

Supporting Information for:

Dispersible Gold Nanorod Dimers with Sub-5 nm Gaps as Local Amplifiers for Surface-Enhanced Raman Scattering

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Nanorod Dimer Synthesis and Characterization:

The method for producing all the dimers in this work was altered from previous publications.^{1,2} Briefly, Au-Ni nanowires were synthesized electrochemically in anodized aluminum oxide (AAO) membranes purchased from Synkera Technologies, Inc. with nominal pore diameters of 35 nm. Au was deposited at -1100 mV (vs. Ag/AgCl reference) using concentrated Orotemp 24 Rack plating solution (Technic, Inc.), and Ni was deposited at -1100 mV using Nickel Sulfamate plating solution (Technic, Inc.) diluted 100 times. After releasing the nanowires from the AAO templates by dissolving the AAO in 0.5 M NaOH, the wires were rinsed by spinning them down

using a benchtop centrifuge at 5000 rpm and subsequently resuspending them in H_2O (with 0.1% sodium citrate) four times. The nanowires were then diluted to 4 mL in H_2O and were vacuum filtered onto larger pore AAO membranes (100 nm Whatman Anodisc 47 membranes), where 1.25 mL aliquots of the nanowires were filtered onto three membranes per synthesis batch. These templates were allowed to dry completely after the initial filtering process before being placed into the electron beam (e-beam) evaporator to deposit the SiO_2 backing material. 7 nm of SiO_2 (as measured by the built-in quartz crystal microbalance) was then deposited on the surface of the AAO membranes at a deposition rate of 0.02 nm/s, covering the exposed side of the nanowires and creating a sheath down the long axis (Kurt J. Lesker PVD 75 e-beam evaporator). 10 mL of 5 M NaOH, followed by 100 mL of H_2O , was then vacuum filtered through the AAO templates to aid minimize the interaction between the nanowires and the AAO surface. Finally, the nanorods were recovered back into solution by sonicating each of the nanowire-coated AAO membranes in ethanol for 30 seconds. After spinning them down several times in ethanol, they were then resuspended in a 50% (w/w) solution of H_3PO_4 in ethanol for 2 hours to dissolve any excess AAO left in solution. After spinning the wires down several more times in ethanol and then water, the remainder of the Ni sacrificial segments were etched in a 25% H_3PO_4 solution in water for 2 hours. With a final rinsing step, the dimers are now ready for further functionalization and Raman characterization. UV-vis spectra were collected on a Cary 5000 UV-vis-NIR spectrometer (Varian), and TEM/STEM images were collected on a Hitachi HD-2300A Scanning Transmission Electron Microscope.

Dimer Functionalization and SERS Measurements:

Particle Preparation and Functionalization. For both ensemble-averaged and single-particle

studies, the nanorod dimers were functionalized with a 1 mM ethanolic solution of 1,4-BDT over a period of 2 h. For single-particle studies, this was done after first dropcasting them on a silicon wafer and mapping the location of particles of interest with an SEM. For the ensemble-averaged studies, ethanol was used to wash the samples several times before resuspension in water to achieve concentration of 3-9 nM. The molecule 1,4-BDT is known to form monolayers on Au and Ag over short functionalization times and has a footprint of approximately 0.54 nm²/molecule.

Raman Spectroscopy Measurements. Normal Raman spectroscopy was done with solutions of ~0.3 M of 1,4-BDT in basic NaOH (~6 M) where the molecule is in anion form and much more soluble. This was verified by the absence of any S-H stretching for solutions containing 1,4-BDT (Figure 4). For these samples $\lambda_{\text{ex}} = 785 \text{ nm}$, $P_{\text{laser}} = 4 \text{ mW}$, $t = 30 \text{ s}$.

Surface-Enhanced Raman Spectroscopy Measurements. The ensemble-averaged Raman spectra were recorded from an aqueous solution of functionalized dimers using a WITec Confocal Raman spectrophotometer coupled to a microscope with 50 \times and 100 \times objectives in backscattering configuration. The 785 nm excitation was from a semiconductor continuous wave diode laser and used with a holographic notch filter with a grating of 600 lines per millimeter. The backscattered Raman signals were collected on a thermoelectrically cooled (-60 °C) CCD detector. Sample cells were constructed by attaching the cap of a microcentrifuge tube to a glass slide. The cap acted as a vessel for the liquid sample, and a glass cover slip (0.17-0.13 mm) was carefully placed on top to eliminate solvent evaporation and to act as a reference point from which the focal volume was lowered to a depth of 200 μm into the sample. SERS data was collected with $\lambda_{\text{ex}} = 785 \text{ nm}$, $P_{\text{laser}} = 3.1 \text{ mW}$, and $t = 20 \text{ s}$.

Processing of the Raman spectra and all data analysis was done with IGOR Pro software

(Portland, OR). All data was baseline corrected before normalization. For the baseline correction, a fourth order polynomial was fitted to the raw Raman spectrum and subtracted.

Sample Calculation of the Enhancement Factor (EF) from Ensemble-Averaged Solution Measurements. The calculation of the EF from the nanorod dimers in aqueous solution was determined using two methods. The first method uses the well-known equation below:

$$EF = (I_{\text{sers}} \times N_{\text{normal}}) / (I_{\text{normal}} \times N_{\text{sers}}), \quad (1)$$

where N_{normal} is the number of molecules in the scattering volume for the ordinary Raman measurement and N_{sers} is the number of adsorbed molecules in the scattering volume for SERS. I_{SERS} is the peak intensity of a band from the SERS measurement and I_{normal} is the peak intensity of the same band from the ordinary Raman measurement. For all EF calculations in this work, the intensity of the 1565 cm^{-1} band from the molecule 1,4-benzenedithiol (1,4-BDT) was used for I_{SERS} and I_{normal} . To determine N_{normal} and N_{sers} we characterized the scattering volume of our Raman micro-probe system. The scattering volume was determined by measuring the waist of the excitation profile and the axial detection efficiency, which can be used to calculate the scattering volume. The first value was determined using a ‘scanning knife-edge method’ where the objective is focused on a silicon substrate and scanned over the edge. To determine the axial detection efficiency the intensity of the silicon band at 521 cm^{-1} was measured as a function of distance from the focal plane of the substrate. Both methods and a detailed discussion on the calculation of the scattering volume can be found in the supporting information of ref [3].

To determine the concentration of nanorod dimers in solution, first the samples were well characterized with TEM/SEM imaging to calculate the average volume of a nanorod dimer and the number of Au atoms per nanorod dimer. The Au^+ concentration of the aqueous solution was then measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES,

Agilent 7500ce) to determine the amount of Au in the sample. This allows one to estimate the number of particles per unit volume. In addition the average surface area of a nanorod dimer can be determined and the number of 1,4-BDT molecules per nanorod dimer can be calculated based on the footprint of the molecule (0.54 nm²/molecule). This allows us to estimate I_{SERS} . A sample calculation is provided below:

$$EF = (I_{\text{SERS}} \times N_{\text{normal}}) / (I_{\text{normal}} \times N_{\text{SERS}}),$$

$$\text{where } I_{\text{SERS}} = 116.5 \text{ mW}^{-1} \text{ s}^{-1} \text{ and } I_{\text{normal}} = 7.7 \text{ mW}^{-1} \text{ s}^{-1}$$

$$EF = (116.5 \text{ mW}^{-1} \text{ s}^{-1} \times N_{\text{normal}}) / (7.7 \text{ mW}^{-1} \text{ s}^{-1} \times N_{\text{SERS}}),$$

$$N_{\text{normal}} = 2.2 \times 10^{-10} \text{ L} \times 0.31 \text{ M 1,4-BDT},$$

Where $2.2 \times 10^{-10} \text{ L}$ is the scattering volume.

$$N_{\text{normal}} = 6.82 \times 10^{-11} \text{ mol} = 4.11 \times 10^{13} \text{ molecules.}$$

$$N_{\text{SERS}} = 5.33 \times 10^{13} \text{ particles/L} \times 2.17 \times 10^4 \text{ nm}^2/\text{particles} \times$$

$$1.85 \text{ molecule/nm}^2 \times 2.2 \times 10^{-10} \text{ L}$$

$$N_{\text{SERS}} = 4.71 \times 10^8 \text{ molecules.}$$

$$EF = (116.5 \text{ mW}^{-1} \text{ s}^{-1} \times 4.11 \times 10^{13} \text{ molecules}) / (7.7 \text{ mW}^{-1} \text{ s}^{-1} \times 4.71 \times 10^8 \text{ molecules})$$

$$EF = 1.3 \times 10^6$$

Sample Calculation of the Enhancement Factor (EF) from Single Dimers. For single dimers, the EF is calculated using the same equation as above but using different acquisition parameters and microscope objectives.⁴ In this case N_{SERS} is calculated from a single nanorod dimer that is located using SEM correlation.

$$EF = (I_{\text{SERS}} \times N_{\text{normal}}) / (I_{\text{normal}} \times N_{\text{SERS}}),$$

$$EF = (49.8 \text{ mW}^{-1} \text{ s}^{-1} \times 1.95 \times 10^{12} \text{ molecules}) / (11.7 \text{ mW}^{-1} \text{ s}^{-1} \times 1.27 \times 10^4 \text{ molecules}),$$

$$EF = 6.6 \times 10^8$$

Samples for correlated SERS/SEM experiments were prepared by drop casting an ethanol suspension of the functionalized nanoparticles onto a substrate that had been patterned with registration marks *via* lithography or by simply scoring the substrate with a diamond pen. The substrate was briefly rinsed with ethanol to remove any dust that may interfere with locating the nanoparticles under a dark-field microscope. The nanoparticles were allowed to dry under ambient conditions and the locations of several nanoparticles (typically 20 to 50) were identified by their Rayleigh scattering and their positions noted for correlation with SEM. After the nanoparticles had been probed with SERS, the sample was immediately imaged by SEM to determine the sizes, shapes, and orientations of the nanoparticles.

FDTD Simulations:

FDTD simulations were completed with a commercially available software package from Lumerical Solutions, Inc. with a plane wave excitation at 785 nm. The geometry of each simulation was designed to match the actual geometry of each dimer as measured in TEM. A mesh size of 0.5 nm was chosen for each dimension. The resulting field plots are plotted on a log scale for clarity.

DDA Simulations:

DDA calculations were performed using the freely available DDSCAT V7.1 software.⁵ The incident wavevector was taken to be along the x-axis and polarization parallel to the long axis of the dimer (along the z-axis) was considered for fixed polarization calculations. For orientationally averaged enhancement calculations, the long axis of the dimer was rotated by 90

degrees (in incremental steps) around the x-axis with polarization along both the y- and z-axes considered. The average of the enhancements at each of these angles was used as the “solution- or ensemble-averaged enhancement.” The dielectric table of Johnson and Christy⁶ for Au was used and for the gold in water calculations the incident wavelength and the refractive index were divided by the refractive index of water (1.331) to get the relative refractive index. A dipole spacing of 1 nm and 0.5 nm was used for the 4 nm and 2 nm interparticle gaps, respectively.

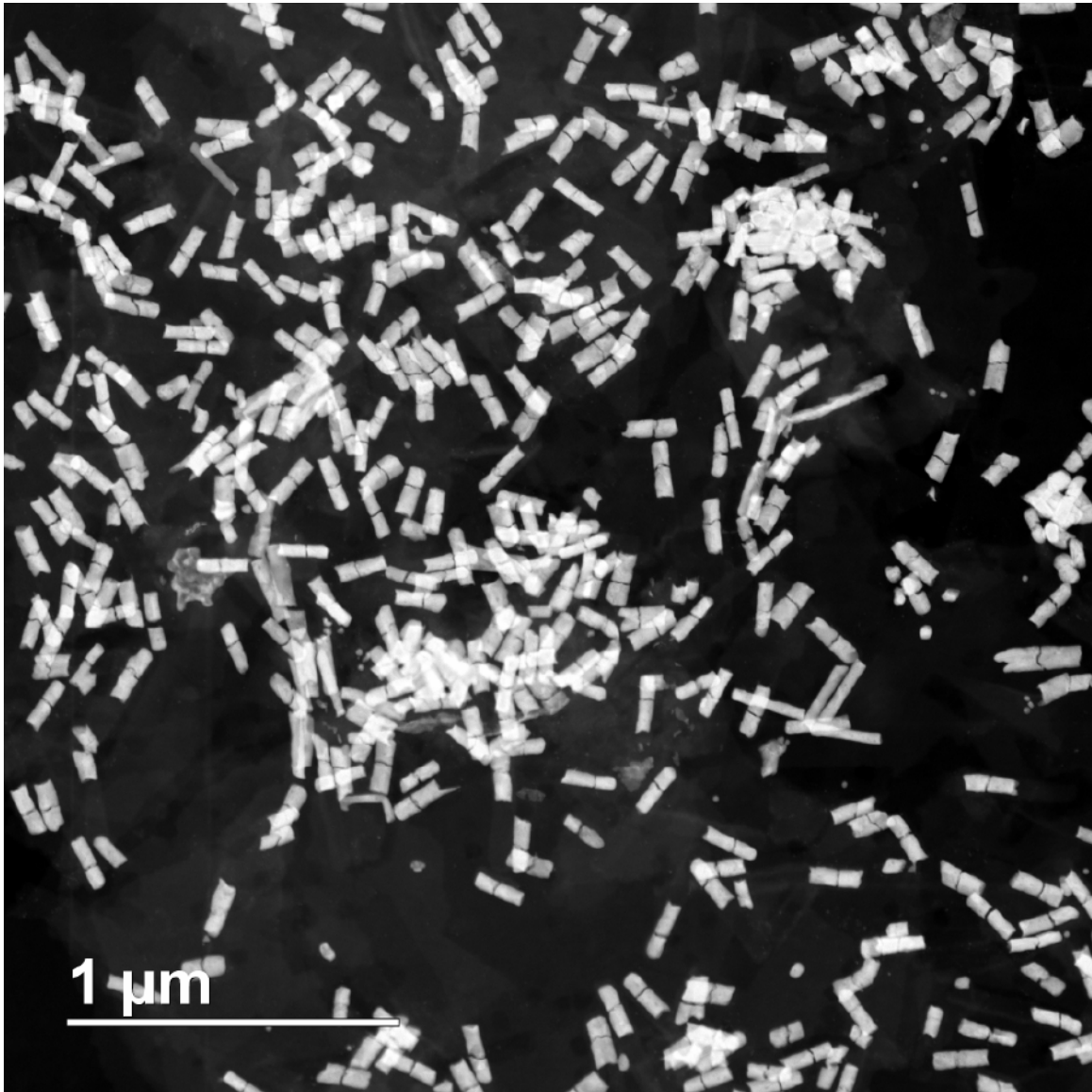


Figure S1. Large-area STEM image of a batch of nanorod dimers fabricated by OWL. The high yield (>96% dimers) and uniformity of the dimers in this sample is easily observable.

Discrete Dipole Approximation (DDA) calculations supporting 785 nm excitation choice

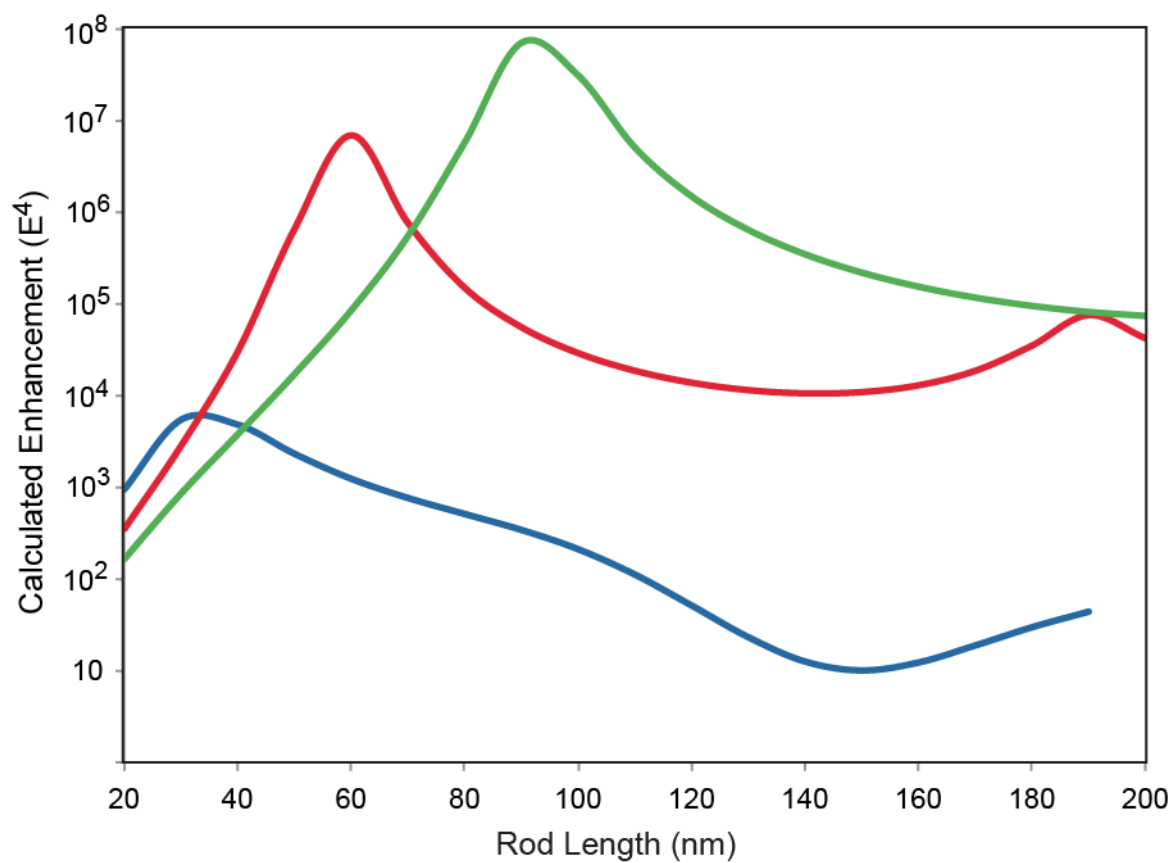


Figure S2. DDA-calculated enhancements (E^4) for gold nanorod dimers of varying rod length and constant gap size of 4 nm in vacuum. The green, red, and blue traces correspond to excitation wavelengths of 785, 633, and 532 nm, respectively.

Dimers used for single-particle SERS study in Figure 3

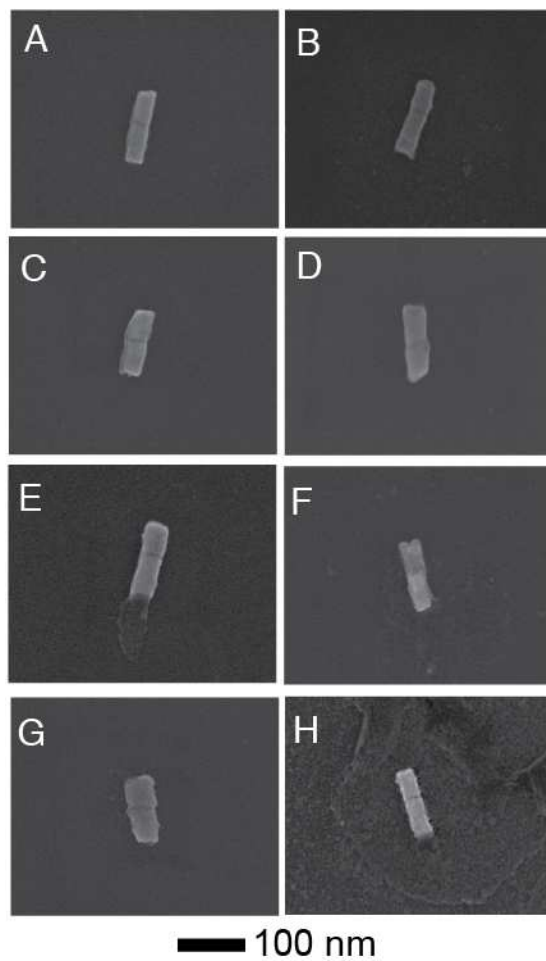


Figure S3. SEM images of the dimers used for the single-dimer SERS data shown in Figure 3. In Figure 3c, spectra for (A-H) are shown in order from top to bottom.

Polarization Dependence Study

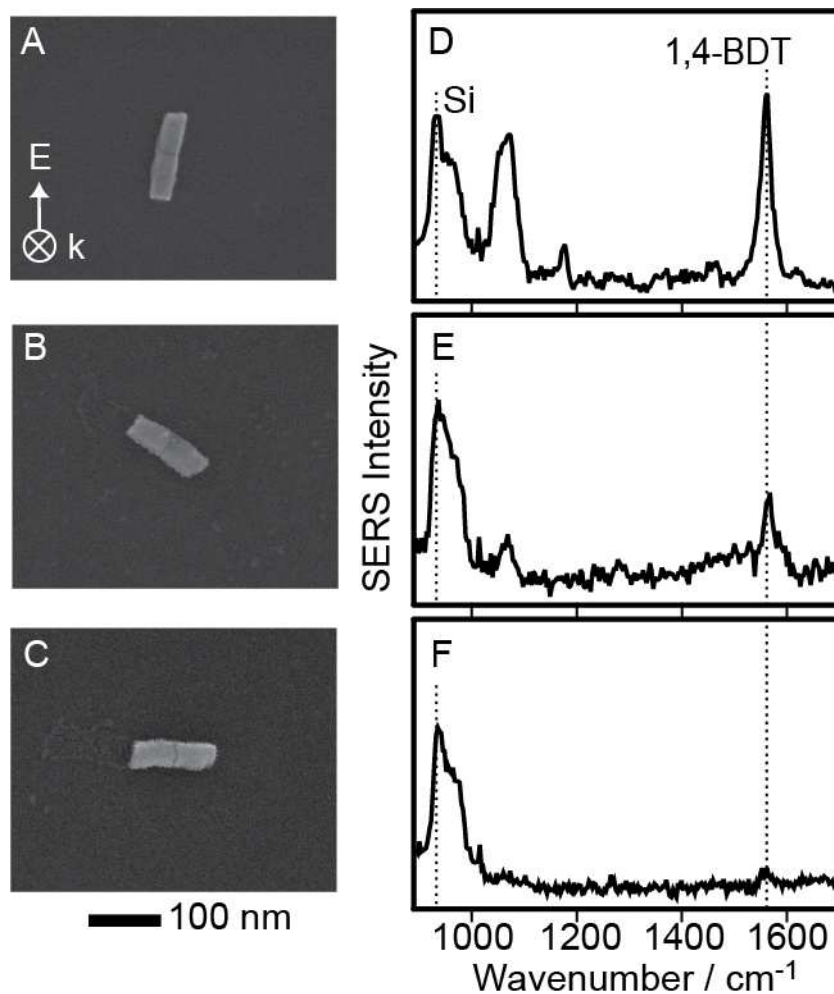


Figure S4. The polarization dependence of the SERS signal from the OWL dimers. (A-C) are SEM images of the dimers used in this study. The inset of (A) shows the direction of excitation light propagation (k) and polarization (E) for each dimer. (D-F) depicts the SERS spectrum collected from the corresponding dimers (A-C) at the same acquisition parameters and laser power (30 mW). The peak for 1,4-BDT clearly decreases as the dimer is rotated further from the ideality of the polarization along the long axis.

References

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