

Supporting Information

Tunable SERS In Gold Nanorod Dimers Through Strain Control On An Elastomeric Substrate

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1 Gold rod dimers fabricated from heterogeneous nanorods

Gold nanorod dimers were fabricated via a modified version of the on-wire lithography (OWL) technique first introduced by Qin et al. in 2006. Rather than using a SiO₂ backbone to retain spacing between individual segments, dimers are fabricated on an elastomer film which allows interparticle spacing to be changed through variation in strain applied to the substrate. The ability to vary this interparticle spacing allows the SERS enhancement factor for individual dimers to be actively and reversibly tuned.

Briefly, heterogeneous nanorods were electrodeposited inside anodic aluminum oxide (AAO) templates (Anodisc, Whatman, Inc.) with rated pore sizes of 200 nm. The templates are coated and sealed on one side via the thermal evaporation of Ag. A commercial potentiostat (PST050, Radiometer Analytical) is used to electrochemically deposit the nanowires into the template with a platinum counter electrode and a Ag/AgCl (sat KCl) reference electrode. The AAO template is placed into a homemade electrochemical cell attached to this setup. The cell is then filled with Ag plating solution (Silver 1025, Technic Inc.), and a thin sacrificial layer of metal is plated at -1000 mV into the pores of the AAO template in order to fill the branched portions of the channels. Upon completion, the electrolyte is removed and the cell is rinsed three times with distilled water to remove the remaining electrolyte solution. Next, the cell is filled with Au plating solution (Orotemp 24, Technic Inc.), and metallic Au is deposited potentiostatically at -1000 mV until an amount of charge corresponding to the desired segment length has passed through the cell. The Au plating solution is removed and the cell is rinsed three times with distilled water. This process repeated to form the opposing Au segment and the sacrificial Ag spacer layer that designates the interparticle gap.

Upon completion of the nanowire deposition, the Ag attached to the AAO is removed by submerging the AAO into a solution of hydrochloric (Fisher Scientific) in order to remove the thermally evaporated and electrochemically deposited Ag layers and is then rinsed in distilled water. The nanowires are released from their template by immersing the AAO in a 3 M solution of

NaOH (Fisher Scientific) for 1 hour until the AAO is completely dissolved, producing free nanowires. Particulate matter resulting from the dissolution of the AAO is removed by washing the nanowires three times in ethanol (Fisher Scientific) via centrifugation for 1 min at 10,000 rpm. To create dimers on the elastomer surface, nanorods are dropcast from solution directly onto the substrate and are blown dry with nitrogen. The substrate is then immersed in a solution of HCl for 10 minutes to remove the sacrificial spacer layer between the two segments.

2 Extinction spectrum simulations for gold nanorod dimers

In figure S1 we have calculated the extinction, scattering and absorption spectra for gold nanorod dimers of diameter 320 nm, comprised of segments 400, 600 and 800 nm in length and with gap sizes 9, 12, and 15 nm wide. Our results indicate that the scattering from these large nanoparticles presents a broad, almost featureless spectrum due to the excitation of higher order modes. The computer model also allows us to compare the scattering magnitude with that of the absorption. Here, our results suggest that the enhancement factor is exclusively dependent on the absorption part of the nanorod extinction spectrum, rather than the scattering which is the bulk contributor to the nanorod extinction.

3 Use of the “ $|E|^4$ ” approximation

The approximation of $|E_{pump}|^2|E_{Stokes}|^2 \approx |E_{pump}|^4$ is an approximation that can be used if the wavelength of the Raman enhanced light is sufficiently close to that of the laser. From Fig, S1, we obtained FWHM of the absorption peaks in a range of approximately 50-75 nm. The resonance of our rough-ended rods is likely to be somewhat broader. The 1080 cm⁻¹ Raman line that we tracked closely in this study lies within the range of the laser wavelength, which gives us confidence that they both lie under the umbrella of the absorption peak. Consequently, although imperfect, the use of E_{pump}^4

to simulate the enhancement appears to be a reasonable approximation in this case.

4 Correlation between macro- and microscopic strain

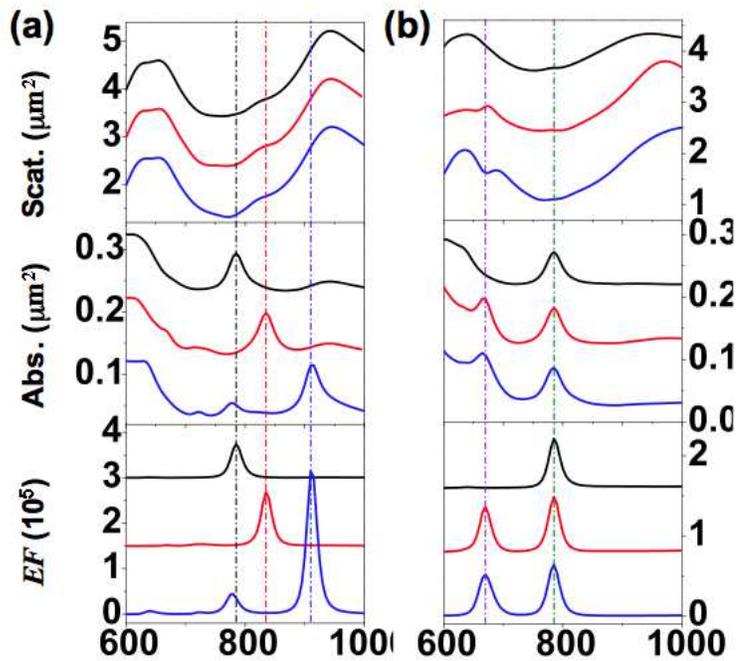
We performed strain measurements on 1 μm diameter polystyrene beads to test the validity of the strain-scaling technique used in these experiments. Specifically, we aimed to check if the $Strain = \frac{\Delta L}{L}$ relation breaks down for any reason (e.g. substrate failure, particle delamination, etc.) above the length scale relevant for our dimer stretching experiments. The polystyrene beads were applied to the substrate which was subsequently imaged in dark field (scattering) mode with a 150 \times objective. Bead pairs that were located along the same line of strain were identified and imaged with a high resolution camera as the applied strain was varied. Images of the displaced bead pairs were processed in ImageJ to measure the change in distance resulting from each level of applied strain. These measurements we repeated three times and the results were averaged. This experimentally measured “microscopic” strain was plotted against the strain extrapolated from the measured change in length of the substrate as measured by a micrometer (figure S2). Our results yielded a nearly 1:1 correlation, suggesting that the relation remains valid in the vicinity of the length scale of interest.

5 Additional SERS experimental results and comparison with simulations

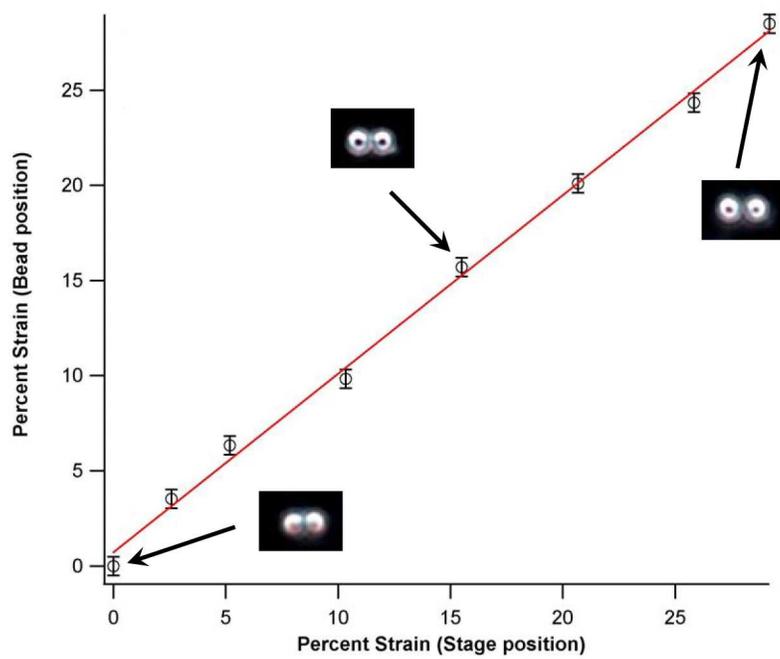
In figure S3 we present additional examples of gap size vs EF measurements taken from other nanorod pairs in this study. All calculated data was taken from Fig. 4 in the main text. Of particular interest here is the SERS enhancement peak in figure S3a which is noticeably different from the simulated results. As we have already shown in our simulations, the location of the maximum SERS enhancement is sensitive to nanorod diameter (Fig.1a in main text) and it possible that a difference in size could have contributed

to this discrepancy. However, there are other features of the geometry of the nanorods used in this experiment that are not accounted for (gap roughness, for instance), so further investigation would be necessary to provide confirmation of this.

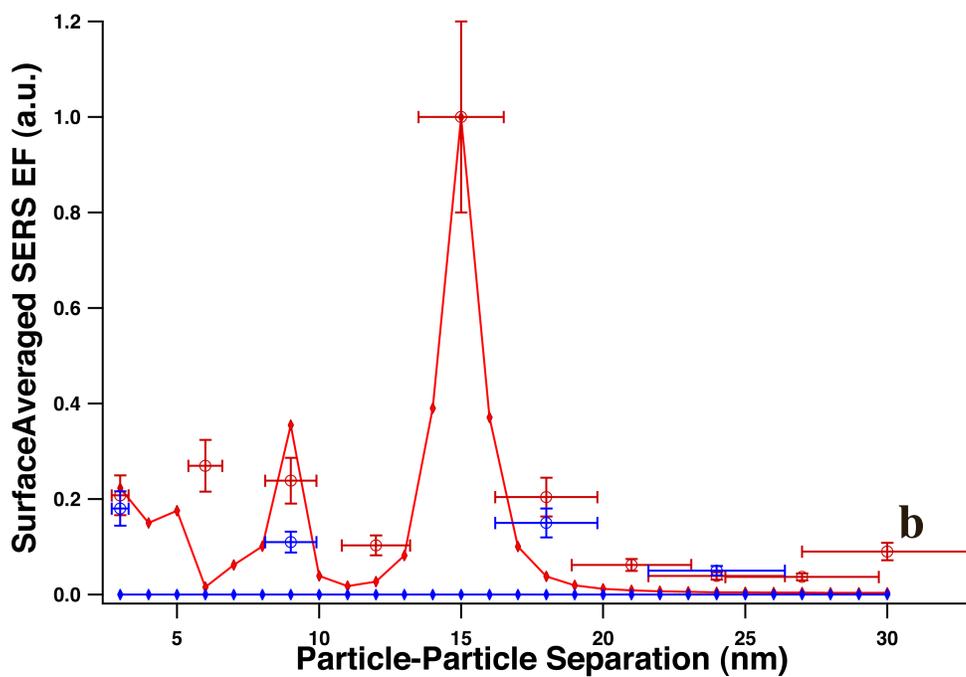
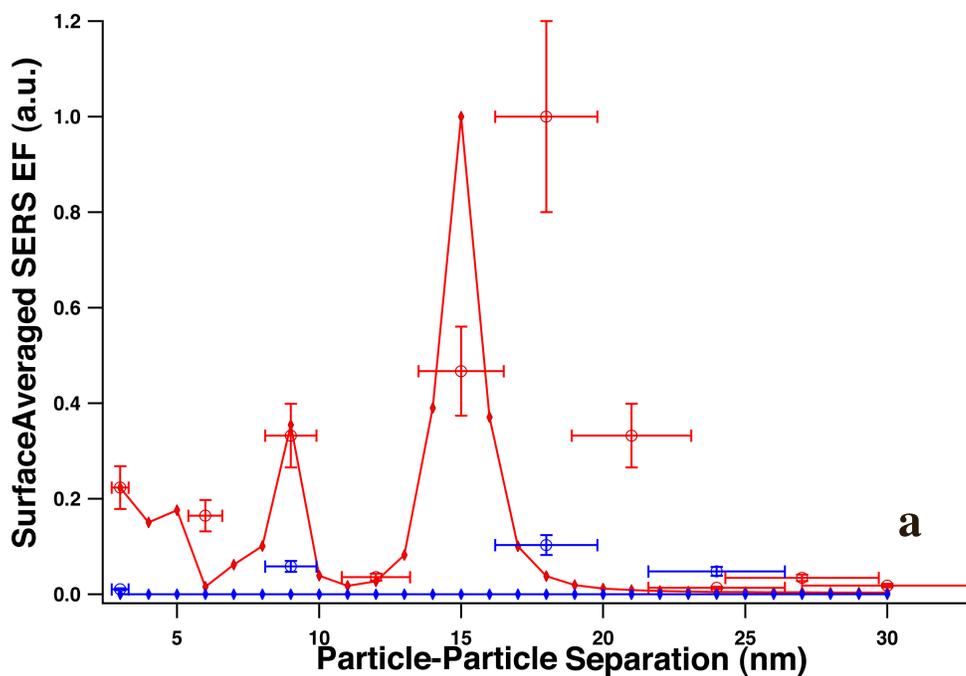
Finally, figure S4 shows EF measurements where very large gap sizes have been taken into account. This figure illustrates that when the two nanorods are separated by a distance greater than 30 nm, the magnitude of the EF drops to and remains at approximately zero. This finding agrees well with electromagnetic theory which suggests that the largest SERS enhancements for a nanoparticle dimer system like the one presented here occurs when the two nanoparticles are close enough to couple through near-field interactions.



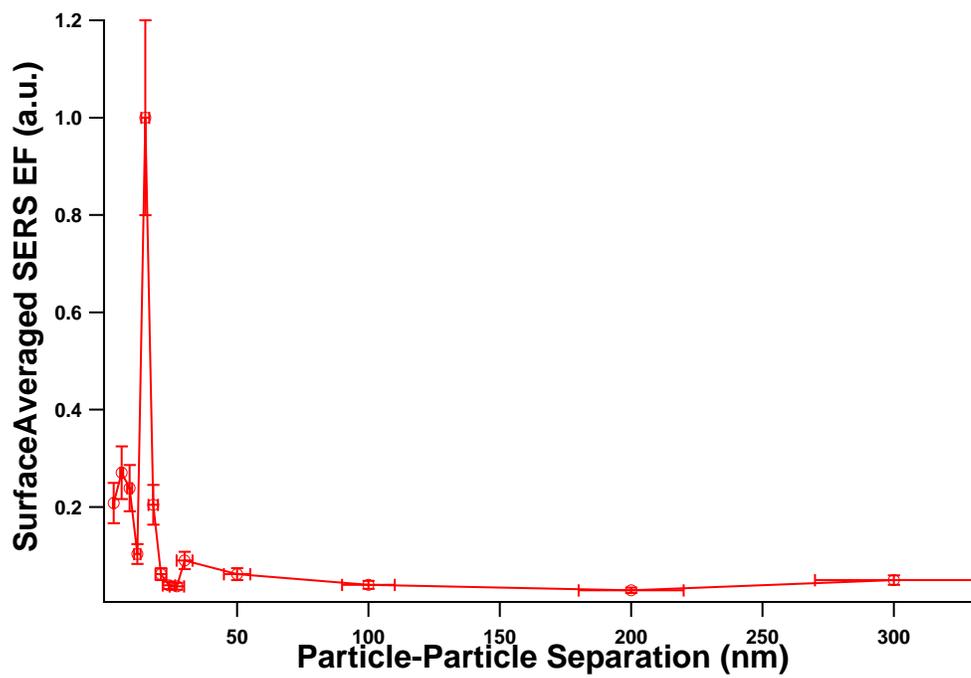
S 1. Scattering (top), absorption (middle) and Raman enhancement factor EF (bottom) for Au rod dimers, (a) for different gap distances: 15 nm (black), 12 nm (red) and 9 nm (blue) and, (b) for different segment length: 400 nm (black), 600 nm (red) and 800 nm (blue). The Raman enhancement peaks always correspond to the absorption peaks, but not necessarily the scattering peak. The segment length $L = 1 \mu\text{m}$ in (a) were unchanged, and the gap in (b) were kept at 15 nm. Diameters of rods were 320 nm in both (a) and (b).



S 2. The trace in this figure depicts the correlation between the macroscopic strain applied to the elastomer substrate (measured with a micrometer) and the microscopic strain measured between polystyrene beads (deduced through digital image analysis). Error bars were calculated from standard error.



S 3. Figures (a) and (b) show experimental data (red and blue circles denoting measurements made parallel and perpendicular to the dimer axis, respectively) taken from two dimer pairs with segments approximately 320 nm in diameter, plotted against the results from FEM simulations (red and blue traces denoting results from parallel and perpendicularly polarized illumination, respectively). Error bars were calculated from the dispersion of the data observed during measurements.



S 4. Experimental measurements of the surface averaged SERS EF (normalized) plotted against interparticle separation with additional measurements of the EF taken at separations ranging from 30-300 nm to demonstrate that the value remains stable around zero for separations larger than approximately 30 nm.