Supporting Information to: Tunable laser interference lithography preparation of plasmonic nanoparticle arrays tailored for SERS

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After the LIL recording step, periodic particle arrays with sub-wavelength size are generated upon development of the positive photoresist, with the height of the features around 100 nm. The dry etching treatment with argon ion beams removes the gold from the areas non-protected with the resist pattern, reducing the height approximately 20 nm. Finally, an oxygen plasma treatment is applied in order to remove the residual of photoresist on top of the prepared metallic nanoparticle arrays. This last step, as can be seen from a cross-section obtained by atomic force microscopy (AFM) in Figure S1, effectively removes the organic resist yielding a final height about 55-60 nm. The time and the power of the oxygen plasma treatment are optimized to ensure removal of the resist while preventing the melting of the gold nanoparticles.

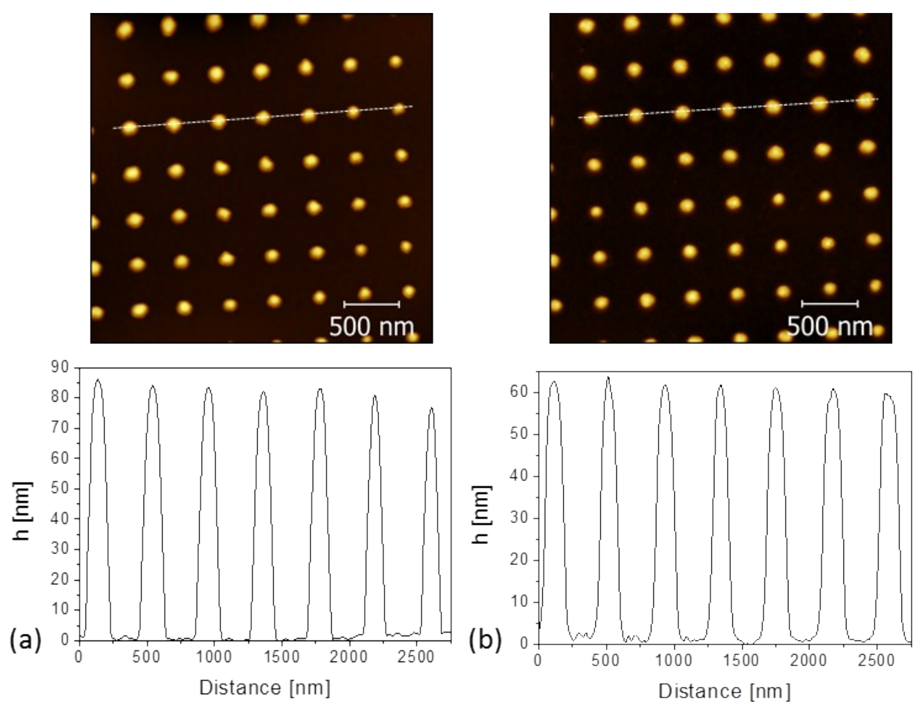


Figure S1. AFM image and modulation depth of the gold nanoparticles arrays after argon milling (a) and oxygen plasma (b) with Λ=460 nm and D=120 nm.

The subsrates S1 (Λ=400 nm and D=215 nm) and S2 (Λ=500 nm and D=165 nm) are tailored to exhibit a localized surface resonance in the vicinity of the laser line at 785 nm. Spectral changes in the transmission spectra for the sample S2 over the plasmonic substrate are measured with both a focused and collimated beam and given in the Figure S2. The study of the morphology performed by AFM for both substrates is outlined in Figure S3.

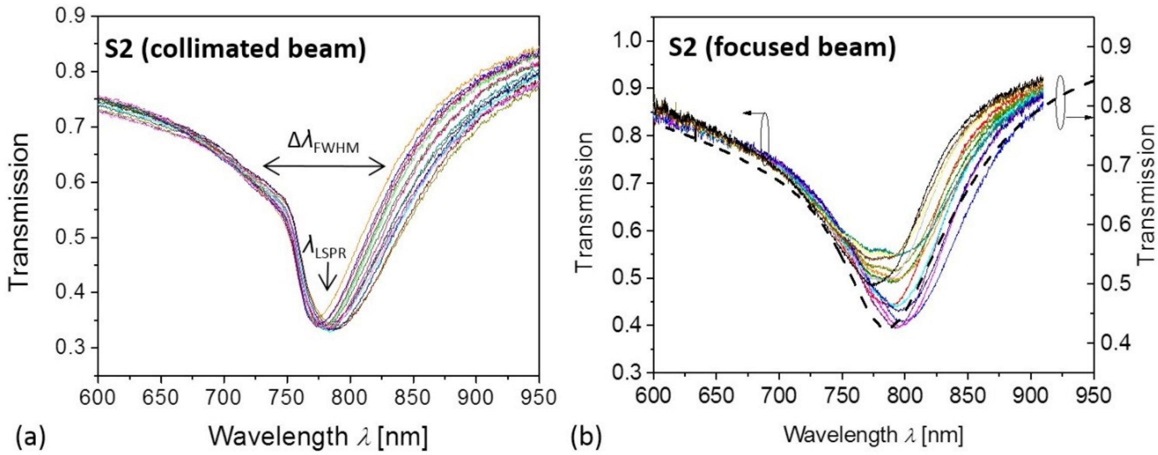


Figure S2. Comparison of the LSPR spectra measured on the substrate S1 on a) series of spots with a large 1 mm diameter arranged over 1 × 1 cm with collimated beam and b) on with focused beam diameter 3 µm scanned over 200 × 200 µm. Dashed line in b) shows transmission spectrum measured with large diameter beam on the same sample for comparison.

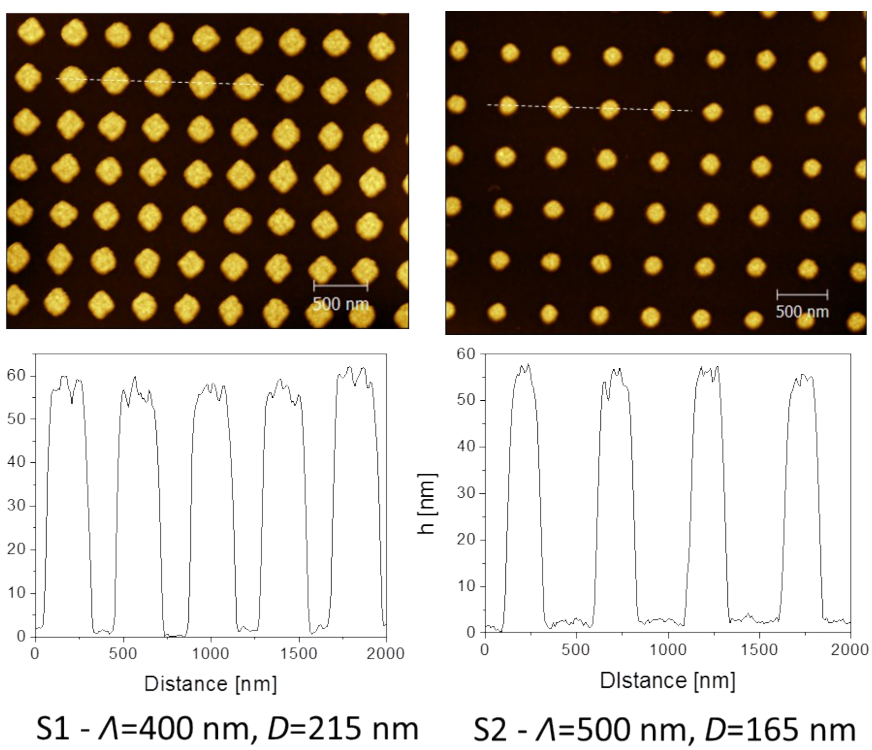
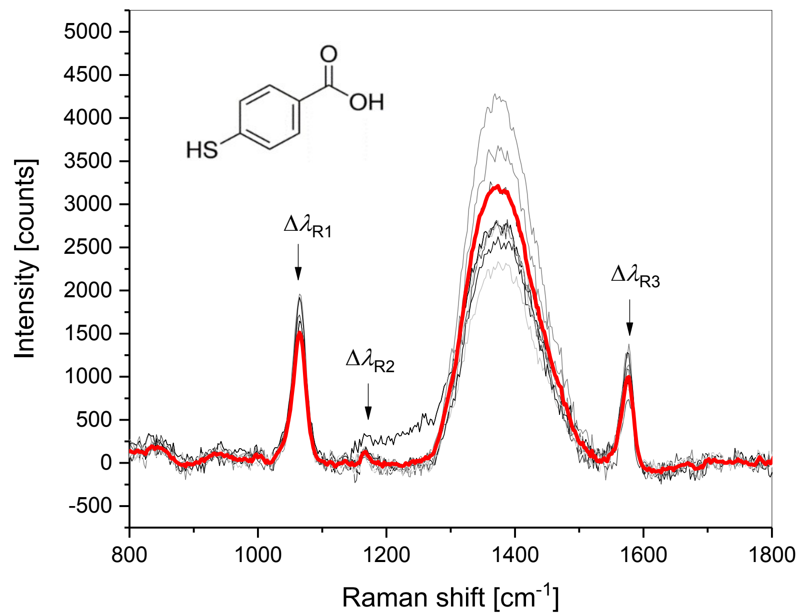
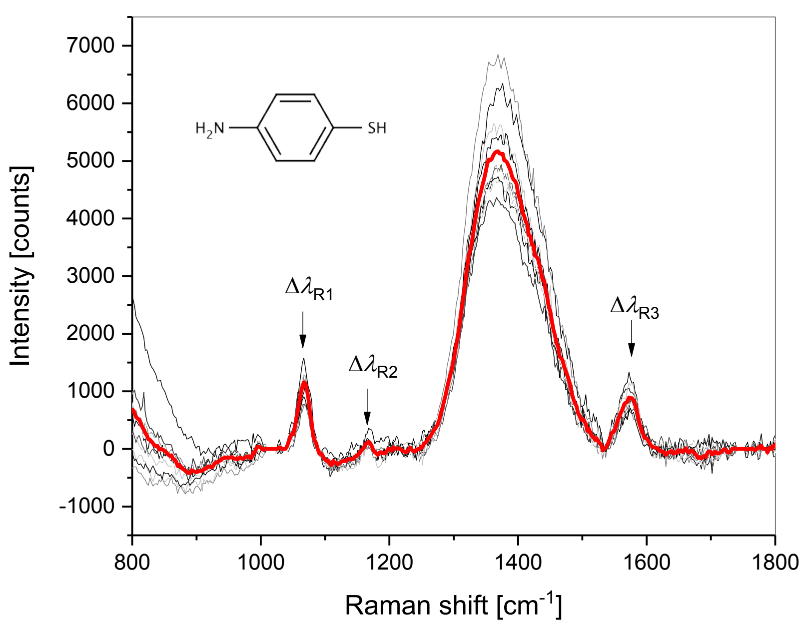


Figure S3. AFM observation of arrays of metallic nanoparticles carried by substrates S1 and S2.

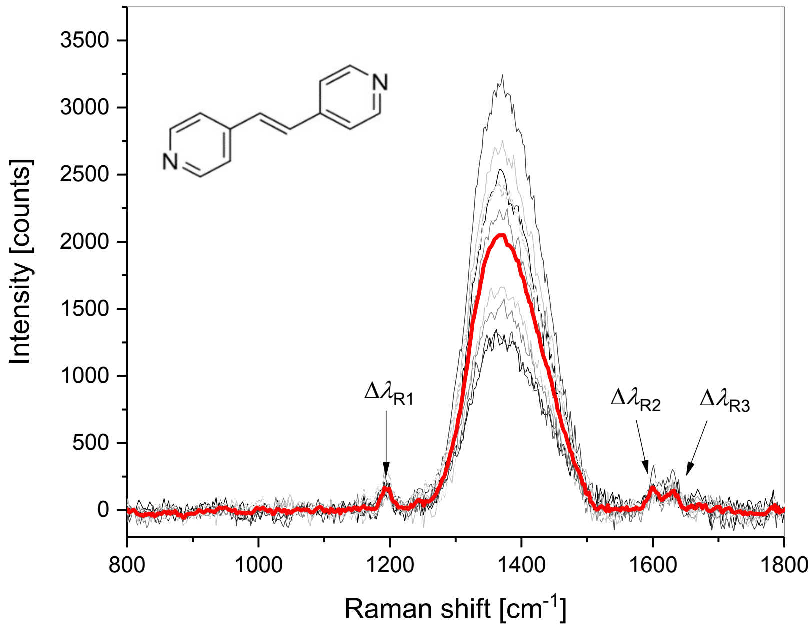
SERS spectra were measured for 4-mercaptobenzoic acid, 4-aminothiophenol and 1,2-di(4-pyridyl)ethylene attached to a substrate with arrays of gold nanoparticles with Λ=500 nm and D=165 nm. These SERS measurements were performed in backscattering configuration at room temperature with ×100 lens and a laser beam at λ_L=785 nm focused at a spot of 1 µm in diameter. The power of the laser beam at the spot was about 2.5 µW and Raman spectrum was accumulated by 30 s. Artefacts corresponding to cosmic rays were removed and raw spectra were compensated for the background. As Figure S4 shows, all measured spectra show broad bands at around 1400 cm^{-1} and 1900 cm^{-1}, which are attributed to the glass substrate. 4-mercaptobenzoic acid shows three peaks at $\Delta\lambda_{R1}$=1065 cm^{-1}, $\Delta\lambda_{R2}$=1166 cm^{-1} and $\Delta\lambda_{R3}$=1576 cm^{-1} with the intensity of 1166, 127 and 886 counts, respectively. Structurally similar 4-aminothiophenol shows three peaks at $\Delta\lambda_{R1}$=1072 cm^{-1}, $\Delta\lambda_{R1}$=1164 cm^{-1} and $\Delta\lambda_{R2}$=1573 cm^{-1} with the intensity 1523, 185 and 1016 counts, respectively. 1,2-Di(4-pyridyl)ethylene shows three weaker peaks at $\Delta\lambda_{R1}$=1095 cm^{-1}, $\Delta\lambda_{R2}$=1600 cm^{-1} and $\Delta\lambda_{R2}$=1632 cm^{-1} with the intensity of 162, 169, and 137 counts, respectively. These observations agree with SERS spectra reported before for other plasmonic nanostructures.[1-3]



a)



b)



c)

Figure S4. SERS spectra of a) 4-Mercaptobenzoic acid, b) 4-Aminothiophenol and c) 1,2-Di(4-pyridyl)ethylene measured on 10 spots arranged on a substrate with *Λ*=500 nm and *D*=165 nm (solid red line represents averaged signal).

References:

1. Yang, W. H.; Hulteen, J.; Schatz, G. C.; VanDuyne, R. P., A surface-enhanced hyper-Raman and surface-enhanced Raman scattering study of trans-1,2-bis(4-pyridyl)ethylene adsorbed onto silver film over nanosphere electrodes. Vibrational assignments: Experiment and theory. *J. Chem. Phys.* **1996,** *104* (11), 4313-4323.
2. Michota, A.; Bukowska, J., Surface-enhanced Raman scattering (SERS) of 4-mercaptobenzoic acid on silver and gold substrates. *J. Raman Spectrosc.* **2003,** *34* (1), 21-25.
3. Hu, X. G.; Wang, T.; Wang, L.; Dong, S. J., Surface-enhanced Raman scattering of 4-aminothiophenol self-assembled monolayers in sandwich structure with nanoparticle shape dependence: Off-surface plasmon resonance condition. *J. Phys. Chem. C* **2007,** *111* (19), 6962-6969.