Supporting information for

Modify morphology of colloidal Ag_2Se nanostructures by laser irradiation

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1. Experimental Section

The synthesis of raw Ag_2Se nanoparticles. 34 mg $AgNO_3$ was first dissolved in 40 ml ethylenediamine, 7.3 mg Se powder was then added into the solution, the reaction was kept for 30 min at room temperature till the liquid color became brick-red. Afterwards, the suspension was centrifuged to separate Ag_2Se nanoparticles and washed several times with ethanol to remove excessive ethylenediamine. Finally, the product was dried by evaporation under ambient conditions.

Laser irradiation of Ag_2Se nanoparticles. A certain amount of Ag_2Se powder was redispersed into 1 ml ethylenediamine by sonification, and the suspension was divided equally into three parts. One part was irradiated by a millisecond Nd:YAG laser with a wavelength of 1064 nm and a power density of 2.4×10^7 W/cm^2 for 30 min, the product was denoted as sample A. The second part was treated by applying the same laser but a higher power density of 5.2×10^{10} W/cm^2 for 10 min, being denoted as sample B. The laser treatment on the third part was same with sample B except that the irradiation time was prolonged to 30 min, and the product was denoted as sample C. All of the three samples were washed successively by ethanol to remove ethylenediamine.

Characterization of the products. The morphology of Ag_2Se nanostructures was observed using a Hitachi S-4800 scanning electron microscope (SEM) and FEI Technai G2 F20 transmission electron microscope (TEM). TEM samples were prepared by dropping the suspension onto copper grids with conductive carbon film. The X-ray diffractometer (XRD) analysis for the crystal structure was carried out in a Rigaku D/max 2500v/pc diffractometer. UV-Vis absorption spectra were recorded in a Hitachi U-4100 spectrometer. The luminescent behavior was detected by using a Hitachi F-4500 fluorescence spectrophotometer.

2. Ag_2Se nanochains and their morphology change under laser irradiation

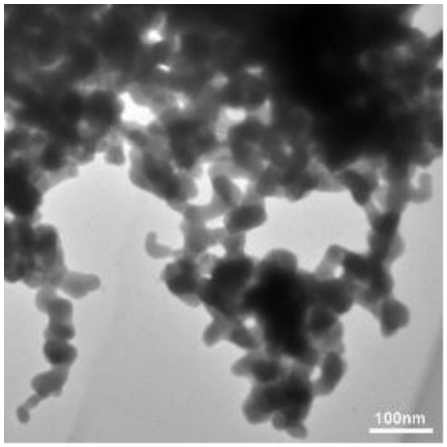

Fig. S1. TEM image of the Ag_2Se nanochains

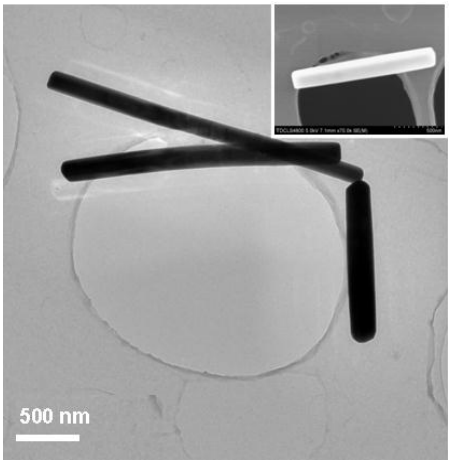

Fig.S2. TEM image of the Ag_2Se nanorods obtained at a low laser power density

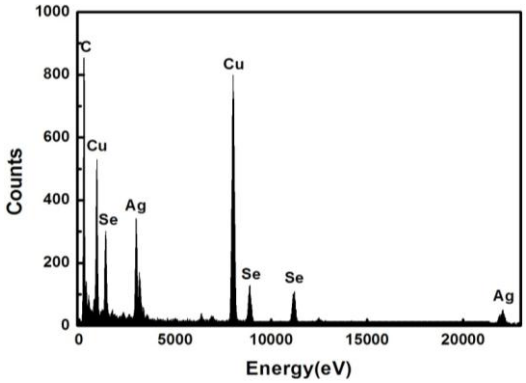

Fig.S3. EDS spectrum of the product obtained at a high laser power density

3. Calculation on the temperature rise due to laser irradiation

① In view of the principles of thermodynamics, we calculated the correlation between laser energy (*Q*) that Ag*2*Se nanocrystals absorbed and their temperature (*T*), as shown in Figure 2 of the manuscript, based on classic thermodynamics [1, 2].

a. $T \leq T_{\alpha-\beta}$ (133°C)

$$Q=c_{\alpha'}(T-T_0)+\Delta Q_1(T,d_0,\tau)+\Delta Q_2(T,d_0,\tau)$$

$$Q=[c_{\alpha'}(T_{\alpha-\beta}-T_0)+\Delta H_{\alpha-\beta}]+\Delta Q_1(T_{\alpha-\beta},d_0,\tau)+\Delta Q_2(T_{\alpha-\beta},d_0,\tau)$$

b. $T_{\alpha-\beta}<T\leq T_m$ (897°C)

$$Q=[c_{\beta'}(T-T_{\alpha-\beta})+c_{\alpha'}(T_{\alpha-\beta}-T_0)+\Delta H_{\alpha-\beta}]+\Delta Q_1(T,d_0,\tau)+\Delta Q_2(T,d_0,\tau)$$

In the formula: $\Delta Q_1(T,d_0,\tau)=h\cdot(T-T_l)\cdot S(d_0)\tau$; $\Delta Q_2(T,d_0,\tau)=\varepsilon\delta T^4\cdot S(d_0)\tau$

In the equations, $T_{\alpha-\beta}$ is α→β phase transformation temperature, T_m the melting temperature of bulk Ag_2Se, T_0. the ambient temperature (300 K), and T_l the temperature of the liquid which is 300 K. $c_{\alpha'}$ and $c_{\beta'}$ correspond to the specific heats of bulk Ag_2Se in α and β-phase, respectively. $\Delta H_{\alpha\rightarrow\beta}$ is the α→β phase transformation heat. d_0 stands for the diameters of nanospheres and nanowires. $S(d_0)$ is the surface area of nanocrystal or nanowire with diameter d_0. δ is Stefan-Boltzmann constant (5.67×10^{-8} W m^{-2} K^{-4}) and τ is the laser pulse width. ΔQ_1 and ΔQ_2 stand for convective heat loss to the surrounding liquid and radiative heat loss respectively, h and ε stand for convection heat transfer coefficient and emissivity, which we calculate using the value of 50 and 1.

The part of heat loss use the nanosphere of 50 nm and nanowire of 100 nm to make an approximate stimulate.

② Measure the energy absorbed by per mole sample when it is induced by different laser parameters. The specific method is measuring the energy through pure ethylenediamine as the same volume as sample A, the minus between the latter and the former is the energy absorbed by Ag_2Se. The value is 0.28 J/pulse.

③ Measure the sample concentration by Atomic absorption spectrometry, the value is $c=2.53*10^{-4}$mol/L, the spot size of laser is 8 mm (LL) and 0.2 mm (HL), the depth of instrument is 2.6 cm. So we can calculate the energy absorbed by per mole of Ag_2Se with single pulse laser are $8.5*10^5$ J/mol.pulse (LT) and $1.4*10^{12}$J/mol.pulse (HT), respectively.

4. Dispersed Ag_2Se nanospheres and their morphology change under laser irradiation

Dispersed Ag_2Se nanoparticles with diameters around 10 nm were synthesized using a solution-phase procedure as previously reported[3]. Briefly, Ag particles were first synthesized by adding 0.5 g $AgNO_3$ in to 10 ml ODA at 180 °C, then 0.12 g Se powder was added into the above system and reaction was kept for another 10 min with magnetically stirring. After the reaction, Ag_2Se particles were collected at the bottom of the beaker, washed several times with ethanol, and then redispersed in ethanol.

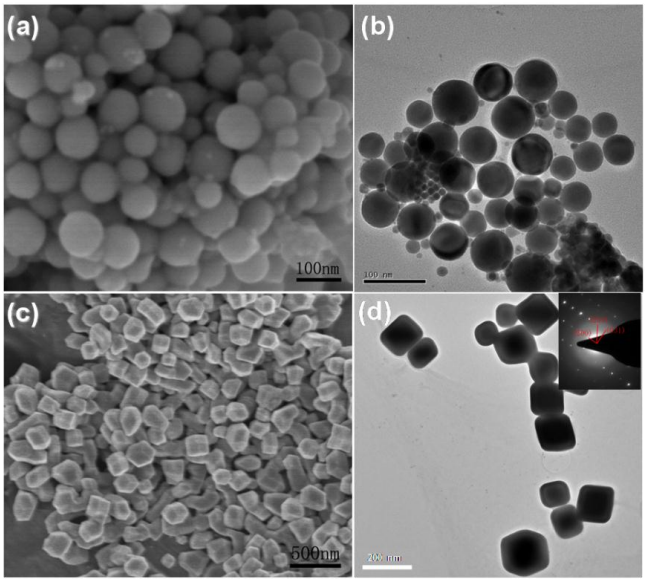

Fig.S4. (a) SEM and (b) TEM images of as-synthesized dispersed Ag_2Se nanoparticles; (c) SEM and (c) TEM images the product after laser irradiation for 30 min at low laser power density.

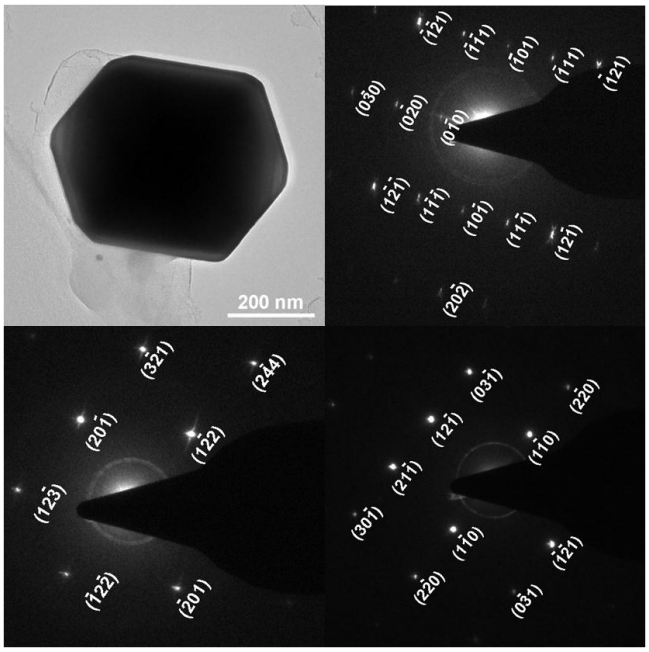

Fig.S5. TEM image and SAED patterns of a Ag_2Se nanocube

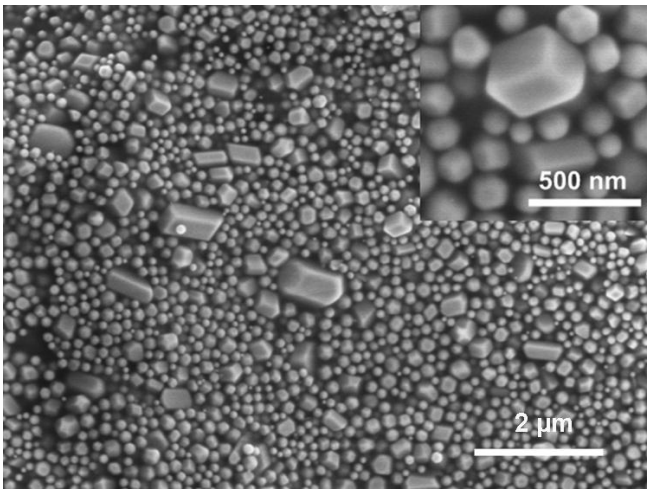

Fig.S6. SEM images of Ag_2Se nanocubes obtaind by furnace heating at 200 °C

1 A. Takami, H. Kurita and S. Koda, *J.Phys.Chem.B*, 1999, **103**, 1226-1232.

2 C. Kothandaraman, *Fundamentals of heat and mass transfer*, New Age International, 2006.

3 D. Wang, T. Xie, Q. Peng and Y. Li, *J.Am.Chem.Soc*, 2008, **130**, 4016-4022.