

SUPPORTING INFORMATION

Gold Nanopyramids Assembled into High-Order Stacks Exhibit Increased SERS Response

Kelsey A. Stoerzinger,[‡] Warefta Hasan,[†] Julia Y. Lin,[†] Alex Robles[†] and Teri W. Odom^{†,‡,}*

[†]Department of Chemistry, [‡]Department of Materials Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

* To whom correspondence should be addressed. E-mail: todom@northwestern.edu.

Telephone number: 847-491-7674

Fax number: 847-497-7713

Email address: todom@northwestern.edu

EXPERIMENTAL METHODS

1. Sample Preparation and Pyramid Assembly Conditions

Dark field scattering measurements of the nanopyrramids were carried out on indium tin oxide (ITO)-coated glass patterned with Au alignment markers. The alignment marks were used to correlate the SEM images of particle structure and orientation with DF scattering spectra and SERS data. The Au markers were functionalized with octadecanethiol (1 mM ODT in water for 24 h) to increase the hydrophobicity of the Au surface (from contact angle $\theta = 41^\circ$ to 110°) and to prevent assembly of the aqueous nanopyrramid suspension onto the markers. The ITO was then functionalized with (tridecafluoro-1, 1, 2, 2-tetrahydro-ctyl) trichlorosilane to increase the hydrophobicity from $\theta = 76^\circ$ to 93° . Aqueous pyramid suspensions were subsequently drop-cast onto the surfaces and allowed to evaporate in sealed dishes at 4°C . The distribution of pyramid low-order and high-order assemblies on ITO was comparable to the results found on surface-modified Si (Fig. 2).

2. Dark Field Scattering Measurements

A broadband white light source (100 W, halogen lamp) was used to illuminate the particles through a DF condenser, and the light scattered from the pyramids was collected by a variable numerical aperture objective (100 \times , NA = 0.5) and dispersed by a spectrometer equipped with a liquid N₂-cooled CCD. The slit width (0.515 mm), lamp voltage (8 V), and exposure times (1 s each for particle and background spectra, 5 μsec for the lamp profile) were kept constant for all measurements.

3. SERS Measurements

The nanopyramidal assemblies were soaked in a 1 mM ethanolic solution of methylene blue for 4 h, rinsed copiously with ethanol, and dried under N₂ gas. The adsorption of the molecule did not alter the structure of the assembly. Raman spectra and images were recorded with a confocal Raman microscope (Alpha, WiTec Instruments) equipped with a piezo scanner and 100 \times microscope objective (NA = 0.90, Nikon). Measurements were collected using a confocal Raman microscope over a $5 \times 5 \mu\text{m}$ region with

a step size of 167 nm and an integration time of 0.5 s. The samples were excited using a linearly polarized He-Ne laser with 1- μm spot size (633 nm, Coherent Inc.) at 100 μW . Care was taken to avoid photobleaching the dye by moving to new regions of the substrate¹ and ensuring that adjacent assemblies were outside of the scan area.

4. Numerical Simulations

We calculated $|E_z|^2$ for a single tip-down (TD) Au nanopyramid and dimers of high-order (H2) and low-order (L2) using commercially available FDTD software (Lumerical). Cross-sections were taken along the central axis in the x-z plane intersecting the tips of TD and H2. For L2, the electric-field intensity was measured in the x-z plane along the long axis of the assembly, where the gap separating the two pyramids was oriented perpendicular to the plane of the detector. The model structures and parameters were chosen to be realistic and as close to the experimental conditions as possible. The pyramids were simulated using experimentally determined dielectric constants for Au,² and the structures were on an ITO ($n = 1.8$) surface and surrounded by air ($n = 1.0$). The electric field intensity maps were calculated at 633 nm, the excitation wavelength used for SERS. The incident light was modeled as a plane wave linearly polarized along the central axis (TD, H2) and long axis (L2) of the nanopyramid and dimer assemblies. Illumination was at normal incidence with a source spot size of 1 μm . The mesh size used in the FDTD program was 4 nm.

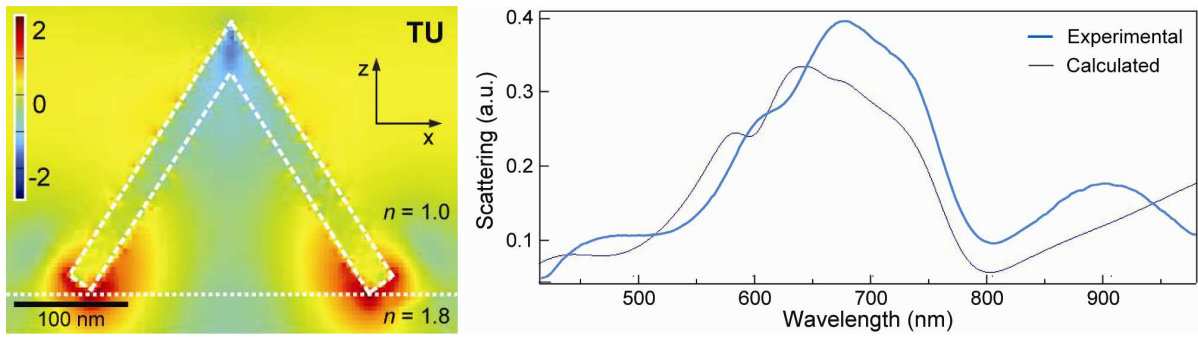


Figure S1. Simulated electromagnetic field intensity of a tip-up (TU) Au pyramid and scattering spectra. (left) Calculated $|E_z|^2$ at 633 nm for a 25-nm thick Au TU nanopyramid. The intensity is plotted on a logarithmic scale. (right) Comparison of FDTD calculated and measured scattering spectra of the TU pyramid. The scattering spectra calculated using a total-field scattered-field source at normal incidence was in excellent agreement with measurements.

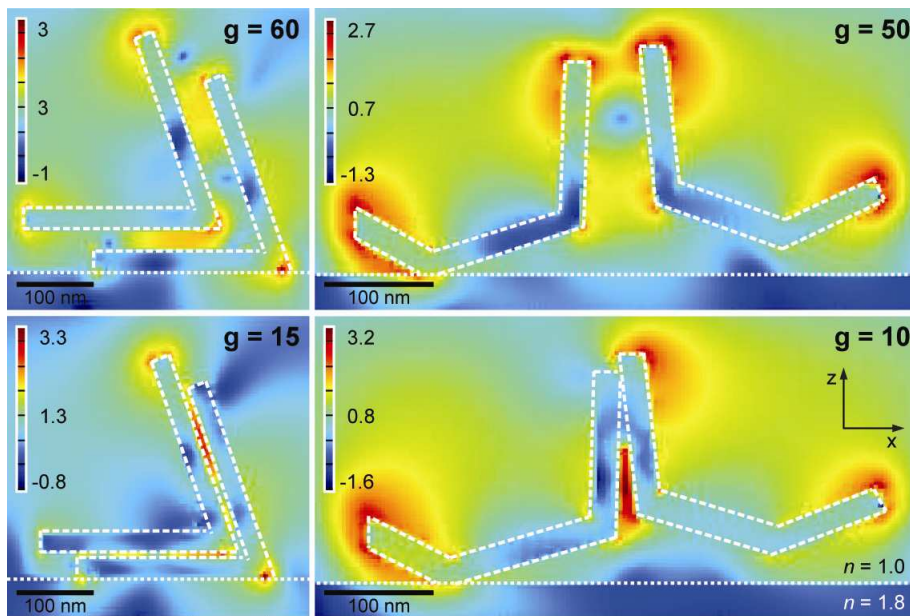


Figure S2. Pyramid dimers with different gaps concentrate electromagnetic fields between adjacent faces differently. Calculated $|E_z|^2$ at 633 nm for (left) high- and (right) low-order dimers with different gap spacing (g) in nanometers. The intensities are on a logarithmic scale.

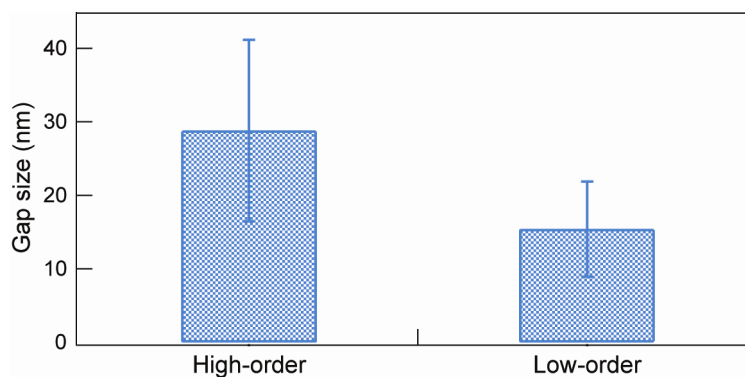


Figure S3. Mean gap sizes for pyramid dimers for 12 H2 and 12 L2 structures. The gap between particles in a single two-particle assembly was determined by averaging the distance taken at five different locations along the gap region of the dimer in the SEM micrographs. Gap sizes were determined using image processing software (ImageJ). Error bars represent standard deviations.

REFERENCES

- (1) Domke, K. F.; Zhang, D.; Pettinger, B. Toward Raman Fingerprints of Single Dye Molecules at Atomically Smooth Au(111). *J. Am. Chem. Soc.* **2006**, *128*, 14721-14727.
- (2) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, *6*, 4370-4379.