Electron Transport in Molecules, Nanotubes and Graphene

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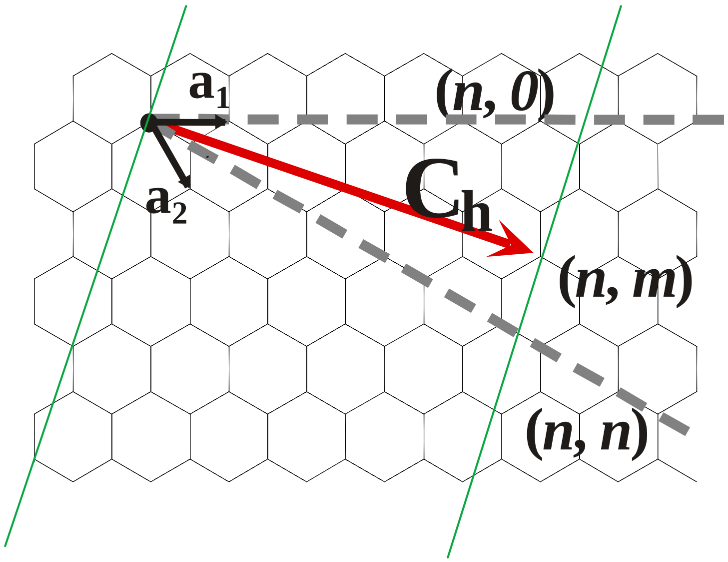
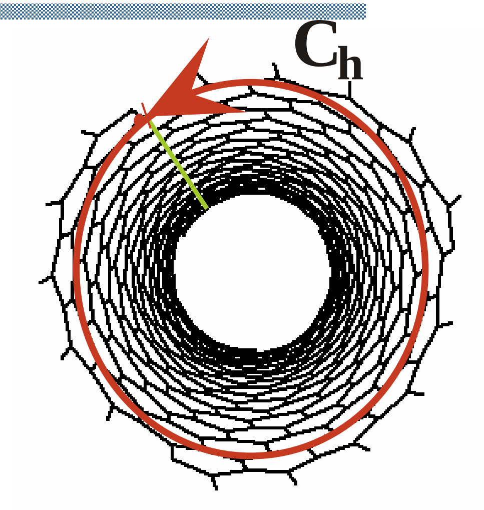
Columbia University and the National Science Foundation
Center for Electron Transport in Molecular Nanostructures

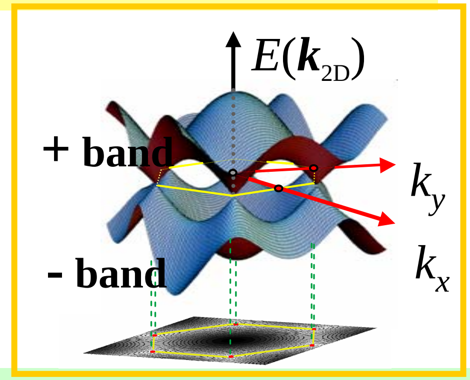
Rolling Up Graphene: Periodic Boundary Condition

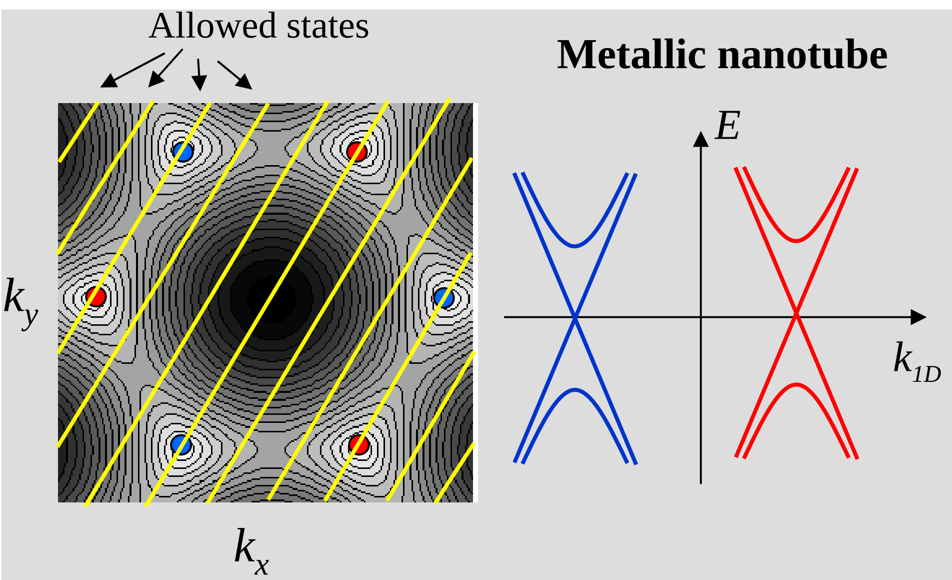


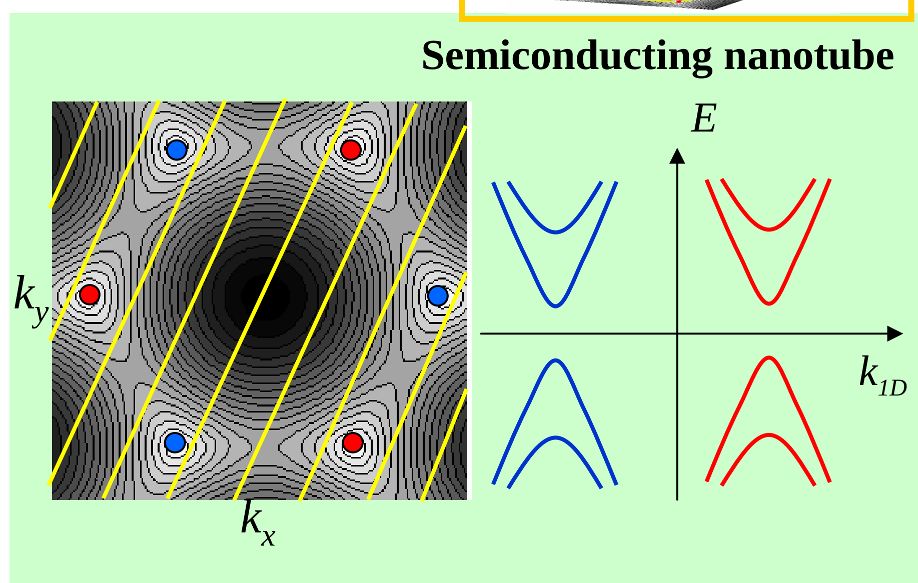


Periodic Boundary Condition

$$C_h \cdot \vec{k}_{\perp} = 2\pi q$$

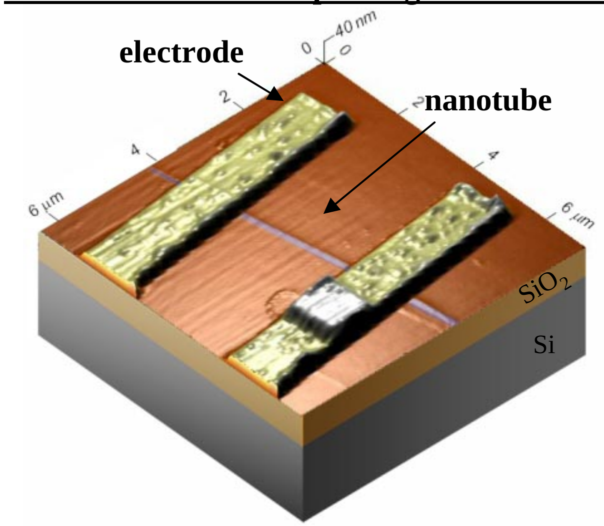


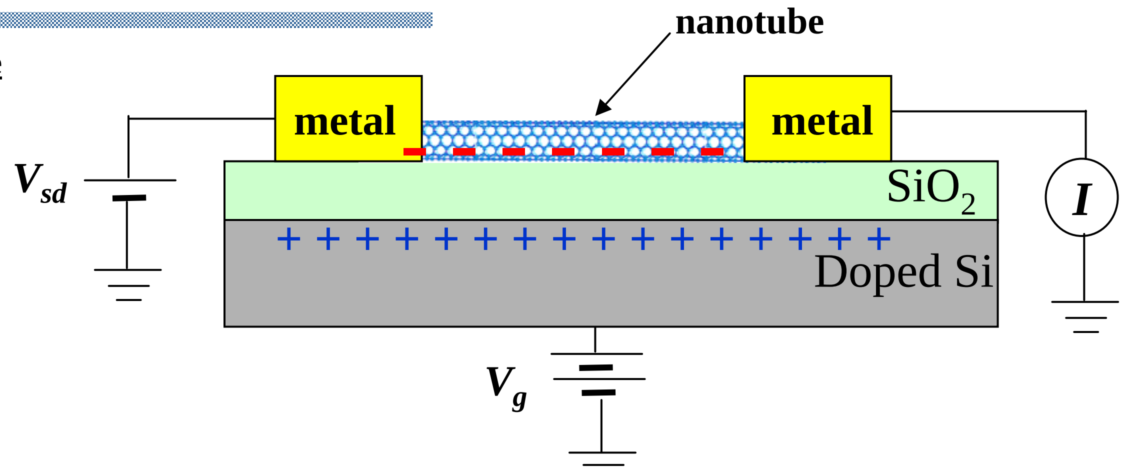




Tuning Carrier Density by Electric Field Effect

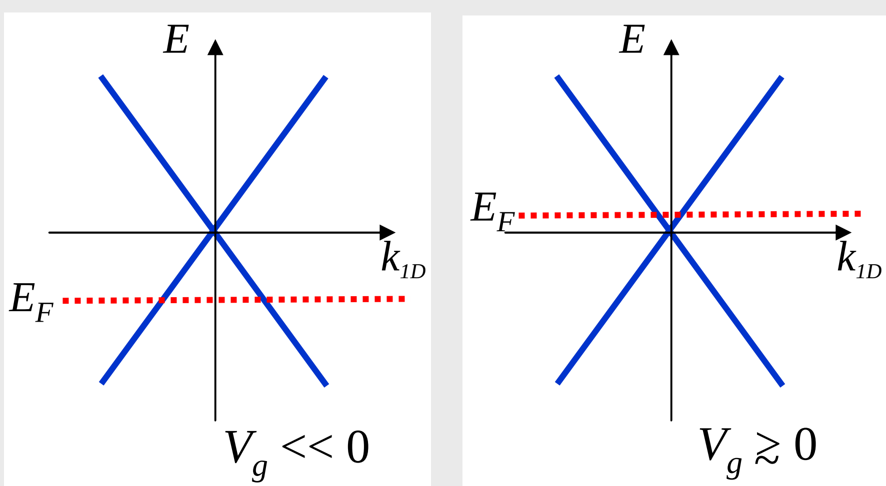
Atomic force microscope image of nanotube device



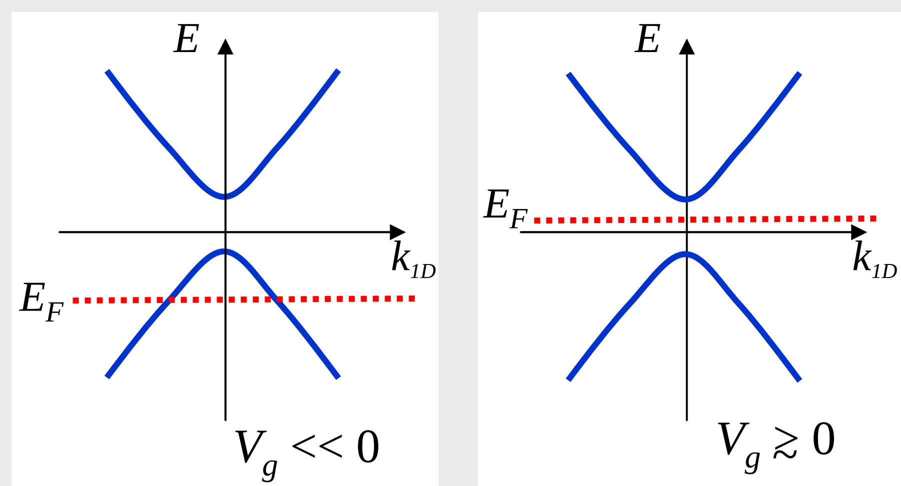


Induced charge: $C_g\, V_g = e\, n = e\,(\text{D.O.S})\, \Delta E_F$

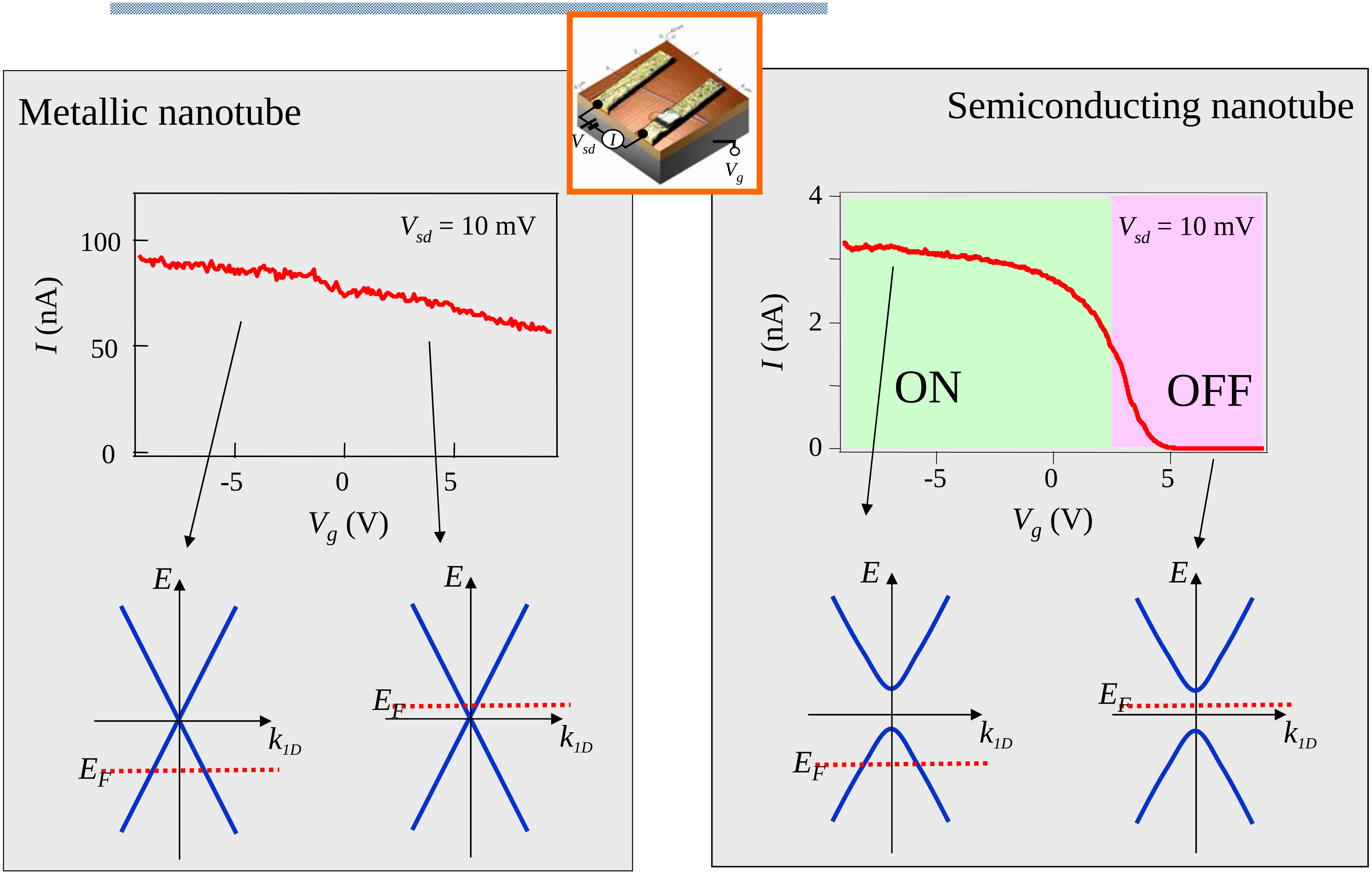
Metallic nanotube



Semiconducting nanotube



Electrical Transport in Nanotube Devices



Controlled Growth of Ultralong Nanotubes

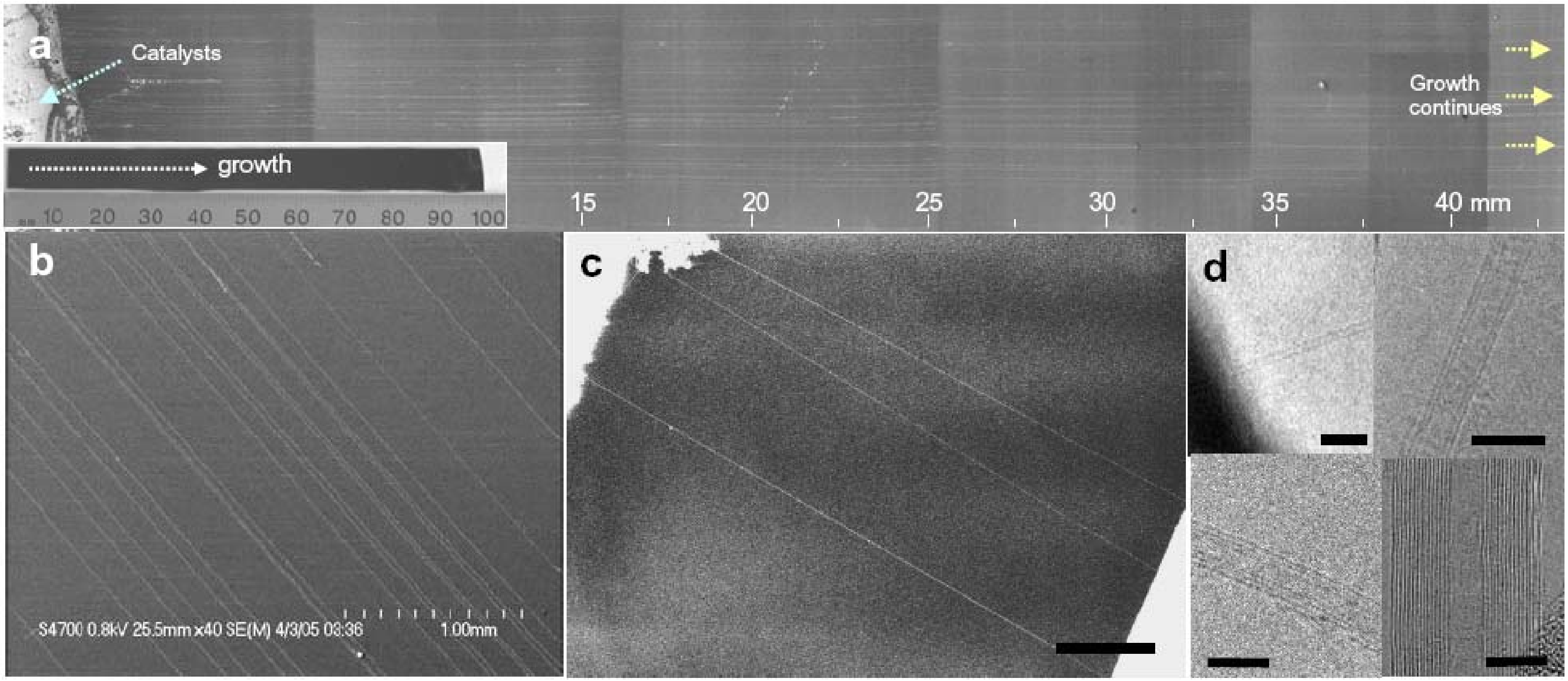
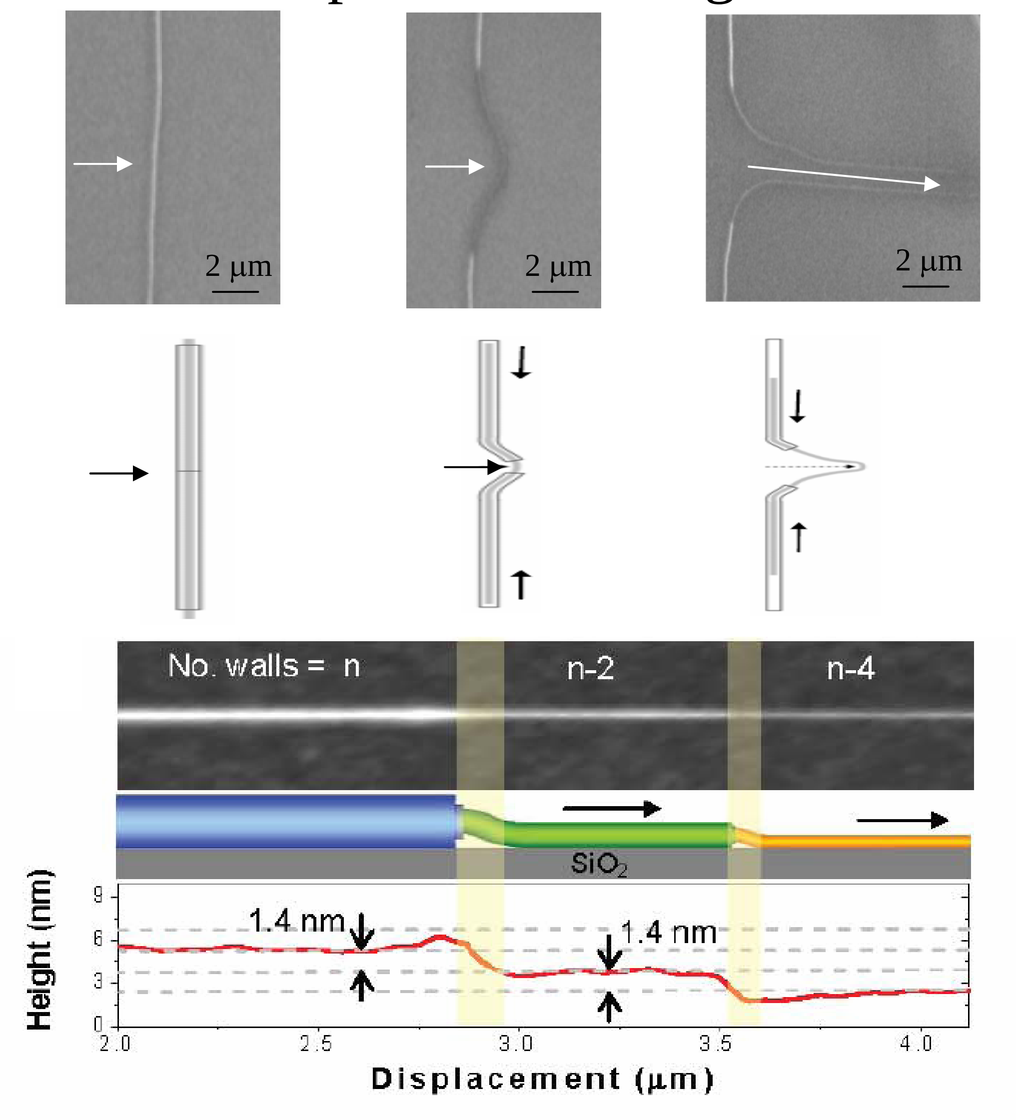


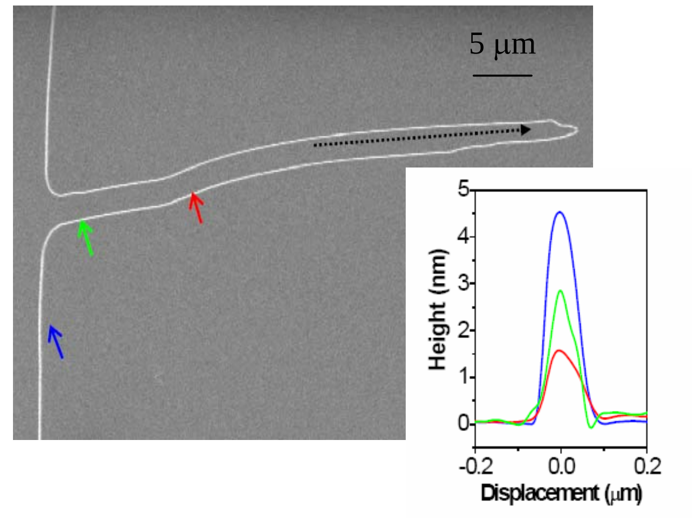
Figure 3. SEM and TEM images of ultralong MWNTs. (a) Schemetic representation for the diameter-dependent stabilization of reaction gas flows. By inserting the smaller tube inside the outer chamber, microscopic turbulent flows can be stabilized into laminar flows with lower Reynolds numbers. (b) SEM image of MWNTs, which are several centimeters long. Scale bar, 2mm. (c) A SEM image of MWNTs grown across a 100 µm slit. Scale bar, 20µm. D, HRTEM images showing single, double, triple, and multi-walled CNTs. Scale bars, 5 nm.

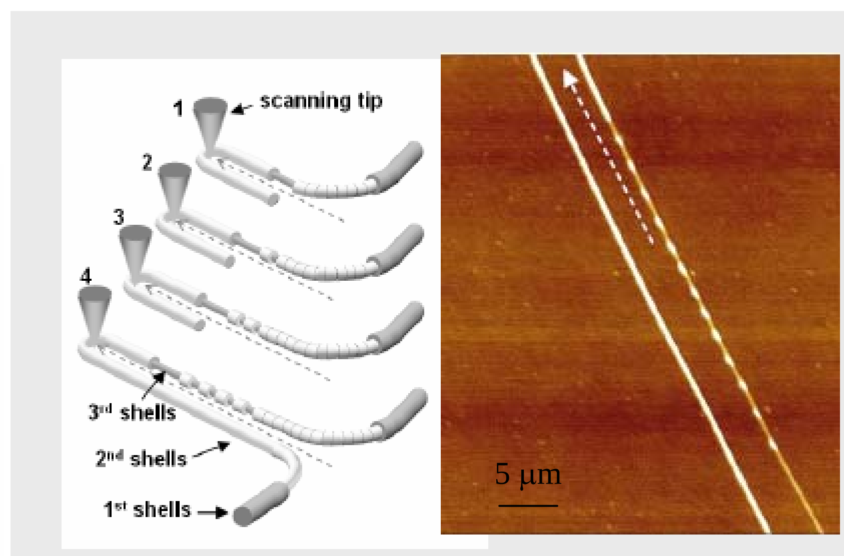
B. H. Hong, J. Y. Lee, T. Beetz, Y. Zhu, P. Kim and S. Kim (2005)

Extraction of Inner Shells from MWNTs

AFM manipulation of long MWNTs

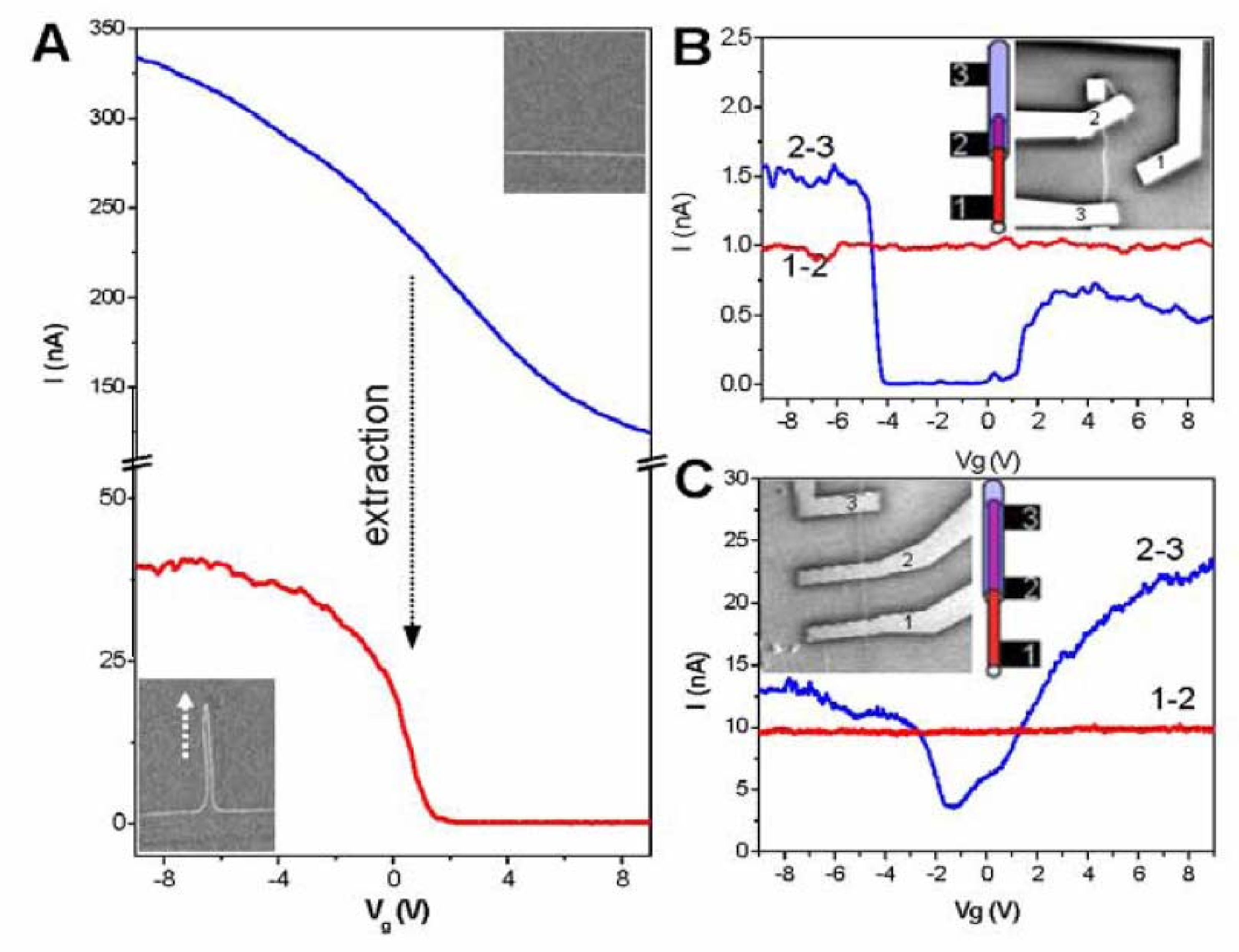






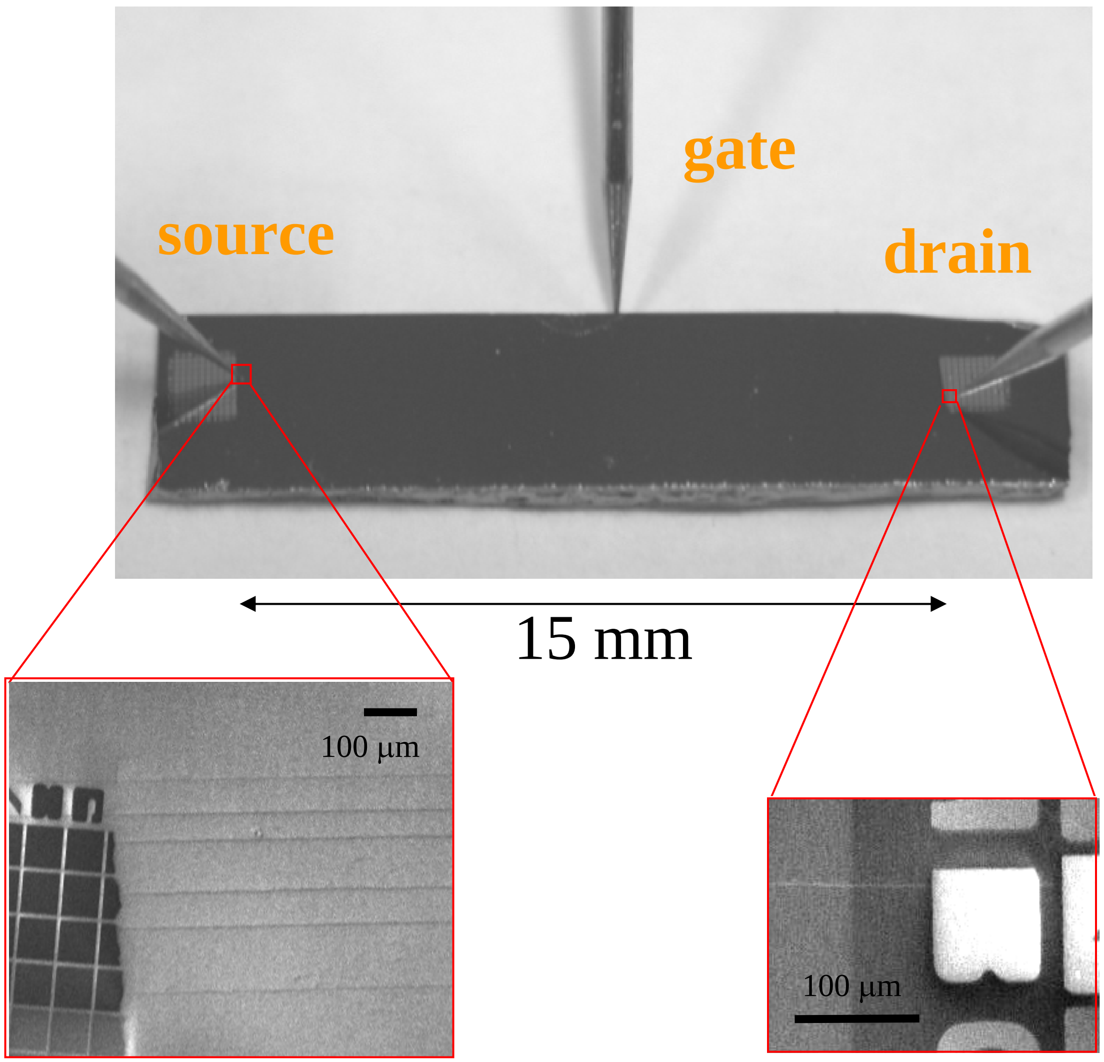
Hong, et al, PNAS (2005)

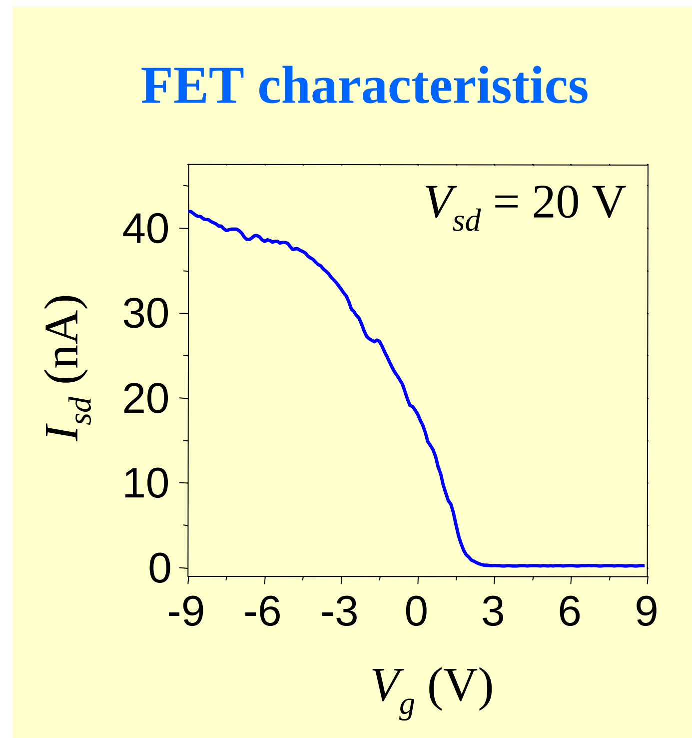
Intershell and Intrashell Nanotube Devices



Hong, et al, PNAS (2005)

Extremely Long SWNT Field Effect Transistor

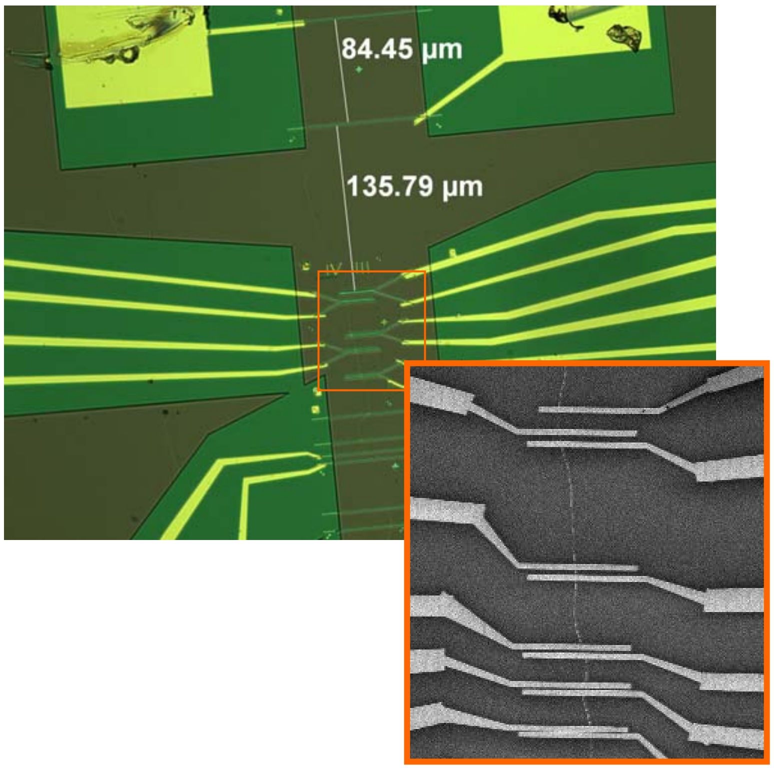


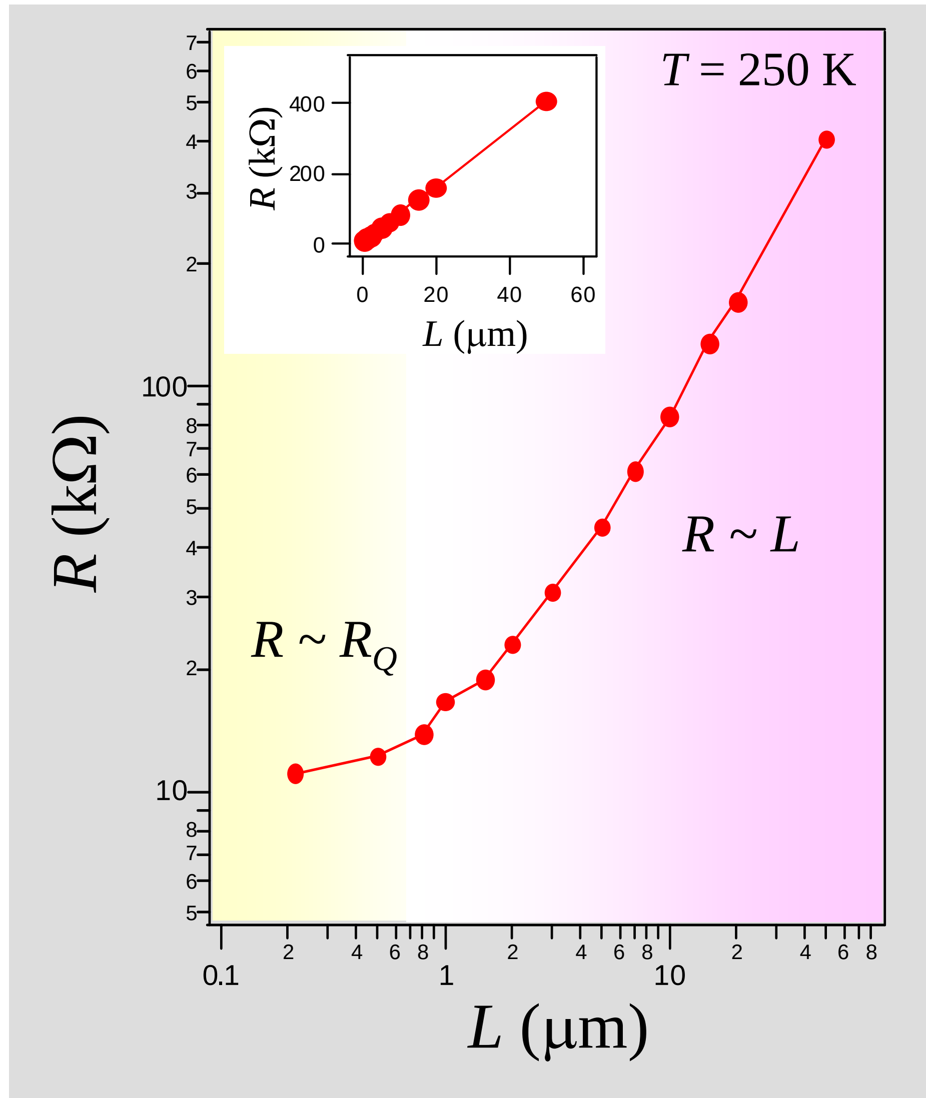


$\rho \sim 10^{-7}\ \Omega$ m

Electron Transport in Long Single Walled Nanotubes

Multi-terminal Device with Pd contact



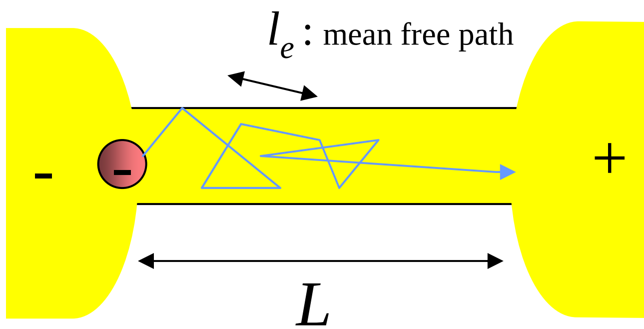


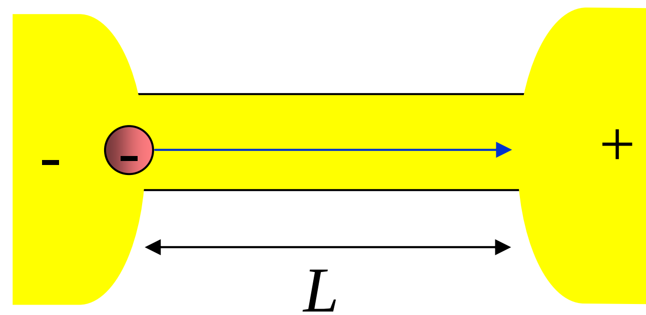
* Scaling behavior of resistance: $R(L)$

M. Purewall, A. Ravi, and P. Kim (2006)

Ballistic Transport and Mean Free Path

Electron Transport in 1D Channel





Diffusive transport: $l_e << L$

$$R(L) = \rho L$$

Ballistic transport: $L < l_e$

$$R(L) = h/N e^2 = R_Q$$

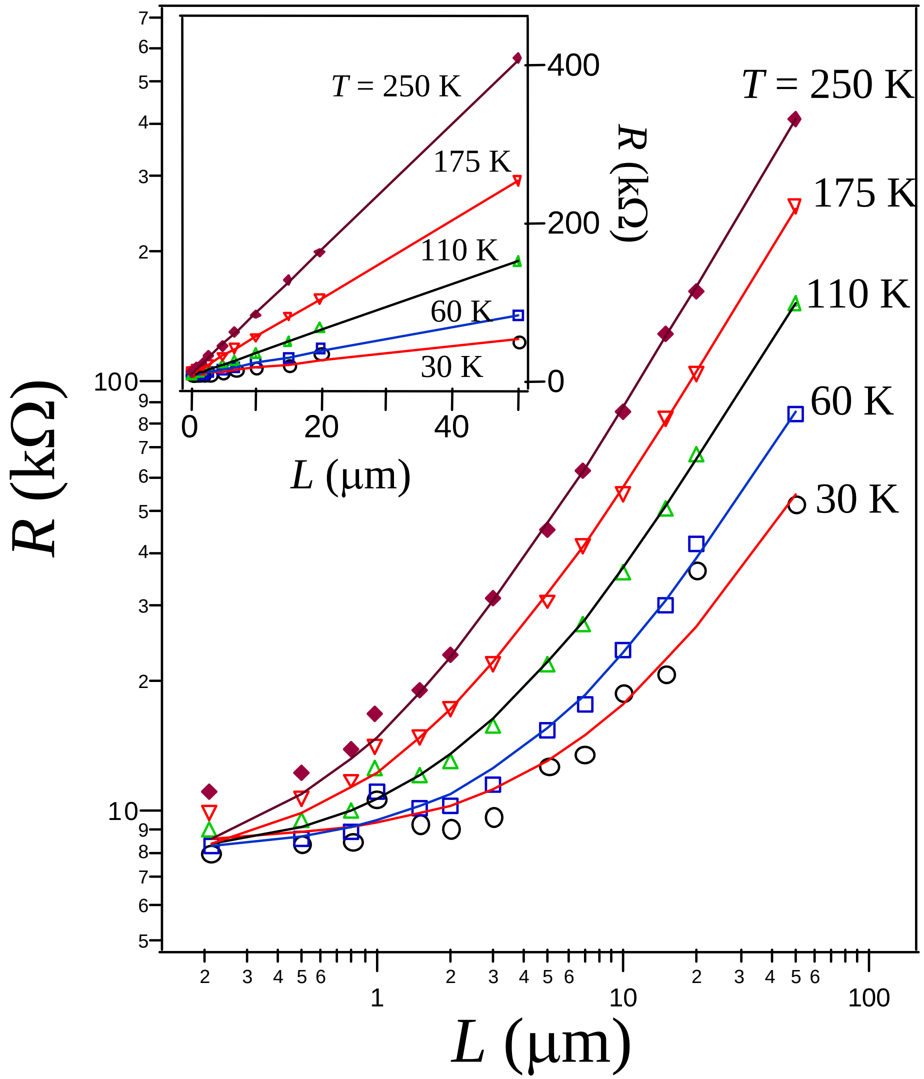
# of channel

Resistance of N- 1D Channel:

$$R(L) = \frac{h}{Ne^2} + \frac{h}{Ne^2}\frac{L}{l_e}$$

For a nanotube, $N = 4$ (2 from spin and 2 from ***K*** and ***K’***)

Electron Mean Free Path of Nanotube

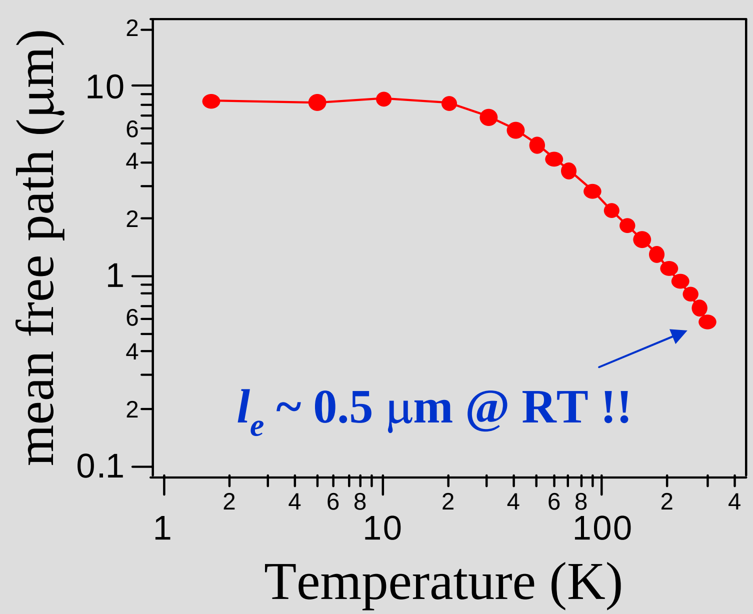


Lines are fit to

$$R(L) = R_c + \frac{h}{4e^2} + \frac{h}{4e^2}\frac{L}{l_e}$$

$$\frac{h}{4e^2} = 6.45\ \text{k}\Omega$$

Non-ideal contact resistance $R_c < 2$ kΩ



Extremely Long Mean Free Path: Hidden Symmetry ?

Carbon nanotube:

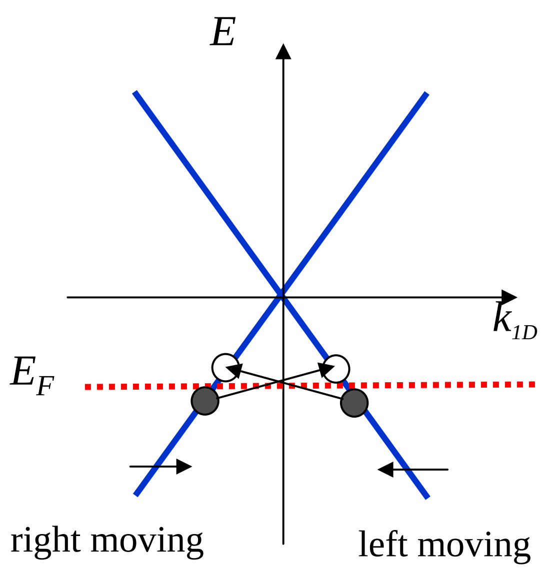
$l_e \sim$ **10 μm @ 1.6 K**

$l_e \sim$ **0.5 μm @ 300 K**

Ga[Al]As HEMT:

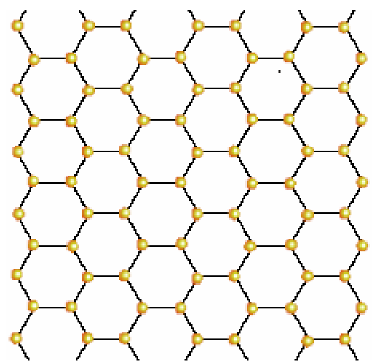
$l_e \sim$ **100 μm @ 1.6 K**

$l_e \sim$ **0.06 μm @ 300 K**



•Small momentum transfer backward scattering must be inefficient.

Selection rules by hidden symmetry in graphene?



T. Ando, JPSJ (1998);McEuen at al, PRL (1999)

Electric Field Effect in Mesoscopic Graphite

APPLIED PHYSICS LETTERS **86**, 073104 (2005)

Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices

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(Received 31 August 2004; accepted 11 December 2004; published online 7 February 2005)

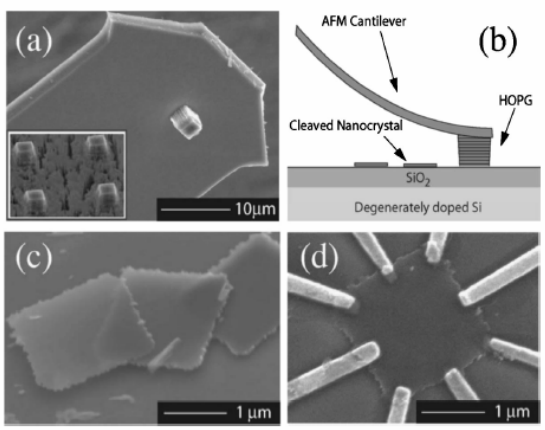
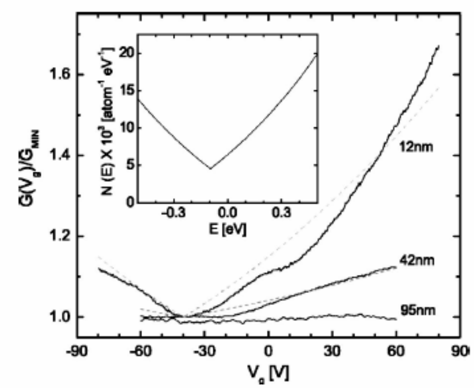


FIG. 1. (a) Scanning electron microscope image of an HOPG crystallite mounted on a microcantilever. Inset: bulk HOPG surface patterned by masked anisotropic oxygen plasma etching; (b) schematic drawing of the microcleaving process; (c) thin graphite samples cleaved onto the SiO_2/Si substrate; (d) a typical mesoscopic device fabricated from a cleaved graphite sample.



PRL **94**, 176803 (2005) PHYSICAL REVIEW LETTERS week endi[ng] 6 MAY 2[005]

Electric Field Modulation of Galvanomagnetic Properties of Mesoscopic Graphite

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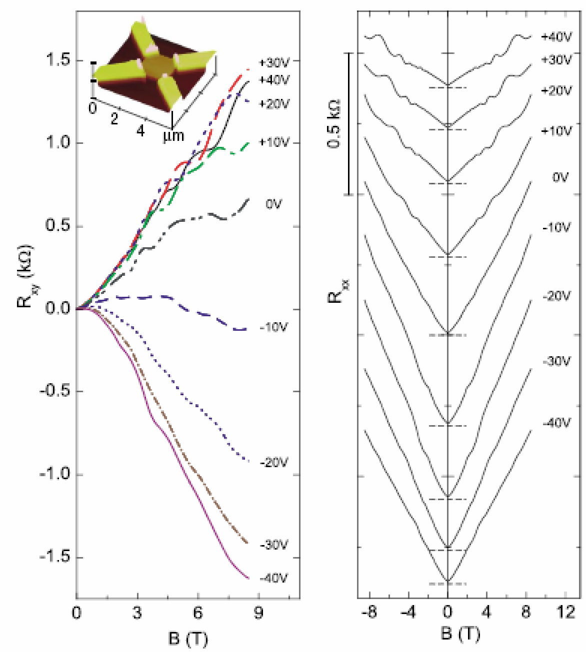

Simple Yet Efficient Mechanical Extraction

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device and, consequently, change an electric current through it. As the semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors (*1*) and carbon nanotubes (*2*). It has long been tempting to extend the use of the field effect to metals [e.g., to develop all-metallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies than traditional semiconducting devices (*3*)]. However, this would require atomically thin metal films, because the electric field is screened at extremely short distances (<1 nm) and bulk carrier concentrations in metals are large compared to the surface charge that can be induced by the field effect. Films so thin tend to be thermodynamically unstable, becoming discontinuous at thicknesses of several nanometers; so far, this has proved to be an insurmountable obstacle to metallic electronics, and no metal or semimetal has been shown to exhibit any notable (>1%) field effect (*4*).

We report the observation of the electric field effect in a naturally dimensional (2D) material few-layer graphene (FLG). name given to a single layer densely packed into a be ture, and is widely used to ties of many carbon-based m graphite, large fullerenes, na carbon nanotubes are usual graphene sheets rolled up int cylinders) (*5–7*). Planar gr been presumed not to exist being unstable with respect t curved structures such as so nanotubes (*5–14*).

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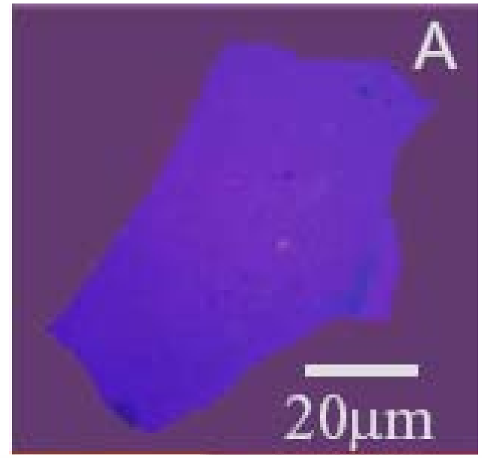
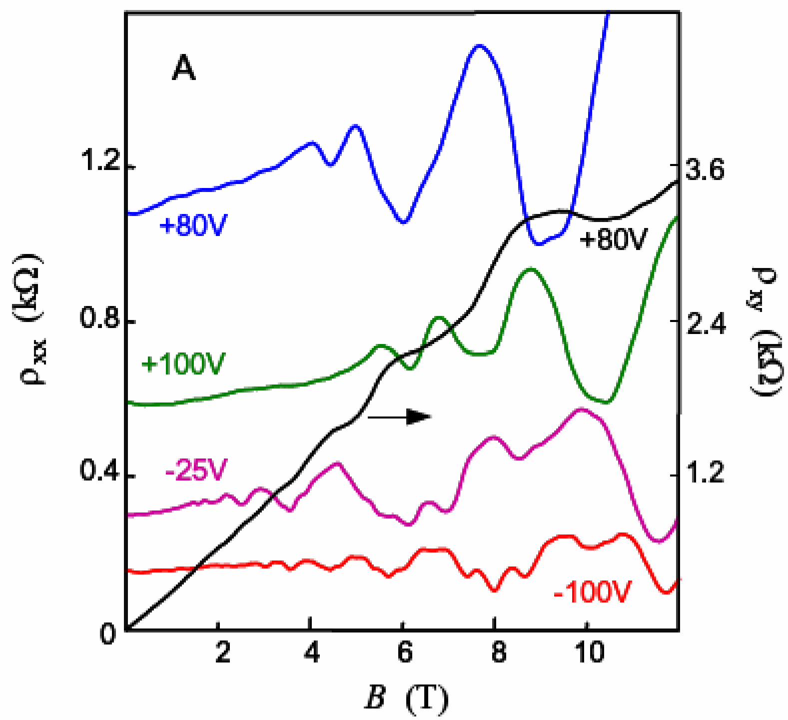
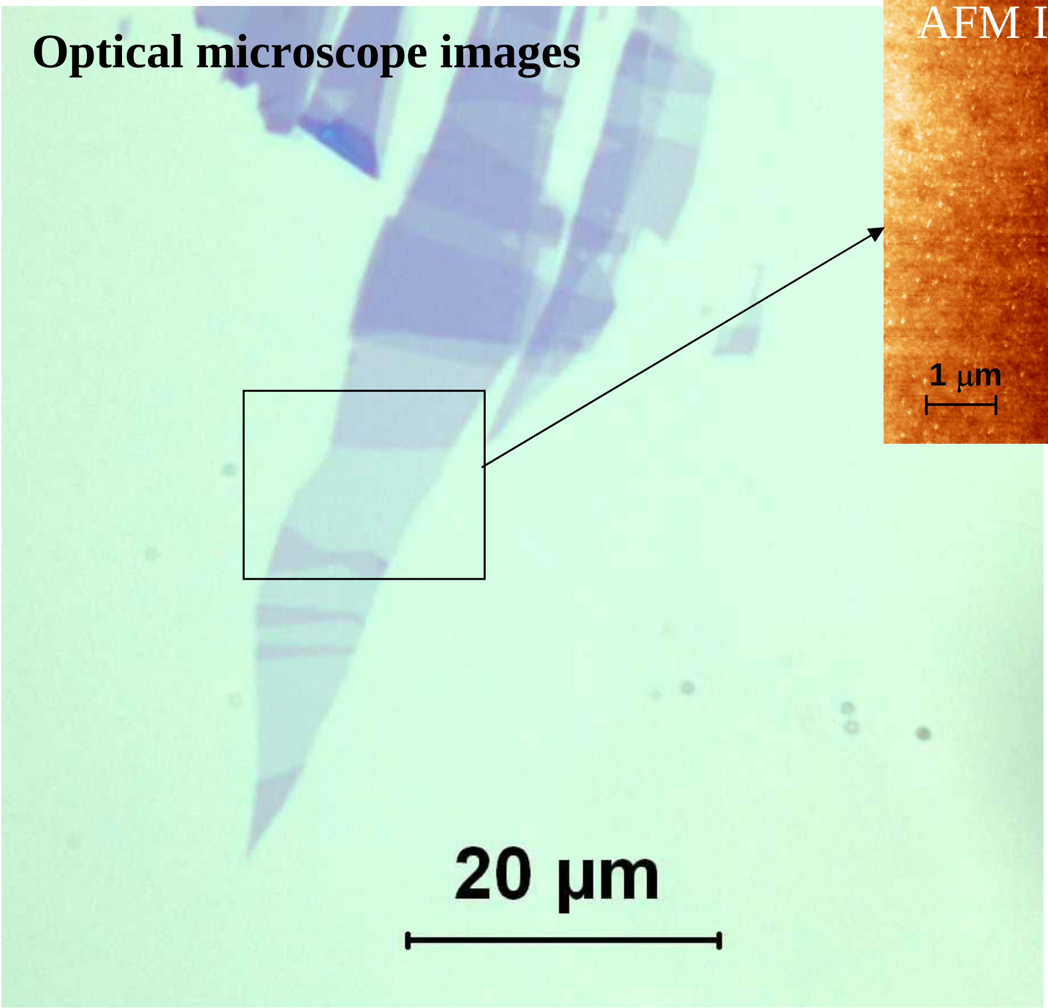
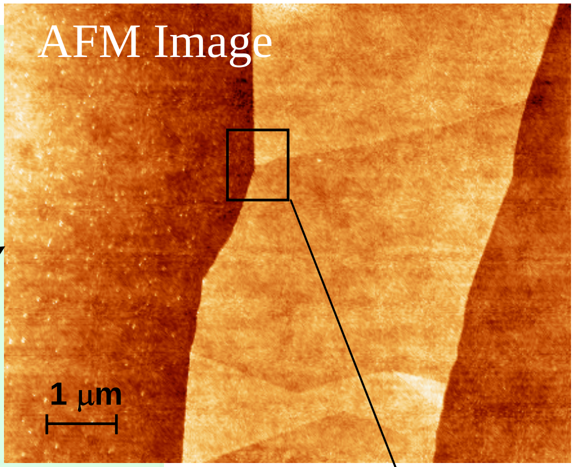


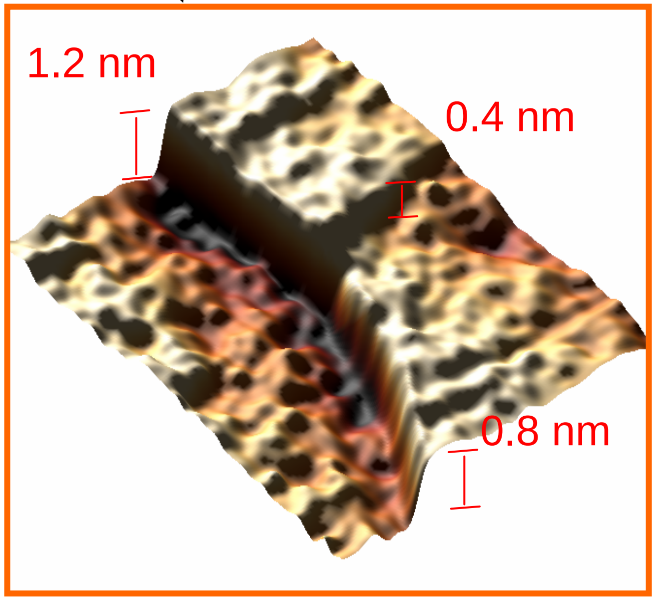


Using Scotch Tape is Essential!!

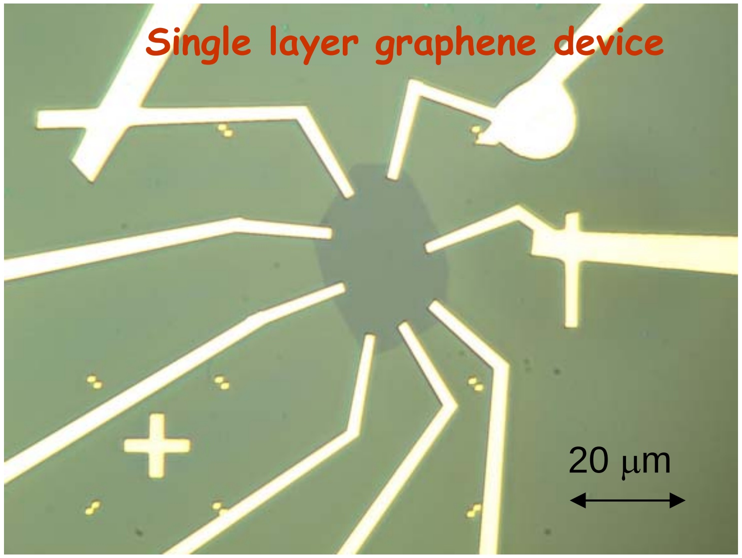
A Few Layer Graphene on SiO_2/Si Substrate

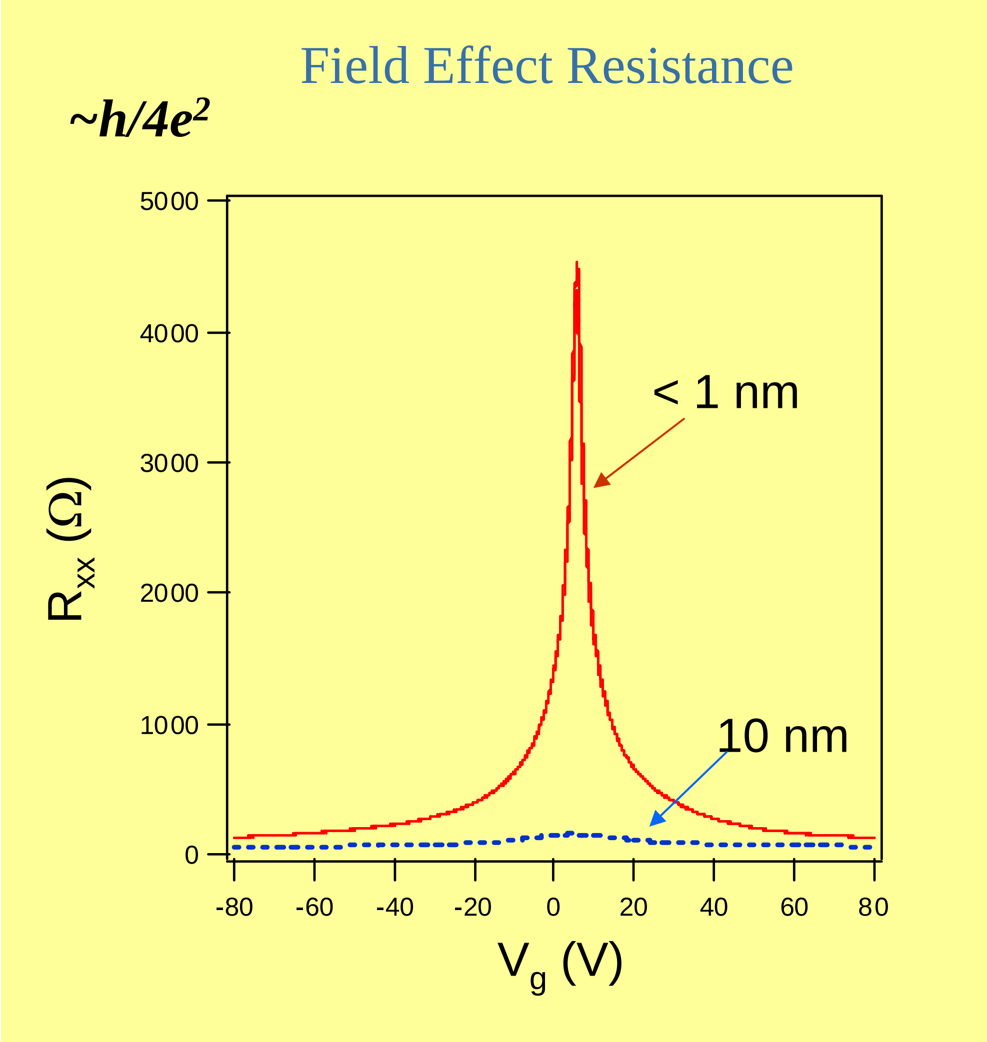






Transport Single Layer Graphene

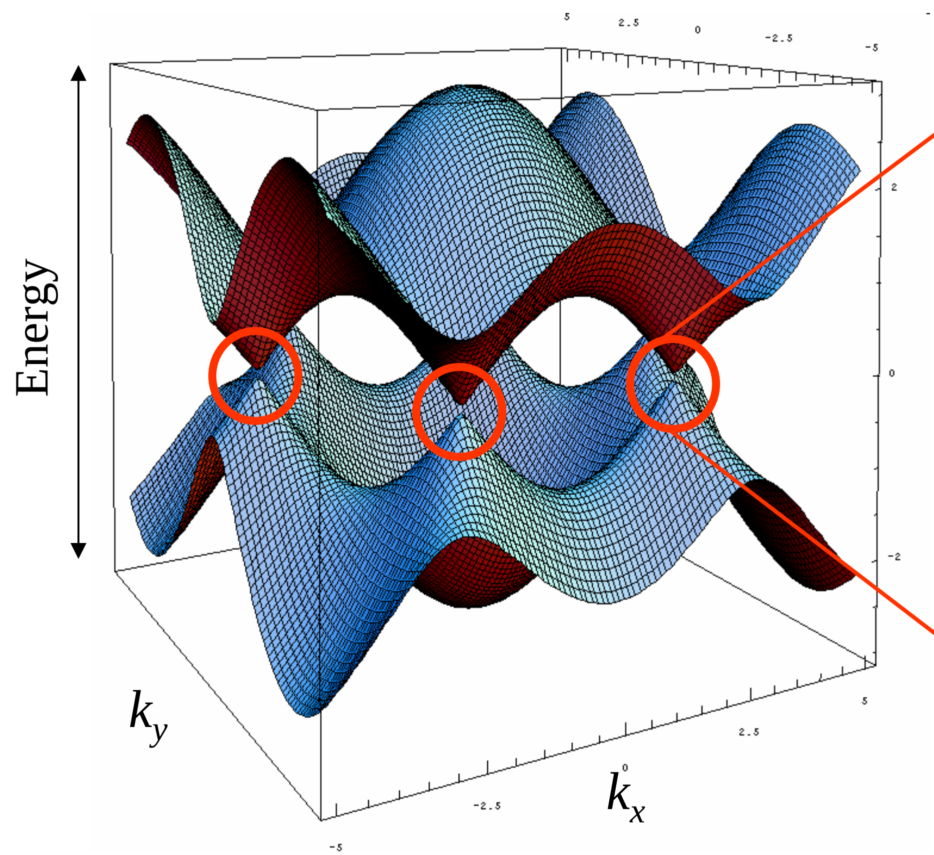


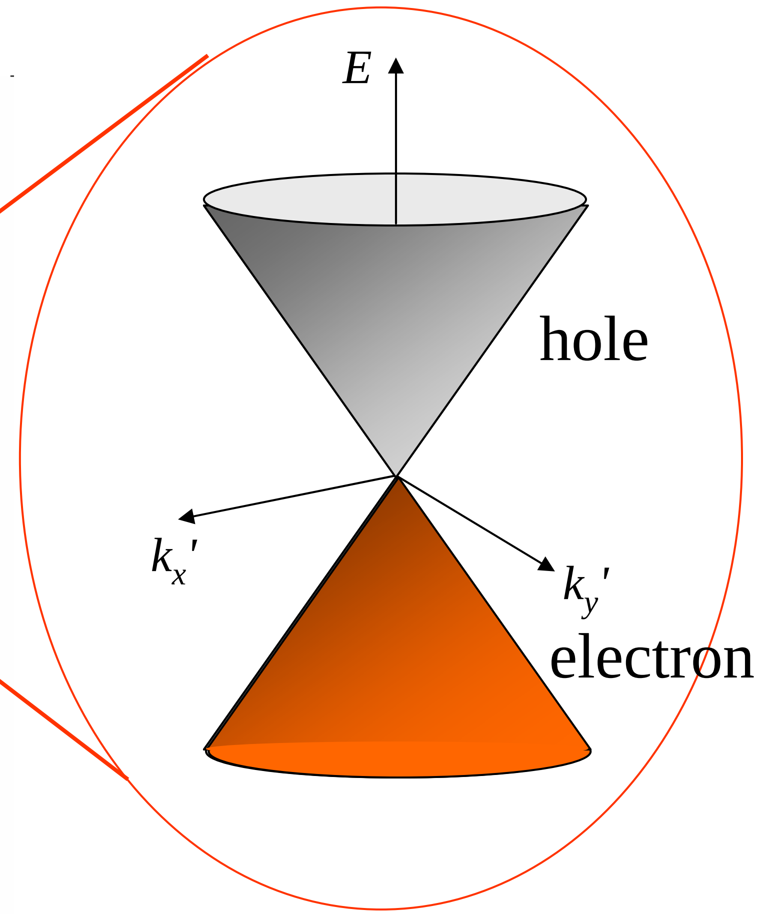


Zhang, Tan, Stormer & Kim (2005), see also Novoselov et al (2005).

Graphene : Dirac Particles in 2D Box

Band structure of graphene





$$E \approx \hbar v_F \left| \vec{k}'_\perp \right|$$

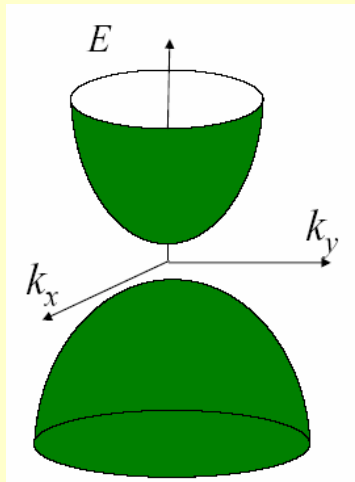
Massless Dirac Particles with effective speed of light v_F.

Graphene v.s. Conventional 2D Electron System

Band structures

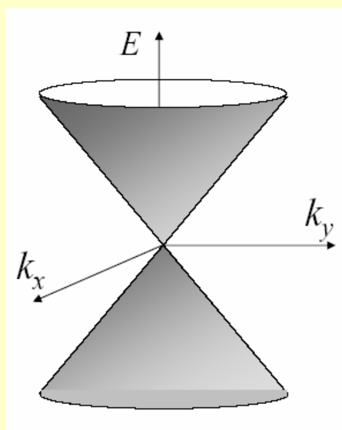
Conventional 2D Electron System

$$E = \frac{\hbar^2 k^2}{2m_e^*}$$

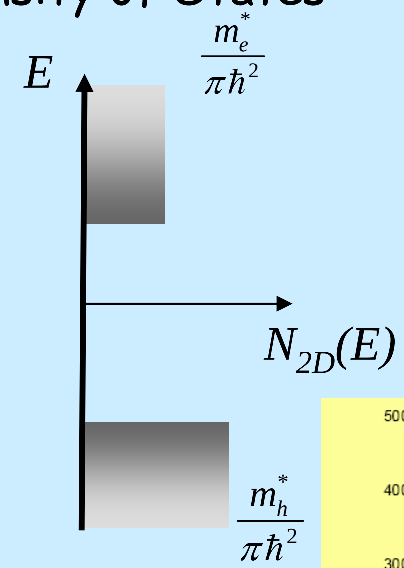


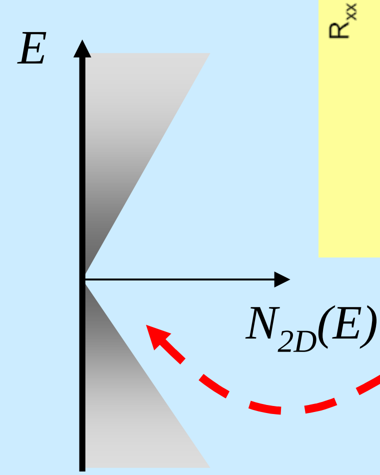
$$E = -\frac{\hbar^2 k^2}{2\left|m_h^*\right|}$$

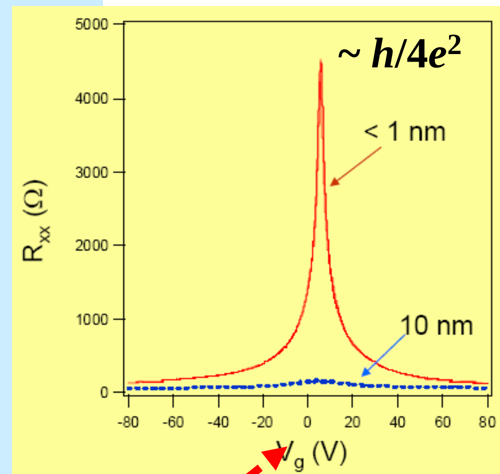
$$E = \hbar v_F \left|\vec{k}'_\perp\right|$$



Density of States







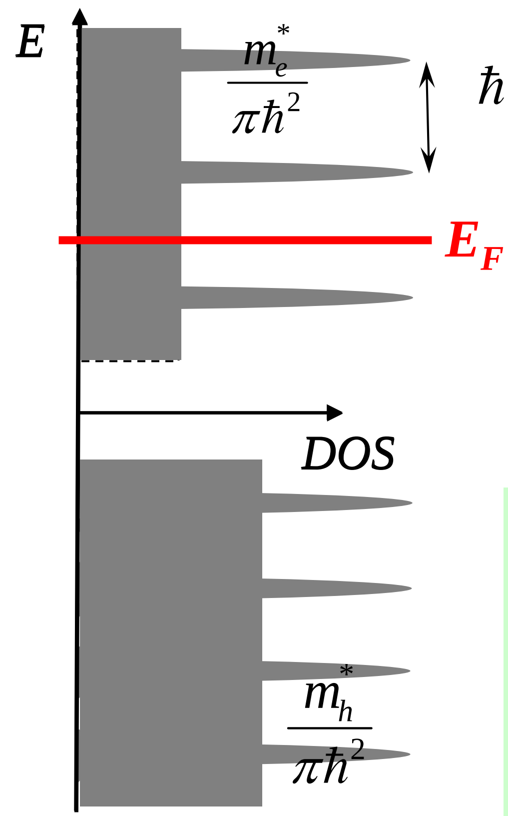
Graphene

- **Zero band mass**
- **Strict electron hole symmetry**
- **Electron hole degeneracy**

2D Gas in Quantum Limit : Conventional Case

Density of States

Landau Levels in Magnetic Field



$$\hbar\omega_c = \hbar eB / m^*$$

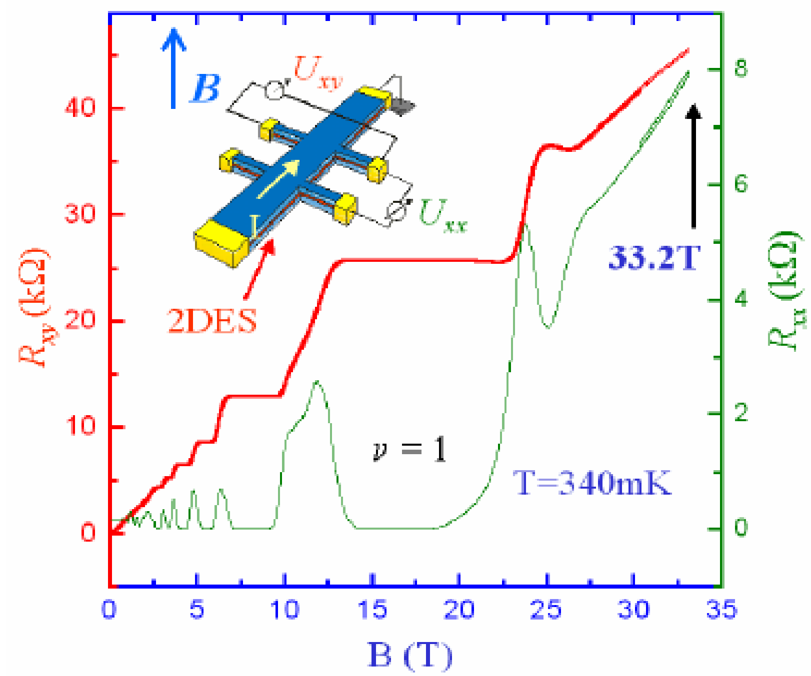
Integer Quantization:

$$R_{xy}^{-1} = \pm \nu \cdot g_s \cdot \frac{e^2}{h}$$

$$\nu = 1, 2, 3 \ldots$$

$$g_s = 2 \text{ (spin)}$$

Quantum Hall Effect in GaAs 2DEG

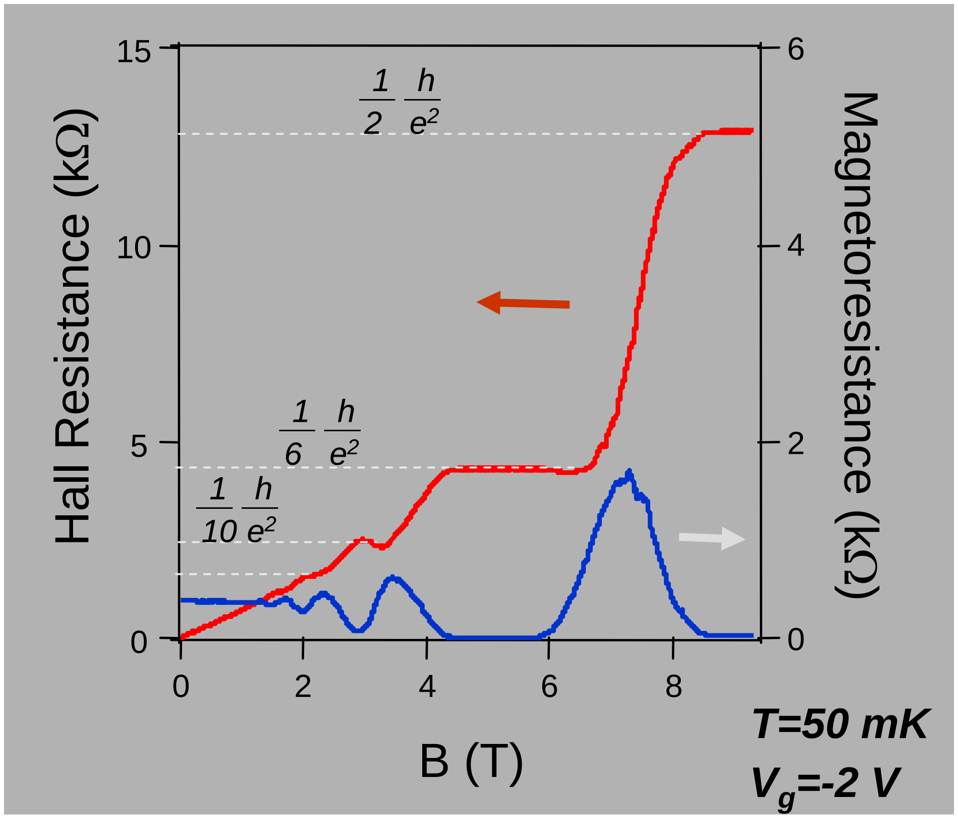


Graphene

- Vanishing carrier mass near Dirac point
- Strict electron hole symmetry
- Electron hole degeneracy

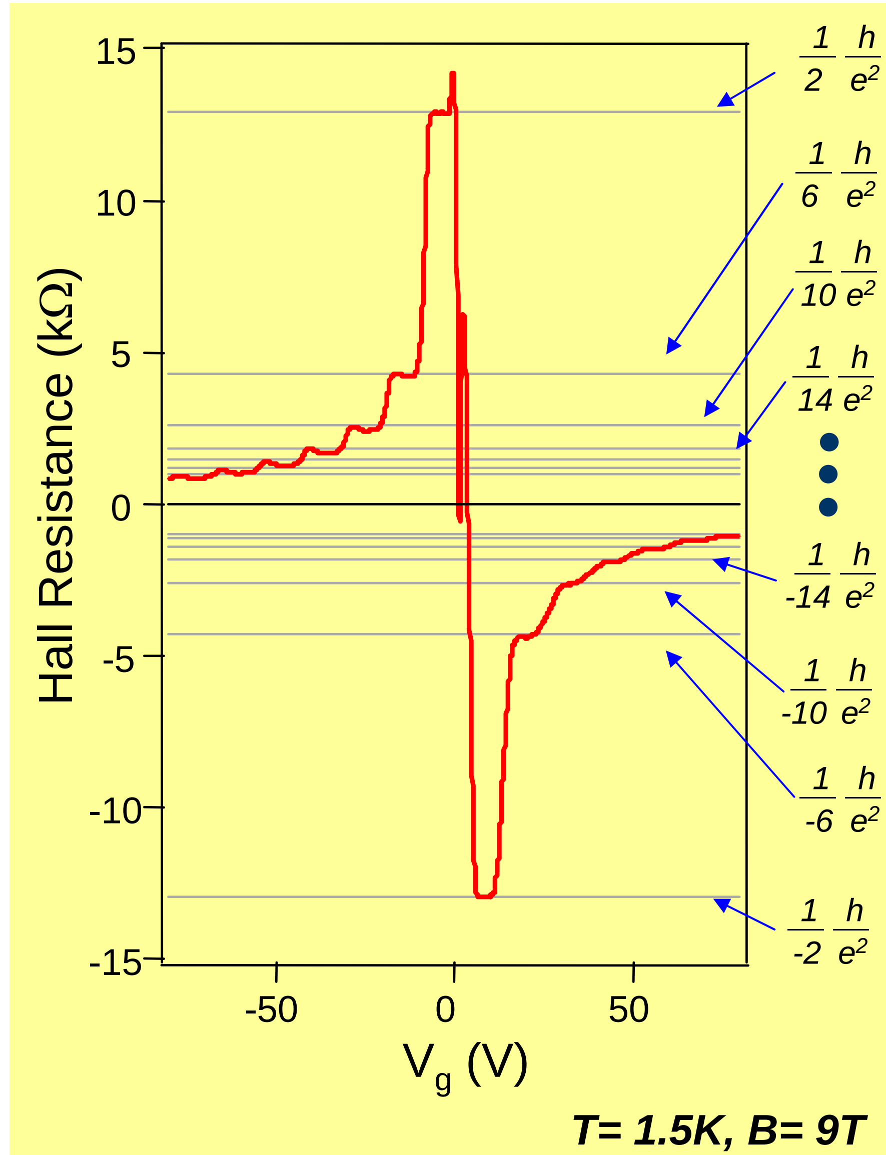
$$\omega_c = \frac{eB}{m^*}$$

Quantum Hall Effect in Graphene



Quantization:

$$R_{xy}^{-1} = 4\left(n + \frac{1}{2}\right)\frac{e^2}{h}$$

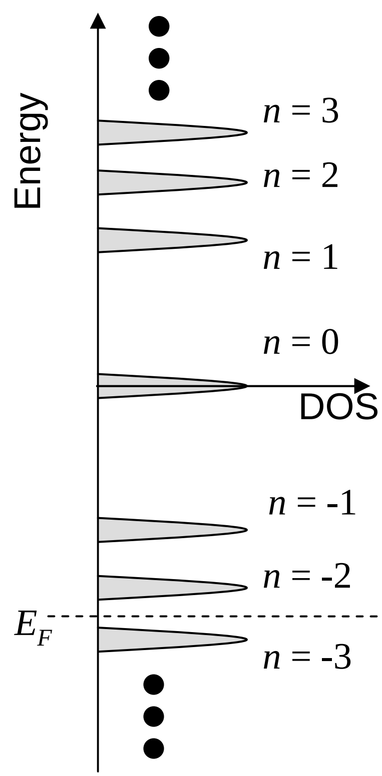


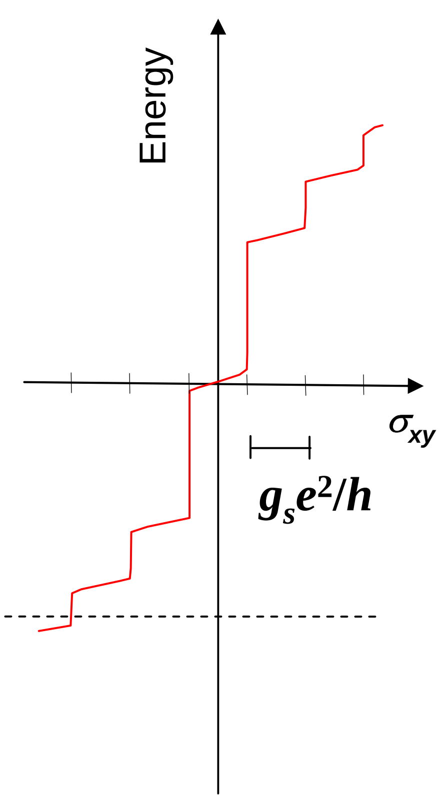
Relativistic Landau Level and Half Integer QHE

Haldane, PRL (1988)

Landau Level $E_n = \pm\sqrt{2e\hbar v_F^2 |n| B}$

Landau Level Degeneracy
$g_s = 4$
2 for spin and 2 for sublattice





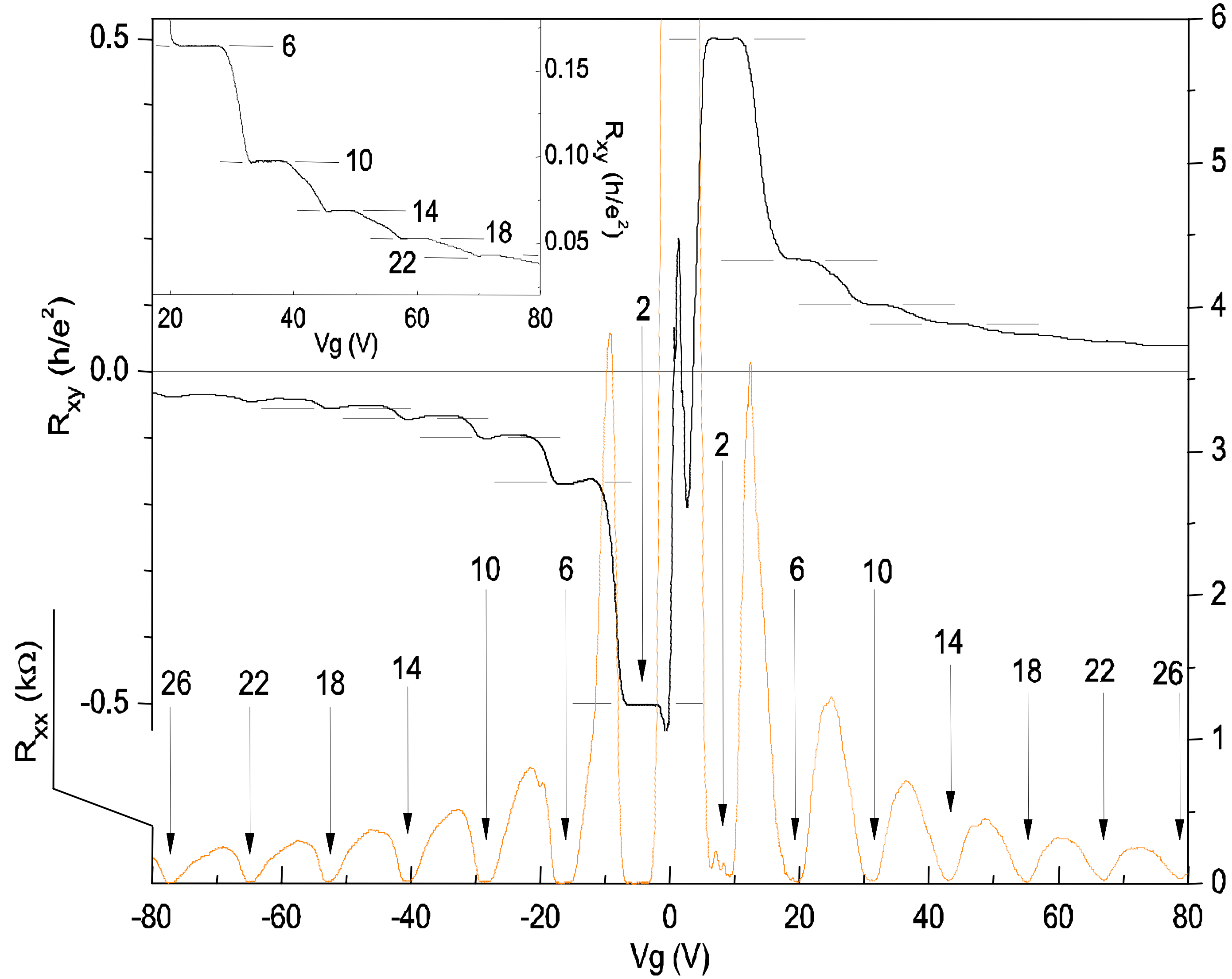
Quantized Condition

$$R_{xy}^{-1} = \pm g_s (n + \frac{1}{2}) \frac{e^2}{h}$$

$$\nu = \pm g_s (n + 1/2)$$

T. Ando et al (2002)

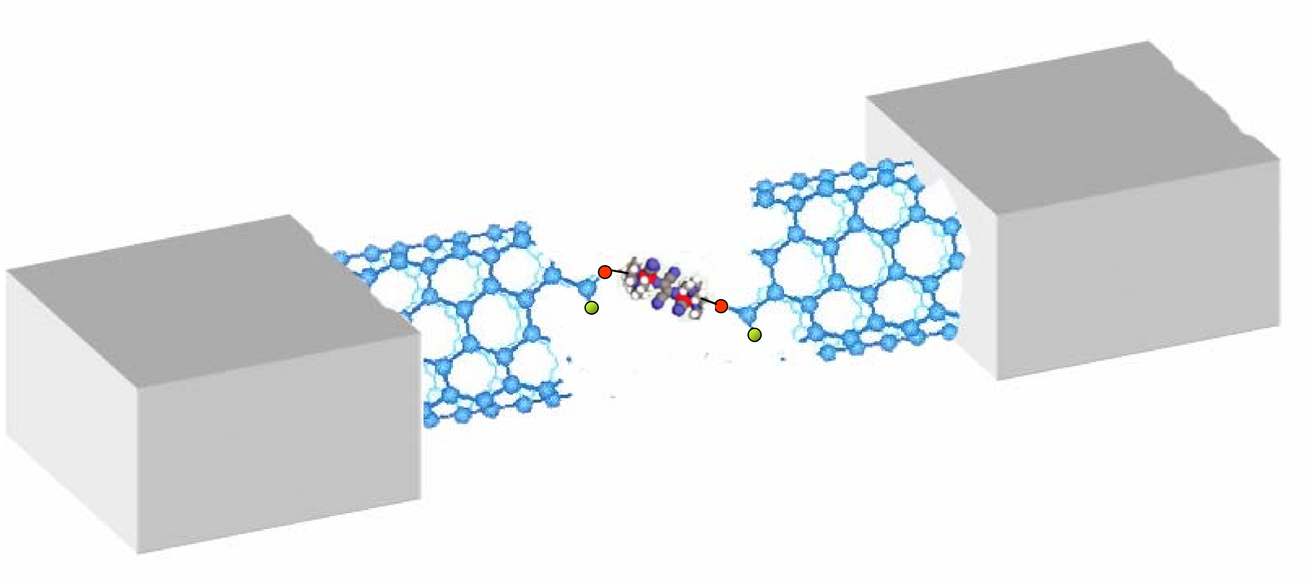
Quantum Hall Effect in Graphene



Mobility
~ 60,000 cm^2/V s

T = 1.7 K
B = 9 T

Nanotube Electrodes for Molecular Electronics

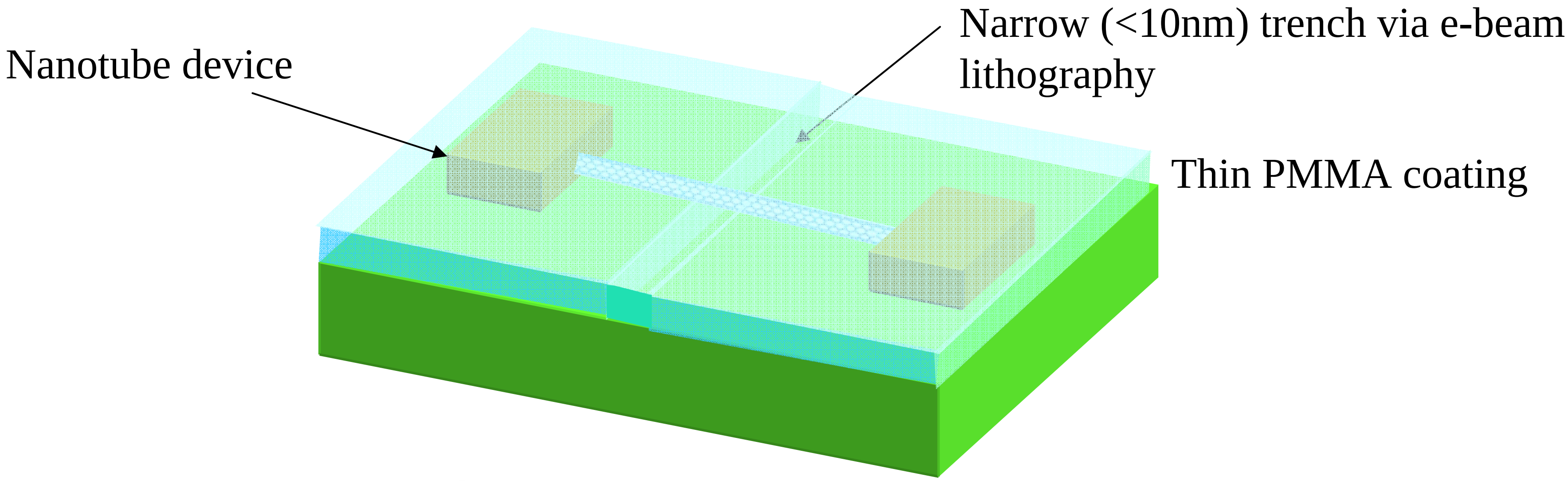


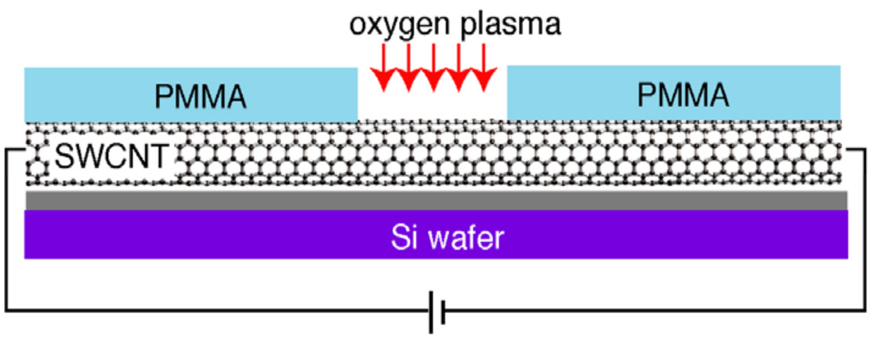
• **Nanotubes are inherently small,**
  yet compatible to microfabrication processes

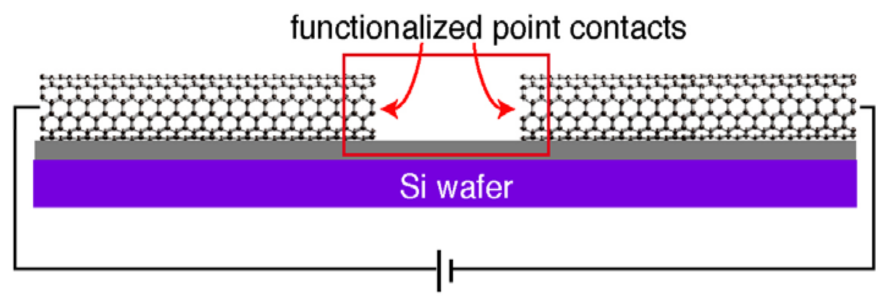
• **Covalent chemistry between electrode and molecules**

• **Potentially good conduction via π-bonding network**

Nanotube Nanogaps







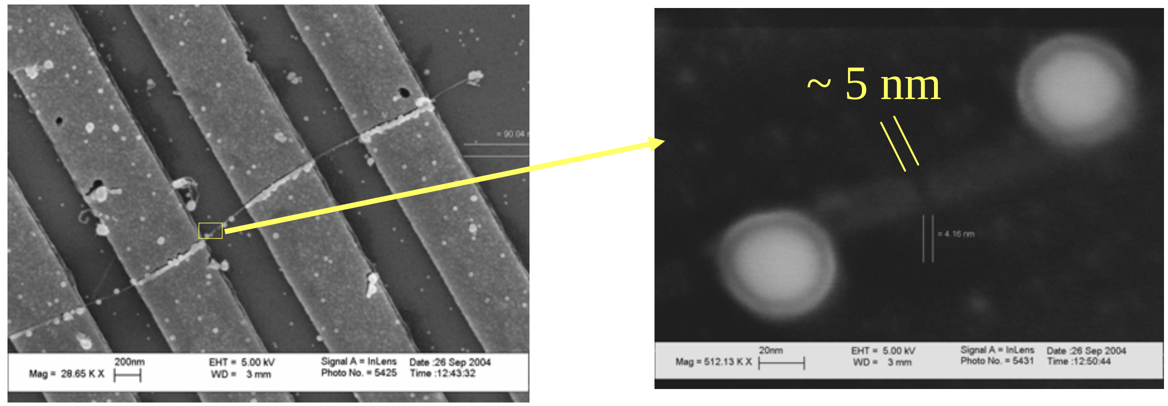
Oxygen Plasma etching creates gaps (0-10 nm) in tubes.

Cut ends likely to be carboxyl-terminated

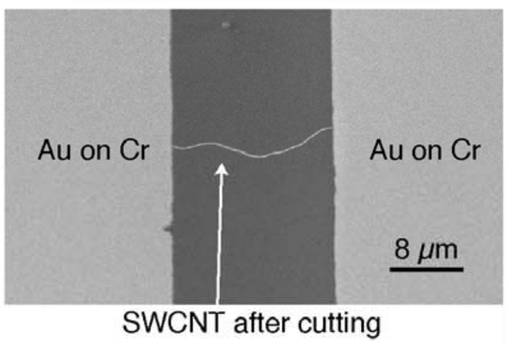
Hone, Wind, Nuckolls, and Kim Collaboration

Nanotube Nanogaps

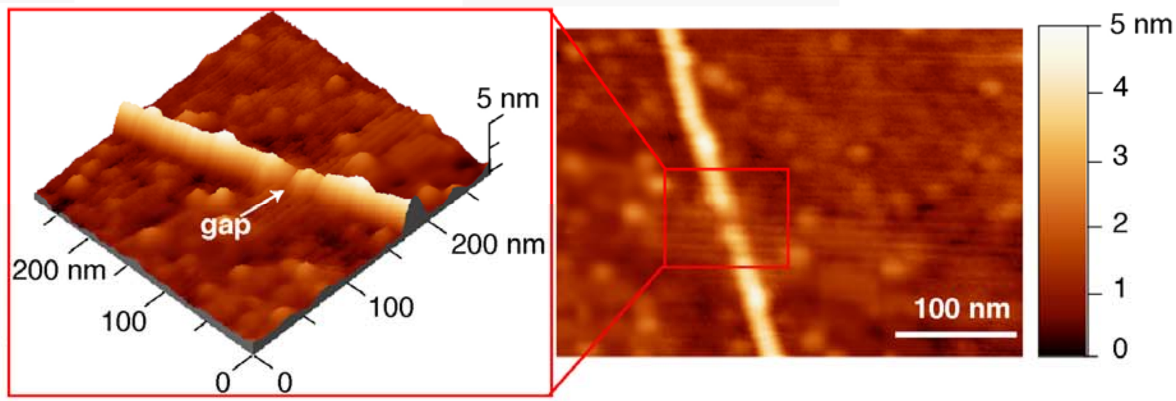
SEM micrograph



SEM micrograph



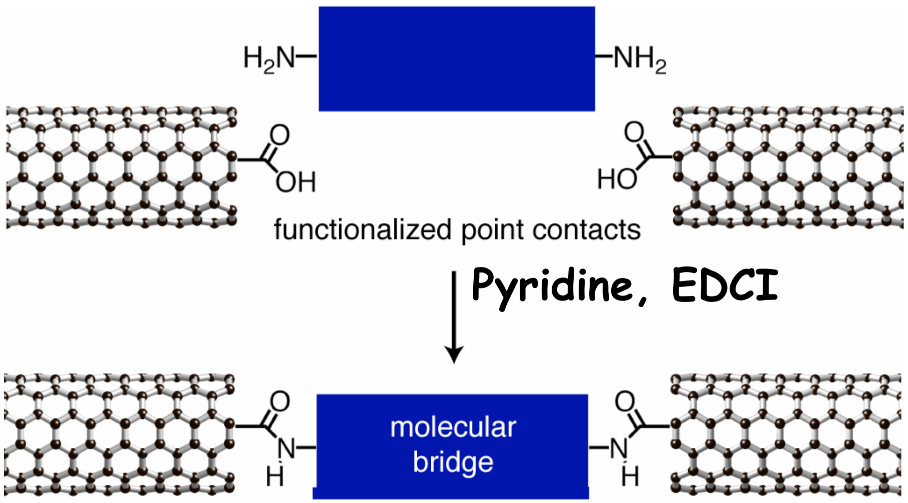
AFM micrograph



Process are optimized to Yield of cut tubes: 25% of ~2600 devices

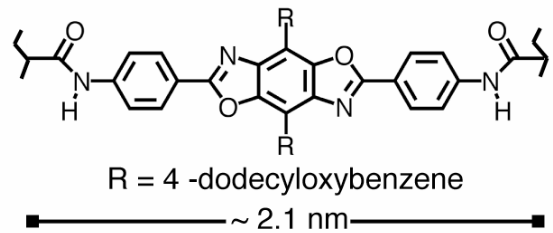
Columbia NSEC (Hone, Wind, Nuckolls, and Kim) Collaboration

Molecular Bridges



- Self-assembled
- Covalently bonded
- Conduction through π-back bone

<u>Bis-oxazole</u>



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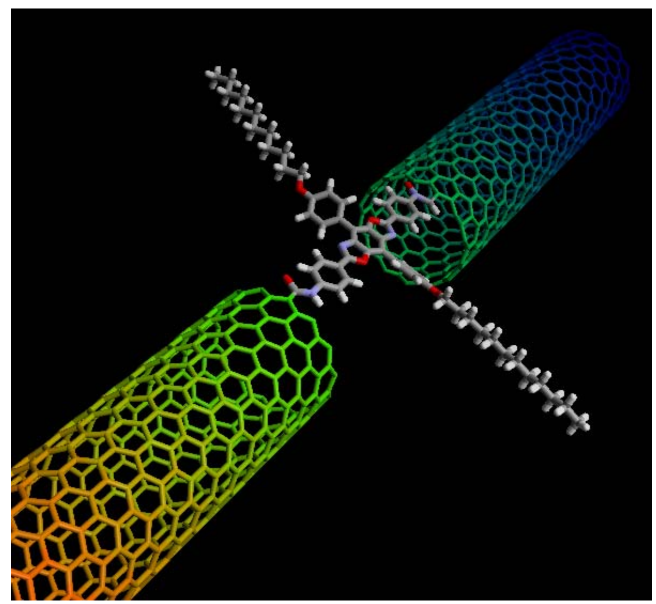
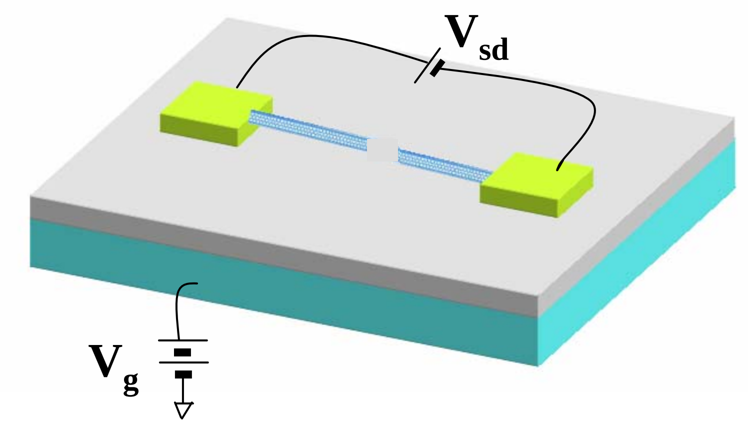


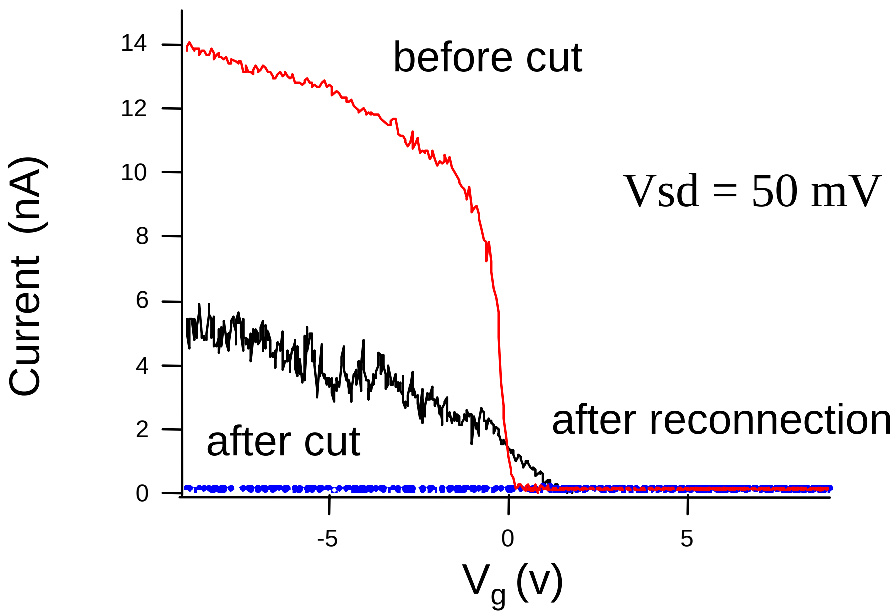
Guo et al., Science (2006)

Does It Work?

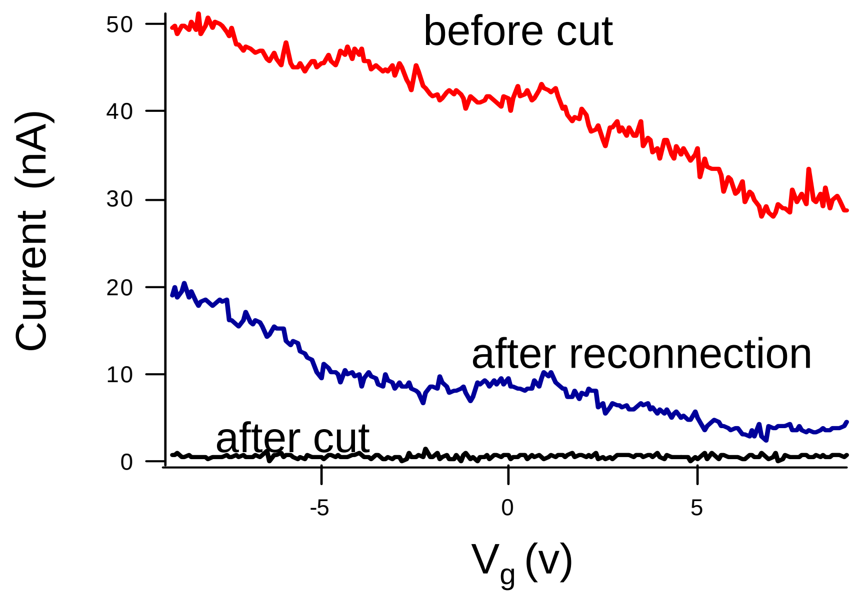


~ 10-15% of reconnection
out of ~ 100 fully cut tubes

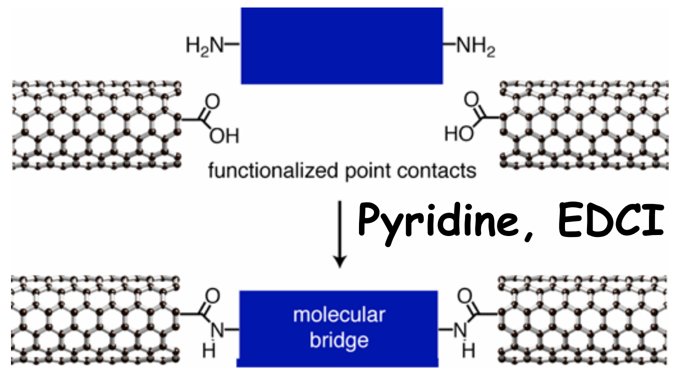
Semiconducting Nanotube + Molecular Bridge



Metallic Nanotube + Molecular Bridge



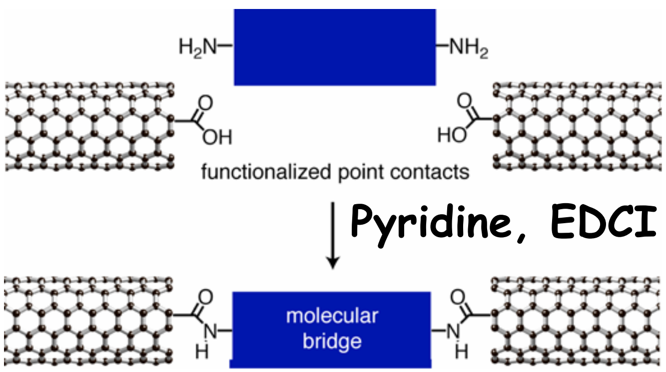
Control Experiments

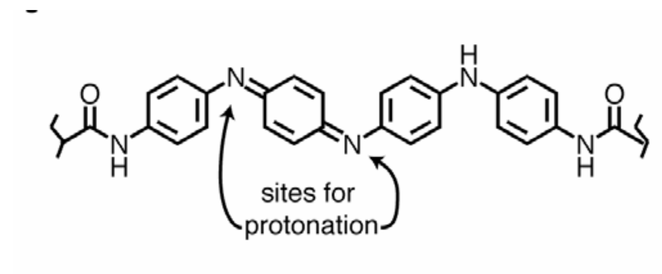


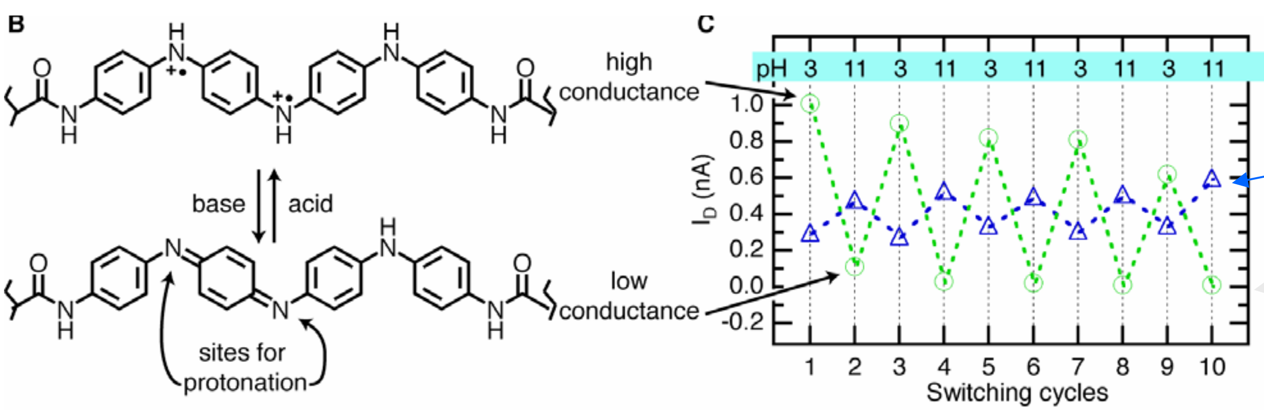
Connection with diamine bisoxazole

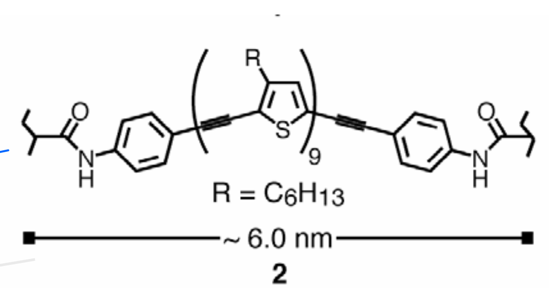
* Pyridine +EDCI without molecules — No connection
* Bis-oxazole without amines — No connection
* Bis-oxazole with Monoamine — No connection
* 1,12 dodecane diamine (insulator) — No connection

Oligoaniline: PH sensing



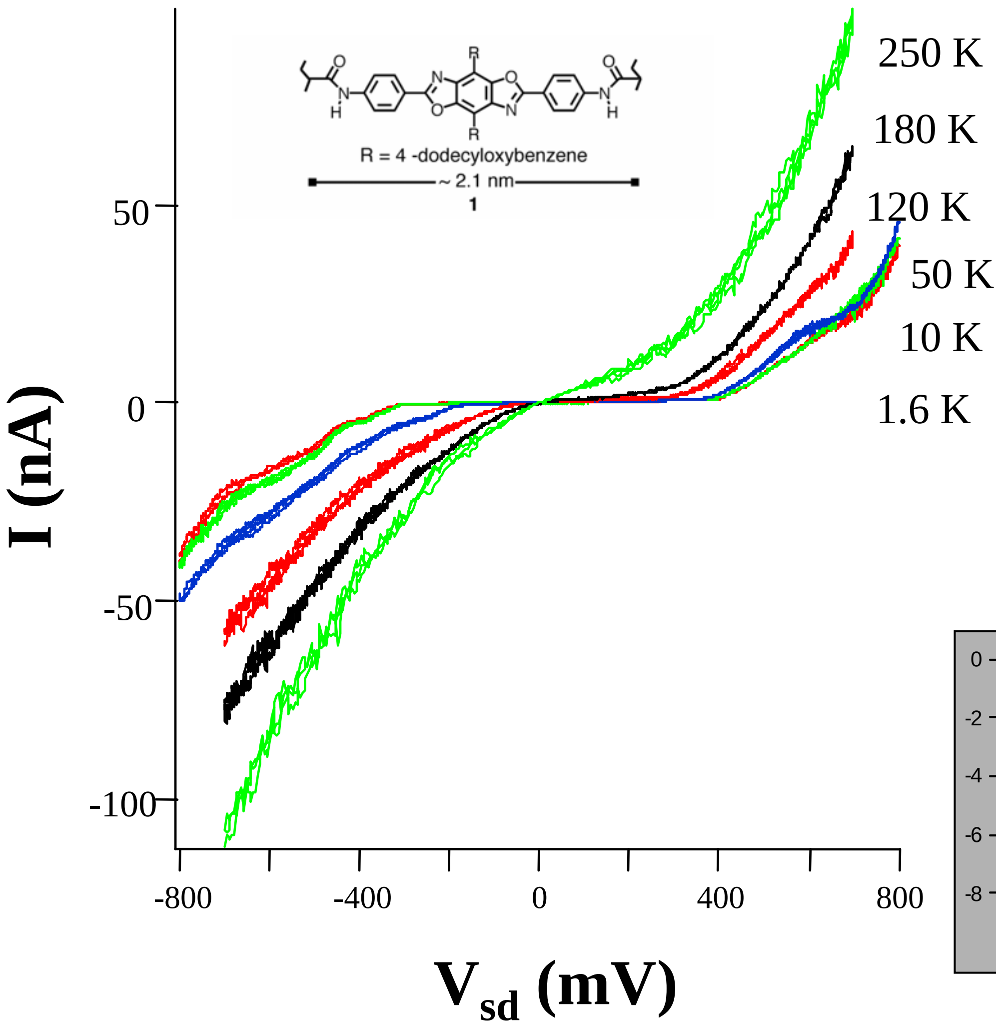


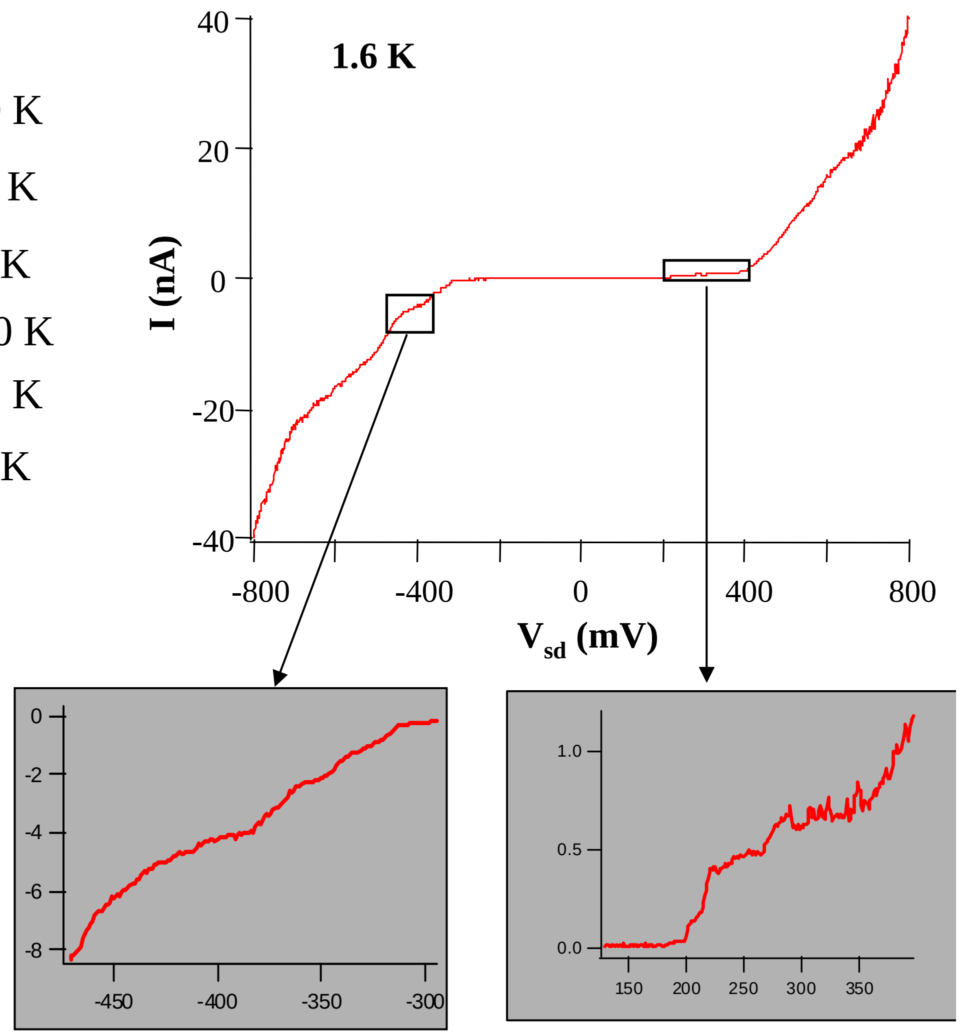




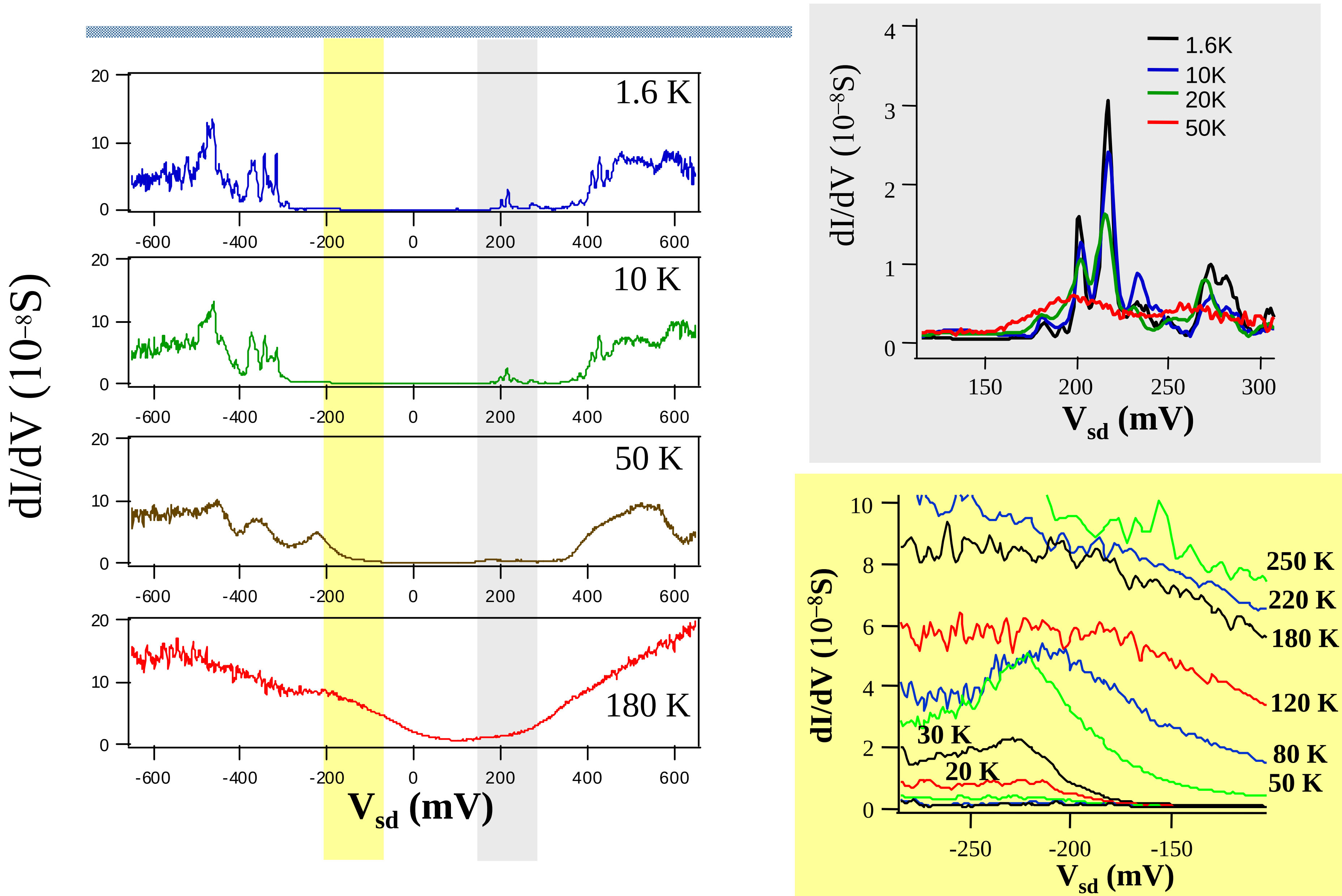
Transport Measurement

Bis-oxazole + metallic SWNT

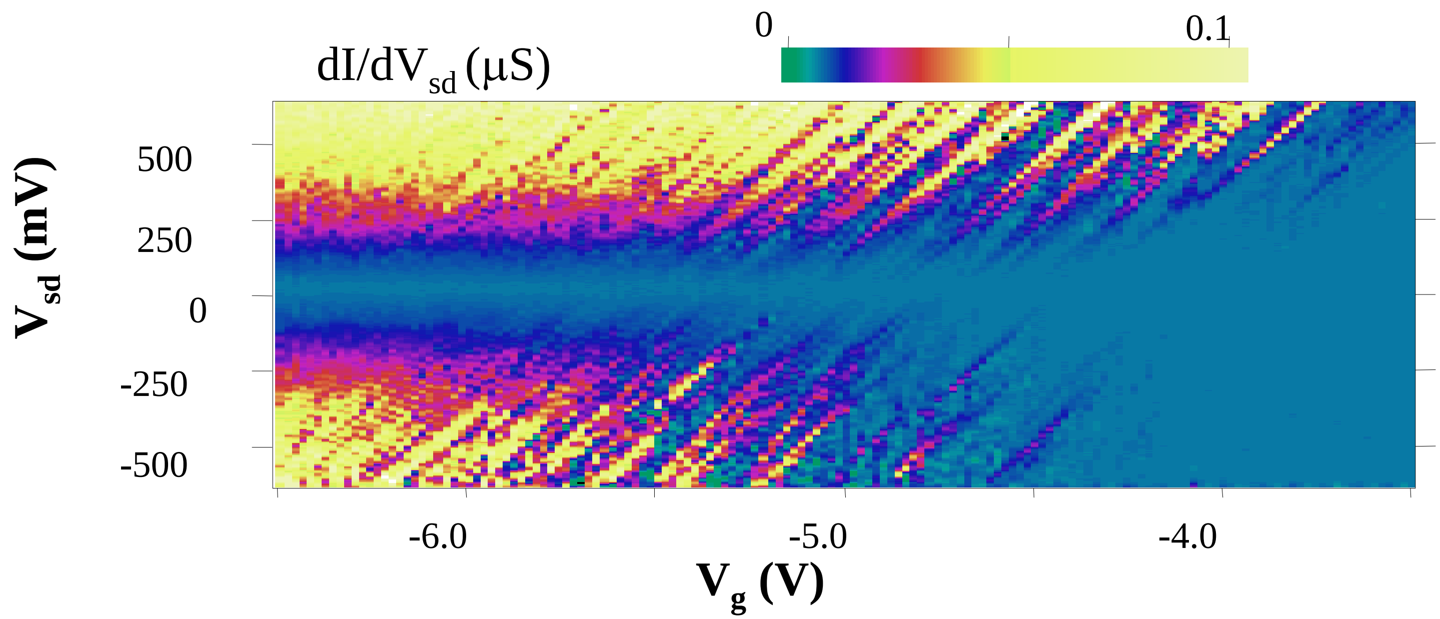


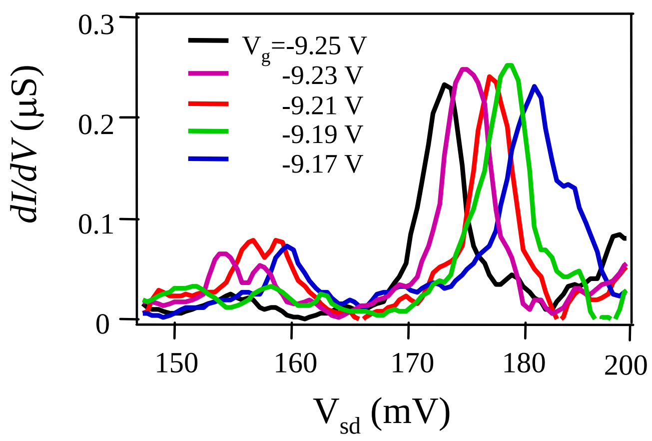


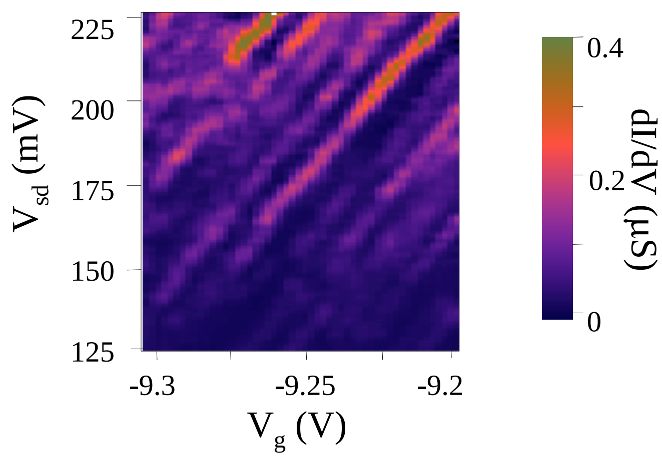
Temperature Dependence Transport Spectroscopy



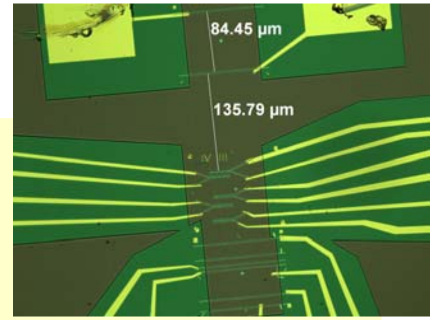
Gate Voltage Dependence



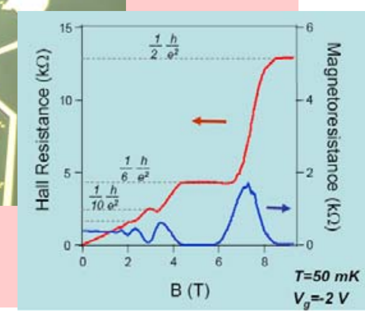




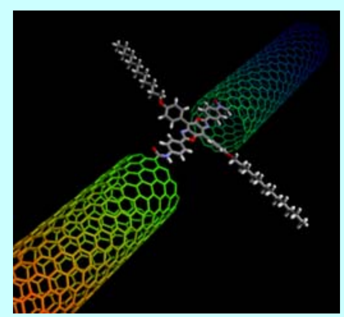
Summary



- Transport in long nanotubes:
  - Subshell extraction in MWNTs
  - Extremely long mean-free path in SWNTs



- Transport in graphene:
  - Unusual quantum Hall effect
  - Graphene nano ribbon devices
  - Gate dependent Raman spectroscopy



- Nanotube electrode for
  single molecular electronics

Acknowledgement

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