

Supplementary Information for “Plasmonic Nanoparticle Arrays with Nanometer Separation for High-Performance SERS Substrates”

Jesse Theiss^a, Prathamesh Pavaskar^a, Pierre M. Echternach^b, Richard E. Muller^b, and Stephen B. Cronin^a

^a *Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089, USA*

^b *California Institute of Technology, Jet Propulsion Laboratory, Pasadena, CA 91109 USA*

Experimental SERS Enhancement Factor Calculation:

Evidence suggests that the SERS enhancement of the 1436cm^{-1} vibrational mode of metal-bonded p-ATP molecule is significantly enhanced due to a charge transfer mechanism in addition to the electromagnetic enhancement for incident radiation at 532nm and 632.8nm^{1-3} . This intense peak is only observed in surface-bonded molecules, which further complicates the comparison of SERS spectra with those of bulk reference samples of p-ATP. The 1077 and 1590cm^{-1} Raman peaks are believed to be primarily EM-enhanced³ and are measurable in unbonded p-ATP, making them well-suited for accurately determining the EF. The EF is defined as:

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

where I_{SERS} is the intensity of the Raman mode taken on the SERS-active substrates and I_{bulk} is the spectral intensity of the same Raman mode for the “crystalline” p-ATP solid. I_{SERS} and I_{bulk} are easily obtained from experiment and normalized for acquisition time and laser power, with an additional factor to account for the decrease in laser power density ($\sim 1/10$) when using an elliptical beam spot. N_{bulk} is the number of molecules within the laser-illuminated volume of p-

ATP solid. Here, this active volume is a cone defined by a focused circular laser spot $0.5\mu\text{m}$ in diameter at the surface, with an estimated penetration depth of $8\mu\text{m}$. Using the density of solid p-ATP (1.18 g/cm^3), N_{bulk} is calculated to be about 2.97×10^9 molecules. We estimate the number of dye molecules bonded to the silver surface in the hot spot area by assuming a coverage of 2nm around the hot spot on each nanoparticle. Multiplying by the respective evaporation thicknesses (15nm and 30nm) yields an overall sidewall coverage area in the nanogap region of about 90nm^2 . The dye is estimated to cover the gold surfaces with a density of approximately $0.25\text{ nm}^2/\text{molecule}^{4-7}$, which yields approximately 360 molecules per nanoparticle pair. The diffraction limited 632.8nm laser spot was passed through a cylindrical lens producing a slightly larger effective sampling area such that approximately 10 nanoparticle pairs contribute to each spectrum measured. We thus take N_{SERS} to be about 3600 molecules. Taking I_{SERS} and I_{bulk} measured to be 1890 and 55800 respectively and adding compensation factors for the reduced laser power density due to the cylindrical lens ($1/10$) and CCD collection method ($1/4$), we estimate a SERS enhancement factor of 1.1×10^6 .

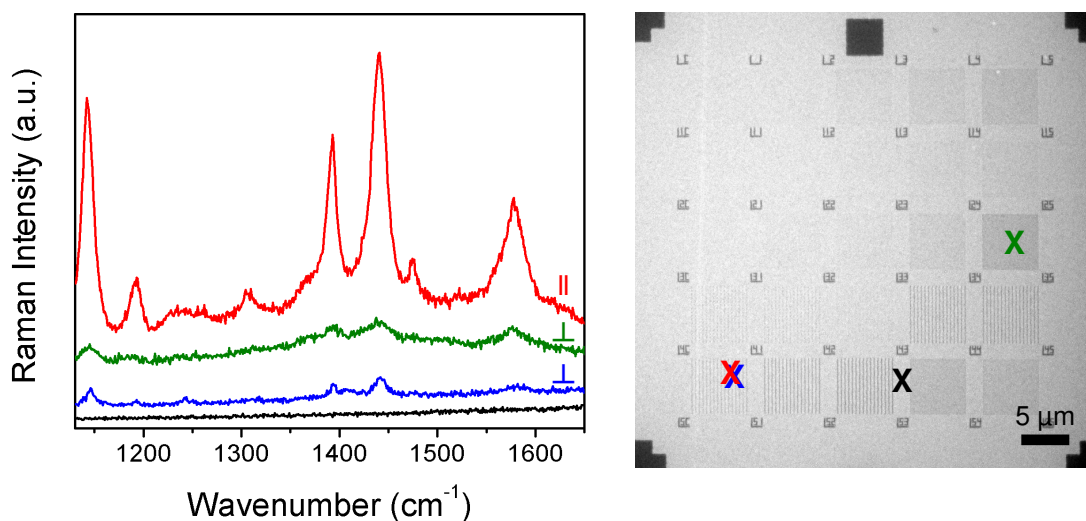


Figure S1. Raman spectra of p-ATP molecules bonded to Ag nanoparticle arrays deposited by angle-evaporation taken at several points corresponding to the TEM shown in the right. The spectrum in red was taken at the location indicated by the red “X” with incident light polarized along the axis of the nanoparticle pairs. The blue spectrum corresponds to the same location taken with light polarized perpendicular to the nanoparticle dimer axis. The black spectrum and the green spectrum correspond to spectra taken at the black and green X’s, respectively.

Figure S1 shows the Raman spectra taken at several different locations on the 5x5 nanoparticle grid array, shown in the TEM image on the right. An increase in Raman intensity is clearly visible for the spectrum taken with light polarized along the axis of the nanoparticle pairs, whereas the intensity is much lower in cells with polarization aligned perpendicular to the nanoparticle pairs.

Gap Size Statistics:

A histogram of the gap size statistics is given below. A Gaussian fit to this data gives a mean and standard deviation of $2.0 \pm 0.9\text{nm}$.

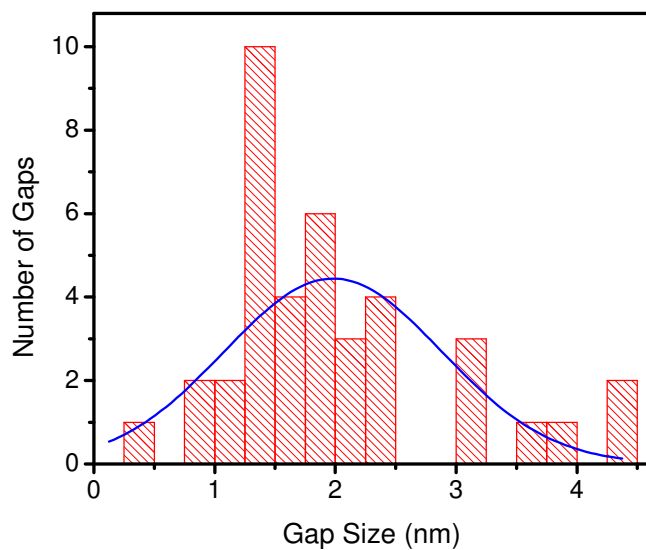


Figure S2. Histogram of gap sizes, as measured by transmission electron microscopy.

REFERENCES

1. Osawa, M.; Matsuda, N.; Yoshii, K.; Uchida, I. *Journal of Physical Chemistry* **1994**, *98*, (48), 12702-12707.
2. Jiang, J.; Bosnick, K.; Maillard, M.; Brus, L. *Journal of Physical Chemistry B* **2003**, *107*, (37), 9964-9972.
3. Baia, M.; Toderas, F.; Baia, L.; Popp, J.; Astilean, S. *Chemical Physics Letters* **2006**, *422*, (1-3), 127-132.
4. Mohri, N.; Matsushita, S.; Inoue, M.; Yoshikawa, K. *Langmuir* **1998**, *14*, (9), 2343-2347.
5. Gole, A.; Sainkar, S. R.; Sastry, M. *Chemistry of Materials* **2000**, *12*, (5), 1234-1239.
6. Su, K. H.; Durant, S.; Steele, J. M.; Xiong, Y.; Sun, C.; Zhang, X. *Journal of Physical Chemistry B* **2006**, *110*, (9), 3964-3968.
7. Yan, B.; Thubagere, A.; Premasiri, W. R.; Ziegler, L. D.; Dal Negro, L.; Reinhard, B. M. *ACS Nano* **2009**, *3*, (5), 1190-1202.