Reproducible Deep-UV SERRS on aluminium nanovoids

Daniel O. Sigle,[1] Elaine Perkins,[2] Jeremy J. Baumberg[1] and Sumeet Mahajan[1#*]*

[1] Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK.
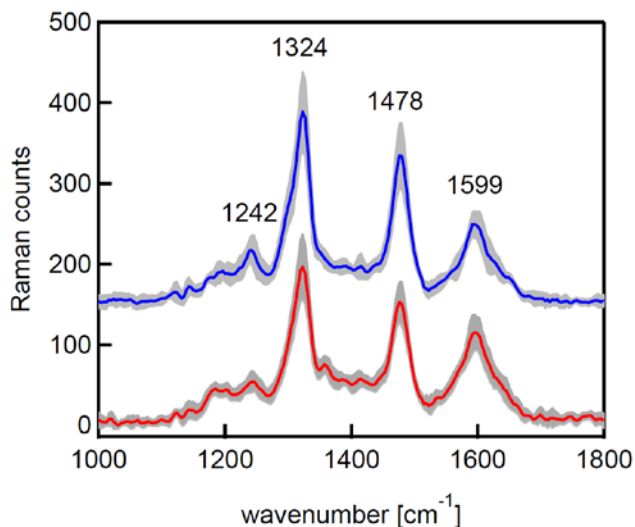[2] Dstl Porton Down, Salisbury, SP4 0JQ, UK.

* jjb12@cam.ac.uk, sm735@cam.ac.uk

[#] Present address: Institute of Life Sciences, University of Southampton, Highfield, Southampton, SO17 1BJ, UK

Supporting Information

Reproducibility of SERS spectra on 100 nm and 200 nm voids

Figure S1. Deep-UV SERRS spectra of adenine on 100 nm (red) and 200 nm void (blue) surface. Both spectra have been averaged over data taken at 6 different locations on three different substrates. The 100 nm void shows a more prominent peak at 1599 cm^{-1}. The standard deviation of the average is indicated in grey. We find a variation in the peak intensities of approximately 15%.
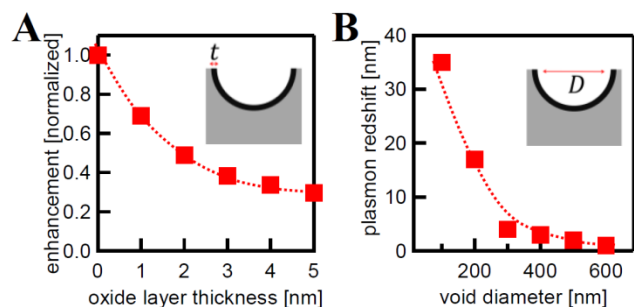
Calculation of enhancement factors

We determine the experimental surface-enhancement in the hot spot region by comparing the peak intensity from the resonant Raman spectrum per molecule in solution with the intensity from the SERRS spectrum per molecule. For the former, we work out an effective detection volume[1] given by a cone with 1/3 x (depth of focus) x (focus area), which allows us to estimate the number of contributing molecules. We determine the number of molecules contributing to the SERRS signal by including all those located in the area of the enhanced field. In order to

determine the volume of the enhanced field region, we approximate the different plasmon modes on our nanostructures given by simulations with regular geometrical shapes. The rim mode is approximated by a torus located along the rim while the volume mode is simplified by two small spheres inside the void. The extent of the modes is given by the volume where the magnitude of the local field enhancement is larger than one half of the maximum ($|E/E_0|^4 > 1/2|E_{max}/E_0|^4$).

Impact of the natural oxide layer on aluminium

Since aluminium surfaces invariably get covered with a self-limiting alumina layer we modeled the impact of this oxide layer on the SERS enhancement on our hemispherical nanovoids. In Figure S2, the simulated $|E|^4$ with respect to the value on a bare surface is depicted for a varying thickness of Al_2O_3 on the surface of a 100 nm void. The natural thickness of this film is approximately 3 nm.[2] The presence of this oxide layer causes a drop of $|E|^4$ to about 40% of the value on a bare aluminium surface, showing that the impact of oxidation under normal conditions is small compared to the several orders of magnitude electromagnetic enhancement. Further, the 3 nm oxide layer causes a shift of the plasmonic resonance frequency to the red. The redshift increases with decreasing void size due to the increasing ratio of oxide layer thickness t to the void diameter D and is approximately 0.6 eV for the 100 nm void. Taking the redshift into account, the centre of the plasmonic resonance is shifted close to the Raman excitation line, which further contributes to the high enhancement observed for 100 nm voids in our experiments.

Figure S2. A: Simulated enhancement for varying thickness of the natural oxide layer of aluminium on a 100 nm void (normalized to the enhancement on a bare Al surface). B: Redshift of the plasmon resonance in the presence of a 3 nm thick oxide layer for different void sizes. Dashed lines are guides for the eye.

References

(1)   Li, L.; Hutter, T.; Finnemore, A. S.; Huang, F. M.; Baumberg, J. J.; Elliott, S. R.; Steiner, U.; Mahajan, S. Metal Oxide Nanoparticle Mediated Enhanced Raman Scattering and Its Use in Direct Monitoring of Interfacial Chemical Reactions. *Nano Lett.* **2012**.

(2)   Jha, S. K.; Ahmed, Z.; Agio, M.; Ekinci, Y.; Loffler, J. F. Deep-UV Surface-Enhanced Resonance Raman Scattering of Adenine on Aluminum Nanoparticle Arrays. *J. Am. Chem. Soc.* **2012**, *134*, 1966–1969.