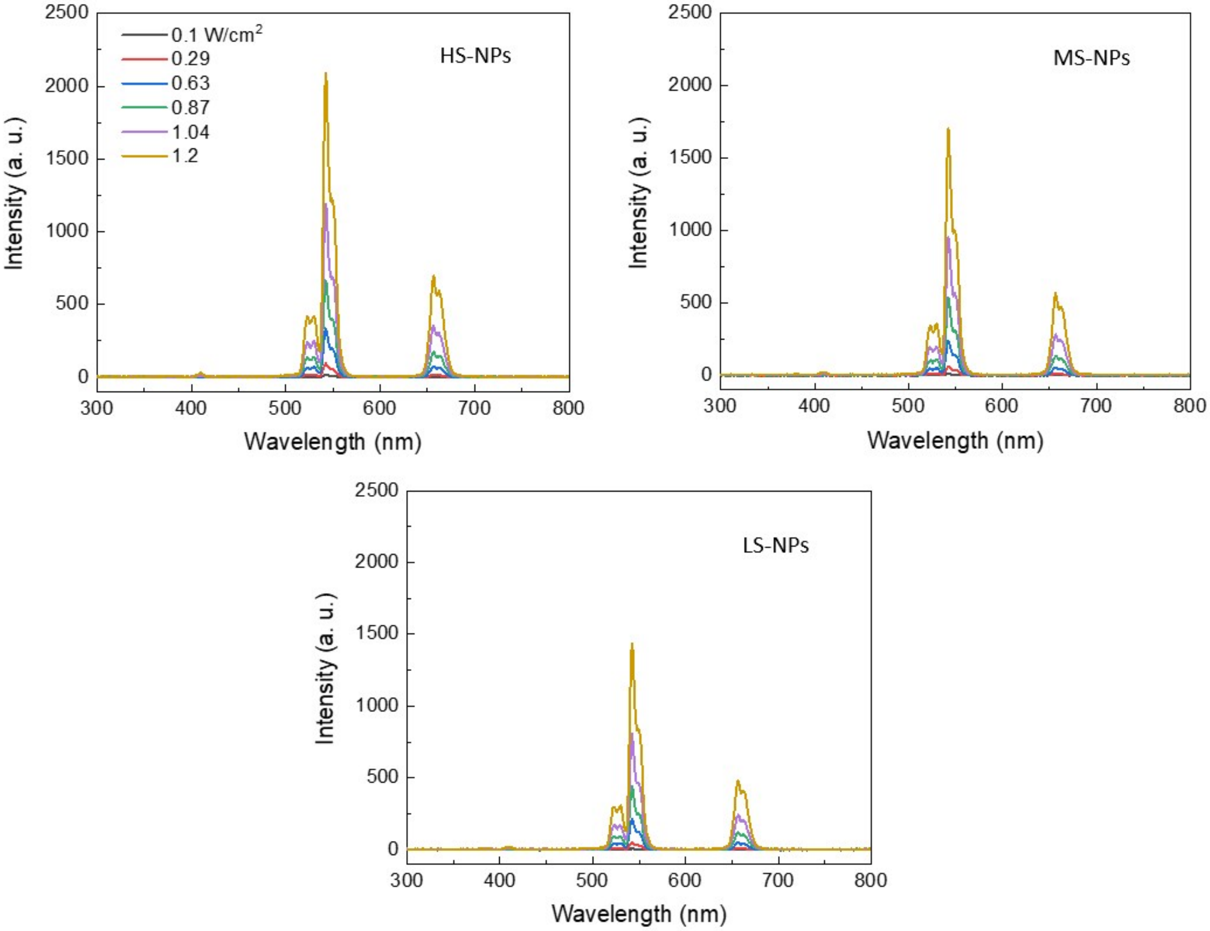


Figure S4. Upconversion luminescence spectra of 3 samples under different excitation power.

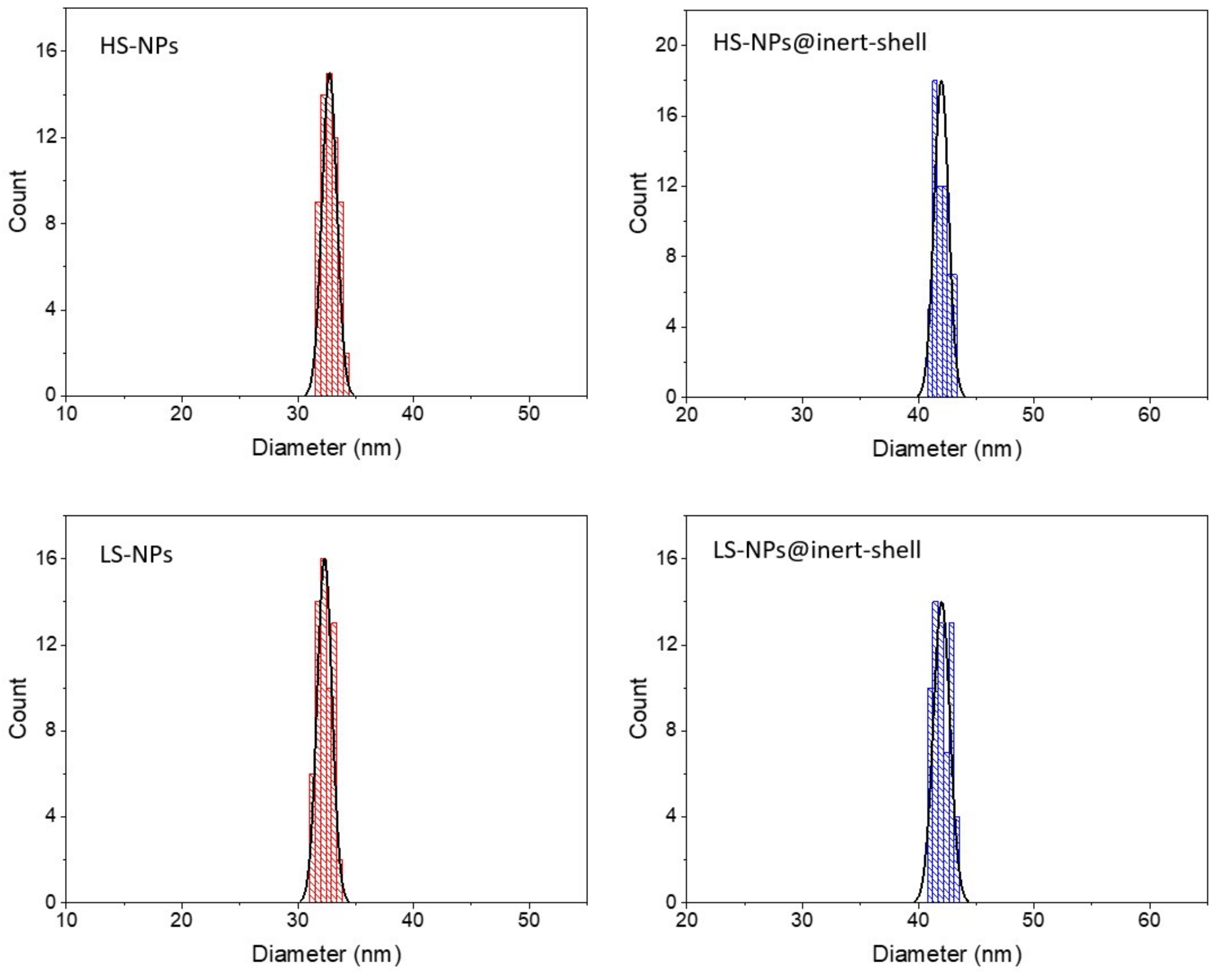


Figure S5. Size distribution histograms of 4 samples in figure 4a-d. The average diameter of the HS-NPs, LS-NPs, HS-NPs@inert-shell, and LS-NPs@inert-shell are 31.8, 32.0, 42.1 and 42.3 nm respectively.

Reference

1. Z. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606.
2. F. Wang, R. Deng and X. Liu, *Nat. Protocols*, 2014, **9**, 1634-1644.