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Supporting Information

Multiplasmon modes for enhancing photocatalytic activity of Au/Ag/Cu₂O core-shell nanorods

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1. Experimental details

1.1 Materials: Sodium borohydride (NaBH₄), chlorauric acid (HAuCl₄·3H₂O), cetyltrimethylammonium bromide (CTAB), ascorbic acid (AA) and silver nitrate (AgNO₃) were purchased from Alfa Aesar. Sodium dodecyl sulfate (SDS), sulphuric acid (H₂SO₄), sodium hydroxide (NaOH) and copper (II) chloride dihydrate (CuCl₂·2H₂O) were at least analytical reagent grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China). Milli-Q water (18 MΩ·cm) was used for all solution preparation.

1.2 Instruments: Extinction spectra were obtained using a Cary 50 UV-vis-NIR spectrophotometer. XPS spectra were collected using an ESCALAB250Xi system. Transmission electron microscopy (TEM) measurements were performed on a TECNAI G2 20 S-TWIN at an accelerating voltage of 200 kV. High-resolution

transmission electron microscopy (HRTEM) images were captured on a FEI TECNAI G2 F20 U-TWIN at an accelerating voltage of 200 kV.

Spectra measurement: All extinction were obtained directly with solution samples, which were put into a 1cm × 1cm quartz cuvette for measurement.

1.3 Preparation of gold nanorods (Au NRs) core

Au NRs were synthesized using a seed-mediated growth procedure.

(1) Preparation of Au seed: CTAB-capped seeds were prepared by chemical reduction of HAuCl₄ by NaBH₄ in the presence of CTAB: freshly prepared and ice-cold NaBH₄ (0.01 M, 10mL) was injected into a mixture of CTAB (0.1 M, 7.5 mL), HAuCl₄ (23 mM, 0.1mL) and deionized water (1.8 mL) under magnetic stirring for 3 min. The color of the solution turned from yellow to brown, indicating the formation of Au seeds. The seed solution was kept undisturbed at 30°C for 2-5 h before use.

(2) Preparation of Au NRs with SPR maximum at ~650 nm (termed as Au-650), ~708 nm (termed as Au-650) and ~808 nm (termed as Au-808).

Au-650: The Au-650 growth solution was made by mixing CTAB (0.1M, 100mL), HAuCl₄ (25mM, 2mL), AgNO₃ (0.1M, 50 μL) and AA (0.1M, 552 μL). The seed solution (120 μL) was added to the growth solution to initiate the growth of AuNRs. The well-mixed solution was kept undisturbed for 12 h, then AA (0.1 M, 552 μL) was added three times at 40 min intervals. The total reaction time was for 24 h.

Au-708: The Au-708 growth solution was made by mixing CTAB (0.1 M, 100 mL), HAuCl₄ (24 mM, 2 mL), AgNO₃ (0.1 M, 120 μL), and AA (0.1 M, 552 μL). The seed solution (120 μL) was added to the growth solution to initiate the growth of AuNRs. The well-mixed solution was kept undisturbed for 12 h, then AA (0.1 M, 552 μL) was added twice at 40 min intervals. The total reaction time was for 24 h.

Au-808: The growth solution of the Au NRs was prepared, which consisted of CTAB (0.1 M, 100 mL), HAuCl₄ (25.5 mM, 1.96 mL), AgNO₃ (0.01 M, 1.0 mL), H₂SO₄ (0.1M, 2 mL), and AA (0.1 M, 0.8 mL). Then 240 μ L of seed solution was added to the above growth solution to initiate the growth of the Au NRs. After 12 h, Au NRs with SPR at 800 nm were obtained.

After synthesis, the reacted growth solutions were centrifuged twice (9200 rpm, 10 min) and the obtained Au-NR precipitates were redispersed in 2 mM CTAB solution.

1.4 Preparation of Au NRs coated with Ag shell (Au/Ag NRs)

Au/Ag NRs were obtained by adding the mixed solution to 100 mL of Au NRs, which consisted of CTAB (0.1 M, 10 mL), AgNO₃ (0.1 M, 0.5 mL) and AA (0.1 M, 5 mL). Then, the solution was kept stirring at 70°C for 8 h. The Au/Ag NRs were centrifugated at 9000 rpm for 5 min twice and redispersed in 100 mL deionized water to remove other ions. By changing the amount of Au NRs, the thickness of Ag shell can be tuned.

1.5 Preparation of Au/Ag/SiO₂ nanorods

The purified Au/Ag were suspended in 10 mL H₂O, then 75 μ L of 0.1 M CTAB and 50 μ L of 0.2 M NaOH solution were added with stirring. 30 μ L aliquot of 20% TEOΣ (ϖ/ϖ) in ethanol was added under gentle stirring trice with 30 min interval. The reaction solution was incubated at 30 °C for 24 h. Then the samples were centrifuged several times and dispersed in ethanol. To remove the CTAB residuals inside the mesoporous structure, 60mg NH₄NO₃ was added and the sample solution was stirred at 60 °C for 1 h. The samples were purified through centrifugation and washed several times with deionized water.

1.6 Preparation of Au/Ag nanospheres

Au/Ag nanospheres were prepared according to ref.1. Typically, 10 mL gold nanospheres suspension ([Au⁰] = 0.25 mM, [CTAB] = 10mM) was first mixed with

36.5 μL of AgNO_3 (0.1 M) and 365 μL of AA (0.1 M). Then, the mixed suspension was put in a 70 $^\circ\text{C}$ water bath for 5 h to complete the Ag overgrowth. The obtained Au@Ag NPs were purified via centrifugation (9000 rpm, 5 min) twice before TEM characterization.

2. Theoretical details

2.1 PIRET caculation

The transfer rate based on PIRET can be caculated as

$$k_{transfer} = \frac{1}{\tau_{donor}} \left(\frac{R_0}{R} \right)^G \quad (1)$$

Where R_0 (given in Angstroms) can be calculated as

$$R_0 = 0.2108(k^2 \Phi_0 n^{-4} J)^{1/6} \quad (2)$$

Where k is an orientation factor usually taken as 2/3, n is the refracitve index, Φ_0 is the quantum yield of the donor, and J is the normalized overlap integral between the donor spectrum F_D and the acceptor spectrum ε_A

$$J = \int F_D(\lambda) * \varepsilon_A(\lambda) * \lambda^4 d\lambda \quad (3)$$

2.2 FDTD simulations

The extinction spectra and electric field enhancements of Au/Ag/Cu₂O nanorods were performed using FDTD Solutions 8.6 developed by Lumerical Solutions, Inc. An electromagnetic pulse with different wavelength range was launched into a box containing the target nanorod to simulate a propagating plane wave interacting with the nanorod. The nanorod and its surrounding medium inside the box were divided into 1 nm meshes. Calculations were done for isolated Au/Ag/Cu₂O nanorod in water (refractive index of 1.33) and excited by linearly polarized light. The nanorods were modeled as cylinders capped with two half spheres at both ends. For the longitudinal

excitation, the incident light was perpendicular to the length axis and polarized along the length axis. For the transverse excitation, both the incidence and polarization directions of the excitation light were perpendicular to the length axis. Palik provided optical constants for Ag and Cu₂O. The optical constant for bulk Au was extracted from Johnson Christy database. Charge pattern were simulated by COMSOL Multiphysics.

2.3 Normalization of the photocatalytic activity based on the surface area

The photocatalytic activity of Au/Ag/Cu₂O NRs with different Cu₂O shell thicknesses was normalized based on the surface area. The same amount but the different thickness of Cu₂O shell leads to the different surface areas for different Au/Ag/Cu₂O core-shell NRs. The normalization was carried out using the equation $(4\pi r^2 + 2\pi r h) * n$, where r , h , and n present the radius of two half spheres of the nanorod, the height of the cylinder of the nanorod and numbers of the corresponding Au/Ag/Cu₂O NRs, respectively. Because each Au/Ag NR was wrapped with Cu₂O as shown in TEM, n is equal to the amount of Au/Ag NRs. The surface area of Au/Ag/Cu₂O (31 nm) was supposed to be 1 and the ratios of other samples compared to Au/Ag/Cu₂O (31 nm) were calculated and listed in Table S1.

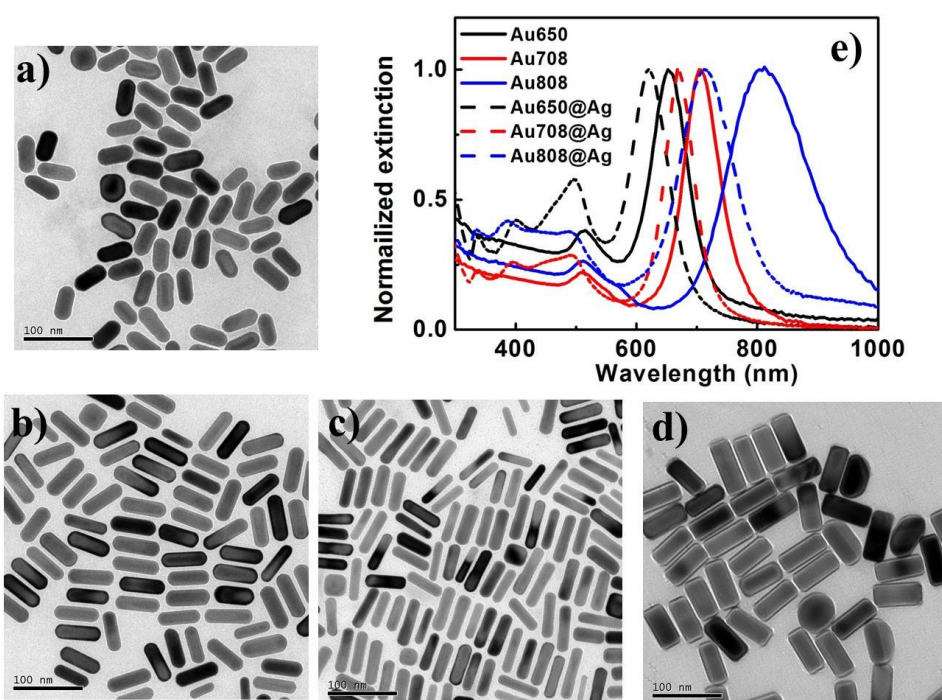


Figure S1 Characterization of Au NRs cores and Au/Ag NRs. (a-c) TEM images of the Au-650 NRs, Au-708 NRs and Au-808 NRs samples. The average diameters and lengths of Au-650 NRs, Au-708 NRs and Au-808 NRs are 23.8 ± 3 nm and 52.1 ± 4 nm with an AR of 2.2 ± 0.2 , 21 ± 2 nm and 62 ± 4 nm with an AR of 3.1 ± 0.3 , 18 ± 2 nm and 73 ± 3 nm with an AR of 4.0 ± 0.3 , respectively. (d) TEM image of the Au-708/Ag NRs sample. (e) Experimental extinction spectra of Au NRs and Au/Ag NRs. The longitudinal plasmon modes of three Au NRs cores are positioned at 650 nm, 708 nm and 808 nm, respectively.

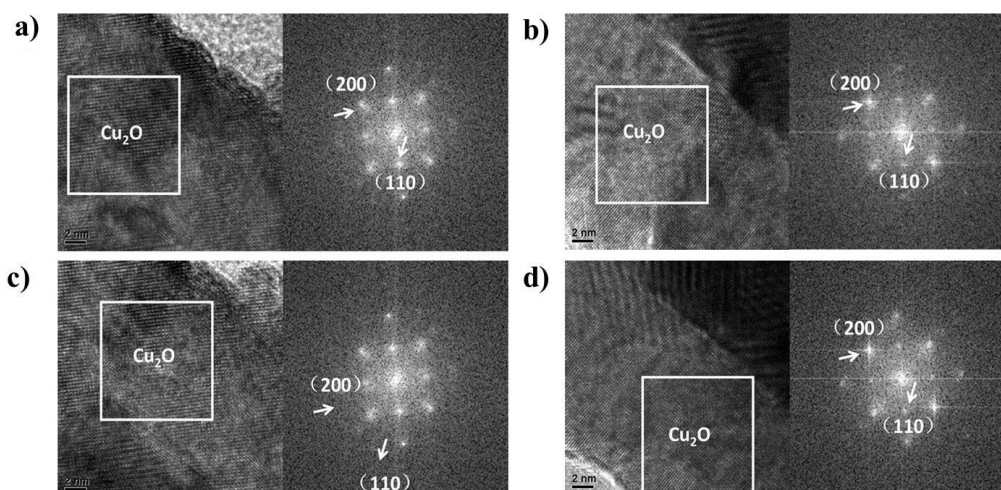


Figure S2 (a-d) HRTEM images of Au-808/Ag/Cu₂O nanorods and the FFTs of HRTEM images.

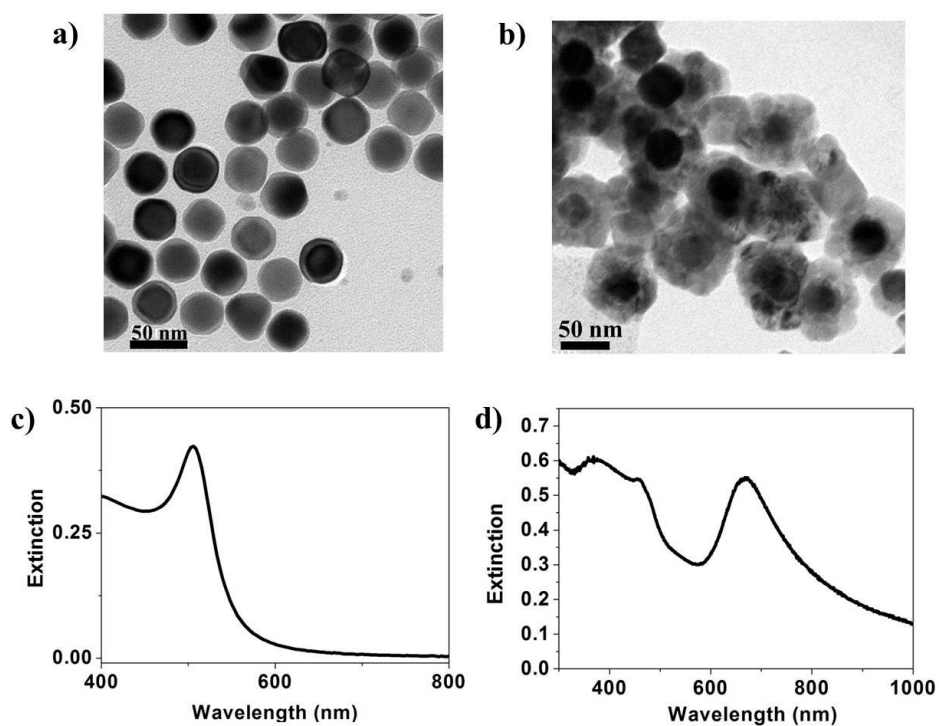


Figure S3 (a-b) TEM images of Au/Ag nanospheres (a) and Au/Ag/Cu₂O nanospheres samples (b). The average diameter of Au nanospheres is 29 ± 3 nm. The Ag and Cu₂O shell thicknesses are ~ 3 nm and ~ 23 nm, respectively. (c-d) Experimental extinction spectra of Au/Ag nanospheres (c) and Au/Ag/Cu₂O nanospheres (d).

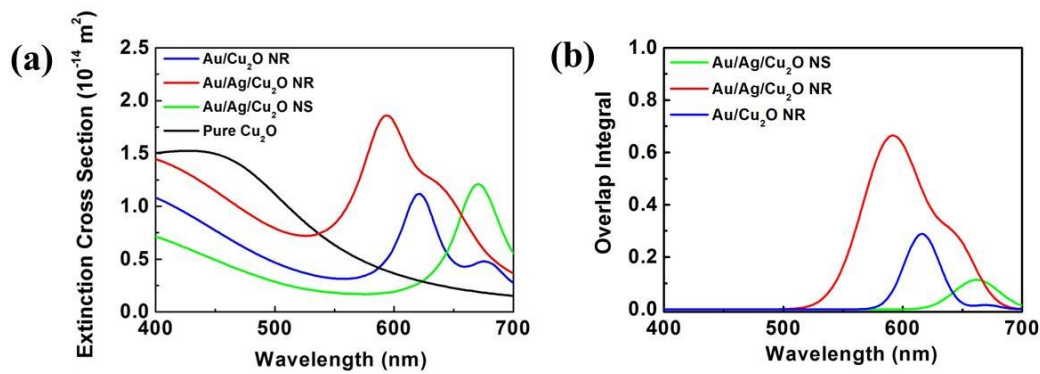


Figure S4 Calculated overlap functions of the Cu₂O band gap and SPR bands with different Au cores. (a) Transverse SPR modes of Au/Cu₂O and Au/Ag/Cu₂O NRs and SPR modes of pure Cu₂O and Au/Ag/Cu₂O nanospheres (NSs). The volumes of Au NS and Au NR cores were fixed at 20000 nm³. (b) The overlap functions of the Cu₂O band gap and SPR. The ARs of Au cores are 4.0. The Cu₂O and Ag shell thicknesses are fixed at 20 nm and 5 nm, respectively.

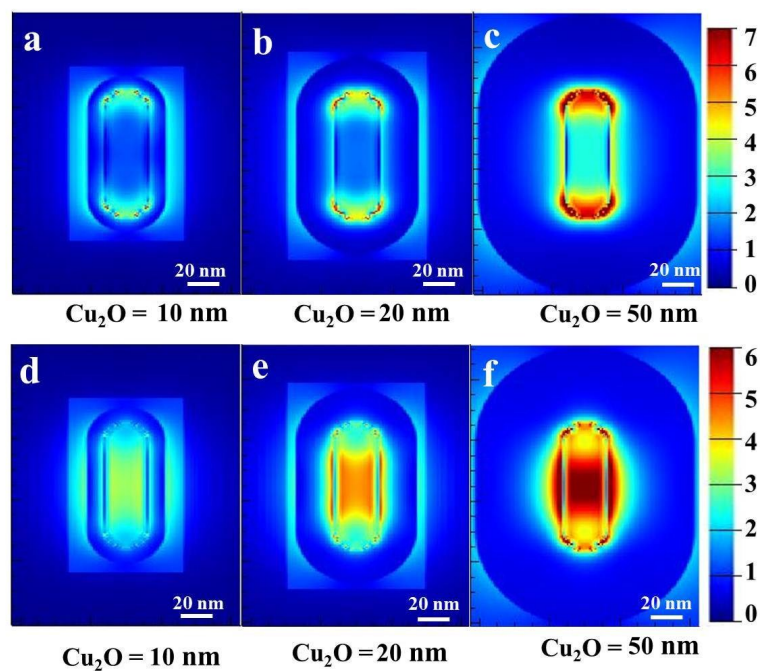


Figure S5 The local EM field distributions of TD (a-c) and TO (d-f) plasmon modes of Au/Ag/Cu₂O NRs with different Cu₂O thickness. (Au core AR = 4, Au core volume = 20000 nm³ and Ag thickness = 3 nm).

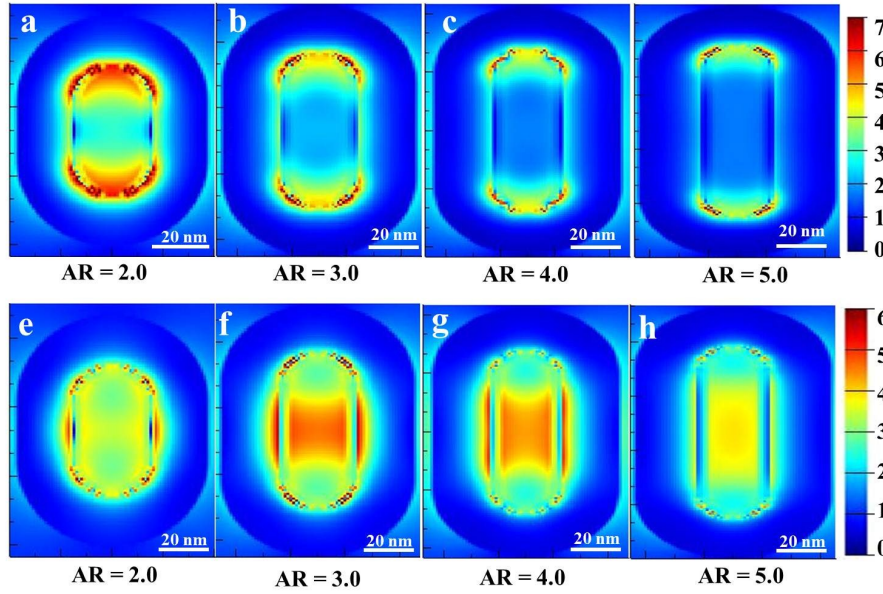


Figure S6 The local EM field distributions of TD (a-d) and TO (e-h) modes of Au/Ag/Cu₂O nanorods with different ARs of Au core. (Au core volume = 20000 nm³, Ag thickness = 3 nm and Cu₂O thickness = 20 nm).

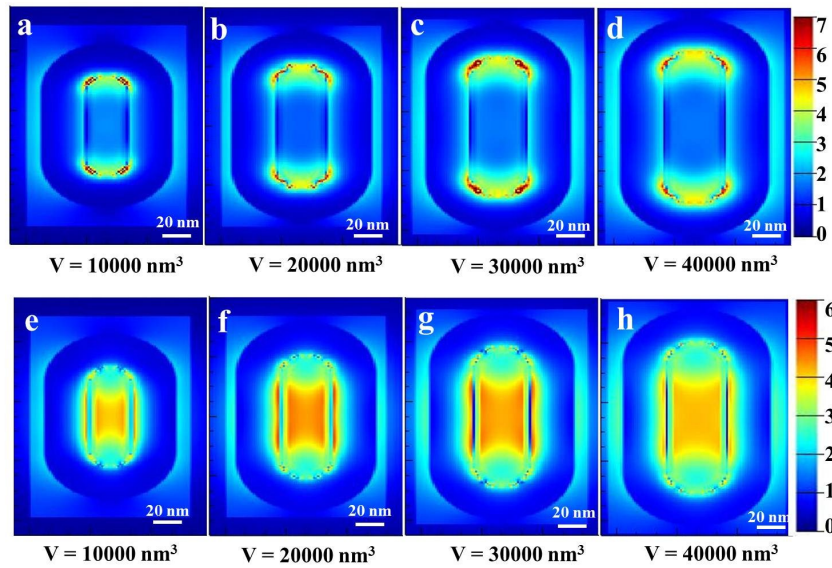


Figure S7 The local EM field distributions of TD (a-d) and TO (e-h) modes of Au/Ag/Cu₂O nanorods with different volumes of Au core. (Au core AR = 4, Ag thickness = 3 nm and Cu₂O thickness = 20 nm).

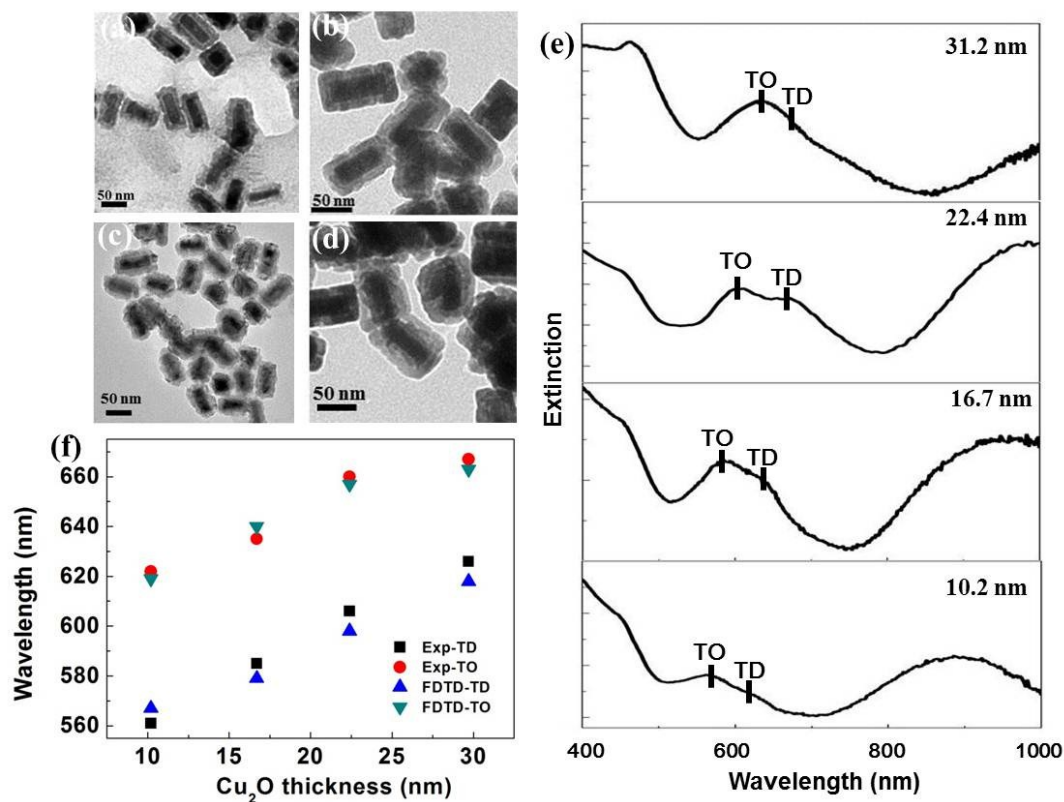


Figure S8 (a-d) TEM images of Au/Ag/Cu₂O NRs with different Cu₂O shell thicknesses of ~10 nm (a), ~16 nm (b), ~22 nm (c) and ~31 nm (d), respectively. (e) Experimental extinction spectra of Au/Ag/Cu₂O NRs. (f) Experimental and simulated transverse SPR peak positions vs. shell thicknesses.

Table S1. Data summary for Au/Ag/Cu₂O core-shell nanorods with different Cu₂O shell thicknesses.

| Sample | Volume of Au/Ag NPs | Shell thickness d | Normalized surface area |
|---------------------------------|---------------------|---------------------|-------------------------|
| Au/Ag/Cu ₂ O (31 nm) | 0.5 mL | 31.2 nm | 1 |
| Au/Ag/Cu ₂ O (22 nm) | 1.0 mL | 22.4 nm | 1.34 |
| Au/Ag/Cu ₂ O (17 nm) | 1.5 mL | 16.7 nm | 1.55 |
| Au/Ag/Cu ₂ O (10 nm) | 3.0 mL | 10.2 nm | 1.96 |

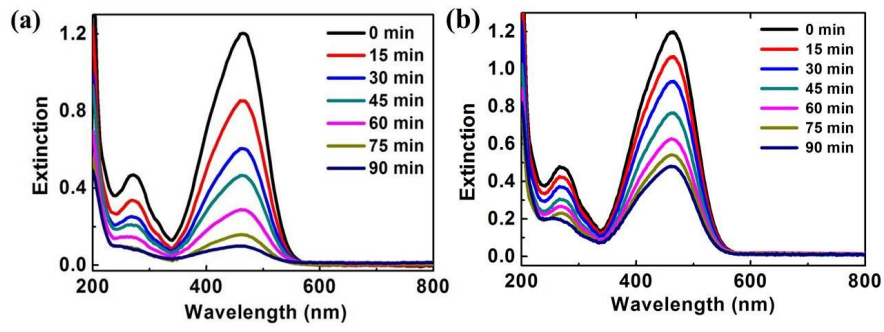


Figure S9 (a-b) UV-Vis extinction spectra of MO under visible light irradiation for different periods in the presence of Au/Ag/Cu₂O NRs (a) and Au/Ag/Cu₂O nanospheres (b).

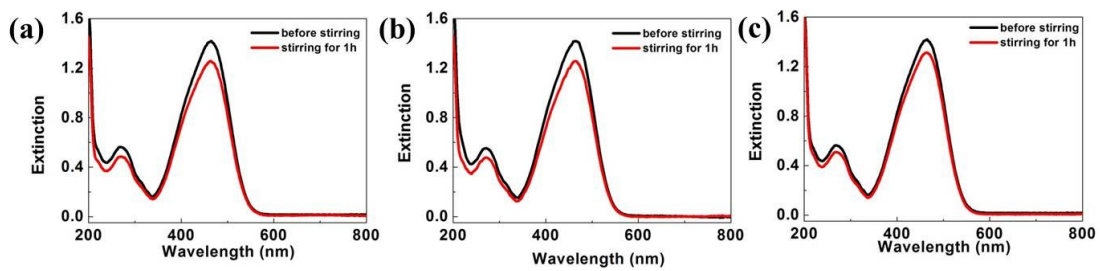


Figure S10 UV-vis absorption spectra of MO in Au/Ag/Cu₂O NRs (a), Au/Ag/Cu₂O nanospheres (b) and Au/Ag NRs suspensions (c) before and after being magnetically stirred for 1h in dark to ensure reach an adsorption/desorption equilibrium between the photocatalysts and MO.

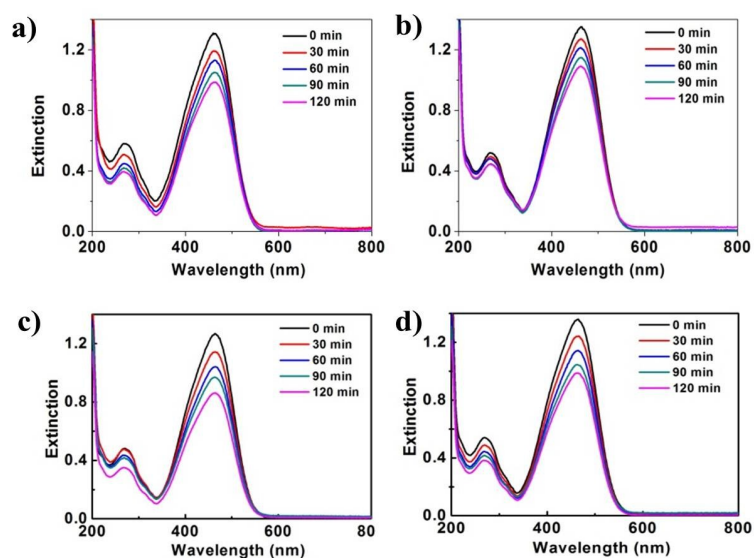


Figure S11 UV-vis absorption spectra of methyl orange as a function of irradiation time at different wavelength (a) 500 nm b) 530 nm c) 580 nm d) 645 nm) using Au-808/Ag/Cu₂O NRs as photocatalysts. 25%, 19%, 32% and 27% of MO degraded after 500 nm, 530 nm, 580 nm and 645 nm light irradiating samples for 120 min, respectively.

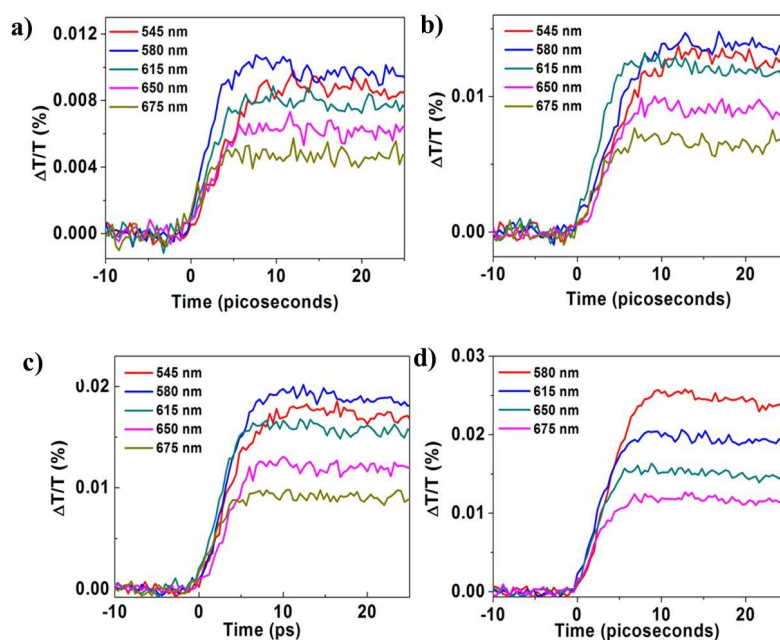


Figure S12 Pump Probe Data obtained from Au-808/Ag/Cu₂O core-shell nanorods. The pump wavelength is tuned from 545 nm to 675 nm with the fluence ranging from

2.5 mJ/cm² to 6.2 mJ/cm². The relative transmission data for the pump laser fluences of (a) 2.49 mJ/cm², (b) 3.74 mJ/cm², (c) 4.98 mJ/cm² and (d) 6.23 mJ/cm² at different wavelengths.

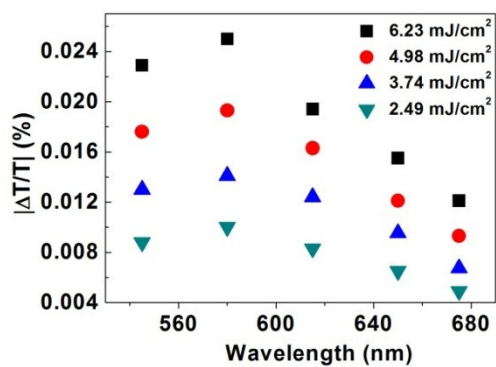


Figure S13 Wavelength-dependent signal amplitudes for Au-808/Ag/Cu₂O nanorods excited by different laser powers.

1 J. Q. Chen, J. Yan, Y. D. Chen, S. Hou, Y. L. Ji, X. C. Wu, *Nano Research* **2018**, *11*, 614-624.