Photothermal Conversion of SiO_2@Au Nanoparticles Mediated by Surface Morphology of Gold Cluster Layer

Lulu Yang[1,2], Zhibin Yan[1,2,3*], Lu Yang[1,2], Jianxin Yang[1,2], Mingliang Jin[1,2], Xiaobo Xing[1,2], Guofu Zhou[1,2], Lingling Shui[1,2,4*]

[1] Guangdong Provincial Key Laboratory of Optical Information Materials and Technology & Institute of Electronic Paper Displays, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, P. R. China;

[2] National Center for International Research on Green Optoelectronics, South China Normal University, Guangzhou 510006, P. R. China

[3] Defense Key Disciplines Lab of Novel Micro-nano Devices and System Technology, Chongqing University, Chongqing, 400044, P. R. China

[4] School of Information and Optoelectronic Science and Engineering, South China Normal University, Guangzhou 510006, P. R. China

* Correspondence: zhibin.yan@m.scnu.edu.cn; shuill@m.scnu.edu.cn; Tel: +86-20-3931-4813

1. Micromorphology of amine grafted silica and gold seed on its surface

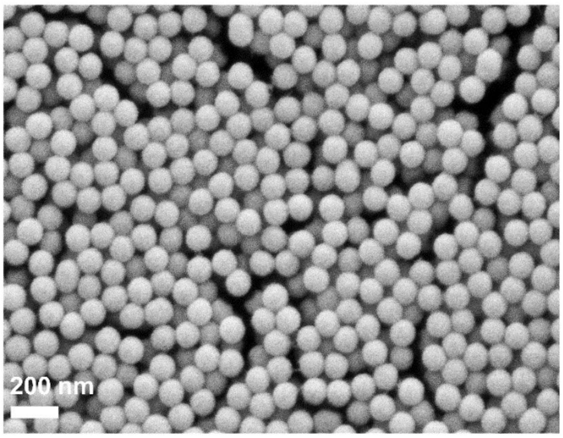


Figure S1 SEM of amine grafted silica core size of 100 nm in diameter.

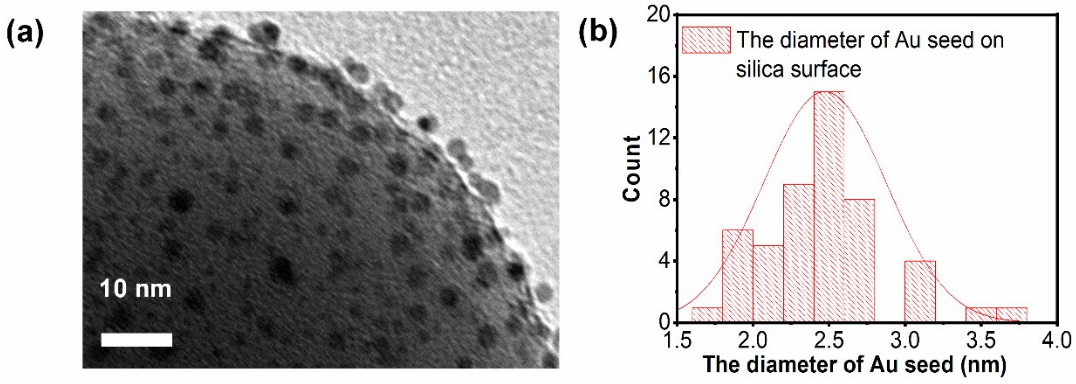


Figure S2 (a) TEM of gold-seeded silica and histograms of gold seed particle size on the its surface.

2. Heat transfer modeling and calculation of photothermal conversion efficiency

Based on the previous literatures[1], the continuum energy balance is used to describe the temperature curve of SiO_2@Au composite nanoparticles suspension. The thermal energy change of the solution depends on the heat input of the laser (Q_I) and the heat emitted to the external environment (Q_{ext}). The energy balance equation is given in equation 1.

$$\sum_{i} m_i C_{p,i} \frac{dT}{dt} = Q_I - Q_{ext} \tag{S1}$$

where m_i and $C_{p,i}$ are the mass and heat capacity of component i in the system, respectively. T is the temperature, and t is time. In the SiO_2@Au suspension considered here, the mass of SiO_2@Au is significantly less than that of water. Hence, the thermal energy of the SiO_2@Au is negligible, and equation 1 is simplified as

$$m_w C_{p,w} \frac{dT}{dt} = Q_I - Q_{ext} \tag{S2}$$

where m_w and $C_{p,w}$ are the mass and specific heat capacity of water, respectively.

The energy produced by SiO_2@Au under laser irradiation is given in equation 3, where I is the incident laser power, A_λ is the absorbance of the nanoparticles solution and η_T is the efficiency of converting light absorption to thermal energy. The path length through the droplet was measured by capturing a picture of the droplet during excitation and directly measuring the distance the light traveled. Once the path length is known then A_λ is determined by scaling the absorbance of the solution in a 1 cm quartz cuvette measured at 532 nm to the path length through the droplet[2].

$$Q_I = I(1 - 10^{-A_\lambda})\eta_T \tag{S3}$$

The dissipates energy of the system to the outside Q_{ext} is proportional to the linear thermal driving force. It's given as

$$Q_{ext} = hA(T - T_i) \tag{S4}$$

Where h is the heat transfer coefficient and A is the cross-sectional area perpendicular to conduction. T is the internal temperature of the system, and T_i is the ambient temperature.

Equation 2 can be recast into equation 5 by collecting terms and a variable change, ΔT, where ΔT is the temperature difference (T-T_i) from the ambient temperature T_i.

$$\frac{d\Delta T}{dt} = \frac{I(1 - 10^{-A_\lambda})\eta_T}{m_w C_{p,w}} - \frac{hA}{m_w C_{p,w}}\Delta T \tag{S5}$$

From here, we would define *B* as the time constant rate of heat dissipation from the SiO_2@Au suspension to the external environment.

$$B = \frac{hA}{m_w C_{p,w}} \tag{S6}$$

When laser is turned off I = 0 in equation 5, the temperature curve is deformed as follows

$$\frac{d\Delta T}{dt} = -\frac{hA}{m_w C_{p,w}}\Delta T \tag{S7}$$

Solving for $T(t)$ using the limit $T(0) = T_m$. The result is

$$T(t) = T_i + (T_m - T_i)\exp(-Bt) \tag{S8}$$

where T_m is the maximum temperature when the laser is turned off.

At thermal equilibrium, where Q_I equals Q_{ext}, the temperature will remain constant, which means $d\Delta T/t = 0$. Equation 5 evolves into

$$\eta_T = \frac{hA\Delta T}{I\left(1 - 10^{-A_\lambda}\right)} \tag{S9}$$

To get *hA*, equation 10 can be given from equation 8

$$t = -\frac{1}{B}\ln\frac{(T(t) - T_i)}{(T_m - T_i)} \tag{S10}$$

After turning off the laser, according to the photothermal response data of the sample, the plot of the natural log of $(T(t) - T_i)/(T_m - T_i)$ as a function of time. After fitting, the slope is -1/B. Know form the equation 6, the value of *hA* can be obtained.

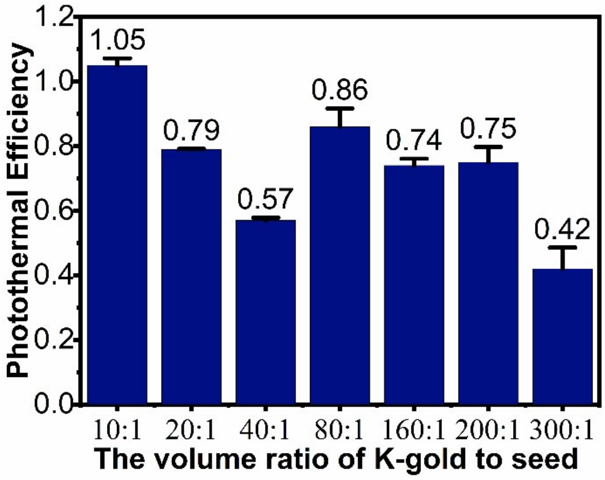


Figure S3 Photothermal efficiency of SiO_2@Au droplets at different seed-to-K-gold volume ratios under 532 nm laser irradiation of 53.6 mW.

3. Instrumentation

The surface topography of SiO_2 was determined by transmission electron microscope (TEM, JEM-1400 PLUS, Japan Electronics) and then the size of gold clusters on the surface of SiO_2 and the distance between gold clusters were analyzed using TEM images by Image J. The absorption spectra of SiO_2@Au suspensions were measured by a UV−Vis spectrometer (Lambda 850, PerkinElmer). All the samples were purified by dialysis through 1000 KD dialysis bags to remove unreacted precursors after the reaction.

4. The measurement of average equivalent circle diameter (D_{ave}) and the average distance (L_{ave}) of gold clusters on the surface of SiO_2@Au under different synthesis conditions

The software of Image J is used to measure the size and spacing of the gold clusters on the surface of SiO2 shown in the TEM (Figure S4). The steps are as follows: first, the irregularly shaped gold clusters are outlined and their area are measured. Then, for each gold cluster, its outline and the outlines of surrounding particles are connected with the line segments, and the shortest distance between them (L) is measured. The line segment cannot pass through the contours of other gold clusters. Finally, the measured area of the irregular gold clusters is equivalent to a circle calculate its diameter, which is called the equivalent circle diameter (D) of the irregular gold clusters. The ratio of the average shortest distance of gold clusters on the surface of SiO2 to the average equivalent circle diameter, L_{ave}/D_{ave}, represents the coupling effect between gold clusters. The smaller the value of L_{ave}/D_{ave}, the stronger the coupling effect between gold clusters.

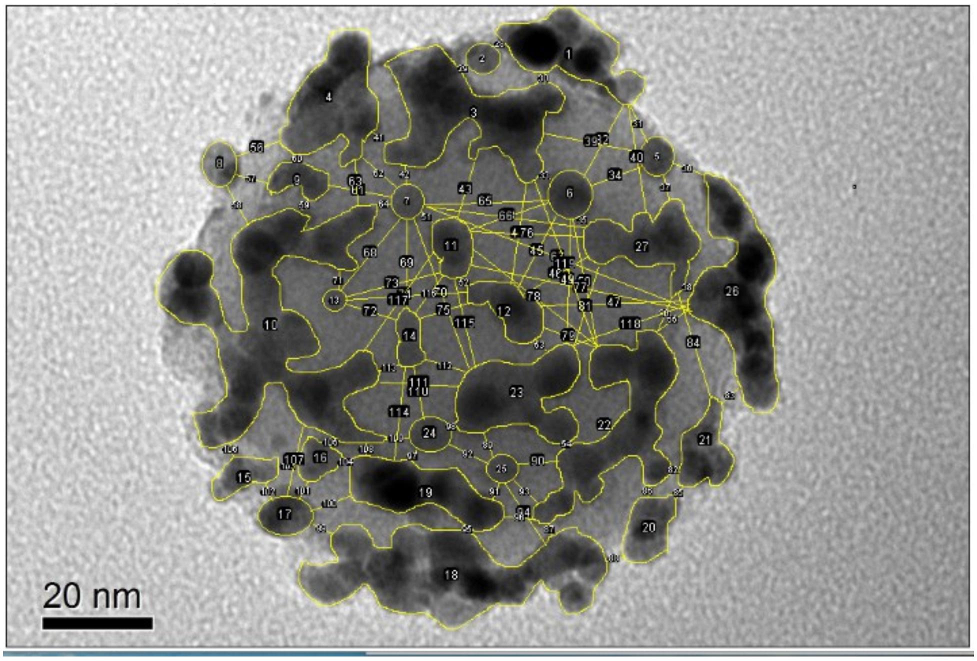


Figure S4 Example of measuring the D_{ave} and L_{ave} by Image J on the TEM image of SiO_2. The boundary of the gold cluster is outlined, and then the area is measured and converted to the equivalent circle diameter. The shortest distance between the boundaries of two gold clusters is considered to be the spacing between particles.

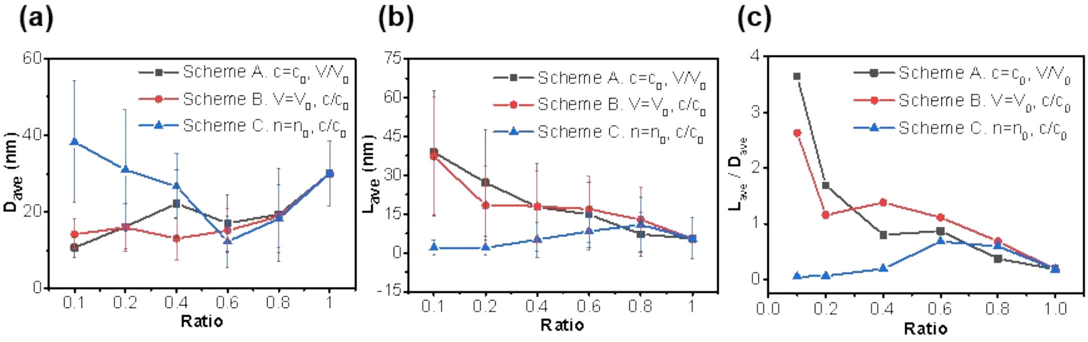
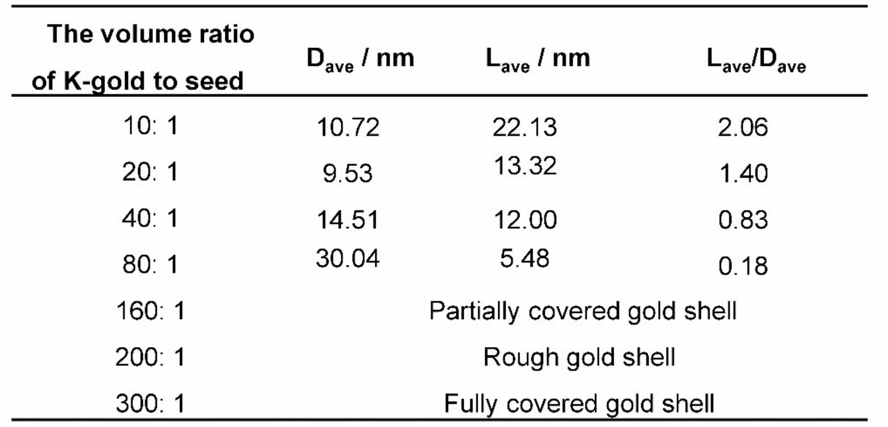


Figure S5 (a) The average equivalent circle diameter (D_{ave}), (b) the average distance (L_{ave}) and (c) the ratio of L_{ave}/D_{ave} of gold clusters on the surface of SiO_2@Au in Scheme A, B and C respectively, and the abscissa represents the ratio of c/c_0 or V/V_0 (80: 1 volume ratio of K-gold to seed and pH=10.31, $V_0 = 4$ ml and $c_0 = 6.6$ mM of $NaBH_4$).

Table S1 The average equivalent circle diameter (D_{ave}) and the average distance (L_{ave}) of gold clusters on the surface of SiO_2@Au at different K-gold-to- seed volume ratios



The volume ratio of K-gold to seed	D_{ave} / nm	L_{ave} / nm	L_{ave}/D_{ave}
10: 1	10.72	22.13	2.06
20: 1	9.53	13.32	1.40
40: 1	14.51	12.00	0.83
80: 1	30.04	5.48	0.18
160: 1	Partially covered gold shell		
200: 1	Rough gold shell		
300: 1	Fully covered gold shell		

5. Peak absorbance wavelength and intensity of UV-Vis absorption spectrum of the SiO_2@Au core-shell nanoparticles with different synthesis schemes

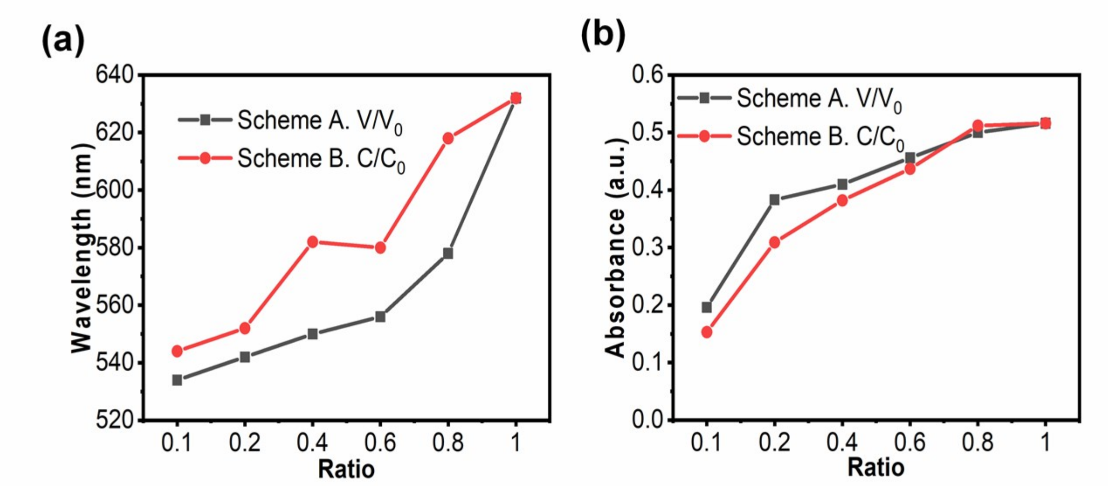


Figure S6. Compare the resonance wavelength (a) and absorbance (b) of the UV-Vis absorption spectrum of the Scheme A with the Scheme B (the abscissa indicates the ratio of V/V_0 or c/c_0).

6. Numerical modelling for thermoplasmonic heating in COMSOL Multiphysics

Table S2 Gold nanoparticle size, interparticle distance and number for each computing case

	Ratio	*D_{ave} (nm)*	*L_{ave} (nm)*	*Number of AuNPs*
Scheme A	0.1	10	26	8
Scheme A	0.6	24	9	3
Scheme B	0.1	14	31	3
Scheme B	0.6	16	9	12
Scheme C	0.1	38	2	1
Scheme C	0.6	12	8	45
Scheme A, B, C	1.0	34	2	2

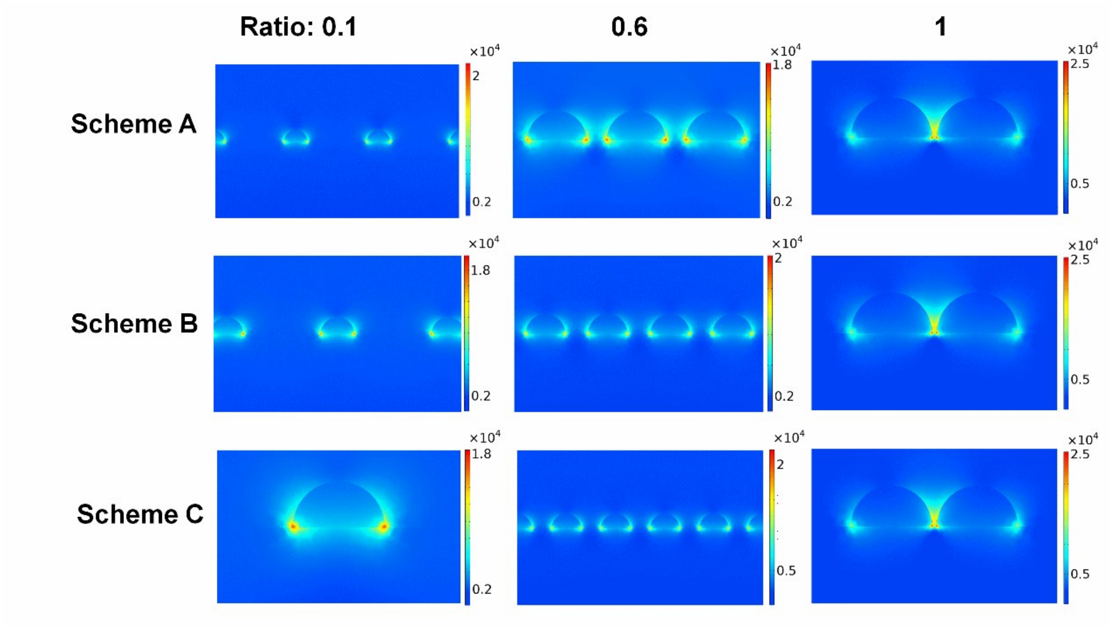


Figure S7. Finite Element Method (FEM) simulations reporting the plasmonic field distribution around the AuNPs arrangement for three representative ratio of 0.1, 0.6 and 1 in Schemes A, B and C. The exciting light is set perpendicular to the interface between water and silica, the polarization direction is along the arrangement direction of the AuNPs. Gold nanoparticle size, interparticle distance and number for each computing case are listed in Table S2.

References:

1. M. P. Hoepfner and D. K. Roper, *Journal of Thermal Analysis and Calorimetry*, 2009, **98**, 197-202.
2. H. H. Richardson, M. T. Carlson, P. J. Tandler, P. Hernandez and A. O. Govorov, *Nano Letters*, 2009, **9**, 1139-1146.