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Was at The Pennsylvania State University**

Local Optical Spectroscopies for Subnanometer Spatial Resolution Chemical Imaging

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Progress

Instrumentation: Evanescently Coupled Visible Photon Scanning Tunneling Microscope

The evanescently coupled photon scanning tunneling microscopes (STMs) have special requirements in terms of stability and optical access. We have made substantial improvements to the stability, resolution, and noise floor of our custom-built visible-photon STM, and will translate these advances to our infrared instrument. Double vibration isolation of the STM base with a damping system achieved increased rigidity, giving high tunneling junction stability for long-duration and high-power illumination. Light frequency modulation with an optical chopper and phase-sensitive detection now enhance the signal-to-noise ratio of the tunneling junction during irradiation.

We have optimized the evanescent coupling of the sapphire crystal with the Au{111} film. Semitransparent thin films (~30 nm) of Au{111} were grown by electron-beam evaporation on epi-polished Al₂O₃(0001) sapphire prisms seeded with 2-nm Nb layers. A diode laser ($\lambda = 405$ nm, 2 mW) and a He-Ne laser ($\lambda = 633.8$ nm, 10 mW) have been used to measure the angle and wavelength dependency of evanescent wave generation by total internal reflection.

Figure 1. (A) A STM image of anthracene-terminated phenylethylenethiol (AnPE) molecules (circled) inserted into n-dodecanethiolate (C12) SAM matrix. (B) The current-voltage characteristics of a single AnPE molecule, showing a substantial increase in current relative to the surrounding matrix. The fluctuations in current are attributed to molecular motion during transition between ON and OFF states. The ability to switch can be photomodulated in our experiments by dimerizing adjacent molecules. The ability to record such spectra is an indication of our enhanced stability.

We have observed conductance switching of isolated anthracene-terminated phenylethylenethiol (AnPE) molecules in self-assembled monolayers (SAMs) with this STM. A promising candidate for molecular electronic devices, these fully conjugated molecules were synthesized by the Alex Jen group at the University of Washington and were selectively inserted into well-ordered *n*-dodecanethiolate self-assembled monolayer (SAM) matrices (Figure 1A). Isolated AnPE molecules showed active stochastic conductance switching (Figure 1B) between high (ON) and low (OFF) conductance states. We observe apparent protrusions several Ångströms beyond the surrounding matrix in STM images when the molecules are in the ON state. Ultraviolet illumination ($\lambda=365$ nm, 0.2 mW) activated a [4+4] cycloaddition reaction, intermolecularly dimerizing adjacent anthracene moieties. This resulted in a dramatic conductance decrease, leading to a photomodulated OFF state (Figure 2) with diminished contrast in STM images.

Figure 2. (A) Schematic illustration of photomodulated conductance switching for isolated anthracene-terminated phenylethylenethiol (AnPE) molecules. (B) Scanning tunneling microscopy images of inserted AnPE molecules with exposure to UV light. Switching frequency is monitored under illumination at noted duration times.

systems to determine their intrinsic photoconductivity (and to optimize our measurements further).

We continue working on the dyad/triad molecules for organic solar power applications. We have achieved submolecular resolution, but required these instrument enhancements in order to enable the key measurements of intrinsic photoconductance. While we have been using two single-frequency photon sources, we will require broadband monochromatic illumination, and have ordered a source for this.

Instrumentation: Evanescently Coupled Infrared Photon Scanning Tunneling Microscope

We continue to use the visible photon STM to guide the development of the infrared excitation STM (IR STM). In our initial experiments, we use similarly prepared substrates, Au{111} on Nb-seeded sapphire prisms, described above. These have a transmission window in the near- to mid-infrared, and are suitable for initial tests and calibrations. Later

With the optimization of the visible-photon STM instrument, we are now prepared to investigate a number of self-assembled molecular and nanoparticle

experiments will employ Ge prisms, with epitaxial metal layers, with broad transmission in the mid- and far-IR.

Our initial IR STM experiments involve small molecules with strong IR absorptions, such as 4'-acetyl-4-mercaptobiphenyl. This molecule was chosen because one can synthetically alter the orientation and position of the carbonyl functional group between the ortho', meta', and para' positions. The ability to alter the angle of the dipole related to the vibration with respect to the surface normal will allow us to elucidate the selection rules for this new spectroscopy. After initial optimization, this instrument will probe the coupling of the different vibrational modes of precise assemblies of single molecules with their surrounding matrices. Ultimately, we will be able to explore surface chemistry by determining bonding changes of molecules in precisely defined (and measured) environments.

Photoisomerization of 1D Assemblies

While control of single molecules and pairs of molecules is interesting, we would like to be able to have molecular actuation of assemblies (in analogy to muscles). This remains a major challenge, and the rules for coupling between active molecules are not yet understood. Proximity of switching molecules in assemblies on surfaces produces results that are not observed in isolated adsorbed molecules. We are using the instruments developed here, in combination with specialized assembly techniques to elucidate the mechanical and electronic coupling within such assemblies. We assembled precisely defined 1D linear chain structures of azobenzene-functionalized molecules, 4-[2-(4-phenylazo-phenyl)-ethoxy]-butane-1-thiol (**1**). The molecules arrange in pairs to make the chains and assemble at the boundaries of decanethiolate (**C10**) domains on Au{111} (Figure 3).

*Figure 3. STM image ($V_s = 1\text{ V}$, $I_{\text{tunnel}} = 1\text{ pA}$) of chains of **1** assembled at the boundaries of **C10** domains on Au{111}. Inset shows chain structure with two chains; each unit of the chain contains a pair of molecules.*

*Figure 4. A) STM image ($V_s = 1\text{ V}$, $I_{\text{tunnel}} = 1\text{ pA}$) of chains of **1** at a boundary of **C10** domain. B) Upon UV illumination, part of the chain isomerizes from trans to cis. STM image ($V_s = 1\text{ V}$, $I_{\text{tunnel}} = 1\text{ pA}$) shows isomerized portion of chain (white square area).*

We controlled *in situ* photo-switching of these 1D assemblies and studied the effects of local environment and coupling on switching efficiency. Upon UV illumination, molecules in chains switch (from *trans* to *cis*) in bundles, suggesting that there is significant coupling between the molecules, resulting in collective behavior (Figure 4). Ongoing work seeks to elucidate the nature of the coupling, (*i.e.*, electronic *vs.* mechanical).

Supported Personnel

Prof. Paul S. Weiss, PI

Dr. Patrick Han, Postdoc (now an Assistant Professor of Physics at Tohoku University)

Dr. Dongbo Li, Postdoc (now a Staff Scientist at Hitachi GST in San Jose, CA)

Dr. Wei Xu, Postdoc (now a Full Professor at Tongji University)

Ms. Moonhee Kim, Graduate Student (now a postdoc at IBM Almaden and Stanford)

Mr. Amit Vaish, Graduate Student (now a postdoc at the University of Delaware)

Publications

“Reversible Photo-Switching of Single Molecules in Controlled Nanoscale Environments,” A. S. Kumar, T. Ye, T. Takami, B.-C. Yu, A. K. Flatt, J. M. Tour, and P. S. Weiss, *Nano Letters* **8**, 1644-1648 (2008).

“Functional Molecules and Assemblies in Controlled Environments: Formation and Measurements,” P. S. Weiss, *Accounts of Chemical Research* **41**, 1772-1781 (2008).

“Cluster-Assembled Materials,” S. A. Claridge, A. W. Castleman, Jr., S. Khanna, C. B. Murray, A. Sen, P. S. Weiss, *ACS Nano* **3**, 244-255 (2009). (minor DoE support)

“Creating Favorable Geometries for Directing Organic Photoreactions in Alkanethiolate Monolayers,” M. H. Kim, J. N. Hohman, Y. Cao, K. N. Houk, H. Ma, A. K.-Y. Jen, and P. S. Weiss, *Science* **331**, 1312-1315 (2011).

Awards

Moonhee Kim won the American Chemical Society, Division of Colloid and Surface Chemistry, Best Poster Award.

Moonhee Kim was awarded the Braucher Research Fellowship.

Paul Weiss gave the University of Oklahoma, Department of Chemistry and Biochemistry, J. Clarence Karcher Lecture.

Paul Weiss gave the Texas A&M University, Department of Chemistry Frontiers Lectures.

Paul Weiss was elected Senior Member of the IEEE.

Paul Weiss gave the Prof. J. W. McBain Memorial Lecture at the National Chemical Laboratory, Pune, India.

Paul Weiss gave the Hong Kong University of Science and Technology, Institute for Advanced Study Distinguished Lecture.

Paul Weiss gave the Thomas Jefferson University, William Potter Lecture.

Paul Weiss was elected a fellow of the American Chemical Society.