

Supporting Information

Surface-Enhanced Raman Spectroscopy - Scanning Electrochemical Microscopy: Observation of Real-Time Surface pH Perturbations

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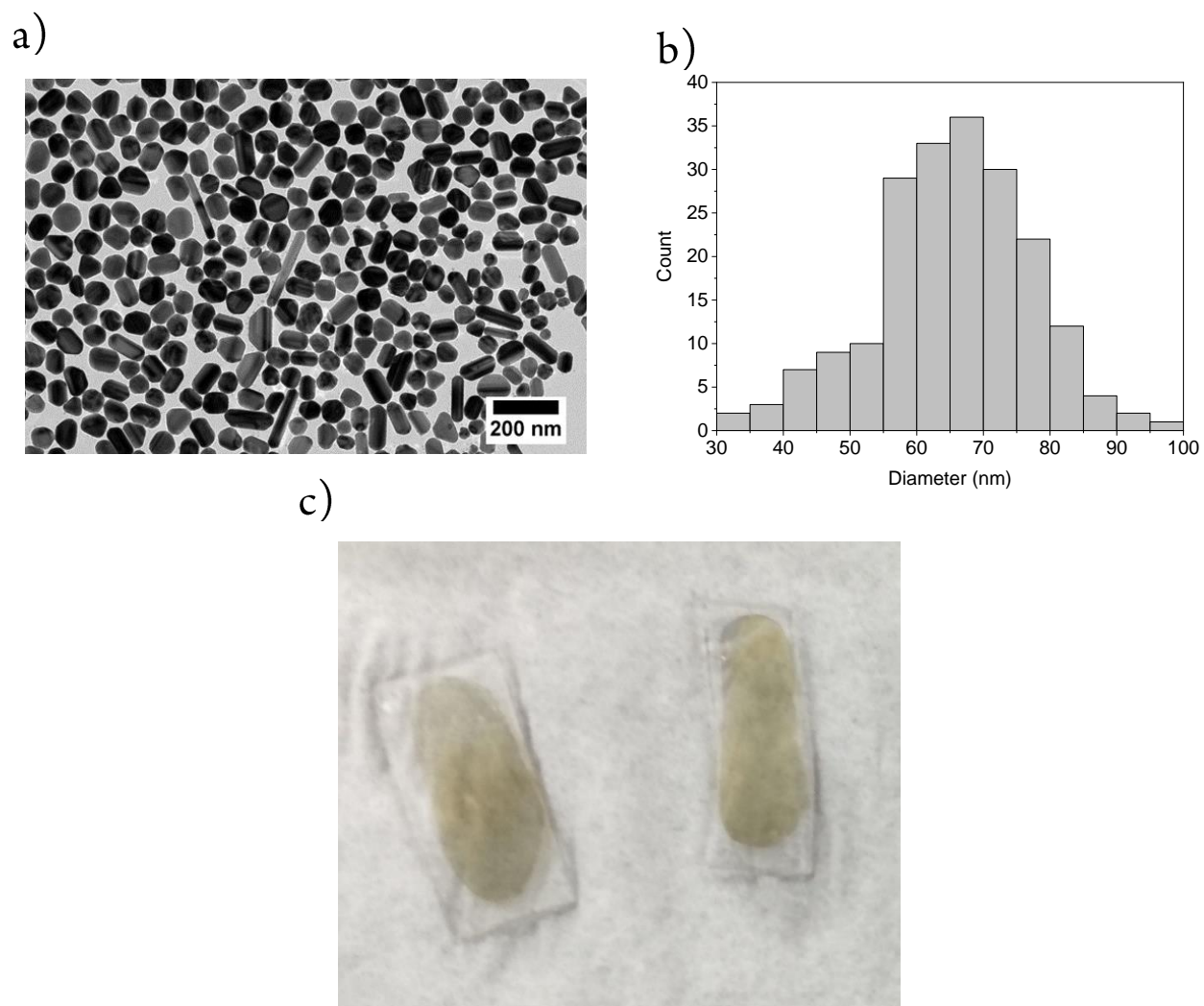


Figure S1: Silver nanoparticle characterization. a) TEM image of AgNPs (obtained on a JEOL JEM-2100 TEM). b) Size histogram of AgNPs. c) Photo of AgNP-modified glass slides.

SECM tip positioning: To approach the 4MPy/AgNP surface, we biased the SECM tip (Pt, 12.5 μm) to -0.8 V to achieve steady-state HER, as shown in Figure S2 (top). While using FcMeOH oxidation to approach fits theory¹ better, we opted not to use it for the initial approach since it interfered with our Raman signal. Still, HER allowed reasonable approaches to the substrate, and we carefully changed the solution to a FcMeOH solution at the end of the experiment. FcMeOH approach curves, illustrated in Figure S2 (bottom), show a better fit to theory and roughly agree with the HER approach curves with respect to tip-substrate distance.

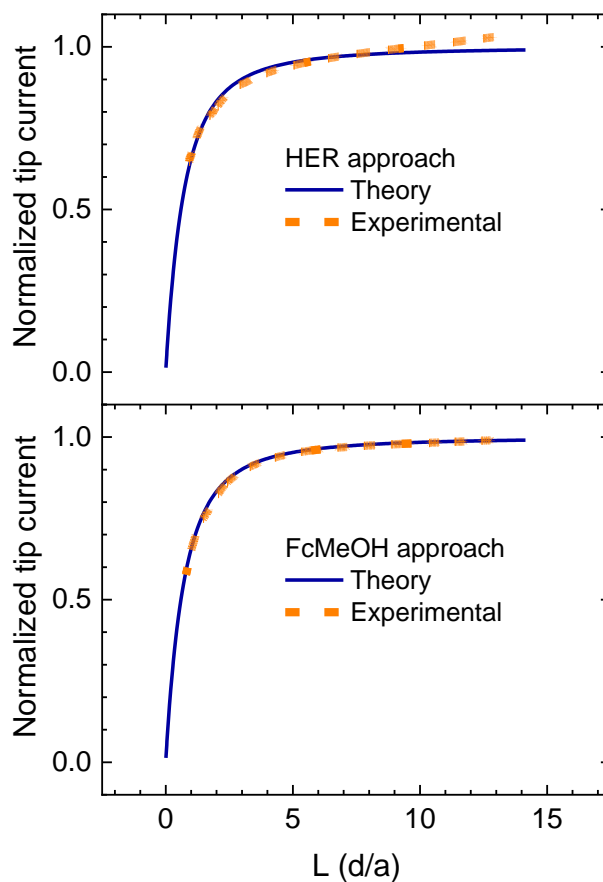


Figure S2: Approach curves for the SERS-SECM chronoamperometry experiment. Top) Initial approach curve for using HER (-0.8 V vs Ag/AgCl). Bottom) Approach curve after experiment using FcMeOH oxidation (0.5 V vs Ag/AgCl).

Peak assignment of 4-mercaptopyridine SERS spectra: Following peak assignments from Zhang, *et al.*,² the peaks at 1010 cm^{-1} and 1100 cm^{-1} are associated with ring breathing, with the 1100 cm^{-1} peak being particularly sensitive to the nature of the C-S bond. Interestingly, we see no significant trend arising between these two peak heights and pH, while others have observed the 1100 cm^{-1} peak increase in relation to the 1000 cm^{-1} peak at high pH values.^{3,4} We note that Yu, *et al.*,³ who observe a greater change in these peaks, used a gold substrate; Hu, *et al.*, used silver and observed smaller changes in these peaks. Thus, we speculate that the SERS material may affect how peaks are affected by pH changes. At low pH values, there is a pair of overlapping peaks just above 1200 cm^{-1} , with the peak closer to 1200 cm^{-1} disappearing at higher pH values. This agrees with other studies^{3,4} and arises because they are both C-H deformation modes, with the left/right peaks associated with

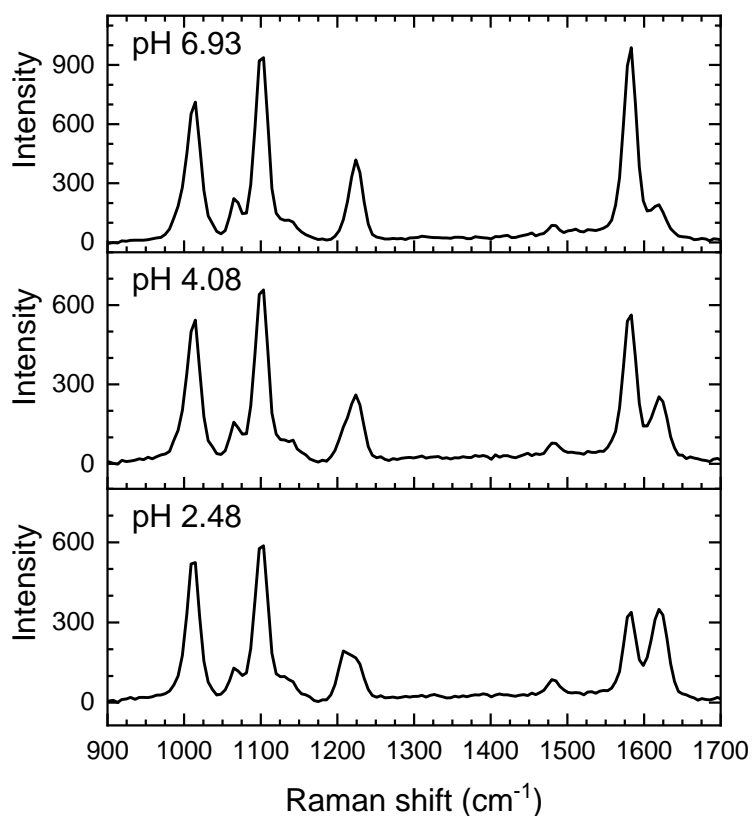


Figure S3: Raman spectra of 4MPy in citrate buffer solutions of varying pH

protonated/deprotonated 4MPy, respectively.

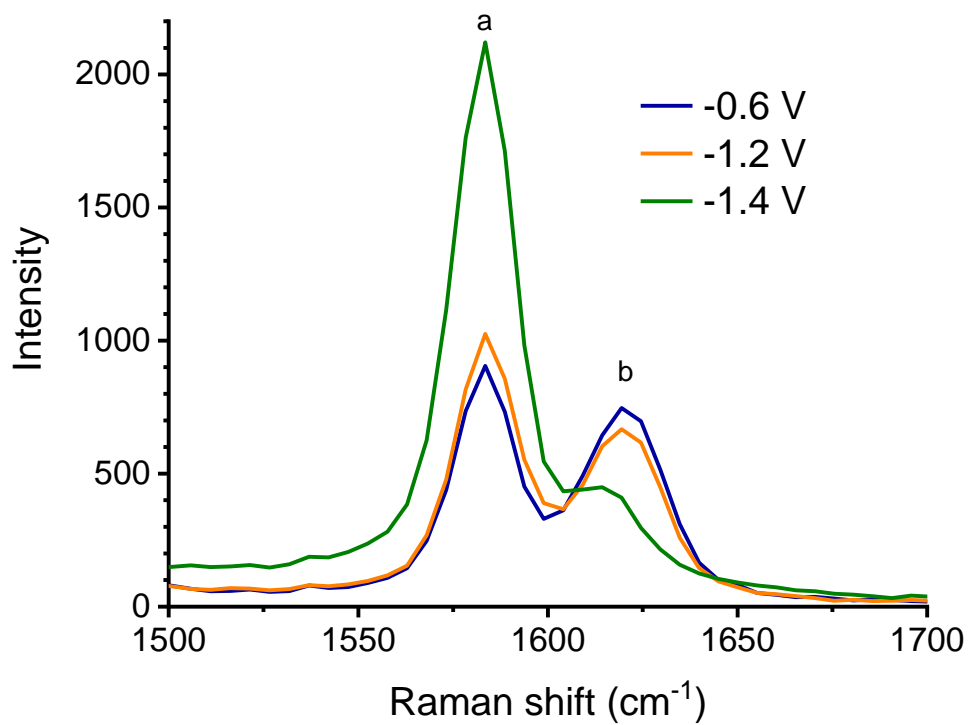


Figure S4: SERS spectra of 4MPy/AgNP surface while holding the tip at varying potentials during the chronoamperometric experiment (Figure 3 in the main text).

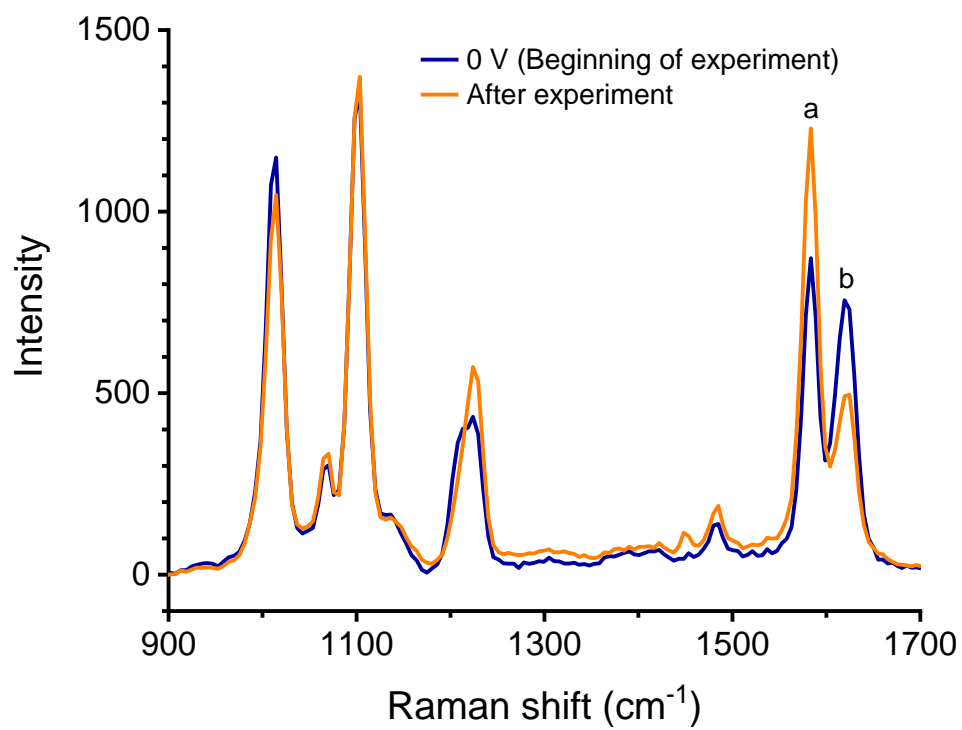


Figure S5: SERS spectra of 4MPy/AgNP surface at the beginning (blue) and end (orange) of the chronoamperometric SERS-SECM experiment.

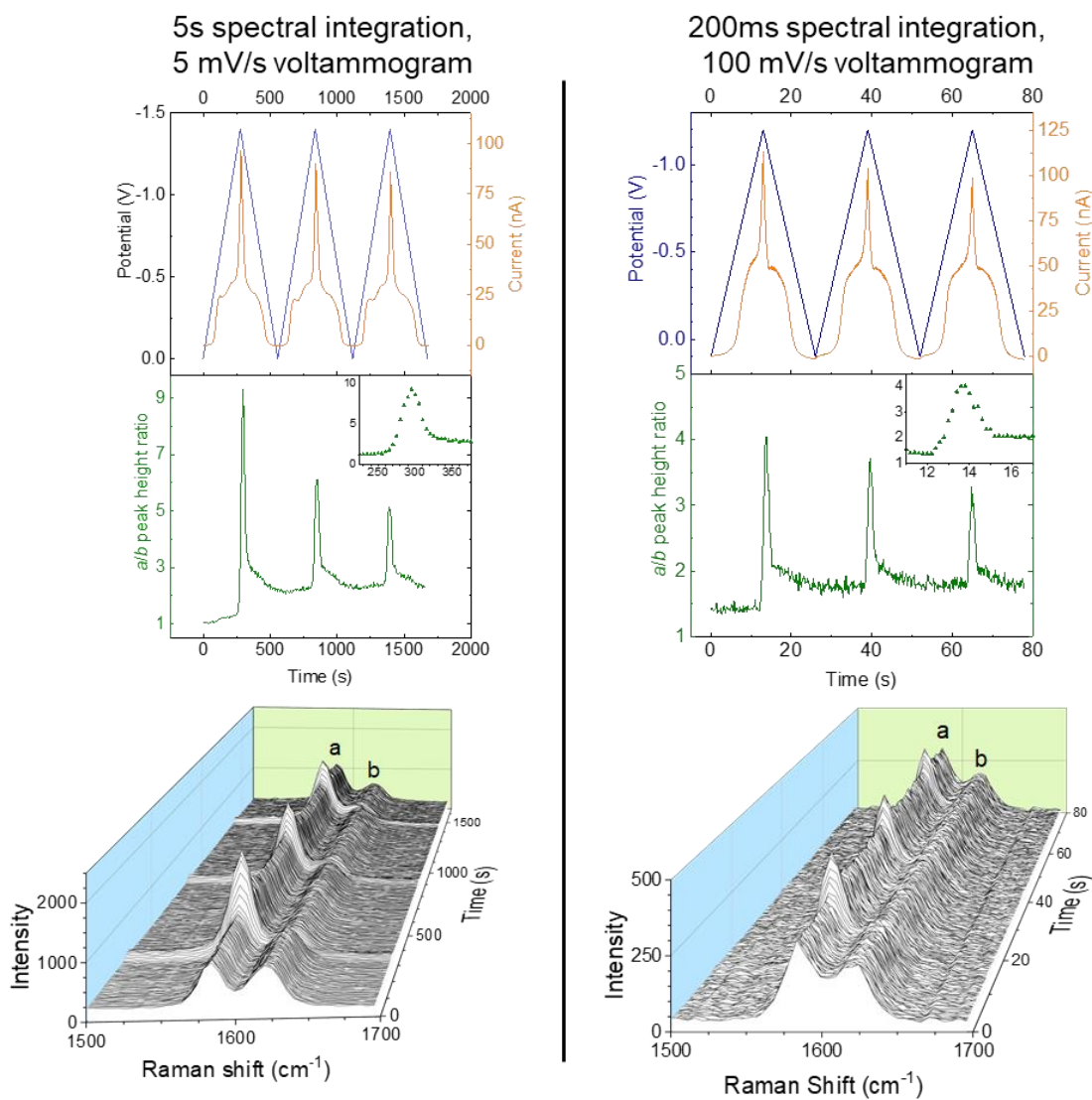


Figure S6: Cyclic voltammetric SERS-SECM experiments with both 5 s integration time (left) and 200 ms integration time (right). The top plots display the tip voltammograms and a/b peak height ratios, while the bottom plots show the spectral region containing these peaks over the course of the experiment. For the 5 s integration experiment, the tip was located 11 μm above the substrate (on a different sample) and the potential scan rate was 5 mV/s.

References

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