Supporting Information

Pinpointing Photothermal Contribution in Photochemical Reaction on Plasmonic Gold Nanoparticles

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Experimental Section

Chloroauric acid ($HAuCl_4 \cdot 4H_2O$, 99.9%), Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, 98.5%), Trisodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 99%), PEG-SH (2000), p-nitrothiophenol ($C_6H_5NO_2S$, PNTP, 99.5%) are all purchased from Sinopharm Chemical Reagent Co., Ltd. The 18.2 MΩ·cm ultrapure water is produced by Millipore water purification systems. All glassware was soaked in piranha solution (H_2SO_4: H_2O_2=3:1) or freshly prepared aqua regia (HCl: HNO_3=3:1) and then cleaned with ultrapure water.

AuNPs with different particle sizes were prepared by sodium citrate reduction method, taking 78.1 nm AuNPs as an example here. Gold seeds of about 45 nm were synthesized according to $HAuCl_4$: Na_3Ct = 1:1, and then amplified by hydroxylamine hydrochloride reduction method. 10 mL of Au (1:1) sols, 9.4 mL of H_2O, 0.2 mL of 100 mM $NH_2OH \cdot HCl$ and 0.2 mL of 1% Na_3Ct were mixed and stirred for 5 minutes, then 0.4 mL of 1% $HAuCl_4$ was added and stirred for 1 hour. Add 2mL of PEG-SH (2000) and stir for another 1 hour. Centrifuge (10000 rpm, 10 min) the above mixture into 2 mL, add water and disperse into 9 mL, add 1mL of 10^{-4}M PNTP and leave it for 2 hours, finally, centrifuge and disperse into 10μL. 21.2 nm AuNPs were made by Au (1:5) sols. Other AuNPs of different particle sizes were prepared with Au (1:1) seed sol by adjusting the different ratio of raw materials.

Normal Raman and SERS mapping experiments were performed with a confocal microprobe Raman system (LabRAM HR800) using a laser of 632.81 nm and an objective lens (×50 LMPLFLN, Numerical Aperturec (NA) = 0.5) to reduce instrumental noise. The laser power was approximately 11.9 mW without filters in light path and attenuated to 1.06 mW by the use of D1 filter. The calculated diameter of the focal spot is 1.544 μm according to the equation $d=1.22\lambda/NA$, and the calculated laser power density at the focal spot is ca. 6.35 mW/μm^2 without filters and 0.57 mW/μm^2 with D1 filter, respectively. The grating is 600 l/mm. The exposure time is 0.5 s for normal Raman mapping and 1 s for SERS mapping, respectively, with only one accumulation.

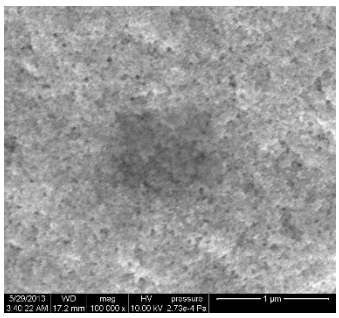
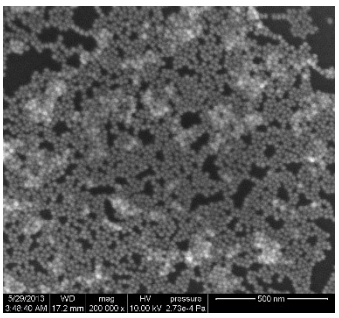
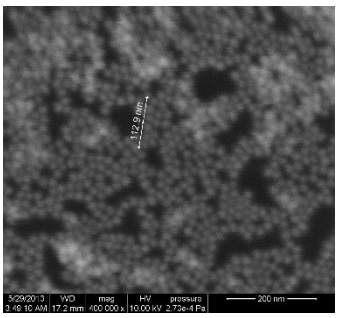
The stokes and anti-stokes SERS spectra was measured on the LabRAM HR

Evolution platform (HORIBA Scientific, Shanghai). The exposure time was 1 s for stokes spectra and 10 s for anti-stokes spectra, respectively, and other experimental parameters including the accumulation of 3 times, the objective lens of ×100 with NA=0.9, the grating of 600 l/mm, the laser power of ca. 2.0 mW without filters.

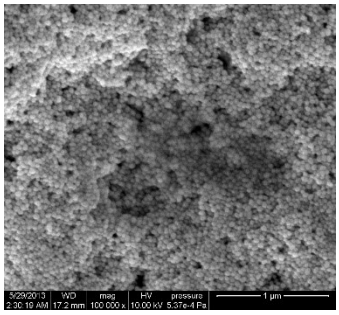
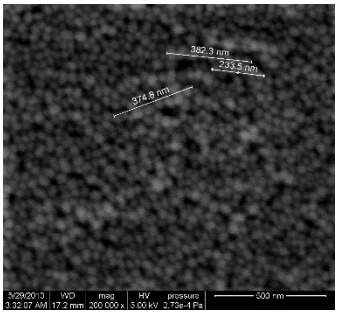
Finite-Difference Time-Domain Simulation Electro-magnetic simulations were performed by FDTD Solutions (version 8.0, from Lumerical Solutions, Inc.). We used a two-particle spherical model with particle sizes ranging from 20 to 500 nm under vertical laser irradiation at 632.81 nm.

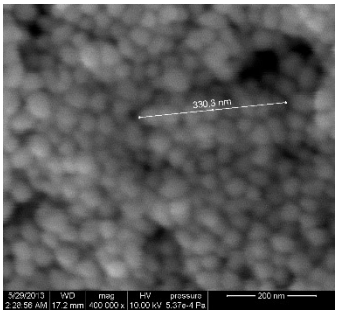
The UV-visible absorption spectra in the liquid phase were measured by a Shimadzu UV-2600 spectrophotometer, and the thin-film UV spectra were measured by Shimadzu UV-3700 instrument.

The SEM images of AuNPs with different particle sizes at three different magnifications are shown below.

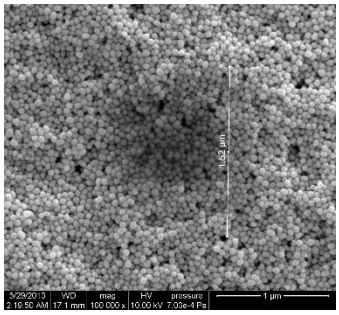




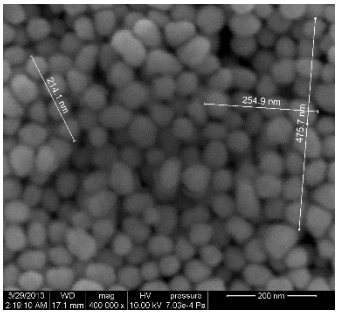
D1≈21.2 nm

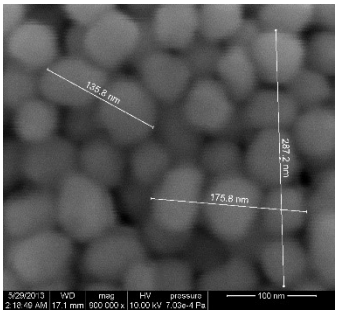





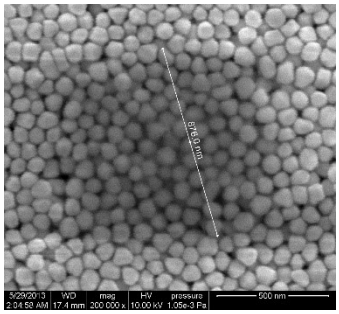
D2≈42.5 nm

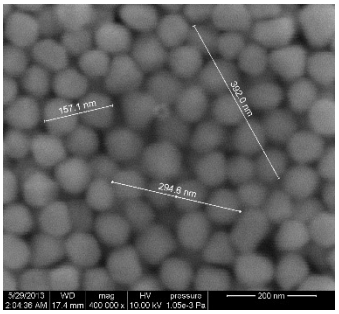


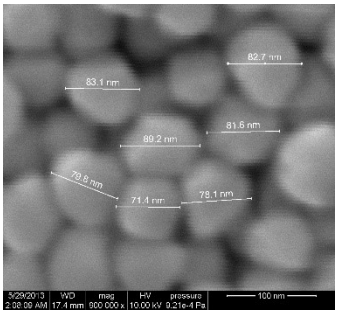




D3≈57 nm







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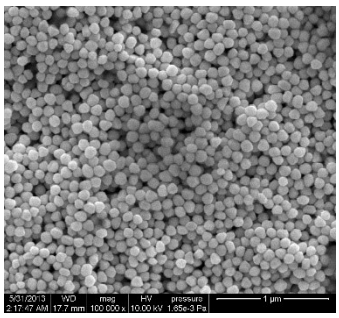
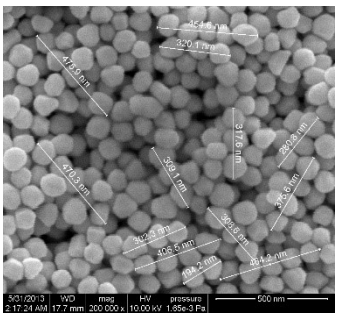
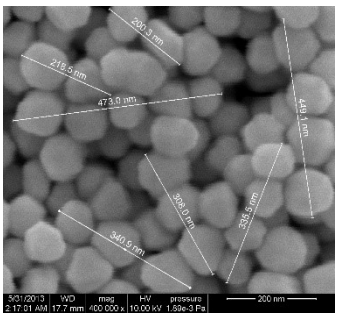
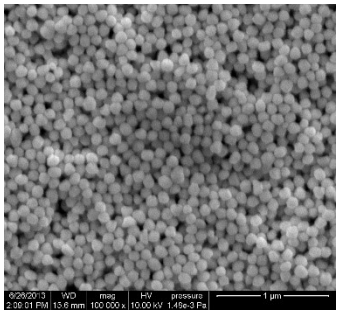
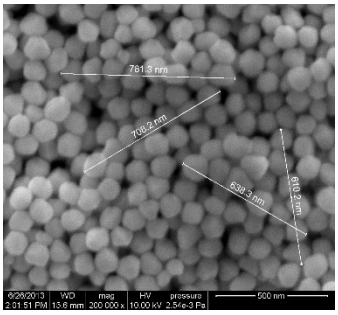
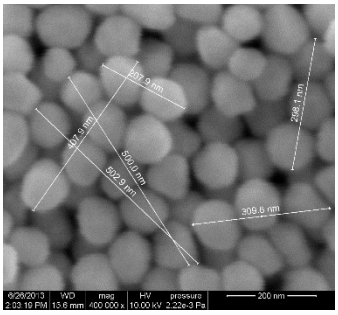
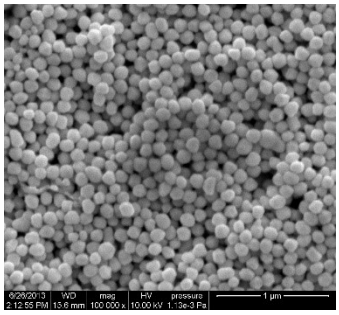
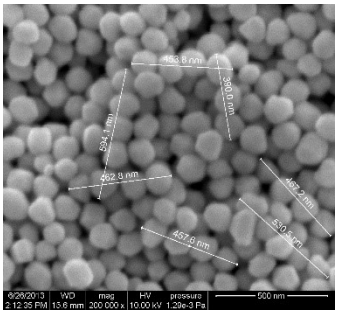
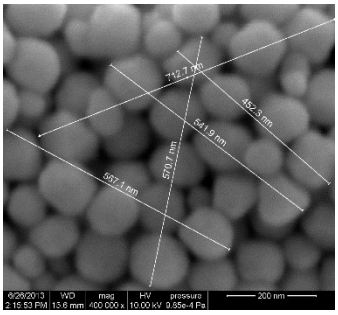




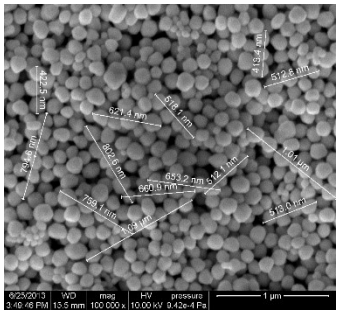
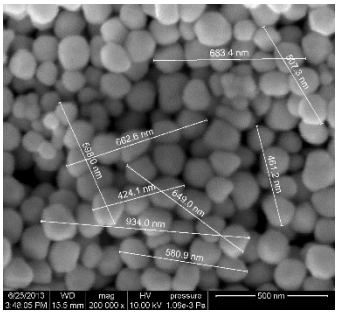
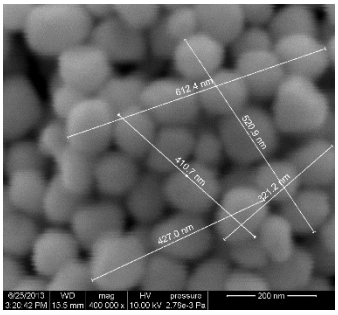
D5≈97 nm

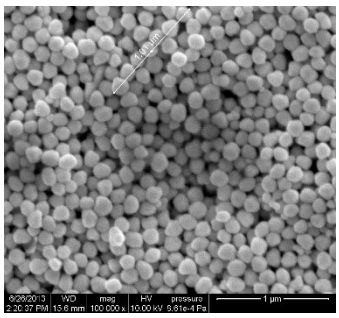
D6≈100.9 nm

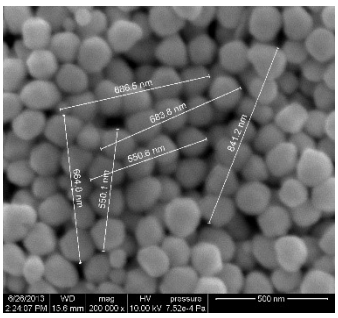




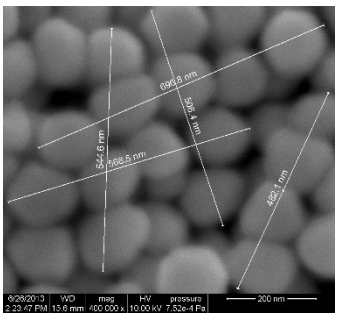
D7≈116.2 nm

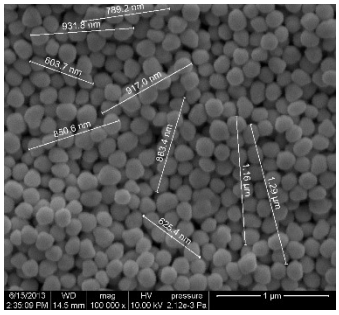
D8≈131.1 nm

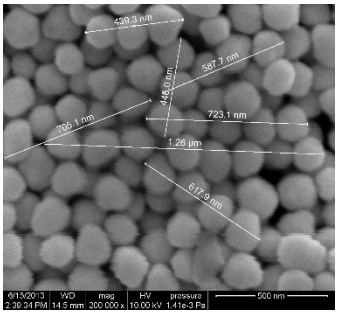


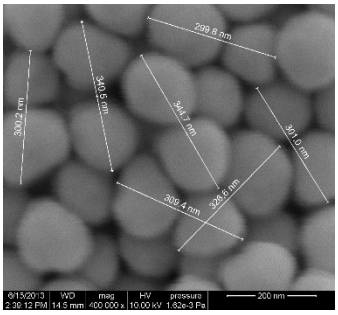




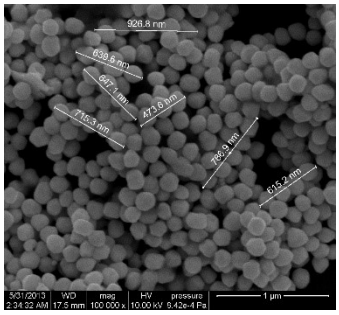
D9≈137.3 nm

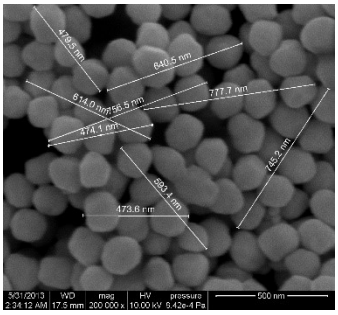


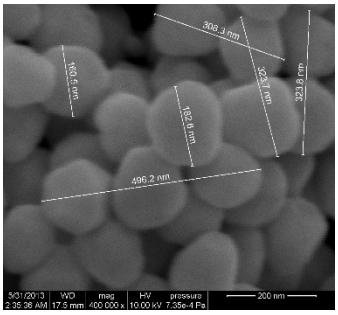




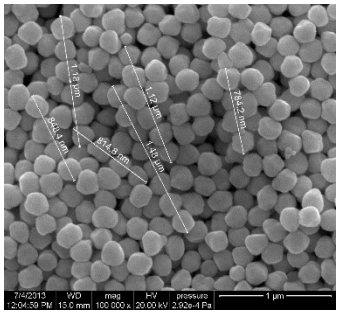
D10≈154.8 nm

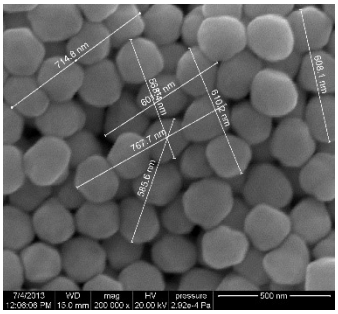


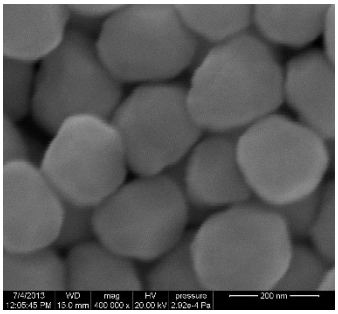




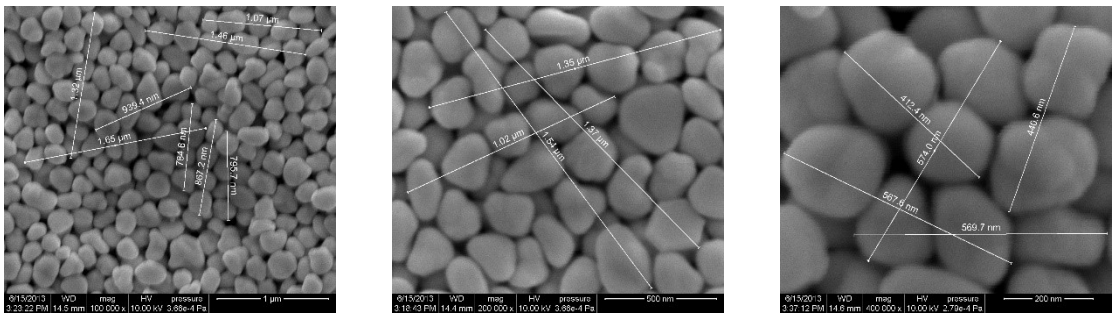
D11≈158.2 nm







D12≈193.6 nm



D13≈209.3 nm

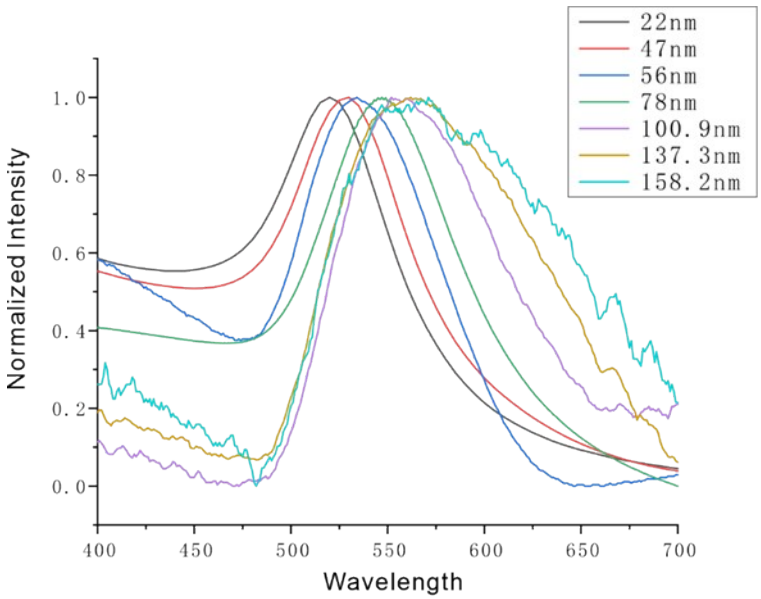


Figure S1. UV-Vis absorption spectra of seven different sizes of gold particles. The UV spectra of gold particles below 100.9 nm (the first four bars) were measured in the liquid phase, and 100.9 nm and above (the last three bars) were measured on thin films.

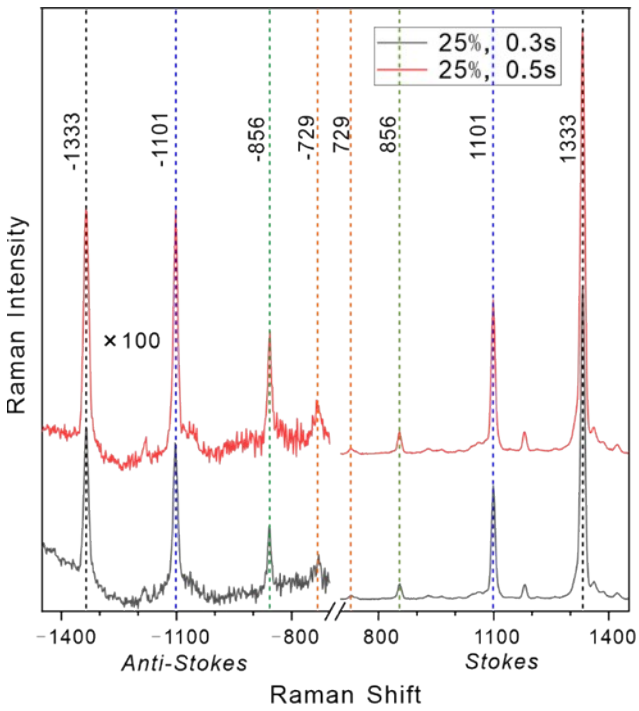


Figure S2. Simultaneous Stokes and anti-Stokes measurements of normal Raman spectra directly on PNTP crystals. A laser of 532 nm and an objective lens (×50 LMPLFLN, Numerical Aperture (NA) = 0.5) were used. Measurements were made at 25% laser power with an integration time of 0.3 s and 0.5 s, respectively. All spectra were obtained by averaging after measurements at five different locations in the selected samples. The laser power of 25% denoted a laser power density of ca. 7.56 mW/μm^2.