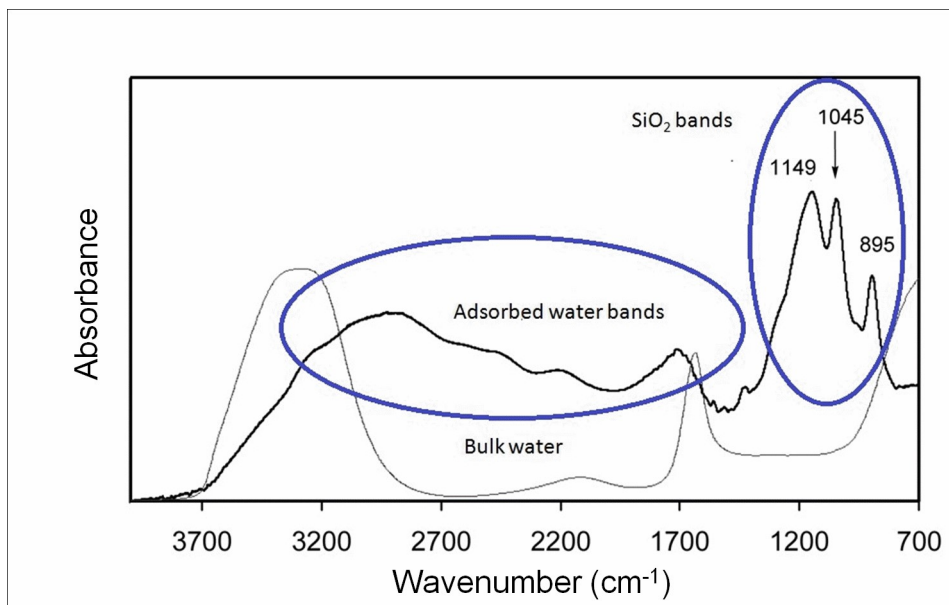


Supplementary material.

1. Treated substrate characterization.

As commented in the main text, the initial treatment of the Si(100) surface with piranha solution leads to a SiO₂ layer that can be detected by FTIR, with clearly visible bands centered at 1045 cm⁻¹ and 1149 cm⁻¹ as shown in Figure S1. These bands are assigned to SiO₂ transverse-optic (TO) oxygen asymmetric (AS1 and AS2) stretch modes [1]. A new band also appears at 895 cm⁻¹, which is assigned to the Si-H stretching in O₃SiH configurations (1). The FTIR spectrum displays other bands at 1700 cm⁻¹ and 2200 cm⁻¹ that are probably due to the presence of water that is adsorbed rapidly as the sample is transferred from a dry nitrogen atmosphere to the FTIR chamber. There is also a broad feature between 2600 cm⁻¹ and 3600 cm⁻¹ from $\nu(\text{OH})$ modes of strongly hydrogen bonded water and silanol group.

In a previous work (43) the comparison between this spectrum and the one of bulk water acquired in Attenuated Total Reflection (ATR) mode demonstrated a clear difference between SiO₂ TO bands and water bands, as observed in Figure S1. This fact confirms that an oxide layer appears after the treatment with piranha solution. That layer is hydrophilic, most likely due to the presence of a large number of silanol groups such as required for the effective coupling of the silane and then the activation with SH groups. The rest of these chemical changes on the substrate cannot be detected by transmission FTIR probably due to the weakness of the IR absorption signals.



2. Ruling out non SERS contributions.

Test experiments employing aggregated nanoparticles reduced by hydroxylamine in wavelength near the center of the absorption band of R6G (531 nm) have been performed. This measurements at 532 nm coming from the second harmonic of a Nd:YAG laser are performed with a 50x objective and a slip aperture of 100 mm in a Horiba Jobin Yvon HR 800 UV spectrometer with a laser power of 10 mW and an integration time of 1 s. These so recorded spectra are, on average, about 10^4 times stronger than the 785 nm one (not shown). This result, performed in conditions in which the possibility of R6G fluorescence contribution diminishes, denotes that the differences in Raman intensity at both wavelengths can be assessed as SERS signal from metal enhancement mainly *via* EM mechanism. On the other hand, in order to confirm that the large surface area of these aggregates is not sufficient to give a Raman spectrum by itself, spectra from similar size aggregates of a non-metal nanoparticles film have been recorded. The experiments have been carried out by incubating during 1 h a solution of R6G 10^{-3} M on sintered substrates of P25 TiO₂ nanoparticles (1). All the efforts were unsuccessful in producing a measurable Raman signal of R6G. In summary, none of the

two effects, both the fluorescence of R6G as the effect of the area, are in contradiction with the fact that real SERS effect is obtained in the following experiments.