## Observation of Considerable Upconversion Enhancement Induced by Cu<sub>2-x</sub>S Plasmon Nanoparticles

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**Figure S1** (a) Typical large-area SEM image: the surface of the surface of  $Cu_{2-x}S$  layer. (b) SEM image of the  $Cu_{2-x}S$  film cross-section. The thickness is 925±20 nm. (c) TEM image: NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> NPs with an average size of 8 nm. (d) Typical large-area SEM image of the NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> layer. (e-h) AFM images: thickness of 4 nm, 8nm, 12 nm, 16nm MoO<sub>3</sub> layer. (i)AFM and SEM images: thickness of the NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> layer.

To obtain the  $Cu_{2-x}S-MoO_3-NaYF_4:Yb^{3+}$ ,  $Er^{3+}$  hybrid structure, the colloidal  $Cu_{2-x}S$  NCs was dissolved in the cyclohexane solution. The glass was dropped vertical

into the solution. With the slowly volatilizing of cyclohexane, the  $Cu_{2-x}S$  NPs were self-organized onto the surface of the glass. The surface morphology of the  $Cu_{2-x}S$  layer is shown in Figure S1a. Figure S1b displays the cross-section of the  $Cu_{2-x}S$  film with approximately 925 nm thickness. Then a thin layer of MoO<sub>3</sub> was subsequently deposited using vacuum vapor deposition system. The thickness of the MoO<sub>3</sub> spacer was controlled to be 4 nm, 8 nm, 12 nm, 16 nm. In order to measure the thickness of MoO<sub>3</sub> layer, we deposited the MoO<sub>3</sub> alone on the glass under exactly the same conditions at the same time. Then a slide was gently made on the surface of the glass with a surgical knife blade, a channel was formed. Figure S1e-h shows the AFM images of the channel area and the thickness is accurately measured. The NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> NPs was spin-coated on top of the smooth oxide layer with approximately 150 nm thickness. Figure S1i shows the TEM image of the NaYF<sub>4</sub> NPs with an average size of 8 nm. The surface of the NaYF<sub>4</sub> layer is smooth and compact shown in the large-area SEM image (Figure S1d).

The thickness of the NaYF<sub>4</sub> layer on the glass was approximately 150 nm shown in Figure S1i. It is hard to determine the thickness of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs on the Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub> hybrids film, therefore, we compared the extinction of NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs on the glass and the Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub> hybrids film, by using the Eqs. A<sub>i</sub> = log(1/T<sub>i</sub>), i = 1, 2(i=1 represents the film on glass, and i=2 represents the hybrid film). It is determined that A<sub>1</sub>=1.95 and A<sub>2</sub>=1.93, which indicates that the effective thickness of the NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> NPs on the Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub> film is close to that on the glass. This suggests that the thickness variation of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> NPs on the glass and the Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub> film should have little influence on the EF.



Figure S2 (a-c) XPS survey spectrum of 6.5 nm, 8.8 nm, 10.8 nm Cu<sub>2-x</sub>S NPs.

The composition of Cu<sub>2-x</sub>S NPs was further confirmed by the XPS spectra, as shown in Figure S2. The XPS spectra indicate the presence of Cu and S in Cu<sub>2-x</sub>S NPs. No obvious impurities were found on the surfaces of the samples, indicating that the as-prepared Cu<sub>2-x</sub>S NPs are relatively pure. The binding energies for Cu  $2p_{3/2}$  are 931.90 eV, 932.30 eV and 933.50 eV for the 6.5 nm, 8.8 nm and 10.8 nm respectively, while the binding energies for Cu  $2p_{1/2}$  are 951.70 eV, 952.10 eV and 953.30 eV respectively. The peaks shift to the high energy side with the size increase of Cu<sub>2-x</sub>S NPs. For the Cu, two contributions are discerned from the dissolved spectra of the Cu  $2p_{3/2}$  peak and Cu  $2p_{1/2}$  peak. The higher binding energy peaks are assigned to Cu<sup>2+</sup>, accompanied by the characteristic Cu<sup>2+</sup> shaking up satellite peaks (938-945 eV),. The lower binding energy peaks are assigned to Cu<sup>+</sup>. The XPS peaks of S could be deconvoluted to the binding energy of S  $2p_{3/2}$  (160.63 eV) and S  $2p_{1/2}$  (163.06 eV).

These are in good agreement with the literature reported results.<sup>[1-3]</sup> The XPS spectra indicate the existence of Cu<sup>+</sup> and Cu<sup>2+</sup>. By the integral spectra of Cu<sup>2+</sup> and Cu<sup>+</sup>, the ratios of Cu<sup>2+</sup> to Cu<sup>+</sup> in different Cu<sub>2-x</sub>S NPs can be determined, then the ratios of Cu to S can be determined further. The Cu to S ratios calculated from XPS spectra are 1.87, 1.83 and 1.71 for 6.5 nm, 8.8 nm and 10.8 nm Cu<sub>2-x</sub>S NPs, respectively, which are well in consistent with the results of EDX.



**Figure S3** The absorption spectra of the  $Cu_{2-x}S$  NPs dispersed in three different solvents: cyclohexane, trichloromethane, tetrachloromethane, with refractive indices of 1.43, 1.45, 1.46. The inset shows the red-shift in the LSPR maximum with increasing solvent refractive index. The NIR absorption bands redshift with increasing the refractive index, as expected from the LSPR feature. The shift indicates the NIR absorption originates from the LSPR in  $Cu_{2-x}S$  NPs. The spectrum of  $Cu_{2-x}S$  film on the glass red-shifts about 40 nm and is broadened, which could be attributed to the coupling of LSPR modes among the different  $Cu_{2-x}S$  NPs.



**Figure S4** Schematic illustration of  $Cu_{2-x}S$  NP sample for Hall effect measurement. The Hall Effect experiment was performed using the HL5500 Hall effect measurement system. The  $Cu_{2-x}S$  NPs was self-assembled on the glass substrate and wiped to form a square (1 cm×1 cm). The thickness of the  $Cu_{2-x}S$  film was about 1 µm. The In-Sn alloy was placed on the four corners of the square as the electrode. The resultes showed that the density of free carriers was  $1.546 \times 10^{18}/cm^3$ .



**Figure S5** (a) The FITR spectra of pure OAm, pure OA,  $Cu_{2-x}S$  NPs and  $Cu_{2-x}S$  NPs after 200°C annealing. (b) The Raman spectra of  $Cu_{2-x}S$  NPs and  $Cu_{2-x}S$  NPs after 200°C annealing.

The Cu<sub>2-x</sub>S NPs for FTIR measurement were washed with ethanol for three times and dried into powder. Then part of the power was annealed for 2 hours at 200°C. The spectrum of Cu<sub>2-x</sub>S NPs was clearly dominated by characteristic vibrations as the N-H stretching band at 3300 cm<sup>-1</sup>, the C-H stretching band at 2854 cm<sup>-1</sup>, 2922 cm<sup>-1</sup> and the C=C bending vibrations at 1647 cm<sup>-1</sup>, which were corresponding to the characteristic vibrations of OAm, indicating that the surface of Cu<sub>2-x</sub>S NPs was capped with OAm as surface ligands. For spectrum of Cu<sub>2-x</sub>S NPs after 200°C annealing, the N-H stretching band at 3300 cm<sup>-1</sup>, the C-H stretching band at 2854 cm<sup>-1</sup>,2922 cm<sup>-1</sup> and the C=C bending vibrations at 1647 cm<sup>-1</sup> disappeared, indicating the OAm ligands disappeared.

Figure S5b shows the Raman spectra of  $Cu_{2-x}S$  NPs and  $Cu_{2-x}S$  NPs after 200°C annealing for 2h. The observation of vibrational modes of  $Cu_{2-x}S$  NPs indicated the presence of OAm on the surface of NPs, the broad bands observed at 1350, 1560, and 1600 cm<sup>-1</sup> suggested the disordered carbon chains. For the  $Cu_{2-x}S$  NPs after 200°C annealing for 2h, the broad bands weakened a lot, indicating the surface ligands disappeared.



**Figure S6** Differential transmission signal from the  $Cu_{2-x}S$  film for dynamics at 900 nm probe wavelength. The dotted lines are the fitting lines.

Scotognella, F. et al<sup>[4]</sup> has investigated the transient absorbance spectra of Cu<sub>1.85</sub>Se NPs. We tested the transient absorbance spectra of Cu<sub>2-x</sub>S NPs using exactly the same methods. The pump pulses are around 1200 nm which is in correspondence with the plasmonic resonance of the sample. The pump-probe setup employed a computer-controlled optical multichannel analyzer and the measured signal is a map of the chirp-free differential transmission  $\Delta T/T = (T_{on} - T_{off})/T_{off}$  as a function of the pump-probe time delay for different probe wavelengths;  $T_{\text{on}}$  and  $T_{\text{off}}$  are the probe spectra transmitted by the excited and unperturbed samples, respectively. Figure S6 reports the temporal dynamics of the relative differential transmission ( $\Delta T/T$ ) probed at 900 nm. The different temperatures were obtained by changing the pump power, which were tested by thermocouple. According to the results by Scotognella, F. et al., the fast decay of the differential transmission occurring within the first few picoseconds after the excitation is related to the fast decrease of the carrier temperature. The decay time constants at 379, 410, 451 and 486 K are determined to be 0.59, 0.54, 0.50 and 0.43 ps, respectively, which originate from the electron-phonon coupling in Cu<sub>2-x</sub>S NPs. This indicates that the electron-phonon coupling increases with the elevated temperature, which may induce the spectral broadening of LSPR peak. Similar conclusion was also drawn by Scotognella, F. et al.



**Figure S7** (a) XRD patterns of  $Cu_{2-x}S$  NPs,  $Cu_{2-x}S$  NPs irradiated by 980 nm laser for 10 min,  $Cu_{2-x}S$  NPs by 200°C (473K) thermal treatment for 2 hours. (b) TEM images of  $Cu_{2-x}S$  NPs without irradiation or thermal treatment. Scale bar: 50 nm. (c) TEM images of  $Cu_{2-x}S$  NPs irradiated by 980 nm laser for 10 min. The  $Cu_{2-x}S$  samples after irradiation are dispersed in cyclohexane for the TEM measurement. Scale bar: 50 nm.

In order to reveal the structure change, the XRD patterns of the  $Cu_{2-x}S$  ( $Cu_{2-x}S$ , x=0.2) NPs before and after laser irradiation or annealing at 200°C for 2h were characterized. Before annealing, the XRD patterns for  $Cu_{2-x}S$  NPs locate at 20 of 27.8°, 32.2°, 46.2° and 54.7°, corresponding to the (0,0,15), (1,0,10), (0,1,20), and (1,1,15) planes of rhombohedral  $Cu_{1.8}S$  phase (JCPDS No. 47-1748). In contrast to the standard card, the XRD peaks for the  $Cu_{2-x}S$  NPs after annealing have a shift of 0.3-0.5° toward small angle side, which could be attributed to the decrease of deficient states ( $Cu^{2+}$ ), as the atomic radius of  $Cu^{2+}$  is smaller than that of  $Cu^{+}$ . This suggests that the deficient states  $Cu^{2+}$  decrease and even disappear after the thermal treatment, which can be further proved by EDX and XPS experiments. The XRD pattern of  $Cu_{2-x}S$  NPs irradiated by 980 nm laser for 10 min (the power density is 1.23W/mm<sup>2</sup>) remains unchanged compared to the as-prepared  $Cu_{2-x}S$  NPs.

The  $Cu_{2-x}S$  samples after irradiation were dispersed in cyclohexane for the TEM measurement. The TEM images of  $Cu_{2-x}S$  NPs,  $Cu_{2-x}S$  NPs irradiated by 980 nm laser for 10 min are shown in Figure S7b, c. It can be seen that the  $Cu_{2-x}S$  NPs are all mono-dispersed, indicating that the NPs did not agglomerate after 10 min laser irradiation.



**Figure S8** (a) EDX spectra of  $Cu_{2-x}S$  NPs, thermal treatment at 50°C (323K), 200°C (473K) for 2 hours respectively. (b) XPS spectra of Cu 2p region of  $Cu_{2-x}S$  NPs after thermal treatment at 200°C (473 K) compared to that at 20°C (293 K). (c) XPS spectra of O1s region of  $Cu_{2-x}S$  NPs without thermal treatment. (d) XPS spectra of O1s region of  $Cu_{2-x}S$  NPs after thermal treatment at 200°C.

The EDX spectra of the  $Cu_{2-x}S$  NPs before and after annealing at 200 °C for 2h were compared, as shown in Figure S8a. It can be seen that the Cu to S ratio becomes bigger after annealing and close to 2.0, indicating the decrease and even disappearance of  $Cu^{2+}$ , which matches well with the XRD patterns. The XPS spectra show that the binding peaks shift about 0.7 eV to the lower energy after 200°C (473 K) thermal treatment, which further confirms the decrease of  $Cu^{2+}$ . The Cu to S ratio calculated from the XPS spectra is 1.82 at 293 K and 2.01 at 473 K. The tendency of both EDX and XPS is increasing to 2. The XPS spectra of O1s region of  $Cu_{2-x}S$  NPs before and after annealing at 200 °C for 2h were compared shown in Figure S8c, d. The XPS spectrum of O1s region before annealing shows a peak at 531.76 eV. For XPS spectrum after annealing, two peaks are distinguished at 531.87 eV and 530.23 eV respectively. The peak at 530.23 eV should be assigned to lattice oxygen which need a bigger binding energy. The peak at 531.76 eV should be assigned to absorbed oxygen.



**Figure S9** Electric properties of  $Cu_{2-x}S$  film after 400°C thermal treatment: the temperature-dependent conductance. The resistance of  $Cu_{2-x}S$  films after thermal treatment was several hundred Ohm, while the resistance was 10<sup>6</sup> Ohm for  $Cu_{2-x}S$  films without thermal treatment. The slopes of the temperature dependent conductivity of  $Cu_{2-x}S$  film after thermal treatment decreased a little and was independent with  $Cu_{2-x}S$  NP sizes compared to the as-prepared  $Cu_{2-x}S$  film.



**Figure S10** The deduced local temperature (based on  $R_{HS}$ ) of the sample as a function of excitation power for  $Cu_{2-x}S-MoO_3-NaYF_4:Yb^{3+}$ ,  $Er^{3+}$  hybrids. The intensity ratio ( $R_{HS}$ ) of  ${}^{2}H_{11/2}-{}^{4}I_{15/2}$  to  ${}^{4}S_{3/2}-{}^{4}I_{15/2}$  is sensitive to temperature and is a critical parameter in discussing the temperature change in upconversion process. Figure S10 displays the deduced local temperature (based on  $R_{HS}$ ) of the sample as a function of excitation power for  $Cu_{2-x}S-MoO_3-NaYF_4:Yb^{3+}$ ,  $Er^{3+}$  hybrids.



**Figure S11** (a) The TEM image of Au nanorod sample. (b)The absorption spectra of Au nanorods solution and film used in this experiment with the apsorption peak centered at 920 nm. The Au nanorods sample was prepared in comparison to the  $Cu_{2-x}S-MoO_3-NaYF_4:Yb^{3+}$ ,  $Er^{3+}$  hybrids. The Au nanorods sample was fabricated under exactly the same condition only replacing the  $Cu_{2-x}S$  layer with Au nanorods. Figure S11a shows the TEM image of Au nanorods with an average size of 45 nm. The absorption spectra of Au nanorods solution and film are shown in Figure S11b. The Au nanorods dissolved in water solution has an absorption peak centered at 920 nm, wihle for the Au nanorods film the absorption spectra is broadened, becoming a broad absorption band.



**Figure S12.** (a-b) The power density dependence of integral UCL intensity of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>, Au-MoO<sub>3</sub>-NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> and Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> hybrids  $({}^{2}H_{9/2}/{}^{4}F_{9/2}-{}^{4}I_{15/2}$  transitions).



**Figure S13** (a) The power density dependence of integral UCL intensity of  $Cu_{2-x}S-MoO_3-NaYF_4$  hybrids with  $Cu_{2-x}S$  film annealed at 200°C for 2 hours. (b) The power density dependence of enhancement factor of  $Cu_{2-x}S-MoO_3-NaYF_4$  hybrids with  $Cu_{2-x}S$  film annealed at 200°C for 2 hours.

The Cu<sub>2-x</sub>S film was annealed at 200°C for 2 hours. Then we fabricated the  $Cu_{2-x}S$ -MoO<sub>3</sub>-NaYF<sub>4</sub> hybrids with  $Cu_{2-x}S$  film annealed and measured the emission The power density dependence of integral UCL intensity of spectra. Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub> hybrids with Cu<sub>2-x</sub>S film annealed was shown in Figure S13a. It can be seen that slopes of three transitions at high excitation power were higher than that at low excitation power, which was similar to the Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub> hybrids without annealed. The power density dependence of enhancement factor was shown in Figure S13b. It showed that the enhancement factor was nearly disappeared, while at high excitation (beyond 0.9 W/mm<sup>2</sup>) the enhancement factor was very high. When the Cu<sub>2-x</sub>S film was annealed and the plasmonic absorption disappeared as shown in Figure 2c (the main text), the enhancement was nearly disappeared at low excitation power. We thought that the enhancement was own to the plasmon resonance at low excitation power which would disappear after annealed. The enhancement at high excitation power was mainly own to the electron diffusion which was influenced little after annealed.



Figure S14 The diffuse reflection spectra for Cu<sub>2-x</sub>S NPs of different size (6-11 nm).



**Figure S15** The time-resolved spectra of  $Cu_{2-x}S$  film and  $Cu_{2-x}S$ -NaYF<sub>4</sub> film. The temporal dynamics of the relative differential transmission ( $\Delta T/T$ ) were probed at 520 nm, pump by 490 nm light. The decay time constant of  $Cu_{2-x}S$  decreased from 10.20 ps to 2.21 ps, indicating the opening of an additional nonradiative relaxation channel for  $Cu_{2-x}S$  film.



























**Figure S16** (a-f) Thicknesses of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> layer in Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> hybrid. Thicknesses are 431, 229, 128, 72, 46, 29 nm from (a) to (f) respectively. (g-j) Thicknesses of NaYF<sub>4</sub>:Yb<sup>3+</sup> layer in Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub>:Yb<sup>3+</sup> -NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> hybrid. Thicknesses are 20, 28, 37, 50 nm from (g) to (j) respectively. The AFM images were scanned on the edge of the NaYF<sub>4</sub> film on the glass substrate. When the thickness was less than 50 nm, the SEM image could not be seen clearly. Therefore, for samples with thickness less than 50 nm, only AFM images were provided.



**Figure S17** (a) The power density dependence of integral UCL intensity of  $Cu_{2-x}S-MoO_3-NaYF_4$  (undoped)-NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> hybrid with various thickness of NaYF<sub>4</sub> (undoped). The NaYF<sub>4</sub> layer does not dope with Yb<sup>3+</sup> or Er<sup>3+</sup>. (b) The power density dependence of UCL enhancement factor of  $Cu_{2-x}S-MoO_3-NaYF_4$  (undoped) -NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> with various thickness of NaYF<sub>4</sub> (undoped).



**Figure S18** (a) Emission spectra for NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> film and NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> /MoO<sub>3</sub>/Cu<sub>2-x</sub>S. (b) The power density dependence of integral UCL intensity of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> film. (c) The power density dependence of integral UCL intensity of Cu<sub>2-x</sub>S-MoO<sub>3</sub>-NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> hybrids. (d) Enhancement factor of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup>/MoO<sub>3</sub>/Cu<sub>2-x</sub>S film compared to NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> film. The fabrication conditions of the NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup>(150nm)/MoO<sub>3</sub>(8nm)/Cu<sub>2-x</sub>S hybrids were exactly the same with that of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup>/MoO<sub>3</sub>/Cu<sub>2-x</sub>S hybrids. Figure S16a showed the emission spectra for NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup>/MoO<sub>3</sub>/Cu<sub>2-x</sub>S hybrids and NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> film. Figure S16b ,c showed the ln–ln plots of <sup>1</sup>I<sub>6</sub>-<sup>3</sup>F<sub>4</sub>, <sup>1</sup>D<sub>2</sub>-<sup>3</sup>H<sub>6</sub>/<sup>3</sup>F<sub>4</sub>, <sup>1</sup>G<sub>4</sub>-<sup>3</sup>H<sub>6</sub>/<sup>3</sup>F<sub>4</sub>, <sup>3</sup>F<sub>2</sub>/<sup>3</sup>F<sub>3</sub>/<sup>3</sup>H<sub>4</sub>-<sup>3</sup>H<sub>6</sub> transitions, corresponding to five photons, four photons, three photons and two photons process respectively. The slopes of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup>/MoO<sub>3</sub>/Cu<sub>2-x</sub>S hybrids did not exhibit a rapid increase compared to NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup>/MoO<sub>3</sub>/Cu<sub>2-x</sub>S hybrids, slightly lower compared to the NaYF<sub>4</sub>: Yb<sup>3+</sup>, Tm<sup>3+</sup> film. For Tm<sup>3+</sup>, there was no energy level exactly matching to the bandgap of Cu<sub>2-x</sub>S semiconductor NPs.

## Note S1. Calculation of Cu to S ratio for different size of Cu<sub>2-x</sub>S NPs

We further calculated the Cu to S ratios for different size of Cu  $_{2-x}$ S NPs. Luther et al.<sup>5</sup> reported that the density of free carrier is  $1.7 \times 10^{21}$ /cm<sup>2</sup> and estimated a copper deficiency of 3.8% assuming each excess hole originates from one copper vacancy.<sup>[5]</sup> The density of Cu (N<sub>Cu</sub>) and S (N<sub>S</sub>) atom in Cu<sub>2</sub>S can be estimated as below.

$$N_{Cu} = \frac{N_h}{3.8\%} = \frac{1.7 \times 10^{21} cm^{-3}}{3.8\%} = 4.47 \times 10^{22} cm^{-3}$$

The density of S atom is half of the density of Cu atom in Cu<sub>2</sub>S.

$$N_S = \frac{N_{Cu}}{2} = 2.235 \times 10^{22} cm^{-3}$$

Based on the absorption spectra in Figure2a,  $N_h$  are calculated to be  $3.1 \times 10^{21}$  cm<sup>-3</sup>,  $3.8 \times 10^{21}$  cm<sup>-3</sup>,  $4.1 \times 10^{21}$  cm<sup>-3</sup>,  $4.7 \times 10^{21}$  cm<sup>-3</sup>,  $5.3 \times 10^{21}$  cm<sup>-3</sup> for the 6.5 nm, 7.8 nm, 8.8 nm, 9.8 nm and 10.8 nm Cu<sub>2-x</sub>S NPs. The Cu to S ratio in Cu<sub>2-x</sub>S is  $\frac{N_{Cu}-N_h}{N_S}$ .

The calculated results are 1.86, 1.83, 1.82, 1.79, 1.76, respectively, corresponding to the 6.5 nm, 7.8 nm, 8.8 nm, 9.8 nm and 10.8 nm  $Cu_{2-x}S$  NPs. The results of EDX analysis are 1.91, 1.86, 1.82, 1.79 and 1.75. The error at most is 2.6%, indicating the EDX analysis is reliable.

## Note S2. The absorption coefficient of NaYF<sub>4</sub>: Yb<sup>3+</sup>(20%), Er<sup>3+</sup>(2%)

According to the Beer-Lambert Law, the absorption coefficient of NaYF<sub>4</sub>: Yb<sup>3+</sup> (20%),  $\text{Er}^{3+}$  (2%) is calculated by

$$\alpha(v) = n(v) \times \sigma(v)$$

where n(v) presents the atomic density per unit volume,  $\sigma(v)$  denotes the absorption cross section and v is the frequency of incident light. For the transition from  ${}^{2}F_{7/2}$  to  ${}^{2}F_{5/2}$  of Yb<sup>3+</sup> (20%) at 980 nm excitation the absorption cross section was about 10<sup>-20</sup> cm<sup>-2</sup>. The atomic density can be calculated as

$$n(\nu) = \frac{n_i(\nu)}{Mr} \times N_A \times 20\%$$

where  $n_i(v)$  is the single atomic density, Mr is the Relative molecular mass, and  $N_A$  is Avogadro constant. And the absorption coefficient of NaYF<sub>4</sub>: Yb<sup>3+</sup> (20%), Er<sup>3+</sup> (2%) at 980 nm was about 2×10<sup>-6</sup> nm<sup>-1</sup>. The absorbance can be calculated by

$$\Delta I(v) = I_0(v)[1 - \exp(-\alpha(v)L)]$$

where  $I_0(\nu)$  is the intensity of incident light, and *L* is the film thickness of NaYF<sub>4</sub>: Yb<sup>3+</sup>, Er<sup>3+</sup> film. Based on the above calculations, we obtained the absorbance of NaYF<sub>4</sub>: Yb<sup>3+</sup> (20%), Er<sup>3+</sup> (2%) at 980 nm was about 2 ×10<sup>-4</sup>.

## **Reference:**

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