Supporting Information for

Single-particle spectroscopic investigation on the scattering spectrum of

Au@MoS₂ core-shell nanosphere heterostructure

Jian You,^{+a} Hao Xie,^{+a,b} Yanhe Yang,^a Weihai Ni *^a and Weixiang Ye *^{a,b}

^aSchool of Physical Science and Technology, Soochow University, Suzhou 215006, China. ^bDepartment of Physics, School of Science, Hainan University, Haikou 570228, China.

⁺ contributed equally

* Corresponding Authors: wxy@hainanu.edu.cn (W.Y.); niweihai@suda.edu.cn (N.W.)

This PDF file includes: Materials and Math

Materials and Methods Figures S1 to S14

Experimental details

1. Materials

All chemicals were obtained from commercial suppliers and used without further purification. Cetyltrimethylammonium bromide (CTAB, \geq 98%) was obtained from Kermel. Cetyltrimethylammonium chloride (CTAC, \geq 96%) was obtained from TCI. Tetrachloroauric (III) acid (HAuCl₄ • 3H₂O), L-ascorbic acid (AA), Sodium borohydride (NaBH4, \geq 98%), Molybdenum (VI) oxide (MoO₃, \geq 99%), and Sulfur (S, \geq 99.9%) were obtained from Sigma-Aldrich. The chemical solution used in this work were prepared with deionized (DI) water (18.2 MΩ). The tube furnace (OTF-1200X) was obtained from Kjmti.

2. Synthesis and characterization of gold nanospheres (AuNSs)

The AuNSs with an average diameter of 89, 106, 133, 155, and 188 nm were synthesized

with the literature method ¹. We first synthesized the small gold nanoparticle with an average diameter of 24 nm as the seed particle. Then, we regrowth the small gold nanoparticle into five different sizes of AuNSs by the seed-mediated method. Specifically, a varying amount of the seed solution (334, 167, 83, 66, and 42 µL) was added into the CTAC solution (0.025 M, 10 mL), respectively. After the sequential addition of AA (0.1 M, 0.25 mL) and HAuCl₄ (0.01 M, 0.5 mL), the mixture solution was placed in an air-bath shaker (45 °C, 160 rpm) and kept for 3 h. The obtained AuNSs were centrifuged and redispersed into a CTAB solution (0.02 M, 10 mL), respectively. The AuNSs in CTAB solutions were mixed with a HAuCl₄ solution (0.01 M, 66 µL) for mild oxidation. The resultant mixture solution was kept in the air bath shaker (45 °C, 160 rpm) for 2 h. Finally, the AuNSs were centrifuged and redispersed into a CTAC solution (0.025 M, 10 mL), respectively. The dimensions of the synthesized AuNSs were determined by Scanning electron microscopy (SEM) using a Regulus 8100 microscope.

3. Chemical vapor deposition of Au@MoS₂ core-shell nanosphere heterostructure

The Au@MoS₂ core-shell nanosphere heterostructures were synthesized by the chemical vapor deposition (CVD) deposition procedure. The AuNSs of different sizes (89 ± 5 nm, 106 ± 6 nm, 133 ± 8 nm, 155 ± 8 nm, and 188 ± 12 nm) were deposited on different clean quartz glasses separately and then soaked in acetone solution over light. The CVD reaction process is:

$$M_{0}O_{3} + \chi/2S = M_{0}O_{3}\chi + \chi/2SO_{2}$$
(1)
$$M_{0}O_{3}\chi + (7-\chi)/2S = M_{0}S_{2} + (3-\chi)/2SO_{2}$$
(2)

In our deposition procedure, 12 mg of MoO₃ in a quartz container were placed in the center of the quartz tube and the quartz glass with AuNSs was covered on the quartz container. 140 mg of Sulfur in another quartz container were placed on the upstream side of the quartz tube, which is outside the furnace (cf. Figure S1). Before we start the reaction process, we flow argon (Ar) gas into the quartz tube with a flow rate of 200 sccm for 30 min to remove the oxygen. Then, the furnace temperature was first raised to 125 °C and kept for 20 min. Following, the furnace was heated to 680 °C at the rate of 10 °C/min, under 100 sccm of Ar. The temperature of the Sulfur was heated up to 155 °C (\pm 3 °C) by the heating belt when the furnace temperature reached 680 °C. The furnace temperature was continued for 7 min with an Ar flow rate of 30 sccm. Finally, the furnace was then slowly cooled down to room temperature with an Ar flow rate of 100 sccm.

4. Single-particle spectroscopy characterizations

The scattering spectra of single AuNSs and Au@MoS₂ core—shell nanosphere heterostructure were recorded on an Olympus BX63F optical microscope equipped with a monochromator (Acton, SpectraPro 2750i) and a charge-coupled device camera (ProEM 16004+ EMCCD) from Princeton Instruments. The EMCCD was thermoelectrically cooled to -60 °C. The particles were illuminated by the white light from a 100 W quartz-halogen-tungsten lamp through an oil-immersion darkfield condenser (NA = 1.2-1.4). The scattered light of the sample was collected through an 50x objective lens (LMPlanFLN, NA = 0.5). The exposure time for collecting the scattering spectra was 30 sec. For recording the scattering spectra of the Au@MoS₂ core—shell nanosphere heterostructures in a water environment, we used a 60x water immersion objective (LUMFLN, NA = 1.1).

5. Finite element method (FEM) simulations

We used COMSOL Multiphysics 5.3a to simulate the optical scattering cross-sections of Au@MoS₂ core—shell nanosphere heterostructure under a linear plane wave with a normal incidence. The diameters of AuNSs were set as 90 nm, 108 nm, 133 nm, 155 nm, and 188 nm, respectively. The AuNSs' dielectric function was taken from Johnson and Christy ². The thicknesses of MoS₂ were 0 to 12 nm, and the interval was 1 nm. The dielectric function of MoS₂ was taken from Baokun Song ³. The quartz substrate was modeled as a semi-infinite layer, and the refractive index was 1.45. The refractive index of the local environment used in the simulation was 1 (air).



Figure S1. MoS_2 layer deposition procedure. (a) The CVD setup mainly includes a temperature controllable furnace and quartz tube. During the deposition process, the sulfur was placed outside the furnace and heated up with an electric heating tape, while the MoO_3 and SiO_2 substrates were placed in the center of the furnace. (b) Typical temperatures and heating time for the deposition process.



Figure S2. Extinction spectra of gold nanospheres with different sizes and the absorption spectra of MoS_2 layer on quartz wafers. (a) The resonance peaks of the absorption spectra of gold nanospheres with different sizes appear in the range of 1.9 to 2.2 eV. (b) The MoS2 layer has two A and B-exciton absorption peaks at 1.85 eV and 2.0 eV.



Figure S3. Additional image for *in situ* single-particle dark-field scattering spectroscopy. In the SEM image, the dark triangulates are MoS_2 layers.



Figure S4. High-resolution SEM images of exemplary single Au@MoS₂. The scale bar is 200nm.



Figure S5. Representative SEM images of the 5 batches of gold nanospheres used in this work. The scale bar is 500nm and the images are ordered by their diameter.



Figure S6. High-resolution SEM images of exemplary individual nanoparticles. The scale bar is 200 nm.



Figure S7. (a) Experimental data of the scattering spectra of 89 ± 5 nm core-shell nanospheres. (b) We selected the similar scattering spectra of the Au@MoS₂ core-shell nanospheres from COMSOL simulation with a different layer thickness (from right to left is 0 nm, 6 nm, 7 nm, and 8 nm) for a better visible comparison with the experimental data.



Figure S8. (a) Experimental data of scattering spectra of 106 ± 6 nm core-shell nanospheres (b) We selected the similar scattering spectra of the Au@MoS₂ core-shell nanospheres from COMSOL simulation with a different layer thickness (from right to left is 0 nm, 4 nm, 5 nm, 6 nm, and 7 nm) for a better visible comparison with the experimental data.



Figure S9. (a) Experimental data of scattering spectra of 133 ± 8 nm core-shell nanospheres (b) We selected the similar scattering spectra of the Au@MoS₂ core-shell nanospheres from COMSOL simulation with a different layer thickness (from right to left is 0 nm, 3 nm, 4 nm, 8 nm, and 9 nm) for a better visible comparison with the experimental data.



Figure S10. (a) Experimental data of scattering spectra of 155 ± 8 nm core-shell nanospheres (b) We selected the similar scattering spectra of the Au@MoS₂ core-shell nanospheres from COMSOL simulation with a different layer thickness (from right to left is 0 nm, 3 nm, 4 nm, 5 nm, and 6 nm) for a better visible comparison with the experimental data.



Figure S11. (a) Experimental data of scattering spectra of 188 ± 12 nm core-shell nanospheres (b) We selected the similar scattering spectra of the Au@MoS₂ core-shell nanospheres from COMSOL simulation with a different layer thickness (from right to left is 0 nm, 4 nm, 6 nm, 7 nm, 8 nm, and 9 nm) for a better visible comparison with the experimental data.



Figure S12. Particle diameter estimation. (a) We have measured the exact size of the gold nanospheres on the quartz substrate by SEM and their plasmon resonance energy by single-

particle dark-field scattering spectroscopy. (b) The plasmon resonance will red-shift to the lower energy by increasing the particle size, which is owing to the retardation effect. The retardation effect is proportional to the particle surface area S for the sphere. We estimated the proportionality factor by fitting the plasmon resonance energy to the radius of the particle.



Figure S13. Simulated scattering spectra of Au@MoS₂ core-shell nanosphere with different layer coverage for the thickness of 8 nm. (a) 108 nm core diameter. (b) 133 nm core diameter.



Figure S14. Size effect on the exciton absorption linewidth of $Au@MoS_2$ core-shell nanoparticles. The A and B-exciton absorption linewidths do not have a strong dependency on the size of the Au spheres' core or the plasmon linewidth, which may mainly depend on the layer thickness of the MoS_2 layer.

Notes and references

- 1. Q. Ruan, L. Shao, Y. Shu, J. Wang and H. Wu, Adv. Opt. Mater, 2014, 2, 65-73.
- 2. P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370-4379.
- 3. B. Song, H. Gu, M. Fang, X. Chen, H. Jiang, R. Wang, T. Zhai, H. Yen-Teng and S. Liu, *Adv. Opt. Mater*, 2018, 7.