Supporting Information

An Optimal Substrate Design for SERS: Dual-Scale Diamond-Shaped Gold Nano-Structures Fabricated via Interference Lithography

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Experimental Procedure

Chemicals used

4-aminothiophenol (Sigma-Aldrich, 97%), SU-8 2010 (microchem), 1-methoxy-2-propanol acetate (SAMCHUN,99%), (3-mercaptopropyl)-trimethoxysilane (Sigma-Aldrich,95%), acetone (Skchemicals,99.5%), isopropanol (Skchemicals 99.5%), ethanol (Fisher scientific,99.9%), chloroauric acid (Sigma-Aldrich, >99.9%), sodium citrate (Sigma-Aldrich, >98%), zinc nitrate hexahydrate (Sigma-Aldrich, >98%), hexamethylenetetramine (HMTA) (Sigma-Aldrich, >98%), sodium hydroxide (Duksan pure chemicals) Ethanol, crystal violet(CV) (Sigma-Aldrich, >90%). All chemicals were used without further purification.

Fabrication of DGN patterns via interference lithography

The Si substrates were cleaned using ultra-sonication with acetone, isopropanol, and de-ionized water for 10 min and dried by nitrogen blowing. A 5nm Cr layer and 300 nm thick Au film was deposited by e-beam evaporator onto the Si substrate. In case of glass substrate, we

treated O_2 plasma after cleaning process. And then coated (3-mercapto propyl)-trimethoxysilane SAMS monolayer onto the O_2 plasma treated glass substrate as adhesion promoter between glass and gold. A gold deposited substrates were immersed in ethanol solution of 10mM 4-ATP(4-aminothiopheol) solution for 12h to make 4-ATP SAMS monolayer on gold film. After 4-ATP treatment, the gold film substrates were rinsed using an ethanol and dried by N_2 blowing. A 500 nm thick photoresist film was obtained by spin-coating at 3000rpm on the gold film substrate square patterns with circular holes were fabricated via interference lithography. The samples were double exposed for 6 x 6s by rotating the sample 90 degrees. Before developing the photoresist using PGMEA, a post-exposure bake was conducted at 75 °C for 10min and hard-bake was conducted at 95°C for 10min. After O_2 plasma treatment (1.5 Torr using Room Air, 18W) for 13 min onto Su-8 patterned gold substrate to make diamond shape, etch the gold partially using metal reactive ion etching (metal RIE) at 4m Torr of Ar/Cl_2 (40sccm:10sccm) condition and the 250W RF power was applied for 150s.

Attachment of gold nanoparticles on the DGN substrate.

30 mM of chloroauric acid was dissolved in ethanol to which 1% wt of sodium citrate dissolved in water was added. The mixture was heated to 100°C for 30 min and then allowed to cool down naturally along with substrate. The pH of the prepared solution was adjusted to be 8~9 using 1M NaOH solution before deposition. The samples were washed with D.I. water and ethanol.

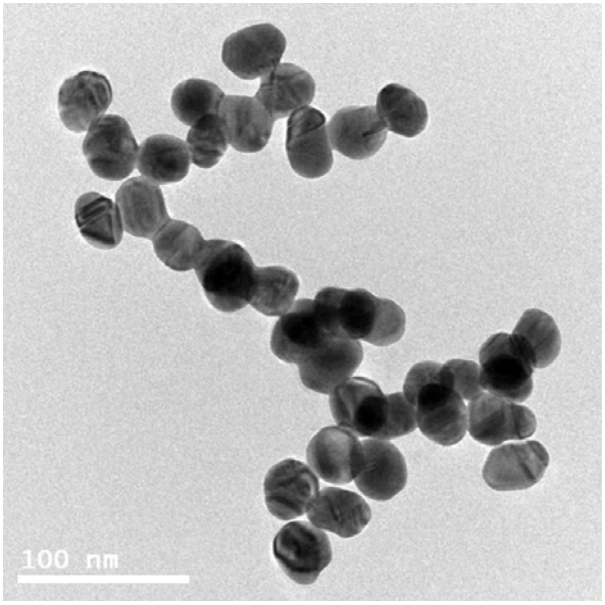

Figure S1. TEM image of as-prepared Au nanoparticles.

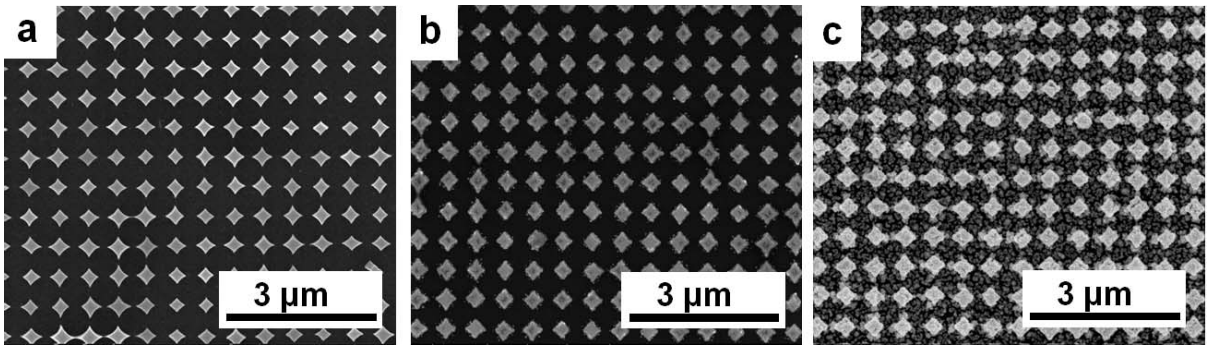

Figure S2. SEM images of Long-range ordered substrate of 350 nm DGN.: a) SU-8 with sharp-edges. b) DGN with 200 nm spacing between edges. c) Dual-scale DGN.

Characterization

The morphology of the DGN was examined using a NOVA NANOSEM 230 FESEM. The powder diffraction data were obtained using a Rigaku D/MAZX 2500V/PC HPXRD. The SERS spectra were acquired using an alpha 300S spectrograph from WITEC. The instrument uses an Olympus BX-40 microscope with a 100 X (0.9 N.A) objective lens with a power of 0.1 mW of the 632.8 nm line from an electrically cooled He-Ne laser. In this work, the sample integration time for single measurement was set to 20 s. In order to estimate the reproducibility of the measurement, the spectra were collected from 10 random locations on each substrate. The diffuse reflectivity spectrum was measured using a Cary 5000 UV/Vis/NIR spectrophotometer (Varian).

EF calculations

The enhancement factor was calculated using the following formula:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{bulk}/N_{bulk}},$$

where I and N correspond to the intensity of the Raman band and number of molecules being probed, respectively, and the subscript refers to the SERS and bulk cases. I_{bulk} and N_{bulk} were estimated from the Raman spectra of $1x10^{-7}$ M of crystal violet solution. N_{bulk} was calculated to be $2.9x10^{5}$. N_{SERS} was calculated to be $7.3x10^{10}$ molecules. The most intense peak at 1172 cm^{-1} in the SERS spectra was chosen to calculate the EF. The enhancement factors were calculated to be $1.88x10^{9}$ for DGN-78, $9.11x10^{7}$ for DGN-44, 2.57×10^{6} for DGN-29,

$2.3x10^8$ for pure 20-30 nm Au particles at 633nm laser excitation. The enhancement factors at 785nm laser excitation were calculated to be $2.77x10^7$ for 78% 350 nm DGN, $1.38x10^7$, $5.26x10^6$ for similar density of 500 nm and 20-30 nm Au particles.

FDTD simulation

The plasmonic behavior for different structural morphology can be determined from Maxwell equations:

$$(1)\quad \nabla \cdot B = 0$$

$$(2)\quad \nabla \cdot D = 0$$

$$(3)\quad \nabla \times H = \sigma E + \frac{\partial D}{\partial t}$$

$$(4)\quad \nabla \times E = -\frac{\partial B}{\partial t}$$

The above equations are solved using the finite-difference time-domain (FDTD).[30-32] An electromagnetic wave of 633nm wavelength propagates perpendicularly to the sample and it is linearly polarized along the vertical direction. The time-averaged light intensity ($|\mathbf{E}|^2$) distributions for the particles are shown in text. The sharp edge shape shows an increase in the electromagnetic field for the DGN and this is particularly pronounced when the polarization of the incident light is parallel to the diagonal of the diamonds as shown in the simulation data.

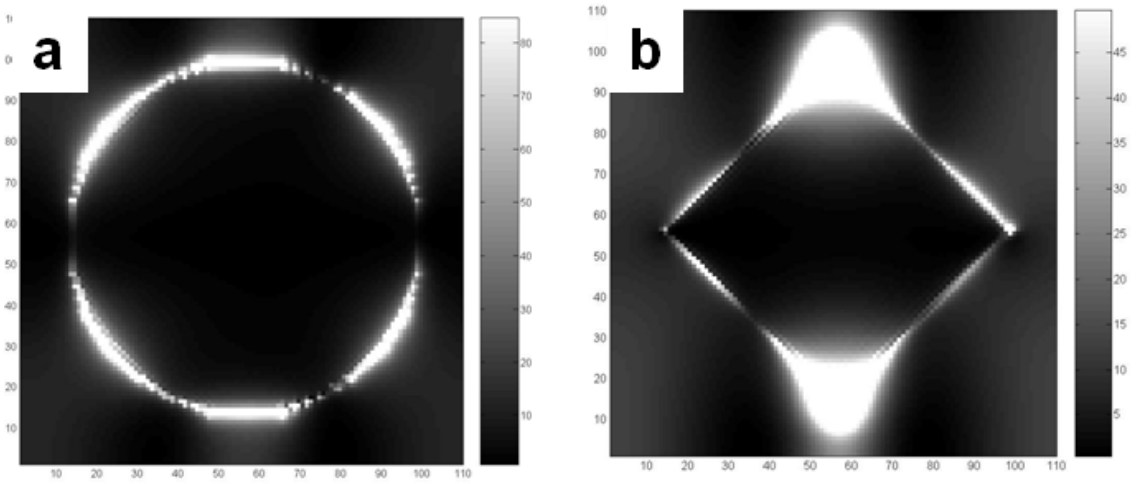

Figure S3. Intensity distribution of simulated electric field on sphere vs diamond shaped nanoposts with the diameter of 350 nm and the period of 500 nm.

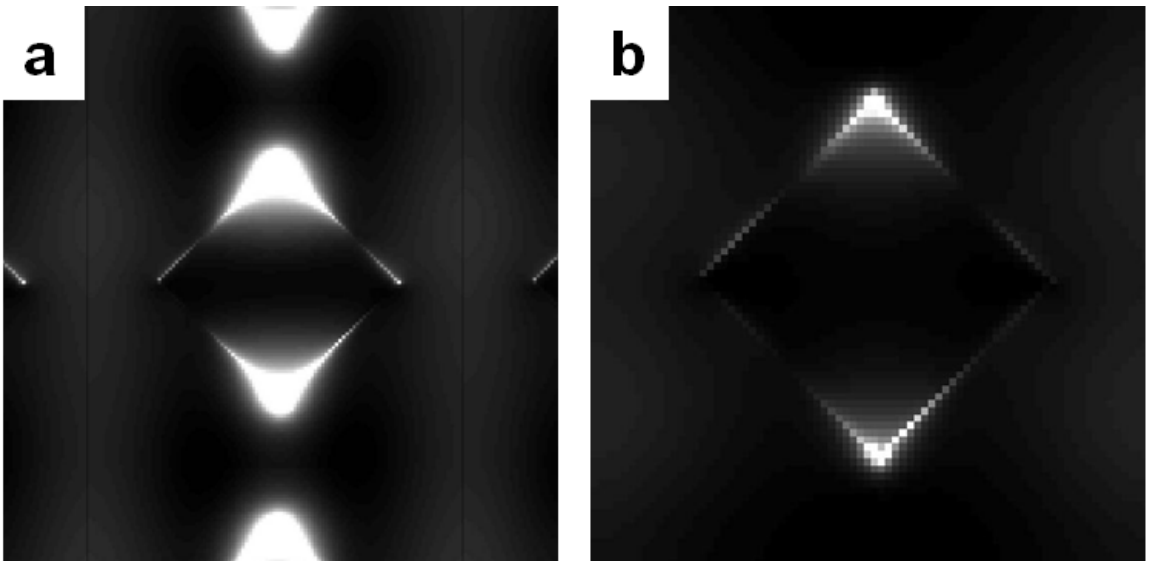

Figure S4. Intensity distribution of simulated electric field on diamond shaped nanoposts with the diagonal dimension of 350 nm (a) and 500 nm (b).

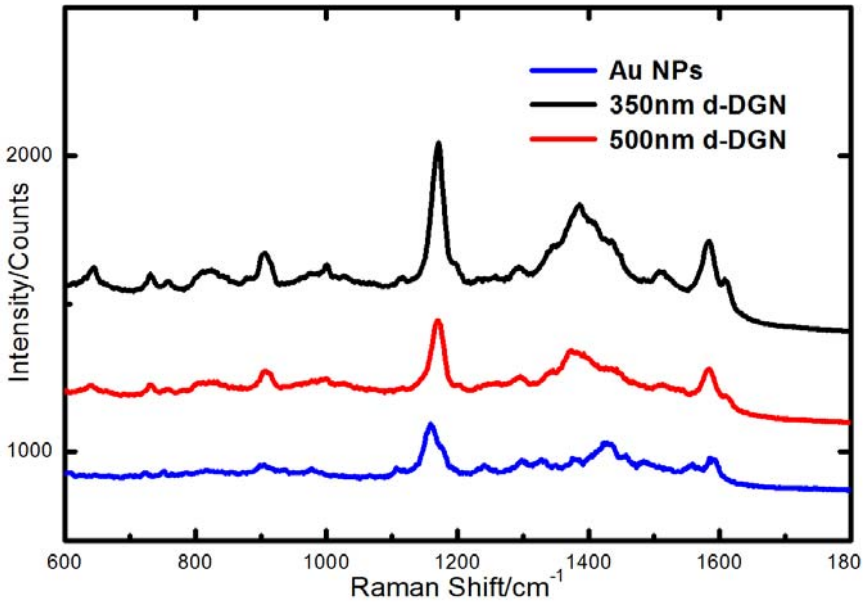

Figure S5. SERS spectra of gold NP substrate, d-DGN-350, and d-DGN-500 at an excitation of 785 nm laser.