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Supplementary Information

Imaging Localized Electric Fields with Nanometer Precision through Tip-Enhanced Raman Scattering

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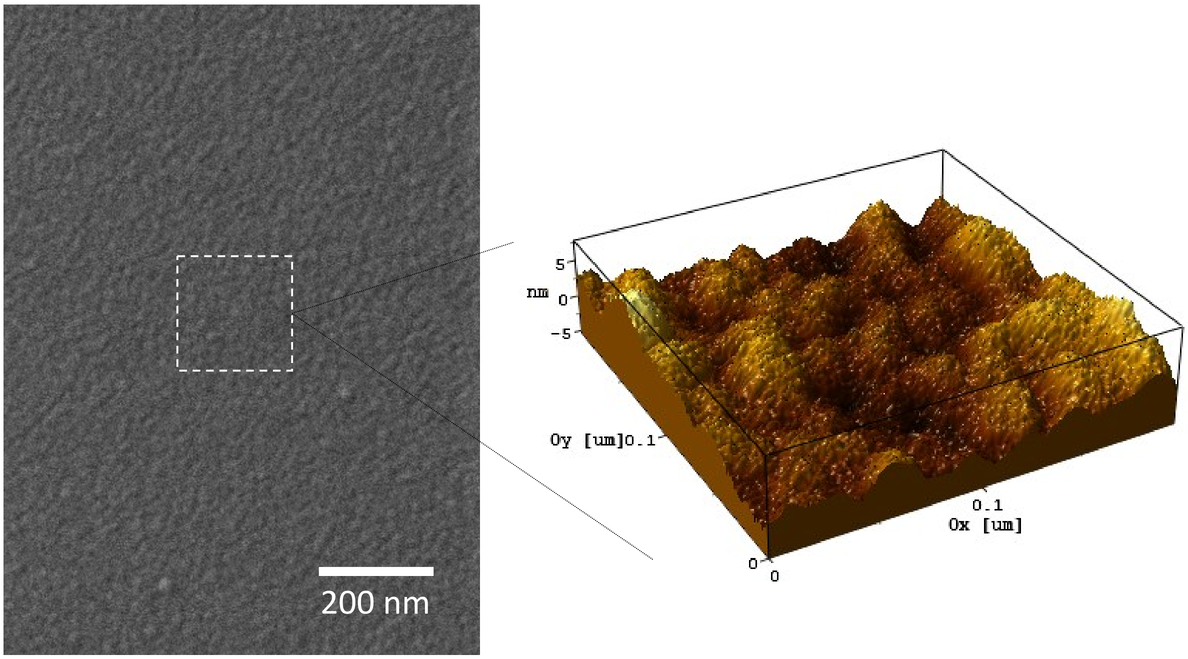

Figure S1. The left panel shows a representative helium ion image of a thin silver film evaporated on a 0.1 mm-thick microscope slide by arc-discharge physical laser vapor deposition (target: Ted Pella Inc., 99.99% purity). The helium ion microscope was operated at an optimal imaging voltage of 30 kV, an aperture size of 10 µm, a spot size of 4 µm, and a beam blanker current of 0.5-1.5 pA. An Everhart-Thornley (E-T) detector was used to image the samples. The working distance was varied in the 5-8 mm range. The right panel shows a topographic AFM image of a 200x200 nm^2 region of the metallic substrate. The typical surface roughness measured from freshly evaporated silver films reveals a root mean square height distribution of ~5 nm. It is important to note that the image shown in the right panel was recorded using an MBN-coated silver AFM probe (tip 1), see below for SEM images and additional information.

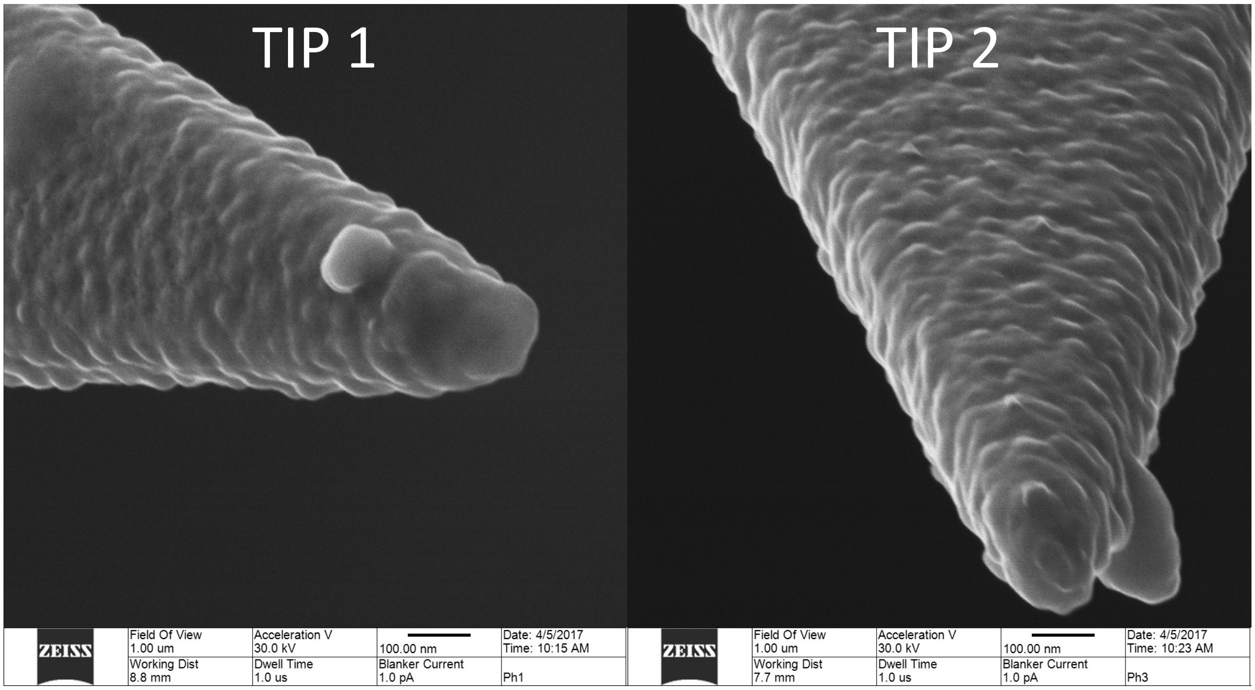

Figure S2. Helim ion images of two different MBN-coated atomic force microscopy tips. These two tips were used to record the TERS point spectra shown in Figure 4 (main text). Nanoscale features that govern the attainable spatial resolution in TERS are visible in the right panel.

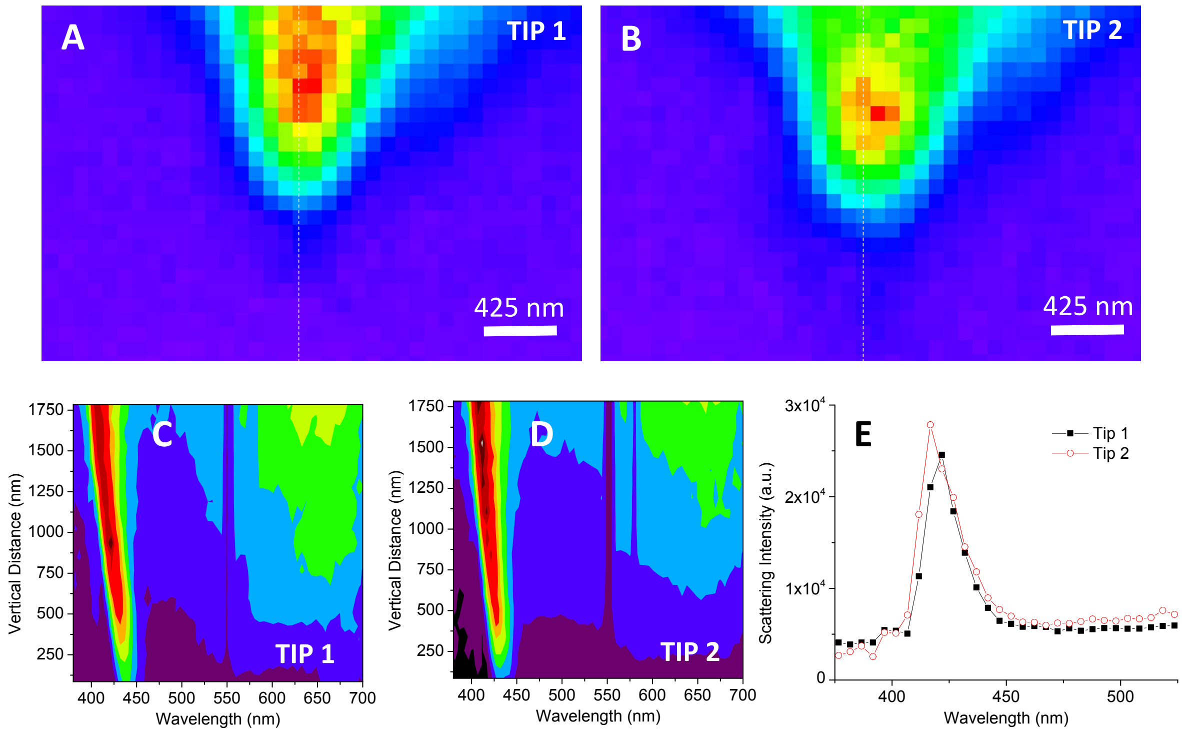

Figure S3. Hyperspectral dark field images of the two MBN-coated tips visualized in Figure S2. The images shown in panels A and B are hyperspectral image slices at 422 nm, near the plasmon resonance maxima of both tips (see panel E). Panels C and D correspond to vertical spectral slices along the dotted white lines highlighted in panels A and B, respectively. Besides minor spectral variations at the apices of the two tips, the scattering profiles are similar in the two cases. These images were recorded using a hyperspectral optical microscope consisting of a hyperspectral detector (SOC710-VP, Surface Optics Corporation) coupled to a confocal optical microscope (Leica, DM4000M). The setup allows us to record spectrally and spatially (diffraction-limited, sampled at 85 nm^2/pixel) resolved optical micrographs by scanning a line detector (at a rate of 10 lines/second) over the field of view dictated by the microscope objective (Leica N PLAN L 100x/0.75 BD). Each element comprising the aforementioned line detector contains spectral information in the 380-700 nm region. The hyperspectral image cubes of the sample were spatially and spectrally normalized to a reference hyperspectral image collected from the light source (depolarized/incoherent) incident onto a diffusive reflection standard (Ocean Optics, WS-1-SL). The recorded images were analyzed using ENVI 5.1 (Exelis Visual Information Solutions).

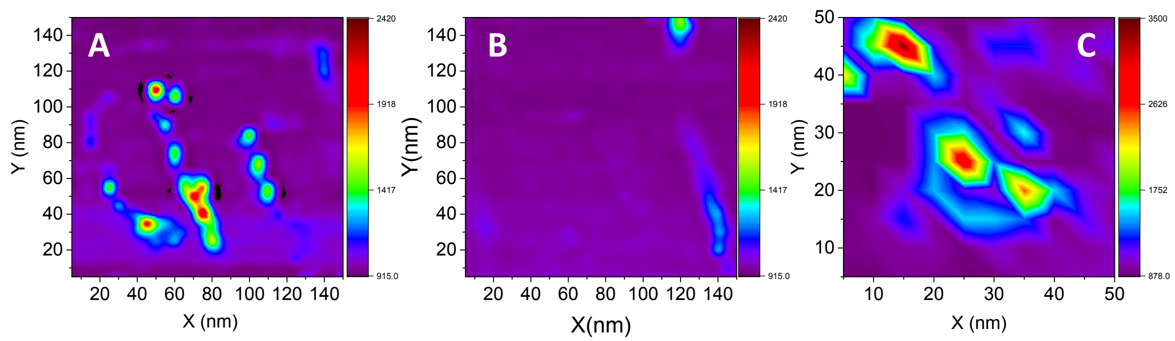

Figure S4. TERS images (5x5 nm^2/pixel) of a sputtered silver substrate (~5 nm rms surface roughness) at 1590 cm^{-1}. BPDT-coated AFM tips were used to record these images. Shown in panels A-C are images recorded from different regions of the substrate. See main text for more details.

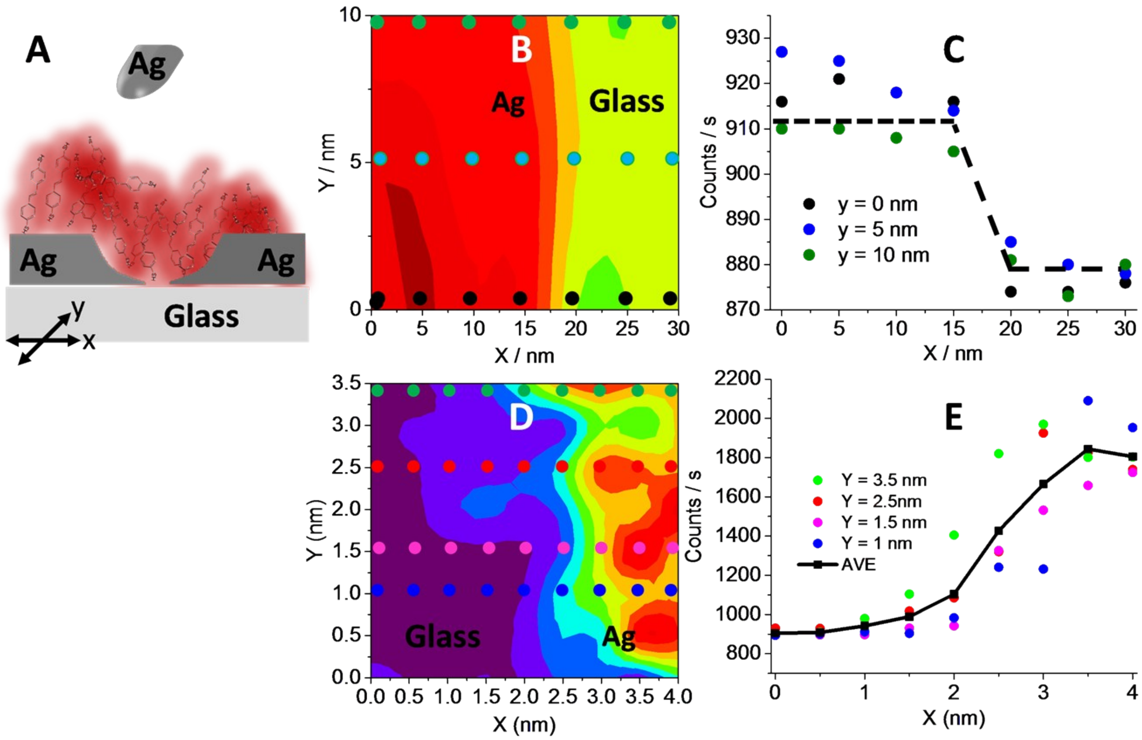

Figure S5. A) A schematic illustration of the experimental construct used to record the images shown in this figure. TERS images of lithographically patterned silver-glass boundaries are shown in panels B (5x5 nm^2/pixel) and D (0.5x0.5 nm^2/pixel). Free ion beam lithography was used to mill the imaged boundaries into a silver film on a glass substrate. The metallic thin film was prepared by arc-discharge physical vapor deposition (target: Ted Pella Inc., 99.99% purity). Intensity cuts taken from the images shown in panels B and D are plotted in panels C and E, respectively. A lateral resolution on the order of 1 nm can be inferred from plots C and E.

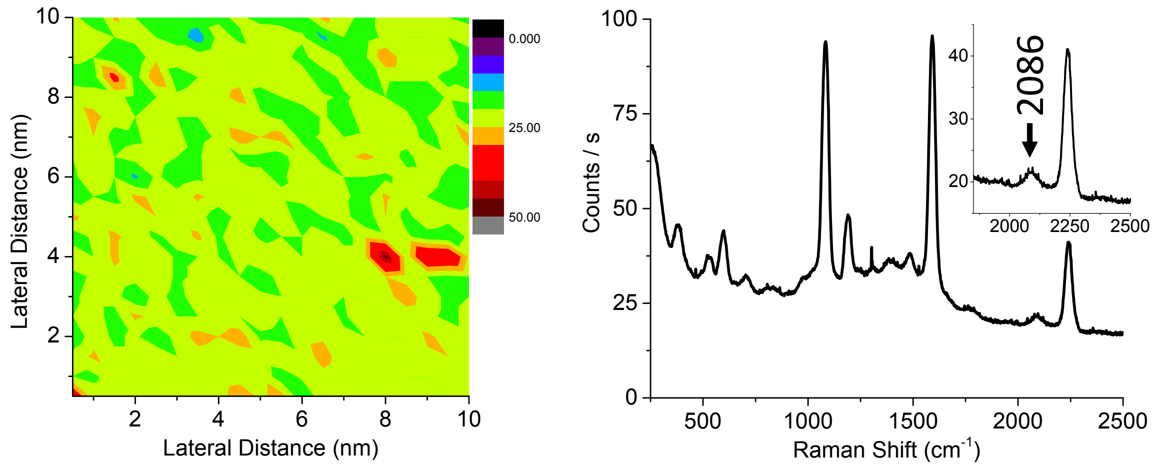

Figure S6. The left panel shows a TERS image (0.5x0.5 nm^2/pixel) of a corrugated silver substrate (~5 nm rms surface roughness) at 2086 cm^{-1}. This image was recorded using an MBN-coated blunted tip (tip 1 in Figure S2). The spectra comprising the hyperspectral image cube from which panel A was taken were all averaged and plotted in the right panel. The 2086 cm^{-1} nitrile vibration is highlighted in the inset of the same panel.

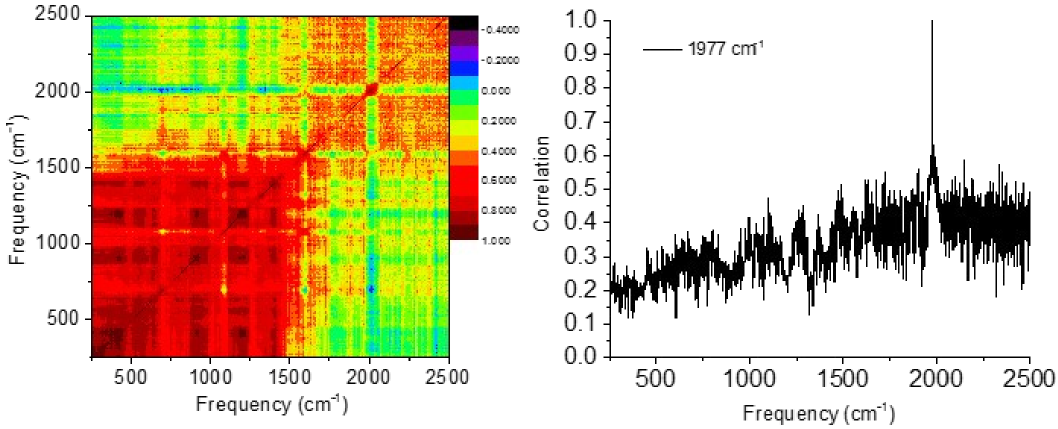

Figure S7. The left panel shows a 2D correlation analysis of the TERS image shown in Figure 5 of the main text. The cross-correlation between two frequencies of the recorded spectra is given by

$$\chi_{i,j} = \frac{\sigma_{jk}}{\sqrt{\sigma_{jj}}\sqrt{\sigma_{kk}}}$$

where σ_{jk} is the covariance, and σ_{jj}, σ_{kk}correspond to the statistical variance at frequencies j and k. A cross-correlation slice at 1977 cm^{-1}, corresponding to a red-shifted nitrile vibration of MBN is plotted in the right panel. The latter-mentioned trace reveals no correlation between the 1977 cm^{-1} mode and any of the Raman lines of MBN. Note that the 1977 cm^{-1} nitrile stretching vibration is correlated to the TERS background. See main text for more details [see refs 33 and 34 in the main text].