Electronic Supplementary Information for “Enhanced detection of thiophenol adsorbed on gold nanoparticles by SFG and DFG nonlinear optical spectroscopy”

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1- Sample preparation

All chemicals are purchased from Sigma-Aldrich.

AuNPs are prepared following Turkevich method

We use 1.7mg of chloroauric acid ($HAuCl_4.3H_2O$ 99.999 %) dissolved in 20mL of Millipore water. The solution was heated up until boiling and stirred vigorously. At that point 0.8mL of $8.5x10^{-4}$ M trisodium citrate ($Na_3C_6H_5O_7$) was quickly added at one time while heating and stirring was kept for 30 minutes. The resulting solution turns successively from light yellow to deep gray and finally dark red after a few minutes. The corresponding UV-visible absorbance spectrum displays the expected absorption peak at 524nm usual for AuNPs in water (see Figure 1-a of the article).

Silanization of the silicon wafer.

A small piece of silicon of $1x1cm^2$ was cut from a wafer purchased from Siltronix and ultrasonically cleaned in methanol. Silanization of this surface was achieved with aminopropyltriethoxysilane (APTES) that binds to the 2 nm thick oxide still lying on top of the silicon. The sample was immersed in a solution of 10% vol of APTES dissolved in methanol for 3 hours. A 1 hour stay in a 110°C oven helped the layer to be reorganized and compacted.

Deposition of the AuNPs from the solution to the silanized silicon wafer.

Then the sample was dipped into the gold colloidal solution for 2 hours. Since at this pH, the amino group is charged positively and the citrate bears negative charges, an electrostatic binding occurs between the nanoparticles and the substrate.

Replacement of the citrate with thiophenol

The sample was then rinsed with Millipore water prior to its immersion in a 10^{-3}M solution of thiophenol (C_6H_5SH) dissolved in dichloromethane (CH_2Cl_2). The thiol moiety displaces the capping layer of citrate and strongly binds to the AuNPs through the sulfur atom. This strong thiophenol adsorption appears to be stable at air at least for several weeks.

2- Large scale AFM images of AuNP on silicon

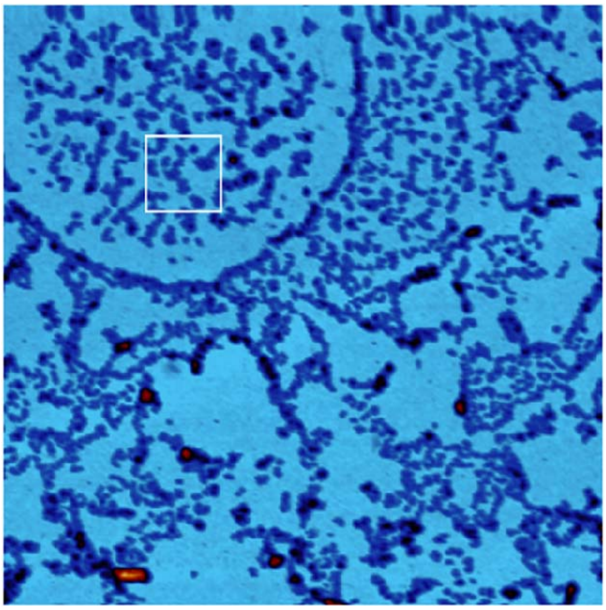

Fig. 7. AFM large scale image of the AuNPs deposited on the silanized silicon substrate (5x5µm). Small clusters of AuNP are formed probably during the drying phase as indicated by the 2µm droplet. White square corresponds to the area scanned in Figure 3 discussed in the text and to image in Figure 8.

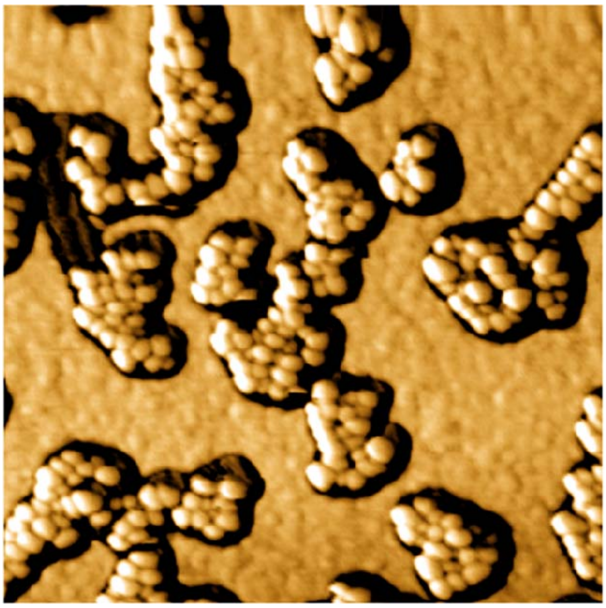

Fig. 8. AFM phase image corresponding to Figure 3 in the text and to the area marked with the white square in Figure 7. The AuNP can be individuated and counted. 296 AuNP are visible on this 760x760nm image.

Fitting parameters for SFG and DFG spectra: the degeneracy of the fitting parameters and how to lift it up

The SFG and DFG spectrum exhibiting a single vibrational mode, are modelled with the equations already given in the text:

SFG:

$$I_{SFG} = \left| C_{SFG}^{eff} e^{i\varphi_{SFG}} + \frac{a_0^{eff}}{\omega_{IR} - \omega_0 + i\Gamma_0} \right|^2 \qquad (1)$$

DFG:

$$I_{DFG} = \left| C_{DFG}^{eff} e^{i\varphi_{DFG}} + \frac{a_0^{eff}}{\omega_{IR} - \omega_0 - i\Gamma_0} \right|^2 \qquad (2)$$

From the experimental spectrum, the plotting software easily returns 5 five fitting parameters, C^{eff}, φ, a_0^{eff}, ω_0 and Γ_0. However, there are two strictly equivalent sets of parameters yielding identical spectra. This degeneracy leads to an ambiguity in the choice of the parameters a_0^{eff} and φ. The correct choice of parameters is important when one seeks to give a physical interpretation of the corresponding values. After some easy manipulations of complex numbers, it can be demonstrated that starting from one set of parameters, the second one is given by the following formula:

$$\text{SFG:} \begin{cases} \tilde{a}_0^{eff} = +\sqrt{\left(a_0^{eff}\right)^2 - 4a_0^{eff} C^{eff} \Gamma_0 \sin\varphi + 4{C^{eff}}^2 \Gamma_0^2} \\ \tan\tilde{\varphi}_{SFG} = \pi - \tan\varphi + 2\dfrac{C^{eff}\Gamma_0}{a_0^{eff}\cos\varphi} \end{cases}$$

$$\text{DFG :} \begin{cases} \tilde{a}_0^{eff} = +\sqrt{\left(a_0^{eff}\right)^2 + 4a_0^{eff} C^{eff} \Gamma_0 \sin\varphi + 4{C^{eff}}^2 \Gamma_0^2} \\ \tan\tilde{\varphi}_{DFG} = \pi - \tan\varphi - 2\dfrac{C^{eff}\Gamma_0}{a_0\cos\varphi} \end{cases}$$

The table below is summarizing all the fitting parameters with the two sets of parameters for each of the three SFG/DFG curves depicted in Figure 4 and Figure 5 of the article. For some parameters, the standard deviation is also given, as returned by the fitting algorithm used to adjust the experimental spectra to equation 1 or 2. Notice that for a given spectrum, the fitted amplitude a_0^{eff} varies considerably between the 2 possible sets: a factor 20 is found for SFG on Au(111). This is a spectacular manifestation of the interference effect between the two complex contributions from substrate and from adsorbate. In the case of a bulk gold substrate, the phase shift is expected around 111°, which points to the set n°1 as indicated with bold character in the table below. To select the correct set of parameters in the case of the AuNP spectra, a comparison of SFG and DFG measurements is necessary. The choice is based on phase φ_{SFG} and φ_{DFG} which have to be very close to each other. This shows that set 2 for spectrum 6-b is clearly inappropriate since it is the only value for φ which is negative. Making the right choice for SFG spectrum on AuNP (spectrum 6-a) is more delicate because the two values obtained for the phase φ are extremely close to each other: 95.9° and 92.3°. In this case, the correct value is found by noting that the amplitudes a_0^{eff} should not vary too much when switching from SFG to DFG. All these considerations are leading to the selection of parameters marked *set 1* in the table 2 and indicated with bold characters. These parameters are used to evaluate the intensity of the vibrational mode of thiophenol on gold that is achieved by calculating the peak (or dip) area, denoted A, of the corresponding Lorentzian function:

$$A = \frac{\pi \times \left(a_0^{eff}\right)^2}{\Gamma_0}.$$

It is worth noting that the resulting vibration mode intensity strongly depends on the chosen set of parameters and can vary by several orders of magnitude.

Table 2 Complete table with the fitting parameters for the SFG and DFG spectra presented in the article (see Fig. 4 & 6). Only one set of parameters corresponds to a physical solution and is with bold characters is the in the table.

	SFG on Au(111) Spectrum 4-a		SFG on AuNP Spectrum 6-a		DFG on AuNP Spectrum 6-b	
	set 1	set 2	**set 1**	set 2	**set 1**	set 2
C^{eff} (√Volt)	**0.33**	0.33	**0.0927**	0.0927	**0.024**	0.024
φ (°)	**115** ±10	91.2 ±0.5	**95.8** ±1.6	92.3 ±0.6	**93.1** ±3.8	-91.3 ±1.7
a_0^{eff} (√Volt/√cm)	**0.23** ±0.05	5.01 ±0.04	**0.36** ±0.02	0.94 ±0.02	**0.28** ±0.01	0.617 ±0.008
ω_0 (cm^{-1})	**3058**	3058	**3058**	3058	**3058**	3058
Γ_0 (cm^{-1})	**8.0**	8.0	**7.0**	7.0	**7.0**	7.0
$A = \frac{\pi \times \left(a_0^{eff}\right)^2}{\Gamma_0}$	**0.024**	9.87	**0.059**	0.39	**0.035**	0.17