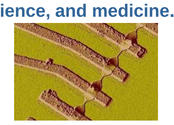
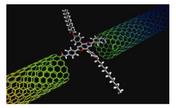
Electron Transport in Molecular Nanostructures

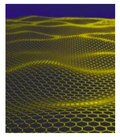
Nanoscale Science and Engineering Center, Columbia University - Grant Number CHE-0641523

James T. Yardley, Managing Director; Tony Heinz and Ronald Breslow, Scientific Directors

COLUMBIA NANOCENTER OVERVIEW

The *Center for Electron Transport in Molecular Nanostructure* at Columbia University seeks to establish the foundation for new paradigms for information processing through the development of fundamental understanding of charge transport phenomena unique to the character of nanoscale molecular structures. Beyond electronics applications, the fundamental studies of molecular transport in the Columbia Nanocenter have the potential to impact other disciplines such as photonics, biology, neuroscience, and medicine.



Basic questions addressed by the Center's research program include:

- What are the fundamental principles that determine the response of a molecular system to application of electric potentials?
- Under what circumstances is the conductance of a molecule quantized?
- What are the design rules governing charge transport phenomena in molecular nanostructures?
- How do we contact molecular systems with metallic electrodes?
- What is the nature of the contact to individual molecular systems?
- How do we design components for molecular circuitry?
- What are the mechanisms for modulation of the conductance of a molecule?
- How can we build molecules containing the operational functions of a transistor?

COLUMBIA NANOCENTER STRUCTURE

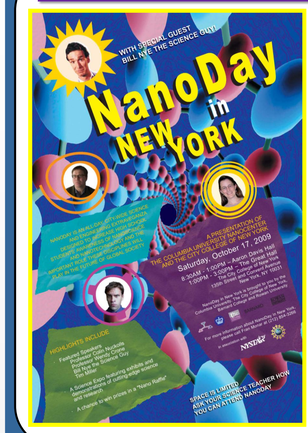
- 16 Principal Investigators from 6 different departments: *Chemistry, Physics, Applied Physics, Electrical Engineering, Chemical Engineering and Mechanical Engineering.*
- Academic affiliates: Barnard College, City College, Rowan University.
- Industrial affiliates: Alcatel/Lucent, DuPont, IBM, Intel, SRC/SIA
- Government Laboratory Partners: Brookhaven National Lab, Molecular Foundry (LBL), Network for Computational Nanotechnology, SRC (NRI).
- Encompasses approximately 75 researchers, including graduate students and postdocs.

Research Thrust Areas:

- *Electron transport and basic physics of graphene and molecular films.*
- *Electron transport in carbon nanotubes.*
- *Electron transport in single molecules.*
- *Non-equilibrium quantum coherent devices in 1-D materials (NRI).*

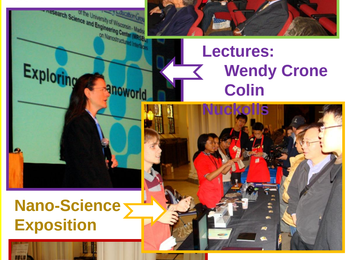
EDUCATION and OUTREACH

NANODAY NEW YORK October 17, 2009



400 New York City High School Students!

Lectures: Wendy Crone Colin Nuckolls

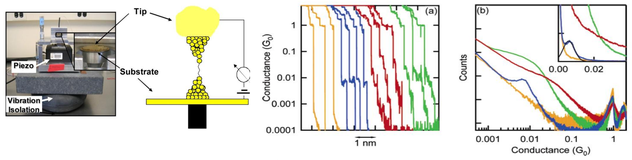


Nano-Science Exposition

Bill Nye, The Science Guy.

TRANSPORT in SINGLE MOLECULES

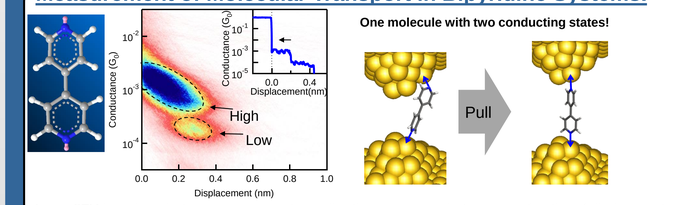
Defined Molecular Conductance in Organic Molecules.



STM-based conductance measurements. (a) Sample conductance traces measured without molecules (yellow) and with 1,4-benzenediamine (blue), 1,4-benzenedithiol (red), and 1,4-benzenediisonitrile (green) shown on a semilog plot. (All data were measured at 25 mV bias, although no bias dependence was found up to 250 mV.) (b) Conductance histograms constructed from over 3000 traces measured in the presence of 1,4-benzenediamine (blue), 1,4-benzenedithiol (red), and 1,4-benzenediisonitrile (green) shown on a log-log plot. The control histogram of Au without molecules is also shown (yellow). Histograms are normalized by the number of traces used to construct the histograms. Inset: same data on a linear plot showing a Gaussian fit to the peak (black curve). Bin size is 10^{-4} G_0.

Mark S. Hybertsen, Latha Venkataraman, Jennifer E. Klare, Adam C. Whalley, Michael L. Steigerwald, and Colin Nuckolls. "Amine-Linked Single-Molecule Circuits: Systematic Trends Across Molecular Families." J. Phys.: Condens. Matter 20, 374115 (2008).

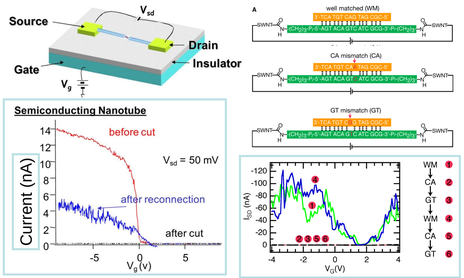
Measurement of Molecular Transport in Bipyridine Systems.



In our STM-based conductance measurements we directly measure conductance as a function of displacement. By building histograms of this data for many measurements, we establish the overall distribution of molecular conductances as a function of displacement. The data strongly support the hypothesis that at short distances a junction forms with C-N-Au angle smaller than 180°. Thus the Au is better coupled to the molecular π-system giving higher conductance. On pulling, the molecule becomes vertical in the junction. In this state the Au is not well coupled to the π-system resulting in lower conductance.

M. Kamenetska, Su Ying Quek, A. C. Whalley, M. L. Steigerwald, H. J. Choi, Steven G. Louie, C. Nuckolls, M. S. Hybertsen, J. B. Neaton and L. Venkataraman. "Conductance and Geometry of Pyridine-Linked Single-Molecule Junctions". J. Am. Chem. Soc. 132, 6817-6821 (2010).

Single Molecule Transistors for Bio-Medical Sensing.



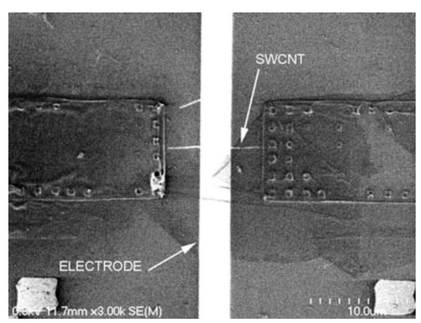
We have developed a system for measuring the conductivity of a single immobilized molecule covalently immobilized within a nanotube gap in a molecular transistor architecture. This allows molecules to be directly wired into metal electrodes through robust amide linkages. The devices are sufficiently robust that aqueous environments can be used. In collaboration with the Jackie Barton group at Cal Tech, we have measured the conductivity of a single DNA duplex when it is wired into a carbon electrode through covalent bonds. Importantly, the presence of intervening mismatches attenuates DNA-mediated conduction leading to as much as 300-fold increase in resistance. These concepts can lead to new precision DNA sequencing technology.

Xuefeng Guo, Alon A. Gorodetsky, James Hone, Jacqueline K. Barton and Colin Nuckolls. "Conductivity of a single DNA duplex bridging a carbon nanotube gap". Nature Nanotechnology 3, 163-167 (2008); Xuefeng Guo and Colin Nuckolls. "Functional single-molecule devices based on SWNTs as point contacts". J. Mater. Chem. 19, 5470-5473 (2009).

CARBON NANOTUBES AND DEVICES

Translocation of DNA Through Single Walled Carbon Nanotubes..

Electron micrograph showing microfluidic chambers with interconnecting carbon nanotube and flow control electrode. Device is fabricated with PDMS, a polymeric material.

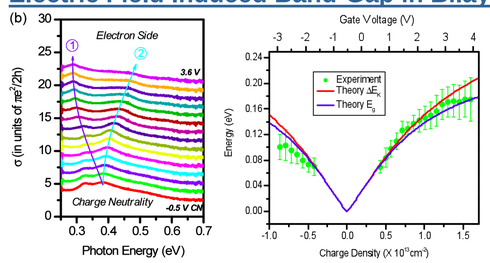


In the group of Colin Nuckolls with additional collaboration with Prof. Stuart Lindsay at Arizona, the Nanocenter has reported for the first time the use of single-walled carbon nanotubes (SWCNTs) as nanopores for analyzing molecular transport properties. Nanopores are orifices of molecular diameter that connect two fluid reservoirs. At this length scale, the passage of even a single molecule generates a detectable change in the flow of ionic current through the pore. In particular, the group has fabricated microfluidic devices in which one single-walled carbon nanotube spans a barrier between two fluid reservoirs, enabling direct electrical measurement of ion transport through the tube. Relative to CNT membranes, this arrangement makes it possible to detect signals from the translocation of a single molecule and to correlate transport with the properties of individual SWCNTs.

Impact: Carbon nanotubes simplify the construction of nanopores, permit new types of electrical measurements, and may open avenues for control of DNA translocation. Such devices may be used as single-molecule Coulter counters and form the basis of proposed new approaches to DNA sequencing.

Reference: Haitao Liu, Jin He, Jinyao Tang, Hao Liu, Pei Pang, Di Cao, Predrag Krstic, Sony Joseph, Stuart Lindsay and Colin Nuckolls. "Translocation of Single-Stranded DNA Through Single-Walled Carbon Nanotubes". Science (Washington, DC, U. S.) 327, 64-67 (2010).

Electric Field Induced Band-Gap in Bilayer Graphene

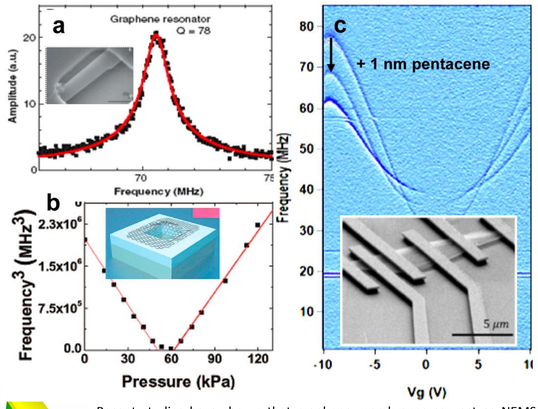


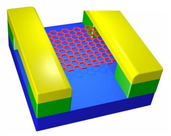
Bilayer graphene is an attractive material for fundamental studies of two dimensional (2D) physics, as well as for many potential device applications. In the bilayer system, the band structure arises from the coupling of two graphene monolayers. This bilayer system shares many of the interesting properties of graphene, but provides a richer band structure. Theoretical studies have predicted that a significant band gap could be induced through the application of a perpendicular electric field, producing a material with an electrically tunable band gap, a phenomenon of great significance for both basic physics and applications. We have observed direct spectroscopic signatures of the opening of a large and tunable band gap in bilayer graphene induced by a perpendicular electric field.

Reference: Kin Fai Mak, Chun Hung Lui, Jie Shan and Tony F. Heinz. "Observation of an Electric-Field-Induced Band Gap in Bilayer Graphene by Infrared Spectroscopy". Phys. Rev. Lett. 102, 256405/256401-256405/256404 (2009).

GRAPHENE: A NEW ELECTRONIC MATERIAL

Electro-Mechanical Resonators in Graphene



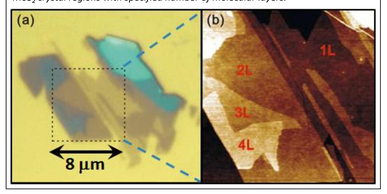


Recent studies have shown that graphene membranes can act as NEMS resonators in the megahertz range. Electrical readout of these devices is important for integration, and is attractive for many applications. In addition, characterization of the basic attributes of these devices, including their response to applied voltage, added mass and changes in temperature, allows detailed modelling of their behavior. These new resonators are voltage tunable and offer detection of mass to very low levels.

Reference: Changyao Chen, Sami Rosenblatt, Kirill I. Bolotin, William Kalb, Philip Kim, Ioannis Kymissis, Horst L. Stormer, Tony F. Heinz and James Hone. "Performance of monolayer graphene nanomechanical resonators with electrical readout". Nat. Nanotechnol. 4, 861-867 (2009).

Single Molecular Sheet of Molybdenum Sulfide: A New Direct-Gap Semiconductor

Optical micrograph of MoS_2 flakes (a) and corresponding AFM image showing MoS_2 crystal regions with specified number of molecular layers.



The material MoS_2 has attracted great interest because of its distinctive electronic, optical, and catalytic properties. We report ultrathin crystals of MoS_2, with thicknesses down to a single molecular monolayer, corresponding to just half a unit cell of the bulk crystal (c = 6.14 Å). With decreasing thickness the MoS_2 crystals exhibit dramatic changes in their electronic structure. Further spectroscopic measurements reveal a systematic change in the electronic properties of the material with crystal thickness and the existence of a crossover from the dark indirect-gap semiconductor to a luminescent direct-gap semiconductor in the limit of single MoS_2 monolayer.

The crossover from an indirect to direct band-gap material arises from a strong confinement-induced increase for the material's indirect band gap. These new nanoscale materials may find exciting new applications in electronic devices, in solid state lighting, or in new mechanical structures

Reference: Kin Fai Mak, Changgu Lee, James Hone, Jie Shan and Tony F. Heinz. "Atomically thin MoS_2: a new direct-gap semiconductor". Phys. Rev. Lett. (2010).

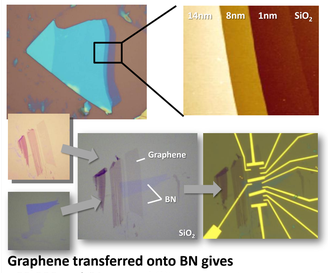
NANOELECTRONICS RESEARCH INITIATIVE*

nanoelectronics RESEARCH INITIATIVE

The Columbia Nanocenter is a recipient of a supplemental award from NSF and from the Semiconductor Industry's Nanoelectronics Research Initiative (NRI) to explore "Non-equilibrium Quantum Coherent Devices in 1-D Materials" as a concept for information processing beyond CMOS silicon.

Graphene: Basis for New Semiconductor Devices

Graphene exhibits extremely high mobilities and offers flexibility to create many new functional electronic devices. However on SiO_2 and other conventional substrates the mobility is substantially reduced due to electron-phonon scattering. Boron Nitride has high energy phonons which couple weakly to electrons and thus offers the possibility for enhanced mobility.



Graphene transferred onto BN gives >60,000 cm^2/V sec mobility at room temperature!

We have fabricated graphene devices on BN substrates that exhibit mobilities almost an order of magnitude better than the corresponding devices on SiO_2. These devices also show reduced roughness, intrinsic doping and chemical reactivity. The ability to assemble crystalline layered materials in a controlled way permits the fabrication of graphene devices on other promising dielectrics and allows for the realization of more complex graphene heterostructures.

Reference: C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard and J. Hone. "Boron nitride substrates for high quality graphene electronics". Nature Nanotech. 5, 722-726 (2010).

*This program is supported by the NSF and the SRC via the Nanoelectronics Research Initiative".

Support for this work was provided by the Nanoscale Science and Engineering Center program of the NSF under Grants No. CHE-0117752 and CHE-0641523 and by the New York State Office of Science, Technology, and Academic Research (NYSTAR).