Supporting Information:

Observing Plasmon Damping Due to Adhesion Layers in Gold Nanostructures Using Electron Energy Loss Spectroscopy

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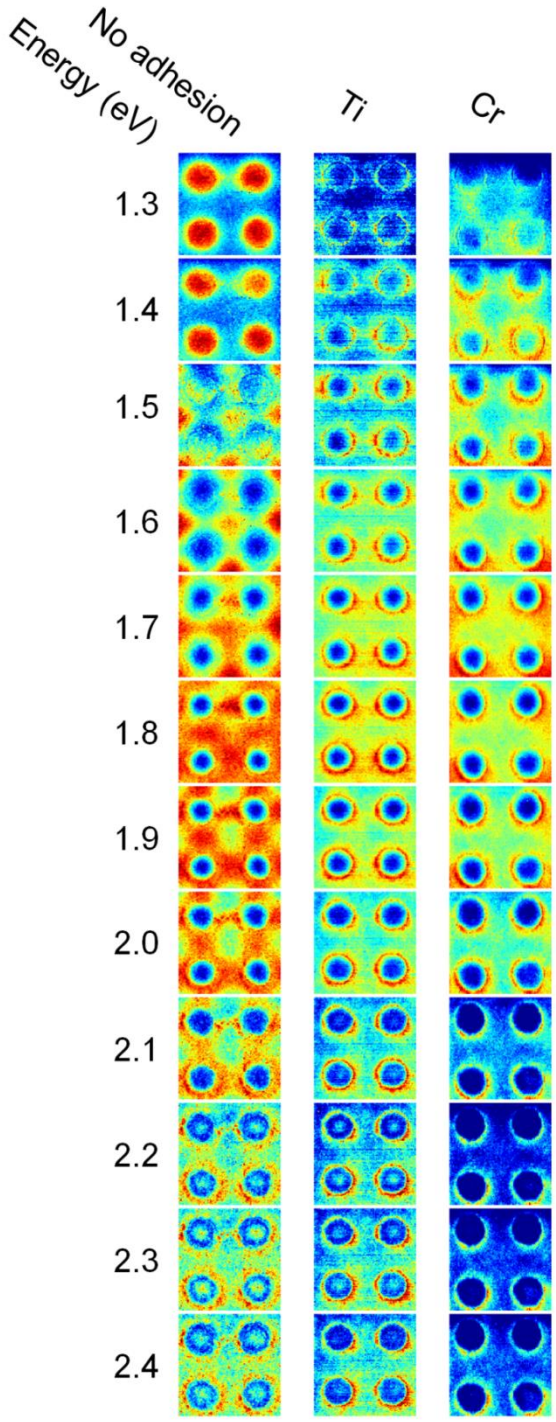
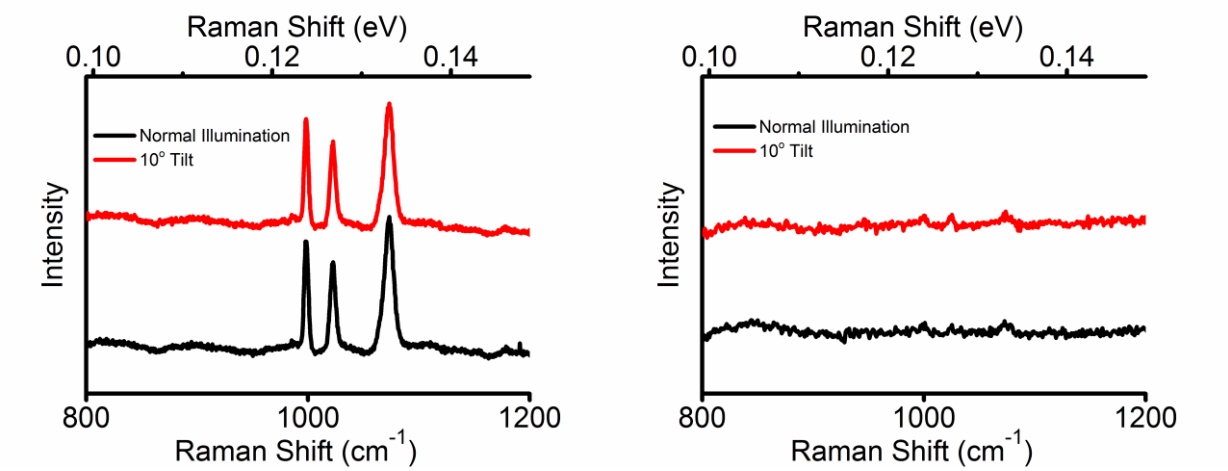
S1: Additional EELS Energy Slices



S1: Energy slices from all three samples at over the whole range of expected plasmon resonance energies. Only the sample with no adhesion layer shows clear periodic resonances at any energy.

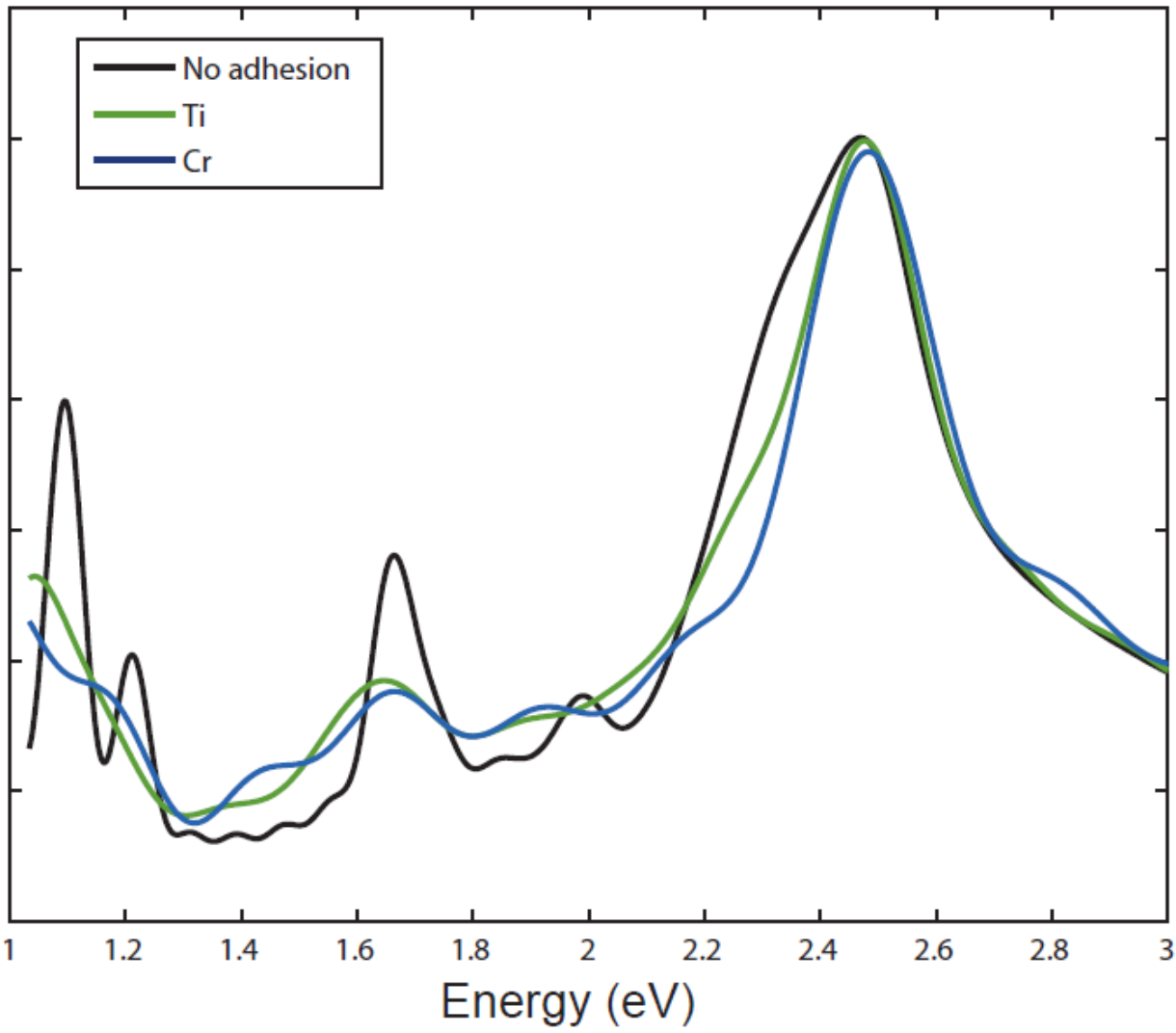
S2: Raman Spectra Collected Under Angled Illumination

Several additional Raman experiments have been performed in order to further support the claim that the plasmon mode at 2.3eV is optically dark. We evaluate two other possible explanations for the lack of SERS signal when illuminating with a 2.3eV laser. While Raman scattering is in general a frequency independent process, resonant conditions between the dye and the laser can also cause a dramatic increase in signal intensity. To confirm that the signal at 785nm is not a result of resonant Raman spectroscopy, the experiment was repeated with a thiophenol, a different dye. The same effect is observed (Figure S2), indicating the effect is independent of which dye is used. To verify the mode at 2.3eV is not excited under oblique illumination, the substrate is tilted by 10^{o} relative to the microscope objective. Again, no significant signal is observed (Figure S2), confirming the mode is optically dark.



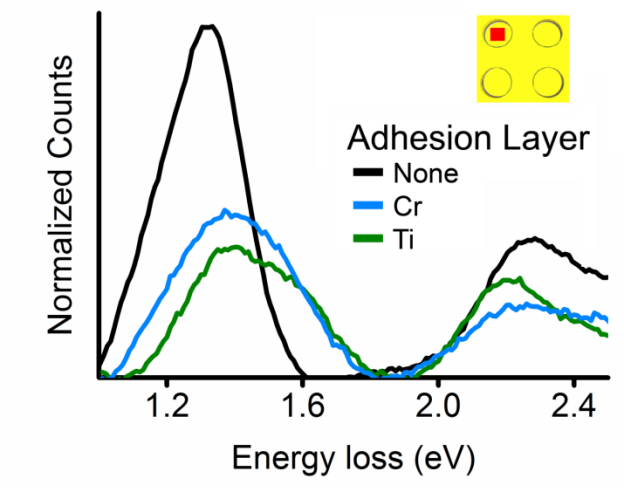
S2: Raman spectra of samples with no adhesion layer coated with thiophenol dye, taken with a 785nm laser (left) and a 532nm laser (right). Spectra were collected under normal illumination as well as with the substrate tilted 10^{o} relative to normal. The 10x microscope objective was used due to its longer working distance to allow for tilting of the sample.

S3: Purcell Factor Simulations



S3: Purcell factor simulation generated by placing a dipole above the array center position. Peaks are present at 1.2-1.3eV, 1.6-1.7eV, 1.9-2.0eV, and a shoulder at 2.3-2.4eV, matching the features measured in EELS (Figure 4). The large feature at 2.5eV is not observed in the experimental data, where it may be heavily damped by the d-band transition of gold, which occurs at approximately the same energy. Introduction of 2nm of Ti or Cr causes broadening and intensity reduction of the resonant modes, as observed in the experimental data.

S4: Background Subtracted Comparison of EELS Peak Intensities



S4: Background subtracted electron energy loss spectra collected from the location indicated by the inset, normalized by the height of the zero loss peaks. The relative intensities for the first peak are approximately 1, 0.48, and 0.37 for samples with no adhesion layer, Cr, and Ti respectively. The values for the second peak are 1, 0.71, and 0.53. As discussed in the main text, the exact values are sensitive to background subtraction.