One at a time: Studies of an Individual Carbon Nanotube

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Basic Energy Sciences
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Outline

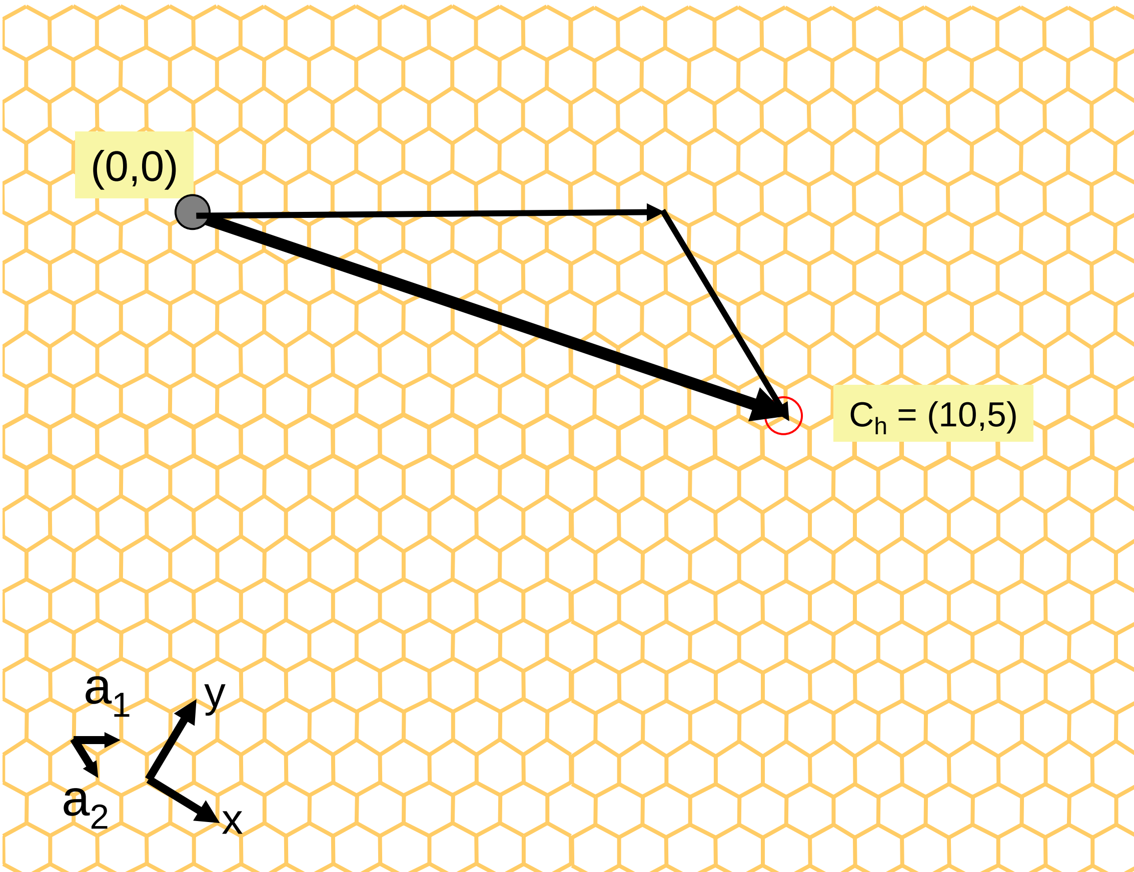
Solid-State Physics

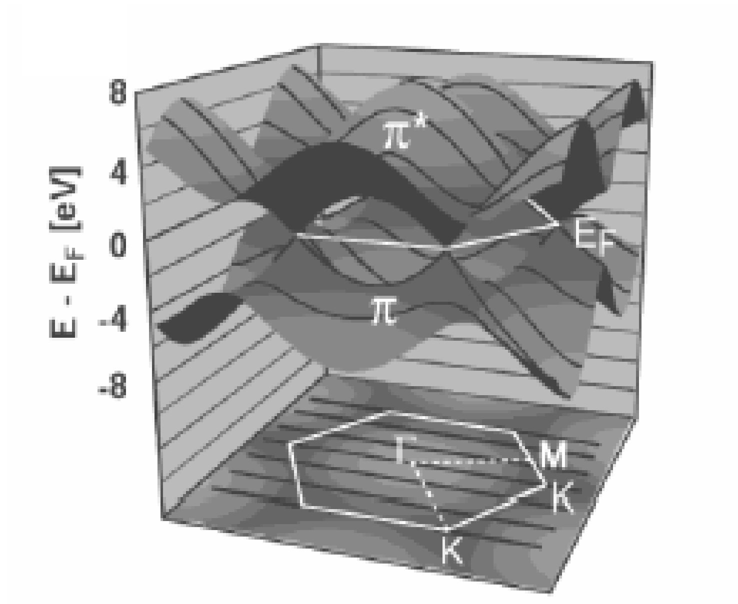
- Background and motivation
  - What are carbon nanotubes?
  - Why are carbon nanotubes interesting?
  - Why do we want to study one individual nanotube?
    - THE NANOMATERIAL DIVERSITY PROBLEM!
- Transport in nanotubes
  - Interface issues
  - Ambipolar transport
- Spectroscopy of individual nanotubes
  - Electroluminescence spectroscopy
  - Photoconductivity spectroscopy
  - Rayleigh scattering
- Structure of the same nanotube
  - Diffraction to get structure
  - BNL Advanced TEM

BioPhysics

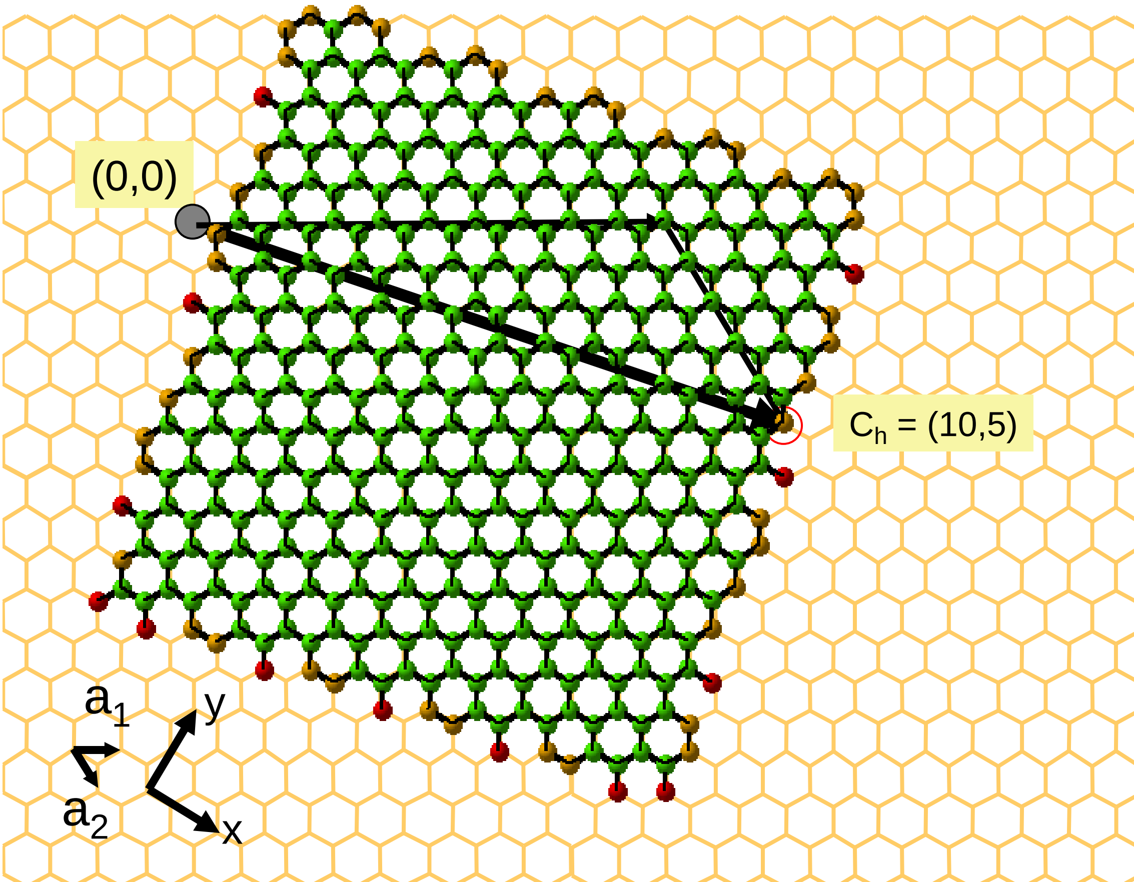
- Biocompatibility
  - Surface functionalization
- Biofunctionalization
  - Highly specific sensing

Carbon nanotubes





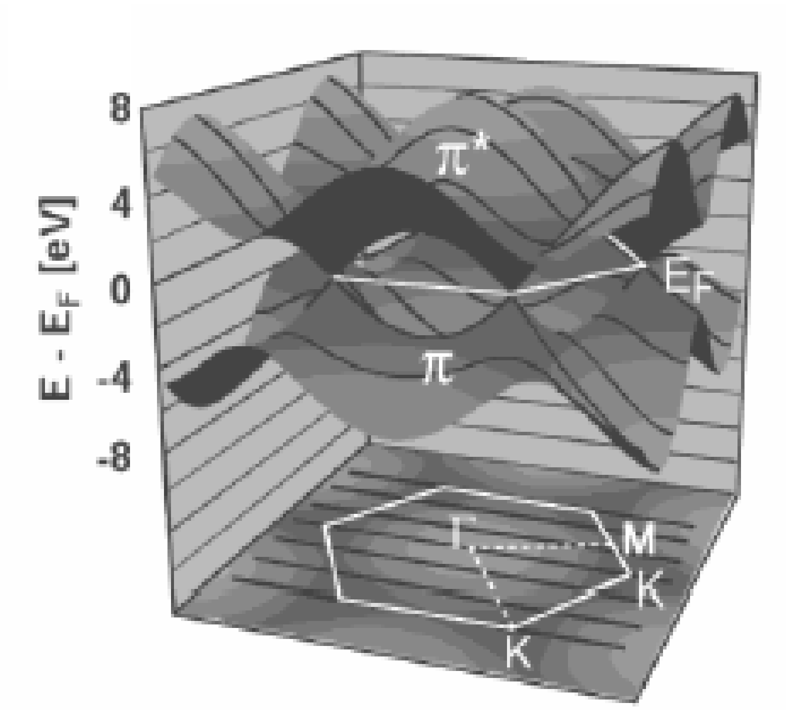
Carbon nanotubes

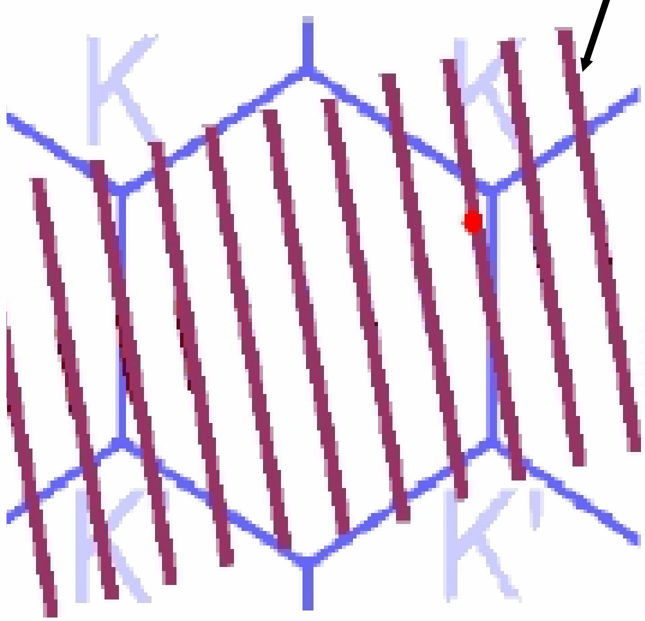


Band structure

- Band folding model
  - Graphene sheet: tight binding model, π bonds determine properties
  - Rolling constraints: electronic structure (n,m) tube is obtained by zone folding the 2D graphene energy dispersion relation with periodic boundary condition around the nanotube

$$k_C\, C = q\, 2\pi$$

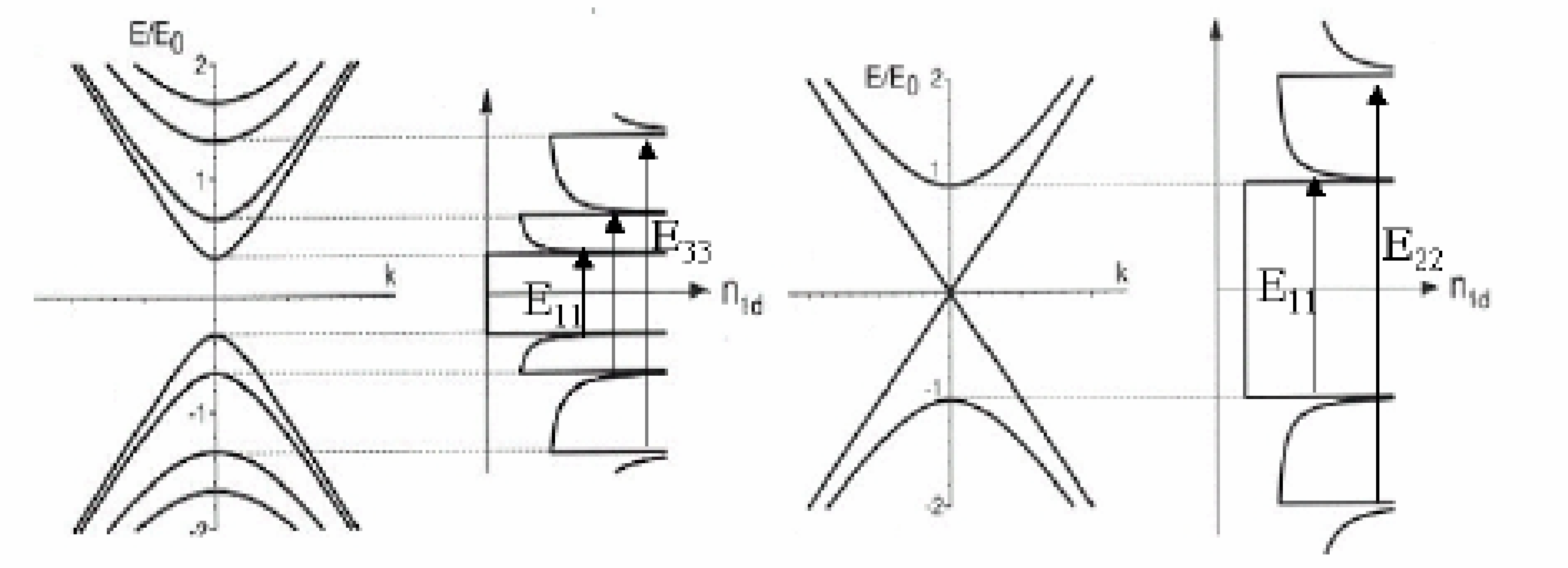




Dispersion

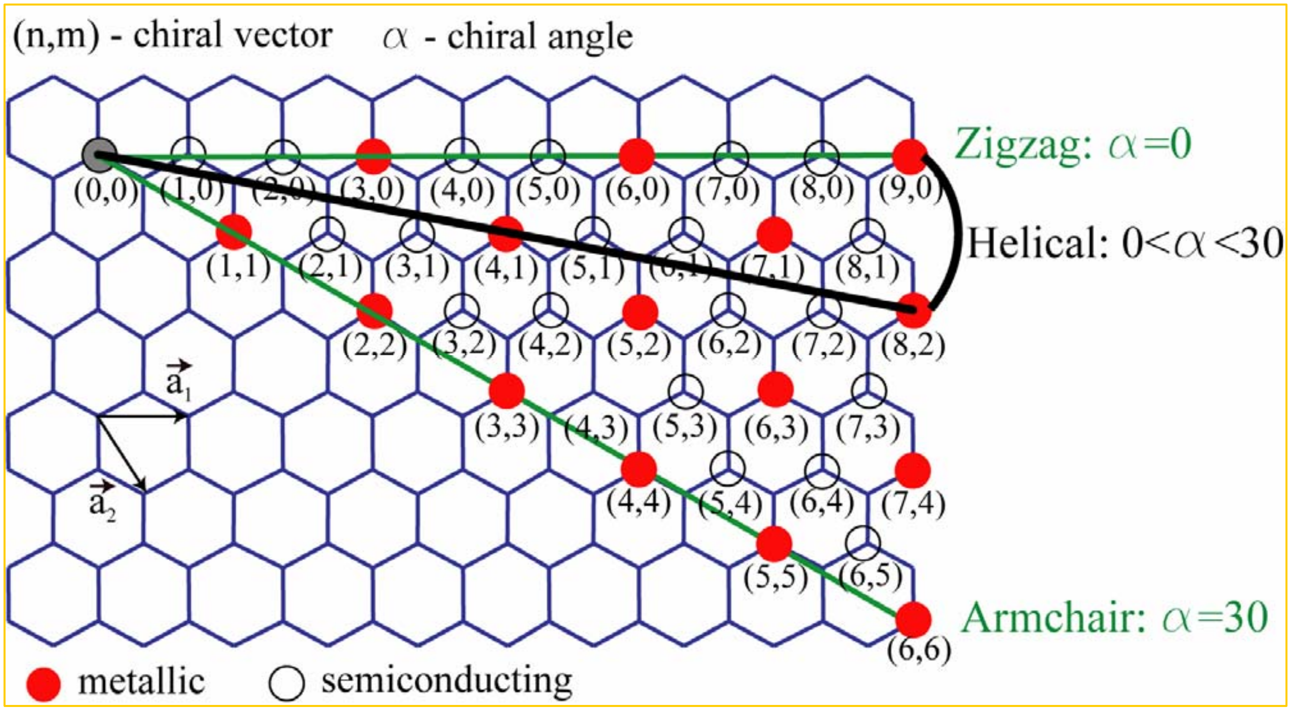
- Metallic or semiconducting depending upon whether K point is included

$n-m \neq 3i$ $\qquad$ $n=m, n-m=3i$



Semiconducting $\qquad$ **Metallic**

Carbon nanotubes



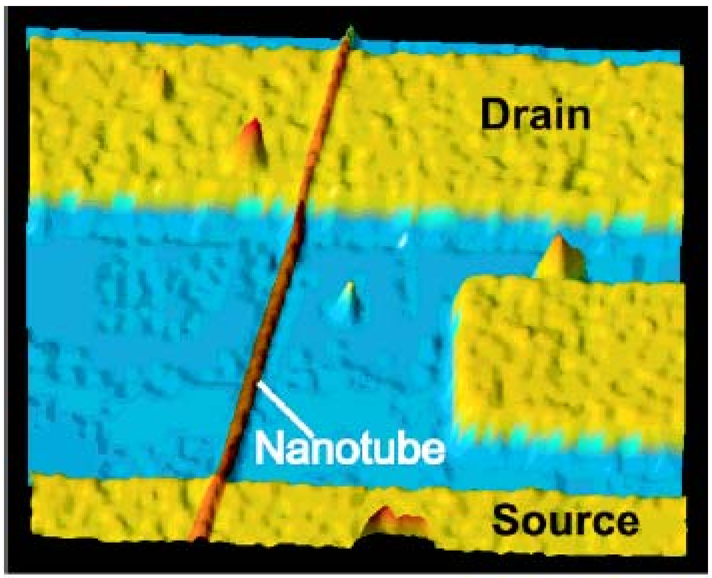
Why do we want to study individual nanotubes?

→ Large diversity of nanotubes

Why are nanotubes interesting?

- <u>Electronics</u>

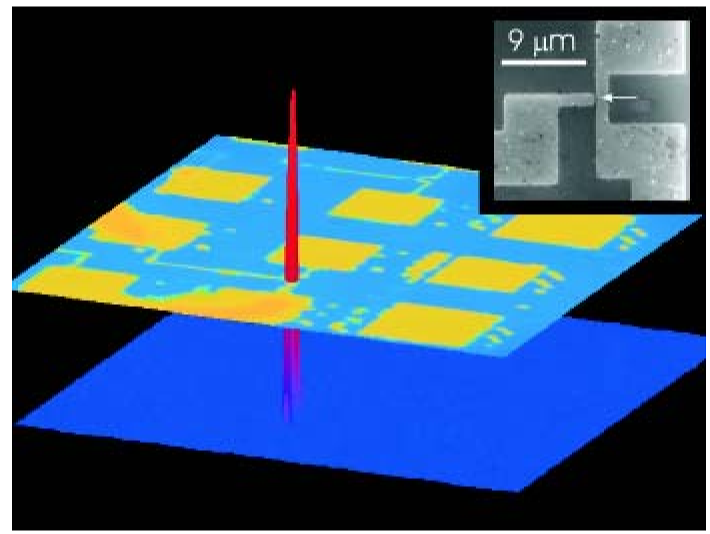
Smallest transistor



S. J. Tans, A. Verschueren, and C. Dekker, Nature **393**, 49 (1998); R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. **73**, 2447 (1998).

- <u>Photonics</u>

Smallest electrically controllable light source



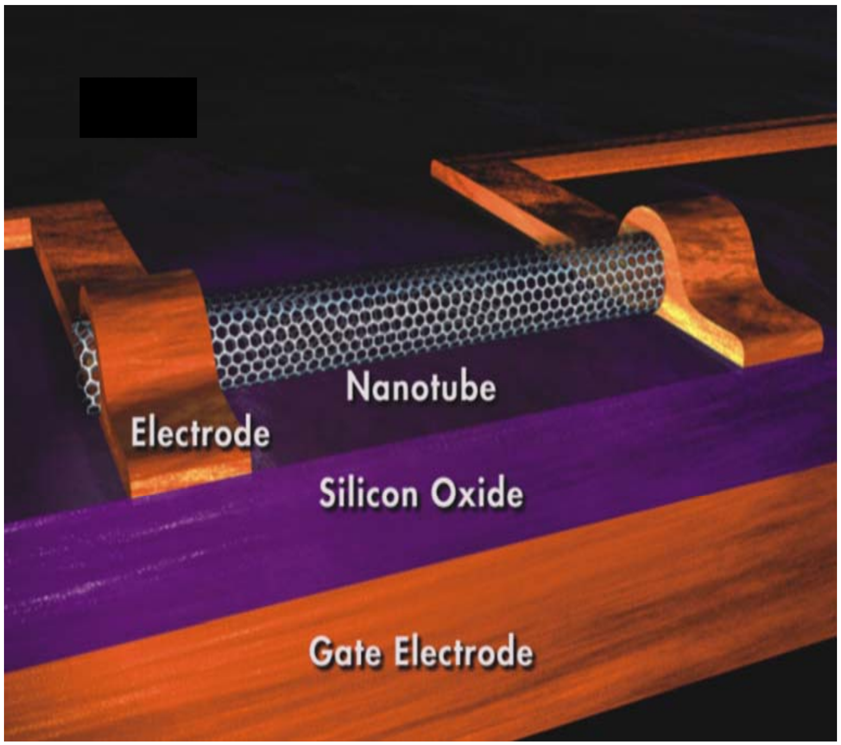
J. A. Misewich, R. Martel, Ph. Avouris, J. C. Tsang, S. Heinze, and J.Tersoff, Science **300**, 783 (2003).

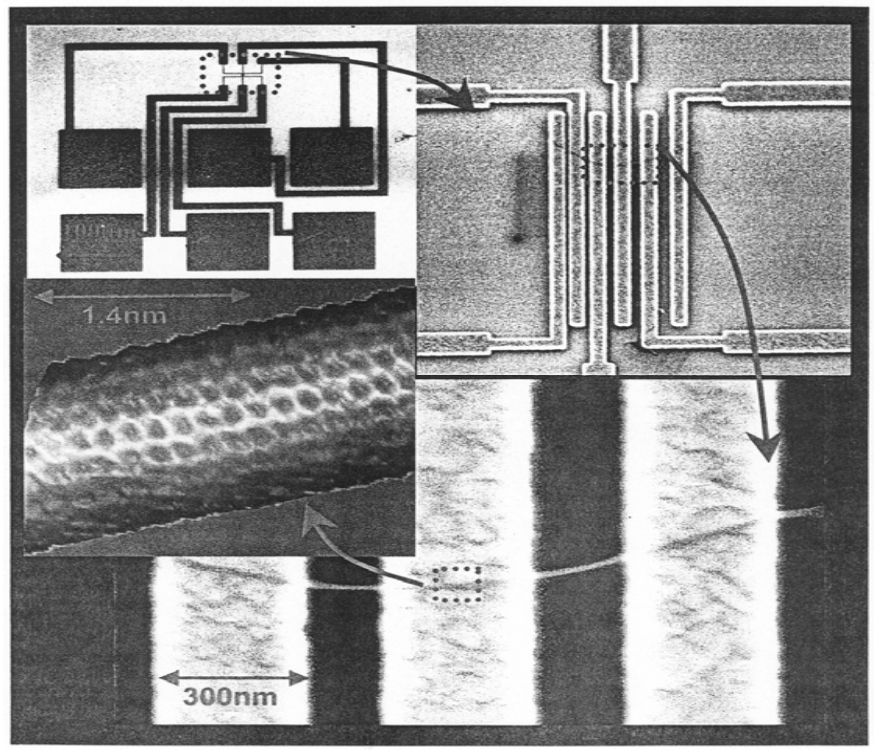
Interesting physical properties

- Charge transport is quasi one dimensional
  - Backscattering is strongly suppressed resulting in ballistic transport or high mobility of electrons and holes
- Low energy dissipation, high mechanical and thermal stability, no electromigration
- High current densities: 10 μA in a 1 nm diameter
  - $> 10^9$ A/cm^2
- Symmetric electron and hole transport (same m*)
  - n-type and p-type conductivity—CMOS
- Direct bandgap
  - Optoelectronics possible
- Challenge
  - Complexity and structural diversity

Fabrication

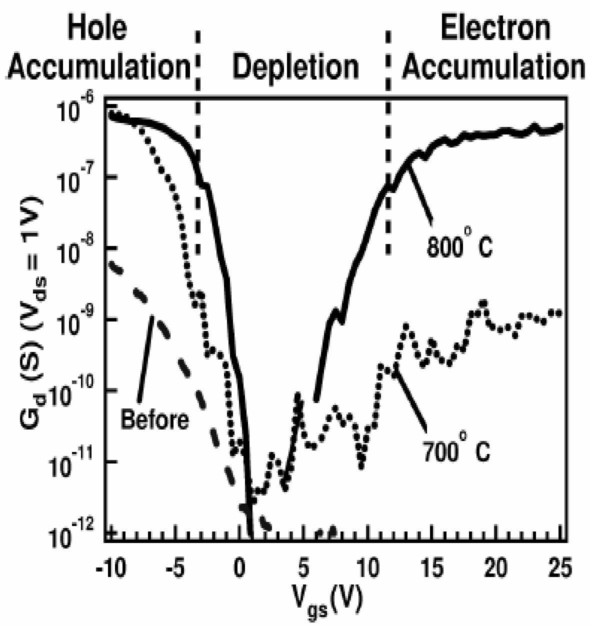
- Disperse nanotubes on silicon wafer (with oxide)
- Add electrodes (e-beam lithography)



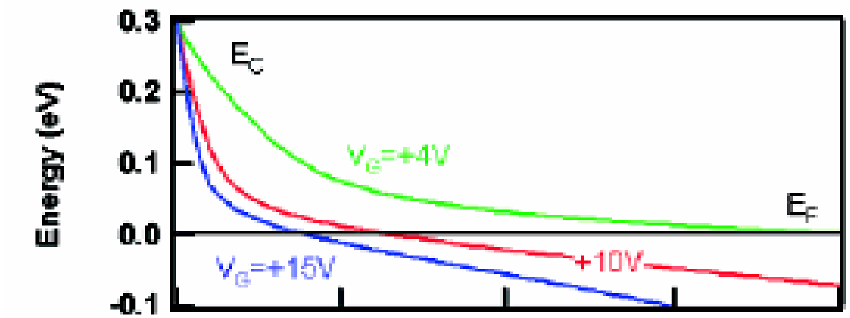


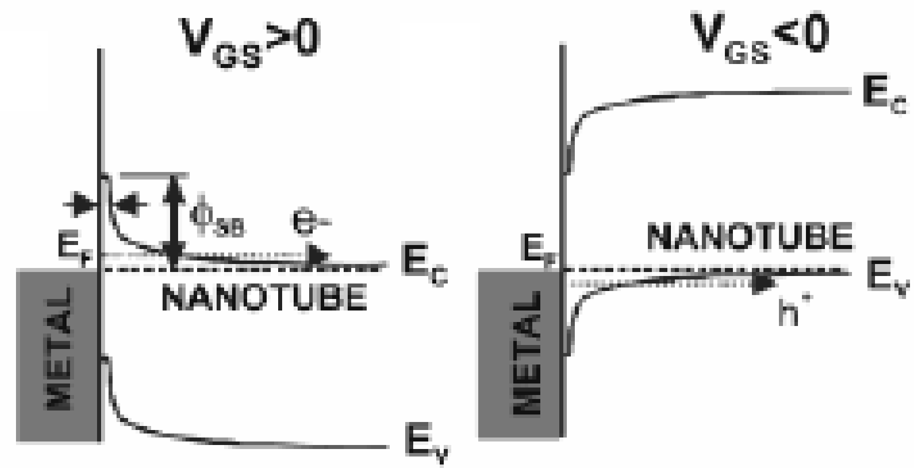
Transport in nanotubes

Contacts often critical in nanotube FET physics



Martel et al.
Phys. Rev. Lett. 87, 256805 (2001).





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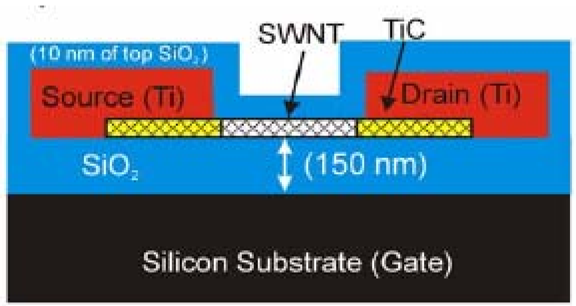
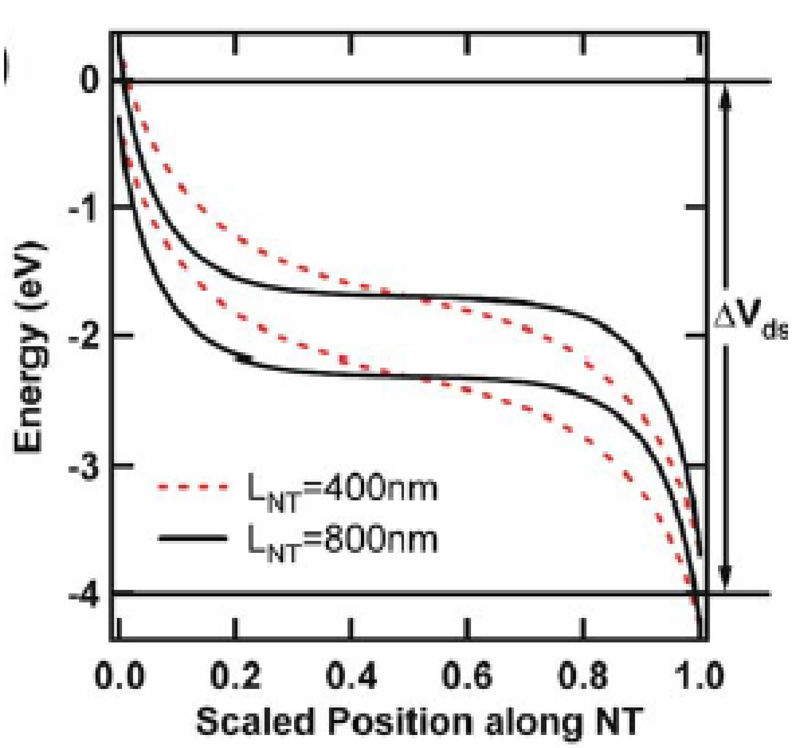
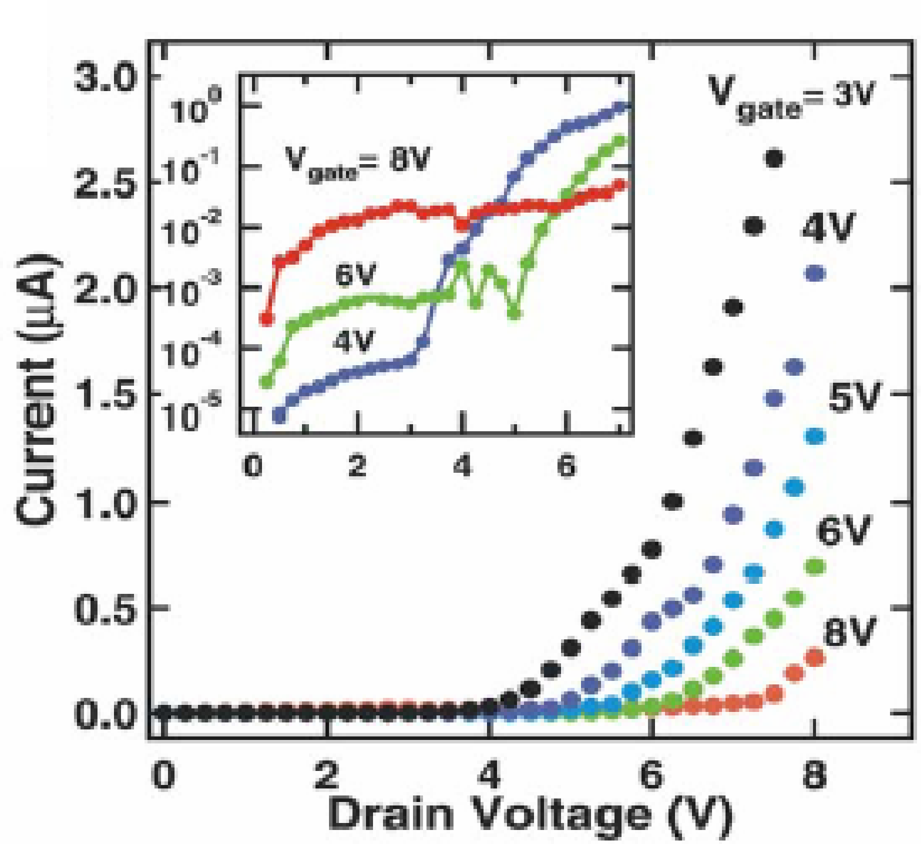
Simultaneous ambipolar transport





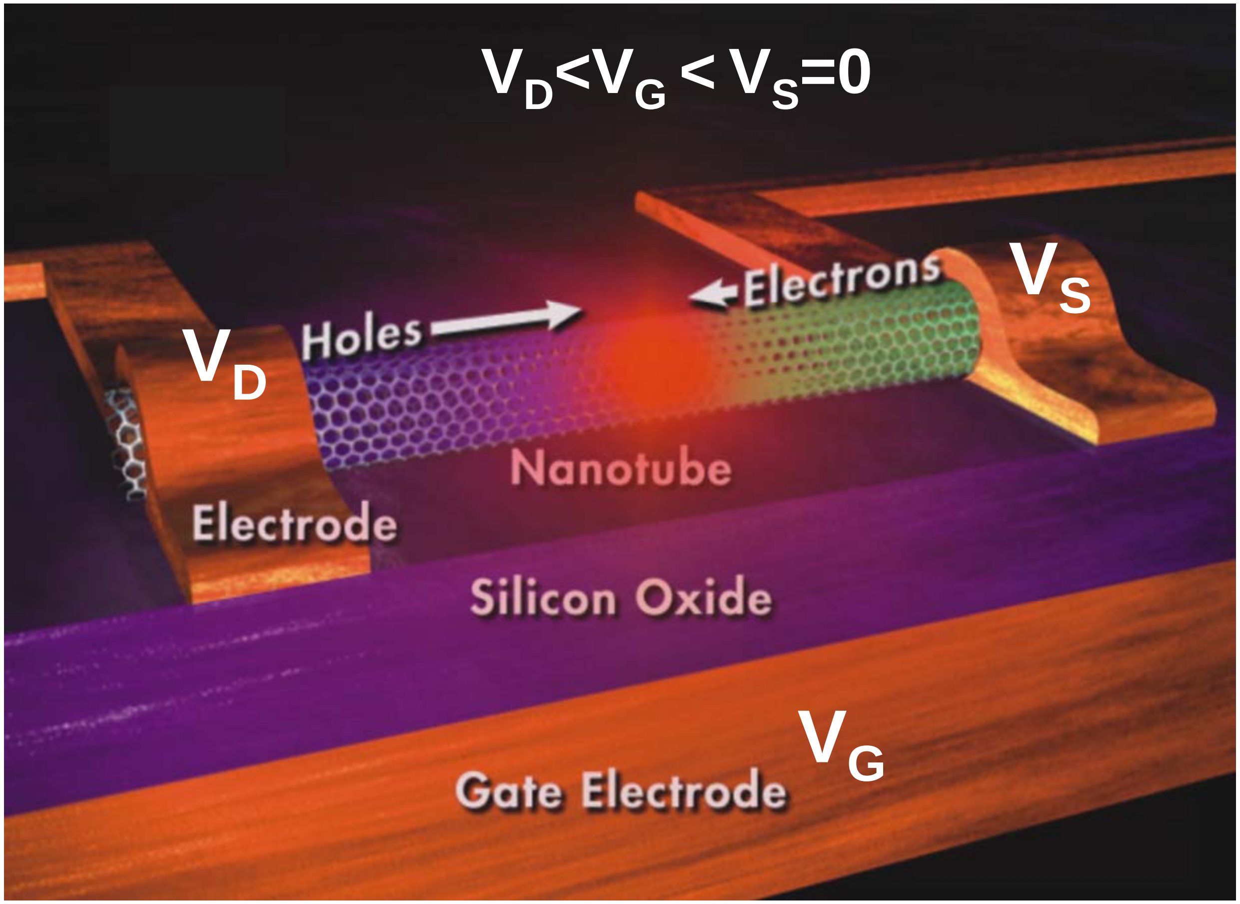
New mode of operation: (Vs<Vg<Vd)



Misewich et al., Science 300, 783 (2003)

Single nanotube emitter

Simultaneous ambipolar transport enables radiative electron-hole recombination



Infrared Spectroscopic Probe Station

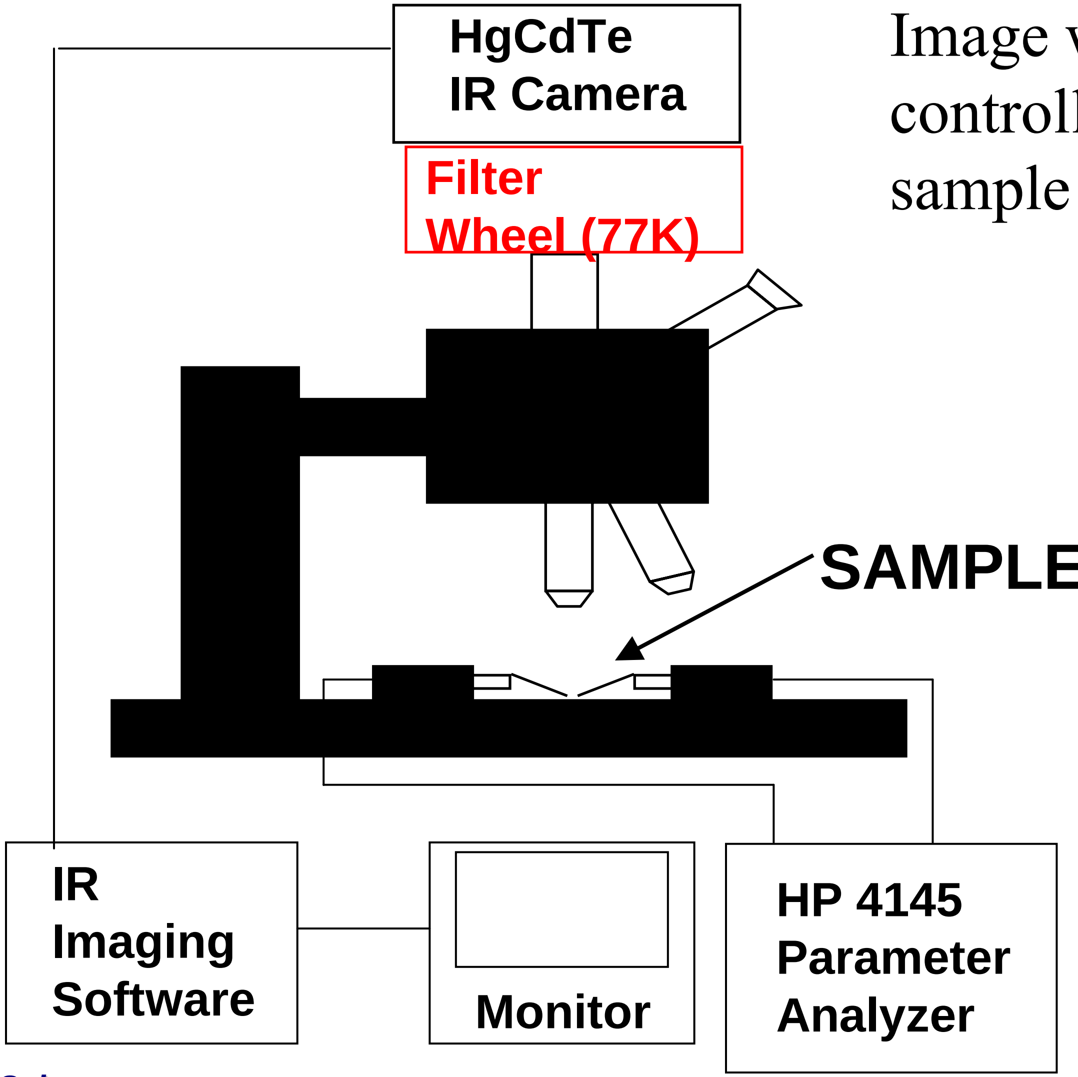
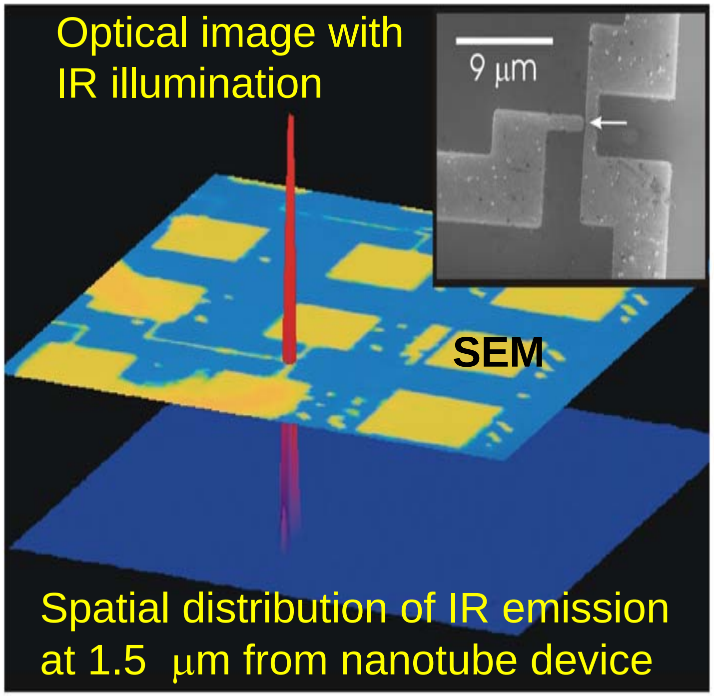


Image while controlling sample currents

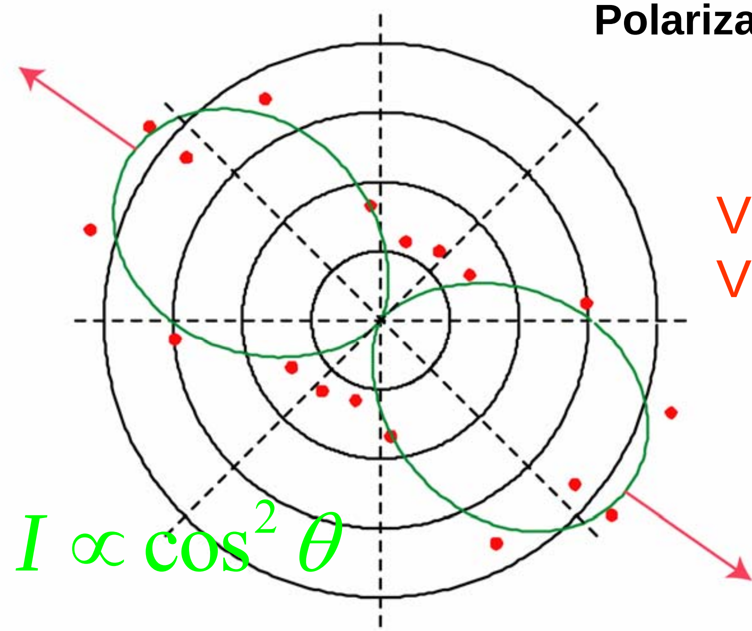
Electroluminescence in individual nanotubes

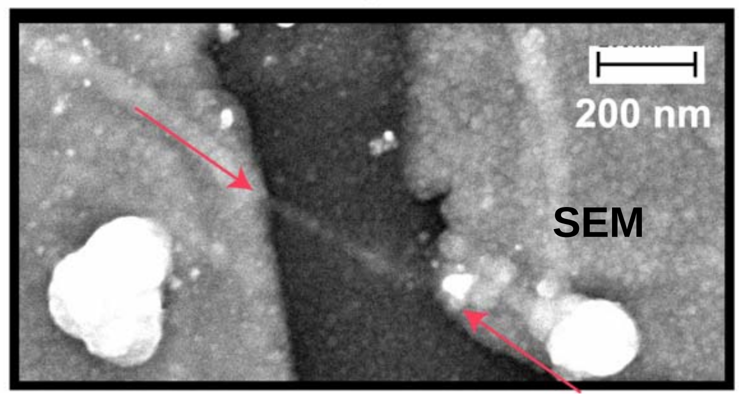
IR Emission



Misewich et al., Science 300, 783 (2003)

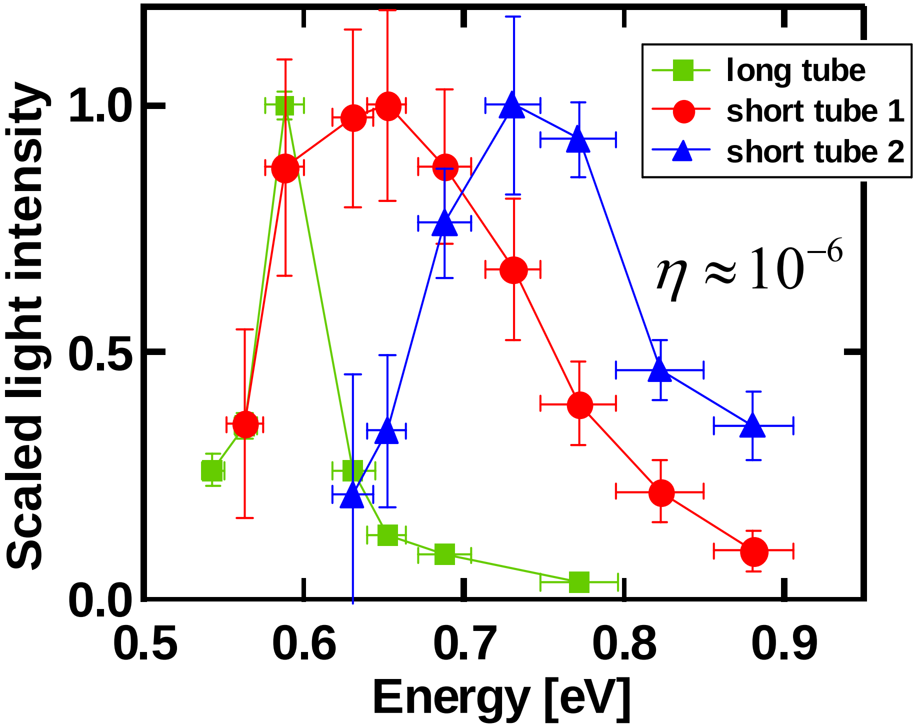
Polarization





BNL/IBM

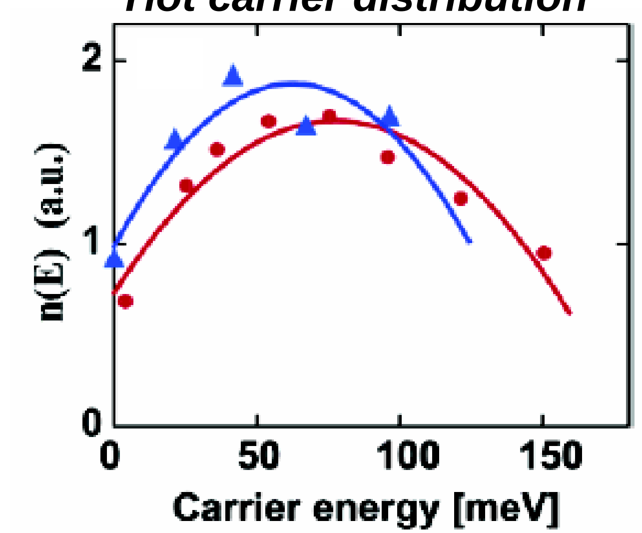
Spectroscopy of single carbon nanotubes



$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{Vm^2\omega^2}\sum_k P_{cv}^2(k)\delta(\hbar\omega - \Delta_k)$$

$$f(E_{gap} + 2E) = \sigma(E_{gap} + 2E)n(E)p(-E_{gap} - E)$$

Hot carrier distribution



$\tau_{optical}$ ~ 20 fs

$\tau_{acoustic}$ ~ 400 fs

Long: 50µm, $\tau_{transit}$~60 ps

Short: 500nm, $\tau_{transit}$~600 fs

Probing fundamental nanotube processes: electron-hole thermalization

Short nanotubes (red and blue spectra): broad asymmetric spectra from hot carriers.

Long nanotubes (green spectrum): narrow symmetric spectrum, thermalized carriers.

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Nano Letters 4, 1063 (2004)

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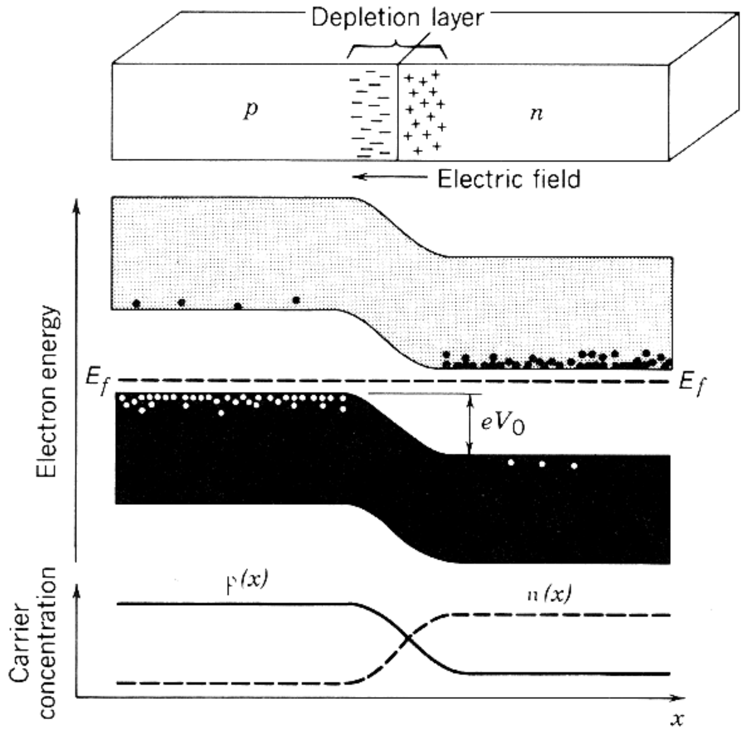
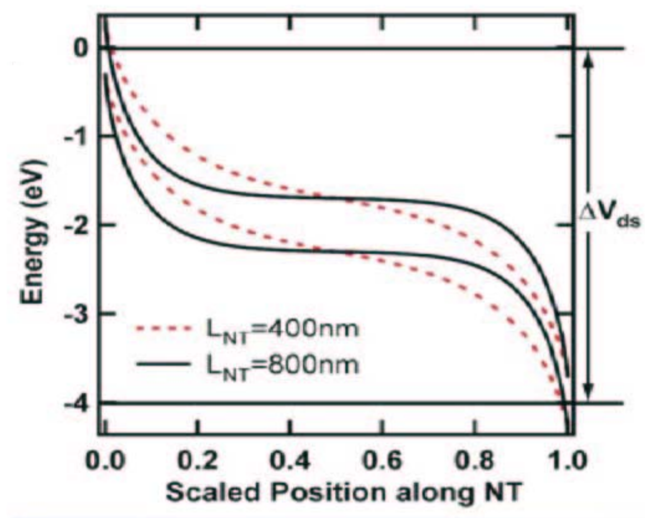
Distinct physics



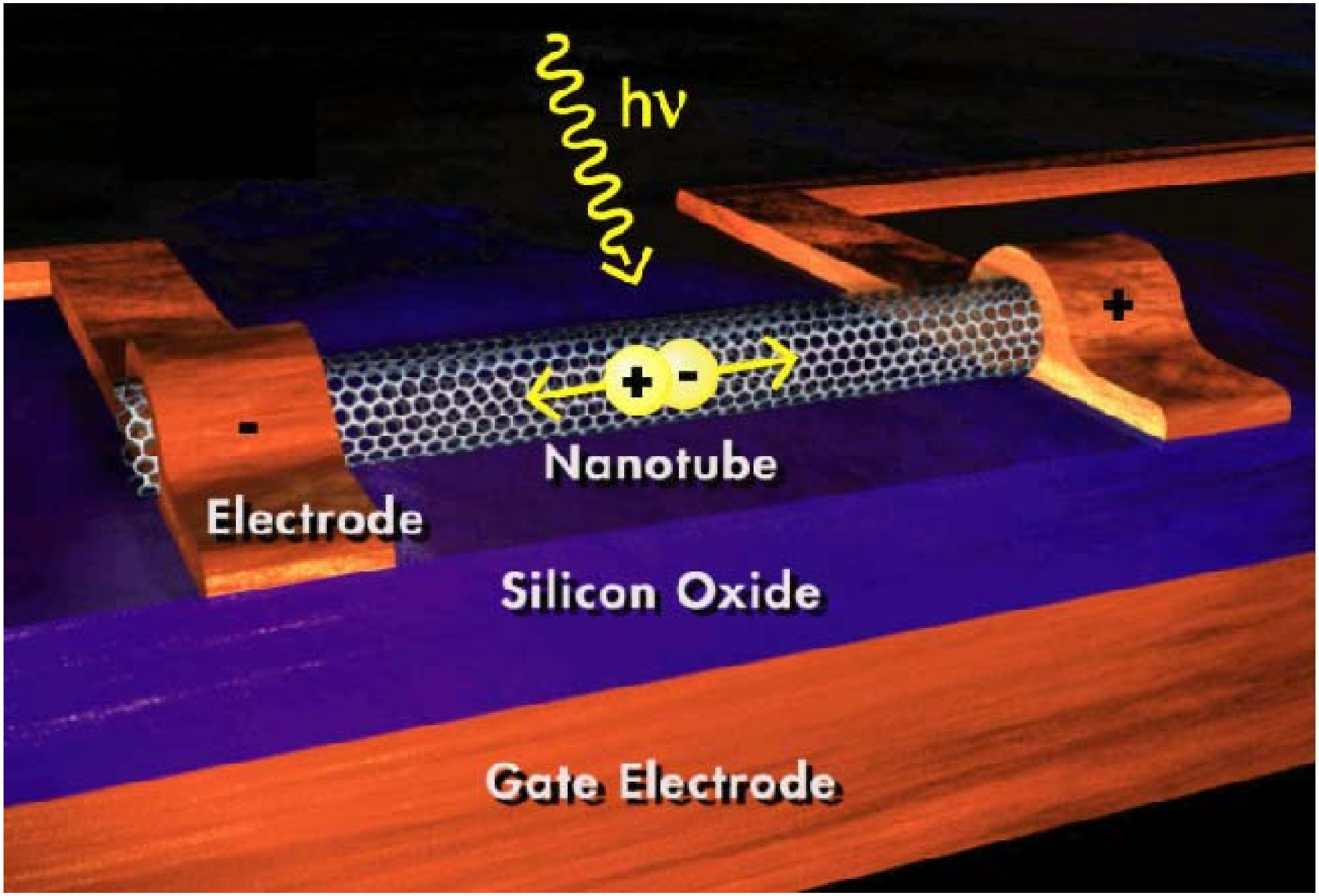
- pn junction
  - 2 terminal
  - Doped p and n regions
  - Injection of both carriers into depletion region—recombination
  - 3d



- Nanotube FET
  - 3 terminal
  - No doping
  - Schottky barrier control
  - Quasi 1-d

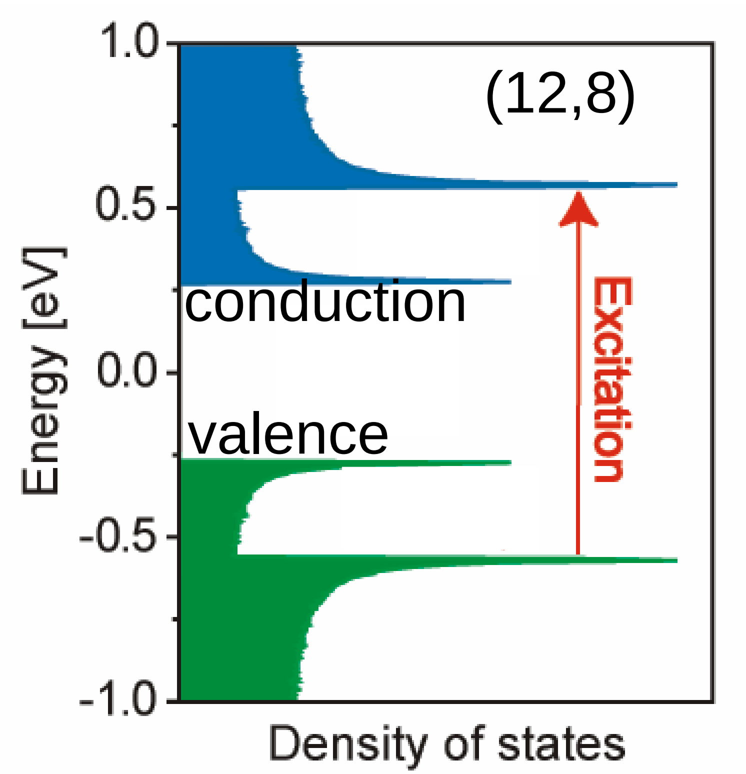
Excitation spectroscopy of single nanotubes

Photoconductivity studies

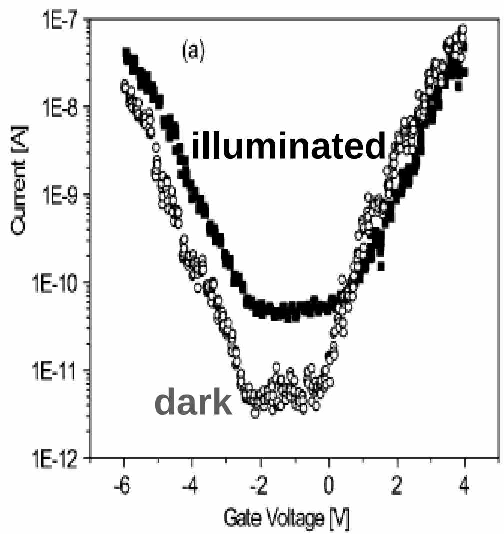


Photoconductivity of individual nanotubes

Probing excited states of single tubes
cw laser excitation of SNT-FET

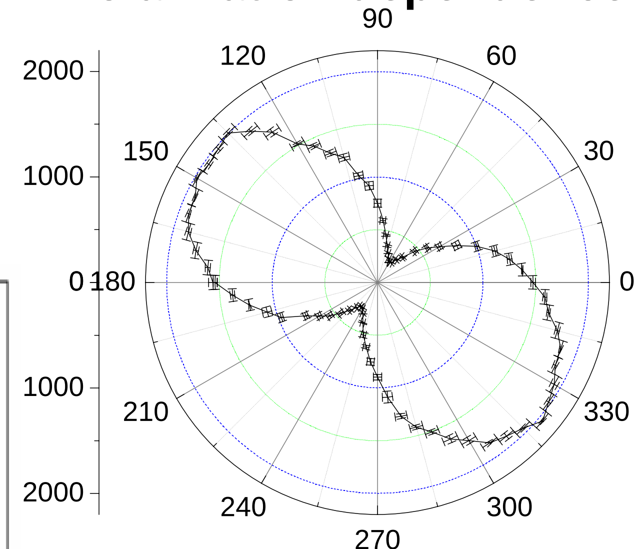


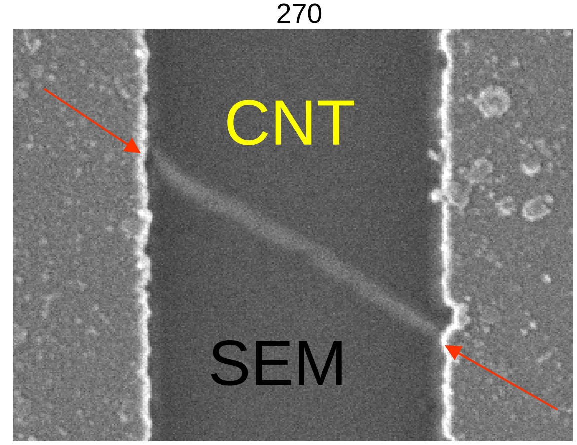
Photocurrent



$$\eta_{QE} \approx 10\%$$

Polarization dependence



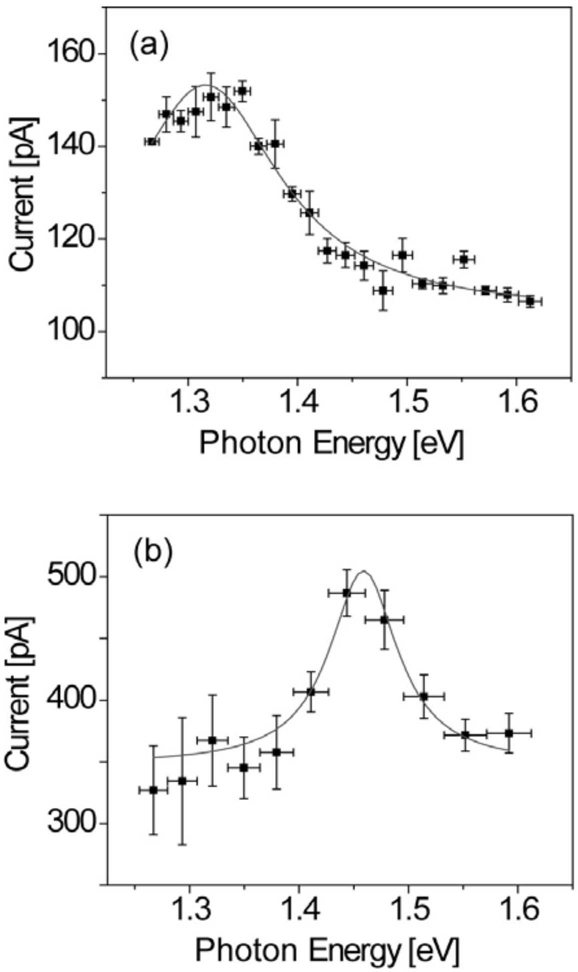


Polarized, efficient detector

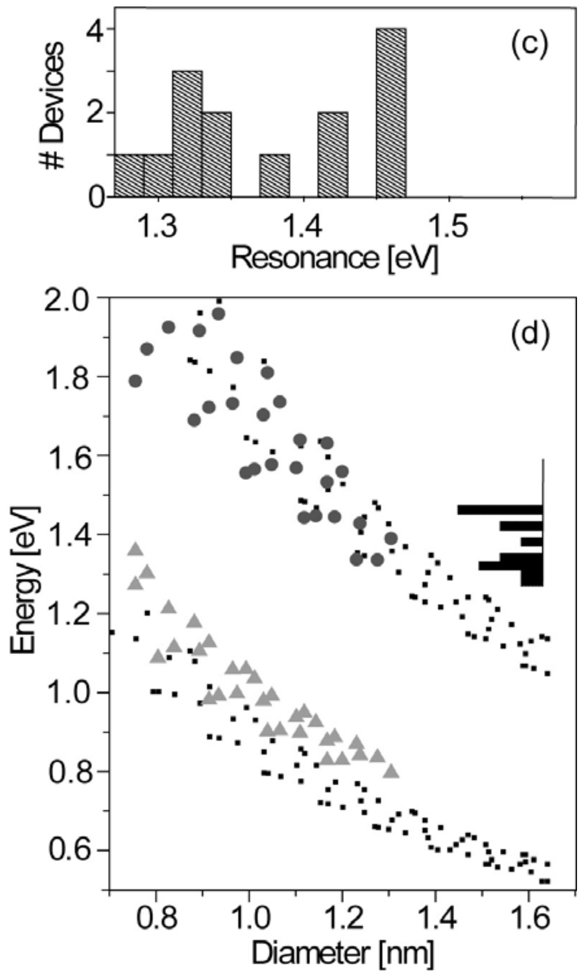
Photoconductivity excitation spectroscopy

Excitation spectroscopy: photoconductivity vs λ_{exc}

Spectra



Nanotube dispersion



Nano Letters 3, 1067 (2003).

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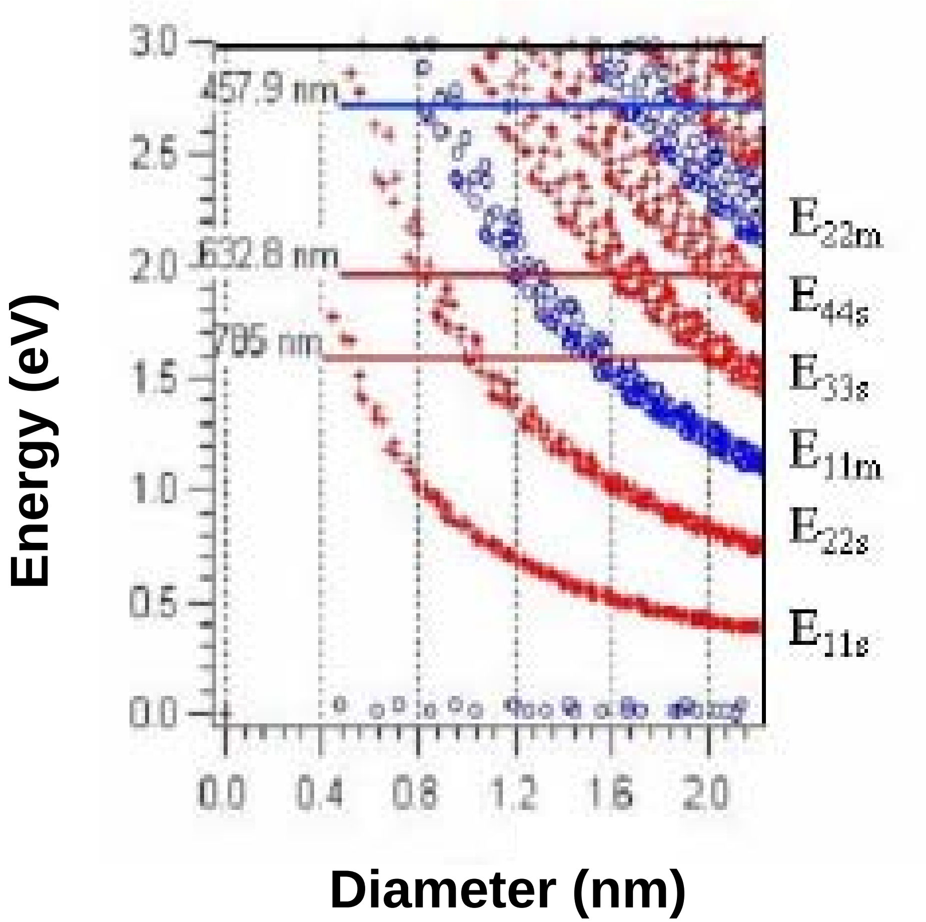
Calculated transitions

- Metallic (blue) and semiconducting (red)



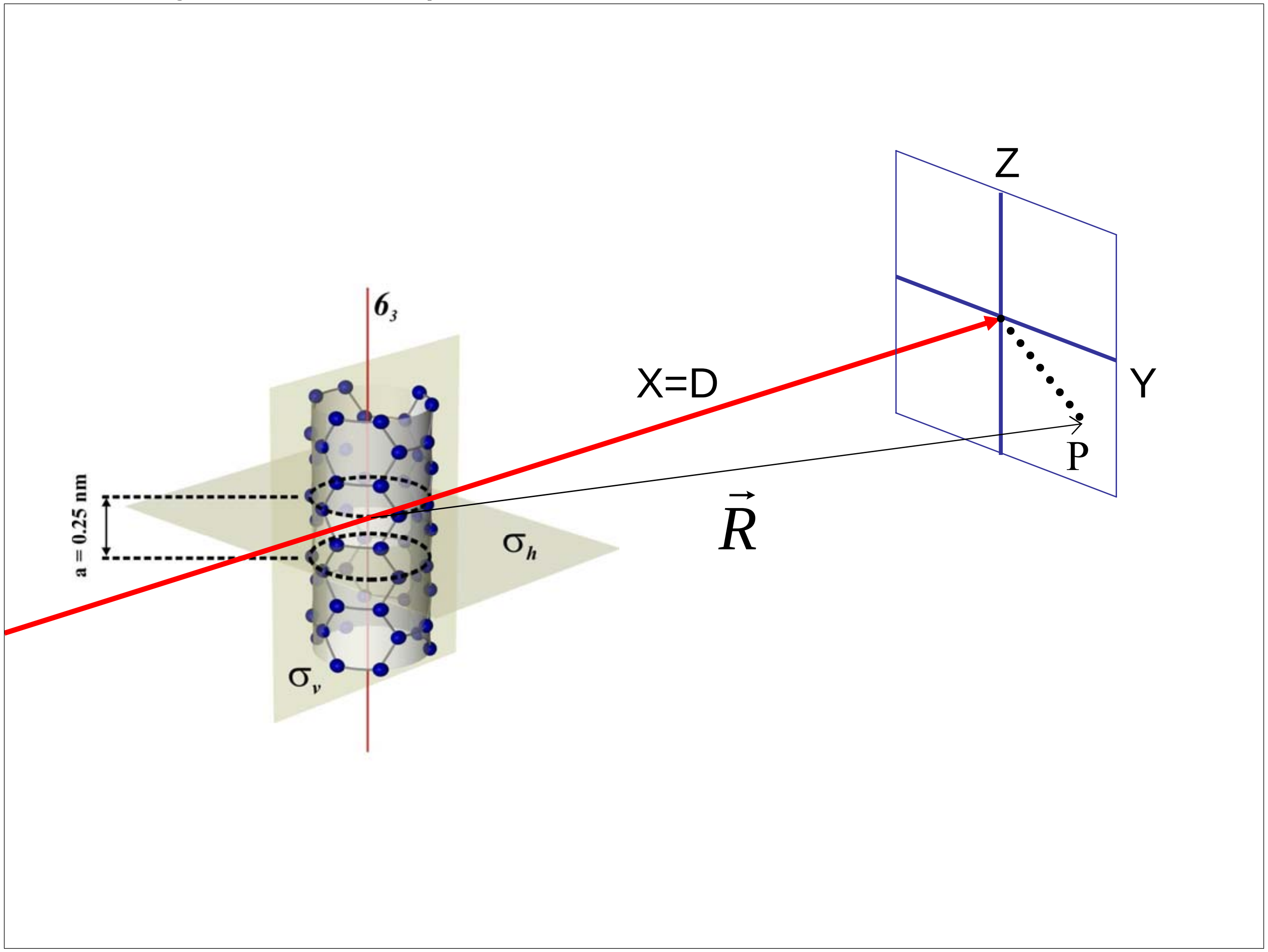
Need to determine which nanotube!

Structural determination via diffraction

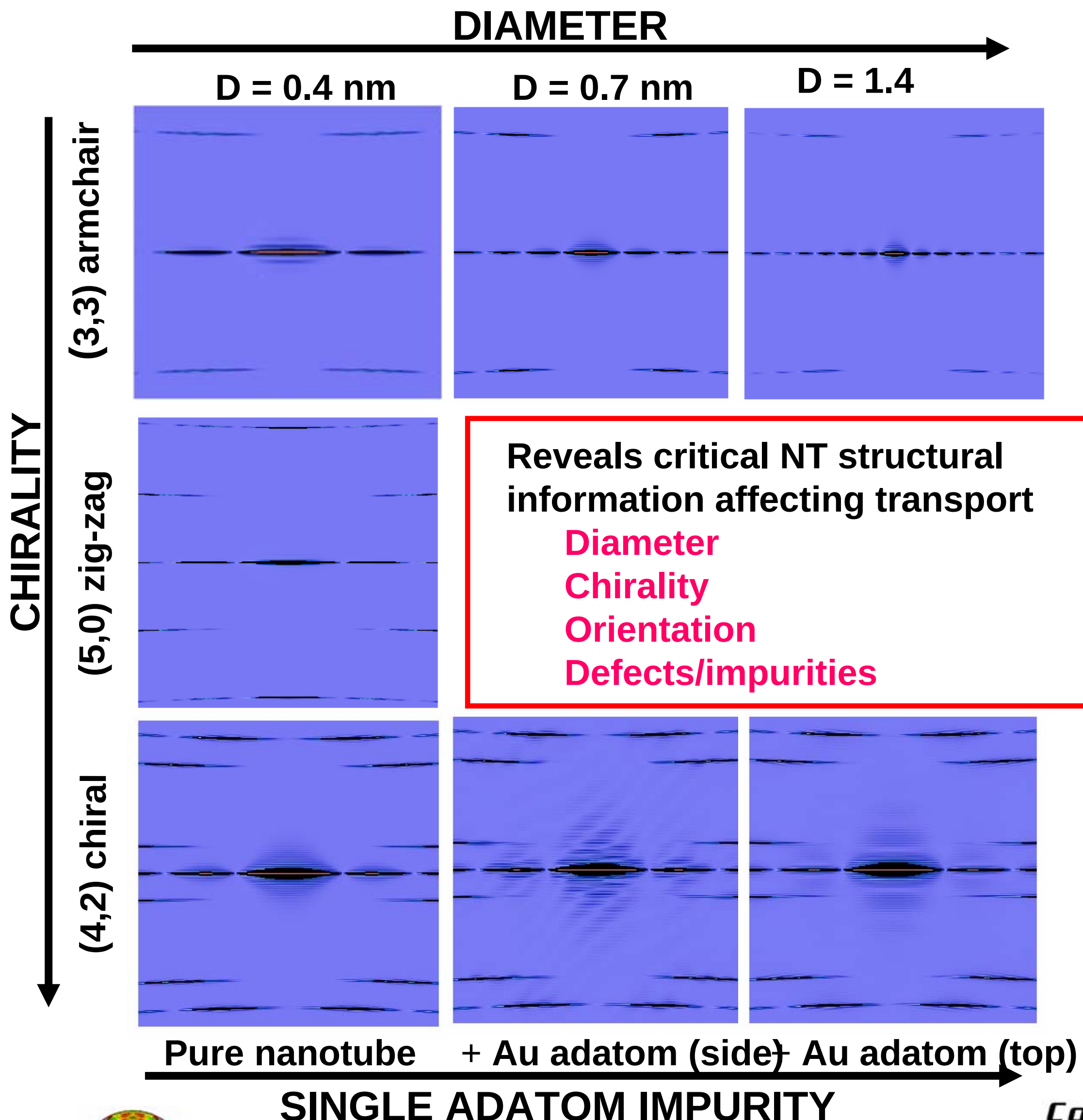
Kataura et al., Synth. Met. **103**, 2555 (1999).

Structure of an individual nanotube: Diffraction studies

Diffraction patterns of single CNTs were simulated on the 256-processor cluster Galaxy at the Computational Science Center, BNL.



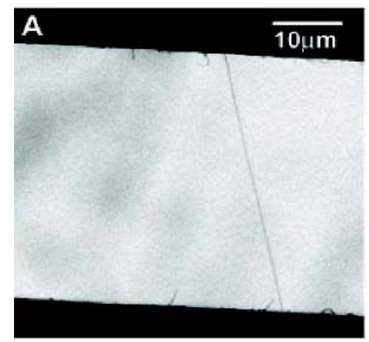
Diffraction from a single carbon nanotube



Reveals critical NT structural information affecting transport
- Diameter
- Chirality
- Orientation
- Defects/impurities

Simulation
- Known scattering factors
- 256 processor cluster (Galaxy,CSC)

Ready for study: SEM of single NT
- Suspended
- Metal contacts



Simultaneous
- Structure
- Transport

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Computational Science Center
Brookhaven National Laboratory

Bozovic, Bozovic, and Misewich

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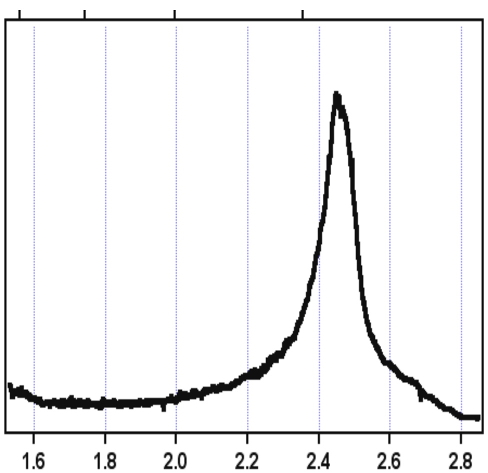
Electronic Structure ⟷ Physical Structure

Rayleigh Scattering Spectroscopy

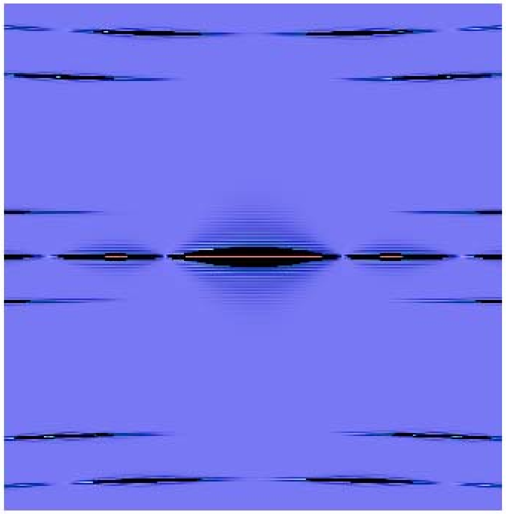
- Resonantly enhanced elastic light scattering [white light scattering from supercontinuum radiation source]
  - $\omega_{scattered} = \omega_{incident}$
- Probe dipole-allowed electronic transitions – analogous to absorption spectrum but easier to measure!



Columbia University (Heinz and Brus groups)

Electron Diffraction

- Electron scattering from parallel 20 nm beam at 200 keV.
- Spacing of equatorial oscillations are directly related to the diameter of the nanotube.
- Location of three first order diffraction spots in each quadrant give the chiral angle.

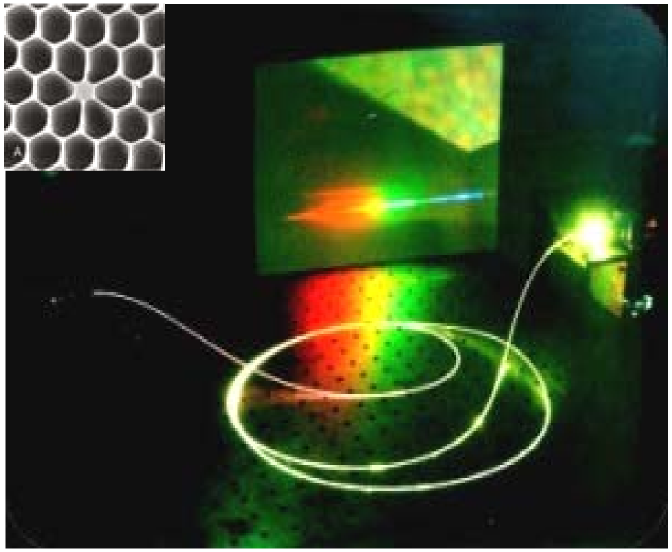


Supercontinuum Light

"White-light" laser: intense light source compatible with confocal microscopy methods.

Microstructured nonlinear fiber with ~ 2 μm core

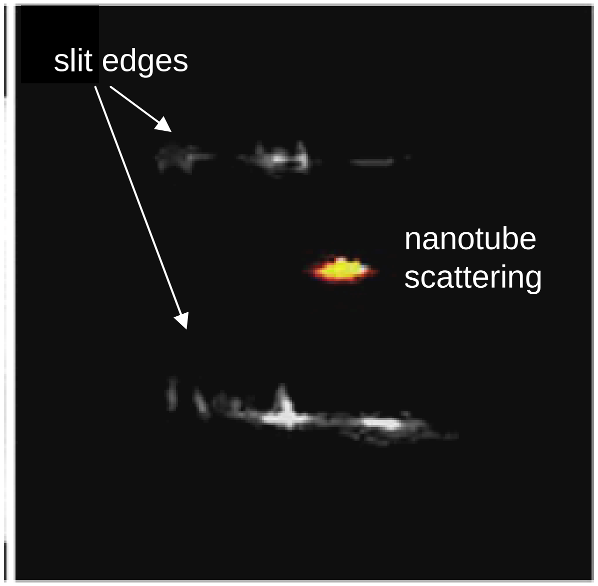
Laser brightness with a large spectral bandwidth (450 - 1450 nm)



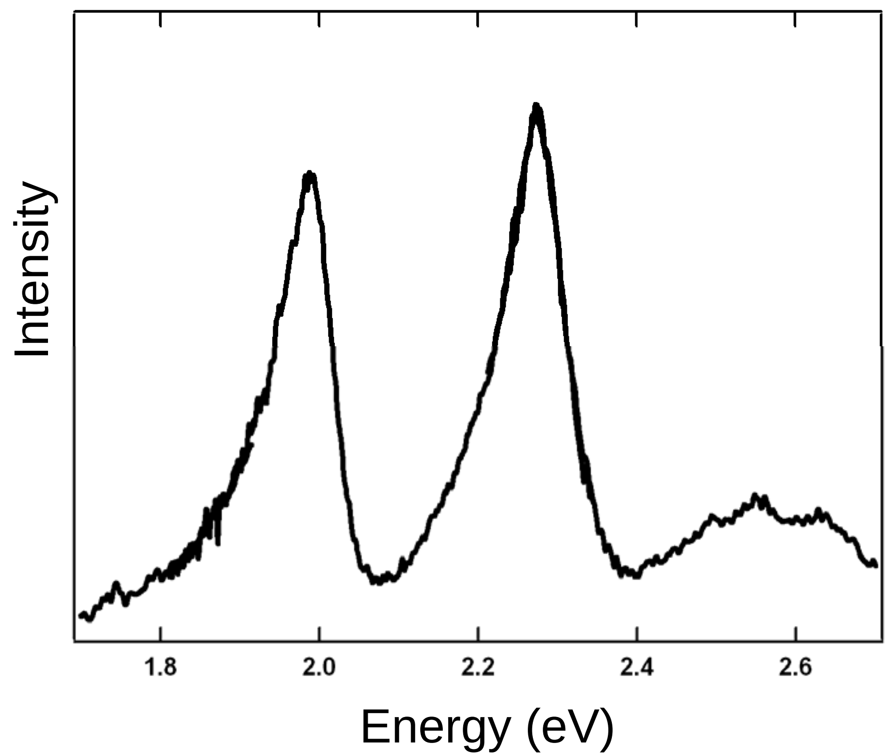
Nanotube Imaging

Look at total integrated intensity on CCD to find tubes. "Map" and correlate to electron microscopy images.

Single tubes scatter light much less than bundles. Distinguishable by the number of peaks in the spectra and width of features.

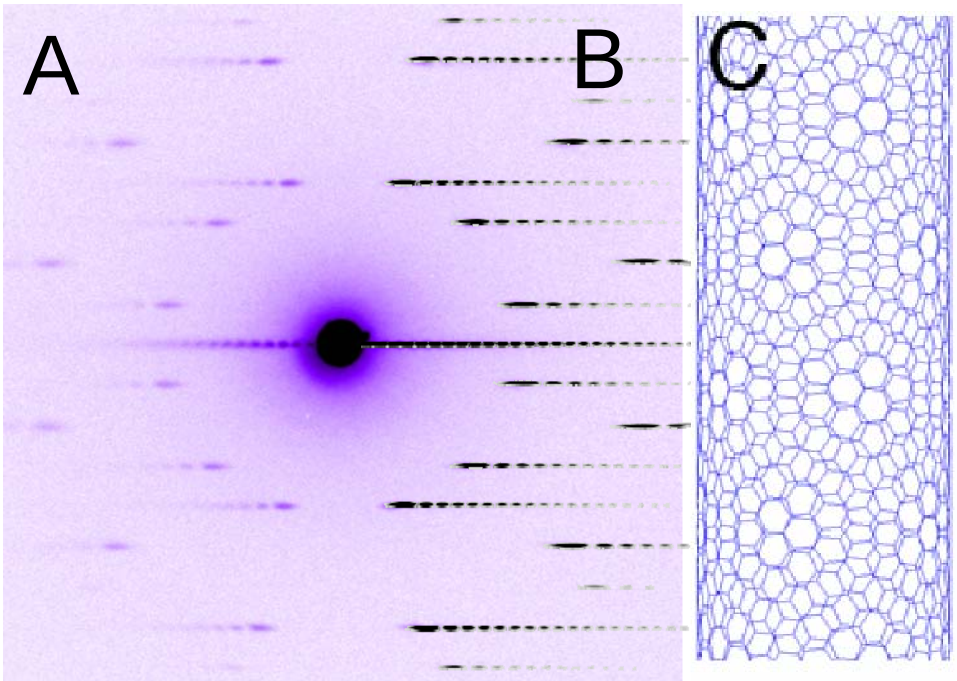


The (16,11) SWCNT



Electronic Transitions: 2.0 and 2.3 eV

Science *312*, 554 (2006)



A: experimental diffraction
B: simulated diffraction
C: model of (16,11) tube

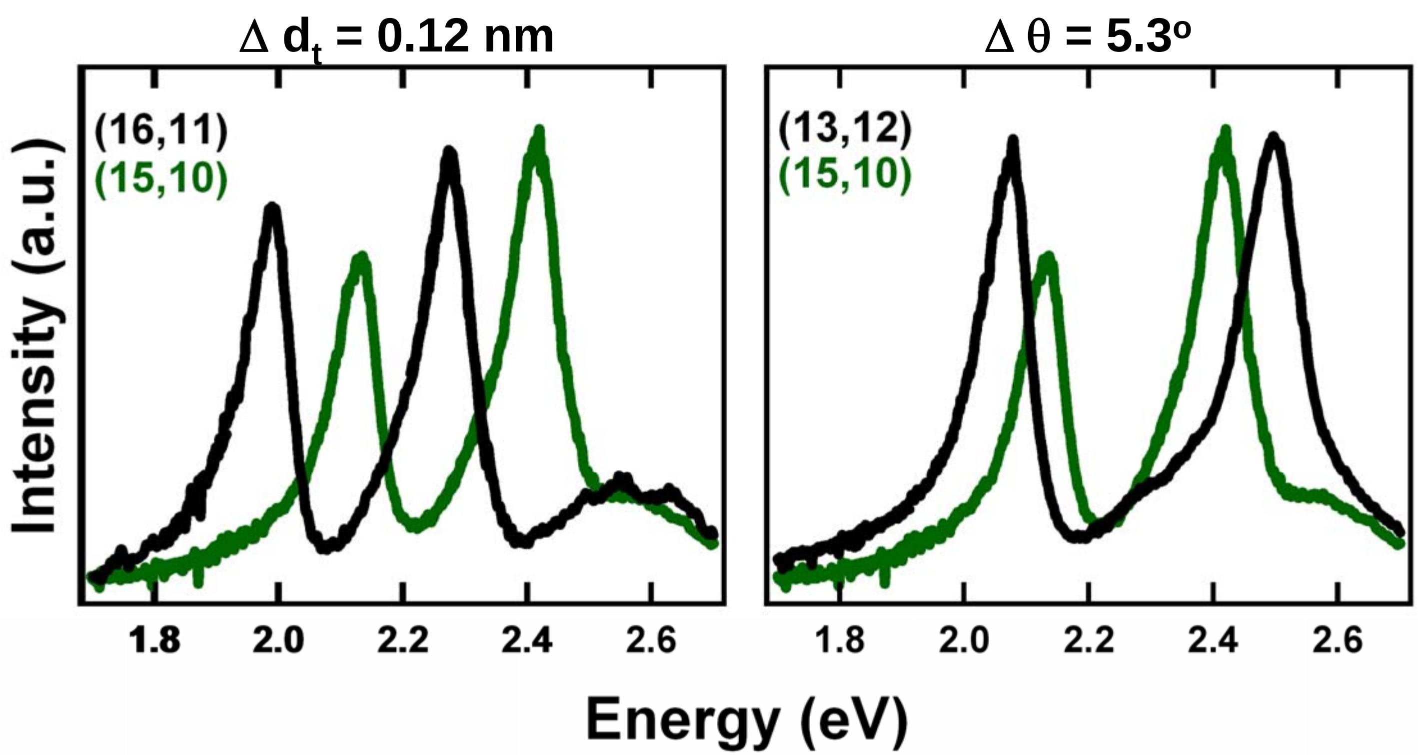
Diameter: 1.83 nm

Chiral Angle: 23.9º

Systematic spectroscopic studies

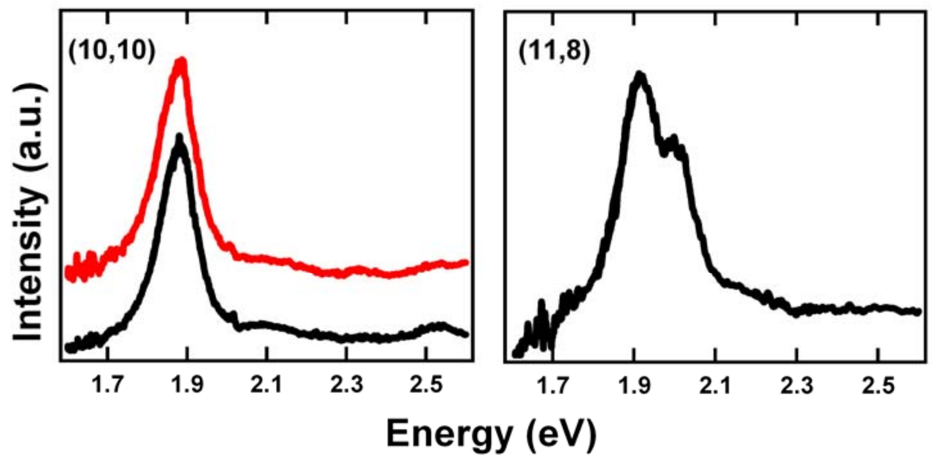
Complete picture for the systematic variation of the SWNT real electronic structure with changing structure

Constant Chiral Angle | Constant Diameter

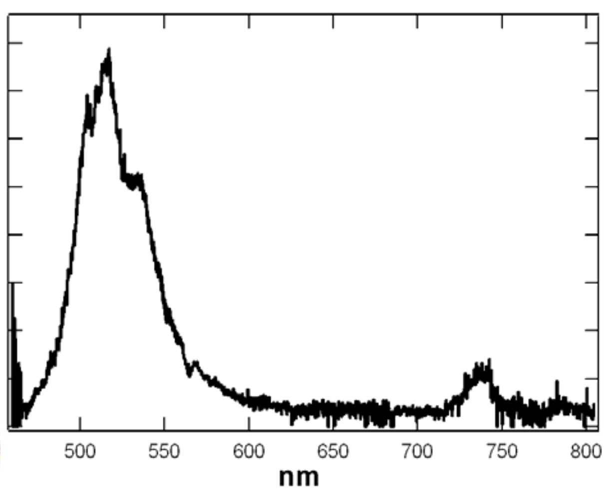


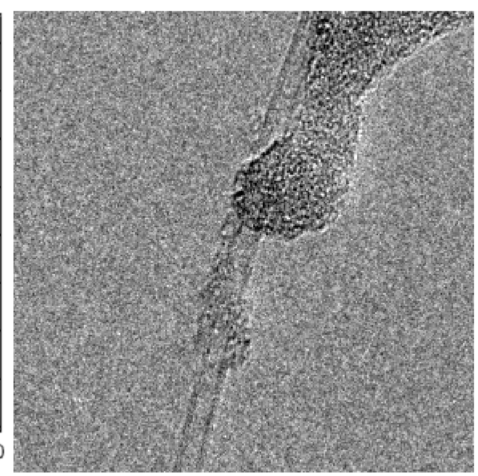
Metallic nanotube spectroscopy

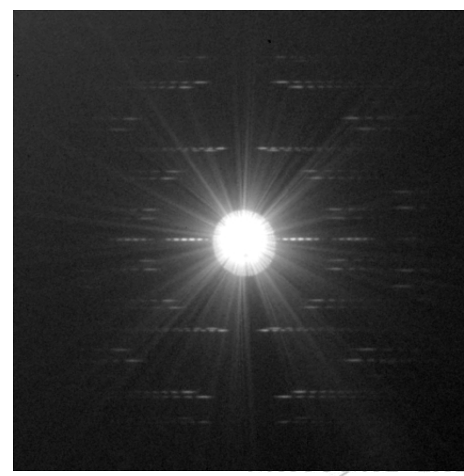
Trigonal Warping Effect in Metallic SWNT



Intertube Interactions in Double-walled Nanotubes





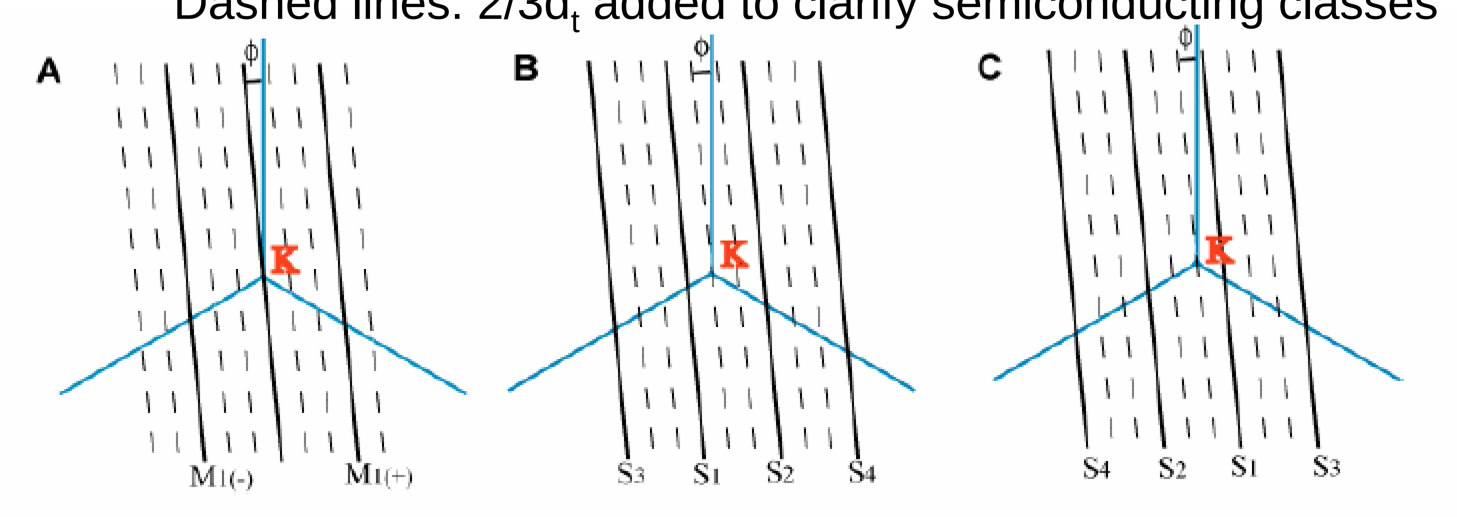


Qualitative agreement with zone folding

- Zone folding around K point in Brillouin zone

  Solid lines: $2/d_t$ available states (boundary conditions)

  Dashed lines: $2/3d_t$ added to clarify semiconducting classes



Metallic (non-armchair)

Semiconducting mod(n-m,3) = 1

Semiconducting mod(n-m,3) = 2

Asymmetry for finite ϕ →

metallic splitting

semiconducting family behavior :

(B odd bands have lower energy than C)

Nanotube chiral resolved spectroscopy

- Build database for understanding of electronic structure
  - Resolve tight binding corrections, many body effects

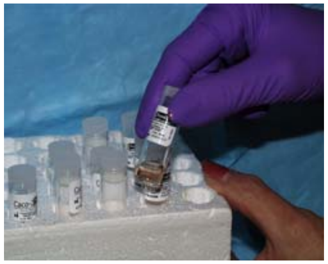
(n,m)	mod(n-m, 3)	d_t (nm)	θ (°)	Transition	E_{ii} (eV)
(16,11)	2	1.83	23.9	S_{33}	2.00
				S_{44}	2.30
(15,10)	2	1.71	23.4	S_{33}	2.15
				S_{44}	2.44
(13,12)	1	1.70	28.7	S_{33}	2.09
				S_{44}	2.52
(13,11)	2	1.63	27.2	S_{33}	2.19
				S_{44}	2.56
(10,10)	0	1.36	30	M_{11}	1.93
(11,8)	0	1.30	24.8	$M_{11(-)}$	1.93
				$M_{11(+)}$	2.02
(20,14)	0	2.35	24.2	$M_{22(-)}$	2.22
				$M_{22(+)}$	2.36

Science *312*, 554 (2006)

From solid-state to biophysics

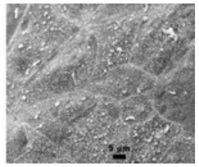
- Biocompatibility of nanotubes
  - Utilize low-Z sensitive TEM and FESEM techniques to image nanomaterial interaction with cells
- Biofunctionalization of nanotubes
  - Spectroscopy: utilize fluorescence microscopy to probe selectivity of protein after functionalization on nanotube
  - Transport: utilize sensitive single nanotube transport measurements to probe for complementary protein

Probing the interaction of nanotube with living cells



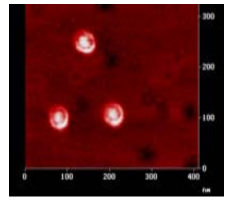
Cell Monolayers

Grown on coverslips in shell vials to confluency



Nanomaterial Syntheis and Purification

Characterization Suite including AFM to check nanoparticles



Nanoparticles added to vials

Vials incubated with rotary mixing (30min-7hr)

Our Model for Testing Nanomaterials uses:

a. monolayers of confluent human epithelial cells, representing the point of first contact for those working with nanomaterials

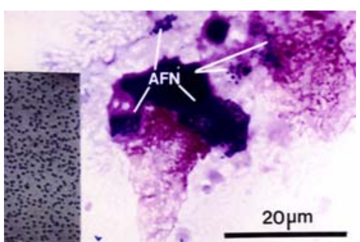
b. multiple methodologies to provide data on cell response & ultrastructure following exposure to nanomaterials;

c. analysis of culture media and washes

providing a rapid profile of cellular responses to a given nanomaterial

Removed media & 2 PBS washes

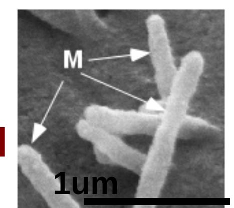
Analyzed for cells, nanoparticles & debris

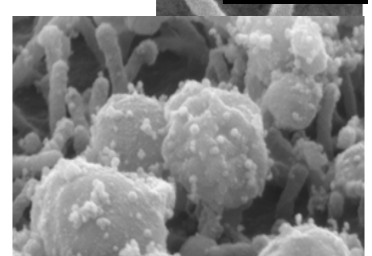


Coverslips removed

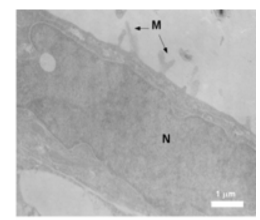
LM Histochemistry:
immuno-staining, vital staining (apoptosis, necrosis…)

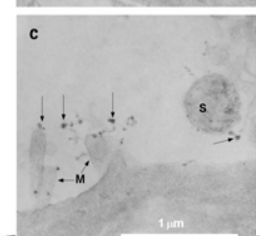
FESEM





TEM

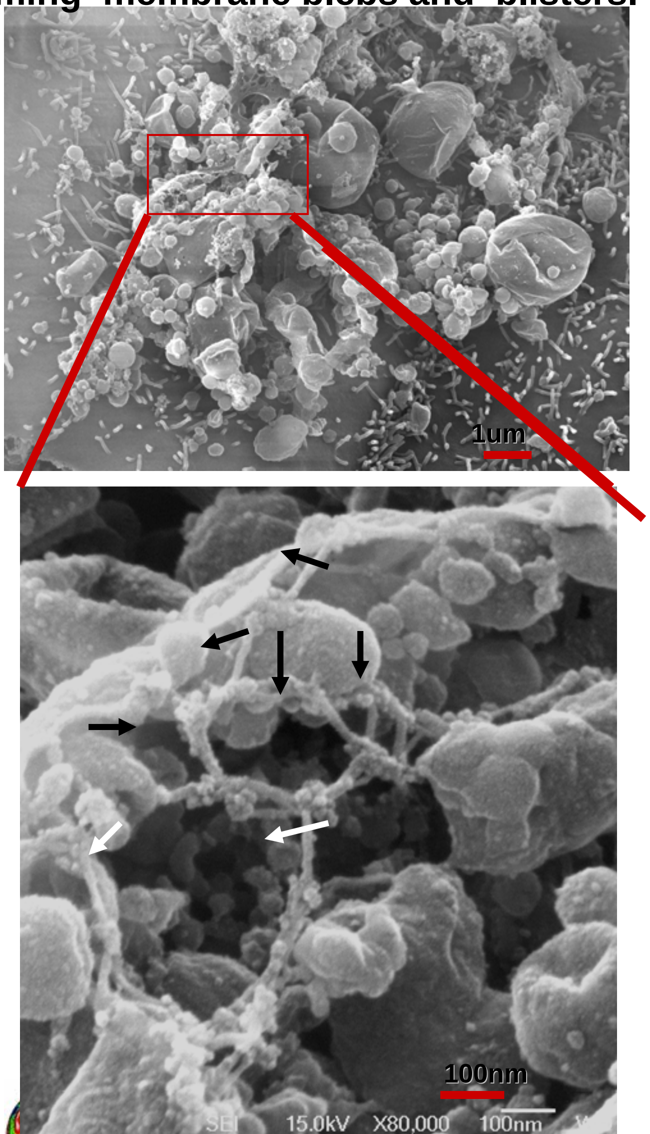


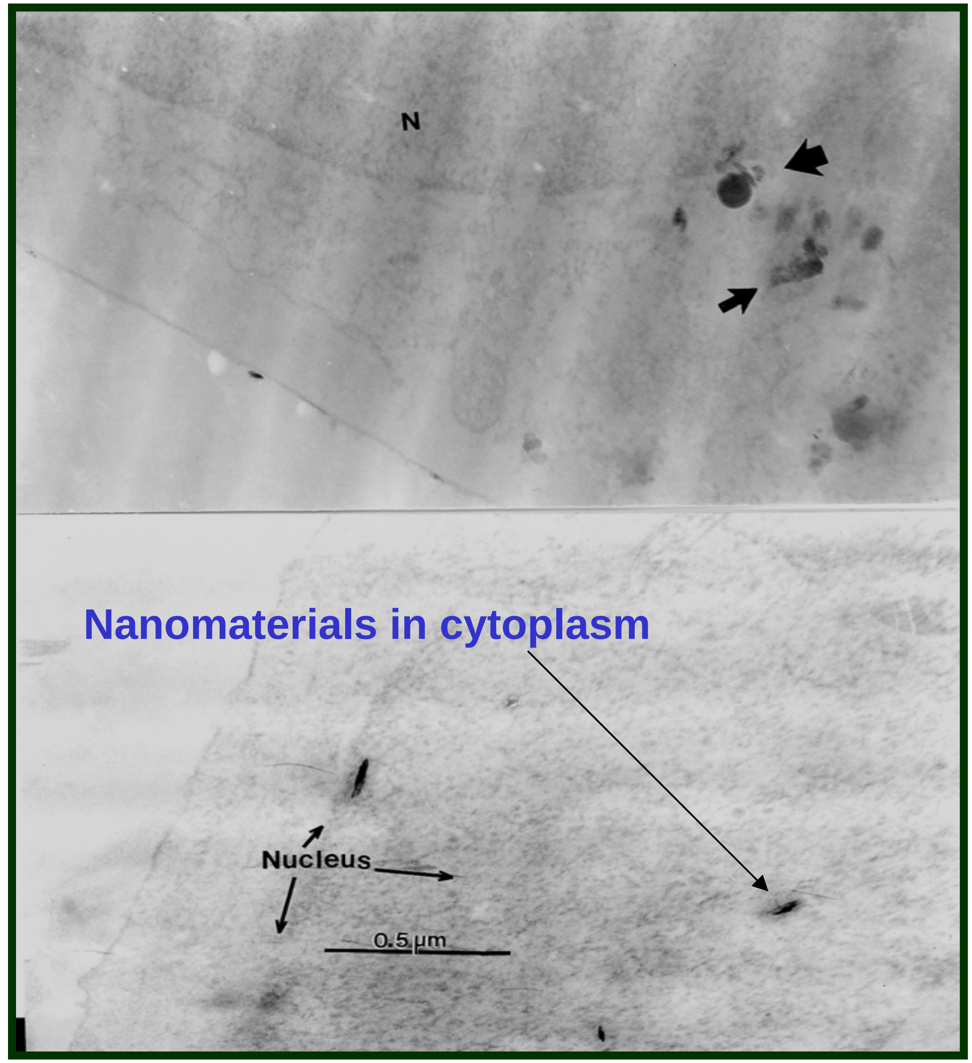


Raw nanotube interaction with human cells

Colon cells 1.5 hour exposure

Rapid abnormal reaction. Colon cells forming membrane blebs and blisters.

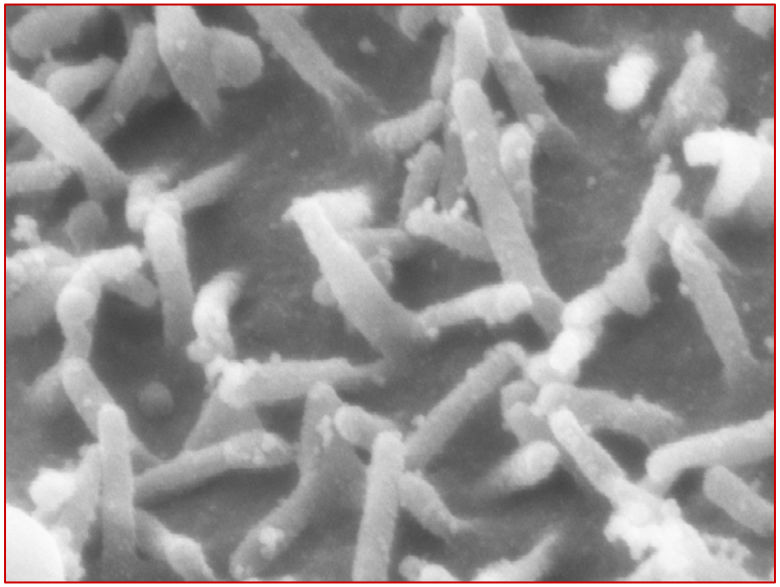




Rapid cell damage and cytoplasm penetration observed for raw nanotubes

Antibody functionalized carbon nanotube

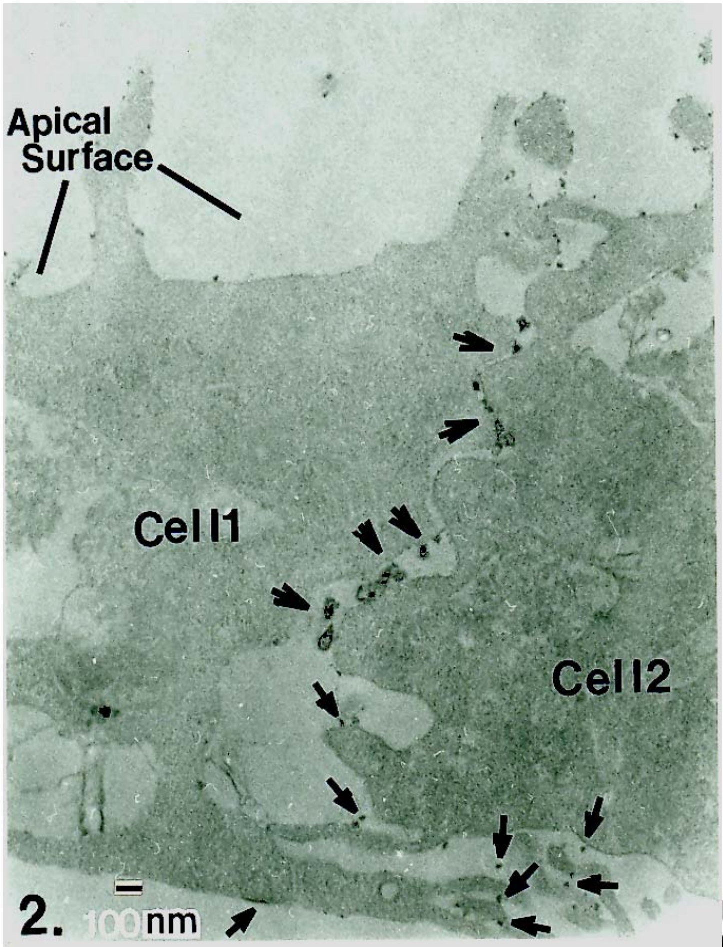
Colon Cells: At 2.5 hr incubation cells treated with mAb-functionalized nanotubes show normal microvilli and surface morphology by FESEM and TEM.



No immediate negative reaction and no cytoplasm penetration observed for antibody functionalized nanoloops

Long term effects yet to be investigated

Lung cells: At 2.5 hr incubation nanomaterial can be seen passing through the intercellular space (arrows) to the basal region of the cell.



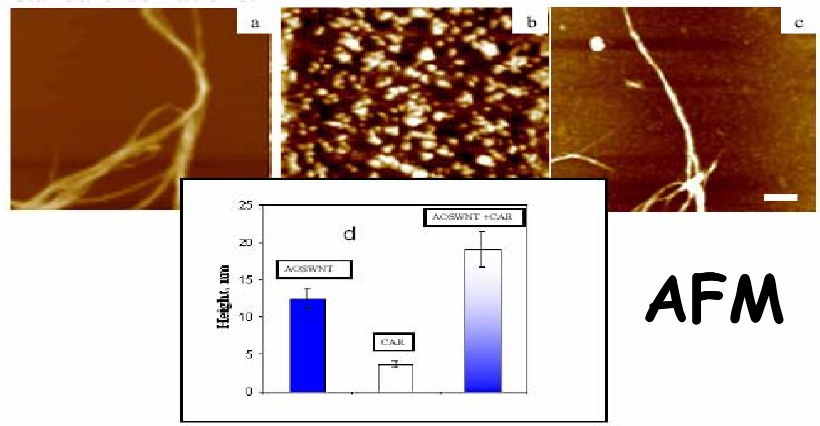
Basic Energy Sciences
Department of Energy

BROOKHAVEN NATIONAL LABORATORY

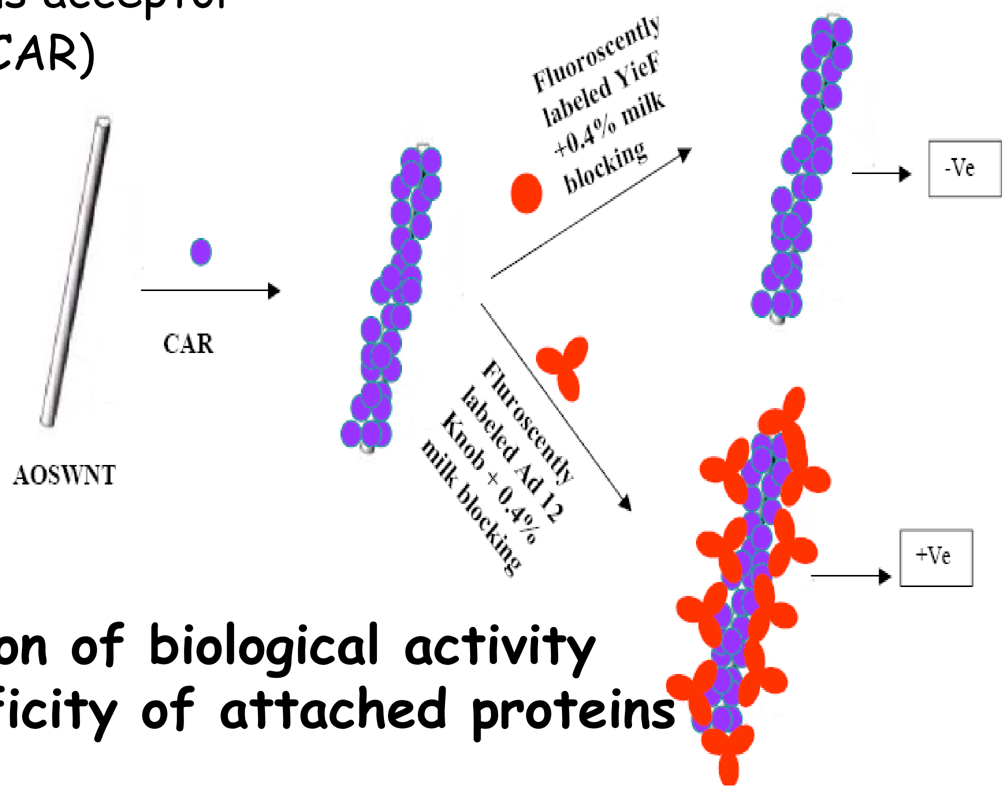
Protein functionalization of carbon nanotubes

Successful attachment of proteins to carbon nanotubes

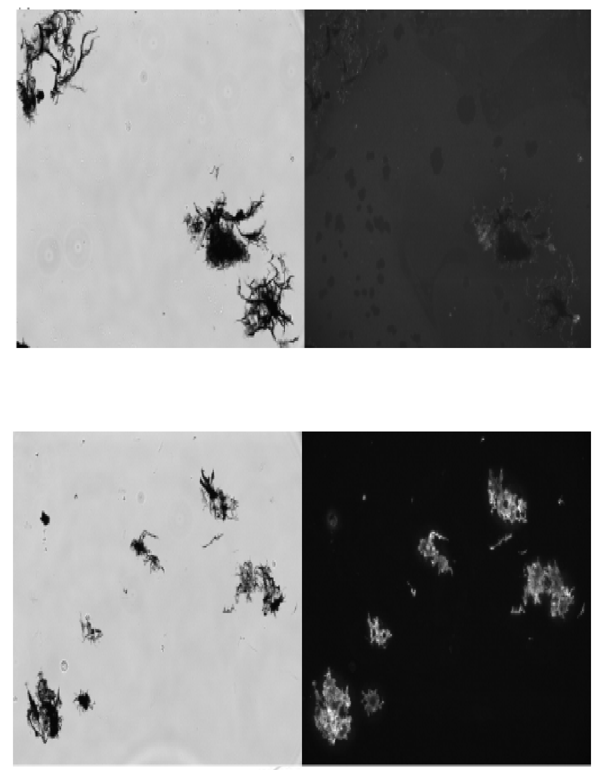
- Adenovirus Ad12 Knob protein
- Complementary human coxsackievirus and adenovirus acceptor protein (CAR)



AFM



Optical **Fluorescence**



Observation of biological activity and specificity of attached proteins

Summary

Solid-state physics

- Transport studies in nanotubes
  - Electrostatic control of band bending
  - Simultaneous ambipolar transport and electroluminescence
- Optical spectroscopy of single nanotubes
  - Dependence of spectrum on nanotube diameter and length
  - Polarization along nanotube axis
- Spectroscopy and structure on same nanotube
  - Directly reveal family behavior and metallic splitting
  - Best approach for determining corrections to tight binding

Biophysics

- Biocompatibility (via TEM)
  - Interaction depends on nanomaterial surface functionalization
- Biofunctionalization (via spectroscopy and transport)
  - Highly sensitive, highly specific protein sensing

Coworkers

- BNL
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  - Stan Wong
  - Aaron Stein
  - Tobi Beetz
  - Yimei Zhu
  - Lijun Wu
- IBM
  - Richard Martel (U. Montreal)
  - Phaedon Avouris
  - Jimmy Tsang
  - Marcus Freitag
  - Yves Martin
  - Vasili Perebeinos
  - Jia Chen
  - Jerry Tersoff
  - Stephan Heinze
- Columbia
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  - Louis Brus
  - Jim Hone
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