Supporting Information

$Au@Cu_7S_4$ Yolk-shell Nanoparticles as a 980 nm Laser-Driven Photothermal Agent with a Heat Conversion Efficiency of 63%

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1. Experimental section

All materials were used as received without further purification.

Preparation of Au nanoparticles

Au NPs were prepared by a standard citrate reduction procedure.[1] Typically, 2.5 ml of 0.1 wt.% $HAuCl_4$ solution was added into 22.5 ml deionized water and then heated to boiling. Under vigorous magnetic stirring, 0.5 ml of 1.0 wt% sodium citrate solution was added dropwise. After reaction for 20 min, heating resource was removed the solution was allowed to cold down naturally. Thus, the Au nanoparticle solution was obtained. Before being used for preparing Au@Cu_2O, these Au nanoparticles were washed with water to remove residual reactants.

Preparation of Au@Cu_2O core-shell nanoparticles

Au@Cu_2O core-shell nanoparticles were prepared according to Wang's report.[2] Briefly, 0.2 g of PVP was added to 10 mL of 0.01 M $Cu(NO_3)_2$ aqueous solution under constant stirring. After PVP powders dissolved completely, a certain amount of as-prepared Au colloid solution was added, followed by immediate injection of 3.5 μL of $N_2H_4 \cdot 3H_2O$ solution (35 wt %). The reaction mixtures were stirred for 2 min, and then the Au@Cu_2O core-shell nanoparticles were collected and finally redispersed in ethanol after thoroughly washed.

Preparation of Au@Cu_7S_4 yolk-shell nanoparticles

Au@Cu_2O nanoparticles prepared from 50 mL of 0.01 M $Cu(NO_3)_2$ aqueous solution was redispersed in 50 ml ethanol. Under vigorous stirring (with an ice-bath), 1.667 ml of 0.15 M Na_2S solution was added. After reaction for 1 h, the products was washed and collected for further characterization.

Characterization

The crystal structure of the samples were investigated by the X-ray diffraction on a Rigaku D/max 2500v/pc X-ray diffractometer at a scanning rate of 8 °/min. Field-emission scanning electron microscopy (FESEM) was conducted on a Hitachi S-4800 microscope. The morphology of products was observed by using an FEI Technai G2 F20 TEM and JEOL100 TEM. Their elemental composition was analyzed with an EDAX Genesis XM2 attached to the G2 F20 TEM. X-ray photoelectron spectroscopy (XPS; PHI 5000Versa-Probe) analysis was conducted using monochromatized AlKα radiation (1486.6 eV) to confirm the chemical states of elements in Au@Cu_7S_4. UV-vis-NIR spectra of the samples were recorded using a U-4100 Spectrophotometer (Hitachi Ltd.).

Photothermal measurements

To measure the photothermal conversion performance of Au@Cu_7S_4 NPs, 0.5 mL of aqueous dispersion of Au@Cu_7S_4 NPs with different concentrations cantanined in a cuvette was illustrated by a 980 nm laser with adjustable power (0 - 0.3 W). During the experimental process, the temperature of the solution was recorded in every 10 seconds using a thermocouple probe with an accuracy of ± 0.1 °C.

2. Calculation of the photothermal conversion efficiency[3]

According to Roper's report, the total energy balance between input and dissipation for the system can be given as:

$$\sum_i m_i C_i \frac{dT}{dt} = Q_{NP} + Q_{sys} - Q_{out} \tag{1}$$

Where m and C are the mass and heat capacity of water, respectively, T is the solution temperature, Q_{NP} is the energy absorbed by NPs, Q_{sys} is the energy imputted by the pure water system, and Q_{out} is heat dissipation of the system.

The heat absorbed (Q_{NP}) by Au@Cu_7S_4 NPs can be shown as:

$$Q_{NP} = I\left(1 - 10^{-A_{980}}\right)\eta \tag{2}$$

Where I is incident laser power in W, η the photothermal conversion efficiency, and A_{980} indicates the absorbance of the Au@Cu_7S_4 NPs at 980 nm.

Q_{out} is linear with system temperature, as expressed as:

$$Q_{out} = hS\left(T - T_{surr}\right) \tag{3}$$

Where h is heat transfer coefficient, S is the surface area of the container, and T_{surr} is ambient temperature of the surroundings.

When the system reaches a steady state temperature (T_{max}), the heat input and output are balanced:

$$Q_{NP} + Q_{sys} = Q_{out} = hS\left(T_{max} - T_{surr}\right) \tag{4}$$

After the laser is removed, the $Q_{NP} + Q_{sys} = 0$, reducing the Eq. 1

$$\sum_i m_i C_i \frac{dT}{dt} = - Q_{out} = - hS\left(T - T_{surr}\right) \tag{5}$$

Rearranging the Eq. 5 would give

$$dt = -\frac{\sum_i m_i C_i}{hS} \frac{dT}{\left(T - T_{surr}\right)} \tag{6}$$

And integrating, give the expression

$$t = -\frac{\sum_i m_i C_i}{hS} ln \frac{T - T_{surr}}{\left(T_{max} - T_{surr}\right)} \tag{7}$$

A system time constant τ_s is defined as:

$$\tau_s = -\frac{\sum_i m_i C_i}{hS} \tag{8}$$

And θ is introduced using the maximum system temperature, T_{max}

$$\theta = \frac{T - T_{surr}}{\left(T_{max} - T_{surr}\right)} \tag{9}$$

Substituting Eq.8 and 9 giving:

$$t = -\tau_s ln\theta \tag{10}$$

Therefore, the time constant for heat transfer from the system τ_s can be determined by applying the linear time data from the cooling period vs. negative natural logarithm of driving force temperature (θ)

Since Q_{sys} can be obtained directly as

$$Q_{sys} = hS\left(T_{max,H_2o} - T_{surr}\right) \tag{11}$$

Eq.4 can be given as:

$$Q_{NP} = I\left(1 - 10^{-A_{980}}\right)\eta = hS\left(T_{max} - T_{max,H_2o}\right) \tag{12}$$

Also

$$hS = -\frac{\sum_i m_i C_i}{\tau_s} \tag{13}$$

With τ_s is equal to 112 s, m is 0.5 g and the C is 4.2 J/g, hS can be calculated to be 18.75 mW/°C. Substituting I = 0.30 W, A_{980} = 2.73, T_{max} - T_{max,H_2O} = 10.1 °C into Eq. 12, the photothermal conversion efficiency can be determined to be 63%

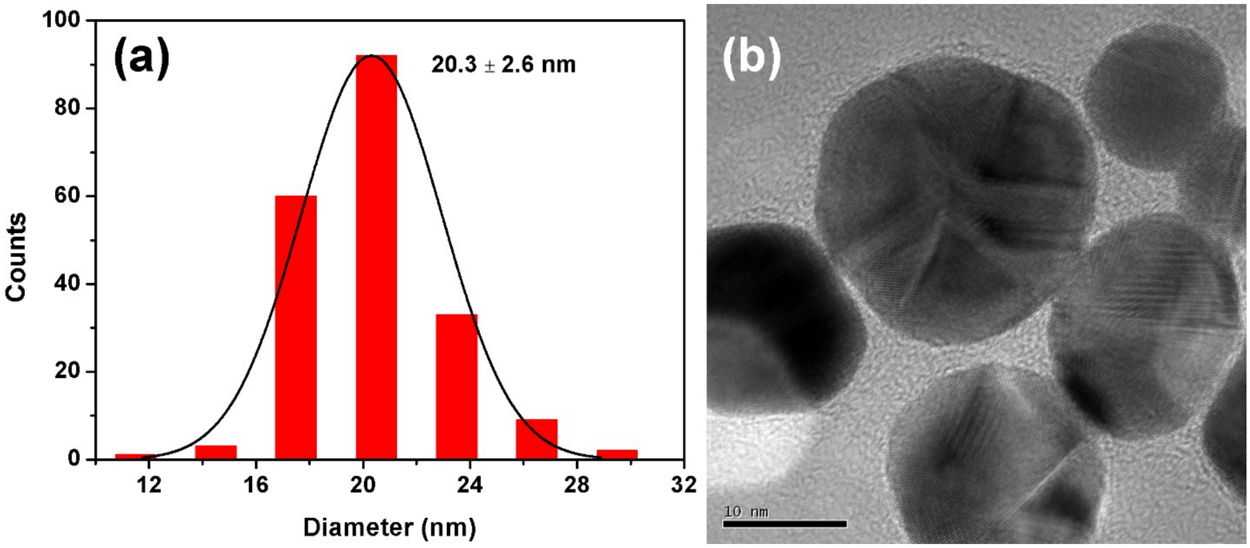


Figure S1. (a) Diameter distribution histogram and (b) HRTEM image of Au nanoparticles.

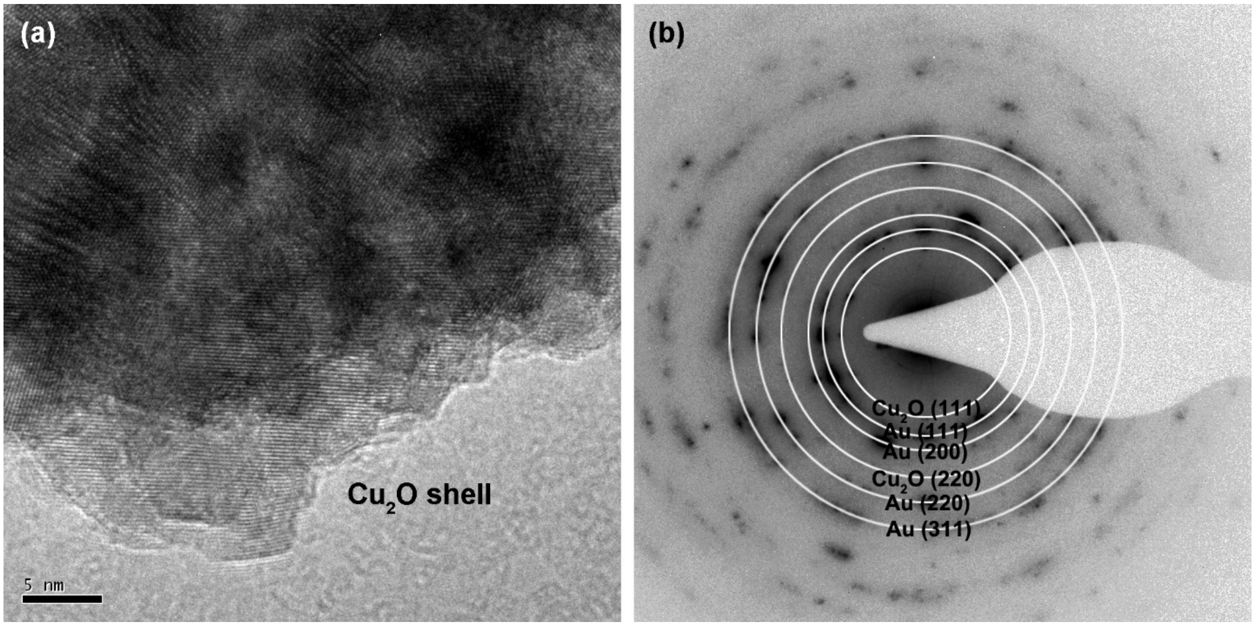


Figure S2. HRTEM image of the Cu_2O shell and the Selected Area Electron Diffraction (SAED) pattern of Au@Cu_2O core-shell NPs.

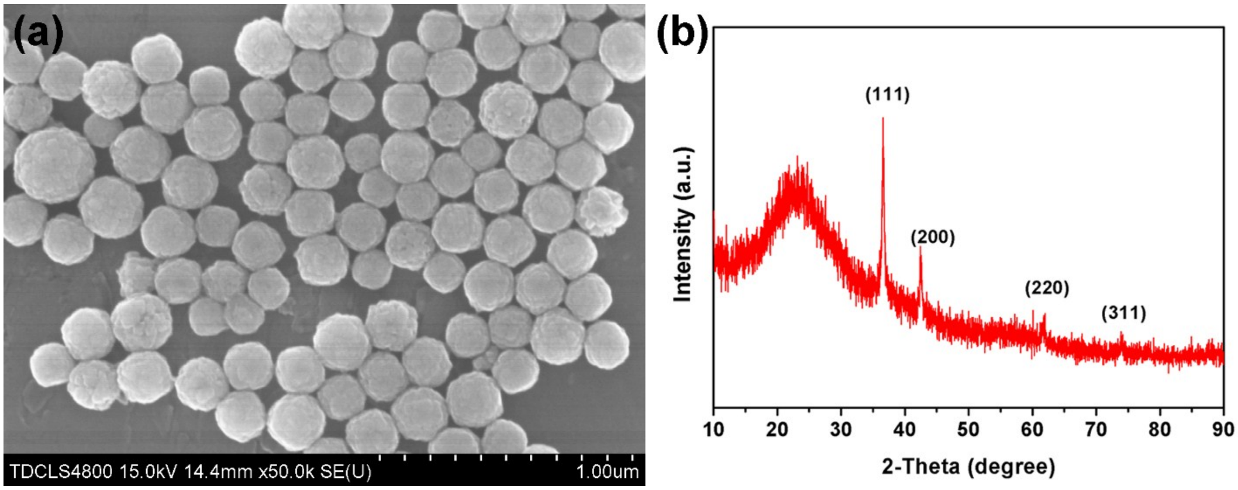
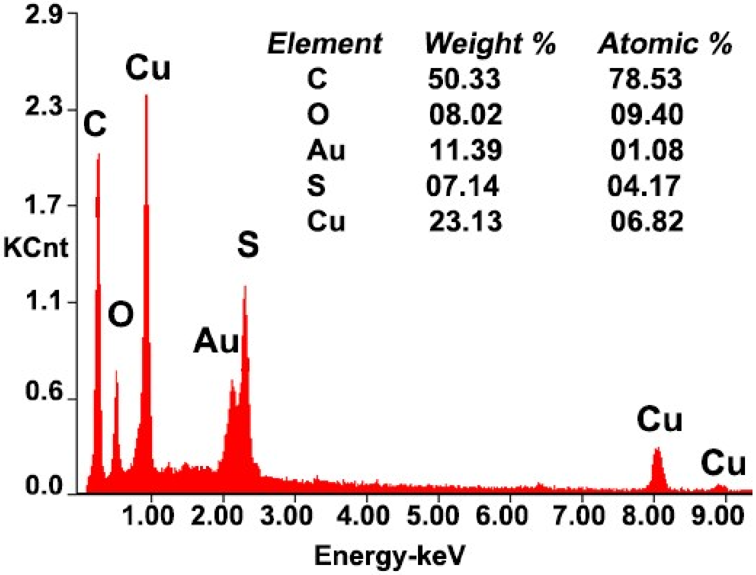


Figure S3. (a) SEM image of XRD patterns of (b) Cu_2O particles prepared in the absence of Au nanoparticles.



Element	*Weight %*	*Atomic %*
C	50.33	78.53
O	08.02	09.40
Au	11.39	01.08
S	07.14	04.17
Cu	23.13	06.82

Figure S4. An integrated EDX spectrum of Au@Cu_7S_4 NPs.

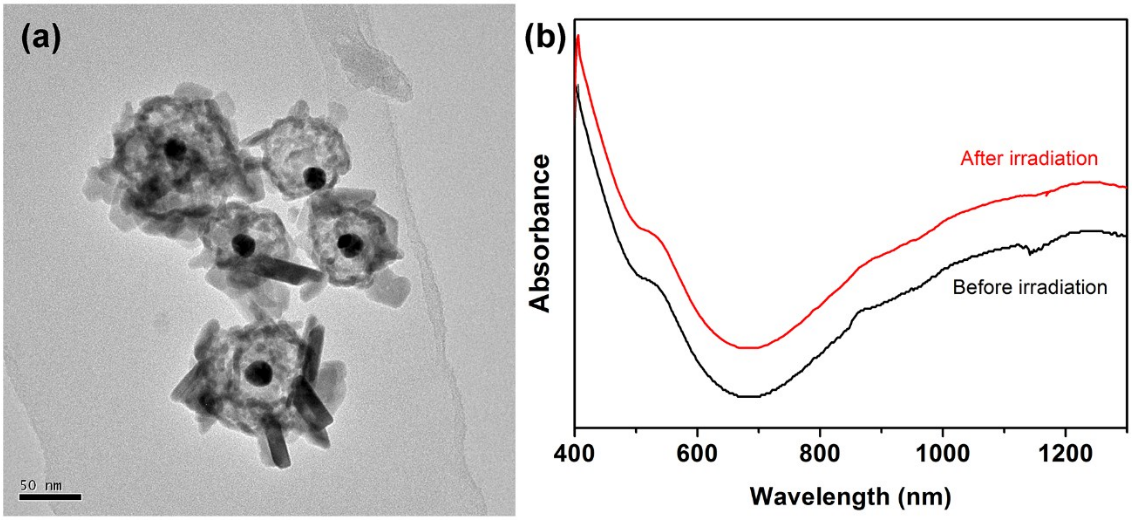


Figure S5. (a) TEM image of Au@Cu_7S_4 yolk-shell nanoparticles recovered after the laser irradiation. (b) Comparison of UV-vis-NIR spectra of Au@Cu_7S_4 aqueous dispersions before and after the laser irradiation. Obviously, negligible changes were observed in the morphology and optical absorption for Au@Cu_7S_4 nanoparticles after laser irradiation, indicating their good photostability.

References

1. X. Ji, X. Song, J. Li, Y. Bai, W. Yang and X. Peng, *J. Am. Chem. Soc.*, 2007, **129**, 13939-13948.

2. L. Zhang, D. A. Blom and H. Wang, *Chem. Mater.*, 2011, **23**, 4587-4598.

3. D. K. Roper, W. Ahn and M. Hoepfner, *J. Phys. Chem. C*, 2007, **111**, 3636-3641.