Controlled Growth of CdS-$Cu_{2-x}S$ Lateral Heteroshells on Au Nanoparticles with Improved Photocatalytic Activity and Photothermal Efficiency

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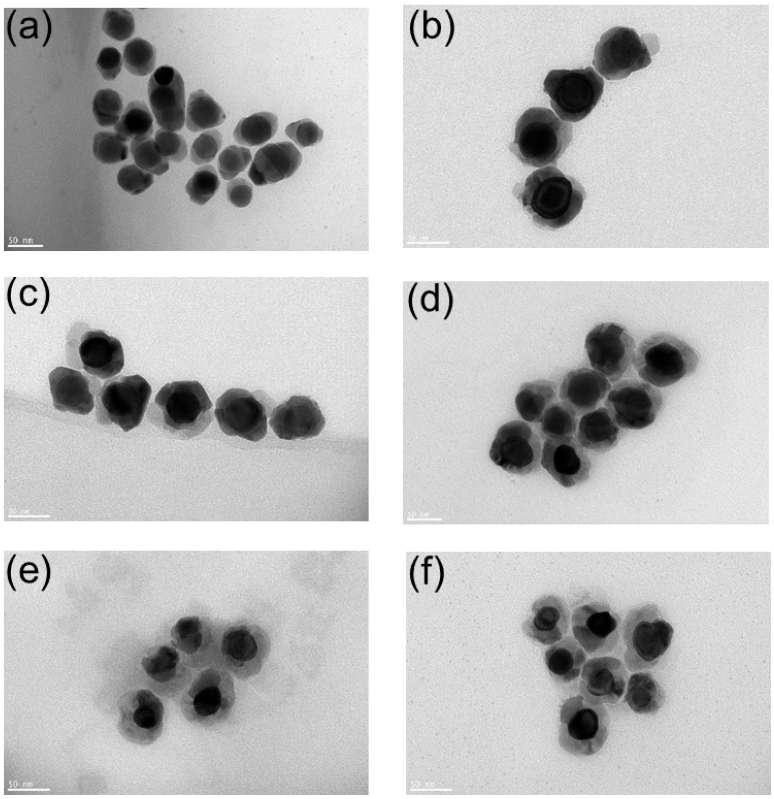


Figure S1. TEM image of (a) Au/Ag_2S core-shell NPs and TEM images of Au/Ag_2S-$Cu_{2-x}S$ core/shell NPs with (b) 6 μL, (c) 10 μL, (d) 20 μL, (e) 40 μL and (f) 80 μL of $CuCl_2$ added.

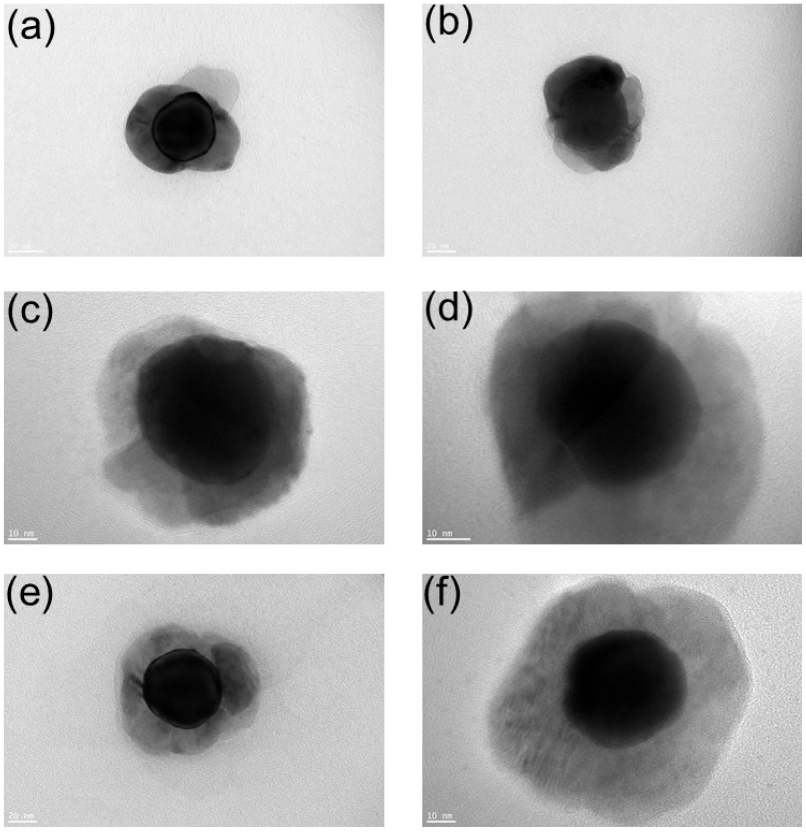


Figure S2. TEM images of single nanoparticle of Au/Ag_2S-$Cu_{2-x}S$ core/shell NPs with (a) 6 μL, (b) 10 μL, (c) 20 μL, (d) 40 μL, (e) 80 μL and (f) 140 μL of $CuCl_2$ added.

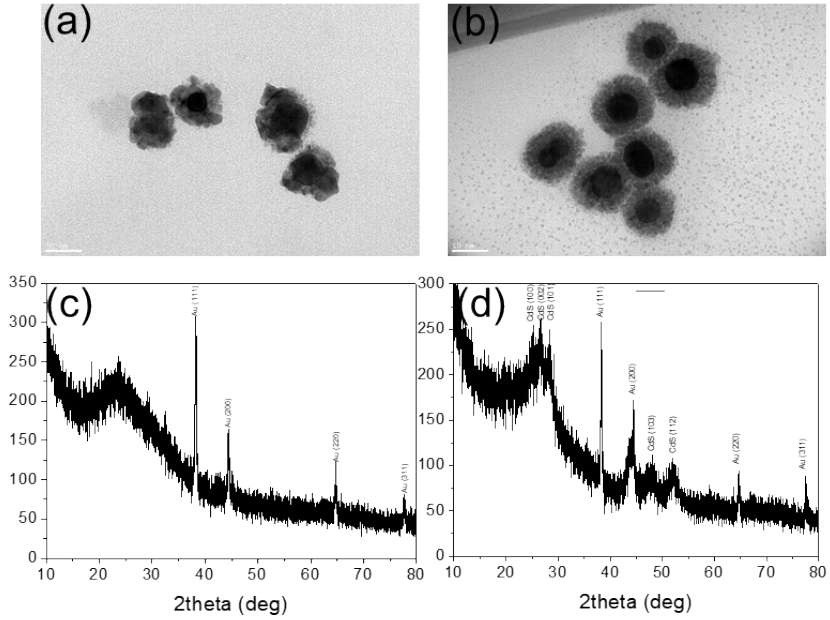


Figure S3.

TEM images of Au/Ag_2S-CdS core/shell NPs with (a) 10 μL and (b) 40 μL of $CdCl_2$ added. XRD patterns of (c) Au/Ag_2S and (d) Au/CdS.

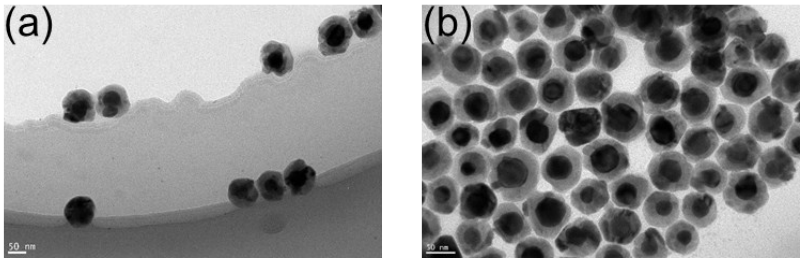
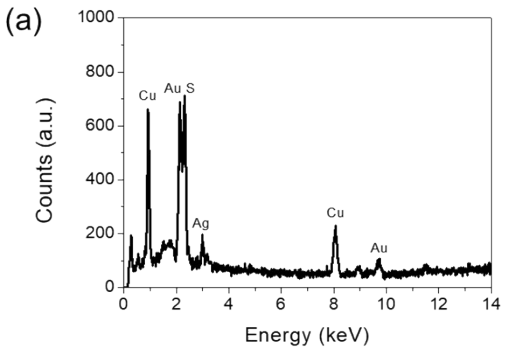


Figure S4. TEM images of Au/CdS-$Cu_{2-x}S$ core/shell NPs with different amounts of $CdCl_2$ added: (a) 6 µL and (b) 10 µL.



Element	*Wt %*	*At %*
S K	19.62	46.00
AgL	09.89	06.89
CuK	25.19	29.81
AuL	45.30	17.29

Element	*Wt %*	*At %*
S K	18.75	45.43
AgL	06.78	04.89
CdL	09.66	06.68
CuK	21.04	25.74
AuL	43.77	17.27

Figure S5. (a) EDS spectrum of Au/Ag_2S-$Cu_{2-x}S$ core/shell NPs with 40 µL of $CuCl_2$ added. (b) EDS spectrum of Au/CdS-$Cu_{2-x}S$ core/shell NPs with 10 µL of $CdCl_2$ added.

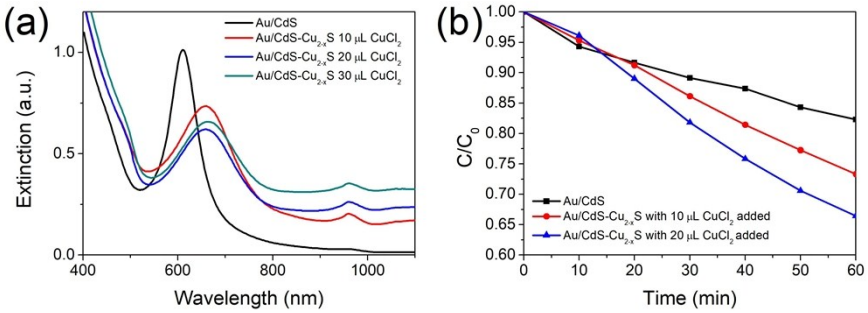


Figure S6. (a) UV-Vis-NIR extinction spectra of Au/CdS with 40 µL of $CdCl_2$ added (refers to the TEM images in Figure S3b) and Au/$Cu_{2-x}S$-CdS with 10-30 µL of $CuCl_2$ in the second step and 40 µL of $CdCl_2$ in the third step added. (b) Photodegradation of RhB versus time for Au/CdS and

Au/CdS-$Cu_{2-x}S$.

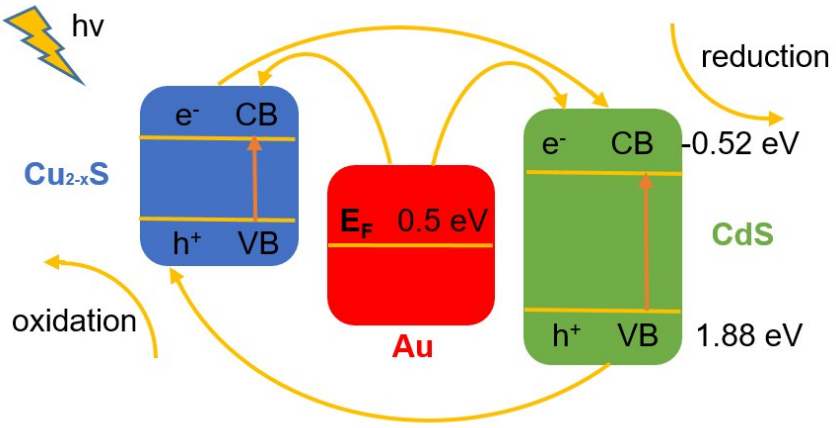


Figure S7. Schematic illustration of the charge transfer mechanism in Au/CdS-$Cu_{2-x}S$ during photocatalytic activity.

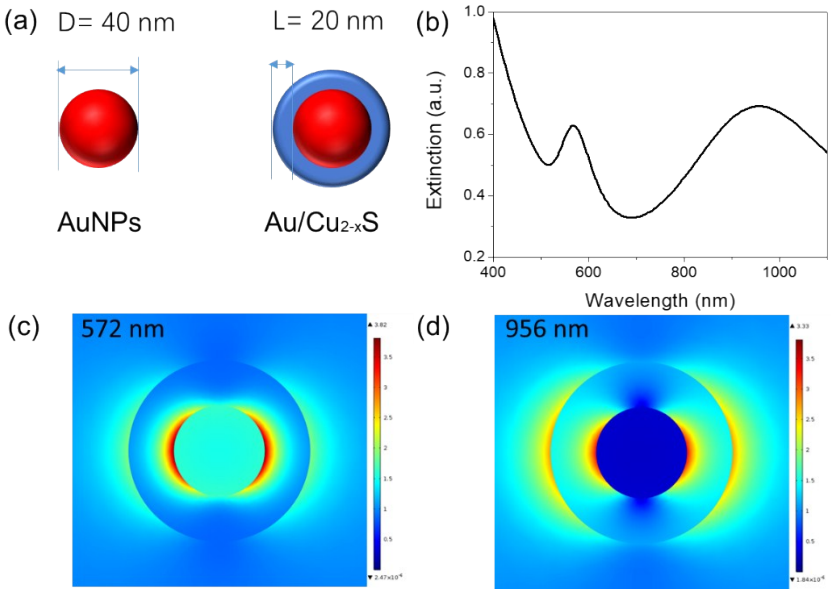


Figure S8. (a) Structure parameters of the Au/$Cu_{2-x}S$ core/shell nanospheres in the simulation. (b) Calculated extinction spectrum of the Au/$Cu_{2-x}S$ core/shell nanospheres in the water. (c,d) Calculated local field distributions of Au/$Cu_{2-x}S$ at two plasmon resonances at 572 nm and 956 nm. The theoretical calculation is based on the finite element method (FEM) and performed by the commercial COMSOL, in which the minimun element size of the FEM mesh is set to be 5 nm. The dielectric constants of Au and $Cu_{2-x}S$ are fitted by the Drude model.

1. Calculation of the photothermal conversion efficiency

We follow Roper's report to calculate the conversion efficiency of the different samples.[1] We use two approximations in the calculation and get the lower limit of the conversion efficiency. We directly use the equations in Tian's report.[2]

$$\eta = \frac{hS(T_{max} - T_{surr}) - Q_{dis}}{I(1 - 10^{-A_\lambda})}, \quad (1)$$

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}}, \quad (2)$$

$$\tau_s = \frac{\sum_i m_i c_{p,i}}{hS}, \quad (3)$$

$$t = -\tau_s ln\theta, \quad (4)$$

where I is incident laser power, η is the conversion efficiency, Q_{dis} is heat dissipated from light absorbed by the quartz cuvette cell itself, h is heat transfer coefficient, S is the surface area of the container, T_{surr} is temperature of the surroundings, T_{max} is the equilibrium temperature, A_λ is the absorbance at the wavelength of λ. Xenon lamp is used as the light resource, and it's hard to calculate the absorbance of the samples in the broadband. We approximate that light is completely absorbed by the samples. We approximate the temperature at 10 min to be T_{max}. The Eq. 1 is then approximated to be

$$\eta = \frac{hS(T_{max} - T_{surr}) - Q_{dis}}{I}. \quad (5)$$

Through linear fitting of t and lnθ, time constant for heat transfer from the system is caculated to be 354 s, 331 s and 322 s, corresponding to Au/Ag_2S, Au/Ag_2S-$Cu_{2-x}S$ and Au/CdS-$Cu_{2-x}S$. In addition, the mass of water is 2 g and the capacity of water is 4.2 J/g, the mass of quartz cuvette is 5.8 g, the capacity of quartz cuvette is 0.775 J/g. Q_{dis} is calculated to be 0.527 W according to the temperature evolution of water. Power density is 2 W·cm^{-2}. Take all the date into Eq. 5, the conversion efficiency is caculated to be 5.3%, 19.3% and 22.4%, corresponding to Au/Ag_2S, Au/Ag_2S-$Cu_{2-x}S$, and Au/CdS-$Cu_{2-x}S$.

2. Calculation of the quantum efficiency and turnover number of the photocatalytic reaction

We follow the reports of Serpone and Hoffmann to calculate the apparent quantum efficiency,[3-4] which is defined as

$$\varphi_x = \frac{\bar{+}(d[x]/dt)}{d[h\upsilon]_{inc}/dt}, \quad (6)$$

where d[x]/dt is the rate of concentration change of the reactant (or product) and d[$h\nu$]$_{inc}$/dt is the total optical power impinging on the sample. We add 1 mg of catalyst to 30 mL of 10^{-5} M aqueous solution of RhB. The light source is a 300 W xenon lamp irradiation with a cut-off filter (λ > 420 nm) and the total optical power impinging on the sample is 2000 mW·cm^{-2}.

Table S1. The apparent quantum efficiencies of the six samples.

Samples	Apparent quantum efficiency
Au/(Ag_2S-$Cu_{2-x}S$)	1.35×10^{-13} mol·(mW·h)$^{-1}$
Au/(CdS-$Cu_{2-x}S$) with 30 μL $CdCl_2$	5.71×10^{-13} mol·(mW·h)$^{-1}$
Au/(CdS-$Cu_{2-x}S$) with 50 μL $CdCl_2$	7.76×10^{-13} mol·(mW·h)$^{-1}$
Au/CdS with 40 μL $CdCl_2$	8.85×10^{-13} mol·(mW·h)$^{-1}$

Au/(CdS-$Cu_{2-x}S$) with 10 μL $CuCl_2$	1.33×10^{-12} mol·(mW·h)$^{-1}$
Au/(CdS-$Cu_{2-x}S$) with 20 μL $CdCl_2$	1.68×10^{-12} mol·(mW·h)$^{-1}$

References:

1. D. K. Roper, W. Ahn, M. Hoepfner, *J. Phys. Chem. C* , 2007, **111**, 3636–3641.
2. Q. Tian, F. Jiang, R. Zou, Q. Liu, Z. Chen, M. Zhu, S. Yang, J. Wang, J. Wang and J. Hu, *ACS Nano*, 2011, **5**, 9761–9771.
3. N. Serpone, A. Salinaro, *Pure Appl. Chem.* 1999, **71**, 303–320.
4. M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev*. 1995, **95**, 69–96.