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The long-term oal of this project is to develop transistors and switches based on single molecules. Since transistors and switches are central components in every electronic circuit and devices based on single molecules are everal orders of magnitude smaller than current semiconductor transistors, this project may lead to the ultimate miniaturization of analog and digital circuitry.

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Controlling Electron Transfer Through Single Molecules

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Final Report
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OBJECTIVES

This project is aimed at probing electron transfer through a single molecule sandwiched between two electrodes ("source" and "drain") in an electrolyte. The electron flow is controlled by the bias voltage between the electrodes, the separations between molecule and the electrodes as well as by a third electrode ("gate") inserted into the electrolyte. The long-term goal of this project is to develop transistors and switches based on single molecules. Since transistors and switches are central components in every electronic circuit and devices based on single molecules are several orders of magnitude smaller than current semiconductor transistors, this project may lead to the ultimate miniaturization of analog and digital circuitry.

The specific objectives of this project are to:

- Investigate how electron transfer through single molecules can be controlled by the electrode voltages and by the molecule-electrode separation.
- Determine how the electron transfer depends on the intrinsic properties of the molecules.

STATUS OF EFFORT

Controlling Electron Transfer Through Single Molecules with Scanning Tunneling Microscope (STM)

We have studied electron transfer through single transition metal atoms/ions and C_{60}. In order to place a metal atom at an appropriate position between two electrodes, we embedded it into an organic matrix. Using this strategy, we have successfully studied electron transfer through several metal atoms as a function of "gate" voltage and "source-drain" bias voltage. A resonant enhancement in the tunneling current that resembles the phenomenon in mesoscopic quantum dot systems has been observed at room temperature. In order to place C_{60} onto an electrode, we have modified C_{60} by attaching a phenanthroline group to it. The phenanthroline immobilizes the C_{60} on the electrode and also isolates the C_{60} electronically from the electrode, which is essential for observing single electron charging effect. The current vs. voltage plots reveals a staircase-like feature that is similar to the well-known Coulomb Staircase in mesoscopic systems. While the phenomena of resonant tunneling and Coulomb blockade in the microscopic molecule systems resemble those observed in mesoscopic quantum dot systems, we have found that molecule-electrode interactions and structural relaxations induced by single electron charging play much more important roles in the microscopic systems than in the mesoscopic systems.

Fabricating Stable Molecular Junctions

The STM approach has provided valuable information about electron transfer through single molecules, but it is not suitable for a practical device. One solution is to replace the STM tip and the substrate with two nanoelectrodes supported on a solid substrate. We have developed a method to fabricate a pair nanoelectrodes separated with a gap on the order of a few atoms. In the method, we start with a thin metal wire laid on a substrate and covered with an insulation layer except a small portion. The small portion is then etched electrochemically during which the conductance of the wire is monitored. When the width of the portion reaches the electron Fermi wavelength, which is on the order of the size of an atom, the conductance becomes quantized at which stage etching is automatically stopped. By gently etching off the few atoms, a gap of a few atoms is formed which can be used to connect to single molecules.

ACCOMPLISHMENTS/NEW FINDINGS

A. Electron transfer through single transition metal atoms/ions

A metal cluster sandwiched between two electrodes is one of the most well studied quantum dot systems. To observe the discrete nature of charge (Coulomb blockade) and energy (resonant tunneling) at room temperature, the cluster has to be smaller than a nanometer. We have been studying electron transfer through single metal atoms embedded in an organic matrix, which allows us to probe both the discrete natures of charge and energy at room temperature.

The existing examples of molecules with a transition metal atom located at the center of an organic matrix are transition metal phthalocyanine or porphyrins. These molecules are attractive because their electronic states can be flexibly modified by placing different metal ions at the center. We have performed a macroscopic measurement of the electron transfer current between graphite electrode and iron phthalocyanine molecules as a function of the electrode potential and observed four pairs of peaks (Figure 1). The four peaks below the x-axis correspond to four successive electron transfers into the molecule from the electrode, and the four peaks above the x-axis are due to the reverse process, electron transfers from the molecule back to the electrode. The symmetry of the peaks indicates that the electron transfer process is completely reversible. These data show that the iron phthalocyanine molecule has at least four distinctive charging states and one can reversibly switch the molecule from one charging state to another by adjusting the electrode potential. In terms of applications in electronics, each charging state may represent a logic state.

Using STM, we have studied an interesting resonant tunneling in the electron transfer through transition metal porphyrins and phthalocyanines. By controlling the "gate" voltage, the resonant tunneling can be turned on and off which may be used as a molecular switch. Some of the findings are summarized below:

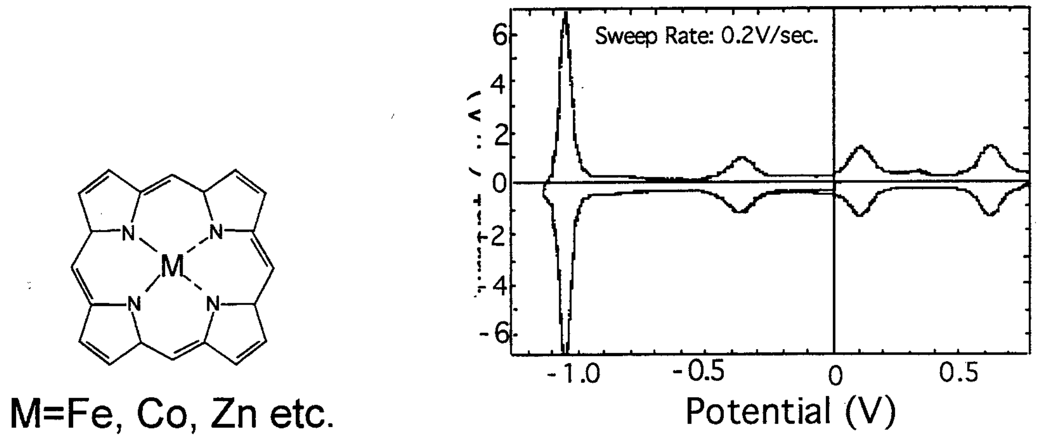

Figure 1. Left: Schematic of a transition metal porphyrin. Right: Electron transfer current between graphite electrode and tetrasulfonated iron phthalocyanine vs. the electrode potential in 0.05 M $KClO_4$.

A1. Resonant tunneling

We have studied resonant tunneling as a function of the "source –drain" bias voltage (Fig. 2) and found a clear dependence of the tunneling on the metal ions which can be attributed to the difference in the electronic states of the different metal ions (in collaboration with Prof. Linsday at ASU). This effect may help us to choose appropriate metal ions to tune the electronic properties of single molecule devices. While the observation can be qualitatively explained in terms of the transport theories developed for mesoscopic systems, several complications, such as molecule-electrode interactions and structural relaxations, were found.

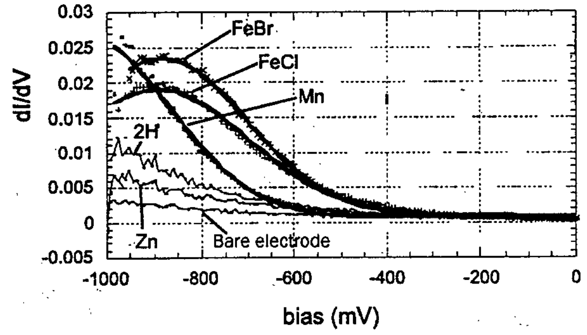

Figure 2. Electron transfer through Fe, Mn, Zn and H embedded in tetraphenol porphyrin.

A2. The importance of molecule-electrode interaction

We have studied Fe-cyclic molecules on both graphite and gold electrodes. On graphite, a clear resonant tunneling was observed as function of the "gate" voltage. However, on gold electrodes, no resonant enhancement in the tunneling current has been observed (Fig. 3). The striking difference is because that the metal ion, Fe, interacts with the metal (gold) electrode much more strongly than it does with the graphite electrode, and the strong interaction changes the Fe electronic states. This result demonstrates the importance of molecule-electrode interaction in microscopic single molecule systems, which is in sharp contrast to the mesoscopic quantum dot systems in which the probing electrodes are not expected to significantly change the electronic properties of the quantum dot.

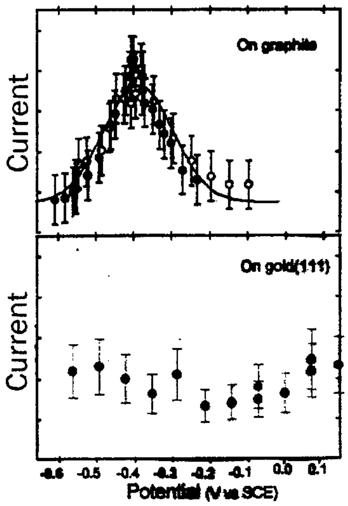

Figure 3. Electron tunneling through Fe-porphyrin on graphite and gold electrodes.

A3. The importance of structural relaxation due to single electron charging

Another important phenomenon associated with electron transfer through single molecules is structural relaxation in the molecules as a result of single electron charging. When charging a mesoscopic quantum dot made of thousands of atoms, the structural rearrangement (relaxation) is usually small. However, adding or removing a single electron to or from a small molecule can lead to a large structural rearrangement. This effect must be considered in the construction of devices based on single molecules. Using an Atomic Force Microscope (AFM), we have been able, for the first time, to directly measure such structural rearrangement in Cytochrome C (metal ion, Fe, embedded in a cyclic compound, which is then wrapped around by chain-like amino acid. Fig. 4-5).

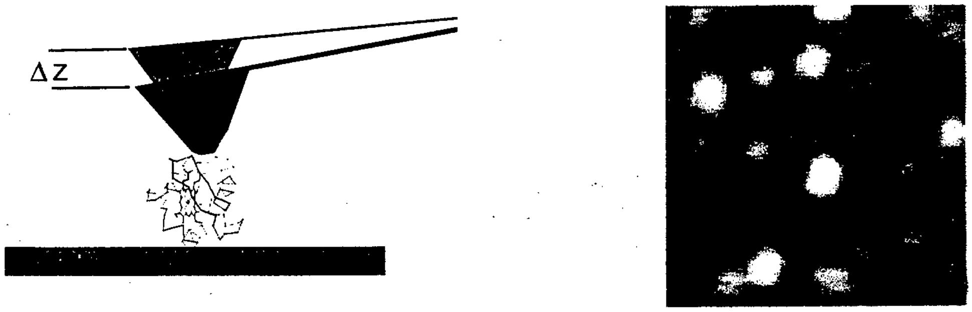

Figure 4. Detecting single electron charging induced structural relaxation in Cytochrome c with Atomic Force Microscope (AFM). The image on the right shows individual molecules as blobs of 20 nm in diameter (the actual diameter is 4-5 nm).

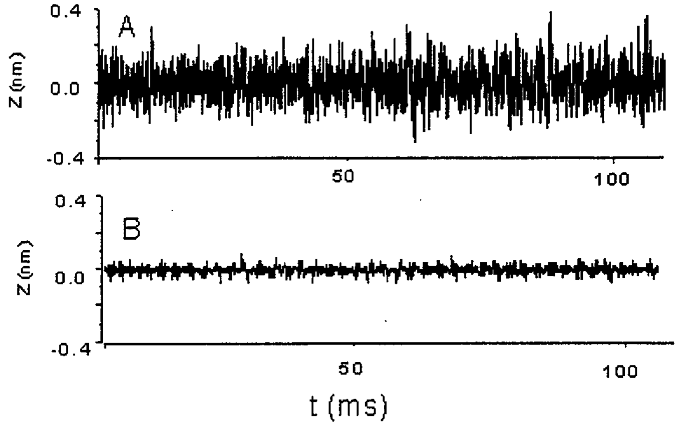

Figure 5. A. Electron charging/discharging induced structural fluctuation in Cytochrome c. B. Background noise.

A4. Theoretical modeling

Theoretical models for describing electron transfer via metal or semiconductor quantum dots (mesoscopic) are well developed. However, as shown above, the models cannot be directly applied to the electron transfer via a single molecule. A successful theory for the electron transfer through single molecules must take into account molecule-electrode interactions and structural relaxation upon charging or discharging. Both effects have been considered in a recent theory by Prof. Wolfgang Schmickler. In collaboration with Prof. Schmickler, we have applied the theory to the electron transfer through a single molecule sandwiched between two electrodes. The calculation explains our experimental data on iron porphyrins reasonably well (Fig. 6).

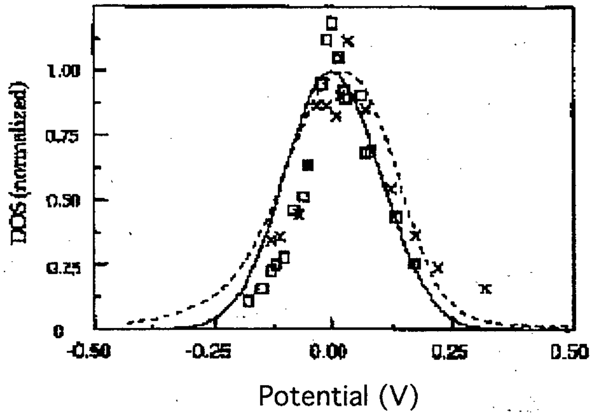

Figure 6. Density of states of iron protoporphyrin. The squares and crosses denote the values derived from the experimental data for a W and for a Pt-Ir tip, respectively. The full line is for a semi-classical model and the dashed from the quantum model.

B. Electron transfer through single C_{60}

We have also studied electron transfer through single C_{60} because of the following reasons: (1). The energy gap between the highest occupied energy level and lowest unoccupied level of C_{60} is about 1.5 eV, much greater than room temperature thermal energy, which makes it easy to probe the discrete nature of energy. (2). The single electron charging energy is significantly greater than room temperature thermal energy because its dimension is about 1 nm, which makes it a good system for studying the discrete nature of charge. (3). The lowest unoccupied energy level has a six-fold degeneracy, which can accommodate up to six electrons. As shown by recent *ab initio* calculations, the accommodation of the six electrons does NOT result in any large structural relaxation, which simplifies data analysis.

B1. Attaching C_{60} onto electrode.

In order to study electron transfer through single C_{60}, one has to be able to attach individual C_{60} onto an electrode. While C_{60} is known to adsorb on a number of metal and semiconductor electrodes, the electronic coupling between C_{60} and the electrode surfaces is usually too strong. To study single electron charging effect, the first challenge is to electronically isolate C_{60} from the electrodes so that the tunneling resistance at the molecule-electrode junctions is much greater than resistant quantum. After many unsuccessful attempts, we have finally found a successful solution by attaching each C_{60} with a phenanthroline group (synthesized by Prof. Echegoyen's lab at University of Miami). The phenanthroline group binds strongly on gold electrode, and, at the same time, serves as a buffer layer that electronically isolates C_{60} from the electrode (Fig. 7).

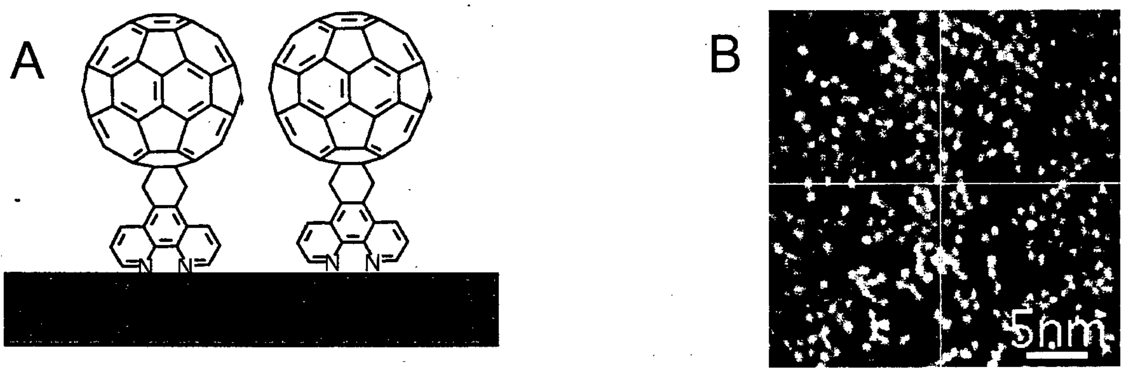

Figure 7. (A). Schematics of phenanthroline-modified C_{60} on gold electrode. (B). STM image of the modified C_{60}.

B2. I-V measurement

With the phenanthroline modified C_{60}, we have performed I-V measurement as shown in Fig. 8A. Staircase-like feature is clearly seen in the plots. For comparison, we have also measured I-V curves of phenanthroline monolayer, which gives the ohmic linear curves as shown in Fig. 8B. While the staircase feature can be qualitatively explained based on single electron charging effect, the discrete nature of energy levels of C_{60} must also be taken into account.

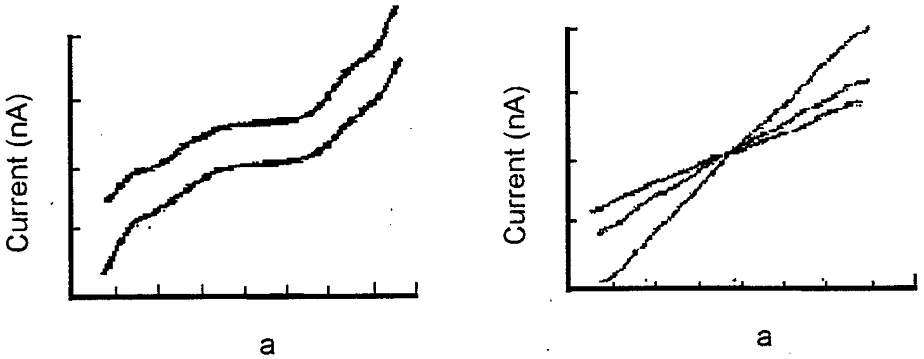

Figure 8. I-V curves of C60-phenanthroline derivative (A) and phenanthroline (B).

C. Fabrication Of Stable Molecular Junctions

For practical applications, the STM approach described above is not suitable because it lacks long-term stability. In order to fabricate stable molecular junctions, we have applied electrochemical deposition/etching method to fabricate probing electrodes with a gap on the order of a few atoms. Bridging the gap with a molecule, a molecular junction may be fabricated.

C1. Conductance quantization in nanowires fabricated by etching/deposition

In order to demonstrate the principle of the method, we started with an STM set-up (Fig. 9) in which an Apiezon wax-coated $Pt_{0.8}$-$Ir_{0.2}$ or Au tip mounted on a modified STM scanner is driven towards a Au(111) substrate in 1mM Cu_2SO_4 + 0.1 M H_2SO_4 until a tunneling current of 20 nA is achieved. The tip is then withdrawn from the substrate and held at a distance varying from 10 to 150 nm. The potentials of the tip and the Au substrate with respect to a reference electrode inserted in the electrolyte are controlled by a bipotentiostat. The tip potential is set at a value in the regime of bulk deposition, while the substrate potential is kept at a slightly more positive potential than the bulk deposition potential so that the deposition of Cu starts predominantly from the tip and grows towards the substrate. When the growing Cu reaches the substrate, a wire between the substrate and tip is formed which is reflected by a sharp increase in the current that flows between the tip and the substrate. We then reverse the process by slowly dissolving the Cu wire by adjusting the potentials to the regime of dissolution, and monitor the current continuously.

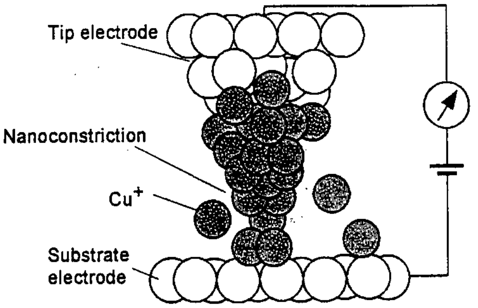

Figure 9. Schematic drawing of the experimental setup for electrochemically deposition of a metallic nanoconstriction.

As Cu atoms are being dissolved away, the wire narrows and eventually breaks during which the conductance decreases in a stepwise fashion with a separation of ~ $G_0=2e^2/h$ between adjacent steps (Fig 10, left). The conductance quantization has also been observed by carefully monitoring the current between the tip and substrate during the growth of the Cu wire (Fig. 10, right). We have plotted the histogram of the conductance values constructed from over 100 curves of 9 separate experiments (Fig. 11). The first three peaks are well defined at $1G_0$, $2G_0$ and $3G_0$ and peaks at higher integer numbers of G_0 are less pronounced, which are similar to those observed in mechanically formed nanoconstrictions.

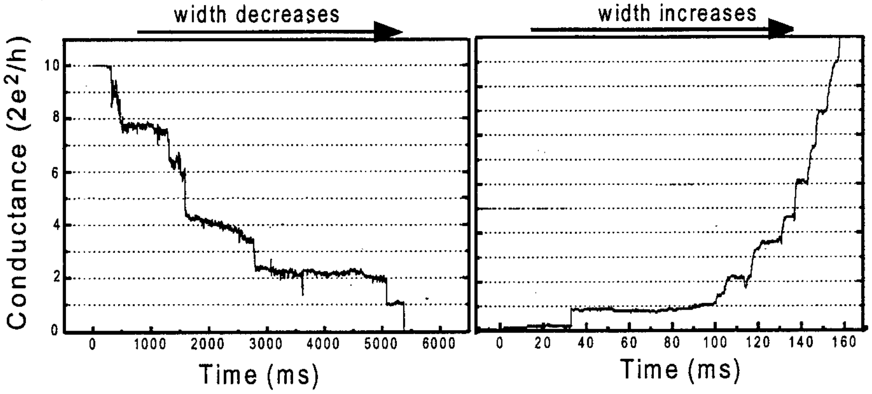

Figure 10. Conductance of a Cu nanowire as its width is being decreased by dissolution (left) and increased by deposition (right).

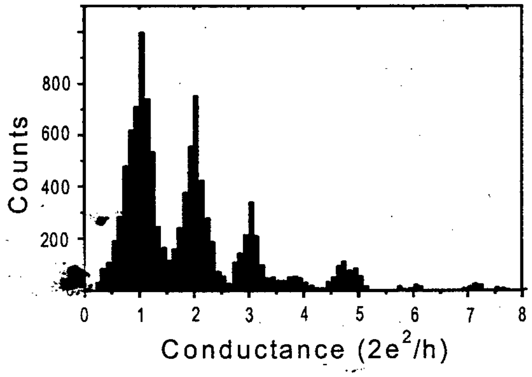

Figure 11. Conductance histogram of metallic nanoconstrictions fabricated by electrochemical deposition and dissolution at room temperature. The peaks occur at the integer values of the conductance quantum, $G_0=2e^2/h$.

C2. Fabrication of stable nanoelectrodes

The STM setup sketched in Fig. 9 has a serious long-term instability problem that is largely overcome by our second setup (Fig. 12). In this setup, a thin metallic wire placed on a flat insulating substrate is covered with an insulating layer except a small region near the center. We then slowly etched the exposed region using a homemade bipotentiostat. When the conductance reached the preset $3G_0$, a built-in automatic switch in the bipotentiostat turned off the etching current. As shown in Fig. 13, the conductance stayed on $3G_0$ from many minutes up to 5 hours and then jumped to lower steps and eventually to zero as the wire finally broke.

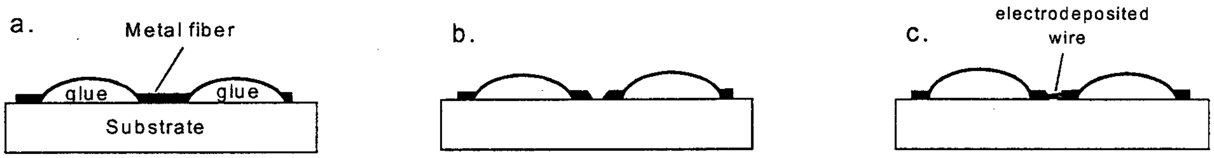

Figure 12 A setup for fabricating stable metallic nanoconstrictions. a. Cover a fine metal wire with glue except the central portion. b. Etch the central portion until the conductance reaches a desired quantum step. c. If the wire is complete broken, it will be reconnected by electrochemical deposition.

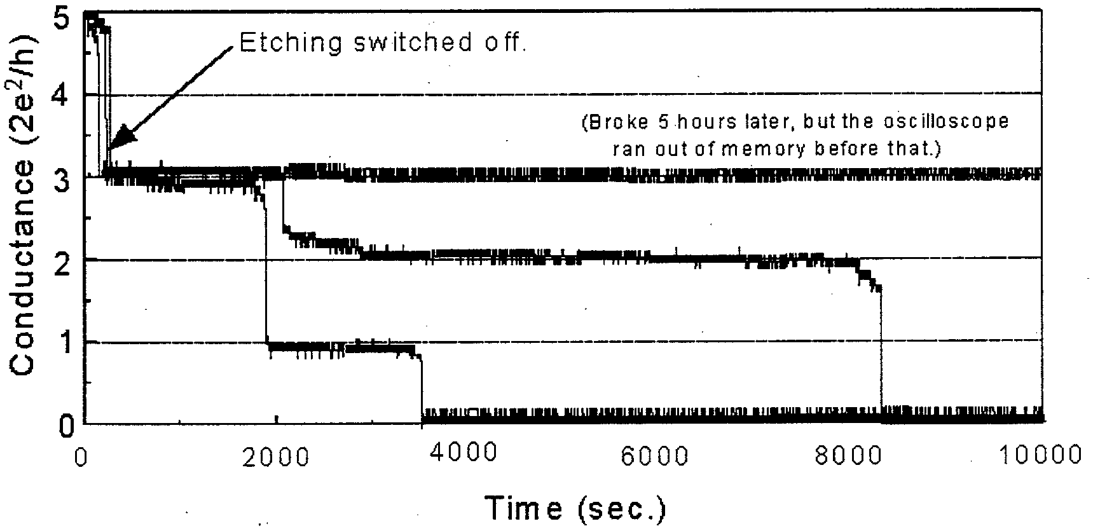

Figure 13. Conductance of Cu nanoconstrictions as their widths is being decreased by etching. The stepwise change is due to conductance quantization. By stopping etching at a selected conductance step (N=3), a nanoconstriction with a desired thickness (conductance) is obtained.

PERSONNEL SUPPORTED

- Faculty
  N. Tao (Principal Investigator).
- Post-Docs
  S. Boussaad (Since May, 1997).
  C.Z. Li (Since Oct., 1996).
- Graduate Students
  F. Cuhna (Graduated with MS in Dec. 1996).
  Q. Jin (Since May, 1996. Graduated with MS in Dec. 1997).
  C. Chu (Graduated with MS in Aug., 1999.).

S. Hong (Graduated with MS in Aug., 1999).
R. Arechabaleta (Since January, 1997).
A. Bogozi (Since January 1998).

- Undergraduate Students
  Bamby Doung (Graduated with BS in 1999).
  John D'Agnese (Since May 1996).
  Mark Adam (Graduated with BS in 1999).
  April Jones (May-August, 1998).
  Joseph S. Bunch (Since January 1999).

*7 of the 13 students and post docs are from under represented minority groups.

PUBLICATIONS

Published or accepted:

1. W. Schmickler and N.J. Tao, "Measuring the inverted region of an electron transfer reaction with an STM", Electrochimica Acta, 42, 2809(1997).

2. F. Cunha, Q. Jin, N. J. Tao and C. Z. Li, "Structural phase transition in self-assembled 1,10' phenanthroline monolayer on Au(111), Surf. Sci., 389, 19-28(1997).

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BOOK CHAPTERS

22. N.J. Tao, "Potential-controlled ordering in organic monolayers", in Imaging of Surfaces and Interfaces, Vol. 5, edited by J. Lipkowski and P. N. Ross, 1999.

INTERACTIONS/TRANSITIONS

Participation/Presentations At Meetings, Conferences, Seminars, Etc

INVITED TALKS:

Geogia Insititute of Technology, Dec., 1999.
45th International Conference on Analytical Spectroscopy, Oct., 1999.
195th Electrochemical Society Meetings, May, 1999.
Washington State U., Sept., 1999.
Univ. of Illinois at Urbana, Feb., 1999.
65th SEAPS Annual Meeting, Nov., 1998.
81st Canadian Chemical Society Conference, Whistler, May, 1998.
Scanning International 97, Chicago, May, 1997.
Scanning Probe Microscopy Workshop, ECS, Texas, Oct., 1996.

CONTRIBUTED TALKS:

American Chemical Society Meetings, New Orlean, September, 1999.
American Electrochemical Society, Seattle, May, 1999.
American Physical Society, Atlanta, March, 1999.
65th SEAPS annual meeting, Nov., 1998.
194th ECS Meeting, Boston, Nov., 1998.
American Vacuum Society, Baltimore, Nov., 1998.
American Vacuum Society, San Jose, Nov. 1997.
National Minority Research Symposium, New Orleans, Nov., 1997.
Air Force Research Annual Meeting, Aug., 1997.
ACS, Orlando, Florida, May, 1997.
American Physical Society, Kansas City, March, 1997.
National Minority Research Symposium, Miami Nov., 1996.
American Vacuum Society, Philadelphia, Oct., 1996.

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

"An ultrasensive surface plasmon spectroscopy", U.S. Provisional Patent, 1999.