

Aqueous Phase Synthesis of Au@Ag₃AuX₂ (X = Se, Te) Core/Shell Nanocrystals and Their Broad NIR Photothermal Conversion Application

Tao Chen^{a, b}, Meng Xu^{b, *}, Muwei Ji^b, Lei Cheng^{a, b}, Jiajia Liu^b, Bing Zhang^a, and Jiatao Zhang^{a, *}

a. School of Chemical Engineering, Zhengzhou University, Zhengzhou, 450001, P. R. China.

b. Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, 100081, P. R. China.

Corresponding Author:

zhangjt@bit.edu.cn

Present Addresses

Beijing Institute of Technology, Beijing 100081, China. Tel.: +86 10 68918065; Fax: +86 10 68918065. E-mail: zhangjt@bit.edu.cn.

Experiment

Chemical and reagents: silver nitrate (AgNO_3 , 99+%), Gold(III) chloride trihydrate (HAuCl_4 , 99.9+%) were all purchased from Aladdin Reagent. Tellurium, selenium, sulfur powder are purchased from traditional Chinese medicine. Hydrazine hydrate and (N_2H_4) and other reagents are purchased from Beijing chemical factors. All of reagents were used without further purification.

Synthesis of Au NCs: Au seed solution was prepared by 2.5 ml CTAC (0.15 M) solution and 1.25 mL of 1mM HAuCl_4 . Then 0.3 ml ice-cold NaBH_4 (10 mM) was added. The seed solution was vigorous stirring for 2 min. After the solution was stirred, it was kept at 25 °C for 1 hour. Then 3.2 ml CTAC (0.2 M) solution was mixed with 0.8 mL HAuCl_4 (0.01 M) solution at 25 °C. 35 ml deionized water was added to this solution, and after gentle mixing, 3.8 ml ascorbic acid solution (0.1 M) was added. After the solution was mixed, 10 μl of the seed solution was added to the growth solution at room temperature. The solution was vigorous shaking for 1 min. After shaken, the solution was aged at 30°C for at least 8 hours.

Synthesis of Au@Ag₃AuTe₂ NCs: The Au NCs colloid (20 ml) was purified by centrifugation (10 min at 7500 rpm) and re-dispersed in CTAC solution (10 mL, 20 mM). Then AgNO_3 (0.7 mL 0.01 M) and ascorbic acid (0.7 mL 0.1 M) were added and stirred for 1 min. and then aged at 30°C for 5 h. After aged, 3 ml tellurium precursor (15 ml Hydrazine Hydrate, and 30 mg Te powder were mixed in 20ml volume autoclave and reacted at 120°C for 4 h to get clear homogenous solution) was added in 10 ml Au@Ag NCs aqueous solution. The mixture was transferred into the 20 ml autoclave and heated at 150°C for 3h. The sample was washed by 1:2 deionized water and centrifuged at 7500 rpm. Then as-prepared Au@Ag₃AuTe₂ NCs were re-dispersed in water.

Synthesis of Au@Ag₃AuSe₂ NCs: For the synthesis of Au@Ag₃AuSe₂ NCs, the experimental procedure was the same as Au@Ag₃AuTe₂ NCs except we used Se powder to replace Te powder.

Measurement of Photothermal Transduction: To evaluate the photothermal transduction of Au@Ag₃AuTe₂ NCs, 1 ml of aqueous dispersion of Au@Ag₃AuTe₂ NCs of different concentrations were put in a cuvette, and exposed to the 808 nm and 1064 nm laser at 0.7W/cm² power densities for 15 min. A thermocouple probe with an accuracy of 0.1°C was inserted into the NCs solutions perpendicular to the laser path to avoid direct light irradiation on the probe. The temperature was recorded every 30 sec.

Structural Characterizations: UV-visible-NIR absorption spectra were measured at room temperature using a Shimadzu UV-3600 spectrophotometer. LRTEM images were obtained by HITACHI H-7650 electron microscopy operating at 80 kV. HRTEM images and energy dispersive spectroscopy (EDS) were obtained using transmission electron microscopy (FEI Tecnai G2 F20 S-Twinworking at 200 kV) equipped with X-ray energy-dispersive spectroscopy detector (XEDS). The XRD pattern of product powder was collected by Bruker D8 multiply crystals X-ray diffractometer (10°/min).

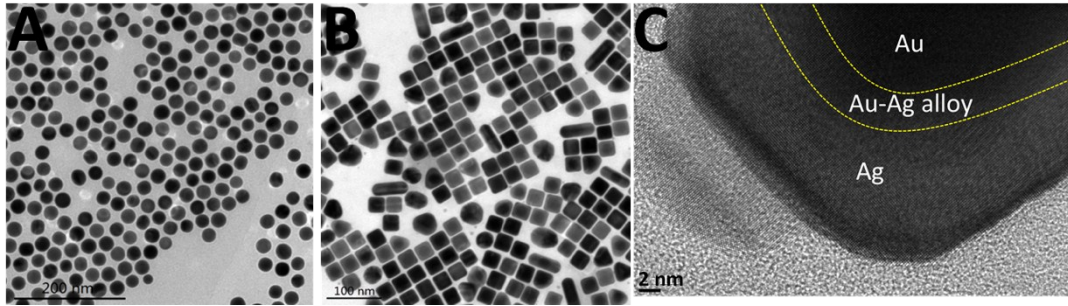


Figure S1. TEM images of the synthesized Au NCs (A), Au@Ag NCs (B) and HRTEM image of the synthesized Au@Ag NCs (C)

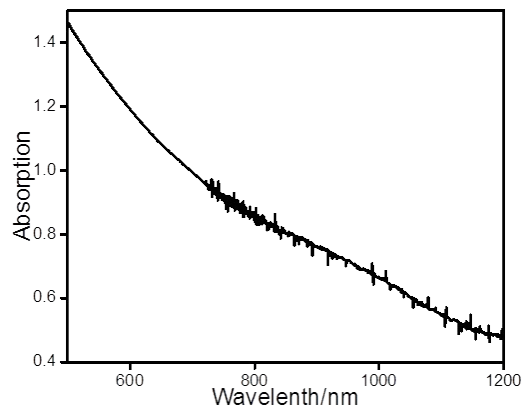


Figure S2. Extinction spectra of the Au@Ag₃AuTe₂ NCs aqueous colloid (200 ppm).

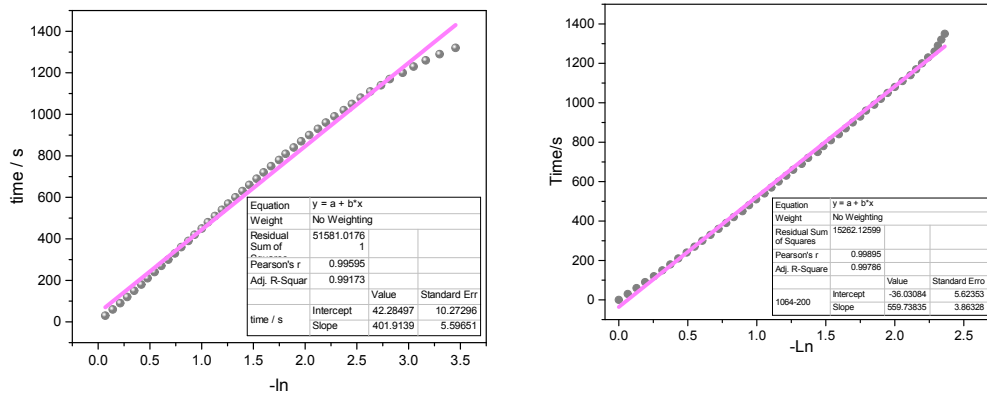


Figure S3. Time constant for heat transfer from the system τ_s , calculated by using the data after cooling period for Au@Ag₃AuTe₂ NCs aqueous, the PT conversion characterization is carried out with 808 nm (left) and 1064 nm (right) laser.

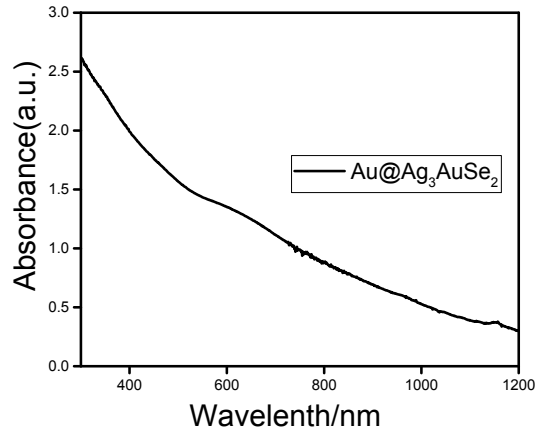


Figure S4. Extinction spectra of the Au@Ag₃AuSe₂ NCs aqueous colloid (200 ppm).

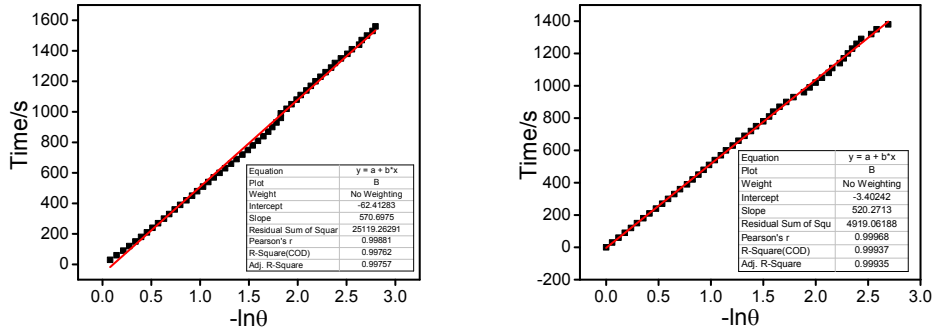


Figure S5. Time constant for heat transfer from the system τ_s , calculated by using the data after cooling period for Au@Ag₃AuSe₂ NCs aqueous, the PT conversion characterization is carried out with 808 nm (left) and 1064 nm (right) laser.

SI-1 Calculation for photothermal conversion efficiency:

The photothermal conversion efficiency (η) is calculated by the following equations, reported by Roper and Hu *et al*^[1,2]:

$$\eta = \frac{hS(T_{max} - T_{surr}) - Q_{dis}}{I(1 - 10^{-A_{808/1064nm}})}$$

(1)

where h , S and Q_{dis} are heat transfer coefficient, irradiated area and the baseline energy inputted by the sample cell, T_{max} and T_{surr} are the highest temperature of system and the temperature of surrounding, I and $A_{808/1064\text{ nm}}$ are the power density and absorption of Au@Ag₃AuX₂ NCs at 808/1064 nm, respectively.

The value of hS is calculated by using the following equations (2) to (4):

$$hS = \frac{\sum m_i C_{p,i}}{\tau_s}$$

(2)

$$t = -\tau_s \ln \theta \quad (3)$$
$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}}$$

(4)

where m and C_p are the mass of sample and the thermal capacity of sample and t is cooling time after irradiation.

For Au@Ag₃AuTe₂ NCs colloid:

The result of that case irradiated under 808 nm laser is that $\tau_s = 401.91$ s, obtained by linear fitting using linear cooling time and negative natural logarithm of temperature. The value of m and C_p are 1 g and 4.2 J/(g·°C). Therefore, hS is calculated to be 10.45 mW/°C by using equation (3). Q_{dis} and $A_{808\text{ nm}}$ are measured independently to be 133.76 mW with power density (I) 0.7 W/cm² and 0.85, respectively. Substituting all of value to parameters into the equation (1), the photothermal conversion efficiency, η , of Au@Ag₃AuTe₂ NCs colloid can be calculated to be 76.7%.

The result of that case irradiated under 1064 nm laser is that $\tau_s = 559.7$ s, obtained by linear fitting using linear cooling time and negative natural logarithm of temperature. The value of m and C_p are 1 g and 4.2 J/(g·°C). Therefore, hS is calculated to be 7.50 mW/°C by using equation (3). Q_{dis} and $A_{808\text{ nm}}$ are measured independently to be 53.28 mW with power density (I) 0.7 W/cm² and 0.59, respectively. Substituting all of value to parameters into the equation (1), the photothermal conversion efficiency, η , of Au@Ag₃AuTe₂ NCs colloid can be calculated to be 49.6%.

For Au@Ag₃AuSe₂ NCs colloid:

The result of that case irradiated under 808 nm laser is that $\tau_s = 570.69$ s, obtained by linear fitting using linear cooling time and negative natural logarithm of temperature. The value of m and C_p are 1 g and 4.2 J/(g·°C). Therefore, hS is calculated to be 7.36 mW/°C by using equation (3). Q_{dis} and $A_{808\text{ nm}}$ are measured independently to be 97.15 mW with power density (I) 0.7 W/cm² and 0.82, respectively. Substituting all of value to parameters into the equation (1), the photothermal conversion efficiency, η , of Au@Ag₃AuSe₂ NCs colloid can be calculated to be 50.7%.

The result of that case irradiated under 1064 nm laser is that $\tau_s = 520.0$ s, obtained by linear fitting using linear cooling time and negative natural logarithm of temperature. The value of m and C_p are 1 g and 4.2 J/(g·°C). Therefore, hS is calculated to be 8.08 mW/°C by using equation (3). Q_{dis} and $A_{808\text{ nm}}$ are measured independently to be 57.37 mW with power density (I) 0.7 W/cm² and 0.41, respectively. Substituting all of value to parameters into the equation (1), the photothermal conversion efficiency, η , of Au@Ag₃AuSe₂ NCs colloid can be calculated to be 34.1%.

Reference:

- [1] Roper, D. K.; Ahn, W.; Hoepfner, M. J. Phys. Chem. C 2007, 111, 3636.
- [2] Tian, Q. W.; Jiang, F. R.; Zou, R. J.; Liu, Q.; Chen, Z. G.; Zhu, M. F.; Yang, S. P.; Wang, J. L.; Wang, J. H.; Hu, J. Q. ACS Nano 2011, 5, 9761.