

Supplementary Information for

**Evidence of a Surface Plasmon-Mediated Mechanism in the
Generation of the SERS Background**

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I. SERS background dependence on the nature of substrate

As a first complementary experiment, we compared the SERS backgrounds measured from two different substrates in the presence of the same p-aminothiophenol (pATP) probe molecule. We fabricated Au SERS substrates in a similar manner as AgFoCC SERS substrates by evaporating metal onto regular arrays of polystyrene nanospheres of 450 nm diameter. The structured Au film exhibits a deep and broad reflectivity dip (see Figure S1) which is comparable with that of AgFoCC SERS substrate relative to the spectral positions of two excitation laser lines discussed in the manuscript. The two substrates exhibit reflectivity (and plasmonic) spectra which are only slightly shifted but both are equally favourable for the enhancement of the Raman signal. This is an important condition to study the SERS background dependence on the nature of substrates.

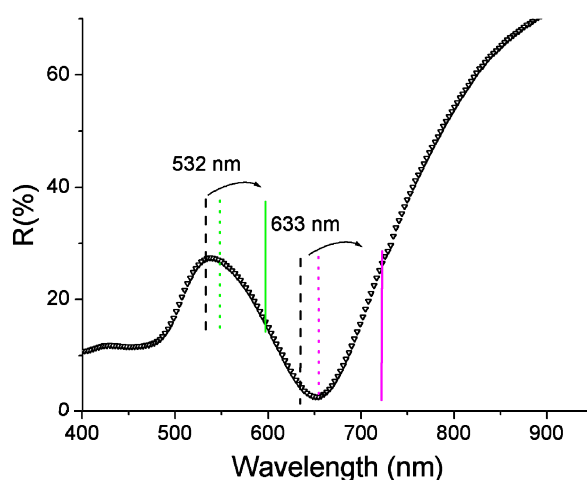


Fig. S1. Reflectivity spectrum of AuFoCC SERS substrate and spectral position of excitation lasers.

As seen in Figure S2 the dependence of the slope of the SERS background on the excitation wavelength, described and discussed in the manuscript, is valid also for Au substrates in the presence of the same pATP adsorbed molecule.

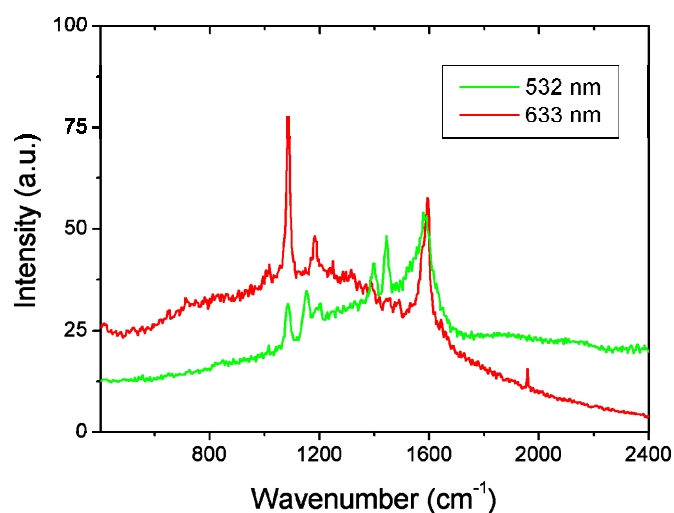


Fig. S2. SERS spectra of pATP on Au substrate (excitation wavelengths indicated in the figure).

Figure S3 presents a typical SERS background pair of images, recorded under 633 nm excitation on gold SERS substrate (AuFoCC), at the two spectral regions indicated by pink lines in Figure S1.

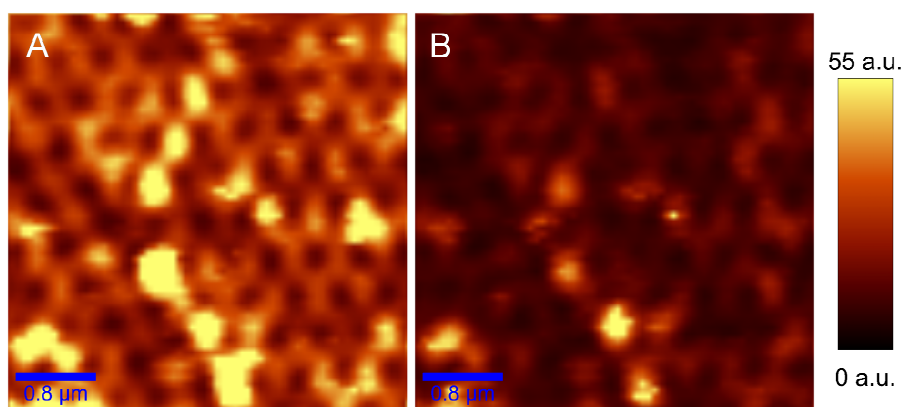


Fig. S3. Images of the SERS background under 633 nm excitation at 525 cm⁻¹ (A) and 2025 cm⁻¹ (B).

That is an important result which proves again that the SERS background is for the most part enhanced when the laser photons are optimally coupled to the plasmons, and, in this case, the nature of the supporting substrate doesn't matter to much.

II. I. SERS background dependence of the nature of probe molecule

As a second complementary experiment, we study the SERS spectra generated from Ag substrates similar to those described in the manuscript in the presence of a different molecule, 11-mercaptoundecanoic acid (11-MUA) which we selected to assume similar chemical binding to the silver surface (through the sulphur atom) as in the case of pATP. The SERS spectra collected for the two excitation wavelengths are presented in Figure S4. Again we found that the dependence of the slope of the background is in direct relation to the profile of plasmon resonance excited by laser photons, as described and discussed in the manuscript, and this remains valid when a different molecule is adsorbed on Ag substrate. Additionally we found some differences between the levels of SERS background related to the two types of molecules adsorbed onto Ag substrate. These results point out the fundamental role of plasmon excitation in the generation of SERS background, which goes over the nature of SERS substrate or adsorbed molecule.

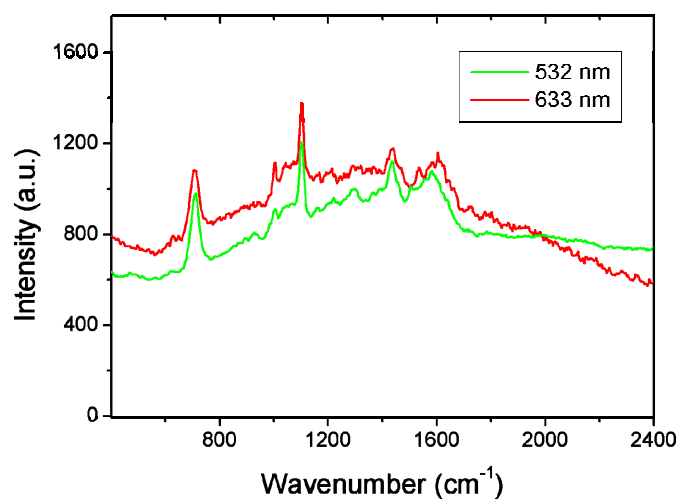


Fig. S4. SERS spectra of 11-MUA on Ag substrate (the two colours are in relation with the excitation wavelengths indicated in the figure).