Electronic Supporting Information: Alkyl-Nitrile Adlayers as Probes of Plasmonically Induced Electric Fields

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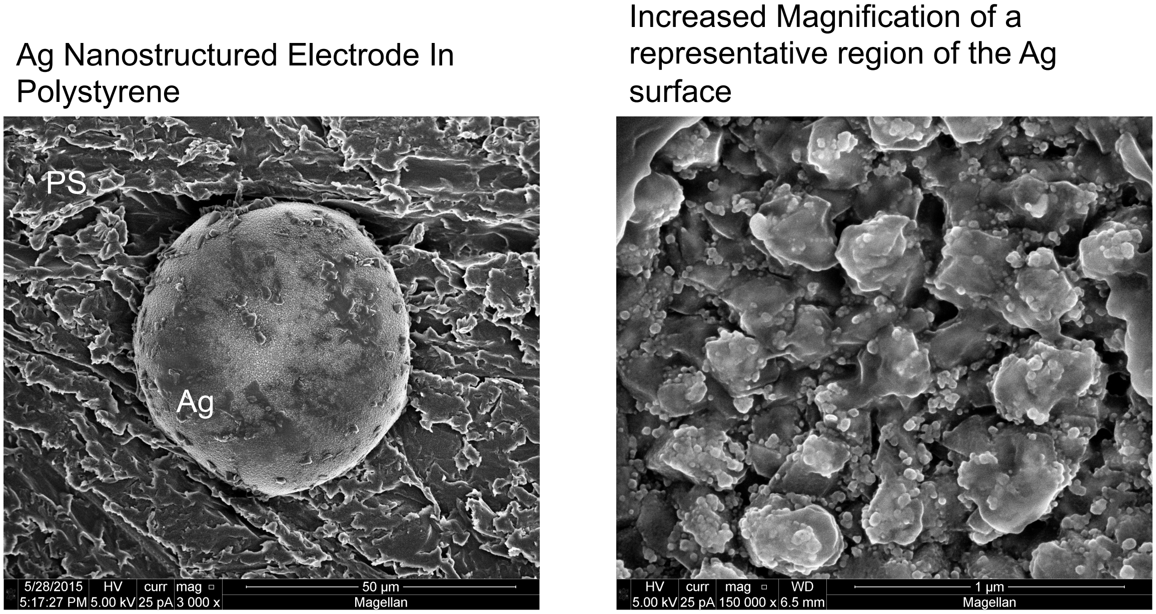
Summary: This electronic supporting information contains Figures S1- S5 referenced in the main manuscript text. Figure S-1 shows the scanning electron micrograph obtained from our deposited silver surface. Figure S-2 shows the spontaneous Raman spectrum of p-mercaptobenzonitrile and n-mercaptobutylnitrile. Figure S-3 shows the electrode and Raman maps obtained for n-mercaptobutylnitrile. Figure S-4 is the power dependent shft in the CN frequency observed for n-mercaptobutyl nitrile. Figure S-5 shows the time variation observed in the SERS spectra of n-mercaptobutylnitrile and p-mercaptobenzonitrile. Figure S-6 shows the fitting results from the CN region of the spectra shown in Figure 7.



Ag Nanostructured Electrode In Polystyrene

Increased Magnification of a representative region of the Ag surface

Whole electrode

150000x

Figure S-1. Scanning electron micrographs of our electrodeposited Ag surface in polystyrene (PS) show a heterogeneous surface on the nanoscale. The images were acquired with 5.00 kV using a Magellan scanning electron microscope. The polystyrene required a thin (1-2 nm) iridium coating to enable imaging.

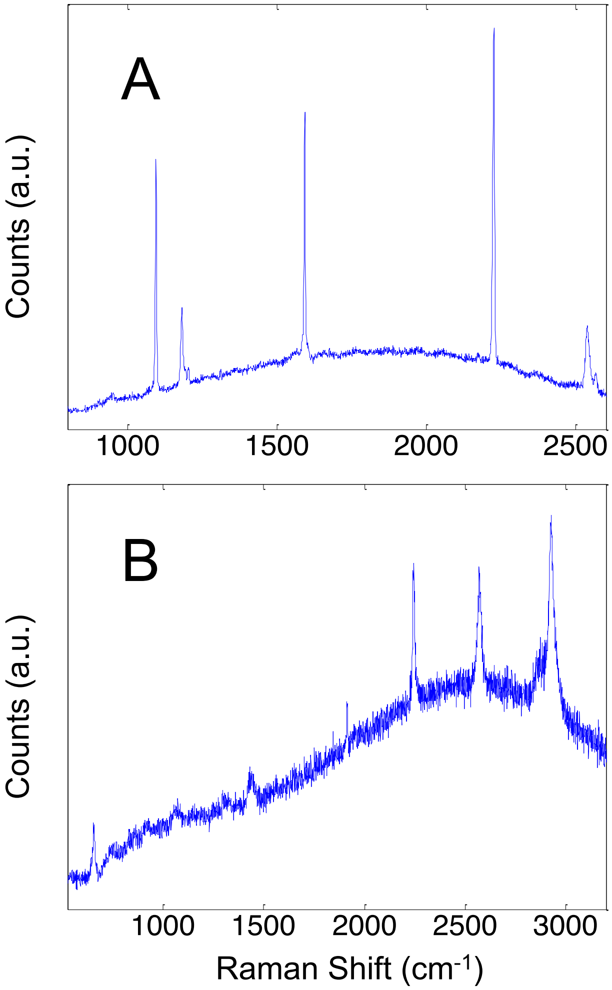


Figure S-2. The figure shows the Raman spectrum of neat p-mercaptobenzonitrile and n-mercaptobutylnitrile. A) The spectrum of crystalline p-mercaptobenzonitrile was acquired with 0.33 mW laser power for 10 s. B) The spectrum of neat n-mercaptobutylnitrile was acquired with 7.7 mW laser power for 10 s.

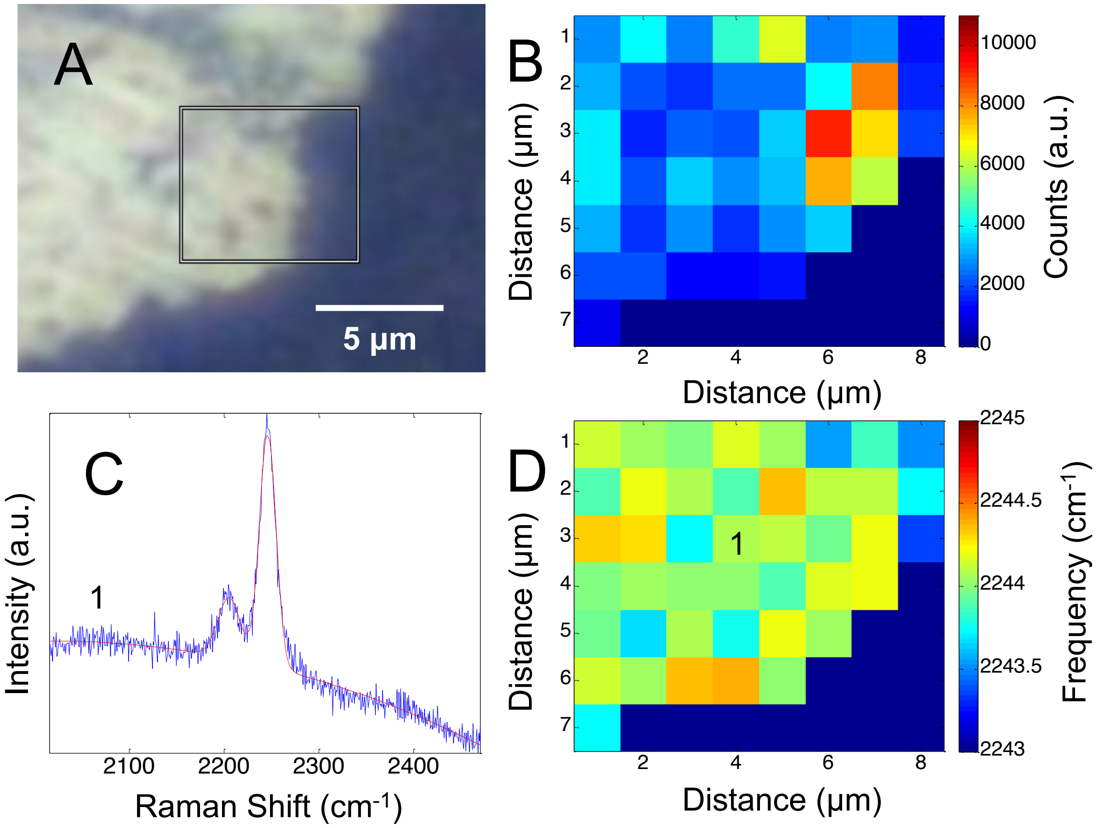


Figure S-3. A) The optical image of the roughened silver surface with n-mercaptobutylnitrile is shown. The box indicates the area where the Raman map (B) was acquired. The CN stretch frequency was determined by fitting a guassian lineshapes to each pixel. The spectrum observed is shown (C). The observed CN stretch frequency is plotted (D), showing a variation of up to 2 cm^{-1} across the electrode. The pixel (1) plotted in C is marked in D.

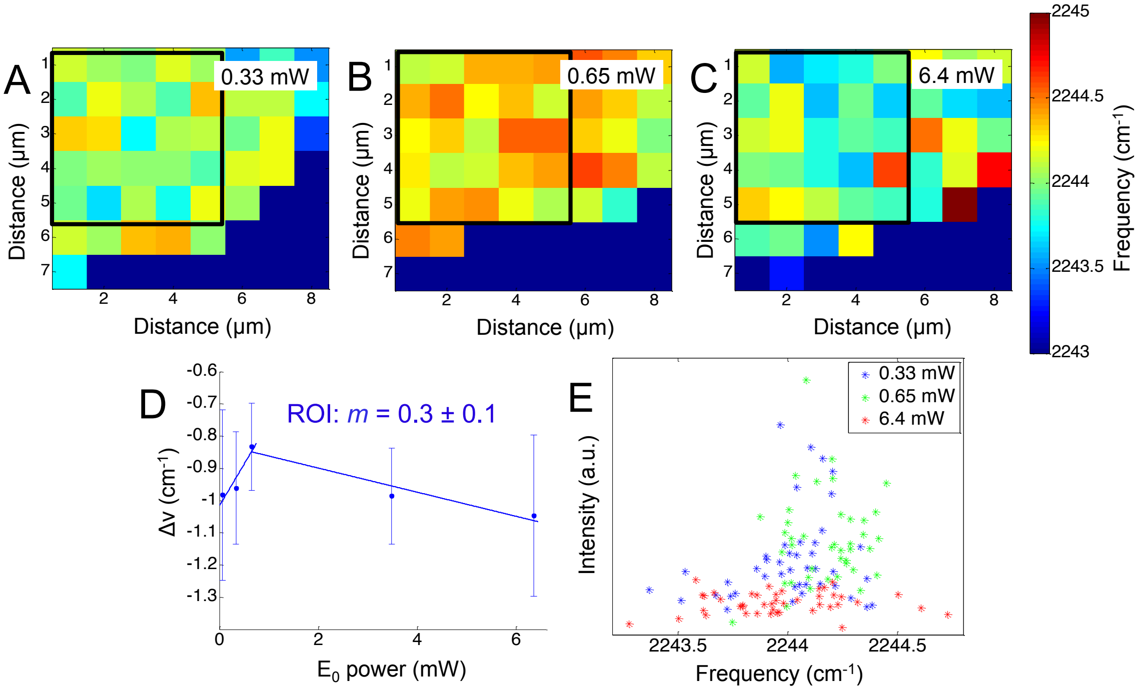


Figure S-4. The Raman maps fo the CN stretch intensity from n-mercaptobutylnitrile are plotted at different incident powers: A) 0.33 mW, B) 0.65 mW, and C) 6.4 mW. The CN frequency continued to shift with changes in the excitation laser power. Gaussian lineshapes were fit to the observed nitrile bands and the frequency of the higher energy component is plotted in D. The initial slope in CN frequency of 0.3 ± 0.1 cm^{-1}/mW was observed, similar to the high enhancement regions of n-mercaptobenzonitrile. Again, the same decrease in the ensemble frequency average was observed for $E_0 > 1$ mW, again suggesting photodegradation of the nitrile probe molecule. The Intensity of the higher energy CN band is plotted against its frequency (E). Compared to the adsorbed CN and the p-mercaptobenzonitrile maps, the CN frequency here was seen to be much more uniform, varying across only ~2 cm^{-1}.

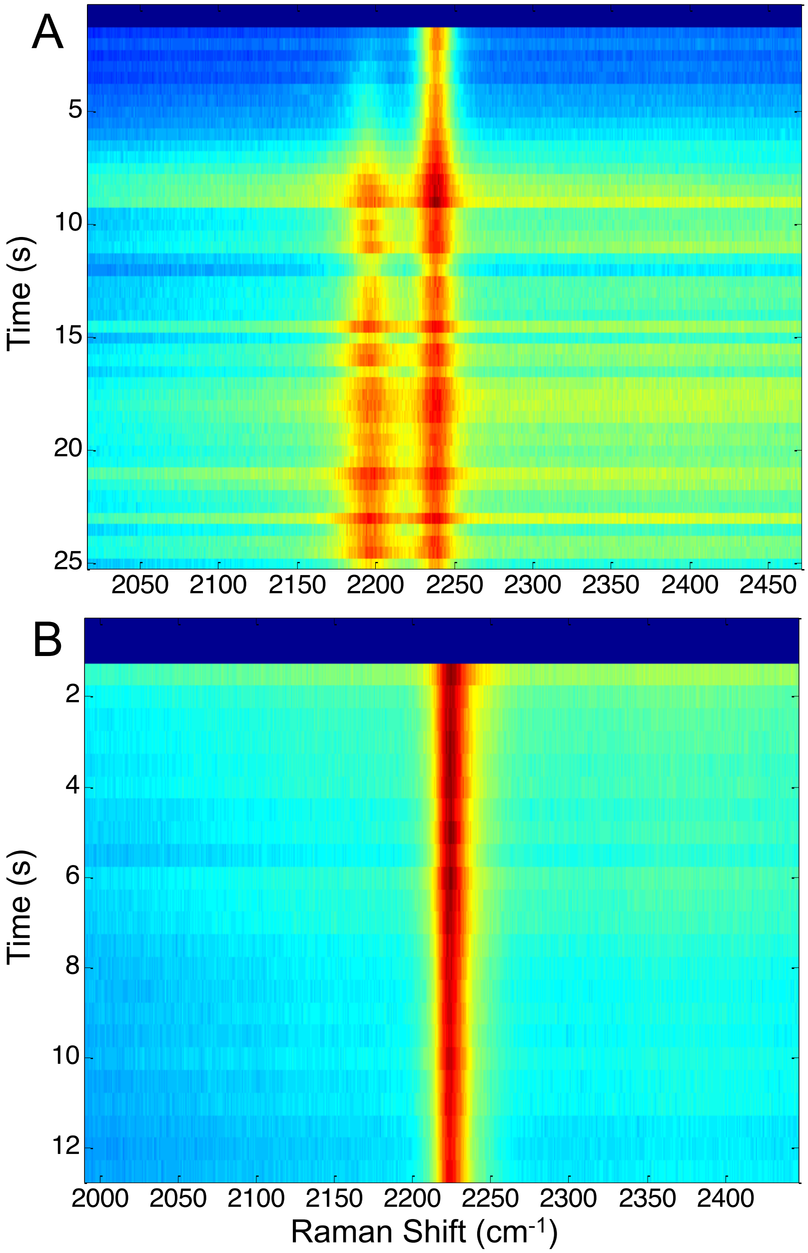


Figure S-5. Kinetic acquisition series of a single location of n-mercaptobutylnitrile (A) and p-mercaptobenzonitrile (B) adsorbed to roughened Ag. Spectra were acquired for 0.5 s (top) and 1 s (bottom) with a laser power of 0.7 mW. The first two spectra were acquired without the laser impinging on the surface to observe the immediate effect of the laser excitation.

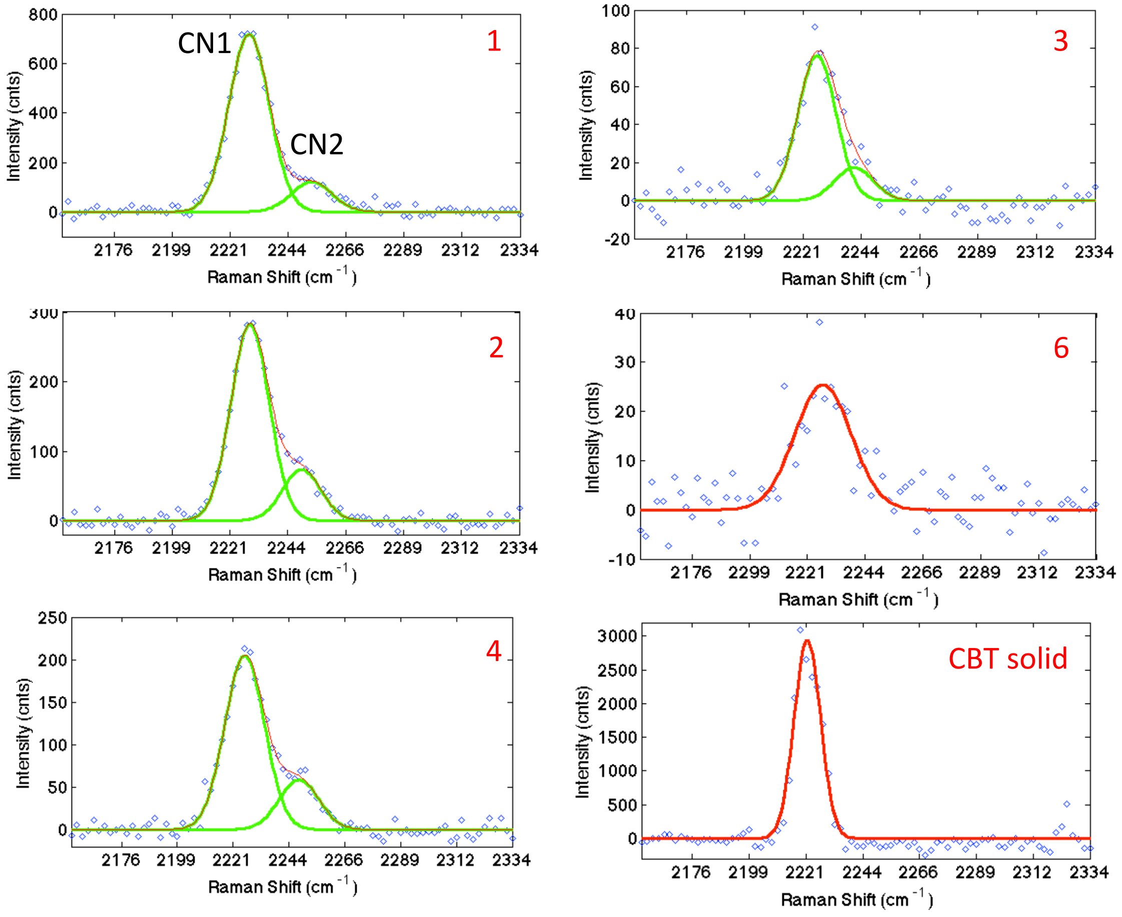


Figure S-6. The CN stretch region of the spectra obtained from Au nanoparticles on the p-mercaptobenzonitrile film in Figure 7 are shown. The spectra were fit with either 1 or 2 Gaussian lineshapes as shown. The numbers in the corners of the spectra correspond to the particle numbers in Figure 7.