

Supporting Information

Decoration of upconversion nanocrystals with metal sulfide quantum dots by a universal in-situ controlled growth strategy

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Experimental section

Materials: All chemical reagents used are analytical grade without any further purification. Yttrium chloride ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), ytterbium chloride ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), erbium chloride ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, (99.9%) oleic acid (OA, 90%), 1-octadecene, (ODE, 90%) chitosan (CS, deacetylation degree $\geq 95\%$, viscosity: 100-200 mPa·s) were purchased from Aladdin Reagents. Cetyl trimethyl ammonium bromide (CTAB, 99%), sodium hydroxide (NaOH, >98%), ammonium fluoride (NH_4F), methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), cyclohexane, sodium sulfide (Na_2S), sodium citrate (Na_3Cit), silver nitrate (AgNO_3), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), copper sulfate ($\text{Cu}(\text{NO}_3)_2$) were all obtained from Beijing Chemical Reagents Materials. Mercaptosuccinic acid (MSA) were purchased from TCI Chemicals Materials. All chemical reagents are of analytical grade and used without any further purification.

Synthesis of OA-stabilized $\beta\text{-NaYF}_4\text{:Yb/Er}$ nanoplates: $\beta\text{-NaYF}_4\text{:Yb/Er}$ nanoplates were synthesized according to the literature methods.^[1] Typically, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (0.8 mmol), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.18 mmol) and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mmol) were added to a 100 mL flask charged with oleic acid (5 mL) and 1-octadecene (15 mL). The resulting mixture solution was heated to 165 °C for 60 min and then cooled down to room temperature. Subsequently, a methanol solution (10 mL) of NH_4F (4 mmol) and NaOH (2.5 mmol) was added and stirred at 50 °C for 30 min to remove the methanol, followed by heating to 100 °C to degas fully and remove oxygen and water under vacuum. Then, the solution was heated to 310 °C under an argon atmosphere for 1.5 h and then cooled down to room temperature. The resulting nanoplates were purified by centrifugation after the addition of ethanol, washed several times with cyclohexane and ethanol, and finally redispersed in 10 mL of cyclohexane for further experiments.

Synthesis of β -NaYF₄:Yb/Er nanoparticles: The synthesis of β -NaYF₄:Yb/Er nanoparticles is consistent with the procedure of nanoplates, except for the solution was heated to 300 °C under an argon atmosphere for 1 h.

Synthesis of β -NaYF₄:Gd/Yb/Er nanorods: β -NaYF₄:Gd/Yb/Er nanorods were synthesized according to the literature methods.^[2] Typically, a deionized water solution (1.5 mL) of 0.3 g NaOH was mixed with 5 mL of ethanol and 5 mL of oleic acid under stirring. To the resulting mixture were selectively added 2 mL of RECl₃ (0.2 M, RE = Y, Yb, Er, Gd). After the solution becomes homogeneous, 1 mL of NH₄F (2 M) is then slowly added into the beaker accompanied by vigorous agitation for 20 min at room temperature. Then the resulting homogeneous colloidal solution was transferred into a 25-mL of Teflon-lined autoclave and heated at 200 °C for 2 h in a furnace. After cooling down to room temperature, the obtained nanorods were collected by centrifugation, washed with ethanol/cyclohexane several times, and finally redispersed in cyclohexane.

Synthesis of CS-functionalized NaYF₄:Yb/Er (NaYF₄:Yb/Er@CS): To obtain water-soluble β -NaYF₄:Yb/Er UCNCs, 0.2 g of CTAB and 40 mL of water were successively added into 50 mL beaker, and the clear solution was obtained after ultrasound and magnetic stirring. The NaYF₄:Yb/Er cyclohexane solution (5 mL) mentioned above was added into the beaker, then the mixture was kept stirring for 2 h to evaporate cyclohexane solvent, obtaining a NaYF₄:Yb/Er–CTAB water solution. NaYF₄:Yb/Er@CS was successfully synthesized according to the literature method.^[3] In detail, 20 mg CS was added to 3 mL acetic acid solution (1%, v/v), then ultrasonicated for 10 minutes until CS was completely dissolved. CS solution was added into NaYF₄:Yb/Er–CTAB water solution and CS functionalized NaYF₄:Yb/Er UCNCs were obtained under bath ultrasonic dispersion for 30 min. The product was centrifuged at 8000 rpm for 5 minutes and washed with deionized water for 3 times. The

synthesized NaYF₄:Yb/Er@CS nanoparticles were dispersed in 10 mL of deionized water for the future use.

Synthesis of hydrophilic NaYF₄:Yb/Er@CS@Mⁿ⁺S by in-situ growth routine: The fabrication of NaYF₄:Yb/Er@CS@Ag₂S NCs has been employed as an example. First, 1 mL synthesized NaYF₄:Yb/Er@CS nanoparticles were diluted to 10 mL with deionized water, followed by addition of AgNO₃ solution (10.0 mM) with various doses (1.0 × 10⁻⁶, 3.0 × 10⁻⁶, 1.0 × 10⁻⁵, 3.0 × 10⁻⁵ mol) and then the mixture was stirred at room temperature for more than 2h. Finally, the corresponding doses (2.0 × 10⁻⁵, 6.0 × 10⁻⁵, 2.0 × 10⁻⁴, 6.0 × 10⁻⁴ mol) MSA solution (0.5 M), and then Na₂S (0.1 M) were added to the mixture drop by drop at the Ag:S ratios of 10:1. The reactant was mixed and stirred under room temperature for 60 min. To study the influence of temperature and reaction time on the growth behavior of Ag₂S on the surface of NaYF₄:Yb/Er, different pH values (pH = 2, 4, 6, 8), different temperatures (20, 35, and 60 °C) and various reaction time (1, 5, 15, 30, 60, and 300 min) were applied to the synthesis of NaYF₄:Yb/Er@CS@Ag₂S NCs. This super facile synthesis strategy is suitable for the growth of ultras-small Ag₂S on various shapes of NaYF₄:Yb/Er, including plates, spheres and rods. Moreover, the *in-situ* growth routine can be extended to prepare NaYF₄:Yb/Er@CS@CuS and NaYF₄:Yb/Er@CS@CdS nanocomposites. For the fabrication of NaYF₄:Yb/Er@CS@CdS, 3.0 × 10⁻⁶ mol Cd(NO₃)₂ solution (10.0 mM) was added to the NaYF₄:Yb/Er@CS solution, then, after more than 2 h of stirring, NaOH (2.0 M) was used to adjust the pH of solution to 9. Finally, MSA solution (0.5 M) and then Na₂S (0.1 M) were added to the mixture drop by drop at the Cd:S ratios of 10:1, the reactant was stirred under room temperature for 5 min, the solution was kept at 90°C for 40 min. For the fabrication of NaYF₄:Yb/Er@CS@CuS, 3.0 × 10⁻⁶ mol Cu(NO₃)₂ solution (10.0 mM) was added to the NaYF₄:Yb/Er@CS solution, then, after more than 2 h of stirring. Then, Na₃Cit solution (0.5

M) and then Na₂S (0.1 M) were added to the mixture drop by drop at the Cu:S ratios of 10:1, the reactant was stirred under room temperature for 15 min.

Characterization: Powder X-ray diffraction (XRD) data were measured on a Bruker D8 Focus powder X-ray diffractometer at a scanning rate of 0.5° min⁻¹ in the 2θ range from 20 to 80° using Cu Kα radiation (λ = 1.5418 Å) operating at an operation voltage and current maintained at 40 kV and 40 mA. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), bright-field TEM image and the corresponding EDX elemental mappings images were obtained on a FEI Tecnai G2S-Twin instrument with a field emission gun operating at 200 kV. Fourier transform infrared spectroscopy (FTIR) were obtained using a PerkinElmer 580B IR spectrophotometer with a KBr pellet technique. The absorption spectrum was measured using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a VG ESCALAB MKII spectrometer. The chemical compositions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, with a Varian Liberty 200 spectrophotometer). The UCL spectra were recorded by using a 980 nm laser diode and a triple grating monochromator (Spectra Pro-2758, Acton Research Corporation) equipped with a photomultiplier (Hamamatsu R928).

In vitro cytotoxicity assay of NaYF₄:Yb/Er@CS@Ag₂S: Typical MTT assays were performed to assess the cytotoxicity of NaYF₄:Yb/Er@CS@Ag₂S nanocomposites. In detail, A549 cells were first put in a 96-well plate (about 5000 per well) and cultured at 37 °C and 5% CO₂ for 24 h in DMEM supplemented with 10% FBS. Then, the cells were washed with PBS and incubated with NaYF₄:Yb/Er@CS@Ag₂S nanocomposites at different Ag⁺ concentrations (0, 12.5, 25, 50, 100, 200 μg mL⁻¹) at 37 °C incubated for another 24 h. After that, 20 μL of MTT with a concentration of 5 mg mL⁻¹ was added to each well and allowed to react with the cells for an additional 4 h. Subsequently, 150 μL of dimethyl sulfoxide

(DMSO) were added to each well to dissolve the MTT formazan crystals formed. Finally, the absorption of each solution was measured at 570 nm by a microplate reader. Cell viability was calculated as a percentage compared with untreated control cells.

In vitro UCL imaging of NaYF₄:Yb/Er@CS@Ag₂S: The *in vitro* upconversion luminescence imaging of A549 cells was carried out by a custom-built instrument for upconversion luminescence microscopy, which was rebuilt from an inverted fluorescence microscope (Nikon Ti-S) with an external laser diode for illuminating the samples. A549 cells were seeded in 24-well culture plates (4×10^4 cells per well) and incubated (37 °C, 5% CO₂) overnight. Then, the original cell culture medium was discarded and fresh culture medium containing NaYF₄:Yb/Er@CS@Ag₂S solution (200 µg mL⁻¹, 0.5 mL) was added into each well and incubated at 37 °C for 3 h. Then, the cells were carefully washed with PBS three times, fixed with 4% poly formaldehyde PBS solution for 15 min, and then washed with PBS three times again.

Photothermal effect of NaYF₄:Yb/Er@CS@Ag₂S nanocomposites: NaYF₄:Yb/Er@CS@Ag₂S nanocomposites aqueous solution with different Ag⁺ concentrations (0, 12.5, 25, 50, 100, 200 µg mL⁻¹) were exposed to the 980 nm laser (1.0 W cm⁻², 10 min). The solution temperature was measured every 10 s by a thermocouple microprobe. To deduce the photothermal conversion efficiency (η), NaYF₄:Yb/Er@CS@Ag₂S (200 µg mL⁻¹) aqueous solution was irradiated with NIR laser until the temperature was steady. Then, the laser was turned off and the system temperature was cooled naturally to the ambient temperature with measuring the temperature every 10 s. The photothermal conversion efficiency (η) was calculated by using equations (1)-(4):^[4,5]

$$\eta = hS (T_{max,nanocomposites} - T_{max,solvent}) / I (1 - 10^{-A_{980}}) \quad (1)$$

$$\tau_s = m_d C_d / hS \quad (2)$$

$$t = -\tau_s \ln \theta \quad (3)$$

$$\theta = T - T_{surr} / (T_{max,nanocomposites} - T_{max,solvent}) \quad (4)$$

where h is the heat transfer coefficient, S is the surface area of the container, $T_{max,nanocomposites}$ and $T_{max,solvent}$ are maximum steady-state temperature for NaYF₄:Yb/Er@CS@Ag₂S nanocomposites solution and water, which are 66.7 and 25.1 °C, respectively. I is the incident laser power (1.0 W cm⁻²), and A_{980} is the absorbance of NaYF₄:Yb/Er@CS@Ag₂S nanocomposites at 980 nm ($A_{980} = 0.11$). τ_s is the sample system time constant, and m_d and C_d are the mass (1.0 g) and heat capacity (4.2 J g⁻¹) of the deionized water used as the solvent, respectively. θ is the dimensionless driving force temperature, T_{surr} is the ambient temperature of the surroundings, T is a temperature for NaYF₄:Yb/Er@CS@Ag₂S aqueous solutions at a constant cooling time (t), and the τ_s was determined to be 243.59 s (Figure 6h). The photothermal conversion efficiency of NaYF₄:Yb/Er@CS@Ag₂S nanocomposites was calculated according to equation (5):

$$\eta = m_d C_d (T_{max,nanocomposites} - T_{max,H_2O}) / I (1 - 10^{-A_{980}}) \tau_s \quad (5)$$

In vitro photothermal effect NaYF₄:Yb/Er@CS@Ag₂S: For *in vitro* photothermal imaging 1 mL of NaYF₄:Yb/Er@CS@Ag₂S aqueous solutions ($Ag^+ = 200 \mu g mL^{-1}$) in cuvette was irradiated for 0 and 6 min (980 nm, 1.0 W cm⁻²). An infrared thermal camera was used to record the temperature of the solution.

The cell live/dead assays were carried out to evaluate the efficiency of the PTT. Briefly, A549 cells seeded into a 24-well plate were divided into four groups (1–4) as follows: (1) control group (PBS solution), (2) NIR laser only group (980 nm, 1.0 W cm⁻², 6 min), (3) NaYF₄:Yb/Er@CS@Ag₂S group ($Ag^+ = 200 \mu g mL^{-1}$), and (4) NaYF₄:Yb/Er@CS@Ag₂S ($Ag^+ = 200 \mu g mL^{-1}$) plus NIR laser (980 nm, 1.0 W cm⁻², 6 min). A mixed solution containing 2 μM of calcein AM and 8 μM of PI was then added to the wells. After being stained for 40 min, cells were washed with PBS and examined by using a fluorescence microscope to detect the live/dead status.

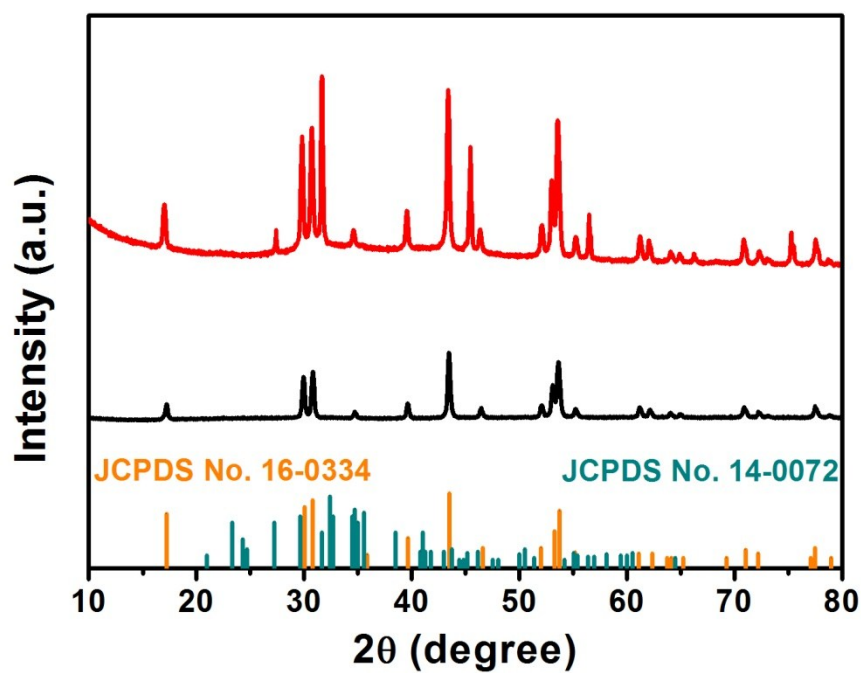


Fig. S1 XRD patterns of NaYF₄:Yb/Er (black line) and NaYF₄:Yb/Er@CS@Ag₂S (red line). The vertical bars show the peak positions and intensities for pure NaYF₄ (JCPDS No. 16-0334) and Ag₂S (JCPDS No. 14-0072) as the references.

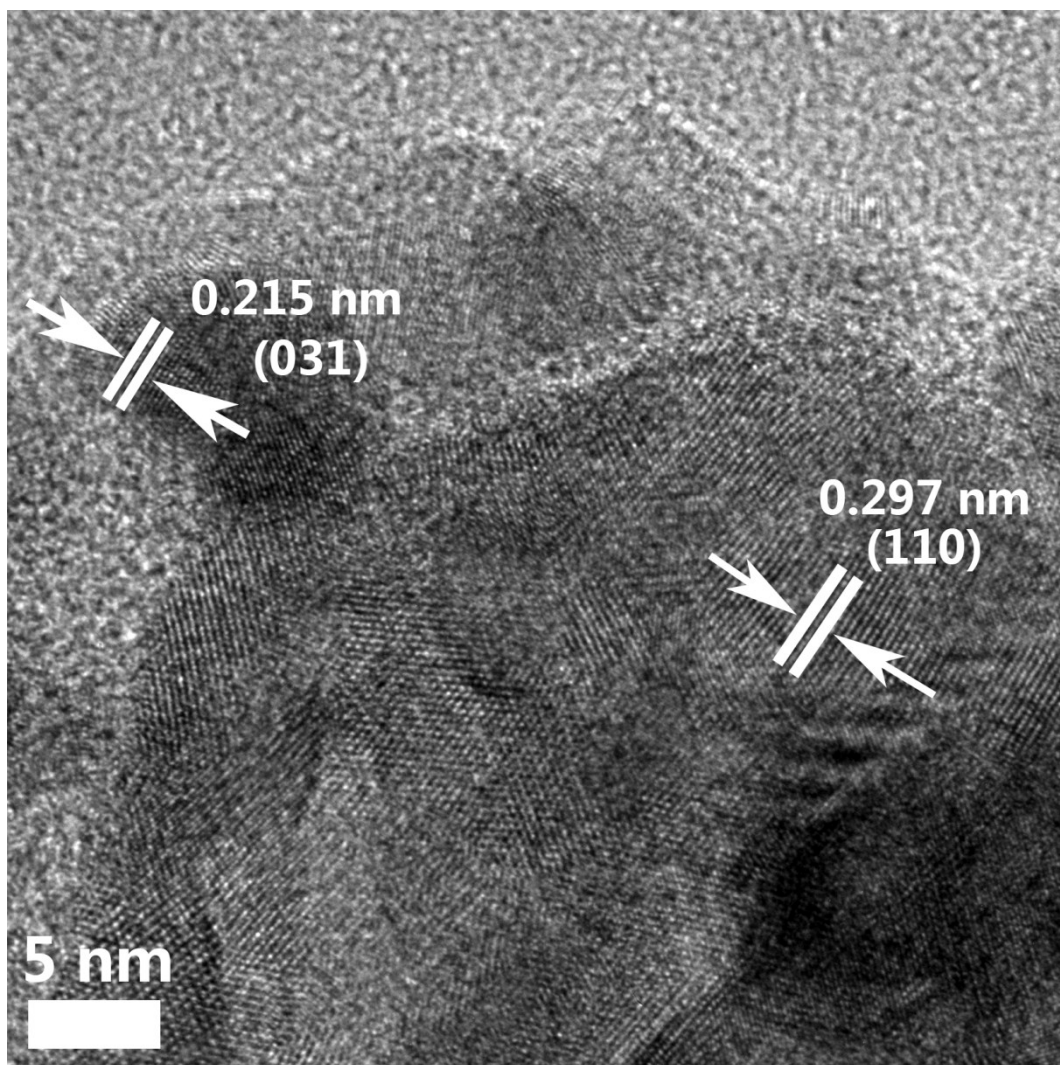


Fig. S2 HRTEM image of NaYF₄:Yb/Er@CS@Ag₂S.

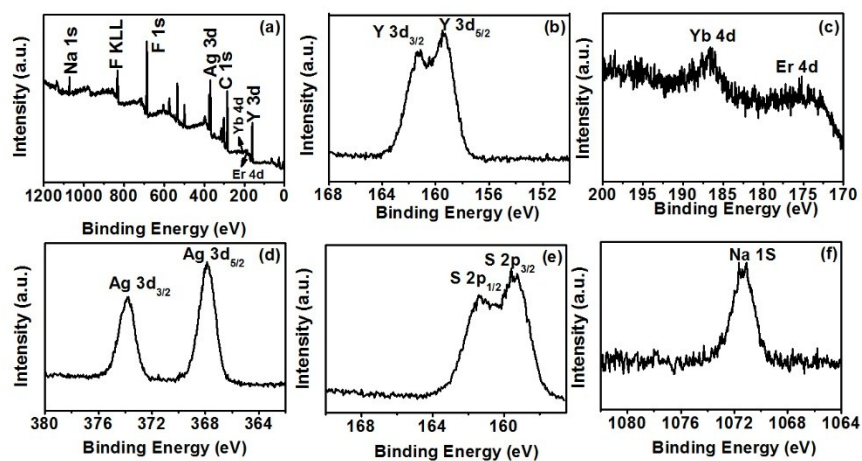


Fig. S3 X-ray photoelectron spectroscopy (XPS) of NaYF₄:Yb/Er@CS@Ag₂S (a) survey, (b) Y 3d, (c) Yb and Er 4d, (d) Ag 3d, (e) S 2p and (f) Na 1s.

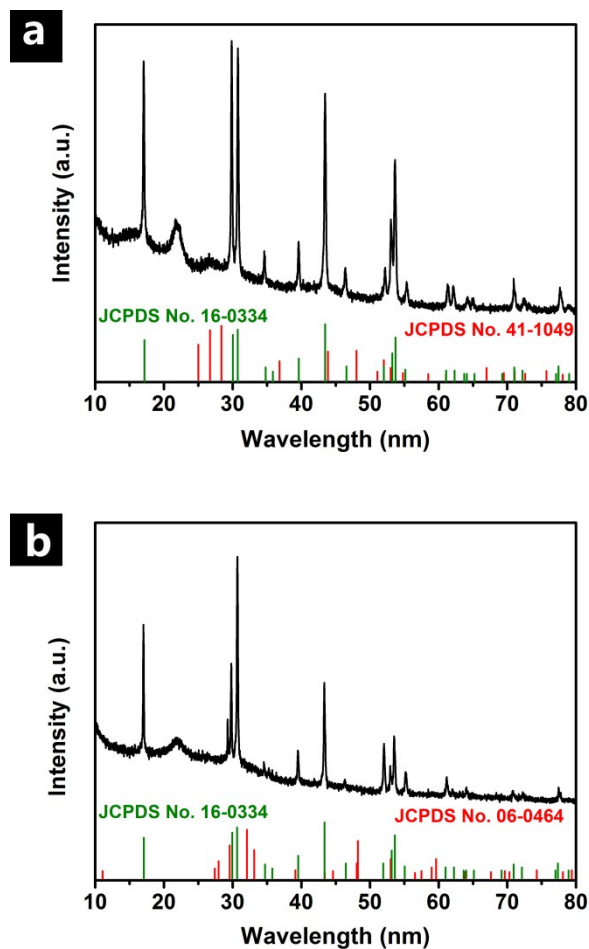


Fig. S4 XRD patterns of (a) NaYF₄:Yb/Er@CS@CdS and (b) NaYF₄:Yb/Er@CS@CuS. The vertical bars show the peak positions and intensities for pure NaYF₄ (JCPDS No. 16-0334), CdS (JCPDS No. 41-1049) and CuS (JCPDS No. 06-0464) as the references.

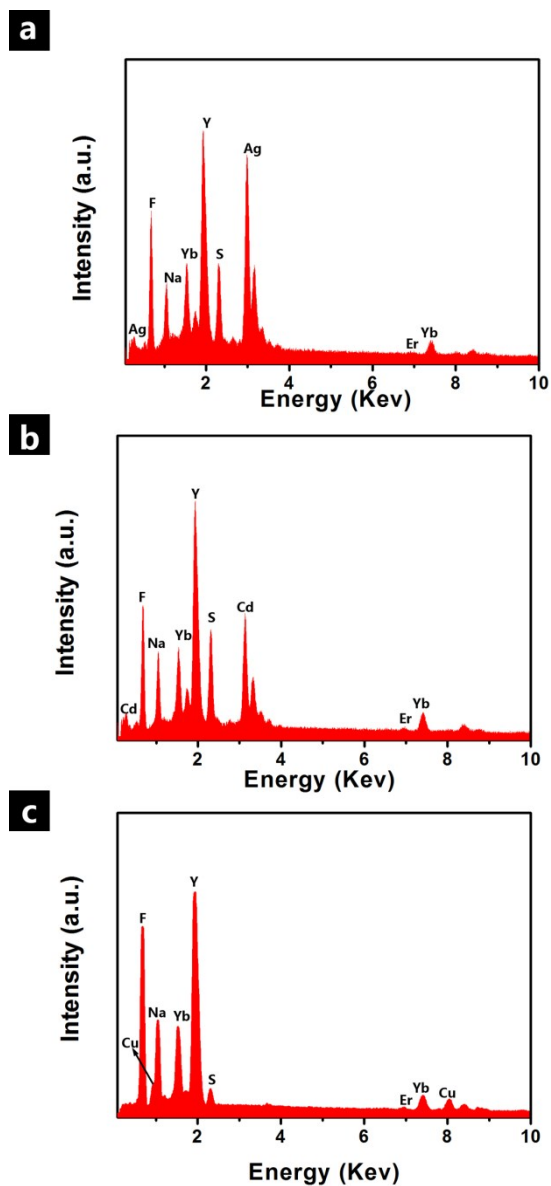


Fig. S5 Energy-dispersive X-ray (EDX) spectra of (a) NaYF₄:Yb/Er@CS@Ag₂S, (b) NaYF₄:Yb/Er@CS@CdS, and (c) NaYF₄:Yb/Er@CS@CuS.

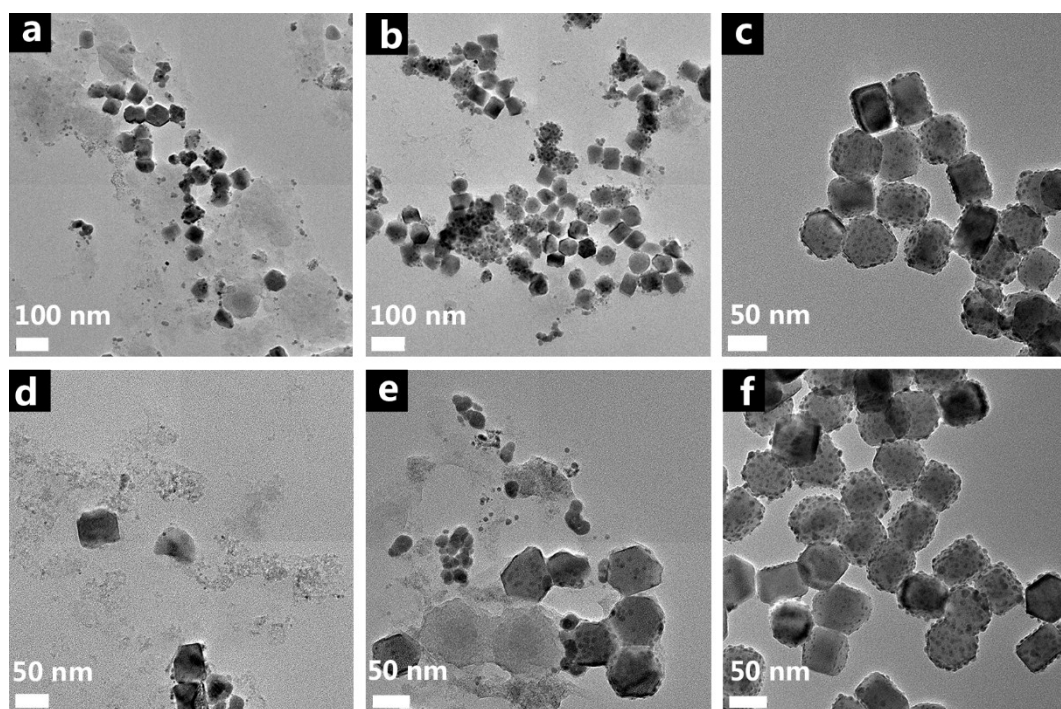


Fig. S6 TEM images of NaYF₄:Yb/Er@CS@Ag₂S nanocomposites synthesized with various pH values, (a, d) pH = 2, (b, e) pH = 4, (c) pH = 6, (f) pH = 8.

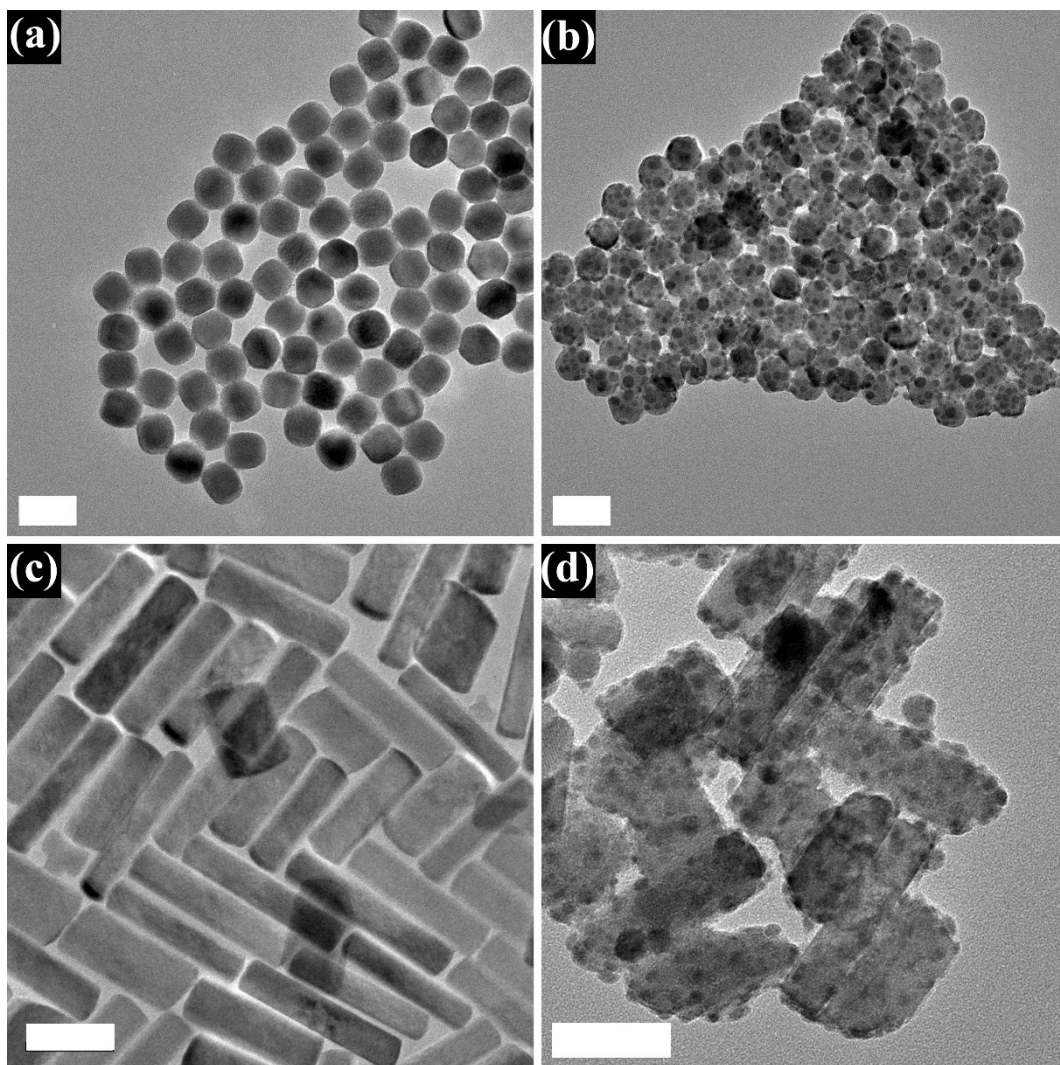


Fig. S7 TEM images of spherical NaYF₄:Yb/Er@CS (a) and the corresponding NaYF₄:Yb/Er@CS@Ag₂S (b), the rod-like NaYF₄:Gd/Yb/Er@CS (c) and the corresponding NaYF₄:Gd/Yb/Er@CS@Ag₂S.

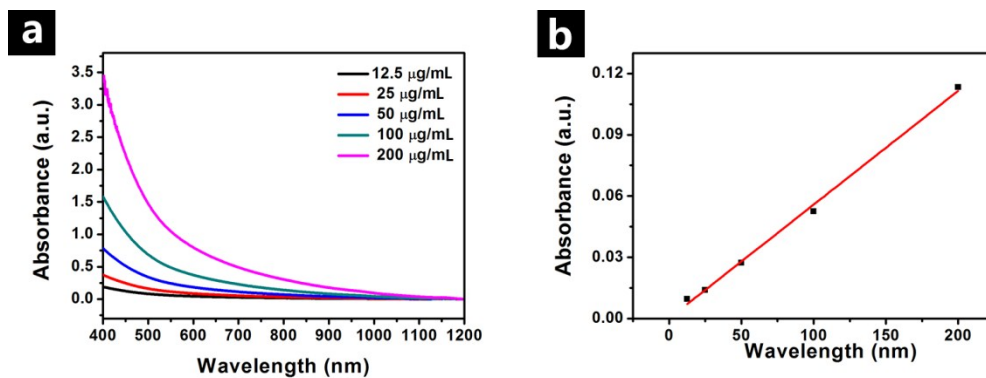


Fig. S8 (a) UV-vis-NIR absorption spectra of NaYF₄:Yb/Er@CS@Ag₂S in water with different concentrations. (b) A linear relationship for the absorbance at 980 nm as a function of the concentration of NaYF₄:Yb/Er@CS@Ag₂S.

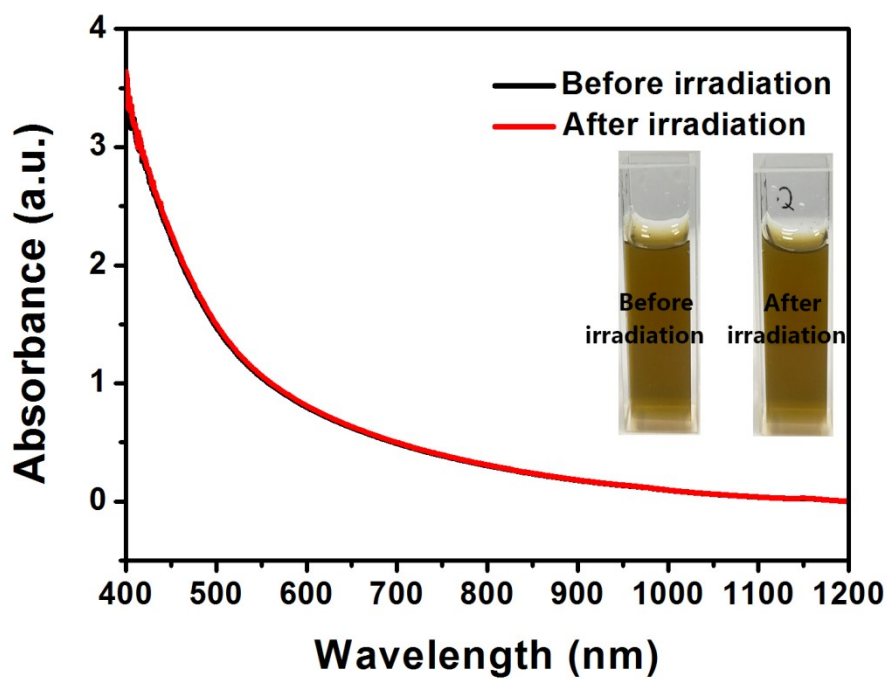


Fig. S9 UV-vis-NIR absorption spectra of NaYF₄:Yb/Er@CS@Ag₂S dispersion before and after 1 h laser irradiation (980 nm, 1.0 W cm⁻²); inset pictures represent the well-dispersed NaYF₄:Yb/Er@CS@Ag₂S solution before and after irradiation.

Table S1. Summary of experiment parameters, morphology, and sizes of the as-prepared NaYF₄:Yb/Er@CS@Ag₂S.

Sample	Ag:Y Ratio	S:Ag Ratio	Reaction Temp (°C)	Reaction Time (min)	pH values	Geometric Shape	Size (nm)
NC1	0.02:1	10:1	10	60	6	Spherical QDs attached on the NCs	2.9 ± 0.2
NC2	0.06:1	10:1	10	60	6		5.1 ± 0.4
NC3	0.2:1	10:1	10	60	6		8.1 ± 0.3
NC4	0.6:1	10:1	10	60	6	Irregular Spherical QDs attached on the NCs	13.9 ± 0.9
NC5	0.2:1	1:1	10	60	6	blurred film adhered to the surface of NCs	-
NC6	0.2:1	2:1	10	60	6		-
NC7	0.2:1	5:1	10	60	6	Spherical QDs attached on the NCs	4.1 ± 0.3
NC8	0.2:1	10:1	10	60	6		8.2 ± 0.5
NC9	0.2:1	20:1	10	60	6	Some spherical QDs attached on the NCs, and some QDs are detached from the surface	6.0 ± 0.9
NC10	0.06:1	10:1	10	60	6	Spherical QDs attached on the NCs	4.9 ± 0.4
NC11	0.06:1	10:1	35	60	6		6.9 ± 0.8
NC12	0.06:1	10:1	60	60	6		9.9 ± 0.5
NC13	0.06:1	10:1	10	1	6		4.8 ± 0.3
NC14	0.06:1	10:1	10	60	6		5.3 ± 0.4
NC15	0.06:1	10:1	10	300	6		7.0 ± 0.8
NC16	0.06:1	10:1	10	60	2	Some Ag ₂ S grows on the surface of NCs, and some are dispersed in the solution.	7.2 ± 0.6
NC17	0.06:1	10:1	10	60	4		6.8 ± 0.5
NC18	0.06:1	10:1	10	60	6	Spherical QDs attached on the NCs	5.2 ± 0.4
NC19	0.06:1	10:1	10	60	8		5.9 ± 0.6

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