

Supporting information

Strong location dependent surface enhanced Raman scattering on individual symmetry-reduced metallic nanoparticle

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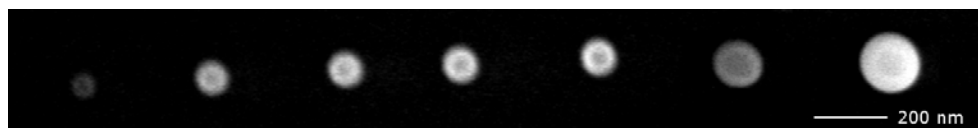


Figure S1. SEM images of different sizes of carbon nanoparticles deposited by EBID on the Si substrate. From left to right: ~ 50, 90, 100, 100, 130 and 160 nm.

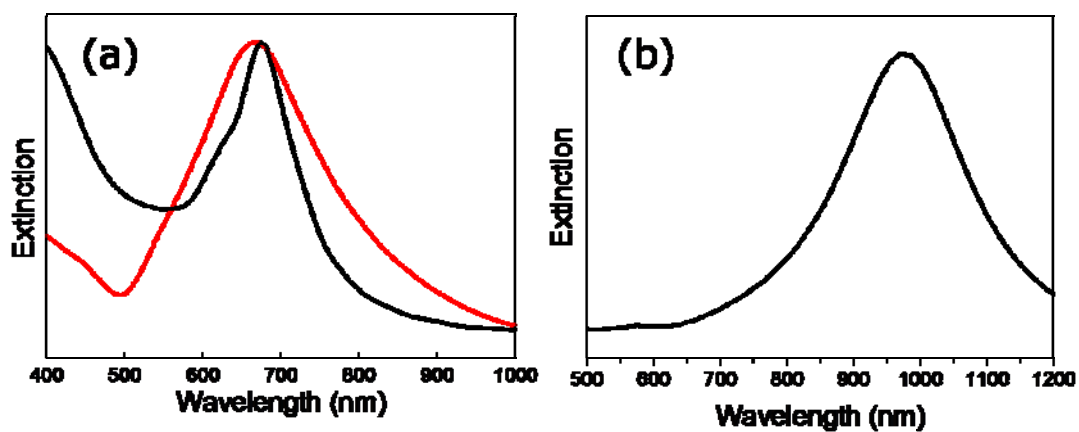


Figure S2. FDTD simulated extinction spectra of (a) Au semishells and (b) Au nanobowls. Red spectrum in the (a) panel shows the experimental extinction spectrum of Au semishells.

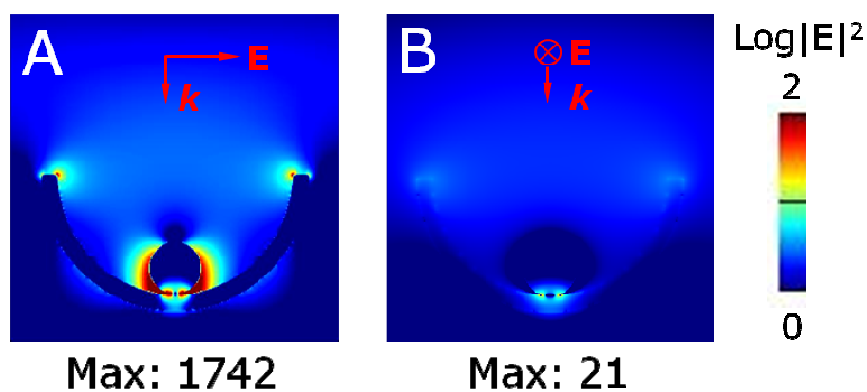


Figure S3. Simulated electric field distribution profiles of a gold nanobowl with a 633 nm incident light polarized (A) in and (B) out of the plane.

Experimental details

1. Au semishells synthesis.

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The fabrication of Au semishells has been described previously [S1]. Briefly, they were prepared by performing an ion milling process on Au nanoshells on the substrate. Au nanoshells (87 ± 10 nm core size and 30 ± 6 nm shell thickness) were synthesized from a chemical plating on the silica nanoparticles [S2]. Monodispersed silica nanoparticles were synthesized by the hydrolysis of tetraethyl orthosilicate (TEOS, Fluka) in basic solution via the Stöber process and functionalized with (3-aminopropyl)triethoxysilane (APTES, ABCR GmbH) in ethanol overnight. These functionalized silica particles were decorated with a small Au colloid (1-2 nm) prepared by the method of Duff et al [S3]. A subsequent reduction of an aged mixture of chloroauric acid (HAuCl_4 , Aldrich) and potassium carbonate (K_2CO_3 , Alfa Aesar) by a solution of formaldehyde (Vel) resulted in a complete Au shell coverage on the nanoparticle surface. The obtained Au nanoshells were purified by repeated centrifugation and washing with deionized water and finally redispersed in deionized water.

The dilute Au nanoshell suspension was drop-casted on a silicon substrate with some recognizable marks and dried under ambient conditions. Then an ion milling process was applied to remove the top part of the shell in an in-house available ion milling system with the parameters: 1 min, 375 V beam voltage, 400 V accelerator voltage, 2.4 sccm Xe flow rate, 2 sccm Ar flow rate and below 8.0×10^{-8} mTorr base pressure in the processing chamber.

2. Au nanobowls synthesis

Au nanobowls were fabricated by applying an ion milling process and a vapor HF etching process on complex Au nanoshells ($\text{Au@SiO}_2\text{@Au}$) on a silicon substrate [S4]. Firstly, 55 ± 7 nm Au NPs were prepared by adding 0.8 ml of 1% (w/v) sodium citrate into a 100 ml boiling aqueous solution containing 0.01% (w/v) HAuCl_4 . Next, 4 ml Au NPs suspension (~ 0.5 mg/ml) was added into 20 ml isopropanol under continuous stirring followed by 0.5 ml ammonia and 54 μl TEOS. The reaction was allowed to proceed for 1 h at room temperature. The obtained silica shell thickness was ~ 100 nm confirmed by TEM images. Following the same procedure of making Au nanoshells described above, the complex Au nanoshells ($\text{Au@SiO}_2\text{@Au}$) colloids with a ~ 25 nm Au shell thickness were obtained. After the $\text{Au@SiO}_2\text{@Au}$ colloids were drop-casted on a silicon substrate and dried under ambient conditions, an ion milling and a vapor HF etching process were applied. The milling time and parameters of the ion milling process is the same as those used in the fabrication of semishells. The vapor HF etching was done in an adapted commercially available system for wafer cleaning [S5]. Nitrogen gas was bubbled through a 49% HF solution in order to get a vapor of HF and water into the reaction hood. The nitrogen flow was adjusted at ~ 0.5 l/min and the temperature in the hood was controlled at ~ 35 °C. In order to get reproducible etching results, the chamber was usually purged by nitrogen gas for 5 min before and after etching process.

3. Carbon nanoparticles by e-beam induced deposition (EBID).

The EBID of carbon nanoparticles was performed in a custom-made device [S6]. Briefly, the liquid precursor hexadecane (Sigma-Aldrich) was placed in the reservoir of an aluminum sealing device, and a silicon-on-insulator (SOI) wafer with nano-channels on freestanding membranes was used as the valve for the precursor vapor leakage. The whole device was loaded into the vacuum chamber of the SEM machine (Philips, XL30 FESEM) with an operation pressure of 10^{-5} Pa. Carbon nanoparticles were deposited under spot mode of

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SEM, with the parameters: 10 kV accelerate voltage, 160 μ A emission current, and spot size of 2. Carbon nanoparticles with various sizes were obtained with a deposition time from 1 to 30 s.

4. Surface-enhanced Raman scattering (SERS) measurement

Raman spectra were recorded on a Horiba Jobin Yvon LabRam HR 800 system in a backscattering configuration. A He-Ne laser at 633 nm with a \sim 1 mW power was used for the Raman measurements in order to match the plasmon resonance of the Au semishells. For the sake of simplicity, the same laser was used for the Au nanobowls for a comparison. A \times 100 objective lens mounted on an Olympus BXFM01LHS microscope was used to focus the laser beam into a spot of approximately 1 μ m in diameter. The spectral resolution of the system is 1.5 cm^{-1} . A piezoelectric micro-positioning platform and an optical microscope were used to find the particles. The integration time of the spectra was 45 s for the Au semishell and 10 s for the Au nanobowl during each measurement.

5. Finite difference time domain (FDTD) calculations.

The extinction spectra and electric field distribution profiles of the Au semishell and the nanobowl were calculated by using the FDTD method (Lumerical Solutions, Vancouver, Canada). The FDTD method is based on the numerical solution of Maxwell's equations and can be used to obtain an adequate profile of the electric near-field distribution around the structures with arbitrary shapes. The simulated particle is illuminated with a total-field scattered-field (TFSF) light source from the top. The polarization of the light is perpendicular to the propagation direction and parallel to the substrate. The wavelength of incident light is varied from 400 nm to 1200 nm and the amplitude is set as 1. The whole simulation region is assumed in air. We use the modeled Au empirical dielectric function [S1]. For normal incident light, we have not found a large influence of the substrate on the plasmon peak of the nanoshells, semishells, and nanobowls, except for a small red-shift of the resonance. Therefore, the simulations we show in this report do not take into account a dielectric substrate for the sake of simplicity.

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