

# SUPPORTING INFORMATION

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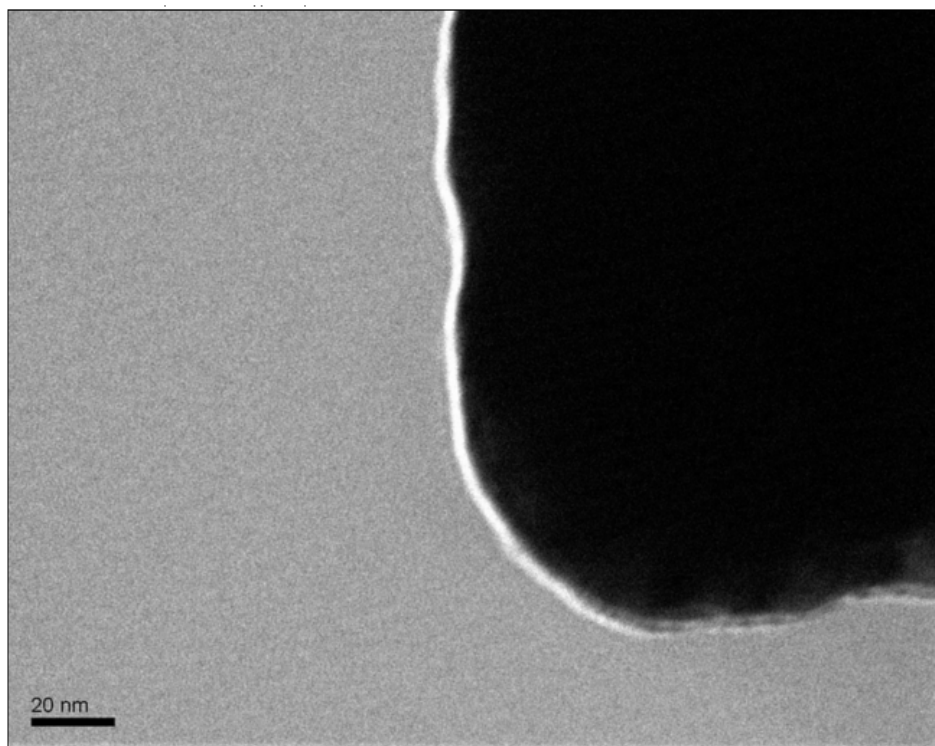
## Prolonged Blinking with TERS Probes

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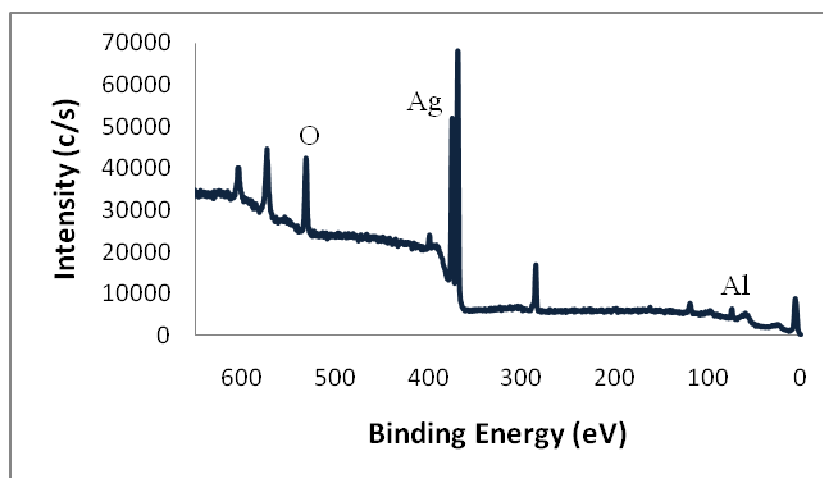
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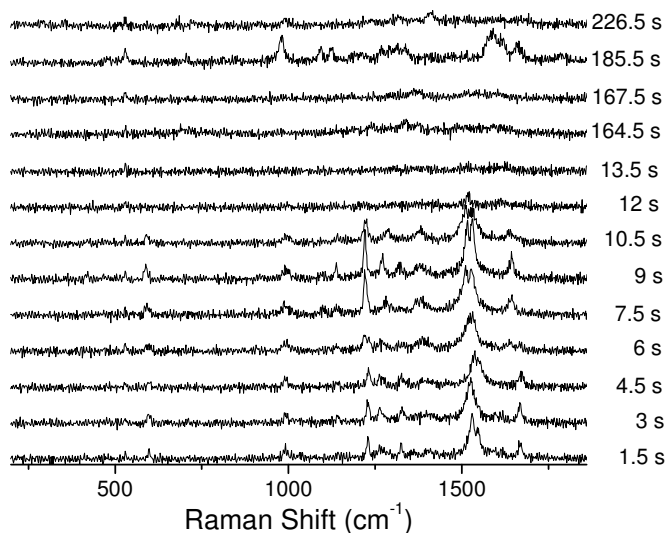


**Figure S1.** TEM image of a protected metalized tip representative of the tips used in the presented experiments. The apex of the tip was approximately 50 nm in diameter with a 3 nm thick protective alumina coating. The tip diameter was less than 100 nm, indicating that the effective thickness of the silver layer on the apex of the tip was substantially less than the nominal value read from the microbalance.



**Figure S2.** X-ray photoelectron spectroscopy spectrum of an alumina coated silver film on a flat silicon wafer. Analysis of the spectrum indicates the concentration of aluminum is 8 at % and that of oxygen is 15 at %. When the oxygen percentage is corrected by subtracting the amount

of oxygen adsorbed onto the surface of a film with no alumina present, a ratio of Al:O of 2:3 is found, confirming the anticipated  $\text{Al}_2\text{O}_3$  oxide stoichiometry.



**Figure S3.** Selected Raman spectra collected from an unprotected metalized tip with the tip hanging in the air, not in contact with any sample. The time labeled on the right is the time elapsed after blowing on the tip. Strong blinking is observed for 12 s after which the spectra do not show any distinguishing peaks. The tip was breathed on again at time 183 s. Blinking was once again observed. This supports a diffusion mechanism because strong blinking is observed as molecules in the breath move into the tip hot spot.