Supporting information:

Gradient Metal Nanoislands as Unified Surface Enhanced Raman Scattering and Surface Enhanced Infrared Absorption Platform for Analytics

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Estimation of Surface Enhanced Raman Scattering Enhancement Factor (SERS EF)

Nanostructured electrodes are extensively used for electrochemical and spectroelectrochemical studies with moderate SERS properties. In order to compare the efficiency of our substrate with that of a typical SER substrate, we have prepared a roughened silver electrode and measured the spectra of adsorbed MBN.

The calculations of the enhancement factor are done according to Ly et al [1]. The Raman Enhancement Factor (REF) is determined by Equation S-1,

$$REF = \frac{I_{SERS}}{I_R}\frac{N_R}{N_{SERS}} = \frac{I_{SERS}}{I_R}\frac{c_R V}{\Gamma_{SERS} A} \qquad \text{Equation S-1}$$

where I_R and I_{SERS} are the Raman intensities of probe molecules in solution and absorbed on the Ag surface respectively. N_R and N_{SERS} refer to the number of molecules in the focus of the laser beam. N_R equals to the concentration of molecules of the solution, c_R=100 mM, times the illuminated volume, N_{SERS} equals to the surface concentration Γ_{SERS} times the illuminated area, A.

The irradiated volume V can be approximated by a cylinder of radius r and height h, while the radius of the focused beam is estimated by McFarland et al to be r=2 µm for the x20 objective independent of the wavelength [2]. The height of the cylinder can be approximated by the depth of focus of a Gaussian beam (Eq.S-2).

$$h = 2r^2\frac{\pi}{\lambda} \qquad \text{Equation S-2}$$

For Γ_{SERS} we used the largest packing density of benzenethiol (BT), $6.8\cdot10^{14}$ molecules/cm^2 [3].

We can estimate the surface area probed by the SERS measurement from the SEM pictures. The average distribution of the size of nanoparticles is measured by ImageJ. We calculate the surface area by considering silver hemi-ellipsoids and relate it to the area of the SEM picture. In this way we have generated an analogy with the roughness factor $RF = \frac{A_{REAL}}{A_{GEOMETRIC}}$ [4]. Therefore, the illuminated area

A, from Eq. S-1, is expressed as $A=RF\cdot\pi r^2$. For the silver electrode the surface roughness factor is determined by BET measurements to be ca. 20 [1].

For the area correlating to the best SERS signal, Figure 2 (b), we have calculated the surface area of half-ellipsoids with major axis 40 nm, minor axis 24, and height 12 nm. This surface area is multiplied by the number of nanoparticles in the image, to extract the A_{REAL}. By dividing with the $A_{GEOMETRIC}$ we get a RF=0.26.

On the basis of these calculations, the enhancement for 647 nm excitation wavelength at the optimal SERS area is $2.5\cdot10^4$ and $1.1\cdot10^4$ for the 1580 cm^{-1} and 2230 cm^{-1} peaks. While the enhancement of an electrochemicaly roughened Ag substrate is $2\cdot10^3$.

Estimation of Surface Enhanced Infrared Absorption Enhancement Factor (SEIRA EF)

Another important step is the evaluation of the molecular signal enhancement by the substrate in the IR region. A method to estimate and compare the enhancement of metal island films from the IR-ellipsometric data was found. Specifically, the parameters of the three main MBN peaks at 1476, 1580, 2230 cm^{-1} were extracted by ellipsometric modelling of an MBN monolayer on a flat gold surface. A model was built consisting of the layers Si/native SiO_2/MBN monolayer. The MBN layer was represented by a combination of three harmonic oscillators to account for the three main peaks, with their already specified parameters and the dielectric constant ε_∞ as a model parameter. The theoretically simulated tanΨ graph was then compared to the experimental data, providing the ratio of the enhancement of the MBN peaks by the existence of silver. The software used was the Sentech SpectraRay3.

Additional gradient sample

As mentioned in the main text, by placing the silicon substrate at a different position during the evaporation, the gradient has a different profile. This difference can be seen in Figure 5, where the SERS and SEIRA response profile of the sample depicted on the left is broader compared to the sample on the right. Figure S-1, shows the corresponding morphologies of the SERS (a') and SEIRA (b') maxima positions in Figure 5, (right). Position a' corresponds to 59% Ag particle density and b' to 78%, which

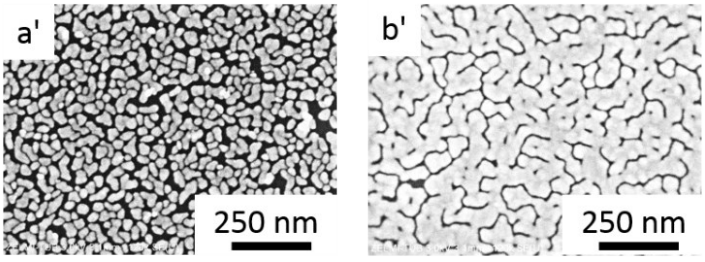

Figure S-1: SEM images of the positions corresponding to the maximum SERS (a') and maximum SEIRA (b') signals of the sample in Figure 5, right.

are similar values compared to the other gradient sample.

Figure S-2, exhibits similar optical behavior as the other gradient sample. At the SERS maximum position (a') the plasmonic resonance has a peak at 620 nm, close to the 594 nm excitation wavelength. Accordingly, position (b') has a plasmonic peak in the NIR, with a plasmonic tail extending to the MIR and providing optimized SEIRA enhancement obtained on the second sample.

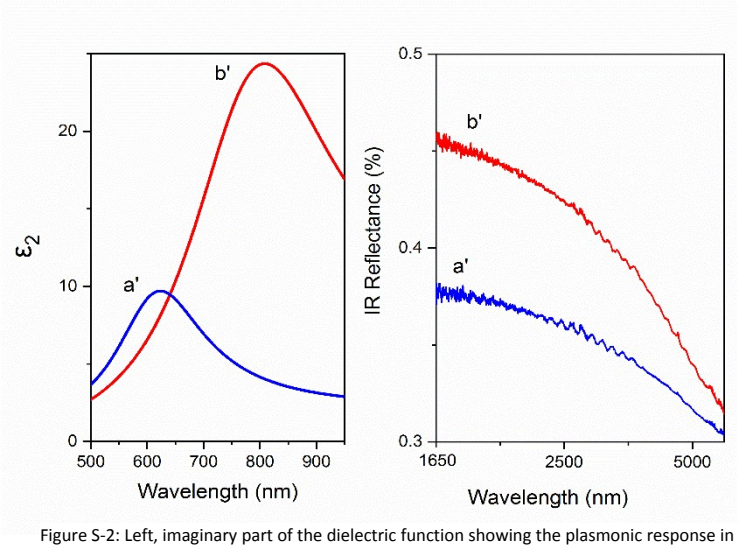

Figure S-2: Left, imaginary part of the dielectric function showing the plasmonic response in the visible for the positions with maximum SERS (a') and maximum SEIRA (b') signals of the sample in Figure 5, right. Right, the continuation of the resonances in the IR range, measured by IR reflectance.

References

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