Center for Electron Transport in Molecular Nanostructures

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The Columbia Nanocenter (NSEC) is dedicated to developing the highest level of fundamental understanding for new and exciting phenomena involving electron transport through single molecules and through nanoscale molecular assemblies [1]. Our research program is exploring three broad scientific propositions:

- **Molecular conduction**: The fundamental phenomena for electron transport through a single molecule represent an exciting opportunity for scientific discovery.
- **Molecular assembly**: Through combination of "bottom up" creation of specific chemical systems and "top down" fabrication, we can explore transport properties of two dimensional assembled and self-assembled nano-structures.
- **Nanoscale characterization**: Characterization of nanoscale molecular assemblies closes the functional design loop linking molecular properties, pathways for assembly and electrical function.

Our interdisciplinary program pursues the synthesis, fabrication, and characterization of three different types of nanoscale molecular systems in intimate contact with electrical contacts: (1) single walled carbon nanotubes, (2) two-dimensional molecular systems and (3) single molecules. The Nanocenter program brings a common intellectual approach to create a fully integrated multidisciplinary program built upon these molecular systems.

Electron Structure and Dynamics in Single Walled Carbon Nanotubes. Our research program is making significant advances toward the synthesis, characterization and understanding of isolated single walled carbon nanotubes. We have, for example, developed a new and unique form of Rayleigh Scattering Spectroscopy which provides rapid spectral signatures for individual nanotubes [2]. We have correlated these spectra with absolute structural determination for a wide variety of carbon nanotube structures [3]. This new spectroscopy provides rapid and precise optical determination of absolute structure and detailed understanding of electronic structure and interactions. This important development will dramatically influence how the scientific community explores the fascinating phenomena associated with carbon nanotubes. We are exploring the electronic properties of excited states of carbon nanotubes as well as the dynamics of these excited states. We have demonstrated that an excited hole-electron pair form a tightly bound "exciton" with strong binding energies (~0.4 eV) which vary with chiral structure [4]. These results show conclusively that strong carrier-carrier interactions play a major role in carbon nanotube transport phenomena. Such fundamental measurements will open up new perspectives in our understanding of the electronic transport properties of carbon nanotubes.

Two Dimensional Molecular Nanostructures. We have begun to develop methodology for the fabrication and electrical characterization of a single two-dimensional planar sheet of carbon: "graphene" [5]. We have confirmed the theoretical predictions based on band structure of the ideal system and we have begun to define the practical capabilities for this system. Our program has demonstrated that graphene offers new 2D electron transport phenomena that will yield exciting physics as well as potential new device concepts. These discoveries will form the basis for extensive explorations of these two dimensional systems.

Working with collaborators at IBM we have been exploring the fundamental aspects of transistor devices built from organic semiconductors. This understanding has allowed us to demonstrate that the molecule-electrode interface is critically important in determining transistor properties and that simple chemical treatment can lower the device resistance by two orders of magnitude for nanometer devices [6]. These results demonstrate how fundamental understanding leads to improved organic electronic materials and devices for practical application. One long-term vision for the Columbia Nanocenter has been the development of the "monolayer FET". Using carbon nanotube electrodes with spacing of about 2 nm we have demonstrated the operation of a nanometer scale monolayer as a field effect transistor and we have shown that these devices may be used as very sensitive chemical sensors [7]. These monolayer electronic devices on nanometer scale all measurement of charge transport in organic monolayer films without domain boundaries.

Conduction in Single Molecules. Although the fundamental characterization of conduction phenomena in single molecules has proven to be a major scientific challenge, we are making major advances toward defining molecular systems that can advance this knowledge. Because of the weak gold-gold bond electrode structures fabricated from gold are usually ill-defined. We have developed a new means for covalently binding molecular systems to Ruthenium [8]. This will open up methodology for exploration of molecular conduction with robust metallic electrodes. We have succeeded in demonstrating direct measurement of conductance for a single molecule covalently bonded across a nanometer-scale carbon nanotube junction. This has provided a very stable system for exploration of molecular conduction and it has allowed us to demonstrate single molecule sensing devices [9].

We have discovered that the gold-amine binding system offers opportunity to study precisely-defined conduction properties. This discovery has allowed us to carry out a systematic investigation of the conductance for individual organic diamine molecules with a wide variety of molecular structures. Thus for example we have shown that for simple alkyl and aryl amines, the observed molecular conductance follows a tunneling model, exhibiting exponential decrease in conductance with increasing molecular length [10]. Conduction for alkyl molecules is lower than for aryl molecules and conductance decays more rapidly with length for alkyl molecules. Our Nanocenter has also explored conductance in a series of molecules based on a simple biphenyl structure in which we can experimentally control twist angle through manipulation of the molecular structure. The experimental measurements for a series of molecules show a clear decrease in single molecule conductance with increasing twist angle (θ), following a $\cos^2\theta$ dependence [11]. These results may be understood in terms of electron transfer theory: For biphenyls, as the twist angle between the two rings increases, the degree of p-conjugation between them decreases. The molecular conductance, which is proportional to the electron transfer rate therefore scales as the square of the π-overlap. We are continuing to investigate the influence of molecular substitution on molecular conductance as well as new molecule-electrode systems. These experiments are already demonstrating a rich variety of behavior and should become a primary tool for explorations of molecular conductance.

References.

[1] Further information about this project may be found at www.cise.columbia.edu/nsec .

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