

Supplementary information

Development of a candidate reference sample for the characterization of tip-enhanced Raman spectroscopy spatial resolution

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1. Etching setup

The STM-TERS silver tips utilised in the studies were etched from a 250 μm diameter silver wire, used as an anode in an electrochemical cell also composed of a gold cathode in the shape of a circular ring with a 10 mm diameter formed from a gold wire with a 1 mm diameter; the wire was placed in the centre of the ring, perpendicular to its plane. The etching solution was a 1:2 v/v solution of perchloric acid and methanol. For each etching, approximately 25 ml of this liquid were poured into the cell in order for the cathode to be just below the surface of the acid. Then, 8.1 V voltage was applied to the electrodes for the time necessary for the tip to be completely formed: at this time a homemade electronic circuit cut the voltage in order to avoid etching the apex further; after this, the tip was thoroughly rinsed in ethanol and nitrogen dried.

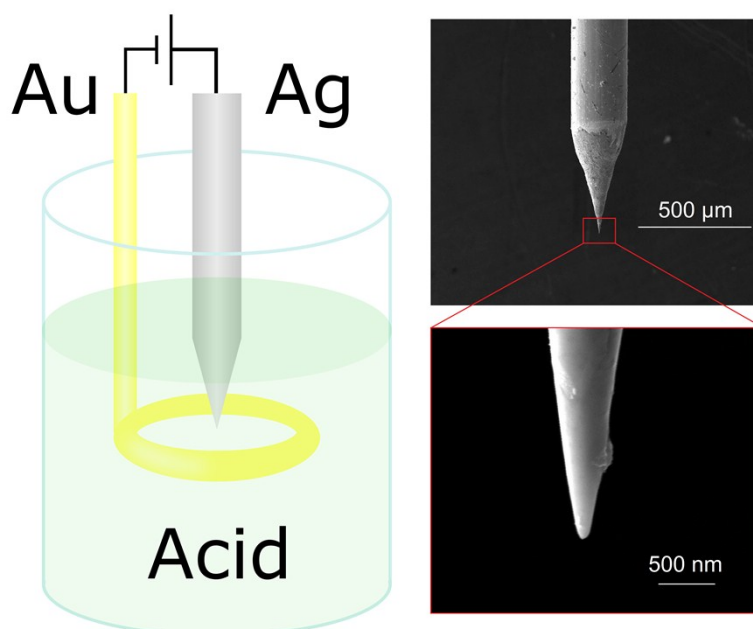


Figure S-1 – Scheme of the electrochemical cell used for STM-TERS tip etching (left, circuit not depicted), and SEM images of an etched tip as an example (right).

2. PMMA mask optimisation

The PMMA mask production was optimised in order to obtain lines with exposed gold of controllable width and shape. In particular, underexposure results in incomplete development of the trenches, and the resulting mask, hence thiol pattern, differs substantially from the initial design, leading to thinner lines, if any; overexposure would result in distorted patterns, since unintended parts of the mask can be developed because of electron diffusion. The electron dose parameter was varied in a dose ranging from 200 to 850 $\mu\text{C}/\text{cm}^2$ and the resulting masks after development, but prior to the thiol solution soaking, were measured via semicontact AFM, and the ideal dose was found to be 670 $\mu\text{C}/\text{cm}^2$. In figure S-2, AFM maps of examples of underexposure, overexposure and optimised exposure are presented.

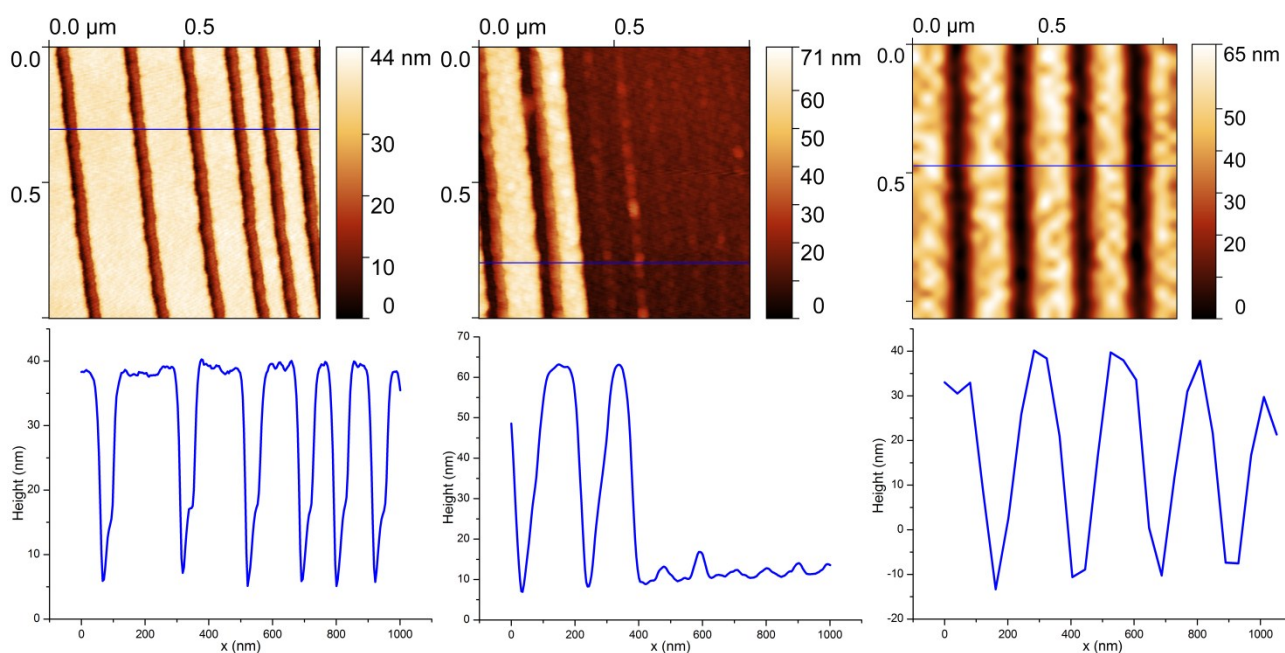


Figure S-1 – Semicontact AFM maps (top) of developed masks after exposure to different EBL doses: 450 $\mu\text{C}/\text{cm}^2$ on the left, corresponding to underexposure (mask height is ~ 50 nm, so in this case the gold is completely covered); 800 $\mu\text{C}/\text{cm}^2$ in the middle, where merged lines because of overexposure can be seen; on the right, a mask exposed to the ideal dose of 670 $\mu\text{C}/\text{cm}^2$, presenting rectangular and separate trenches with the same depth as the mask height, hence with a bare gold surface at the bottom available for bonding with the thiol after the next step in the sample fabrication. In the bottom row, line profiles corresponding to the blue lines in the maps are displayed.

3. Tip spectra after mapping

In figure S-3, TERS spectra of the tips utilised for the TERS maps in figures 4-7 after said measurements are shown, in order to evaluate the entity of the tip contamination (if any) during the measurement. These spectra were taken with the same experimental conditions as each pixel in the maps (633 nm He-Ne laser, 100x, 0.7 NA objective, 0.25 mW laser power, 0.5 s acquisition time, 0.1 V STM bias voltage, 0.5 nA tunnel current feedback), immediately after the corresponding maps, on a clean gold surface equivalent to the ones employed in the candidate reference sample production. These measurements show no detectable tip

contamination during or after the scan for the thiophenol samples, while the spectrum taken after the map on the MMC sample shows signs of the molecule on the apex.

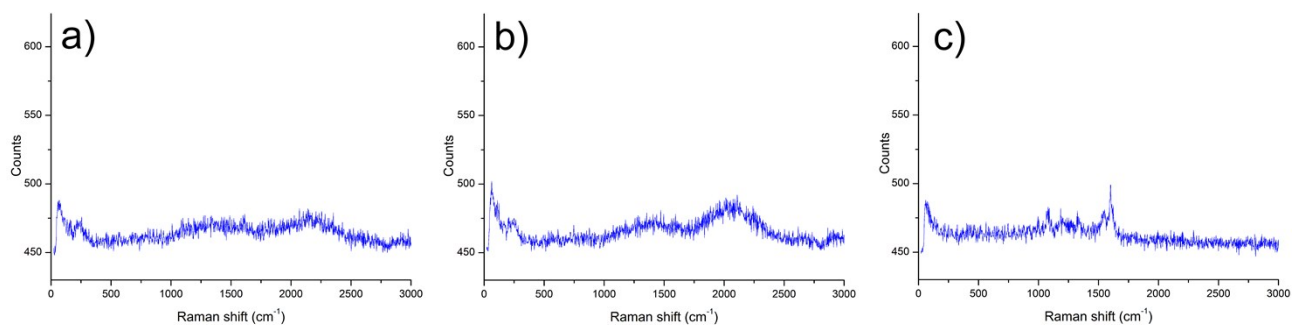


Figure S-3 – Spectra of the TERS tips in images 4-7, approached to clean Au surfaces immediately after the maps to check tip contamination. (a): spectrum of the tip after map shown in figure 4 – no thiophenol signal was measured; (b): spectrum of the tip after the map shown in figure 5, showing no thiophenol signal; (c): spectrum of the tip after the map shown in figures 6 and 7, showing faint MMC signals.