Supporting Information

Gold nanothorns – macroporous silicon hybrid structure: a simple and ultrasensitive platform for SERS

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Experimental Details

Macro-PSi formation

Macro-pores of 1-2 microns were generated on a single-side polished (100) p-type silicon substrate with a resistivity of 20 - 30 Ω.cm using a conventional electrochemical anodization method. The etching process was carried out using a homemade single cell tank with a Pt wire cathode and a copper plate to form the ohmic contact between silicon and power source. A current density ranging from 1 to 100 mA/cm^2 was applied to the system for etching times of 1 to 120 minutes. Various combinations of hydrofluoric acid (HF) and dimethyl formaldehyde (DMF) were used as the electrolyte. Wafers were previously diced into 1.5×1.5 cm^2 squares and sonicated in a (1:1) mixture of acetone and ethanol for 10 min in order to remove organic contamination and then dipped into a 1M HF solution to remove the native oxide layer. After etching, samples were immersed in ethanol for 5 min and then dried under a N_2 stream where needed as a dry sample; otherwise, the samples underwent gold coating.

Gold nanoparticles coating

Gold nanostructures on the top of macro-PSi were prepared using a simple immersion deposition method at room temperature. An aqueous solution of 0.02 M $HAuCl_4$ (Sigma) and 2.9 M HF (Merck) was prepared. As-prepared PSi chips were submerged into the solution for different times to achieve the desired particle size and surface coverage. Samples were rinsed with copious amount of DI water several times to remove residual HF from the surface and then were dried under a N_2 stream.

Electron microscopy

High-resolution transmission electron microscopy (HRTEM) was carried out using a JEOL JEM 2011 microscope with point resolution of 0.23 nm and equipped with a Gatan 894 UltraScan 1000 CCD

camera. Scanning electron microscopy and energy dispersive X-ray analysis were done using a JEOL JSM-7001F SEM.

SERS measurements

The Raman spectra were obtained using a Renishaw Invia micro-Raman System coupled to a HeNe laser (633 nm) and a Peltier cooled CCD detector. The system is equipped with a 1200 lines/mm grating, a motorized xyz stage for mapping and employs an edge filter for Rayleigh scattering rejection. Slit opening and slit beam centre size were selected at 65 µm and 1917 µm, respectively and the exposure time was fixed at 10 sec. Sampling was carried out using a Leica (50 x, NA = 0.75) visible microscope. The laser irradiation used for all the samplings was 0.6 mW.µm^2.

Figure S1. SEM images of the initial macro-PSi substrate. (a-c) top view at different magnifications and (d) cross section view.

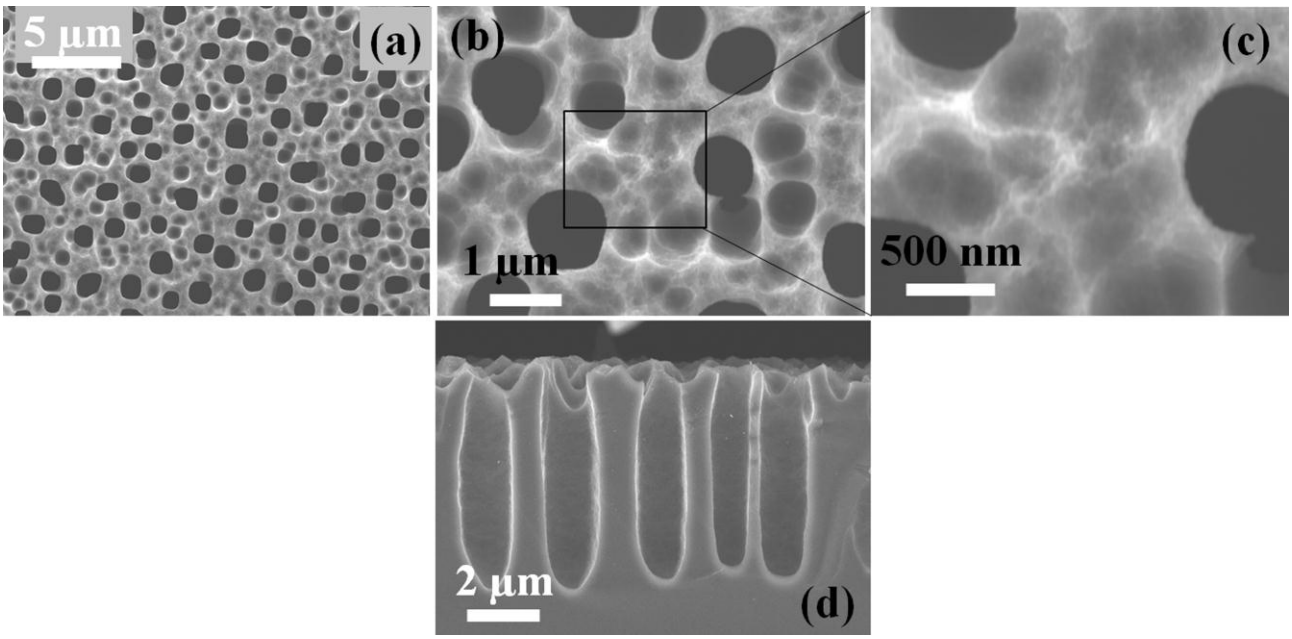


Figure S2. TEM images of the initial stage of the particle growth.

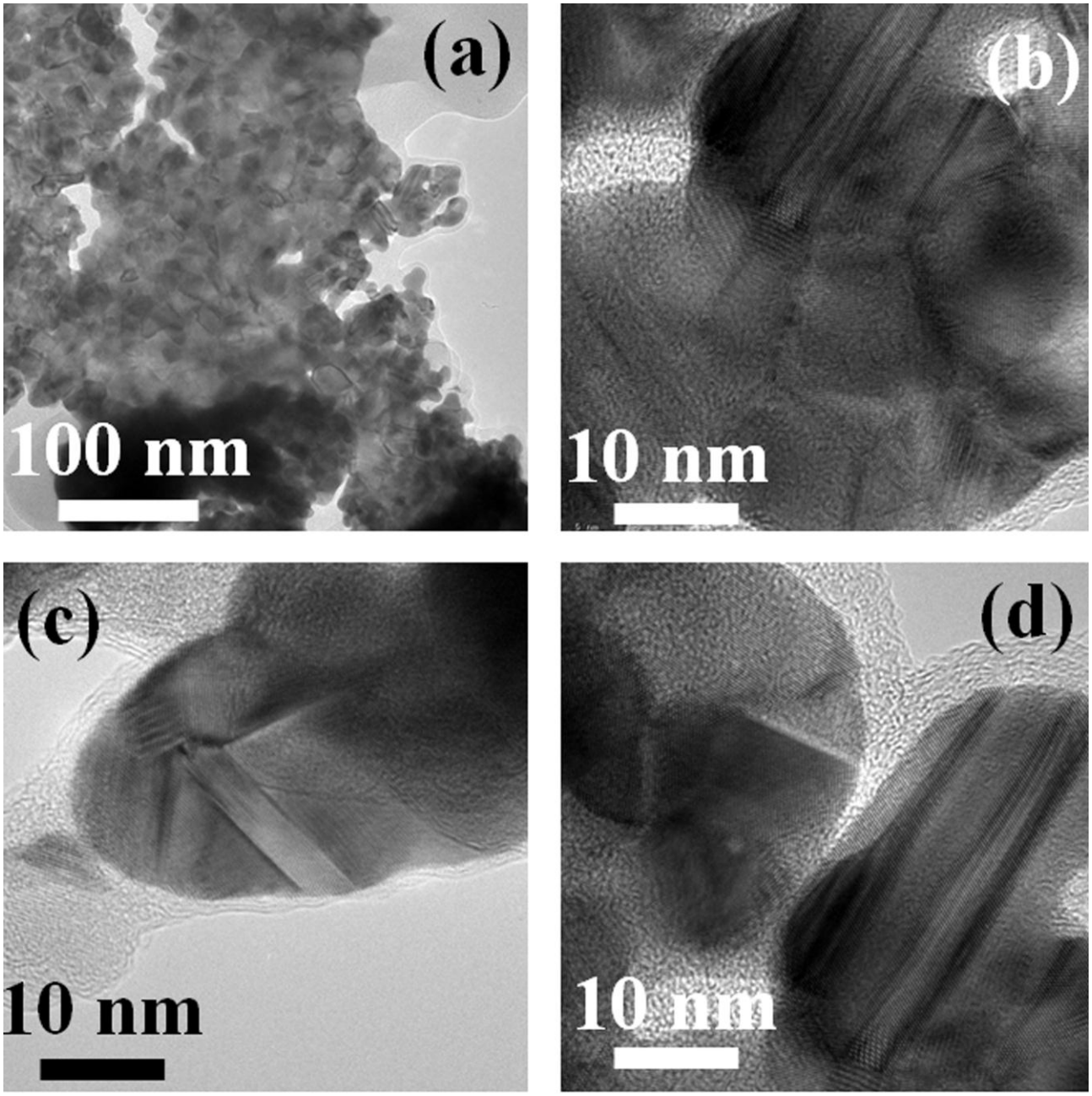


Figure S3. HRTEM images of nano-thorns.

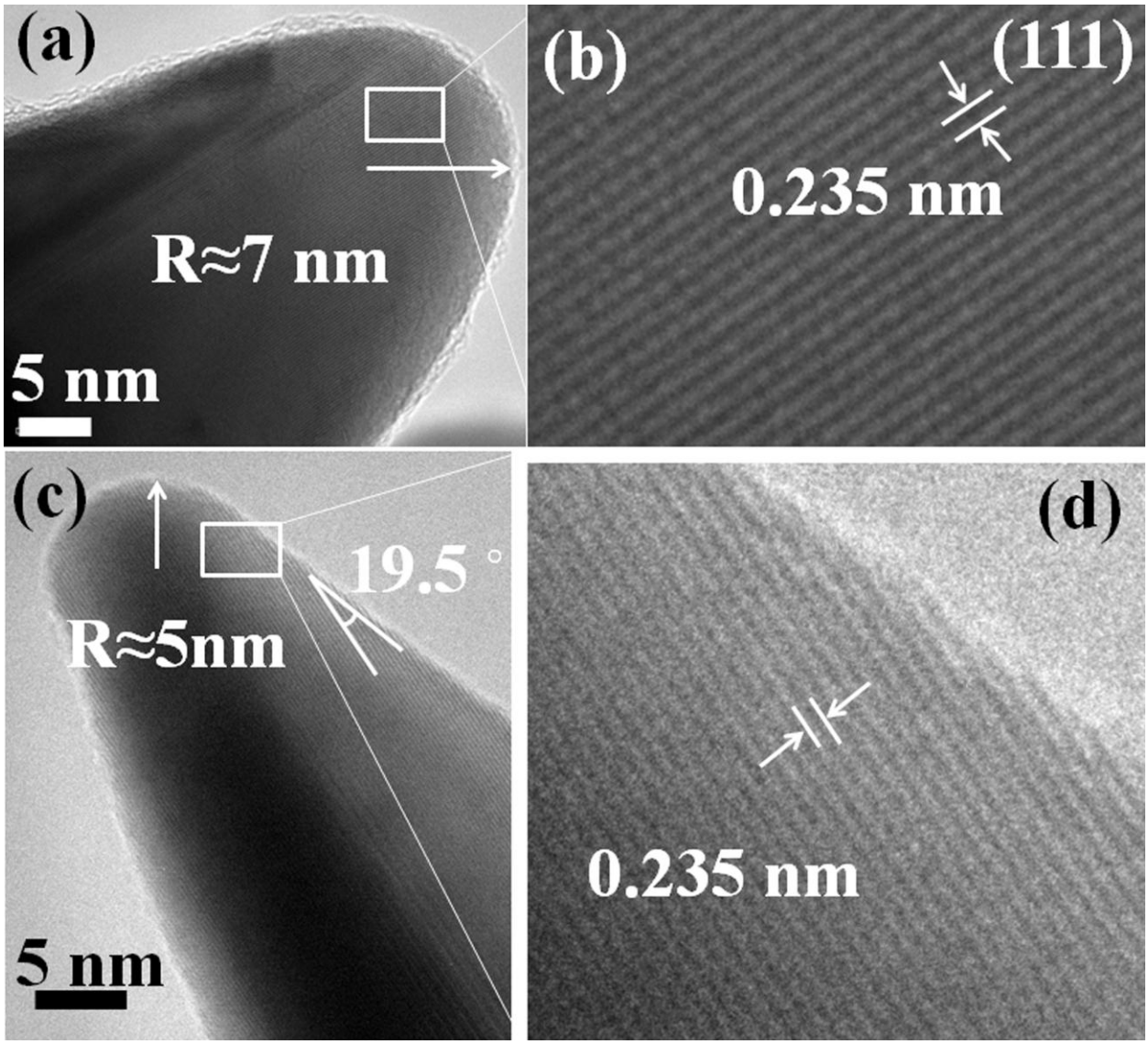
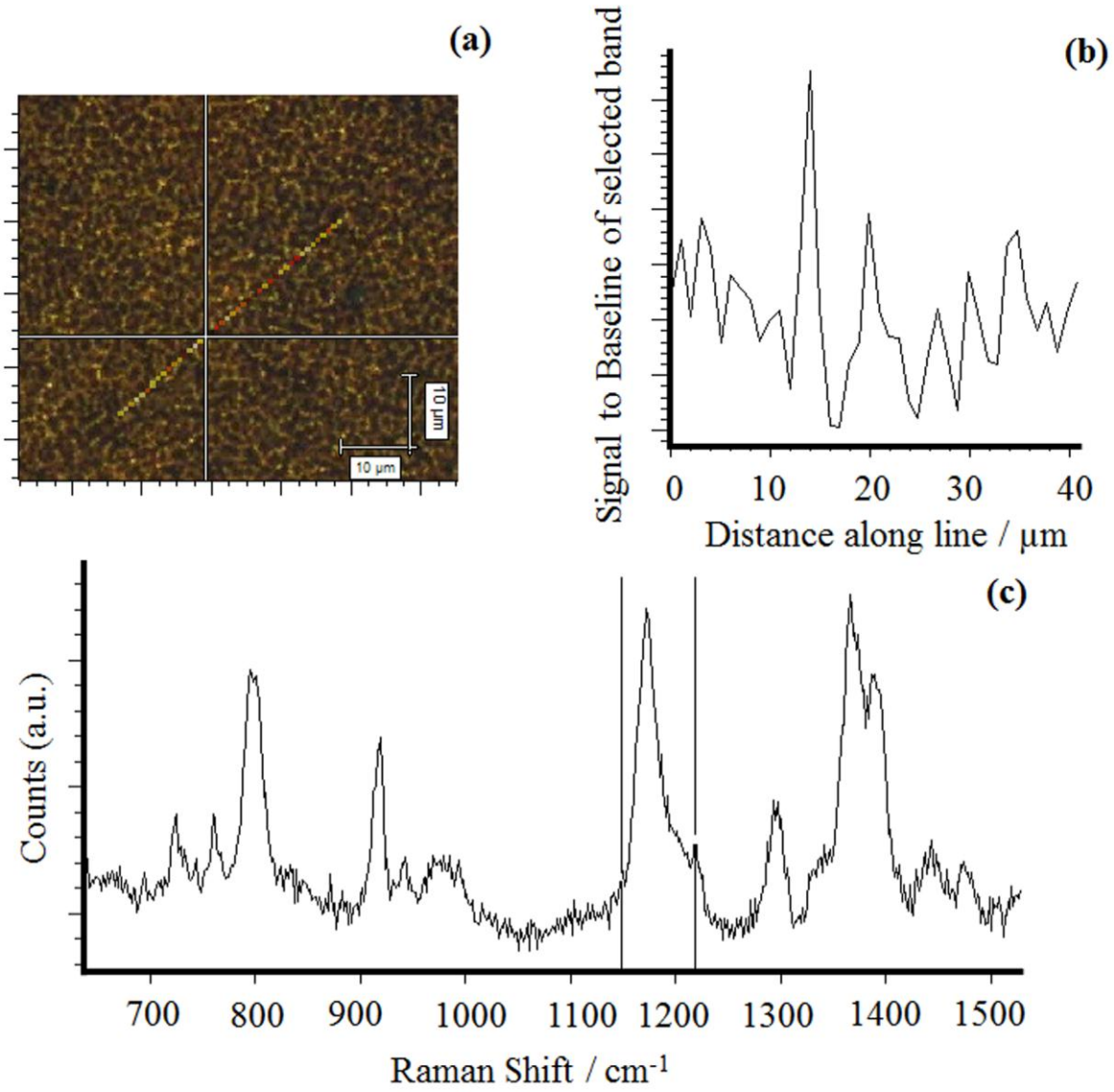


Figure S4. Raman mapping information. (a) Optical micrograph of the sample showing the location of the line scan (dotted line), (b) scan statistics of the 1170 cm^{-1} band shown in the Raman spectrum (c) of the first point on the line scan; this band is indicated by parallel lines.



Enhancement factor estimation:

To estimate the enhancement factor of the gold nano-thorn / macro-PSi substrate, we used the standard equation

$$EF = \frac{I_{SERS} / N_{Surf}}{I_{RS} / N_{Vol}} \qquad (1.1)$$

where, I_{SERS} and I_{RS} are the intensities of the same scattering band in the SERS and non-SERS spectra of CV, respectively. N_{Surf} and N_{Vol} are the number of analyte molecules that yield I_{SERS} and I_{RS}, respectively. Therefore the equation gives the Raman signal enhancement of a particular scattering band per molecule of the analyte. The best scattering band for this estimation is the band that gives the largest intensity ratio I_{sers} / I_{RS}. Interestingly, in our experiments this ratio does not vary substantially from band to band. The ring C−C stretching at 1617 cm^{-1} was chosen to estimate the enhancement factor. The first challenge to estimate EF is the actual scattering volume in non-SERS measurement. The confocal height of the Raman microscope was estimated ~4 µm, from depth of field considerations. The laser spot diameter was estimated to be ~0.9 µm (previously measured in the lab), leading to a scattering volume of ~2.5 $µm^3$. Therefore, the number of CV molecules contributing in non-SERS measurement will be around 1.3×10^{10} as CV powder was used (to be more rigorous, we assumed a porosity of 70% for the powder under the laser beam). In order to estimate N_{Surf} we need to know the number of gold nanoparticles under the laser probe and the number of coated CV molecules contributing in SERS measurement. Given the difficulties in the active surface area of the metal coating on the reported sample, a silicon wafer (not PSi) coated with the same method was used. It is obvious that the active surface area of the reported sample is significantly greater than that we used to estimate metallic surface area, therefore EF will be higher in the actual condition. We found an average number of 100 for gold nanoparticles (according to SEM images) and a total

average effective metallic surface area of ~4 μm^2 (considering the height of grooves formed at inter particle positions) which leads to ~3000 CV molecules under SERS probe when a 1 nM analyte solution was used. Thus, EF was estimated to be in the order of 10^8 which can include an error of about 10^2 due to assumptions made to estimate the values of N_{Surf} and N_{Vol}. However this error can be compensated by the underestimations introduced by assuming a flat silicon surface coated by uniform gold nanoparticles.

Figure S5. Flat silicon surface coated by gold nanoparticles to estimate the active metallic syrface area. The circle shows the laser beam size, approximately.

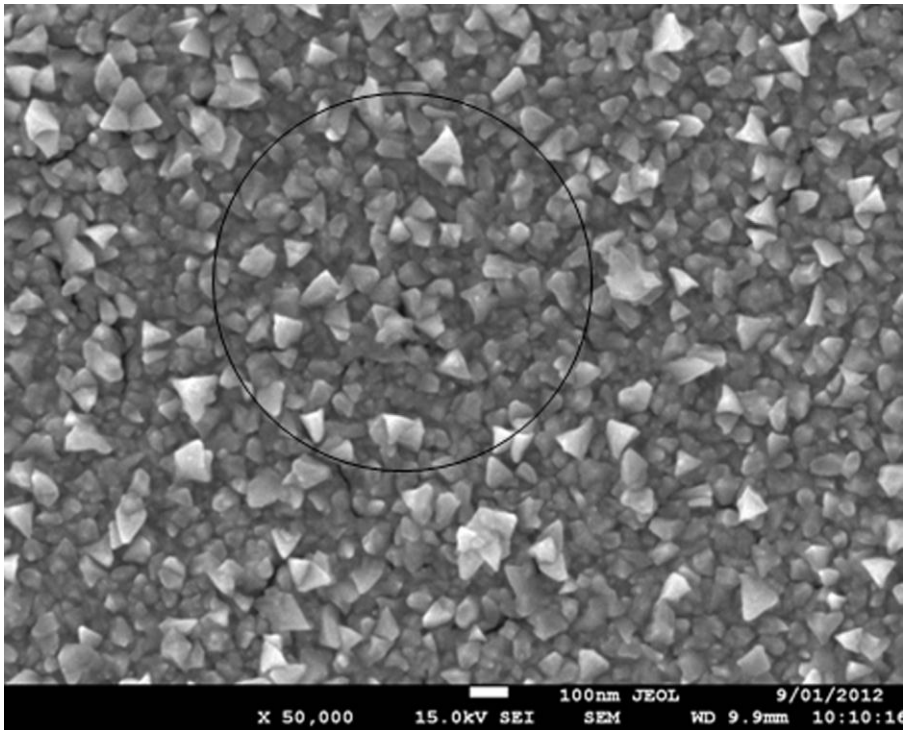


Figure S6. The original SERS scattering spectra of CV @ gold nano-thorn / macro-PSi sample for three different concentrations.

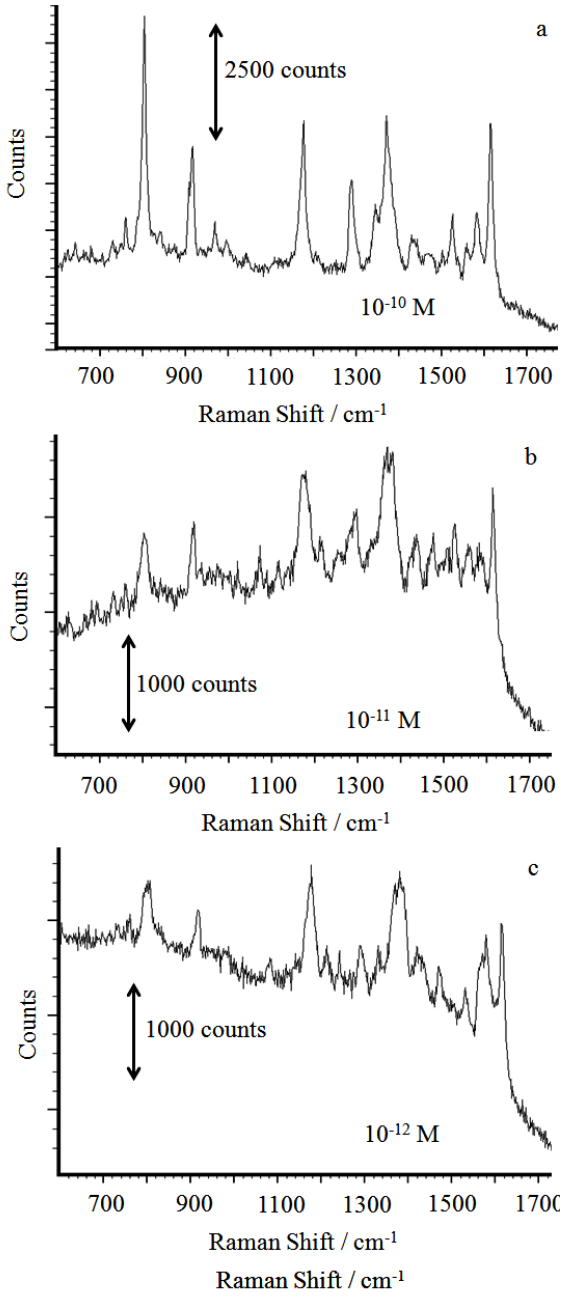


Figure S7. SERS spectra of the fresh and aged substrate with 10-6 M CV.

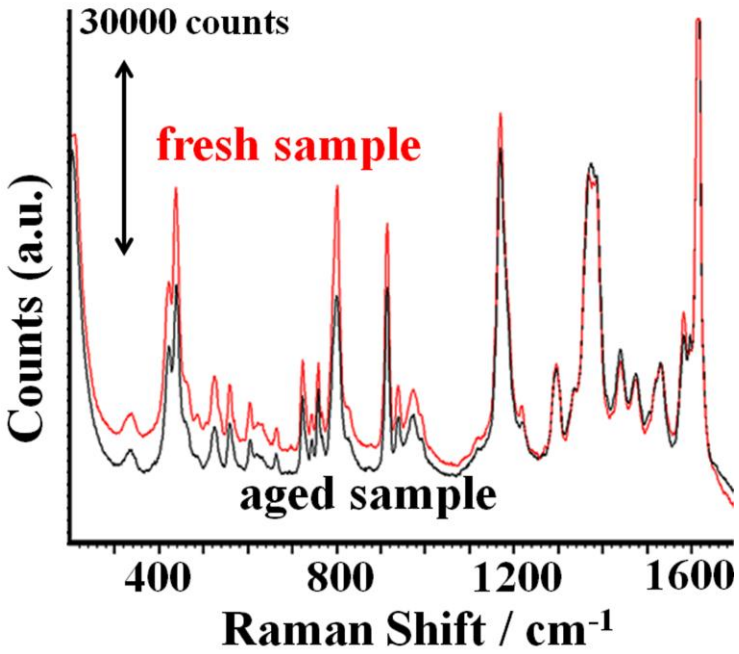


Figure S8. The intensity to baseline distibution of the selected bands of 10^{-9} CV @ gold nano-thorn / macro-PSi sample. Representing data recorded from (a) three samples and (b) different points at the same sample.