

Supplementary Information

Asymmetric Seed Passivation for Regioselective Overgrowth and Formation of Plasmonic Nanobowls

Zachary J. Woessner,^a George R. Lewis,^b Sandra L. A. Bueno,^a Emilie Ringe,^{b,c*} and Sara E. Skrabalak^{a*}

^a Department of Chemistry, Indiana University – Bloomington, 800 E. Kirkwood Ave., Bloomington, IN 47405, USA.

^b Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, United Kingdom, CB3 0FS.

^c Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, United Kingdom, CB2 3EQ.

*Corresponding authors: er407@cam.ac.uk and sskrabal@indiana.edu

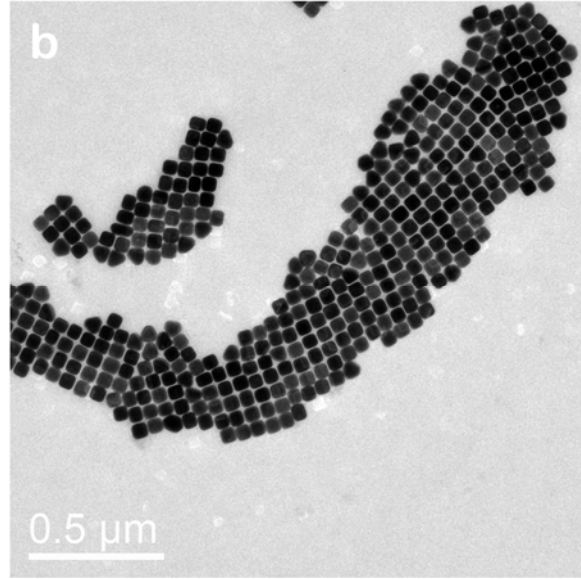
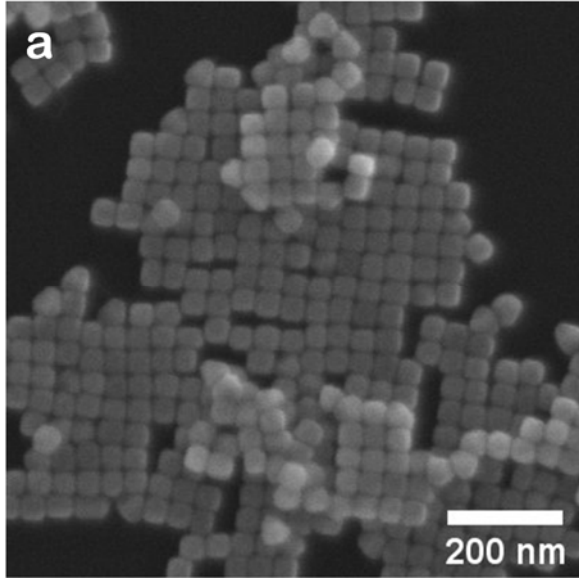


Figure S1. (a) SEM and (b) TEM images of cubic Au NPs used in the synthesis of cubic Au NPs asymmetrically passivated with PSPAA.

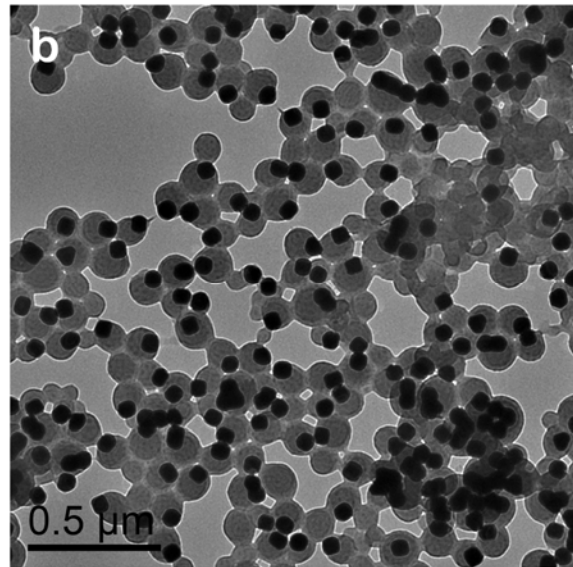
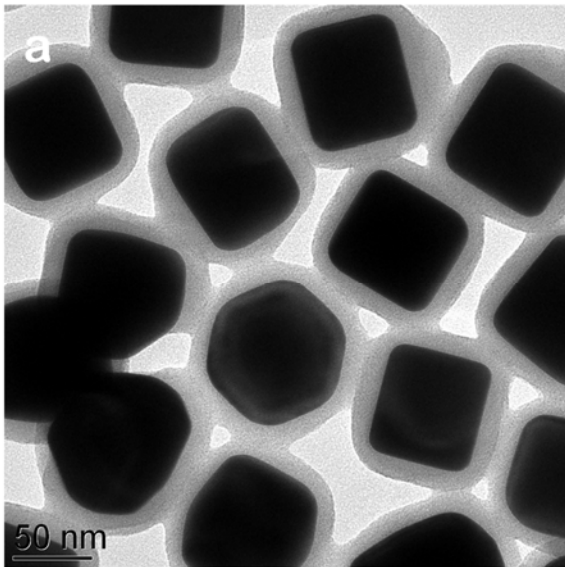


Figure S2. TEM images of cubic Au NPs coated with PSPAA (a) without and (b) with CTAB present during the coating step.

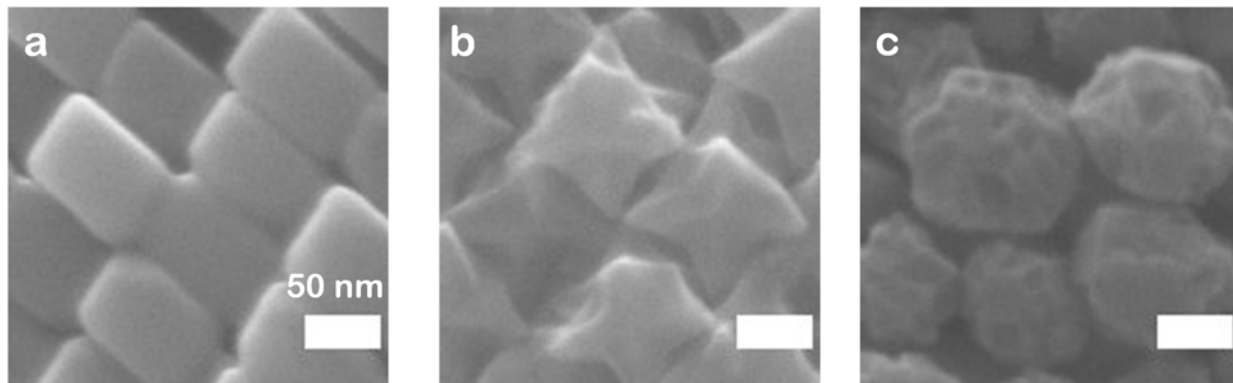


Figure S3. SEM images of NPs obtained through the reduction of (a) HAuCl₄, (b) HAuCl₄ and H₂PdCl₄, and (c) HAuCl₄ and AgNO₃ onto similar concentration of cubic Au seeds without a PSPAA shell.

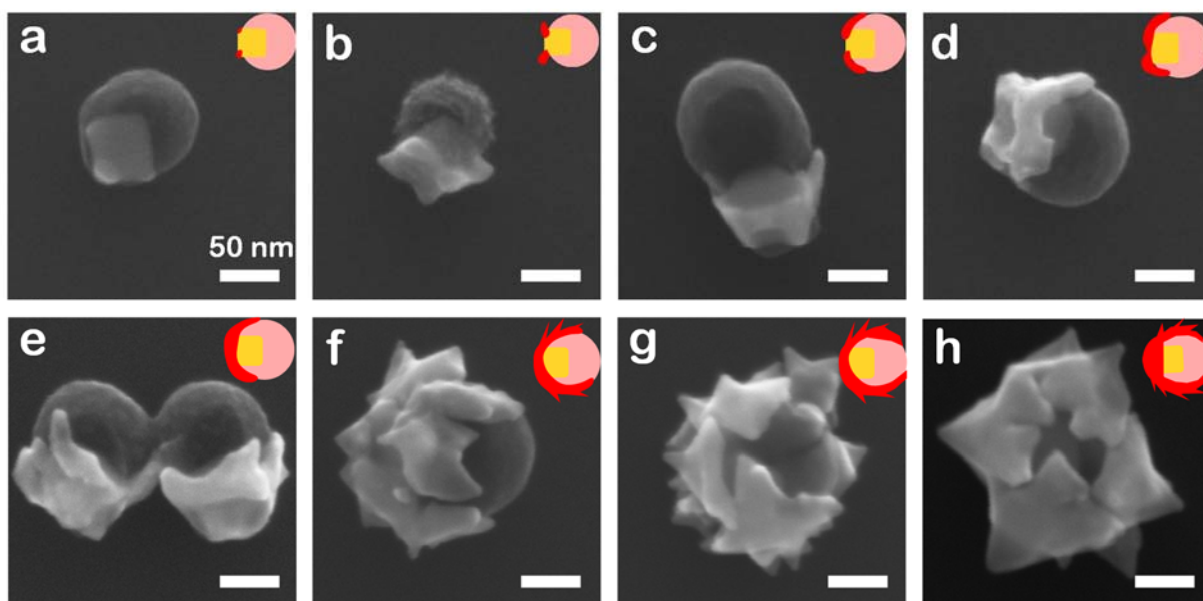


Figure S4. Representative SEM images of products obtained from AuPd overgrowth from asymmetrically passivated Au nanocubes, with different amounts of Au and Pd precursors added in a 10:1 ratio Au:Pd with (a) 1%, (b) 2.5%, (c) 5%, (d) 7.5%, (e) 10%, (f) 25%, (g) 50%, and (h) 100% of the highest precursor concentration added. PSPAA has not been removed. Scale bars 50 nm throughout.

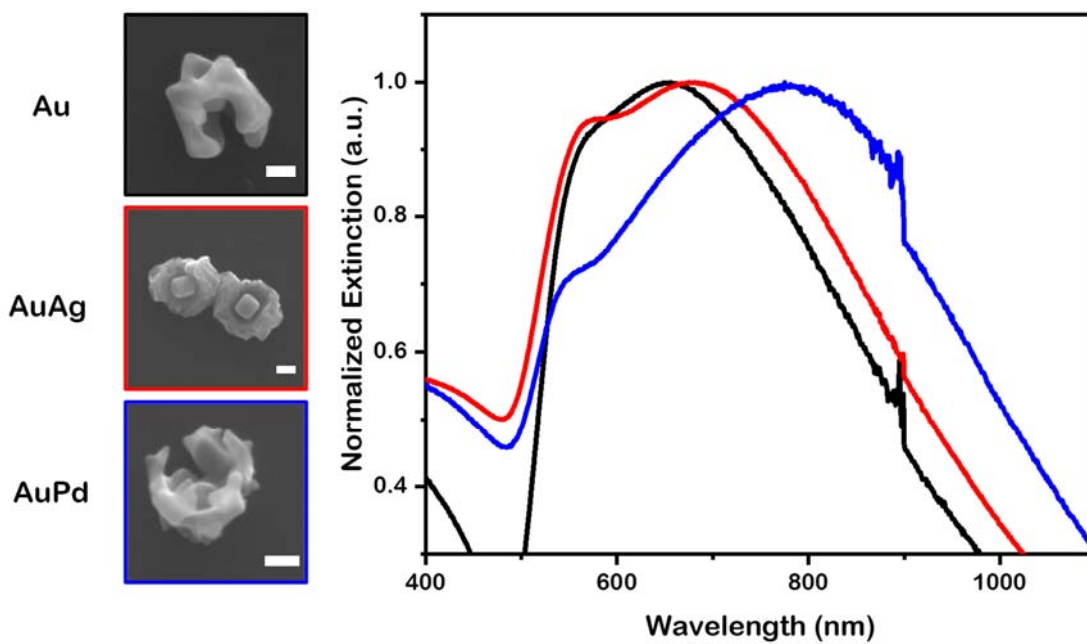


Figure S5. (left) SEM image depicting NP morphology where color outline maps onto (right) LSPR of (black trace) Au nanobowls, (blue trace) Au-Pd nanobowls, and (red trace) Au-Ag nanobowls dispersed in water. Data intensity change at 900 nm is an artefact of lamp changeover wavelength. LSPR normalized to wavelength maximum. Scale bars 50 nm throughout.

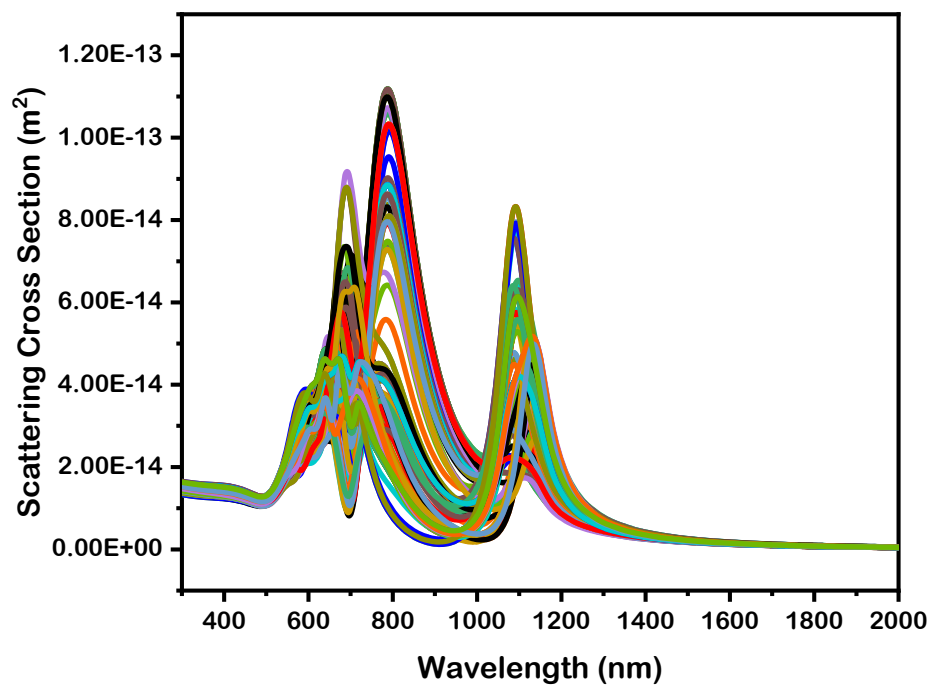


Figure S6. Far-field scattering cross section of the nanobowl from Figure 5 at each orientation simulated.

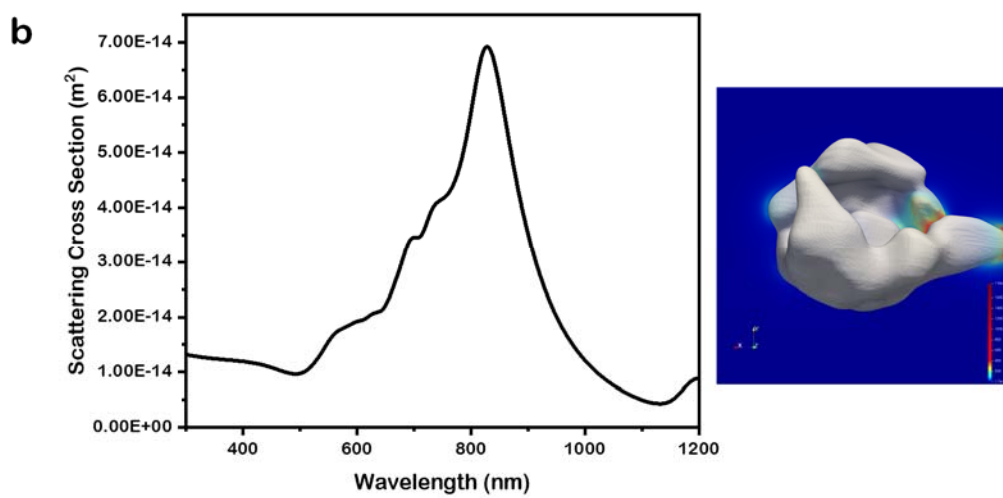
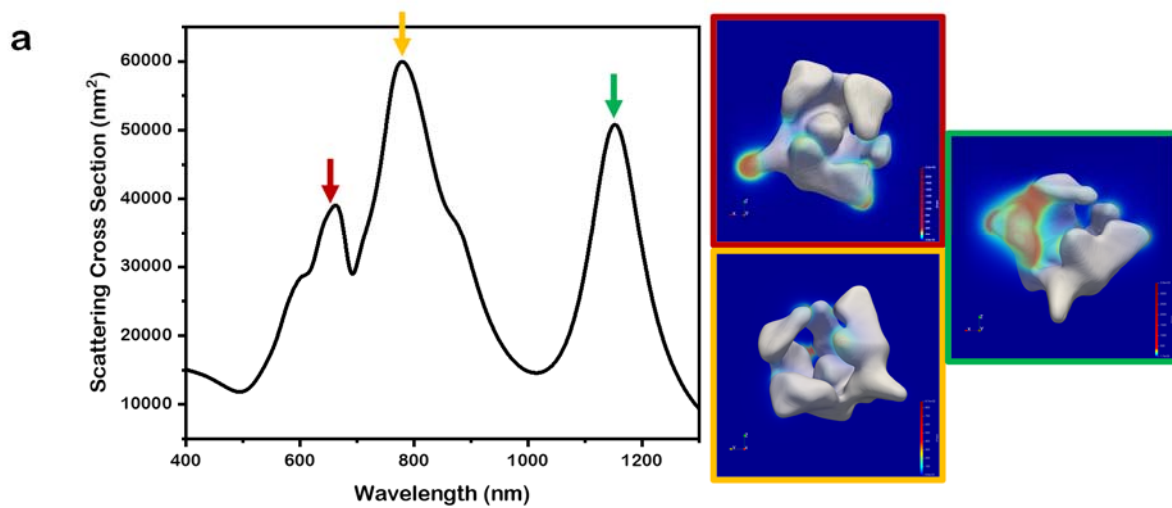


Figure S7. Far-field scattering and near-field enhancement for two different Au nanobowl tomography models.

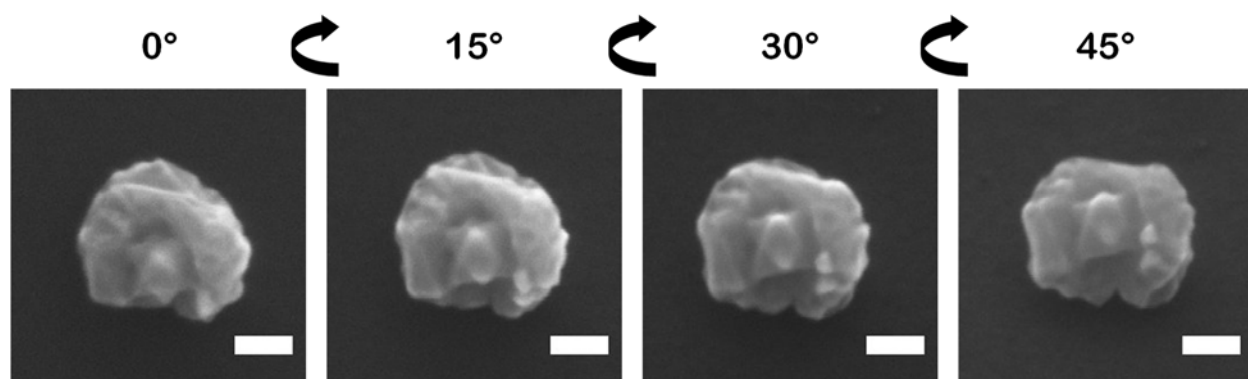


Figure S8. SEM tilt series of ruffled Au-Ag nanobowls grown from ocotopodal Au-Pd NPs asymmetrically passivated with PSPAA. Scale bars 50 nm throughout. Angle indicates angle of SEM stage used during image acquisition.

Saturation Conditions for SERS Raman Markers.

By titrating equal volumes 2-NSH with different concentrations into the same volume of nanobowls (concentration kept constant between experiments), saturation conditions were found for the exterior of the nanobowl (through titration with PSPAA coating the interior) and for the entire nanobowl (through titration with PSPAA removed). Saturation conditions were considered at the concentration when Raman intensity at 1377 cm^{-1} remained constant with increasing 2-NSH concentration added. Exterior thiol saturation was achieved with addition of 2 nmol 2-NSH (titration of 25 μL of 80 μM 2-NSH, Figure S9). The entire nanobowl was saturated with addition of 2.75 nmol 2-NSH (titration of 25 μL of 110 μM 2-NSH, Figure S9). By difference (entire saturation – exterior saturation), the interior of the nanobowls would be saturated with 0.75 nmol thiol. EFs then were normalized by the number of molecules saturating the system. Thiol in subsequent systems were added in excess for each condition ($[\text{thiol}] = 10\text{ mM}$) to ensure saturation. After functionalization, samples were washed in triplicate to remove excess thiol.

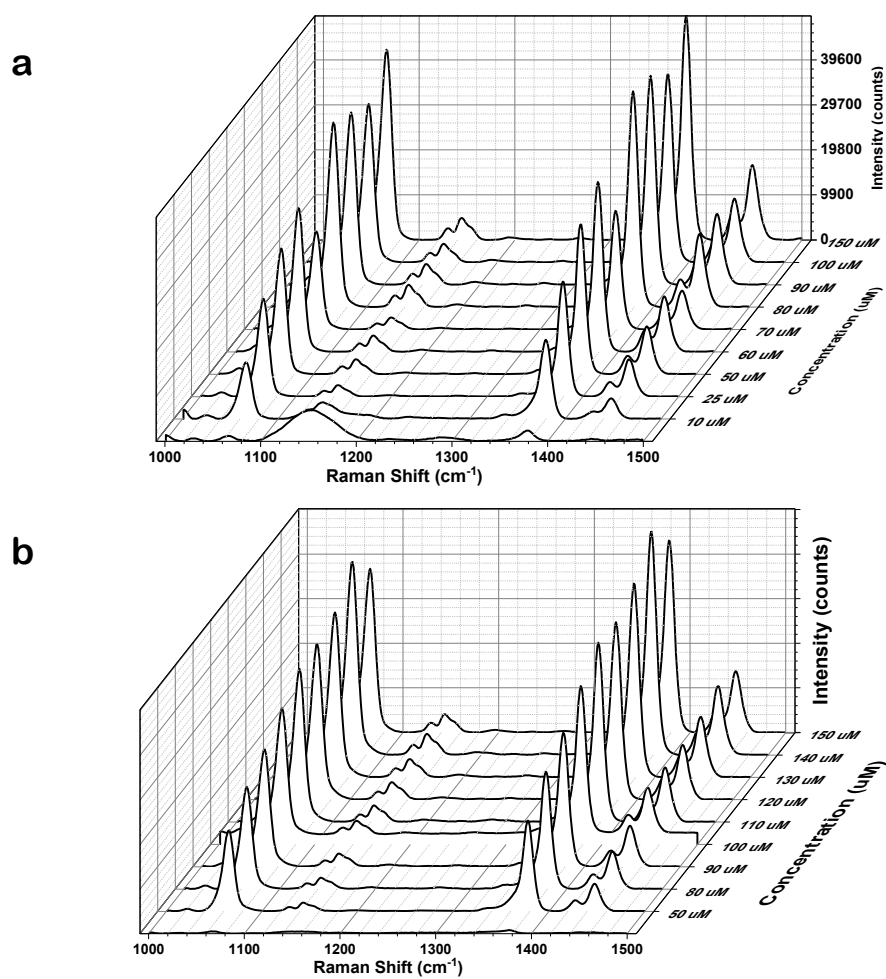


Figure S9. Surface enhanced Raman scattering profiles for Au@Au nanobowls (a) with PSPAA and (b) without PSPAA present. Changeover point occurred after 80 μM 2-NSH was added for (a) and after 110 μM 2-NSH was added for (b). Changeover point indicates saturation conditions for the molecules on the surface.

SERS EF Calculation.

The SERS E.F. was calculated using the following equation:

$$E.F. = \left(\frac{I_{sers}}{I_{bulk}} \right) \times \left(\frac{N_{bulk}}{N_{sers}} \right)$$

where I_{sers} and I_{bulk} are the Raman intensities of either 2-naphthalenethiol (2-NSH) or 4-mercaptobenzonitrile (4-MBN) adsorbed on the sample. N_{bulk} is the number of Raman marker (either 2-NSH or 4-MBN) in the volume of the normal Raman signals, and N_{sers} is the number of Raman marker (either 2-NSH or 4-MBN) adsorbed on the plasmonic nanobowls for SERS signal. For 2-NSH, the ring breathing mode at $\sim 1175 \text{ cm}^{-1}$ was chosen to calculate the E.F., and for 4-MBN, the nitrile stretch at $\sim 2225 \text{ cm}^{-1}$ was chosen to calculate the E.F. N_{bulk} was calculated using the following equation:

$$N_{bulk} = \frac{V \times D}{M_w} \times N_A = \frac{\pi \times r^2 \times h \times D}{M_w} \times N_A$$

Where V is the effective excitation volume, D is the density of the Raman marker (1.55 g/cm^3 for 2-NSH and 1.18 g/cm^3 for 4-MBN), M_w is the molecular weight of the Raman marker (160.24 g/mol for 2-NSH and 135.19 g/mol for 4-MBN), and N_A is Avogadro's number, r is the radius of the laser beam ($\sim 1 \mu\text{m}$), and h is the focal depth of the laser ($\sim 4 \mu\text{m}$). N_{sers} was calculated using the following equation:

$$N_{sers} = A \times D \times N_A$$

Where A is the approximate surface area of the SERS substrate (calculated to be $\sim 9.54 \times 10^{-8} \text{ cm}^2$ through averaging surface area calculations of 3 reconstructions), D is estimated coverage of a single monolayer of coated marker ($7.8 \times 10^{-10} \text{ mol/cm}^2$ for 2-NSH and $4.5 \times 10^{-10} \text{ mol/cm}^2$ for 4-MBN), and N_A is Avogadro's number.