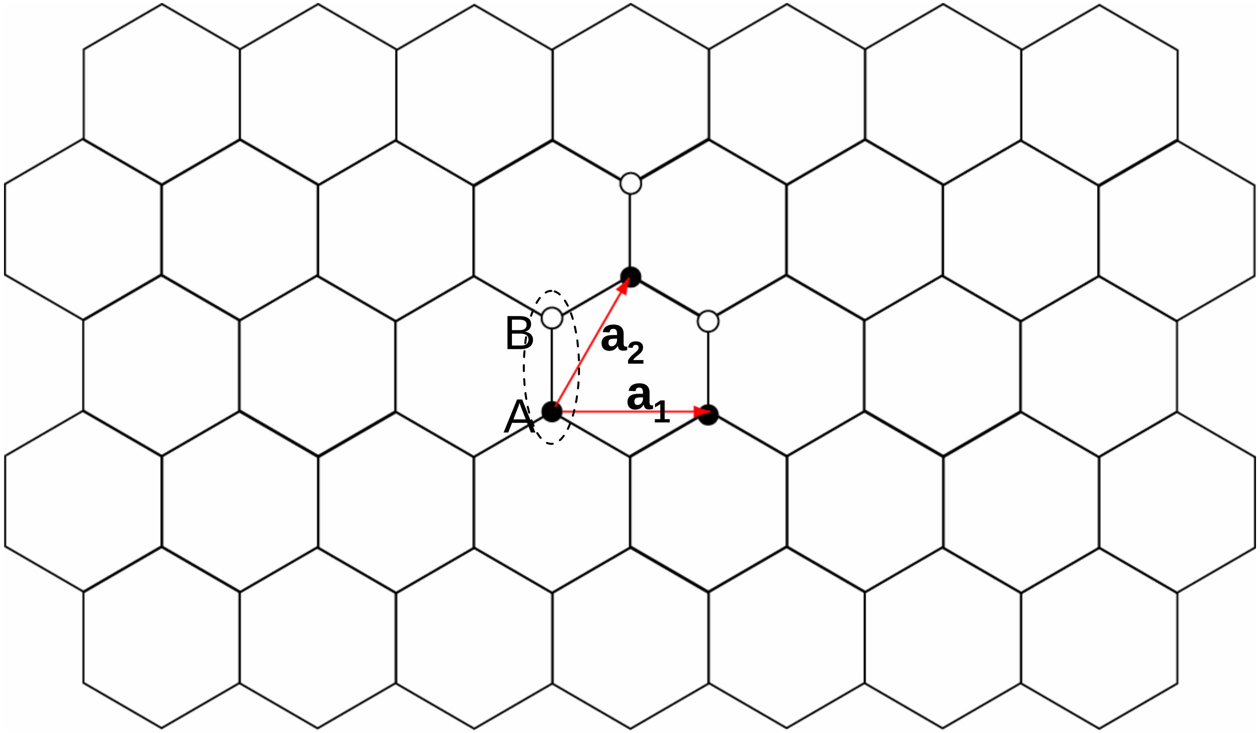
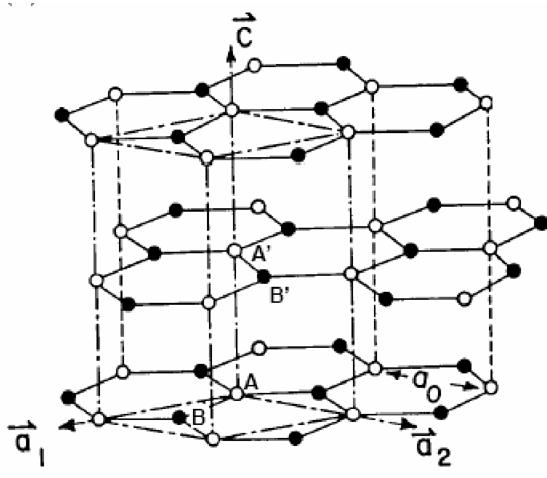
Carbon Nanotubes: Band structure, growth and applications

10/20/05

Graphene structure

Graphene: a single layer of graphite





Graphite structure

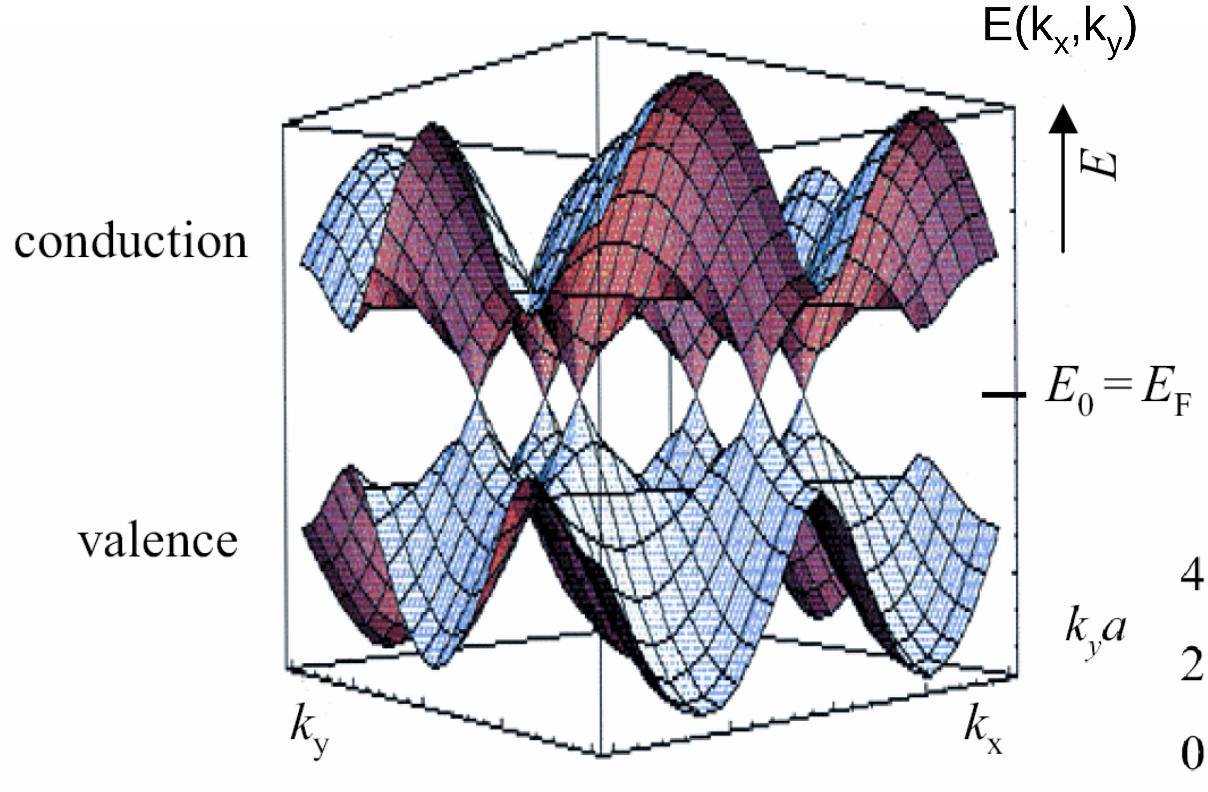
sp^2 bonded carbon.
Each atom connected to 3 neighbors w/ 120 degree bond angles. Honey-comb structure.
Hybridized π bonding across whole sheet.

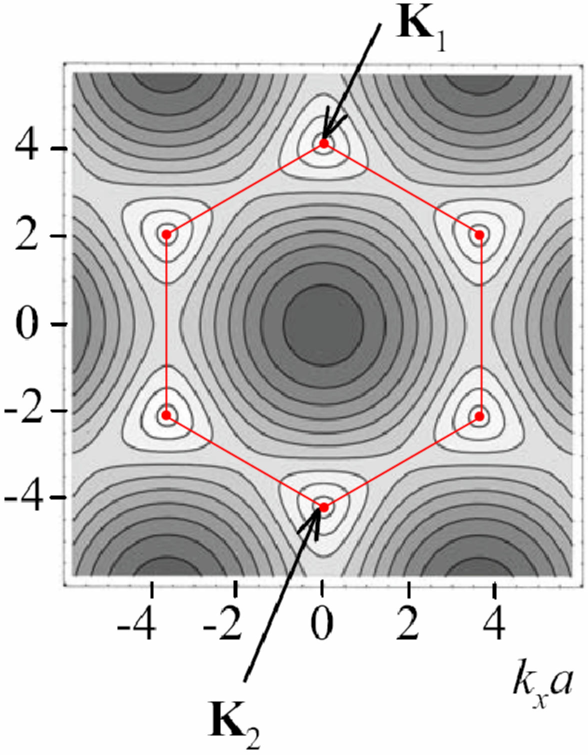
Each base consists of two atoms, A, B

Lattice vector, $\mathbf{a}_1$, $\mathbf{a}_2$

$|\mathbf{a}_1|=|\mathbf{a}_2|=a$, lattice constant

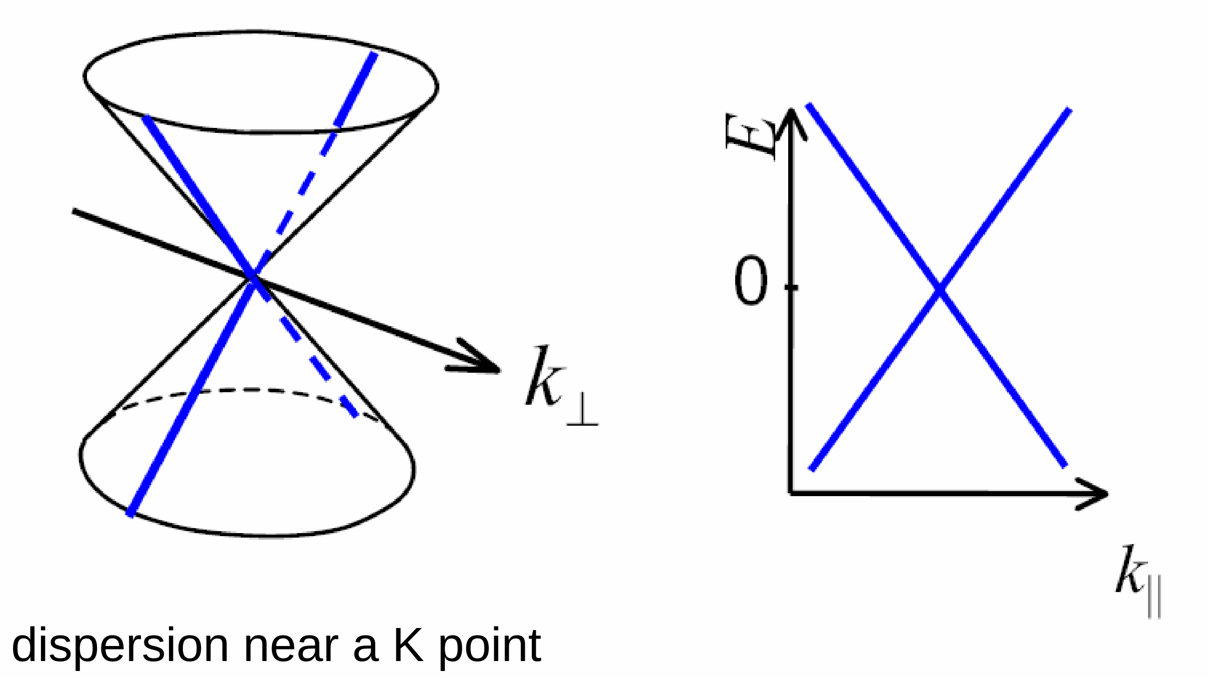
Graphene band structure





Conduction band and valence band meet at 6 **K** points in the Brillouin zone.
Result: graphene is a “gapless” semiconductor.

Dispersion relation

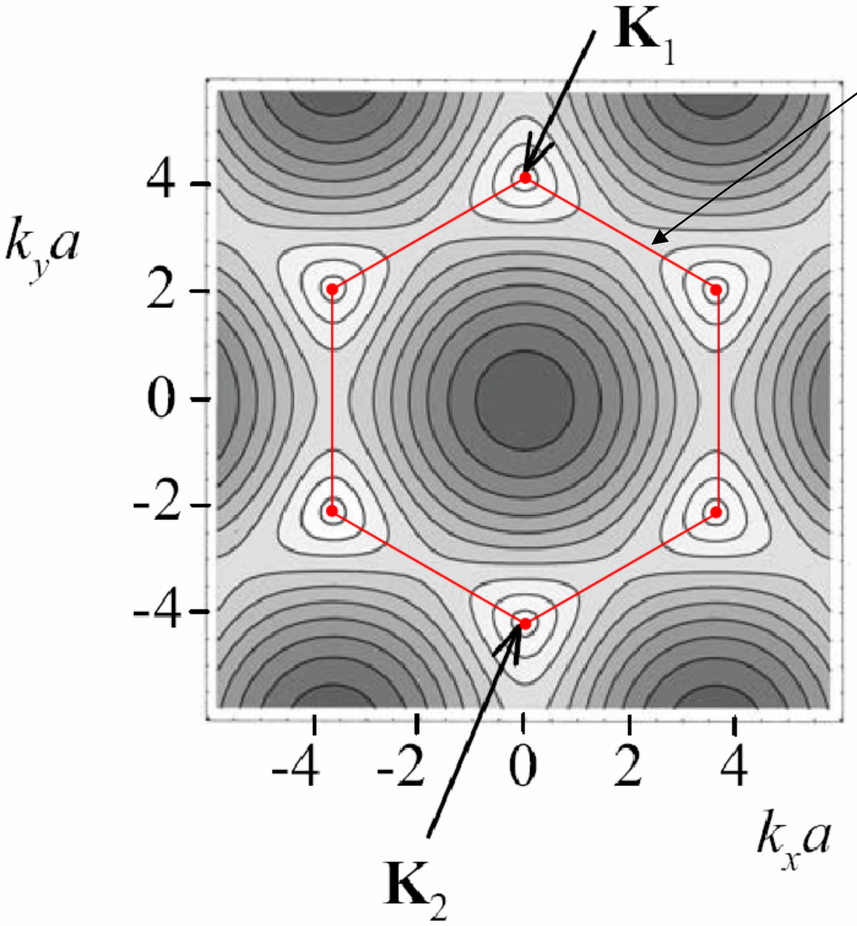


Cone-like dispersion near a K point

$E(k) = \hbar k v_F$ (compare to $E(k) \propto k^2$ for a nearly-free electron)

$V_F = 8 \times 10^5$ m/s

Orbital degeneracy



First Brillouin zone

- Only two non-equivalent K points (the upper left and upper right K points are equivalent to K_1 through the reciprocal lattice vectors, the lower left and lower right K points are equivalent to K_2)

- Only need to consider states near K_1, K_2. $K_2 = -K_1$

- Due to symmetry, for every state near K_1, there is a corresponding state near K_2. (Orbital degeneracy.)

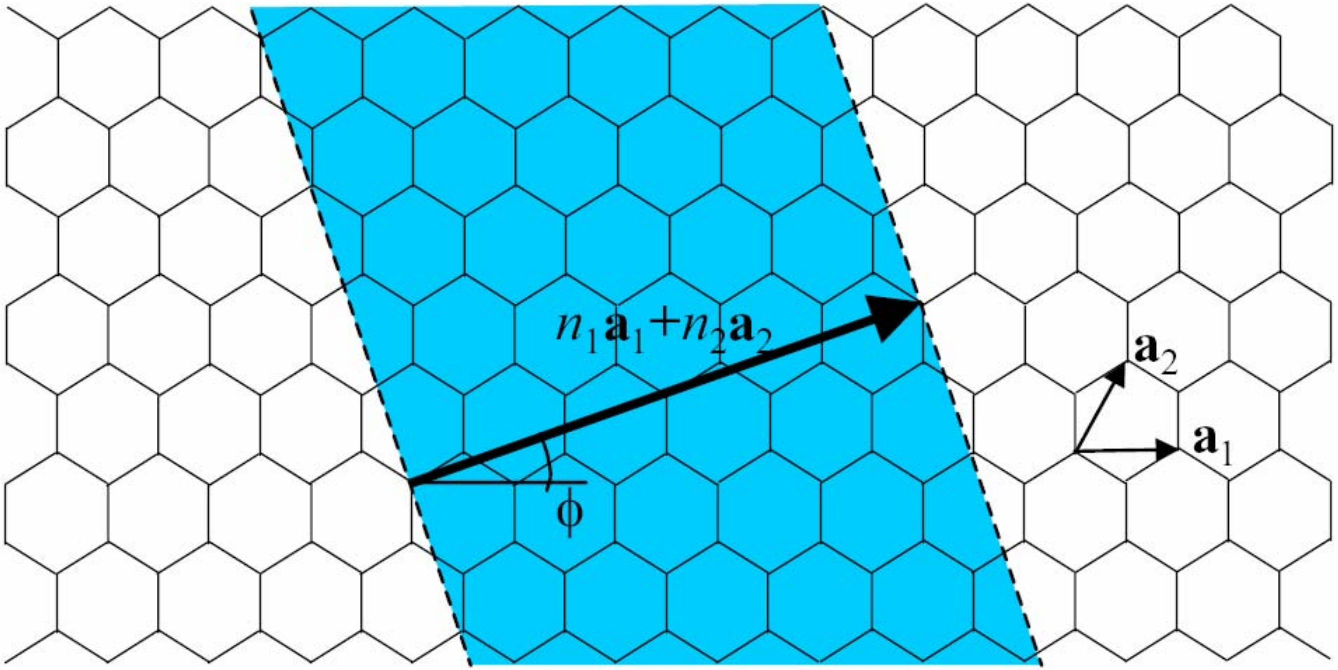
$K1 = 1/a(0, 4\pi/3)$

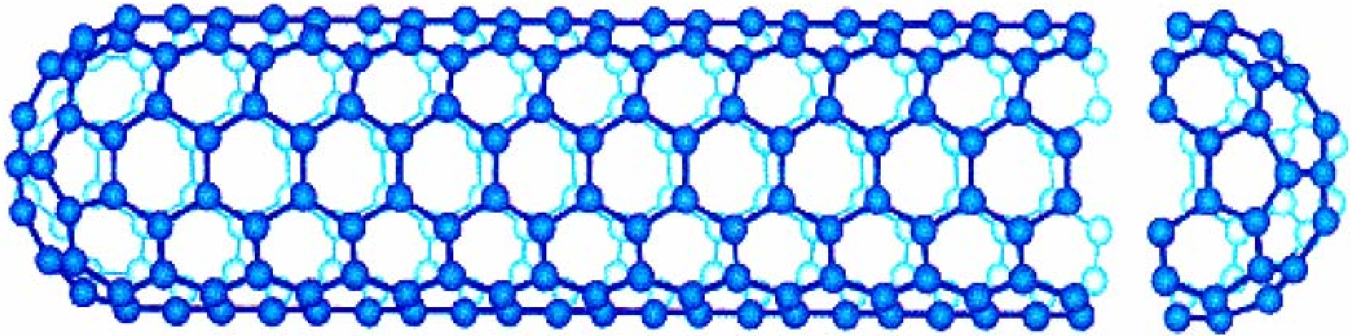
$K2 = 1/a(0, -4\pi/3)$

4-fold degeneracy.
(2-fold orbital + 2-fold spin)

Carbon nanotube

rolling up the graphene sheet along vector $n_1a_1+n_2a_2$

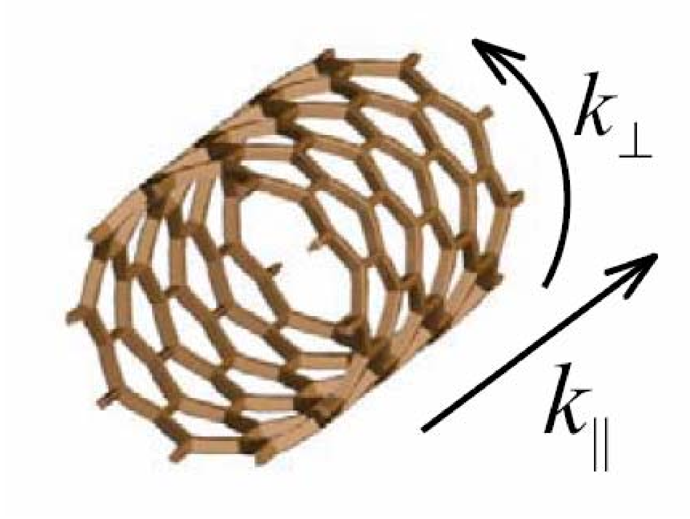




$(n_1, n_2)=(5,5)$

Zigzag: $n_2=0$, armchair: $n_1=n_2$. Chiral angle 0-30°

Quantization of $K_\perp$



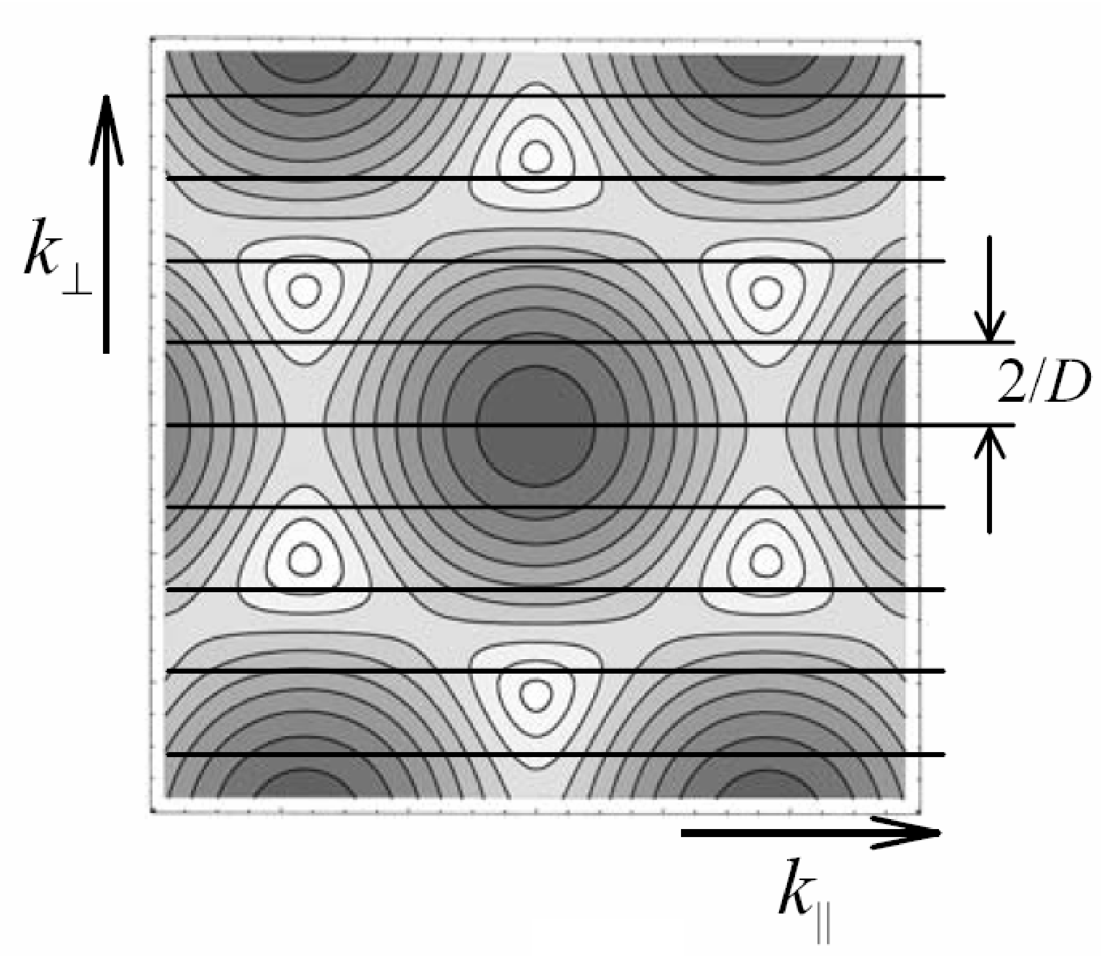
$$k_\perp \pi D = 2\pi \cdot j$$

D, tube diameter, *j*, integer

$\Delta k_\perp$=2/D

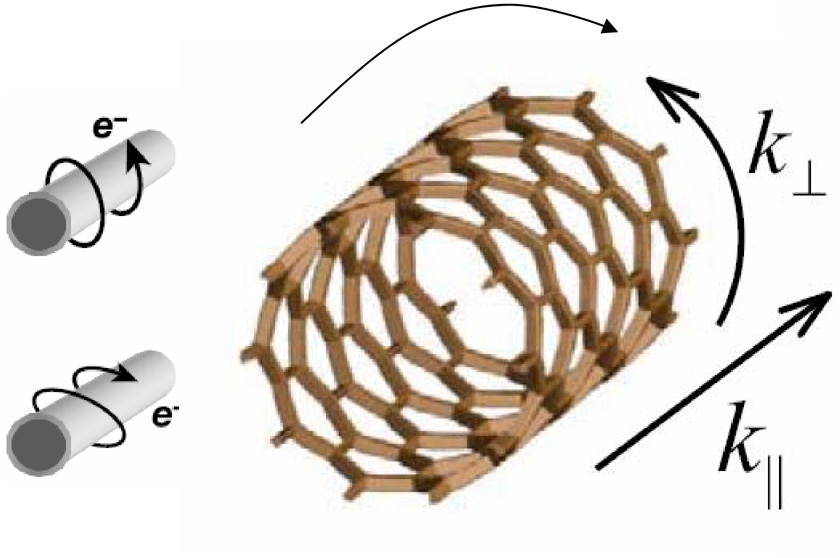
V_F=8x10^5 m/s

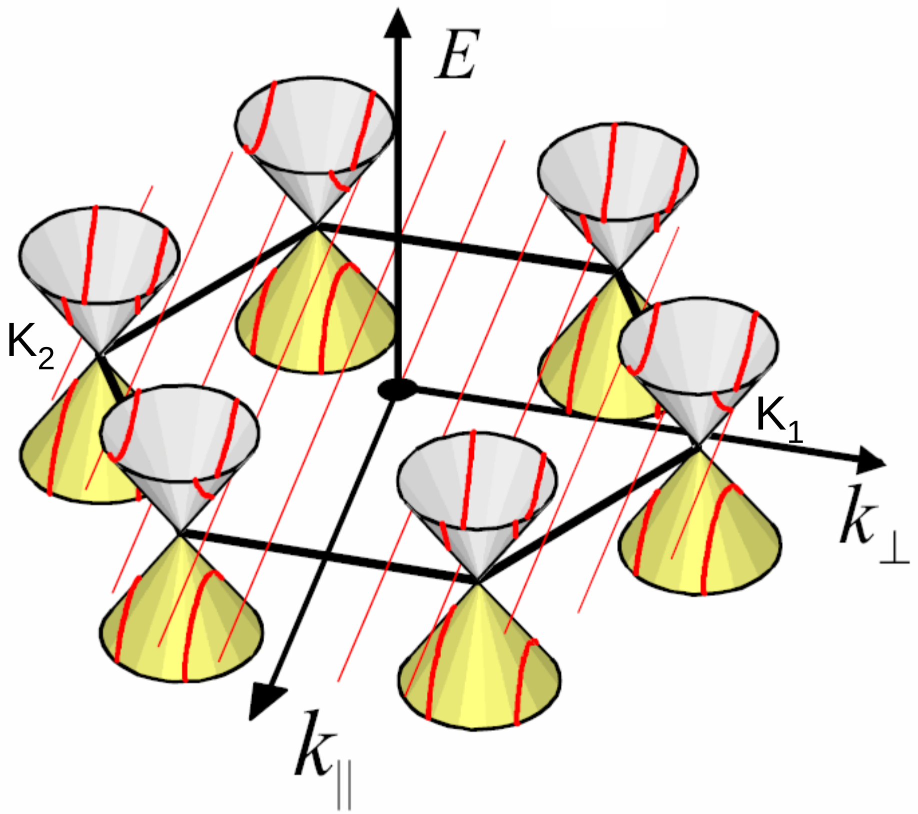
$\Delta E = \hbar v_F \Delta k_\perp$ ~1eV/D (nm)



Truly 1D system

1D subbands

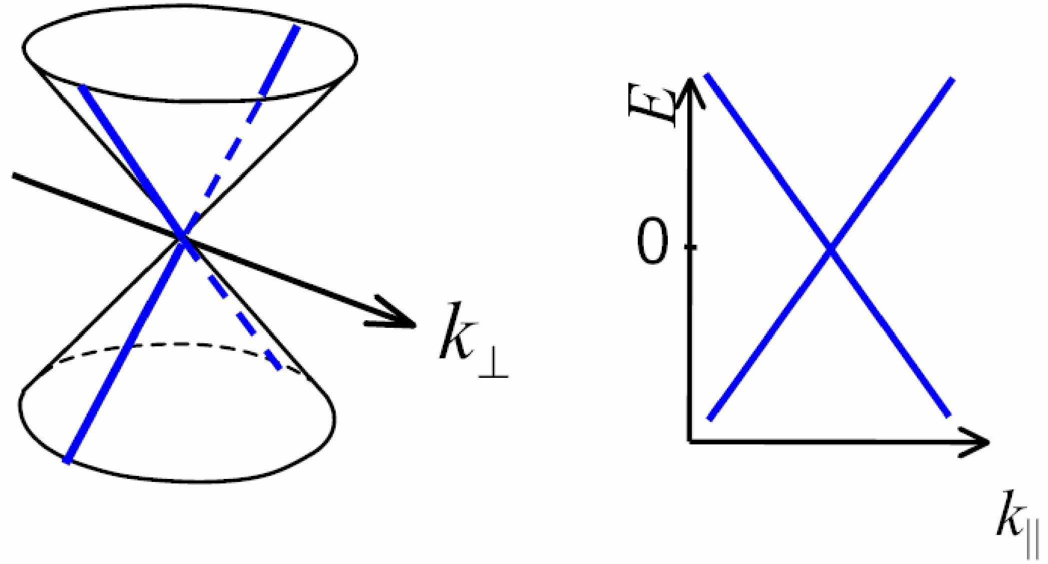




- 1D subbands obtained by slicing the cones at the discrete $K_\perp$ values
- Once again, only need to consider subbands close to K_1 and K_2
- Orbital degeneracy, for each subband near K1, there is a corresponding subband near K_2=-K_1 (clockwise and conterclockwise moving orbitals)

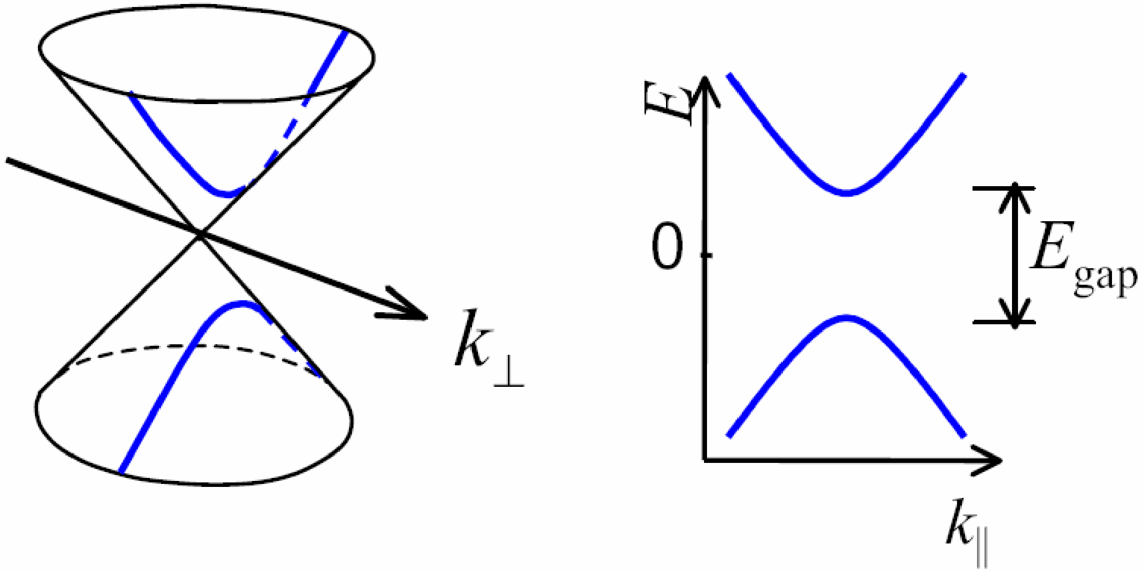
Metallic vs. semiconducting nanotubes

n_1-n_2=3q,
one of the slices crosses K_1, metallic nanotubes



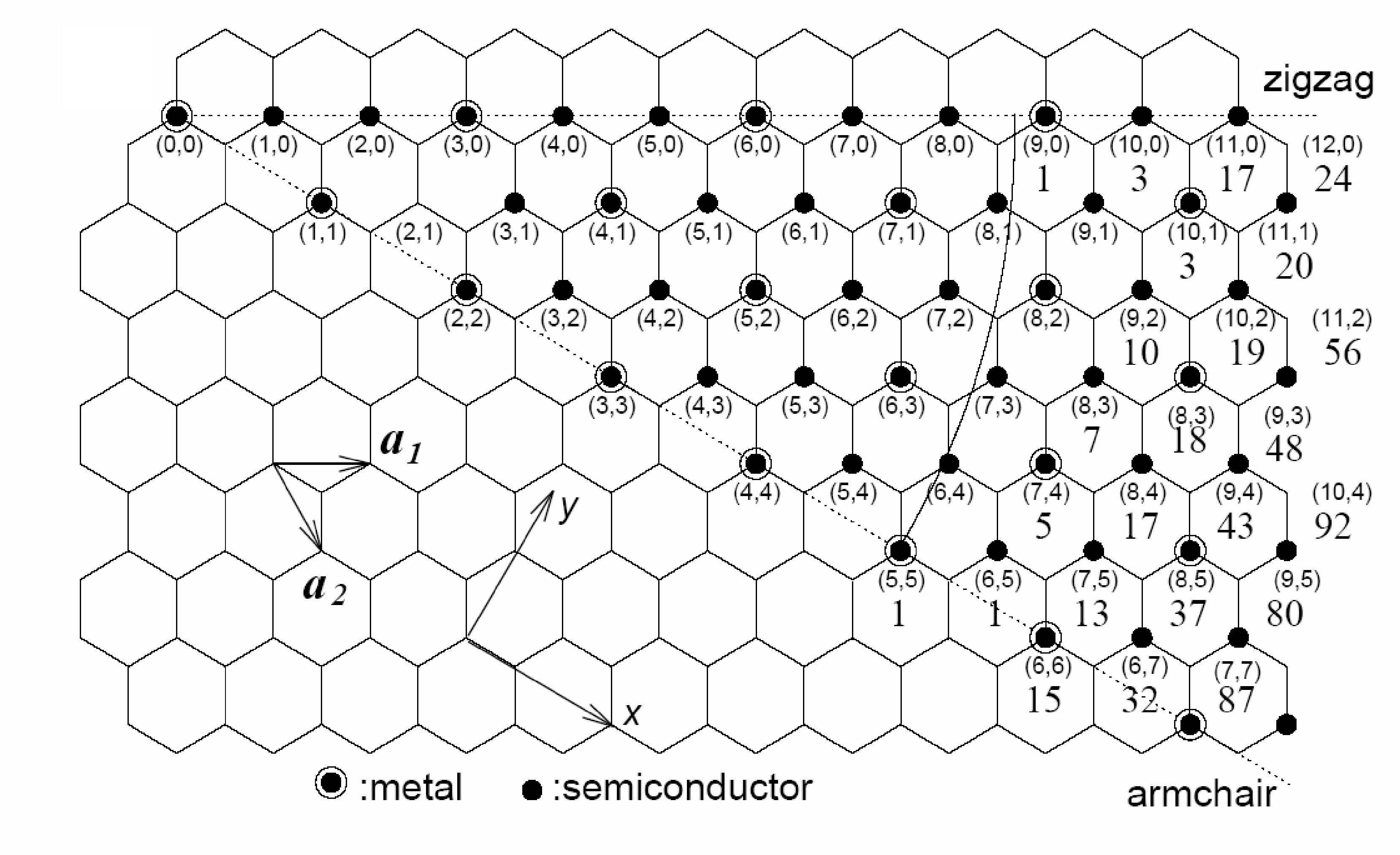
(armchair tubes (n_1=n_2) are metallic)

n_1-n_2≠3q,
No slice crosses K_1, semiconducting nanotubes



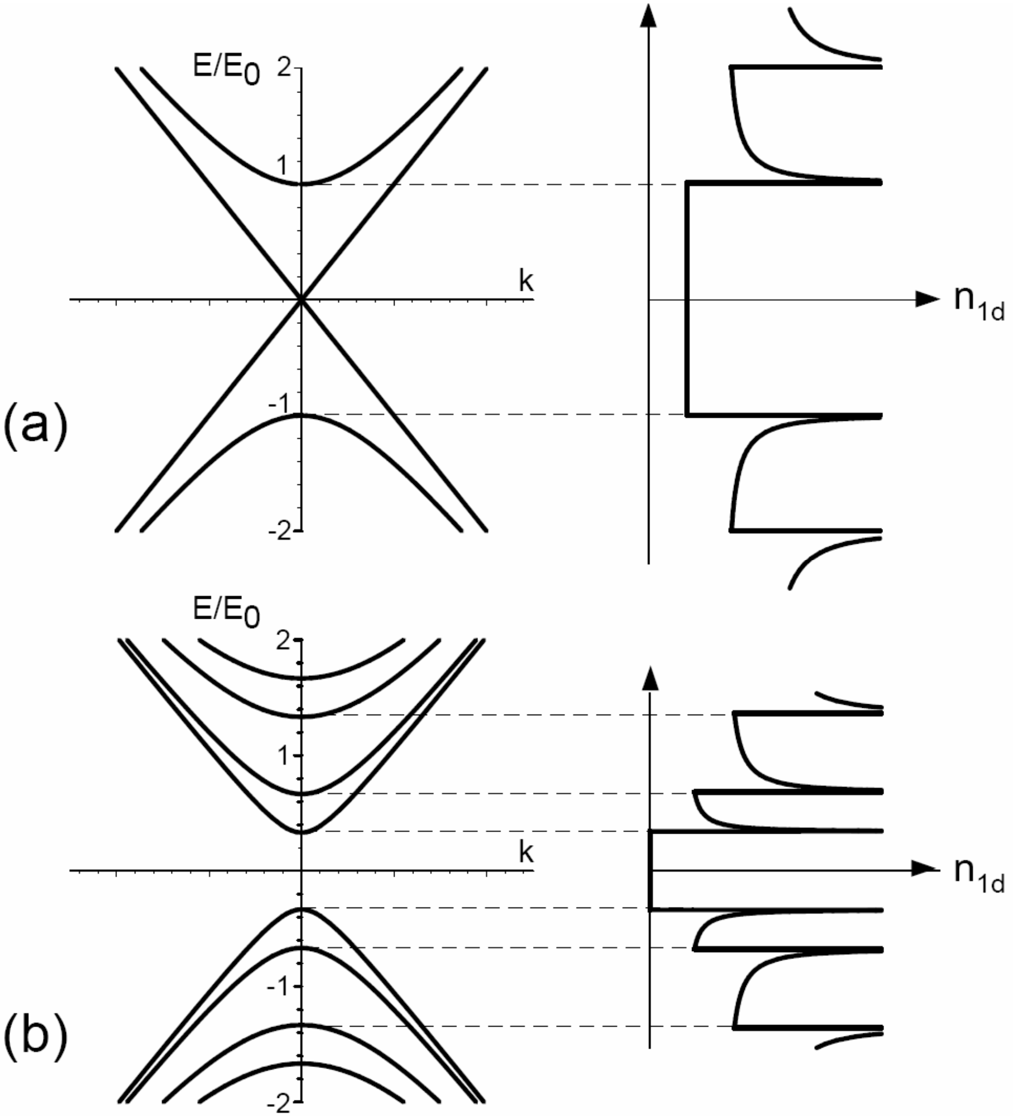
E_g~0.7eV/D (nm)

Metallic vs. semiconducting nanotubes



1D subbands

density of states



metallic tubes

DOS = constant
at small E_F

$$n = 4 \times \frac{2k_F}{2\pi}$$

$$E = \hbar v_F k_F$$

$$D(E) = \frac{dn}{dE} = \frac{4}{\hbar \pi v_F} = \text{const}$$

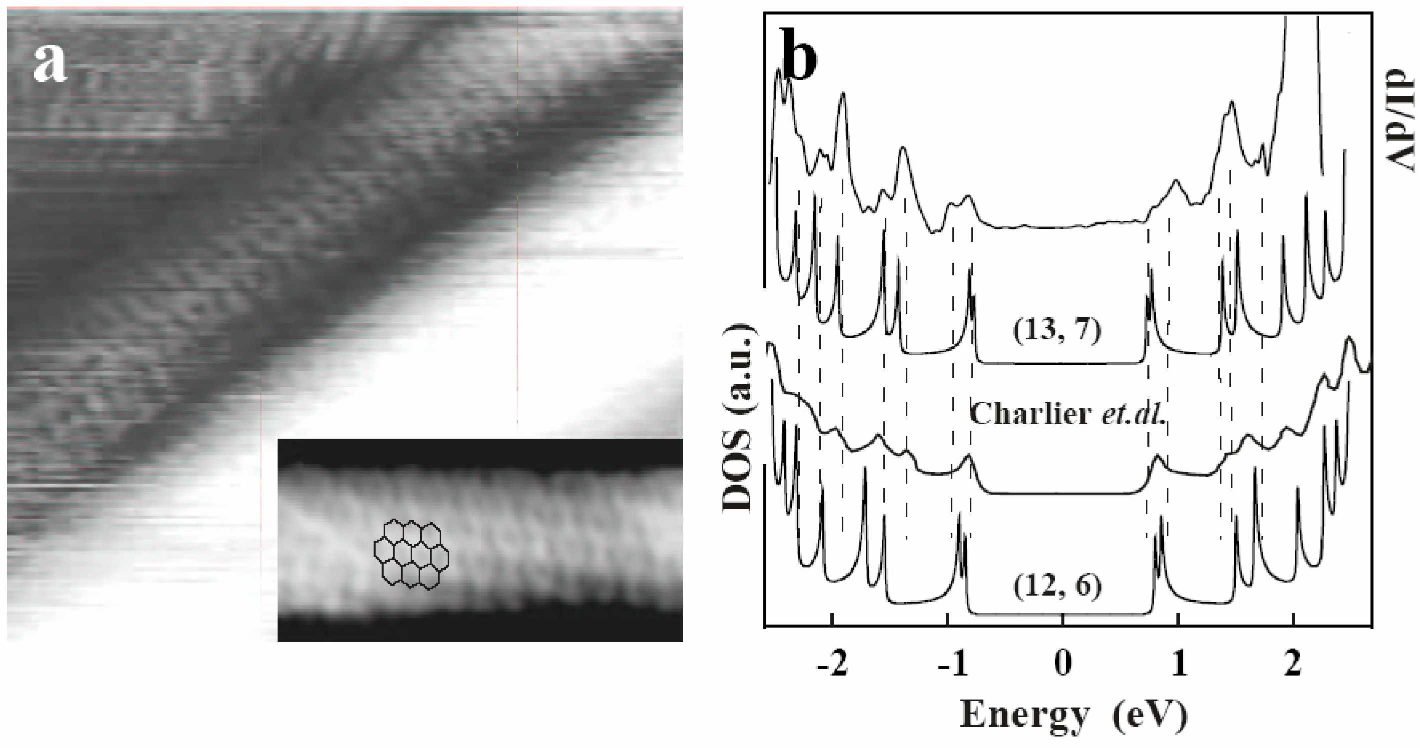
semiconducting tubes

DOS = 0 at small E_F

van Hove singularities

1D subbands, STM studies

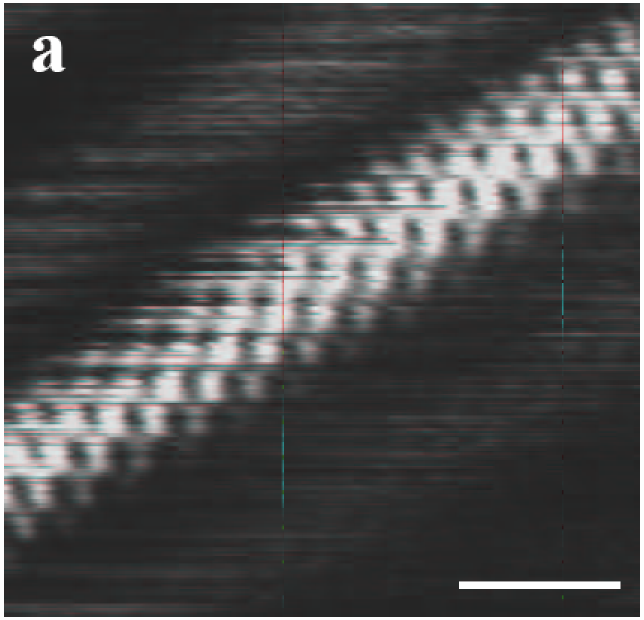
image from Charlie Lieber group at Harvard

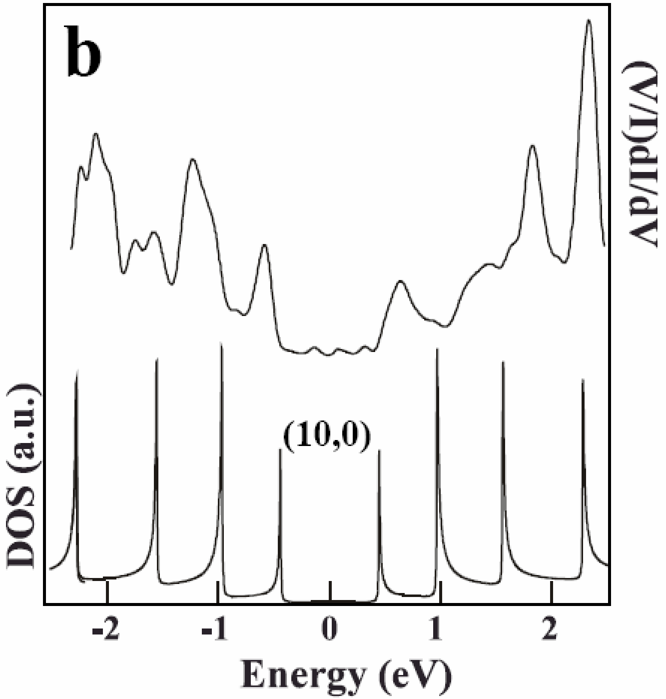


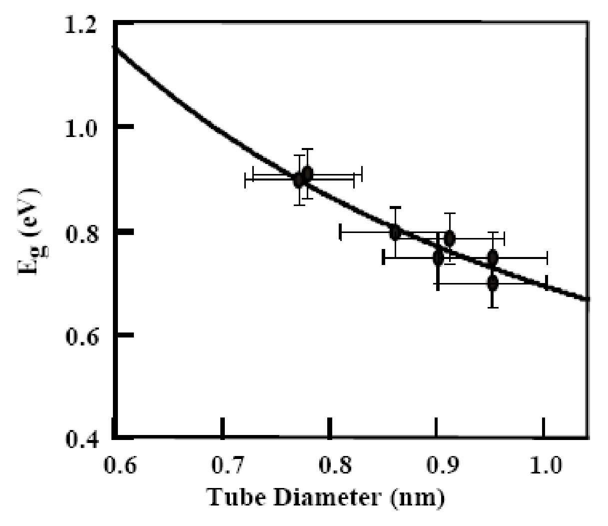
Odom, Nature, **391** (1998)

1D subbands, STM studies

image from Charlie Lieber group at Harvard



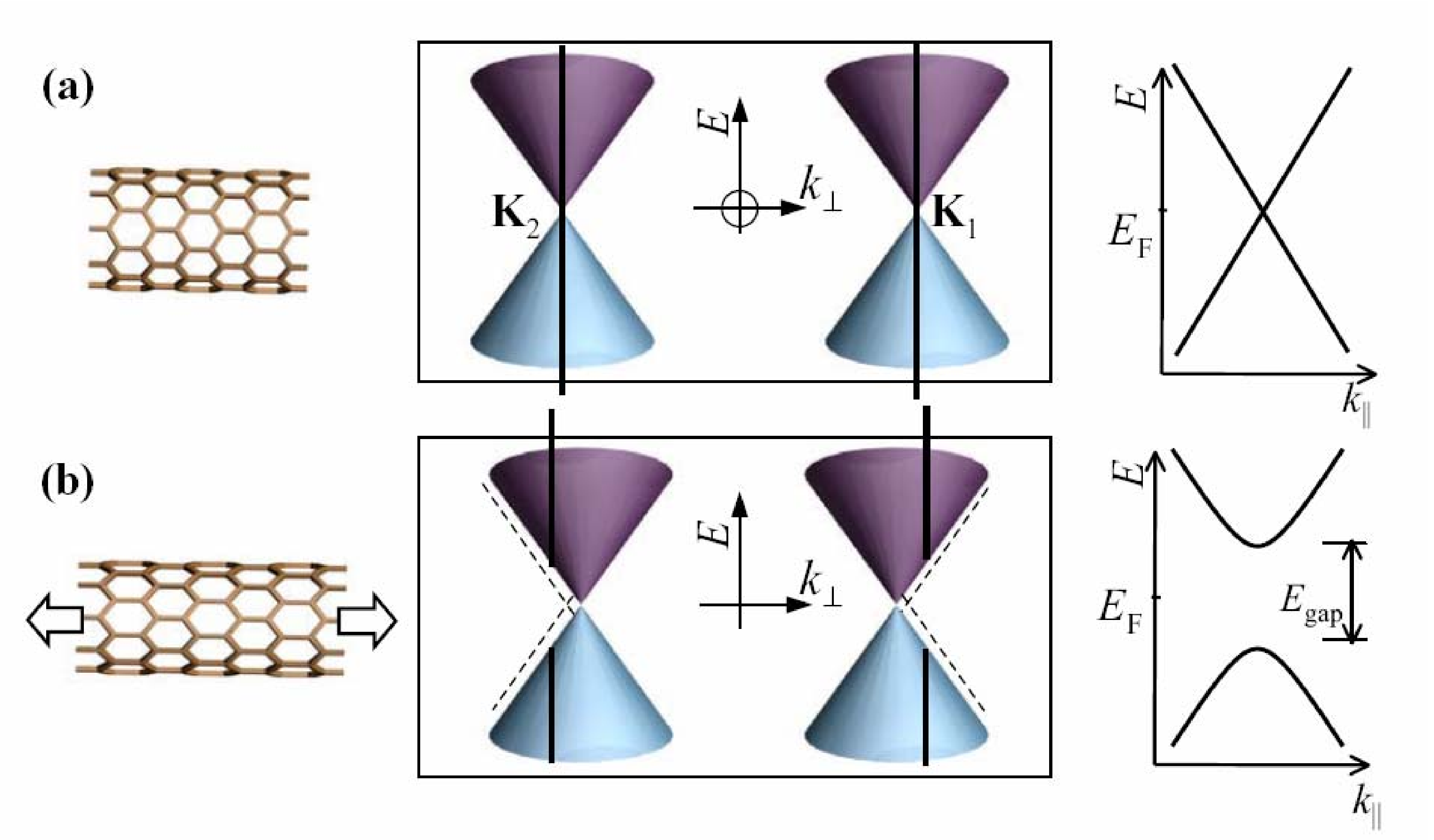




E_g~0.7eV/D(nm)

Odom, Nature, **391** (1998)

Effects of strain

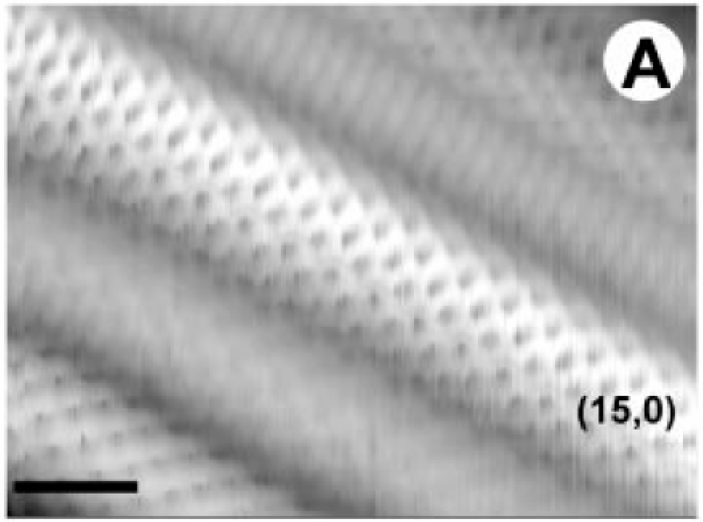


Armchair: no effect
Zigzag: a small band gap developed

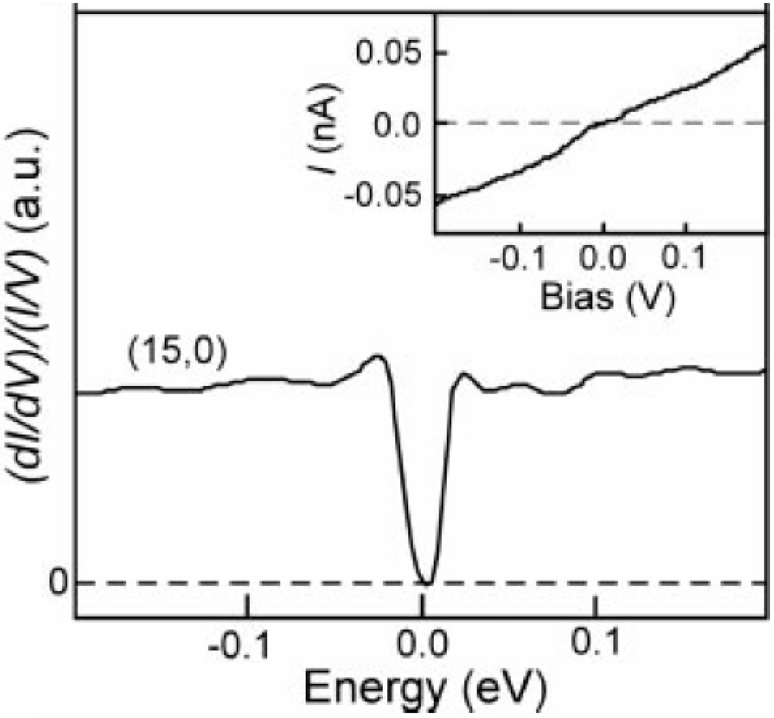
Orbital degeneracy is preserved

Effects of finite curvature

image from Charlie Lieber group at Harvard



Ouyang, Science, **292**, 702 (2001)

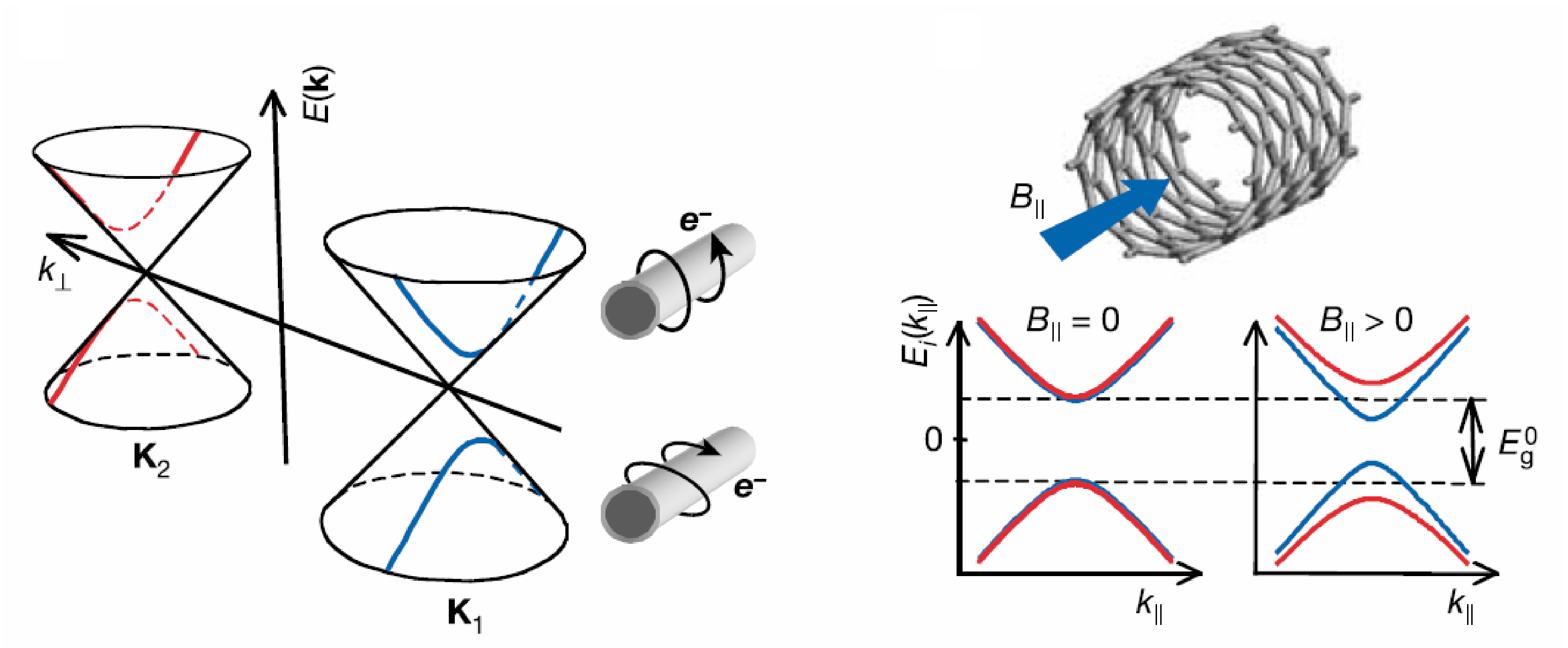


Same as strain effects

A small band gap developed for zigzag and chiral tubes due to the finite curvature of the tube itself. Small bandgap semiconducting tubes. E_g<0.1eV, compared with true semiconducting tubes (Eg~0.7eV).
Armchair tubes remains metallic.

Effects of a parallel magnetic field

Minot, Nature, **428**, 536 (2004)



1D subbands with $K_\perp>0$ and $K_\perp<0$ gains difference phase due to B
Orbital degeneracy broken
Eg can be tuned by B

History

- Discovered 1991 by Ijima *et al.* in Japan - byproduct of carbon arc furnace synthesis of C60.

- Yield of tubes, particularly SWNT, much enhanced when tiny amount of transition metal (Ni, Fe, Co) added to furnace - 1992.

- Laser ablation method - lots of SWNT - 1993.

- Field emission from nanotubes ~ 1995.

- HiPCO, CVD methods ~ 1998.

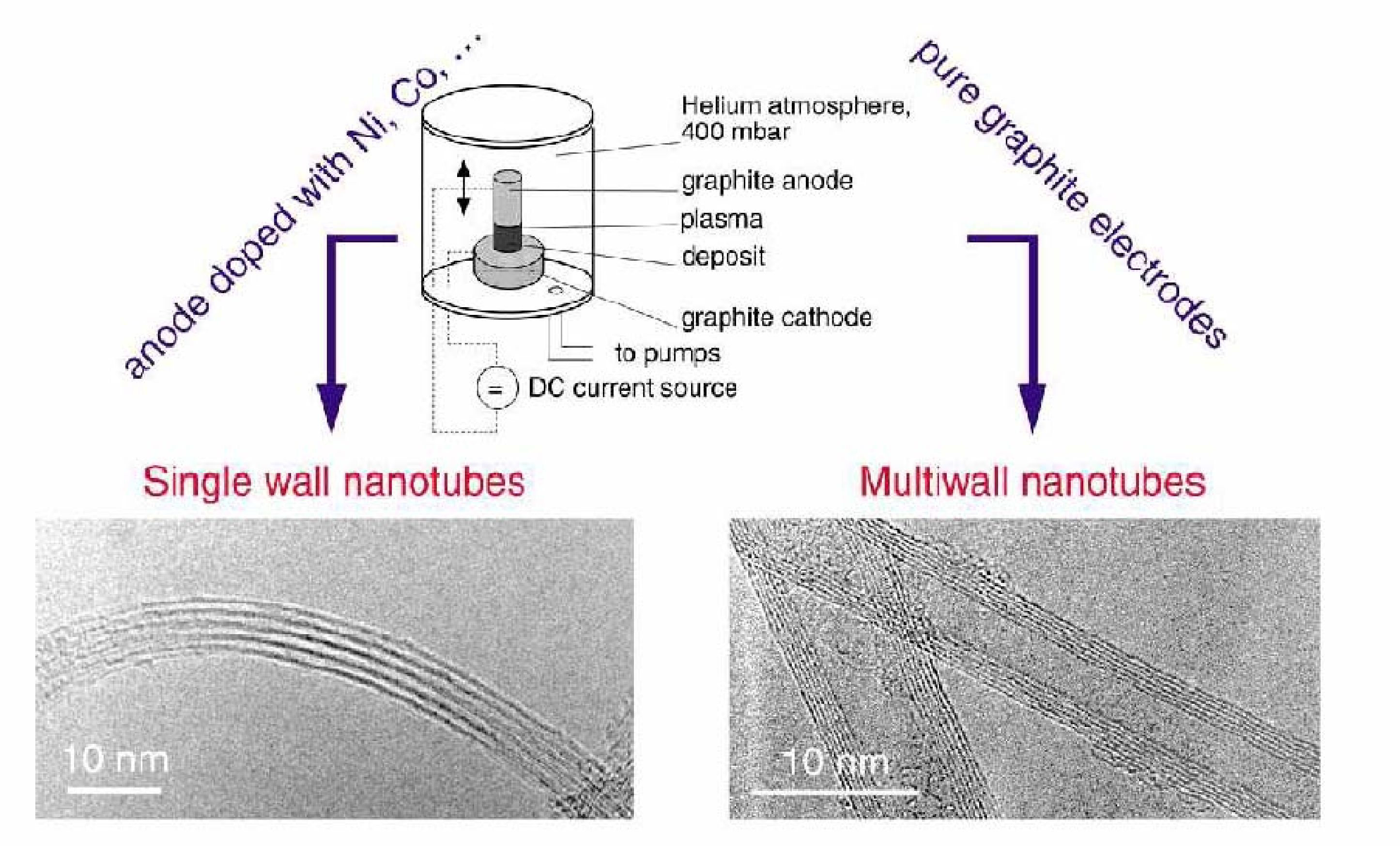
- First nanotube nanoelectronic device - SET - 1997.

- Ballistic transport verified – 1999.

- CNT FET device with Ohmic contacts - 2003

Carbon arc discharge

image from Ecole Polytechnique in Lausanne



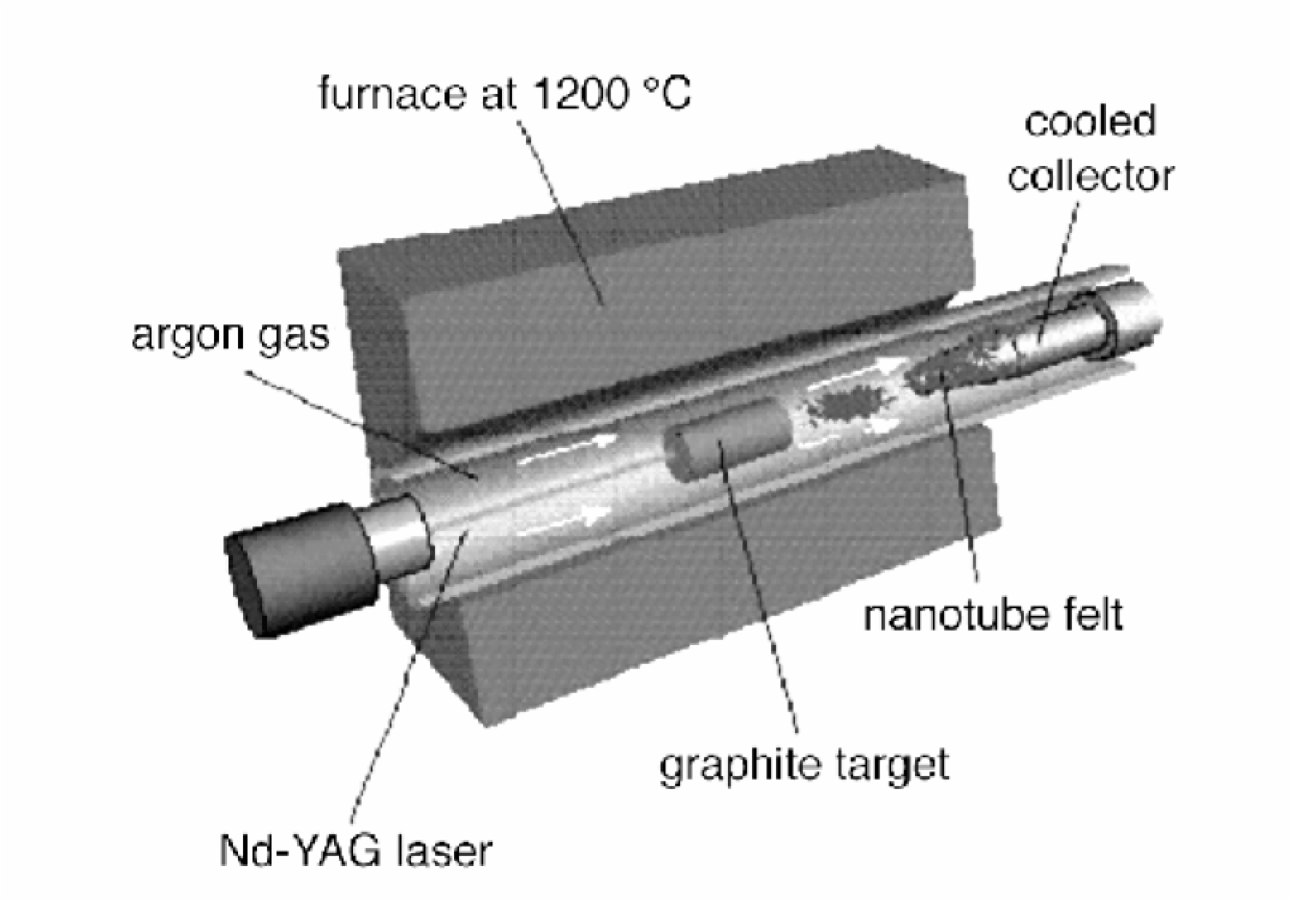
Condensation of carbon atoms from solid carbon source

CNT, no dangling bonds, lower energy compared to other forms of carbon

Resulting tubes are bound together by van der Waals interaction

Laser ablation

image from Yakobson/ Smalley Am. Sci. article



Intense laser pulses to ablate a solid carbon target
Nanotubes carried by inert gas flow and collected at the cold fingers
Once again, typical results are nanotube ropes

HiPCO (high-pressure CO)

- Flow high pressure carbon monoxide past catalyst particles at high temperatures.

- Industrially scaleable!

- Can now produce largely single-walled nanotubes in kilogram quantities.

Smalley group at Rice

Laser ablation

TEM images of multiple-walled nanotubes and rope of single-walled nanotubes

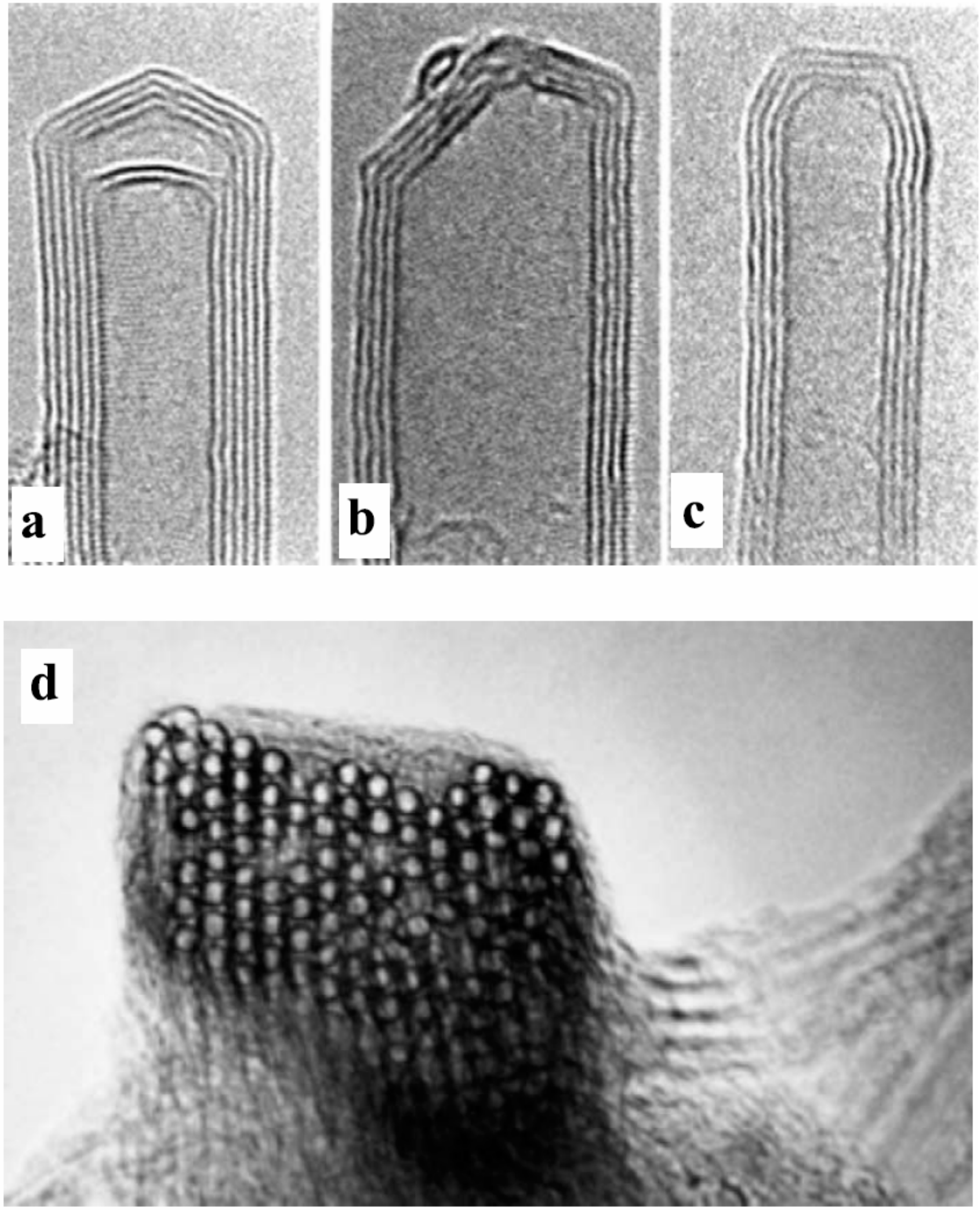
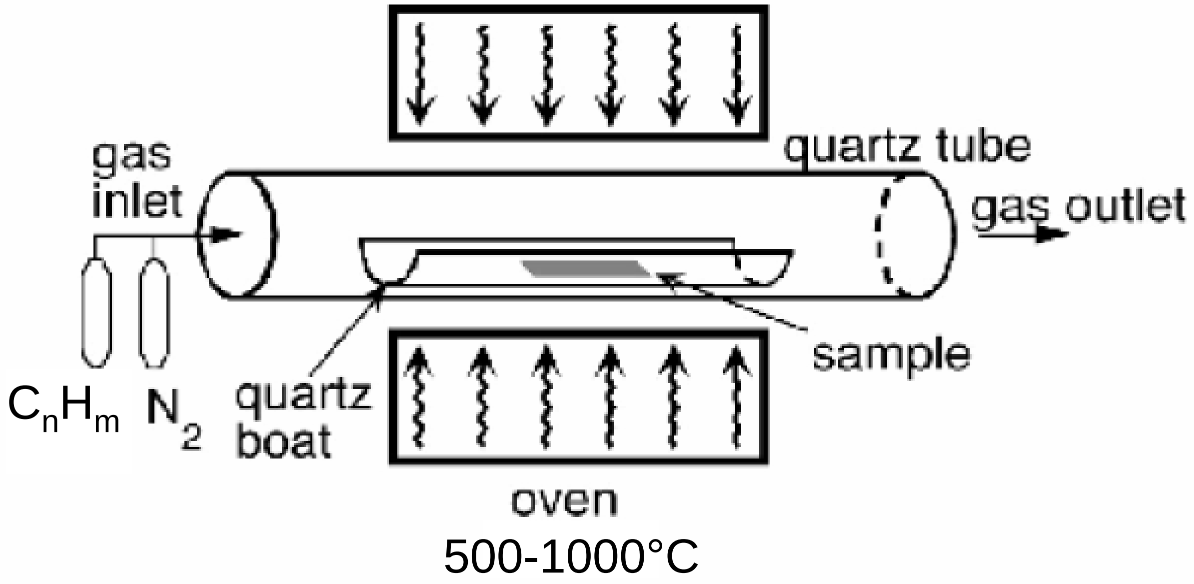


image from Rick Smalley's group at Rice

CVD

image from Ecole Polytechnique in Lausanne

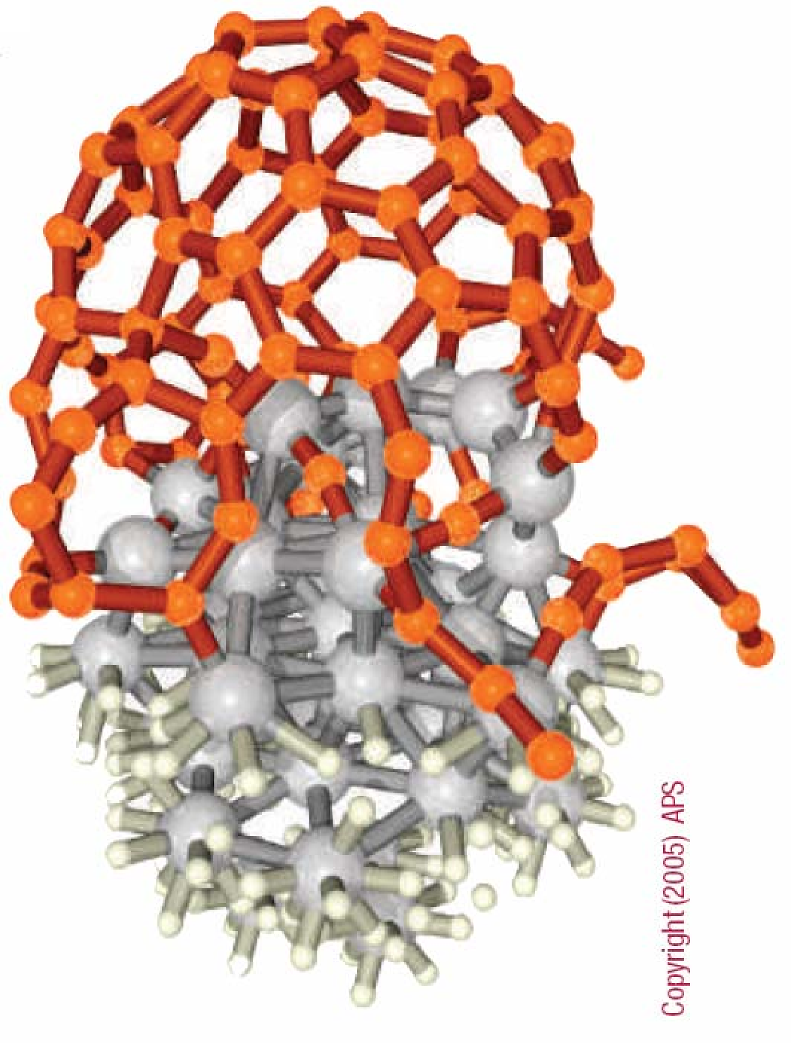


Most used method for generating high quality, individual SWNTs

Key parameters:

- Hydrocarbon precursors
- Catalysts
- Growth temperature

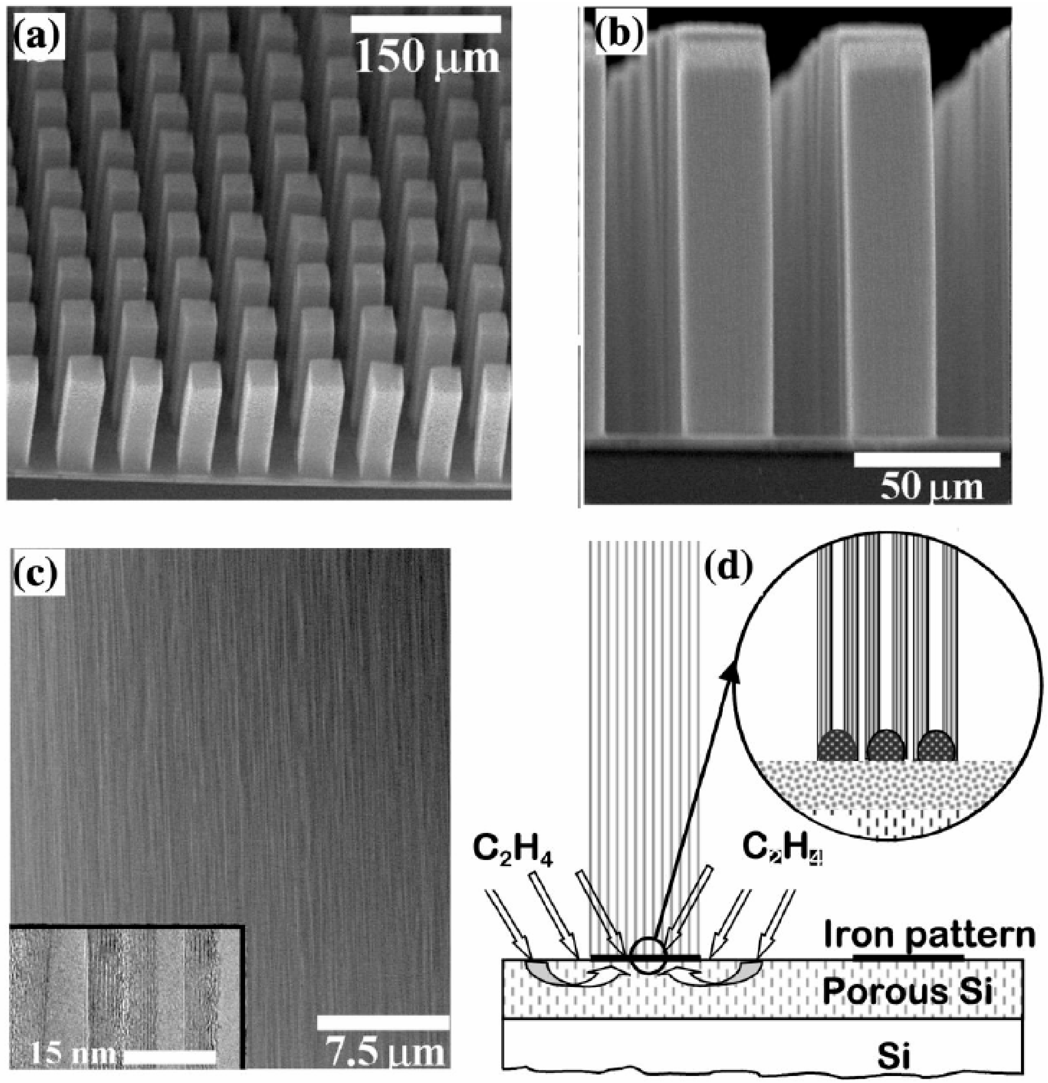
Raty, PRL **95,** 096103 (2005)



Molecular dynamics simulations show the carbon atoms on the catalyst surface “slef-assembly” into the tube form

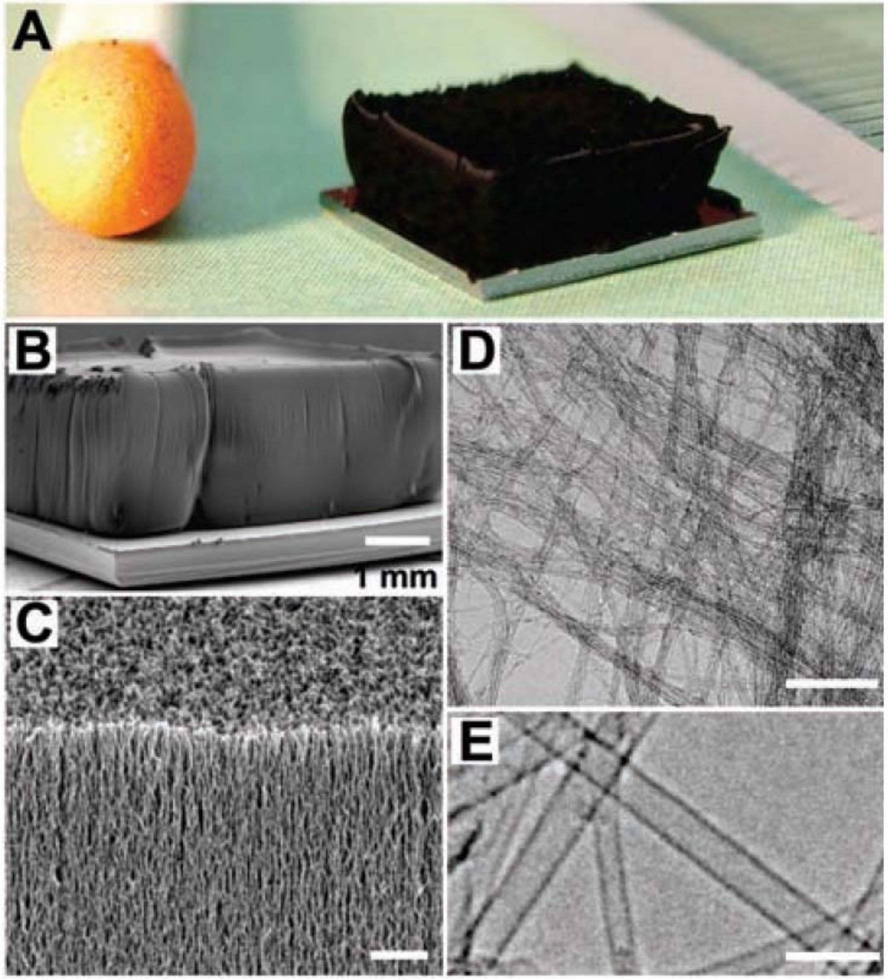
Patterned growth of MWNT

image from Hongjie Dai group at Stanford



Patterned growth of MWNT

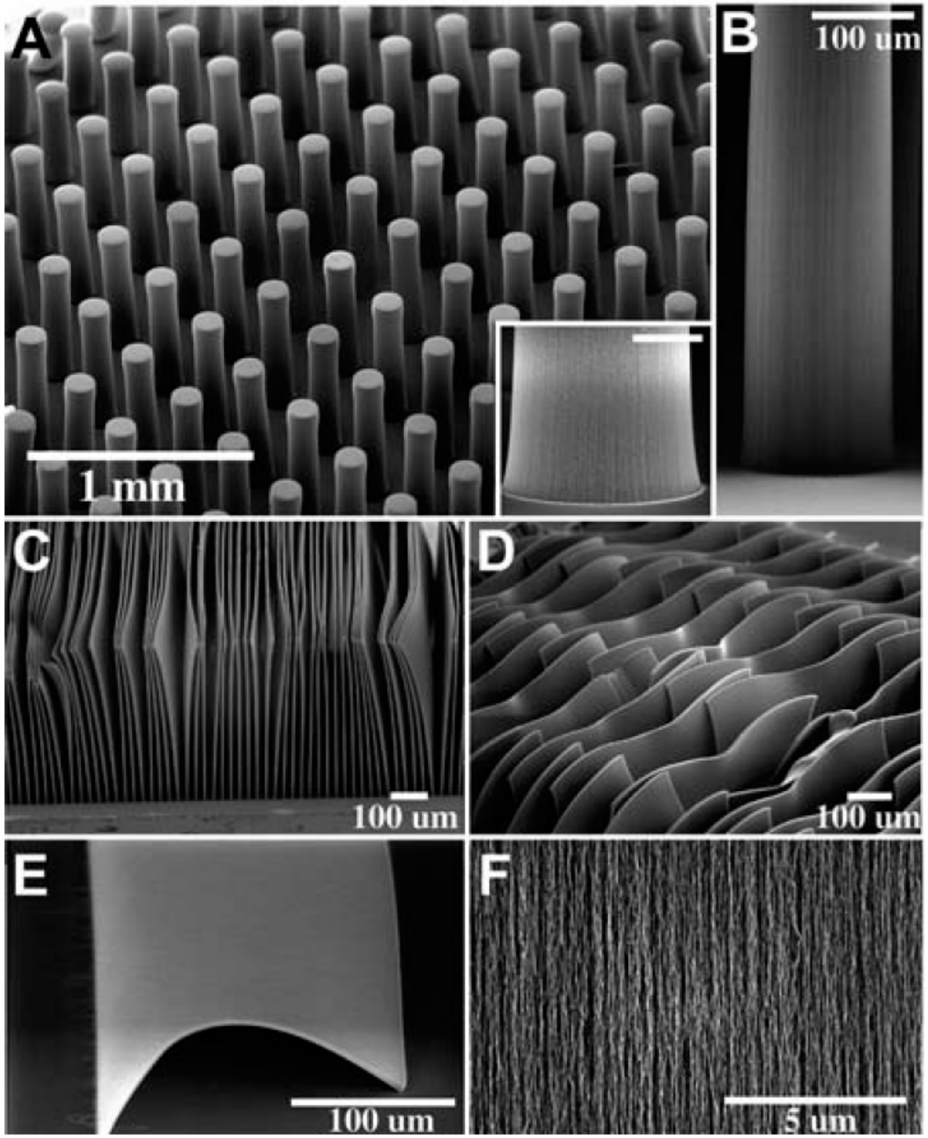
Hata, Science, **306**, 1362, (2004)



- •Ethylene as carbon source
- •Fe catalyst
- •Certain amount of H_2O vapor as weak oxidizer to remove amorphous carbon contamination

Patterned growth of MWNT

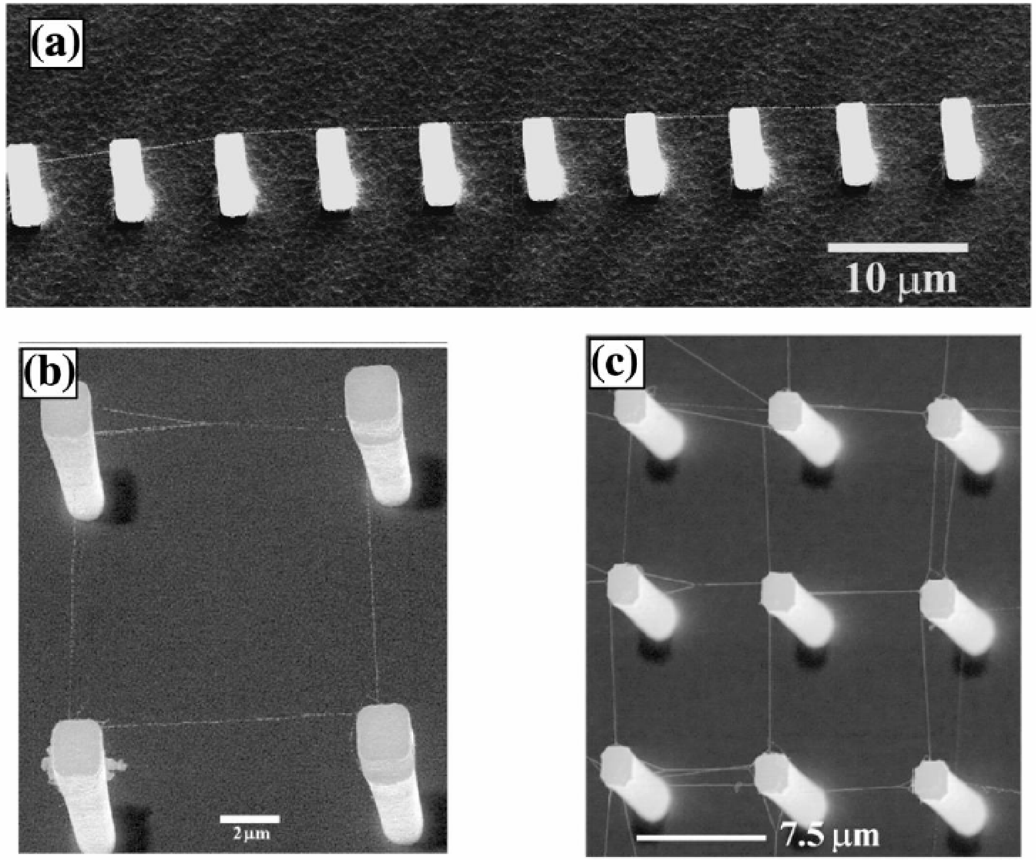
Hata, Science, **306**, 1362, (2004)



Flexible CNT sheets

Patterned growth of MWNT

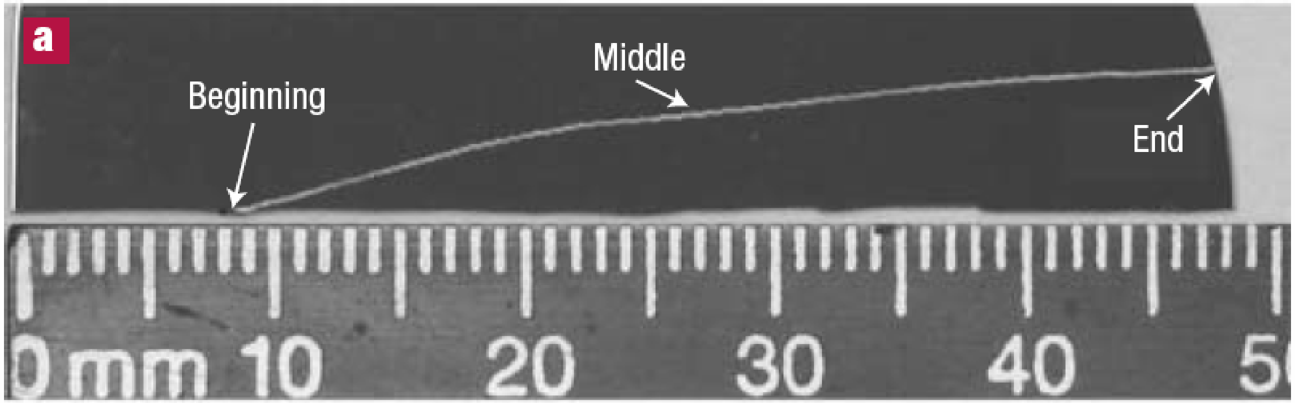
image from Hongjie Dai group at Stanford

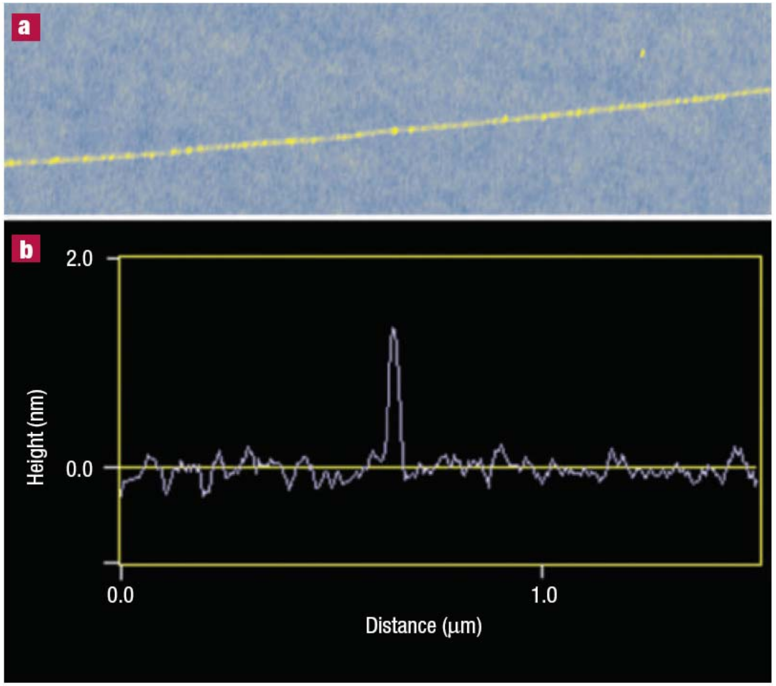


SWNT “power lines” grown between pre-patterned Si pillars

Growth of long nanotubes

Zheng, Nature Mater, 3, 673 (2004)



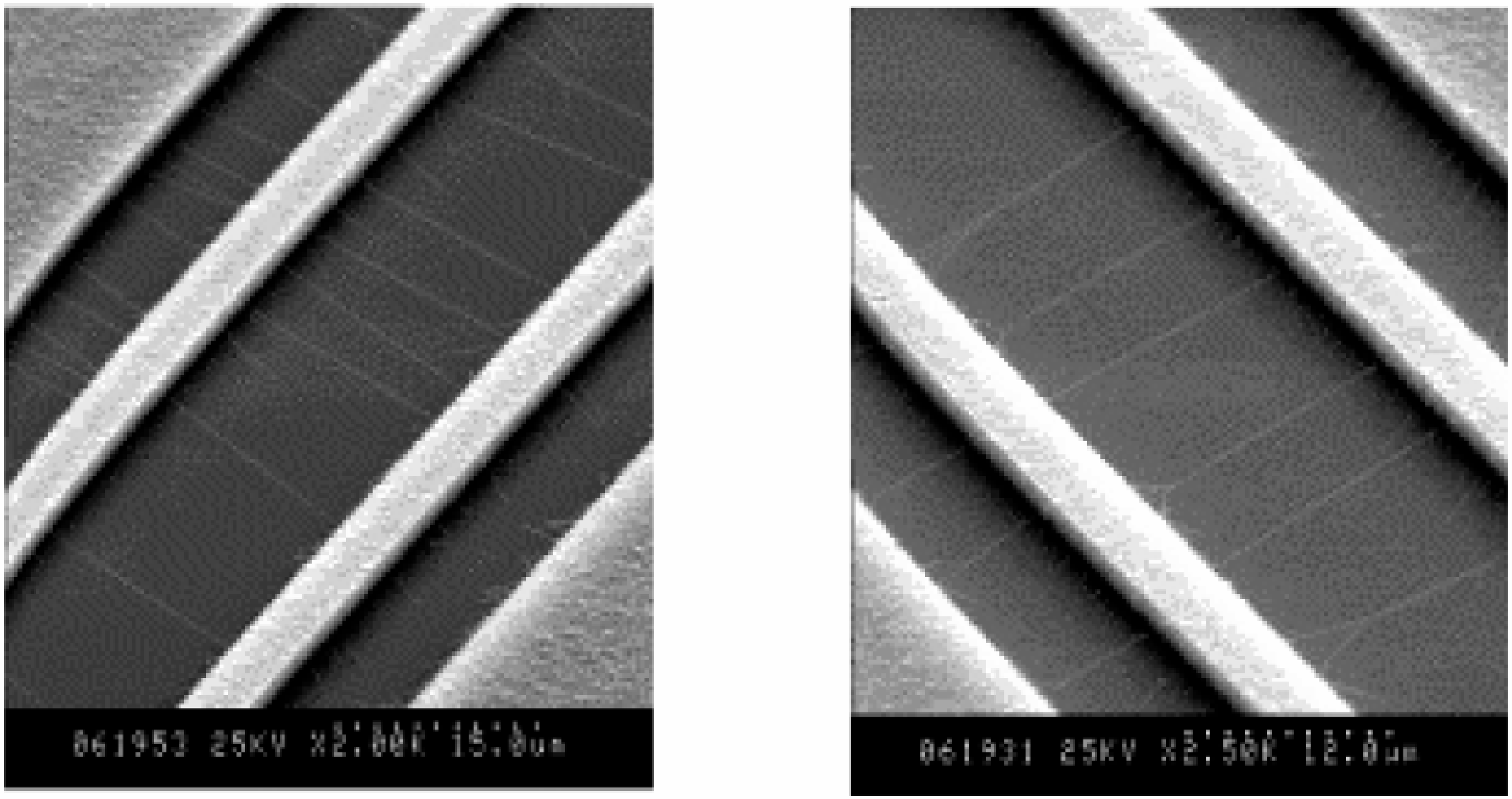


230 SEM images patched together

4cm long SWNT

Directed growth

image from Hongjie Dai group at Stanford



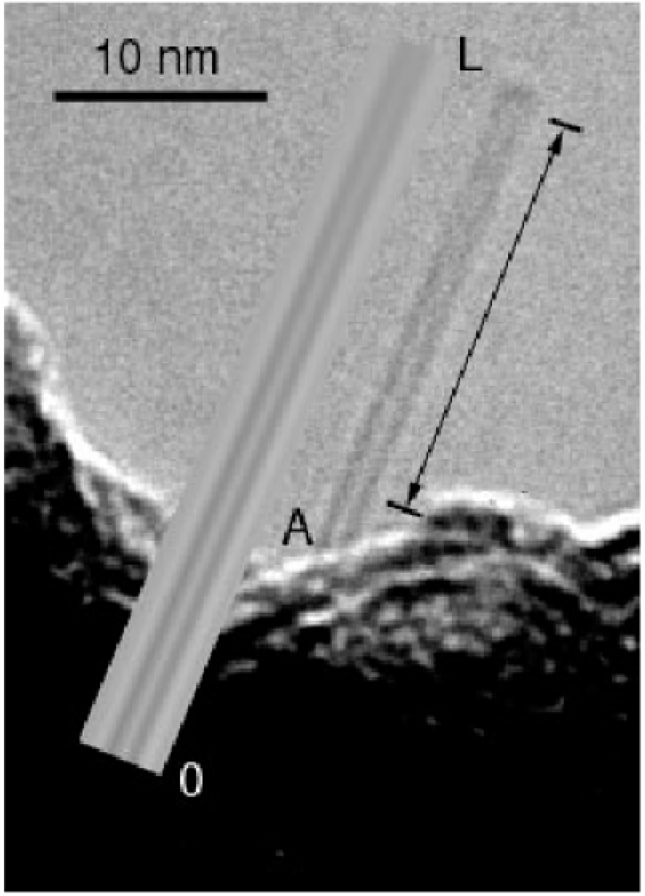
Electric field during growth aligns growing tubes.

Mechanical properties

Bulk solids deform and fail due to motion of dislocations (imperfections) and sliding of grain boundaries.

Perfect nanotubes lack these mechanisms - should be very strong!

Can infer elastic modulus from clamped vibration amplitude due to thermal agitation.



$$\sigma = \underbrace{Y}_{} \frac{\delta\ell}{\ell} \qquad \text{(equivalent to } f = kx\text{)}$$

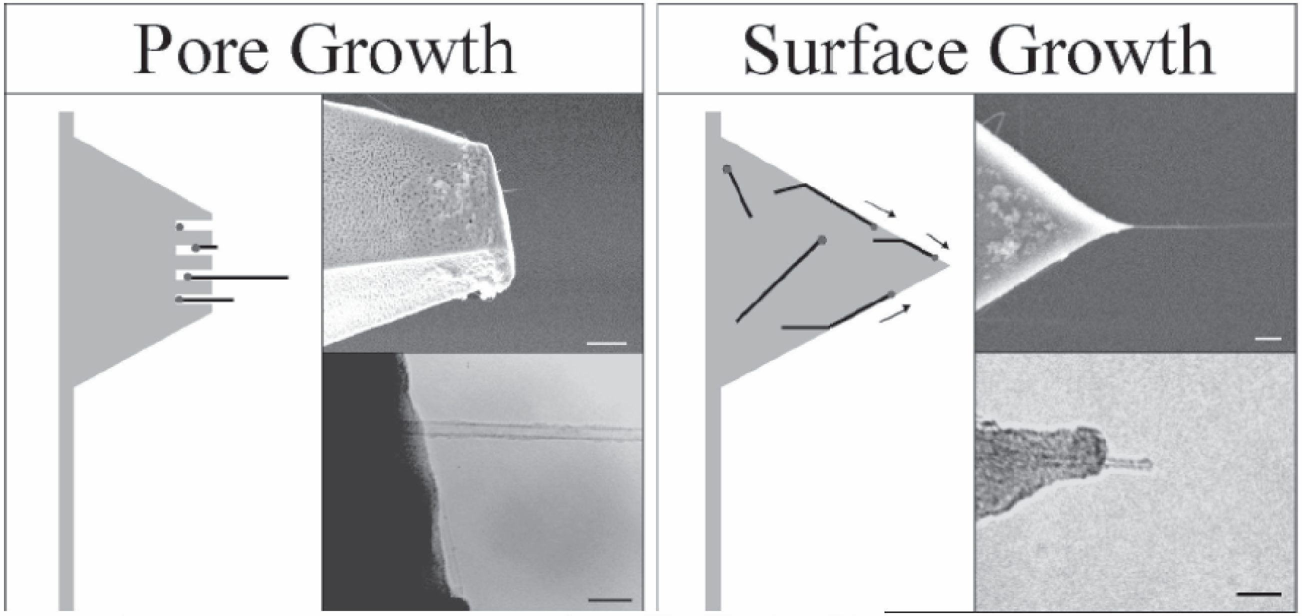
Result: Young's modulus = 1.2 TPa

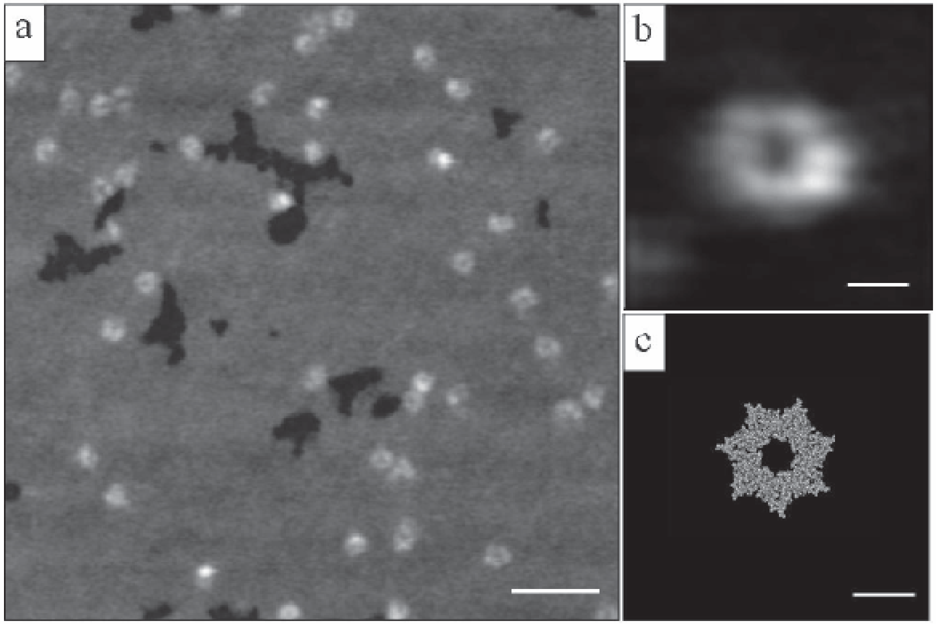
For comparison, steel $Y = 0.19$ TPa

M.M.J. Treacy et al., Nature, 20 June 1996.

Nanotubes as AFM tips

image from Charlie Lieber group at Harvard





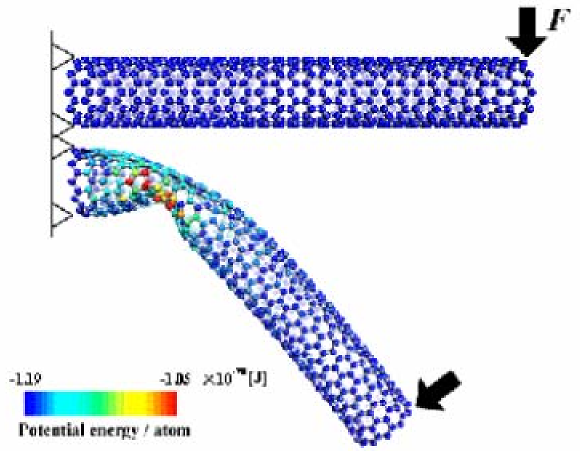
Extremely tiny radius of curvature allows ~ 1 nm lateral resolution - the best there is.

Image of CroEL proteins

Mechanical properties

Tubes are extremely robust.

Buckle reversibly rather than failing catastrophically.



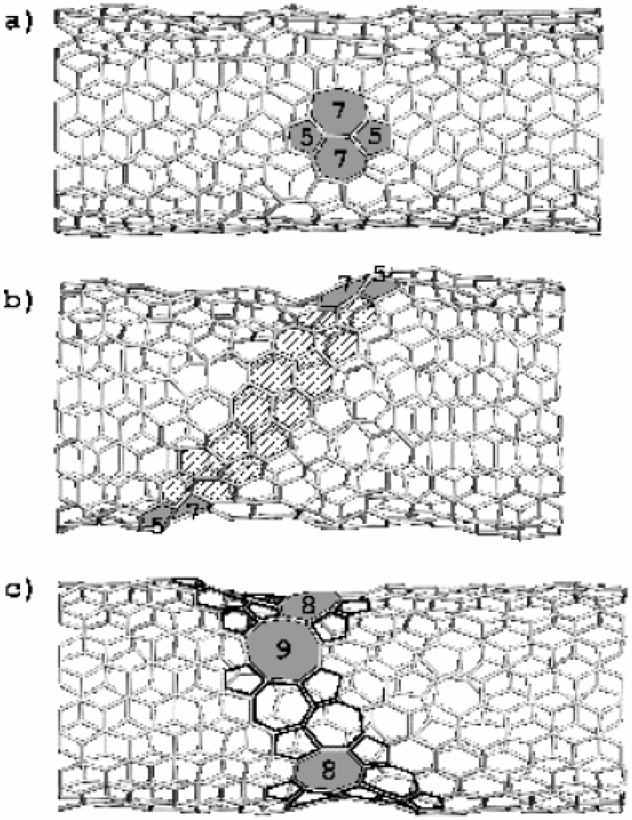
How do nanotubes break?

Image from Boris Yakobson.

Nucleation of defects - pentagon/heptagon pairs.

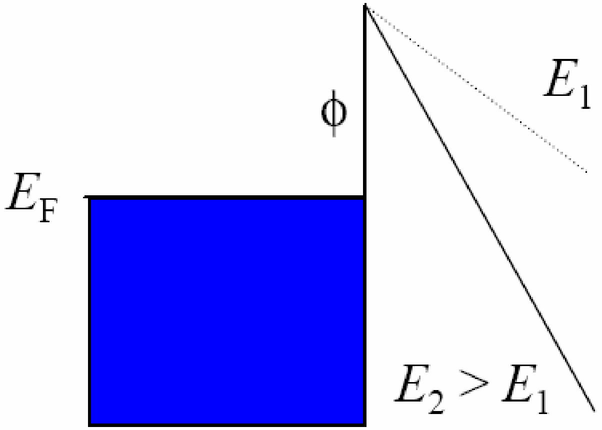
These pairs migrate and leave behind a band of smaller-diameter tube.

Enhanced stress causes more defect nucleation.

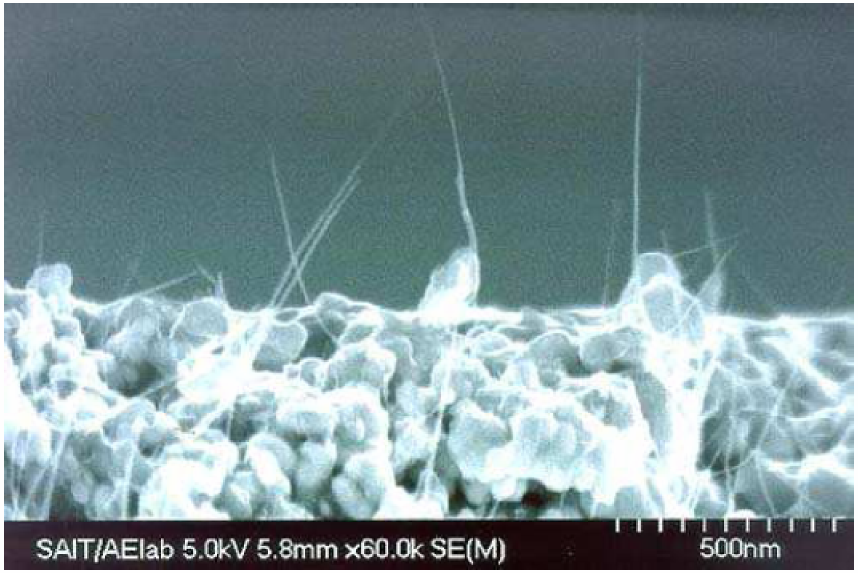


Nanotubes for field emission

- Emission of electrons from metals is enhanced at large electric fields.
- Electric fields near a tip with radius of curvature *r* go like 1/*r* for a given voltage.
- Nanotubes are incredibly sharp tips ($r < \sim 1$ nm), so they can emit efficiently at low voltages (a few V).



Samsung, SWNT protruding from a metal cathode.



Field emission displays

Emitted electrons can hit phosphor-coated transparent ground plane (ITO).

FEDs tend to be very bright and very fast compared to LCDs.

Field emission displays are the most realistic short-term electronic application of nanotubes.

30-inch carbon nanotube based field emission display demonstrated by Samsung

Nanotubes for gas storage

Nanotubes have very high specific surface areas.

Hydrogen has a substantial chemisorption energy onto nanotubes - greater than room temperature!

Controversial results show that 1 g of SWNT material could adsorb up to ~ 0.1 g of hydrogen. Effective packing density is vastly higher than storing hydrogen as a high pressure gas.

Possible applications for hydrogen-powered cars, fuel cells, etc.

Adsorption detectable through electrical properties: sensors

Separating chiralities

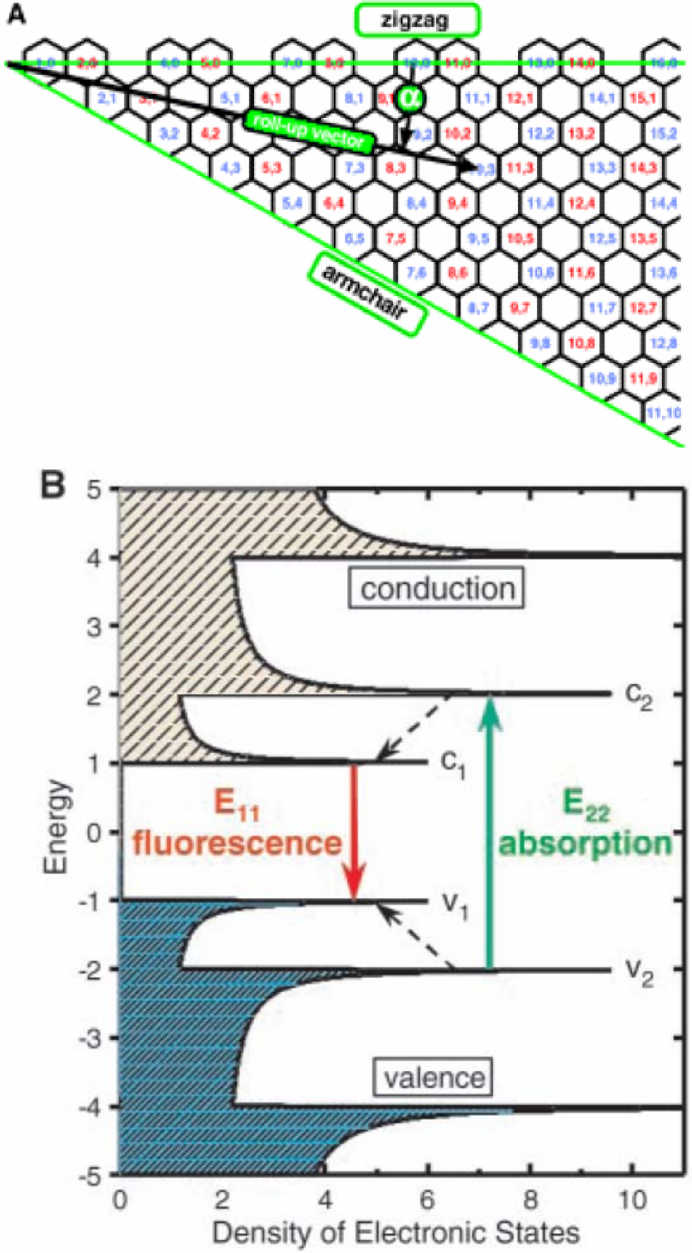
Known fabrication methods all produce a variety of tube chiralities.

Separating tubes by type is extremely difficult.

One very recent development for assessing distribution of tube types: spectroscopy of individual, encapsulated tubes.

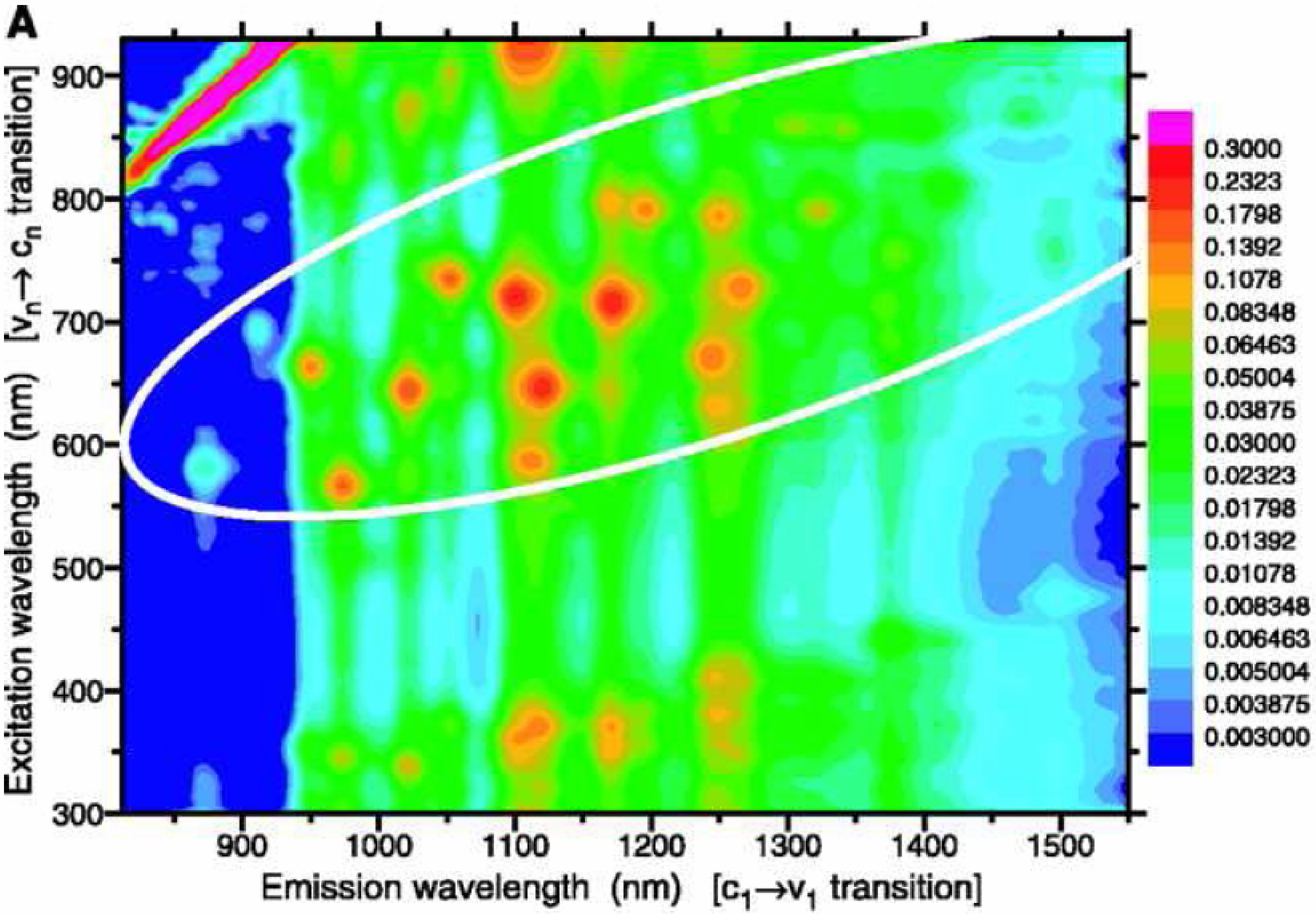
Fix excitation on absorption peak, and look for emission peaks.

Van Hove singularities in d.o.s.



O'Connell et al., Science 297, 593 (2002).
Bachilo et al., Science 298, 2361 (2002).

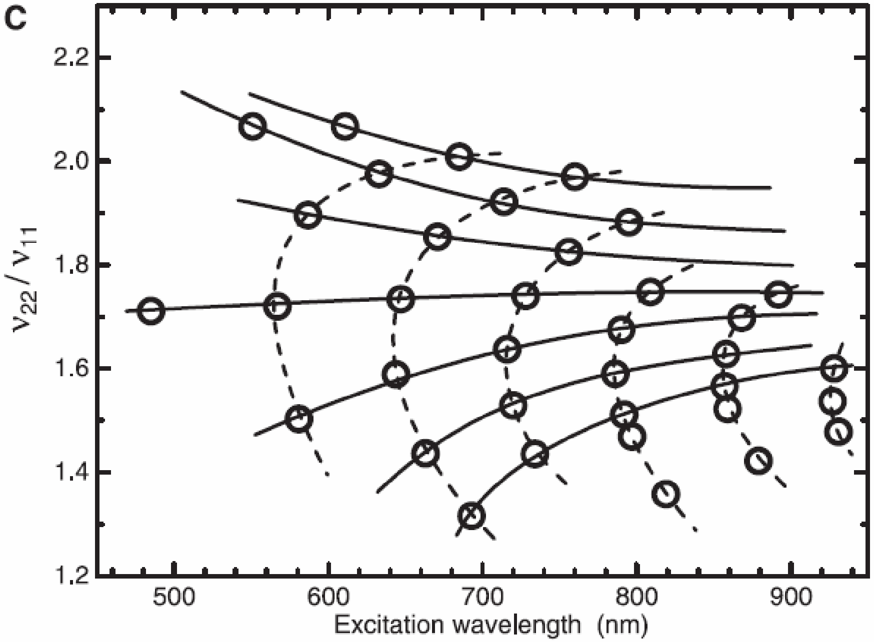
Separating chiralities



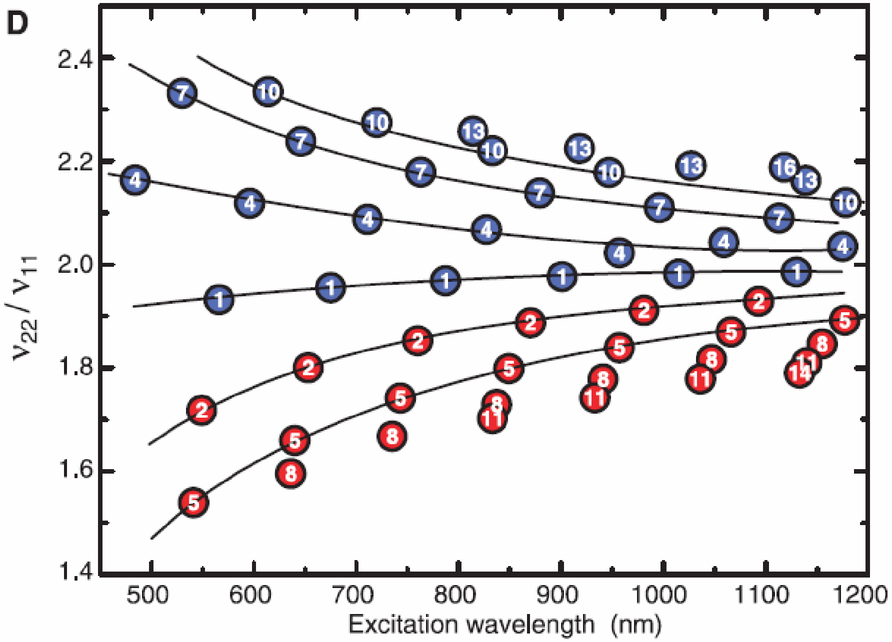
Bachilo et al., Science 298, 2361 (2002).

Determine chiralities

Bachilo, Science, **298**, 2361 (2002)



experiment



Theory

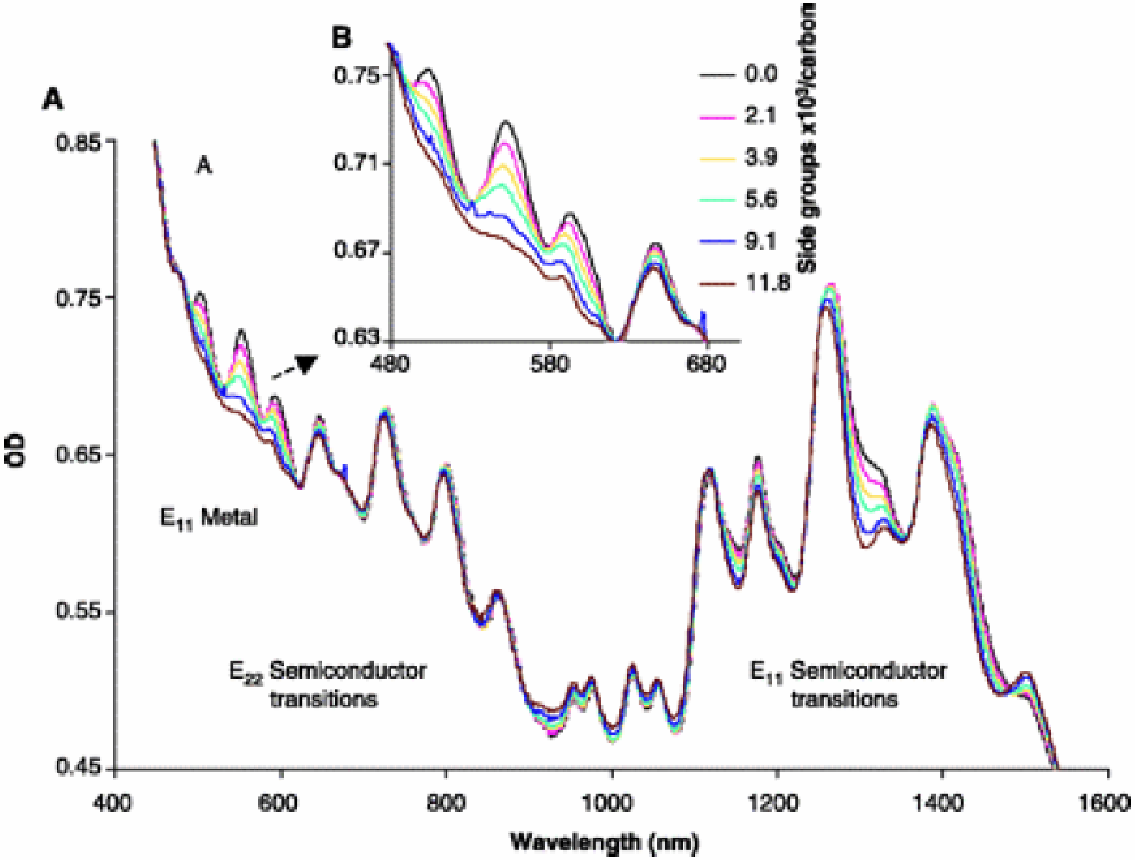
Positions of E_{22} absorption and E_{11} emission determines the tube type

Chirality-specific chemistry

Now that we can identify the types of tubes present, it would be great to be able to chemically manipulate particular types:

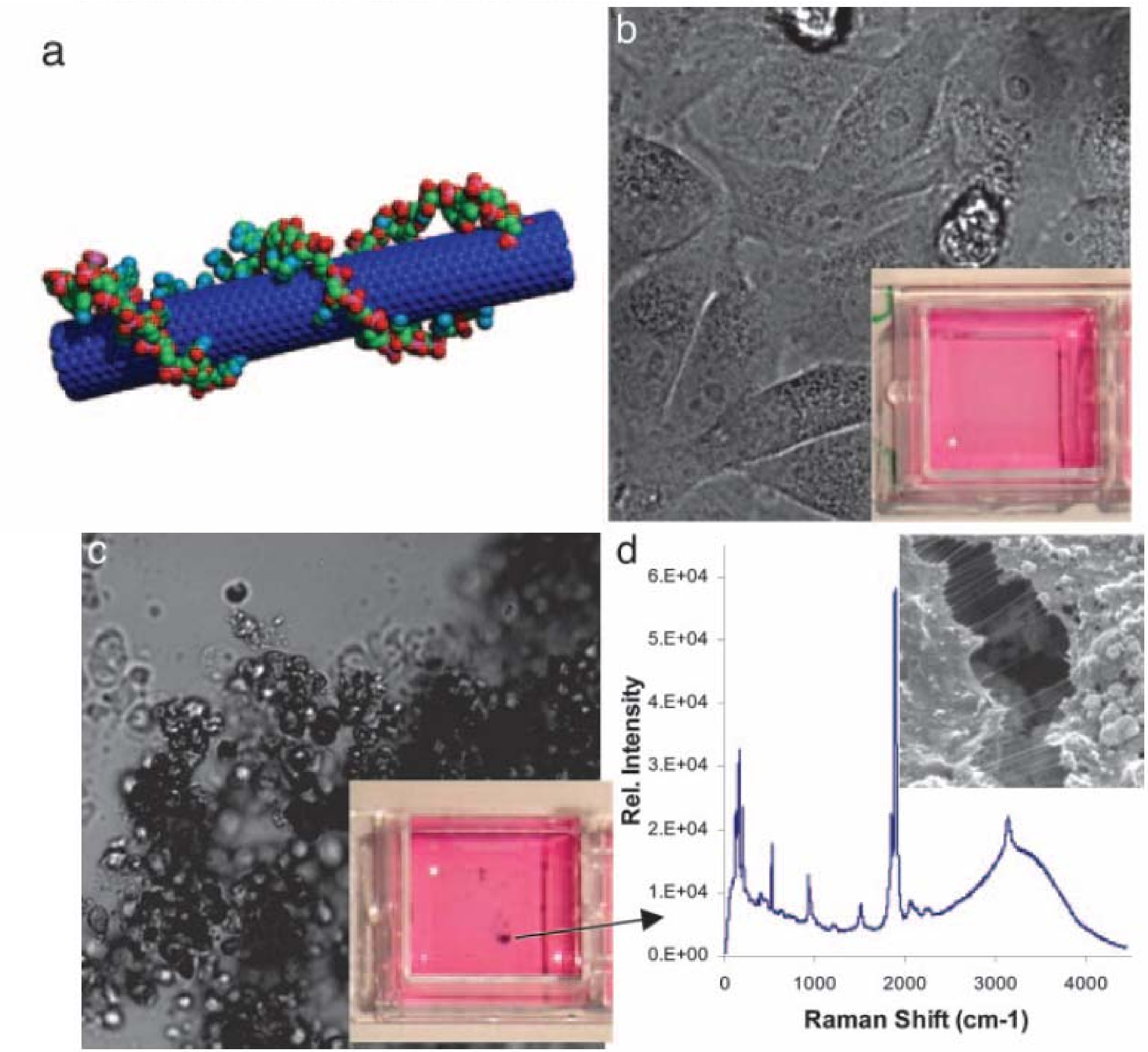
Selective chemistry can now be performed that *reversibly* alters the properties of just metallic tubes!

Covalent bonding between the Diazonium reagents and the nanotube determined by the DOS at the Fermi level
(only bonds to metallic tubes)



Strano *et al.*, Science **301**, 1519 (2003).

Wong, PNAS, **102**, 11660 (2005)



Local heating of the nanotubes kills HeLa cells with near-infrared (NIR) light 700- to 1,100-nm (transparent to biological systems)

Conclusions

- Carbon nanotubes are remarkable materials.
- Molecular structure directly related to impressive electrical, mechanical, physical, and chemical properties.
- Most promising short-term technological uses: field emission displays, light / strong materials, hydrogen storage.
- Outstanding challenges: bulk fabrication, selecting tube types, mastering chemistry of these and related compounds, “the wiring problem”.
- Potentially revolutionary, especially considering the material was *unknown* 15 years ago.

Next class

Nanotube based electronic devices