UCLA College | Physical Sciences Chemistry & Biochemistry

Chem 218: Student Exit Seminar

NANOSCALE VIBRATIONAL SPECTROSCOPY OF GOLD-CYANIDE SELF-ASSEMBLIES: FROM MONOLAYERS TO CRYSTALLITES

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ABSTRACT: My thesis work focuses on the integration of scanning tunneling microscopy with infrared spectroscopy, to provide unprecedented Ångstrom-scale resolution in surface imaging with spatially correlated chemical specificity. Scanning probe techniques generally lack chemical information. Inspired by recent advances coupling optical spectroscopies with scanning probe microscopies, I have developed a nanoscale infrared spectroscopic method applying scanning tunneling microscope probe tips as nanoantennas to obtain multiplexed molecular vibrational signals utilizing a Fourier transform interferometer at room temperature and ambient pressure. The sensitivity of the tunneling junction and nanoscale probe area enables the measurement of vibrational spectra orders of magnitude below the diffraction limit. I substantiated the effectiveness of this instrument by designing an air- and temperature-stable model system characterized by infrared absorption that couples to the electronic states of the gold substrate. Specifically, aurous cyanide (AuCN) self-assembled monolayers satisfy these requirements with the added benefit that its IR absorption lies outside of the carbon dioxide and water windows, thereby maintaining a high signal-to-noise ratio for these experiments. These atomically pristine hexagonal close-packed AuCN monolayers exhibit a strong absorption at 2140 cm^{-1}. Upon thermal annealing, the surface rearranges into a ribbon structure with a blue-shifted absorption to 2230 cm^{-1}. The unique vibrational contrast in AuCN monolayers resulting from thermally induced structural changes serves as an ideal model system for the new infrared scanning tunneling microscope (IR-STM). Upon prolonged vapor deposition, the self-assembled cyanide monolayers reconfigure into large-scale AuCN crystals, giving two distinct morphologies and significantly different vibrational modes, compared to the AuCN monolayer structures. Once again, temperature can tune gold-cyanide orientation and long-range ordering. This work provides new insights for controlled surface-mediated crystal growth in AuCN systems. Ultimately, combining with the chemical information gained from the developed IR-STM, surface-mediated growth will enable new methodologies for fabricating next-generation nanoscale semiconductors. Nanoscale semiconductors based on AuCN that are similar to nanoribbon structures have been demonstrated to be useful for nanoelectronics as well as in catalytic applications.

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