Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Supporting information

# Enhancing Gold Nanoparticle Immobilization on Thiolated Silica: Utilizing Neutral Ligands to Achieve Maximum Surface Coverage for Improved SERS Substrates

*Orisson P. Gomes[1,2], Sanggon Kim[1,5,]* Paulo N. Lisboa-Filho[3], Augusto Batagin-Neto[4], Yves De Koninck[1,5], Younes Messaddeq[1,]**

*1 Center for Optics, Photonics and Lasers (COPL), Department of Physics, Université Laval, Québec, QC G1V 0A6, Canada*

*2 São Paulo State University (UNESP), School of Sciences, POSMAT, Bauru/SP 17033-360, Brazil*

*3 São Paulo State University (UNESP), School of Sciences, Department of Physics, Bauru/SP 17033-360, Brazil*

*4 São Paulo State University (UNESP), Campus of Itapeva, Itapeva/SP 18409-010, Brazil*

*5 CERVO Brain Research Centre, Quebec Mental Health Institute, Department of Psychiatry and Neuroscience, Université Laval, Québec, QC G1E 1T2, Canada*

**SERS enhancement factor (EF) calculation**

The total number of 4-MBA molecules present in a bulk 4-MBA was determined using the following equation.[1,2]:

$$N_{bulk} = \frac{\rho V N_a}{M}$$

where $\rho$ represents the molecular density of 4-MBA (1.489 g/cm$^3$), $V$ is the laser-excited volume within the bulk material, $N_a$ is Avogadro's constant (6.02 $\times 10^{23}$ molecules/mol), and M is the molecular weight of 4-MBA (154 g/mol). The laser-excited volume $V$ is calculated as $V = A_{Laser} z$, with z being the depth of the field for the Raman spectrometer and $A_{Laser}$ being the laser-irradiated area. For a 633 nm laser used with a 50x objective lens (0.5NA), $A_{Laser}$ was found to be 2.72 μm² (beam radius: 0.93 μm, as shown in **Figure S1a**).

To establish the depth of the field (DOF, $z$), we utilized a single-crystal silicon wafer to map the depth profile of our Raman spectrometer. The silicon wafer was moved vertically in 2 μm increments, and the Raman spectra were recorded, as depicted in **Figure S2a**. **Figure S2b** displays the Raman spectra of the Si wafer as a function of the distance from the focal plane to the Si substrate surface. The intensity profile of the peak at 520.6 cm$^{-1}$, shown in **Figure S1b**, delineates the DOF as 49.4 μm. Given that the Raman scattering for bulk 4-MBA was measured at the focal plane on the 4-MBA bulk surface, we utilized half of the DOF value for $z$ in our calculations.

The total number of 4-MBA molecules forming a monolayer on AuNPs was calculated using the equation:

$$N_{SERS} = A_{AuNP} N_{AuNP} \sigma$$

where $\sigma$ indicates the surface density of the 4-MBA on the AuNP surface, estimated at 5.263 nm$^{-2}$.[3] $A_{AuNP}$ is the surface area of a single AuNP (0.013 μm²) and $N_{AuNP}$ is the count of the AuNPs within the area illuminated by the laser. The number of AuNPs, $N_{AuNP}$, which is 438, was calculated as:

$$N_{AuNP} = A_{Laser} / A_{C-AuNP} \xi.$$

In this equation, $A_{C-AuNP}$ stands for the cross-sectional area of a single AuNP and $\xi$ represents the surface coverage rate (0.533).

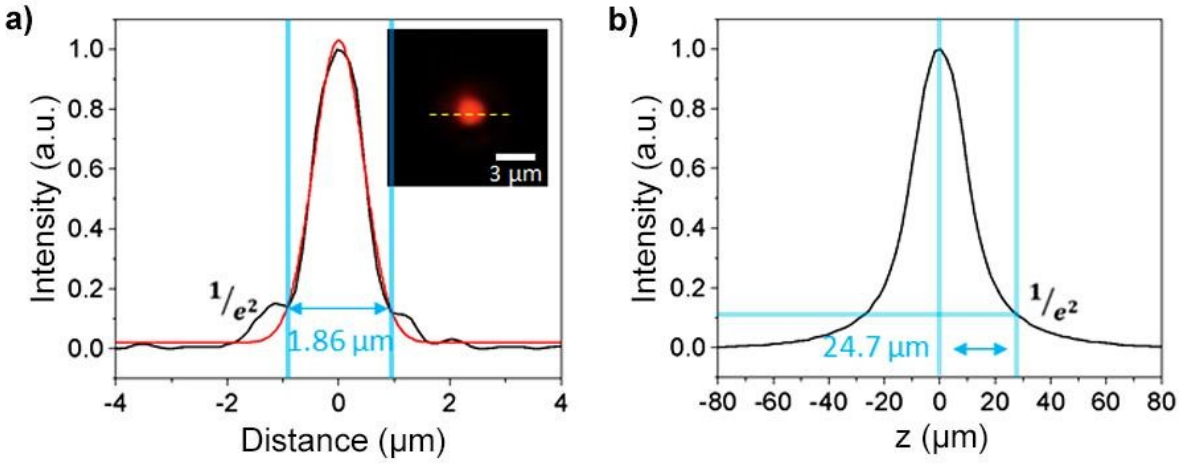


**Figure S1.** Laser beam (633 nm) profile and Raman intensity-depth profile based on the integrated intensity of the 520.6 $cm^{-1}$ band for a silica wafer.

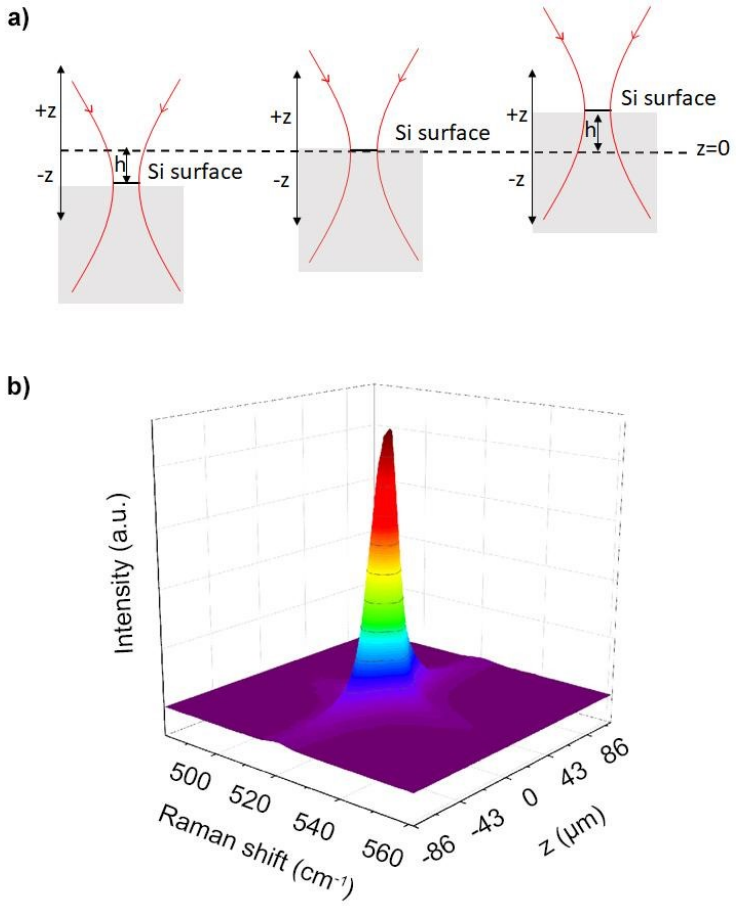


**Figure S2.** Schematic illustrating how a specific plane of illuminated bulk material (Si wafer) contributes to $I_{bulk}$, demonstrating the method for determining the depth dependency of the Raman signal.

## References


1 W. B. Cai, B. Ren, X. Q. Li, C. X. She, F. M. Liu, X. W. Cai and Z. Q. Tian, *Surf. Sci.*, 1998, **406**, 9–22.

2 A. B. Serrano-Montes, D. Jimenez de Aberasturi, J. Langer, J. J. Giner-Casares, L. Scarabelli, A. Herrero and L. M. Liz-Marzán, *Langmuir*, 2015, **31**, 9205–9213.

3 E. M. Perassi, C. Hrelescu, A. Wisnet, M. Döblinger, C. Scheu, F. Jäckel, E. A. Coronado and J. Feldmann, *ACS Nano*, 2014, **8**, 4395–4402.