Introduction to Nanotechnology
Chapter 5 Carbon Nanostructures
Lecture 1

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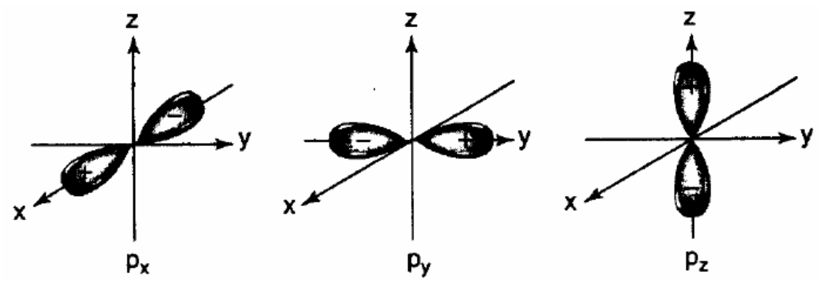
Section 5.2.1

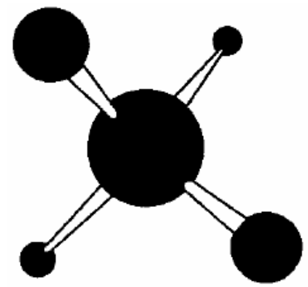
Nature of the Carbon Bond

Carbon contains 6 electrons: $(1s)^2$, $(2s)$, $(2p_x)$, $(2p_y)$, $(2p_z)$



dumbbell structure

p_x, p_y, p_z orbitals of carbon atom



tetrahedral structure

sp^3 hybridization in CH_4

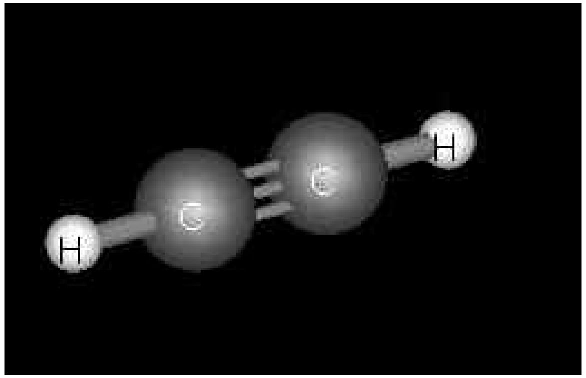
Admixture of the 2S and 2P wavefunction

$$\Psi = s + \lambda_x p_x + \lambda_y p_y + \lambda_z p_z$$

Table 5.1. Types of sp^n hybridization, the resulting bond angles, and examples of molecules

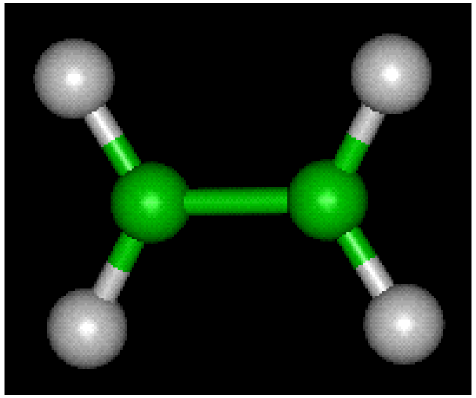
Type of Hybridization	Digonal sp	Trigonal sp^2	Tetrahedral sp^3
Orbitals used for bond	s, p_x	s, p_x, p_y	s, p_x, p_y, p_z
Example	Acetylene C_2H_2	Ethylene C_2H_4	Methane CH_4
Value of λ	1	$2^{1/2}$	$3^{1/2}$
Bond angle	180°	120°	109°28′

acetylene



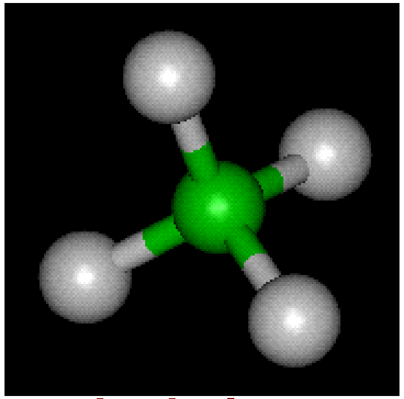
linear compound

ethylene



planar compound

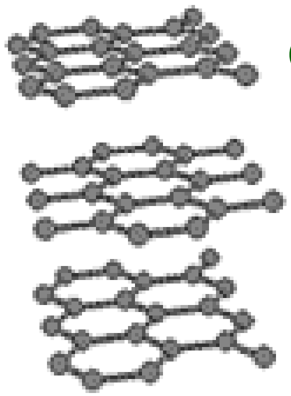
methane



tetrahedral compound

Green = Carbon White = Hydrogen

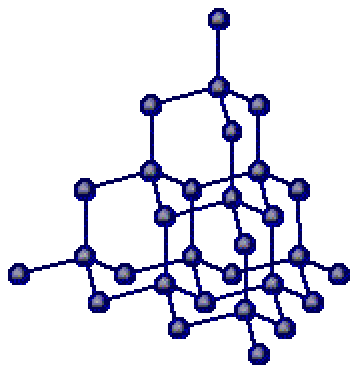
Solid state carbon structures: Graphite and Diamond



Graphite sheet: hexagon bond through sp2 hybrid bonds

3 nearest-neighbor carbons

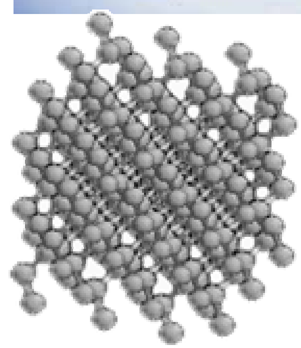
carbon bond angle =120^{o}



Diamond : tetrahedral bond through sp^3 hybrid bonds

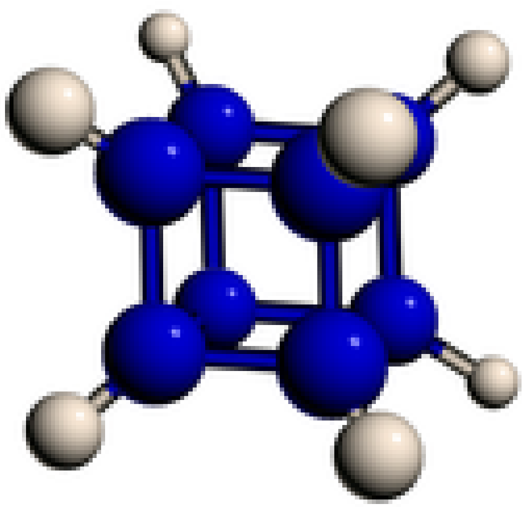
3 nearest-neighbor carbons

carbon bond angle =109^{o}



Hydrocarbon molecules with different carbon bond angles

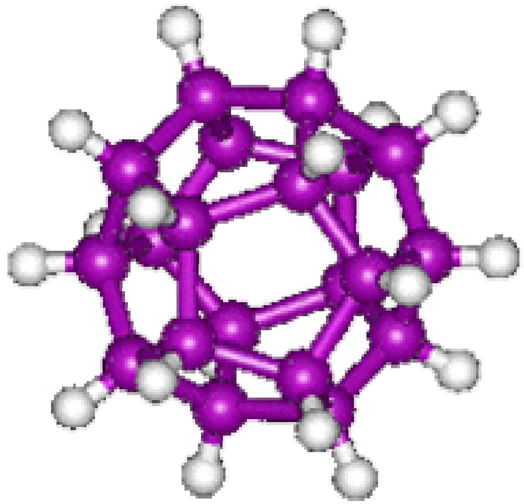
cubane: C_8H_8



square carbon

Carbon angle = 90º

$C_{20}H_{20}$



dodecahedron

Carbon angle = 108º~110º

Joined carbon pentagons

small Carbon Clusters and discovery of C_{60}

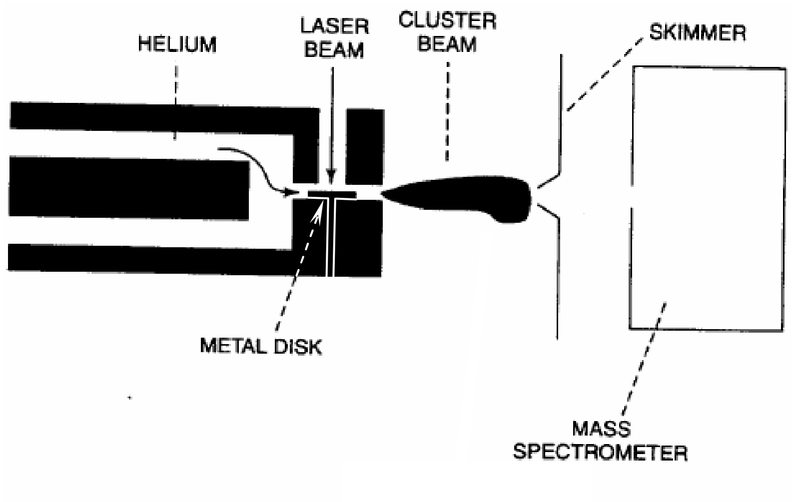


Fig. 4.2 Apparatus for laser evaporation of nanoparticles

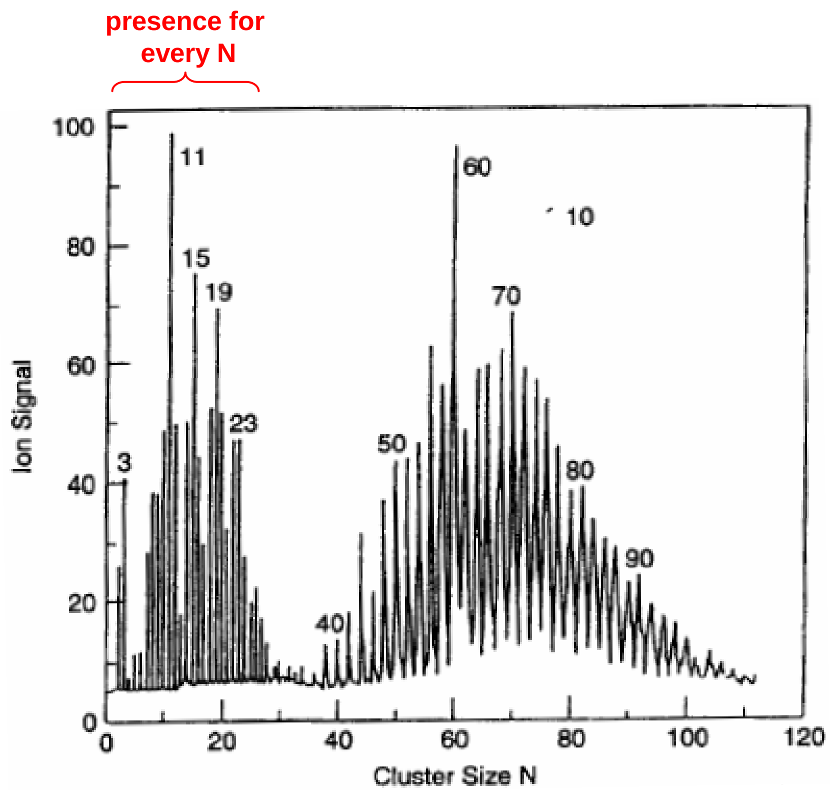
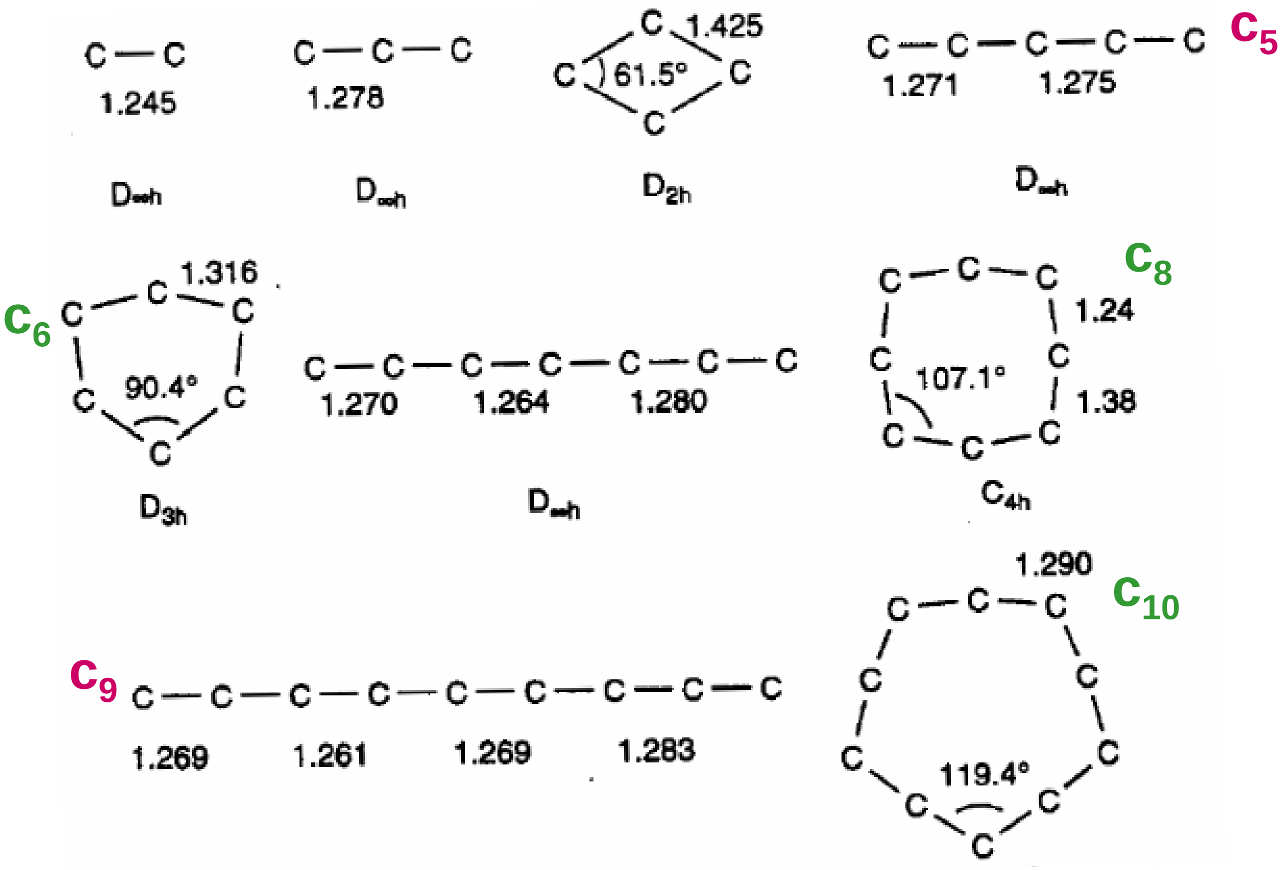


Fig. 5.3 Mass spectrum of Carbon clusters. The C_{60} and C_{70} peaks are evident.

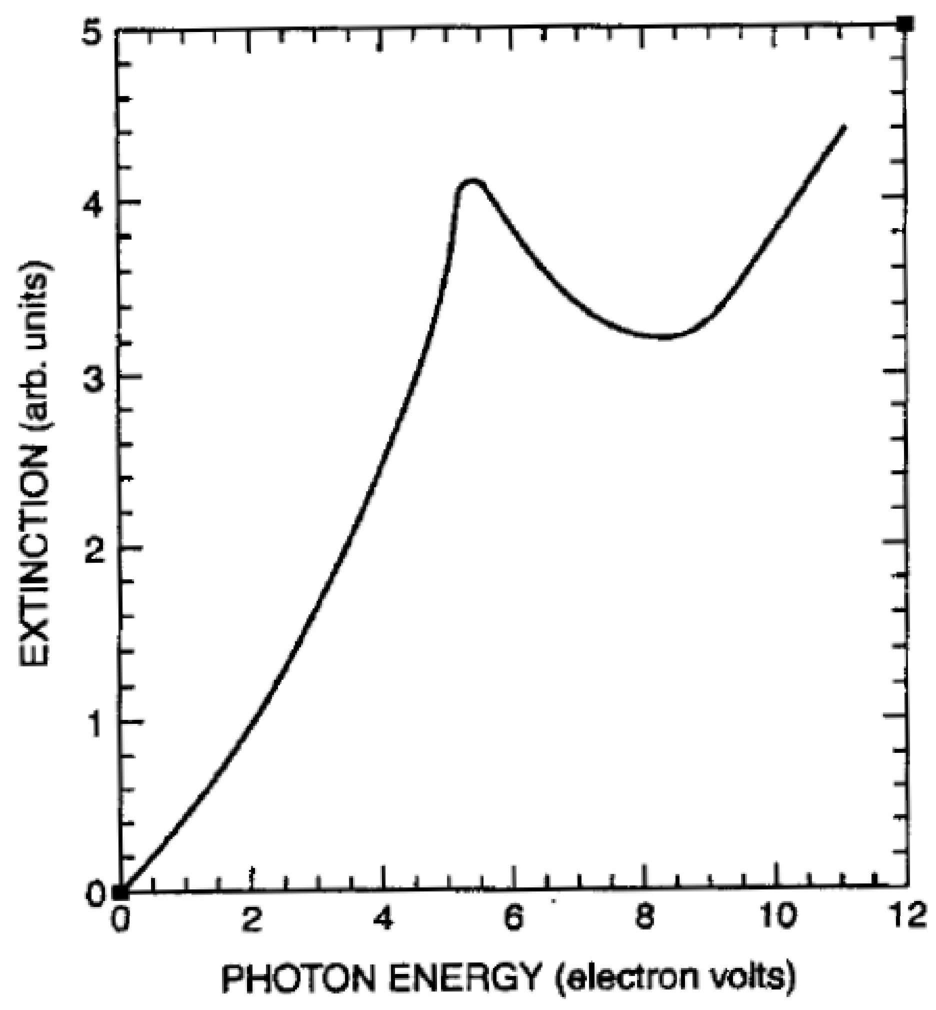
Fig. 5.4 Result of molecular orbital theory for the structure of small clusters



Odd N: linear structure, sp hybridization

Even N: closed structure

Optical extinction



Carbon Star (Red giant)

C_{60} molecules are created in the outer atmosphere of a “red giant”

Optical spectrum of light coming from stars in outer space. The peak at 5.6eV (220nm) is due to absorption from C_{60} presented in interstellar dust.

Structure of C_{60}

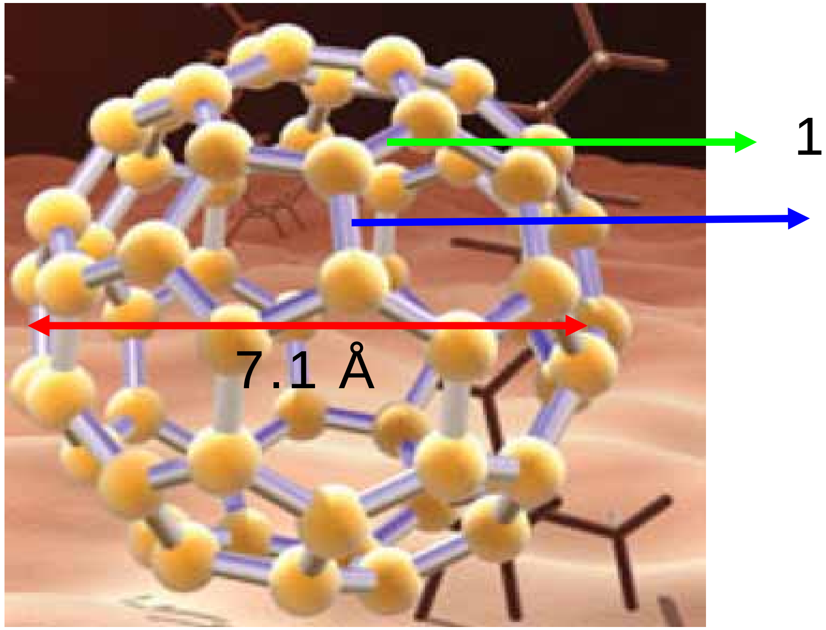


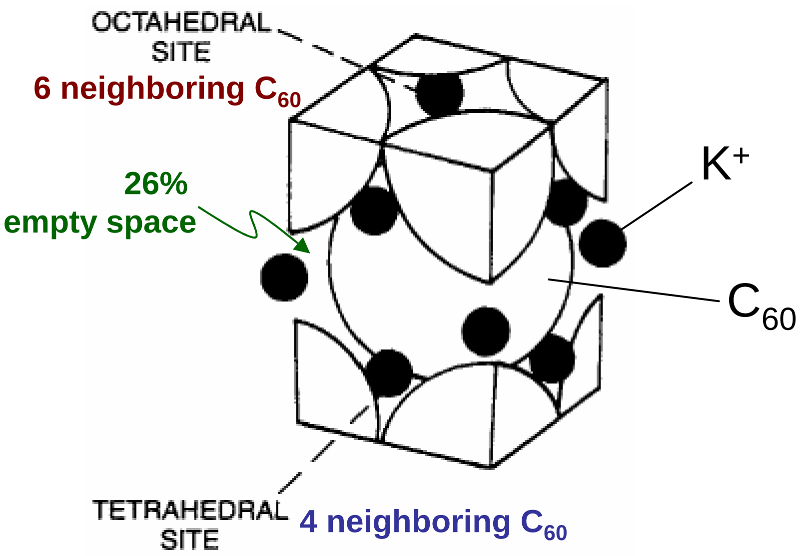
Fig. 5.6 structure of C_{60} fullerene molecule

- Each C_{60} contains 12 pentagonal and 20 hexagonal
- The pentagons are needed to produce closed (convex) surfaces, and hexagons lead to a planar surface.

C_{60} crystal:

- In C_{60} crystals, C_{60} molecules are held together by van der Waals force, arranged in FCC structure with 1nm center-to-center distance.

- Dissolves in common solvents like benzene, toluene, hexane
- Readily vaporizes in vacuum around 400°C
- Low thermal conductivity
- Pure C_{60} crystal is an electrical insulator
- C_{60} crystal doped with alkali metals shows a range of electrical conductivity: Insulator (K_6 C_{60}) to superconductor (K_3 C_{60}) < 30 K!



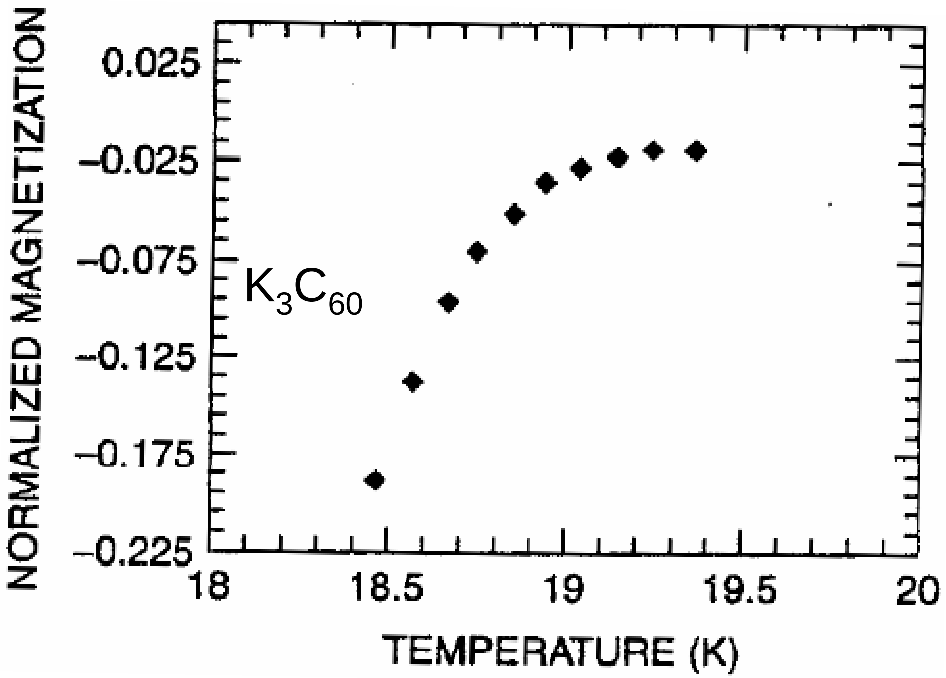
C_{60}^{3-} with 3 ionized K^+

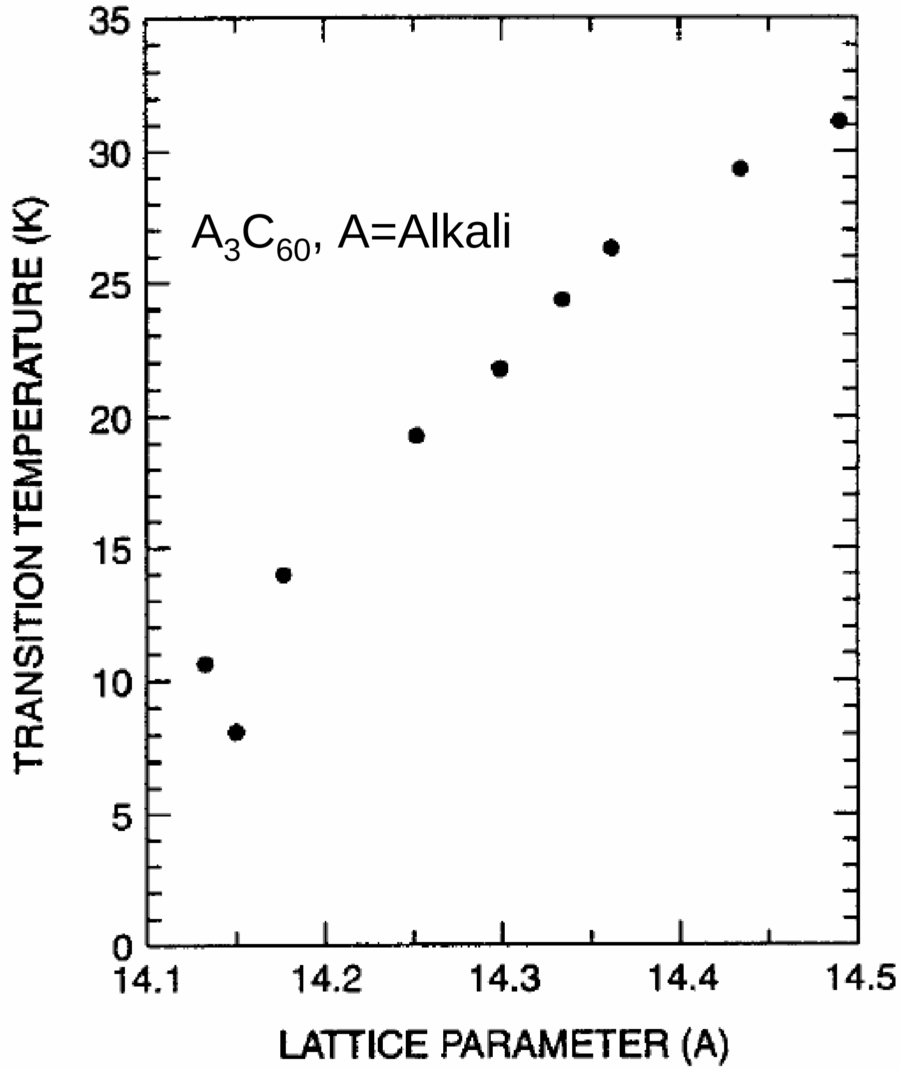
Highly disordered material

Other superconducting compounds:
Rb_3C_{60}, Cs_3C_{60}, Na_3C_{60}

Superconductivity in K_3C_{60}

K_3C_{60} :18K
Cs_2RbC_{60} : 33K





~~J. H. Schön, Ch. Kloc and B. Batlogg~~

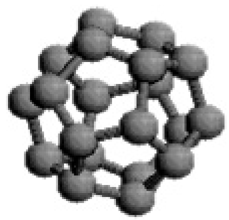
~~Superconductivity at 52 K in hole-doped C60~~ ~~*Nature* 408, 549-552(30 November 2000)~~ retracted

~~High-Temperature Superconductivity in Lattice-Expanded C60~~ 117k ~~*Science* 28 September 2001: Vol. 293, pp. 2432 - 2434~~ retracted

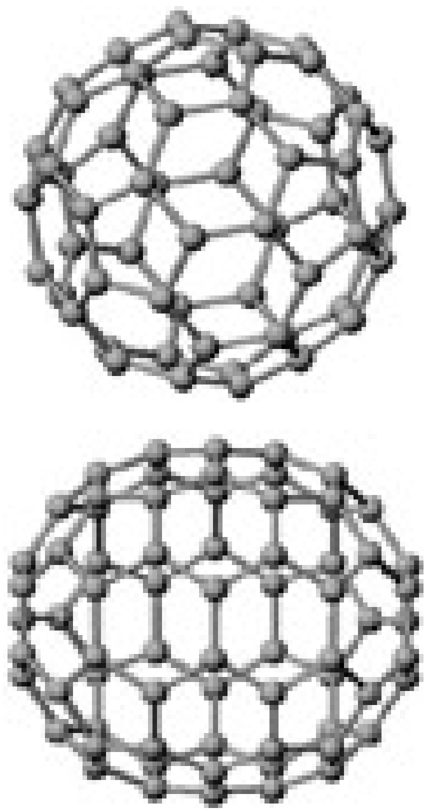
Various sizes of fullerenes

The Smallest Fullerene

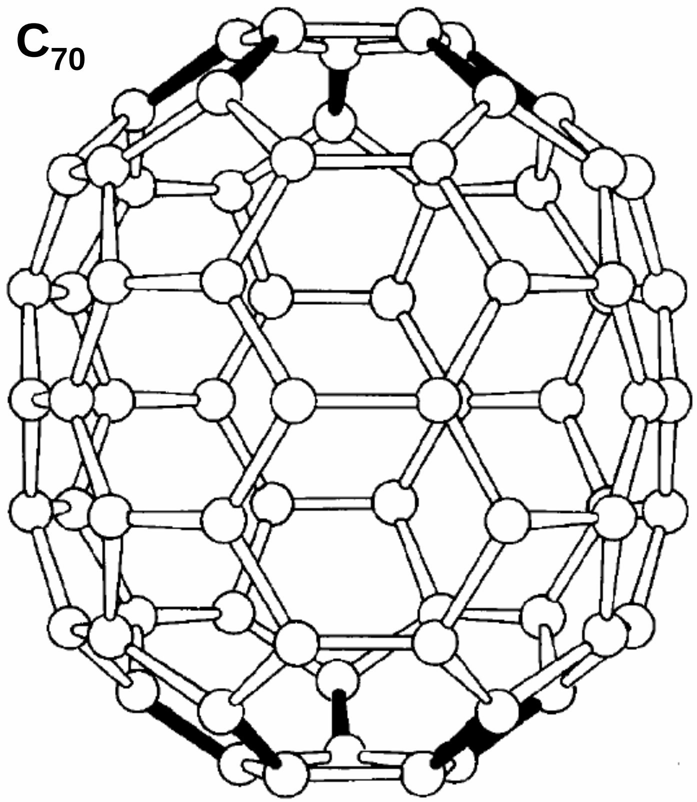
C_{20}

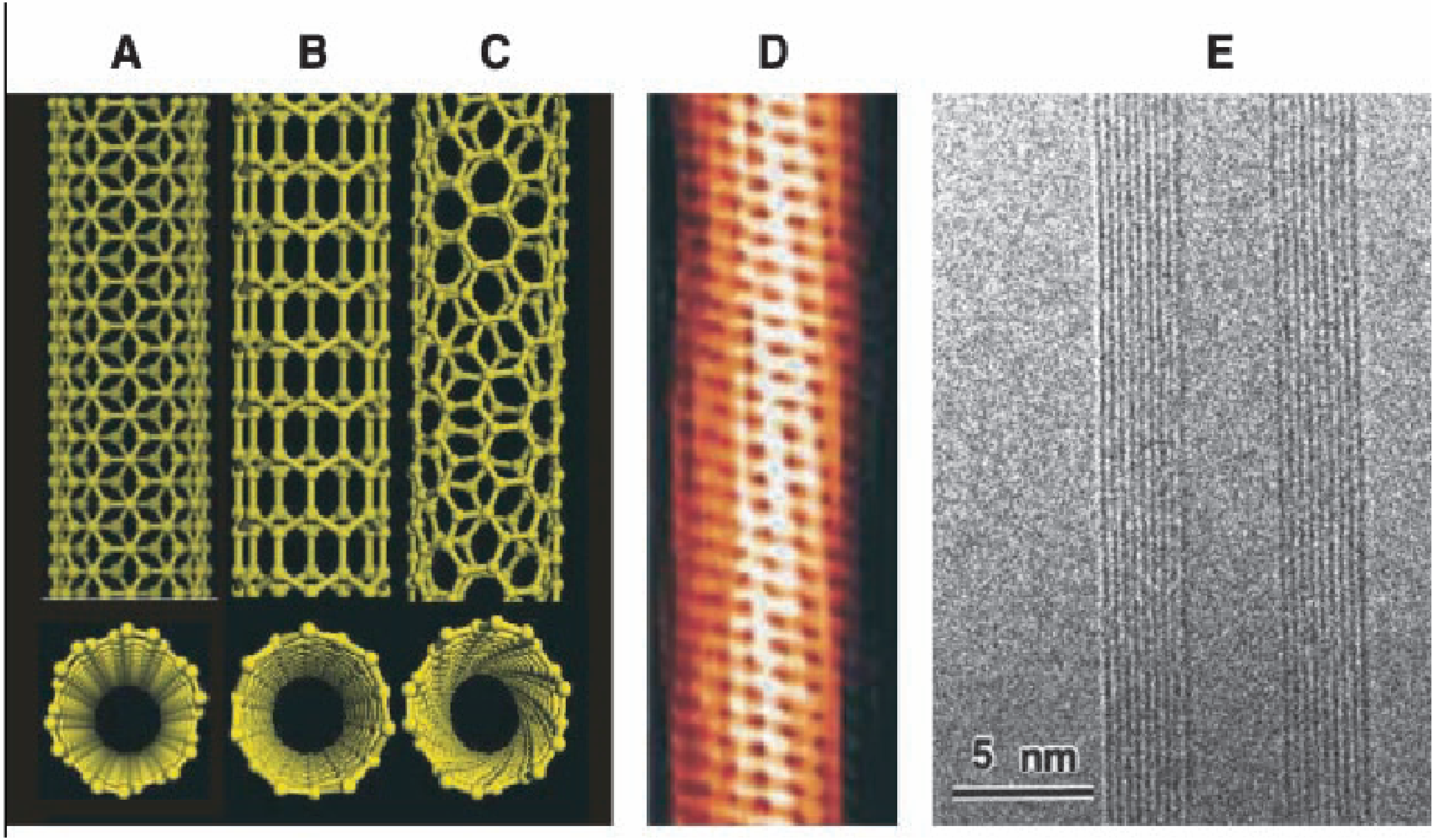


Gas-phase production and photoelectron spectroscopy of the smallest fullerene, C_{20} [Nature, 407, 60 (2000)]



C_{70}

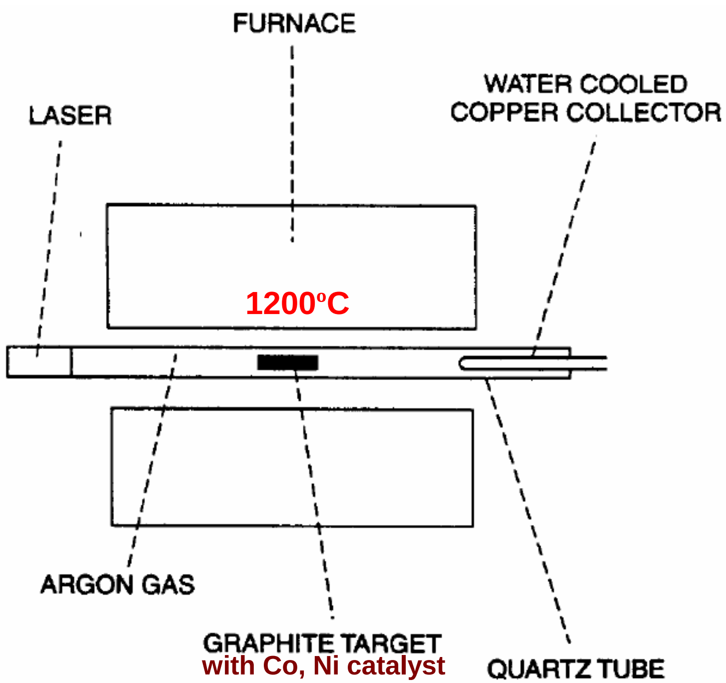




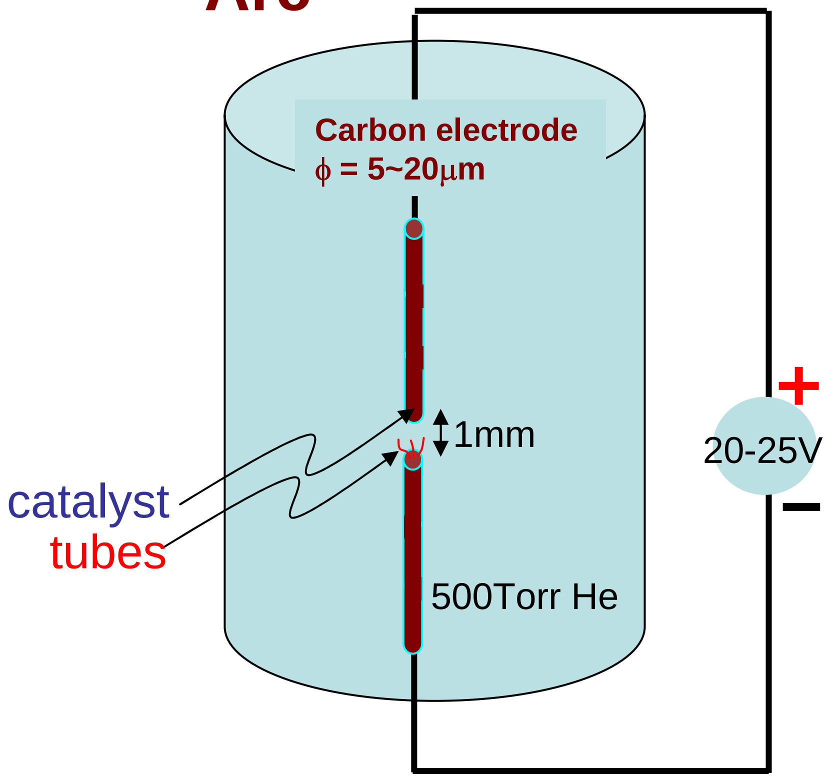
(a) Armchair (b) zigzag (c) chiral (d) by STM (e) by TEM, multiwalled

Fabrication:

Laser evaporation

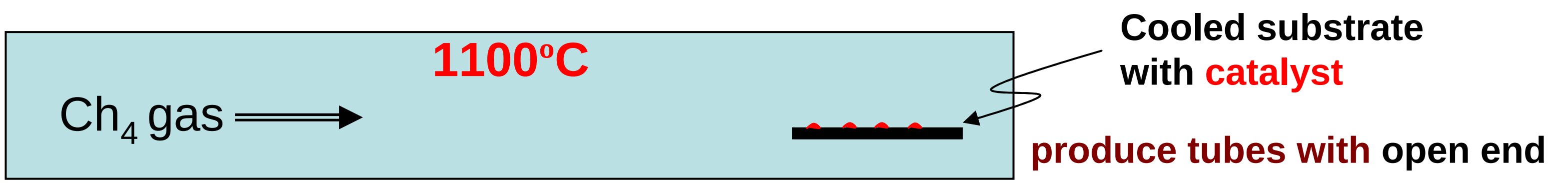


Arc



Chemical vapor deposition:

method: methane (CH_4) 1100ºC, with catalyst Co or Ni



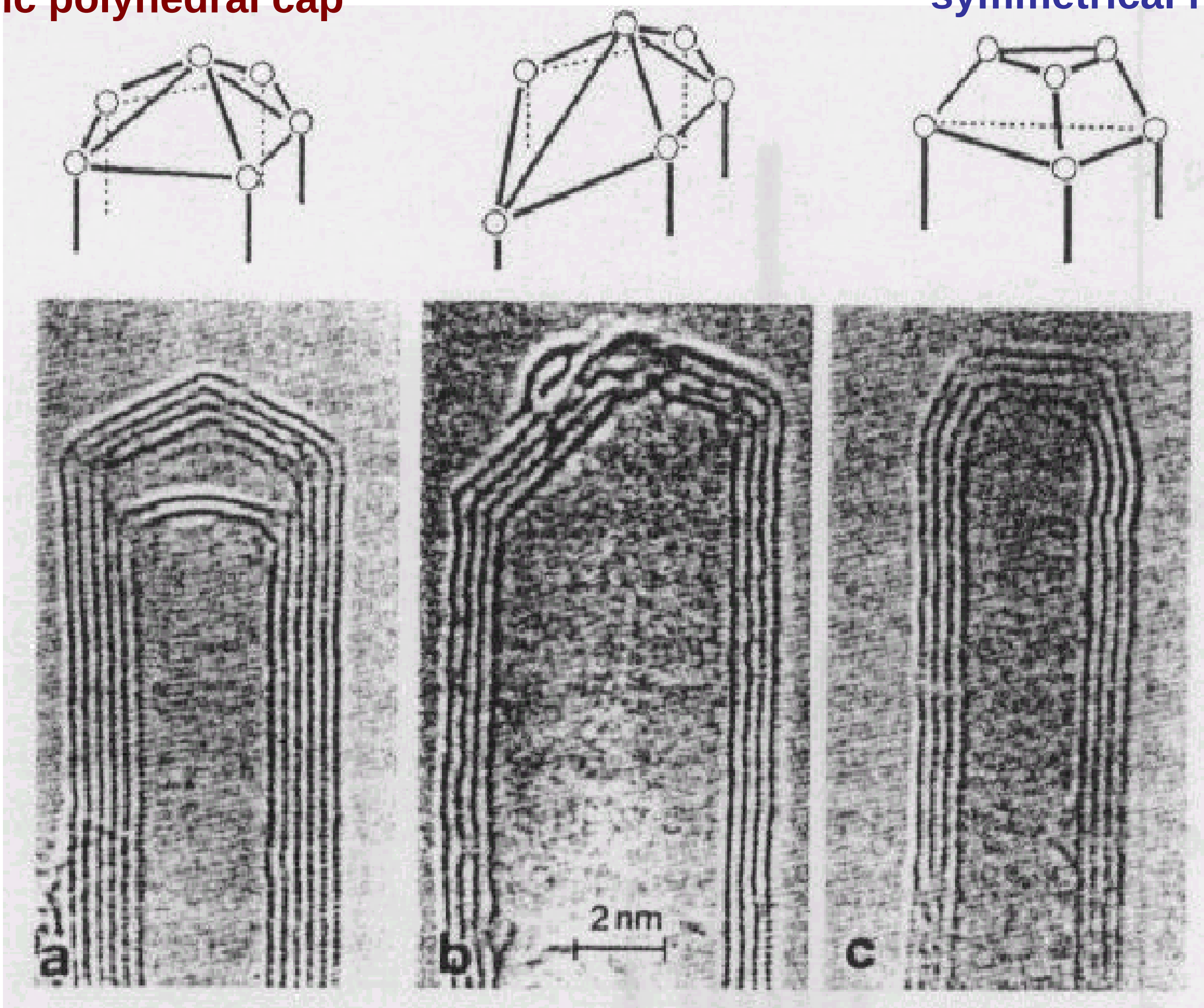
Capped nanotubes

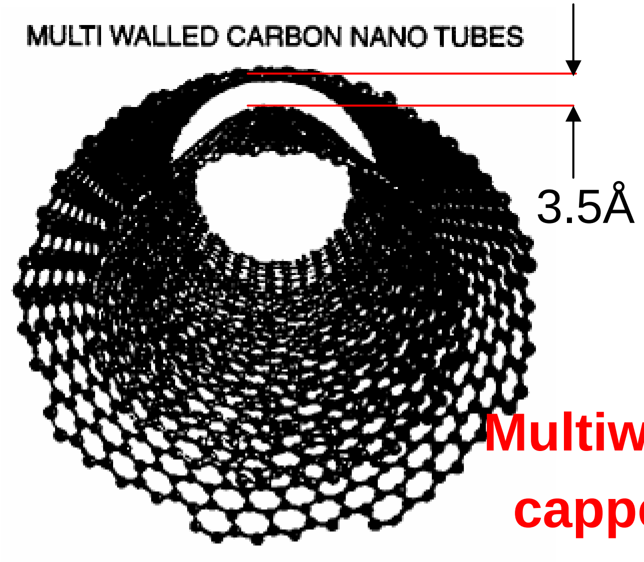
Three common cap terminations

symmetric polyhedral cap

asymmetric polyhedral cap

symmetrical flat cap





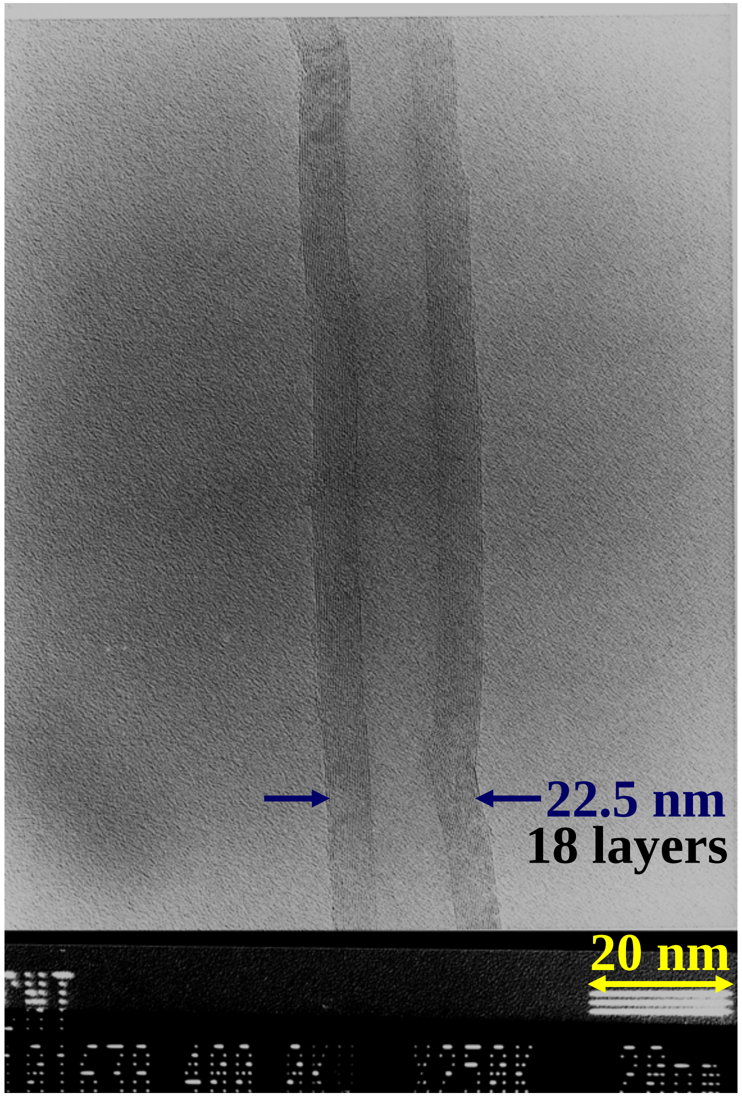
Multiwalled carbon nanotubes

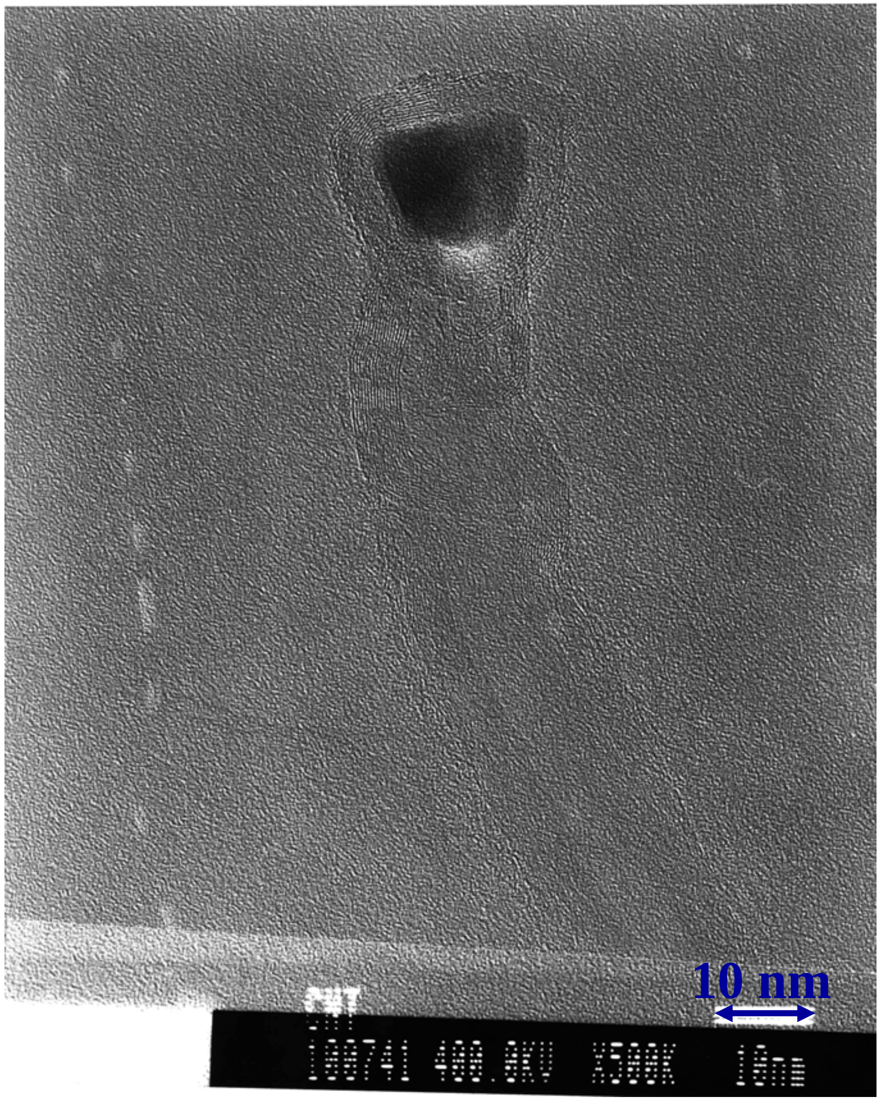
Multiwalled nanotube consists of capped concentric cylinders separated by ~ 3.5 Å

- **Typically, outer diameter of carbon nanotubes prepared by a carbon arc process ranges between 20 and 200 Å, and inner diameter ranges between 10 and 30 Å.**

- **Typical lengths of the arc-grown tubules are about 1 μm, giving rise to an aspect ratio (length-to-diameter ratio) of 10^2 to 10^3.**

Tubes produced by CVD in our lab.





TEM 相片：陳貴賢，林麗瓊

Ropes of single-walled carbon nanotubes

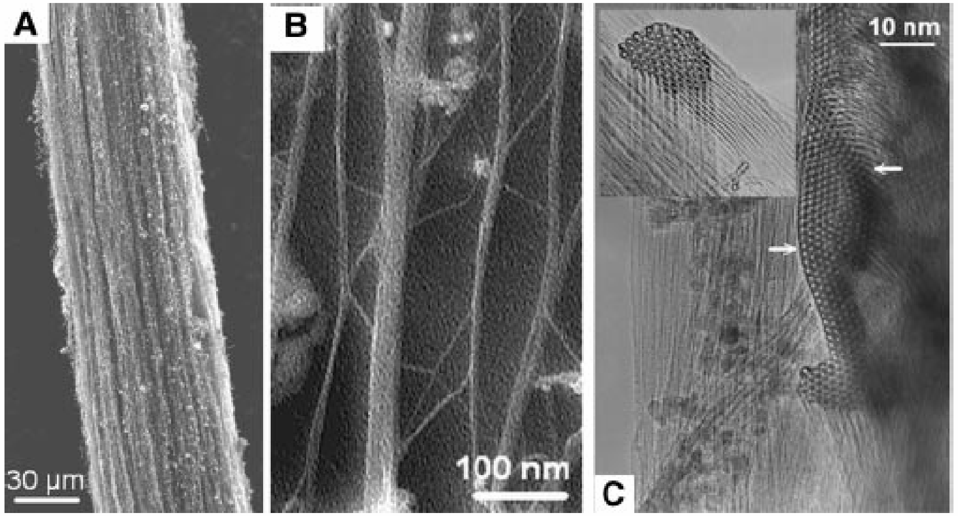
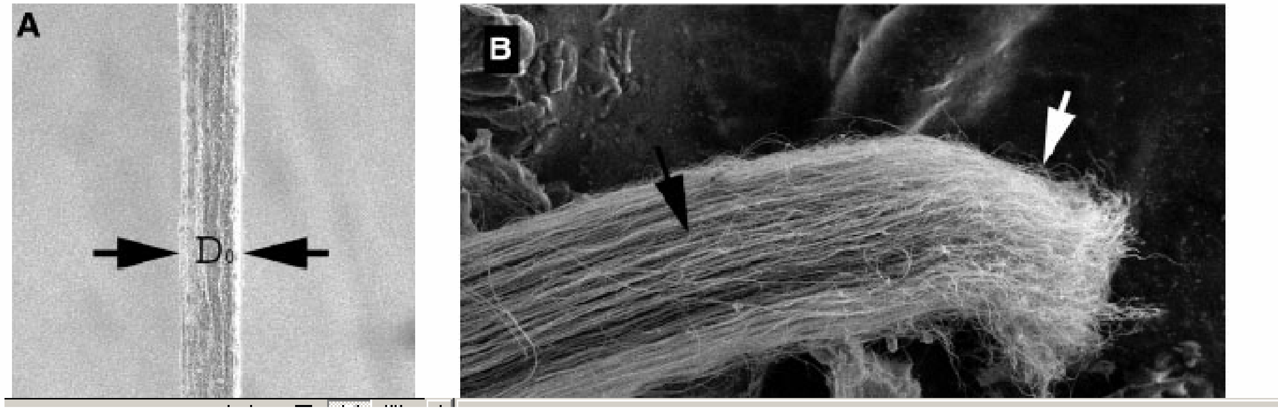


Fig. 2. (**A**) Low-magnification SEM image of a long SWNT strand. When the strand is peeled carefully along the length, a thinner SWNT rope is obtained. (**B**) High-resolution SEM of an array of SWNT ropes peeled from the strand. (**C**) HRTEM image of a top view of a SWNT rope. For HRTEM observation, we selected a SWNT rope, tore it with tweezers, and affixed it on the HRTEM grid by wetting it with a drop of ethanol or acetone. White arrows indicate the arrangement of the triangle lattice of a large area in a SWNT strand. The inset shows a cross-sectional view of a polycrystalline bundle.



Forests of multiwalled carbon nanotubes

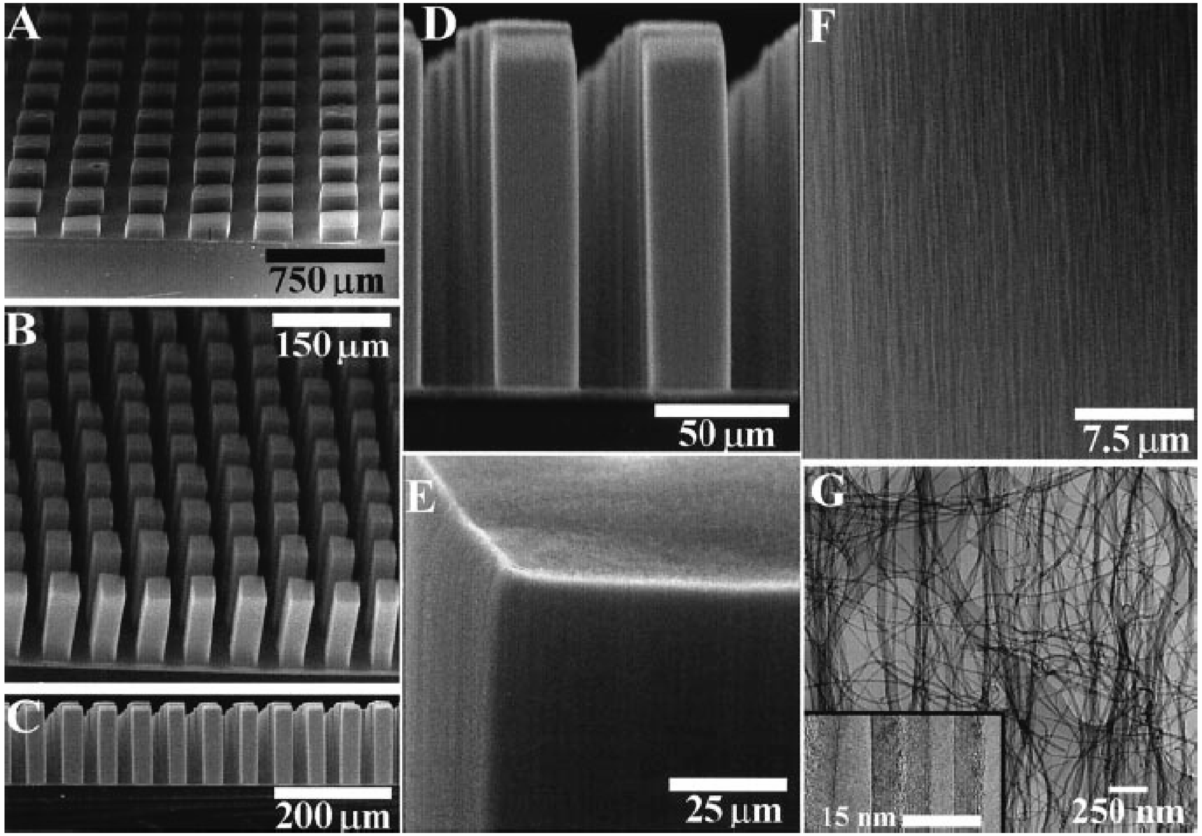
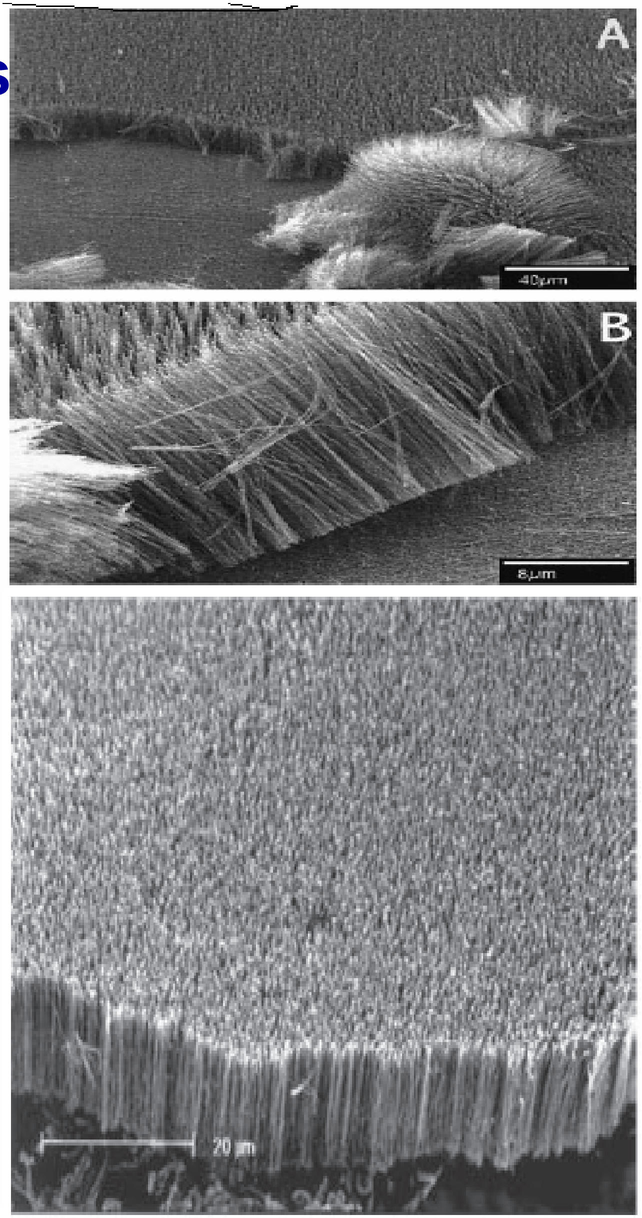


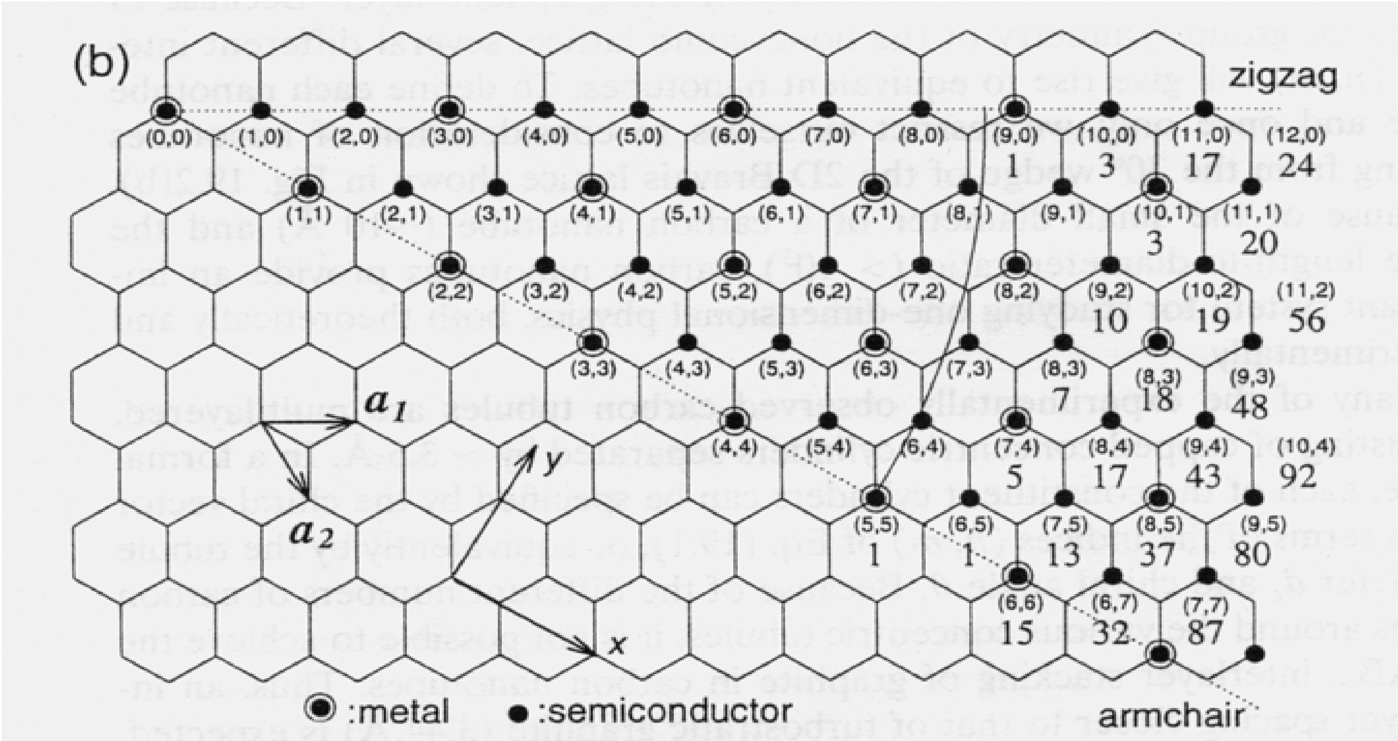
Fig. 2. Electron micrographs of self-oriented nanotubes synthesized on n^+-type porous silicon substrates. (**A**) SEM image of nanotube blocks synthesized on 250 µm by 250 µm catalyst patterns. The nanotubes are 80 µm long and oriented perpendicular to the substrate [see (F)]. (**B**) SEM image of nanotube towers synthesized on 38 µm by 38 µm catalyst patterns. The nanotubes are 130 µm



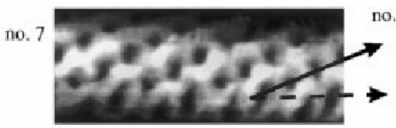
Three categories of single-walled carbon nanotubes:

Three major categories of nanotube structures can be identified based on the values of *m* and *n*

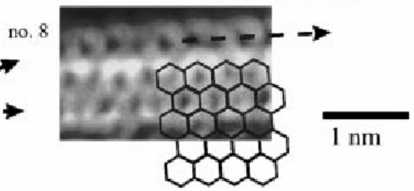
***m* = *n* "Armchair"**
***m* = 0 or *n* = 0 "Zigzag"**
$m \neq n$ "Chiral"



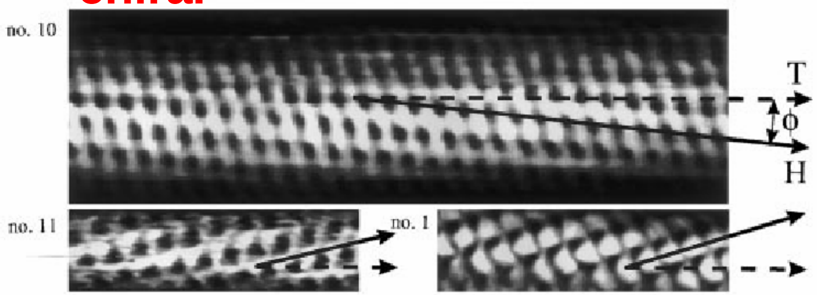
zigzag



armchair

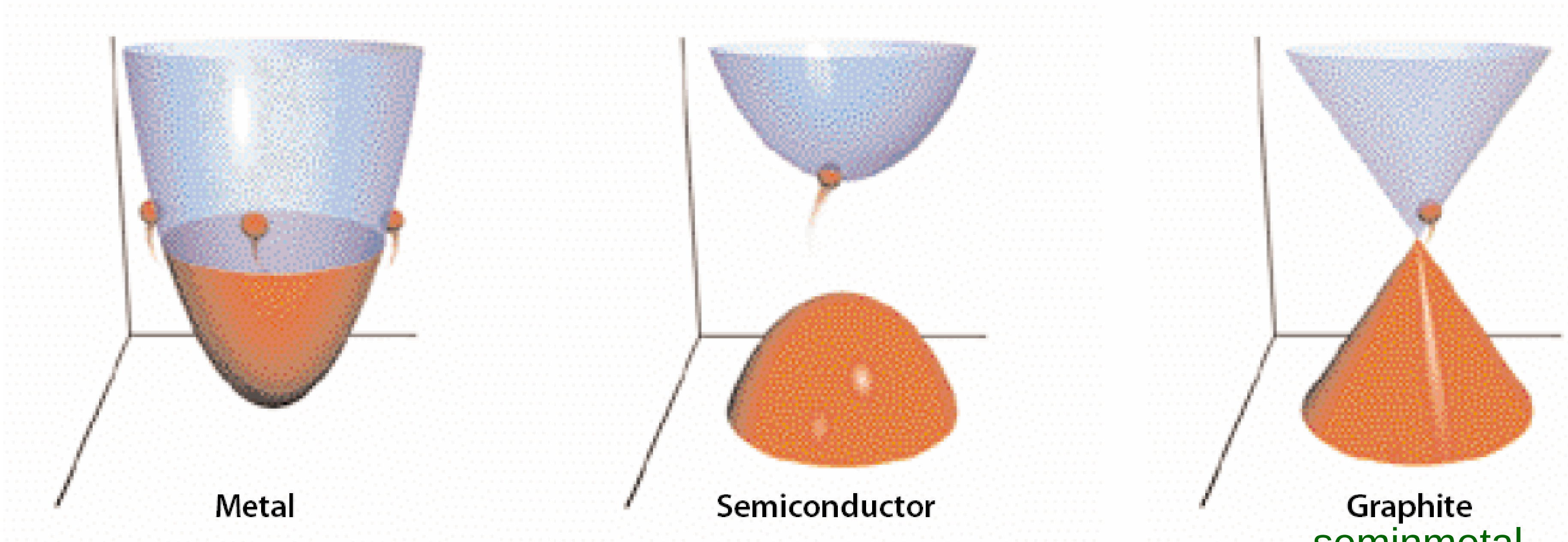


chiral



Nature 391, 59, (1998)

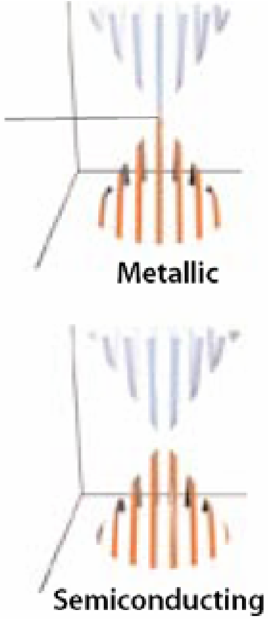
A Split Personality



ELECTRICAL PROPERTIES of a material depend on the separation between the collection of energy states that are filled by electrons (*red*) and the additional "conduction" states that are empty and available for electrons to hop into (*light blue*). Metals conduct electricity easily because there are so many electrons with easy access to adjacent conduction states. In semiconductors, electrons need an energy boost from light or an electrical field to jump the gap to the first available conduction state. The form of carbon known as graphite is a semimetal that just barely conducts, because without these external boosts, only a few electrons can access the narrow path to a conduction state.

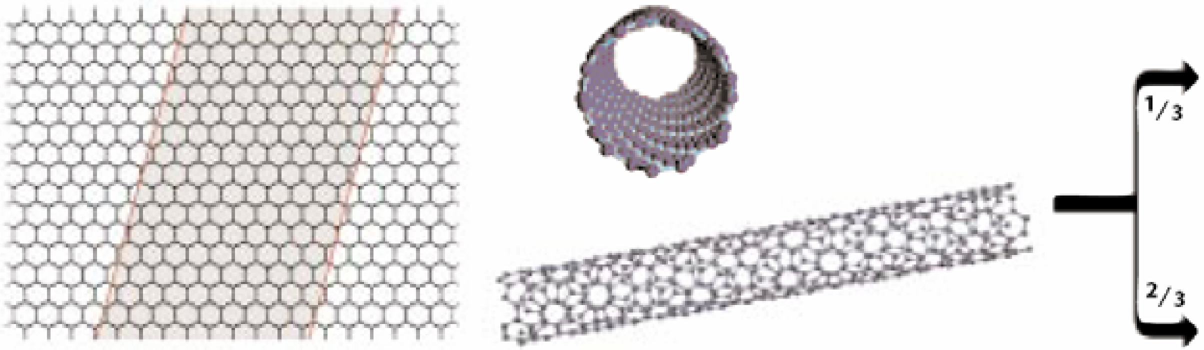
Scientific American December 62 2000

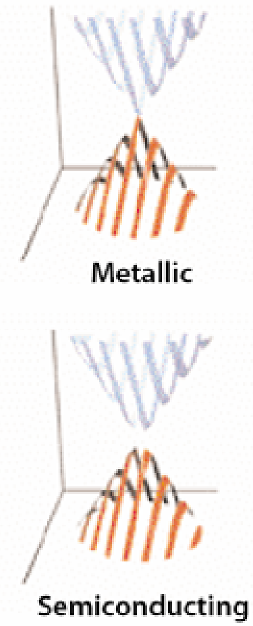
“Zigzag”



STRAIGHT NANOTUBES look like a straight swath cut from a sheet of graphite (*left*) and rolled into a tube (*center*). The geometry of nanotubes limits electrons to a select few slices of graphite's energy states (*right*). Depending on the diameter of the tube, one of these slices can include the narrow path that joins electrons with conduction states. This special point, called the Fermi point, makes two thirds of the nanotubes metallic. Otherwise, if the slices miss the Fermi point, the nanotubes semiconduct.

“Chiral”





TWISTED NANOTUBES, cut at an angle from graphite (*left*), look a bit like barbershop poles (*center*). The slices of allowed energy states for electrons (*right*) are similarly cut at an angle, with the result that about two thirds of twisted tubes miss the Fermi point and are semiconductors.

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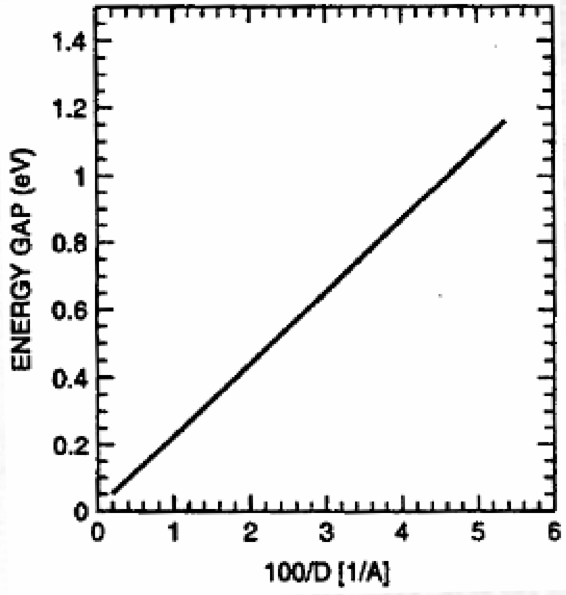
“Armchair” always metallic

Energy for zigzag nanotubes



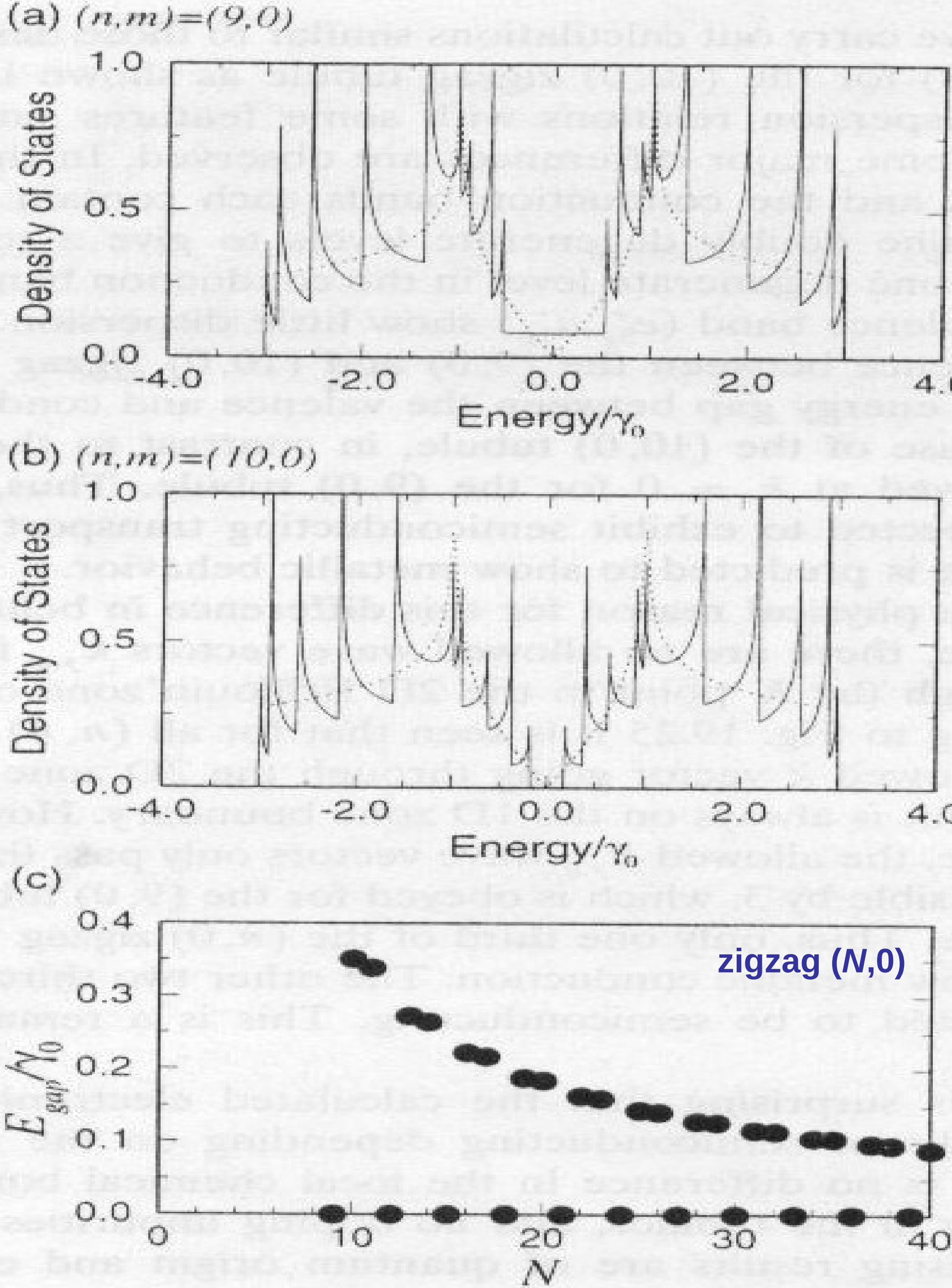
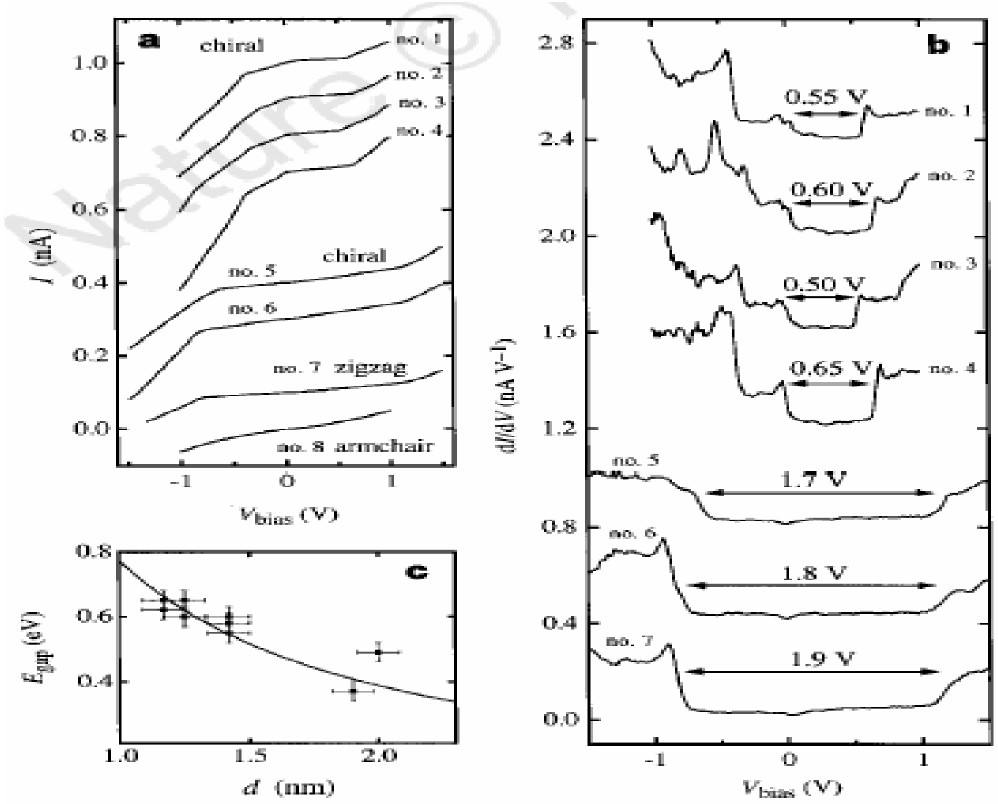
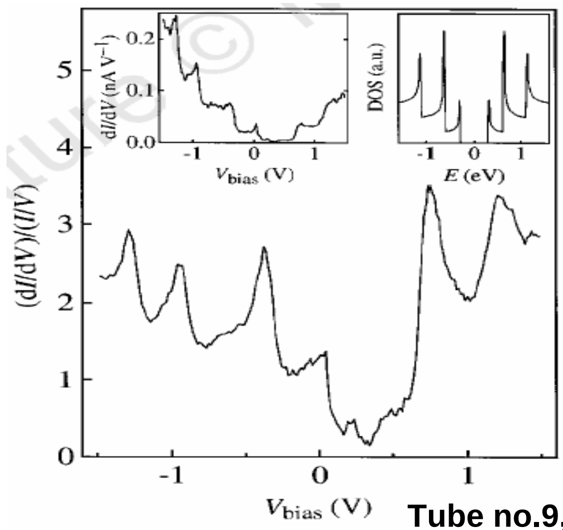


Fig. 19.27. Electronic 1D density of states per unit cell for two (n, m) zigzag tubules based on zone folding of a 2D graphene sheet: (a) the (9, 0) tubule which has metallic behavior, (b) the (10, 0) tubule which has semiconducting behavior. Also shown in the figure is the density of states for the 2D graphene sheet (dashed curves) [19.98]. (c) Plot of the energy gap for $(n, 0)$ zigzag nanotubes plotted in units of γ_0 as a function of n, where γ_0 is the energy of the nearest-neighbor overlap integral for graphite **≈2.5eV**

Nature 391, 59, (1998)



van Hove singularities in the DOS, reflecting the one-dimensional character of carbon nanotubes.



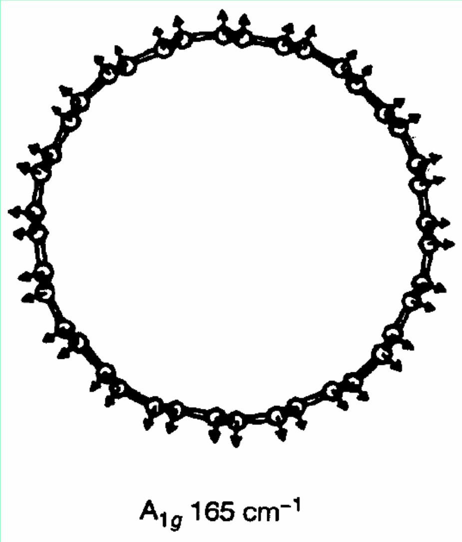
Tube no.9, (16,0)

Curves Nos 1-7 show a low conductance at low bias, followed by several kinks at larger bias voltages, however, the armchair tube does not show clear kinks in the range -1 to +1 V.

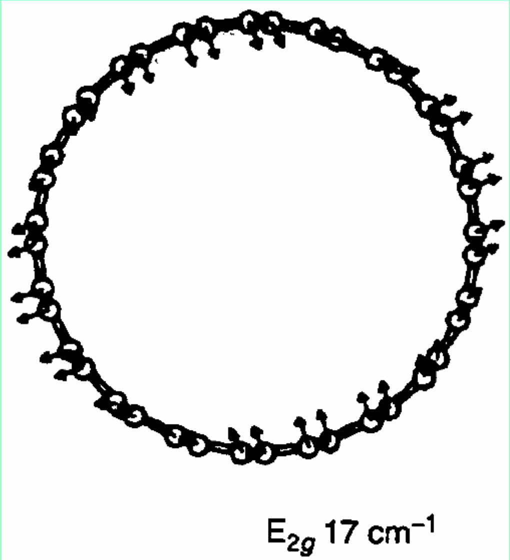
Gaps are indicated by arrows. Two categories of gaps: one with gap values around 0.5 - 0.6eV(semiconducting); the other with significantly larger gap values,1.7 - 1.9eV (metallic).

Gap *Egap* versus diameter *d* for semiconducting tubes: solid line denotes a fit of $E_{gap} = 2\,\gamma_0\, a_{C\text{-}C}/d$ with $\gamma_0 = 2.7$eV.

Cross-section view of the vibration modes

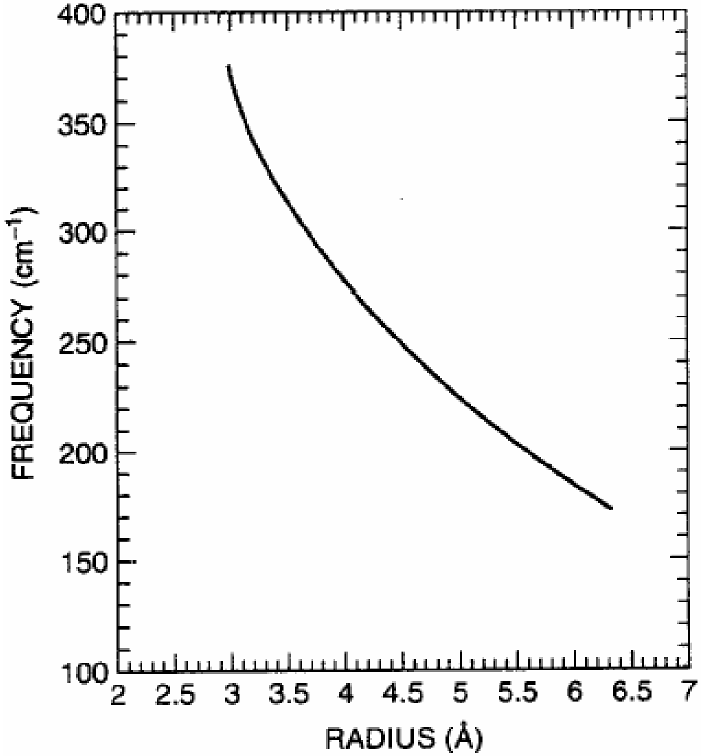


Symmetric stretch



Asymmetric stretch

Determination of the tube diameter from A_{1g} Raman vibration frequency



$$d = a\sqrt{n^2 + nm + m^2}/\pi, a = 0.142\sqrt{3}\text{nm}$$
$$\theta = Tan^{-1}\left(-\sqrt{3}m/(2n+m)\right)$$

One can then "guess" a set of (m,n) from

APL 60, 2204 (92)

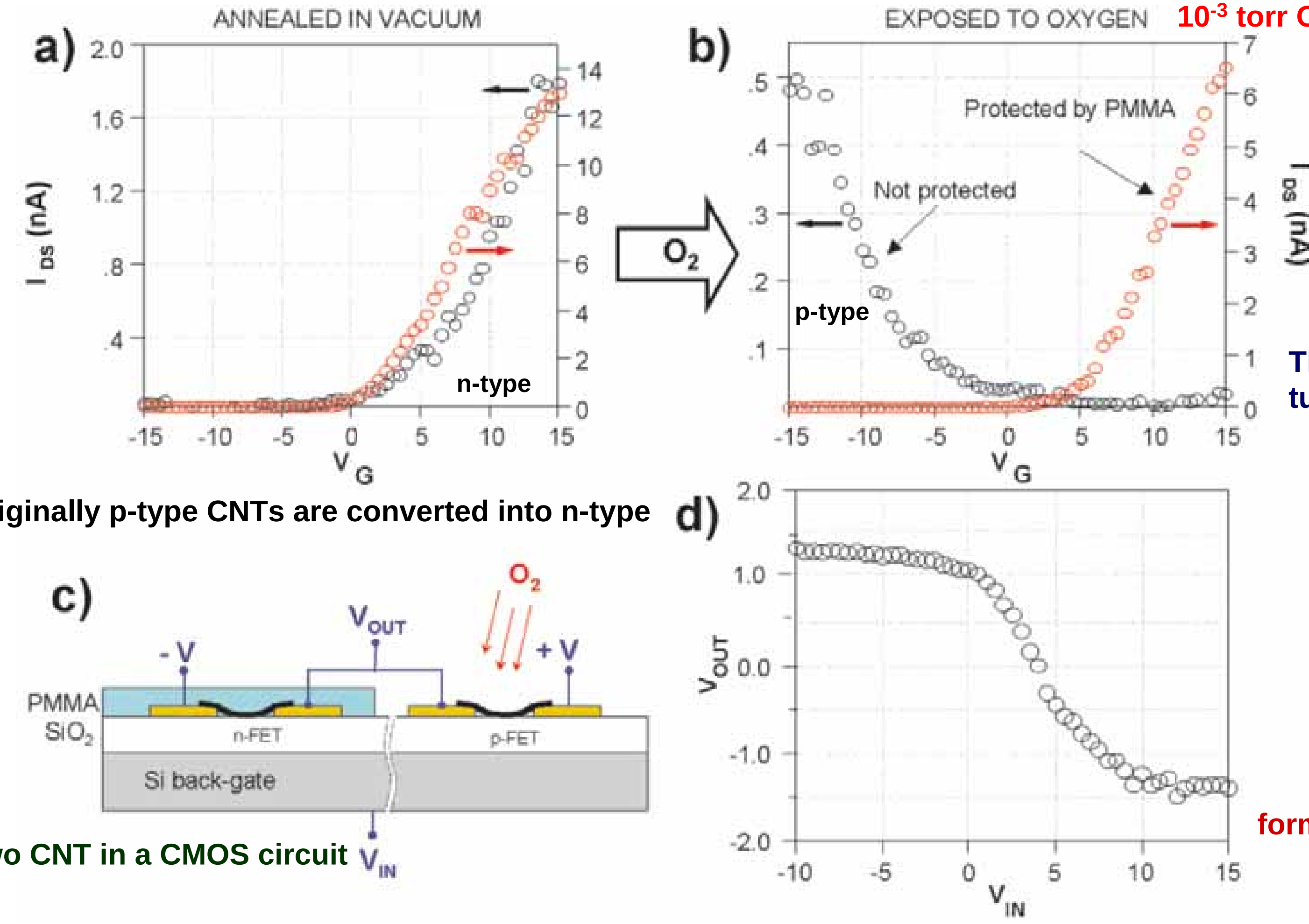
Figs. 5-19 and 5-20

Properties of Carbon Nanotubes:

- High carrier mobility – ballistic transport(<1-10μm);~>10,000 cm^2/V-sec(>10μm) (Si<500 cm^2/V-sec).
- High current carrying capabilities: $J=10^9 A/cm^2$ (Most metal fails at $<10^6 A/cm^2$, Si ~ $10^3 A/cm^2$).
- No Interface states - any dielectric is in principle possible (Si devices need SiO_2).
- Potential for optical devices – direct bandgap material, bandgap determined by diameter (Si is indirect).
- Potential for sensor applications – all the atoms are on the surface.
- Diameter determines semiconducting (2/3) vs metallic tubes (1/3), and placement.

http://www.cns.cornell.edu/documents/CornellUniversity_PN_Diode_2005_Final_1of3_000.pdf

A SWCNT “NOT” GATE



10^{-3} torr O_2 for 3min

The unprotected one turns back to p-type

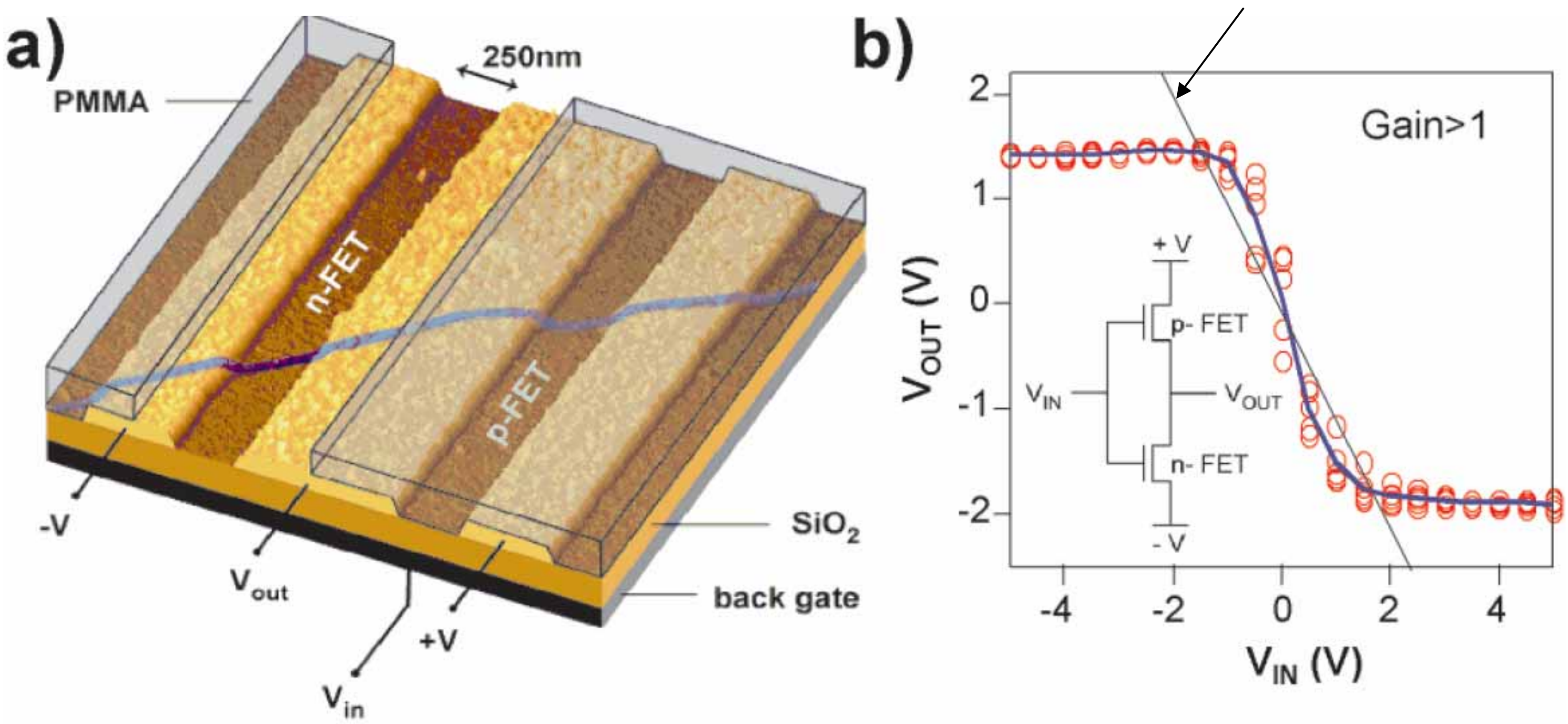
Two originally p-type CNTs are converted into n-type

Wiring two CNT in a CMOS circuit

form an inverter

V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris
Nano Letters, 1, 453 (2001)

A SWCNT CMOS device



1. Two p-type CNT FETs in series
2. Potassium bombardment on the unprotected one results in a p→n conversion
3. CMOS CNT FET with gain ≡ (V_{out}/V_{in}) > 1

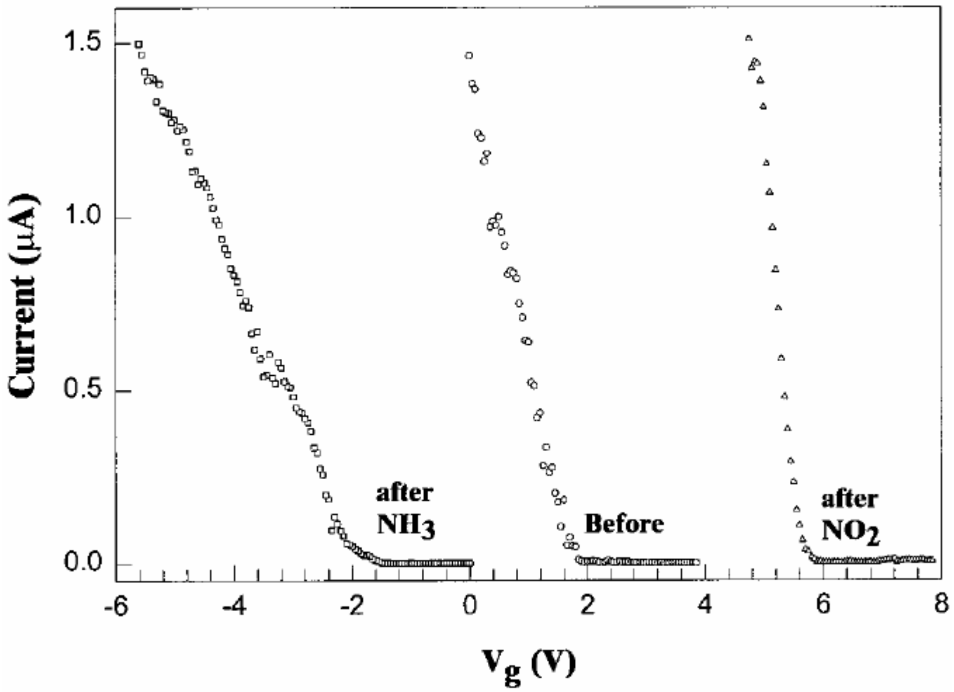
V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris
Nano Letters, 1, 453 (2001)

Nanotube Molecular Wires as Chemical Sensors

Science, 287, 622 (2000) **J. Kong et al**

NH_3 : suppresses conduction
NO_2 : increases conduction

NO_2 binding causes transferring of charge from CNT to NO_2, resulting increased hole concentration in CNT.



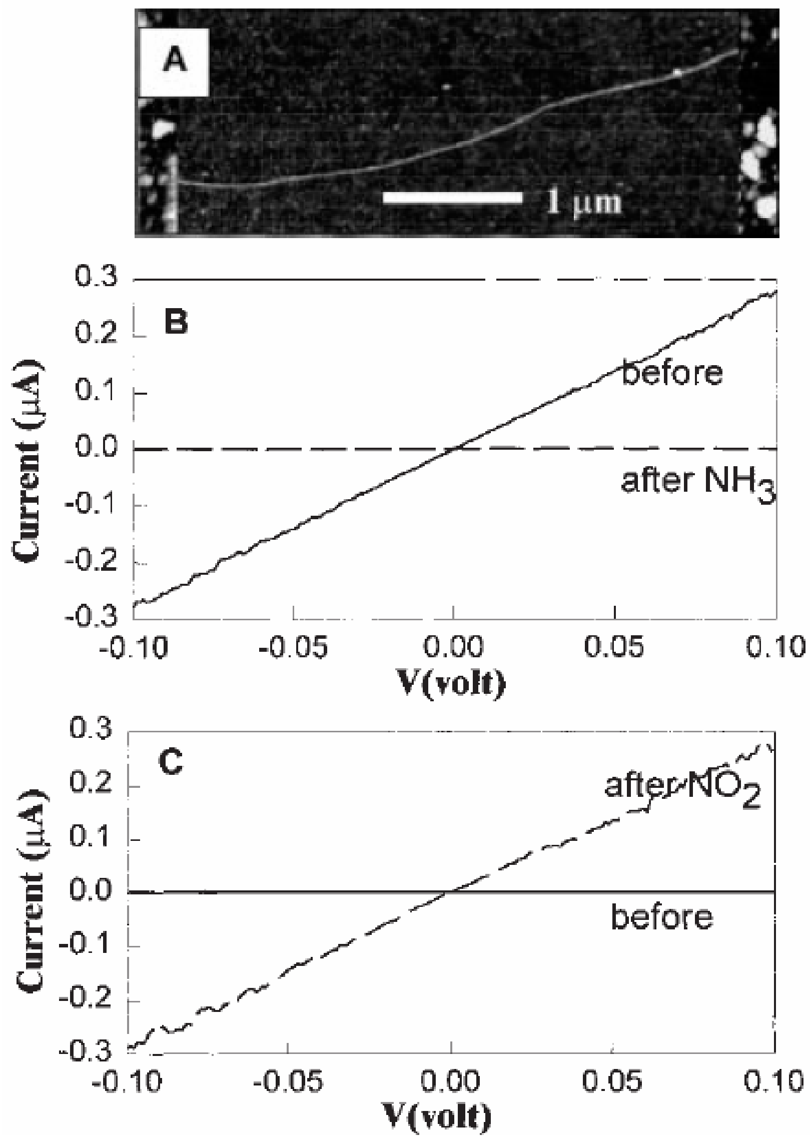


Fig. 5.25 of the text book

Application in Field Emission Display

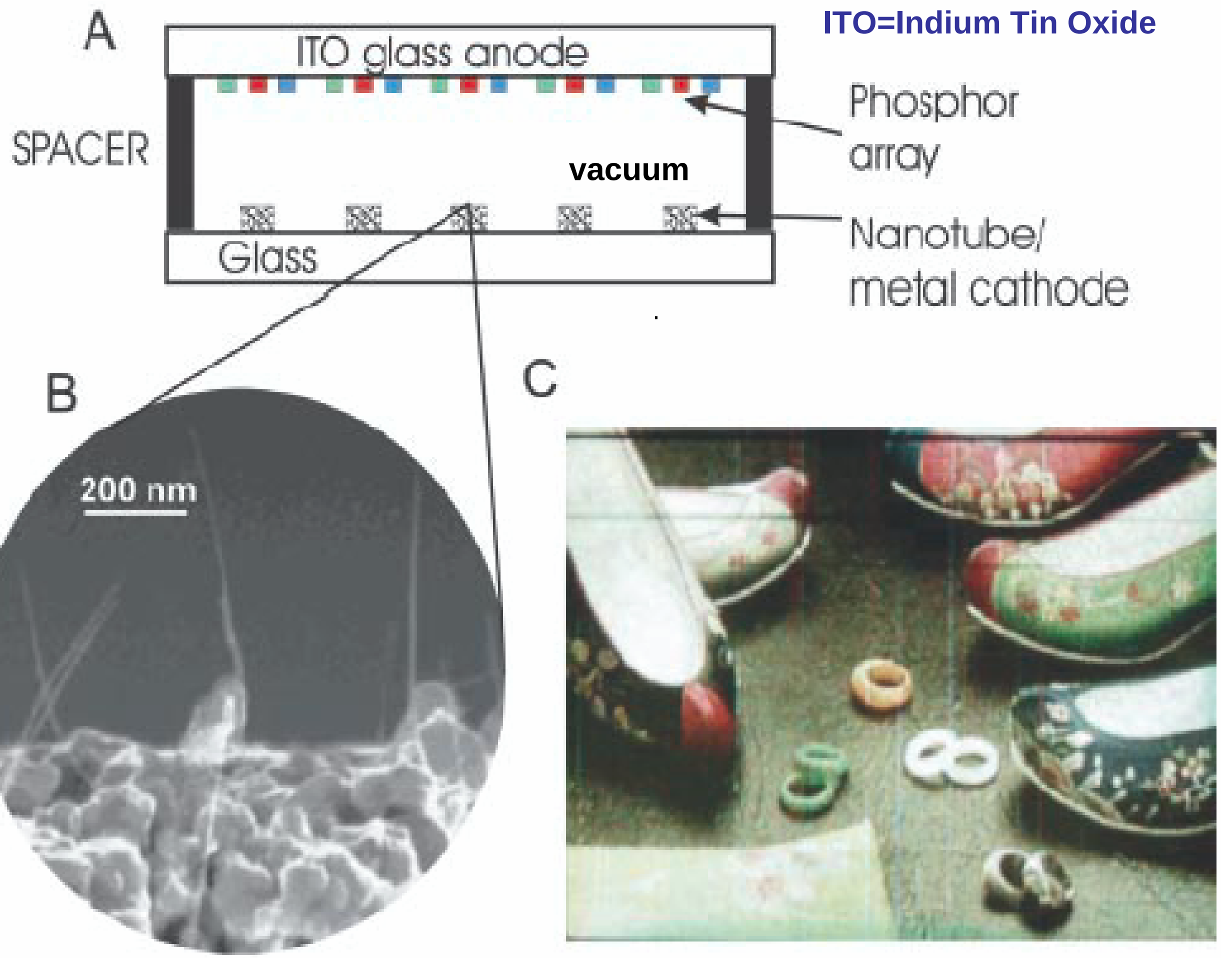
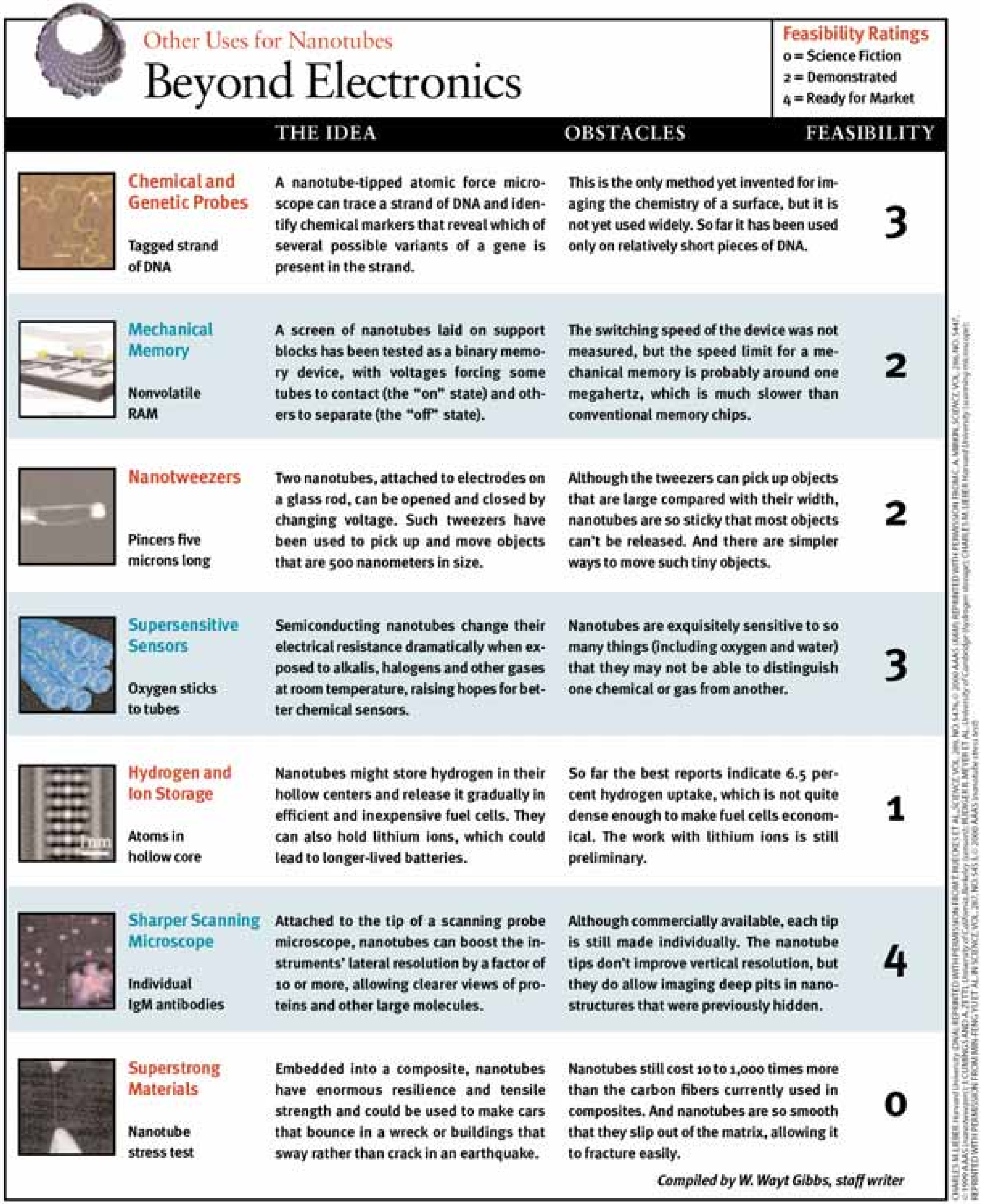


Fig. 2. (**A**) Schematic illustration of a flat panel display based on carbon nanotubes. ITO, indium tin oxide. (**B**) SEM image (49) of an electron emitter for a display, showing well-separated SWNT bundles protruding from the supporting metal base. (**C**) Photograph of a 5-inch (13-cm) nanotube field emission display made by Samsung.

prospective



Other Uses for Nanotubes

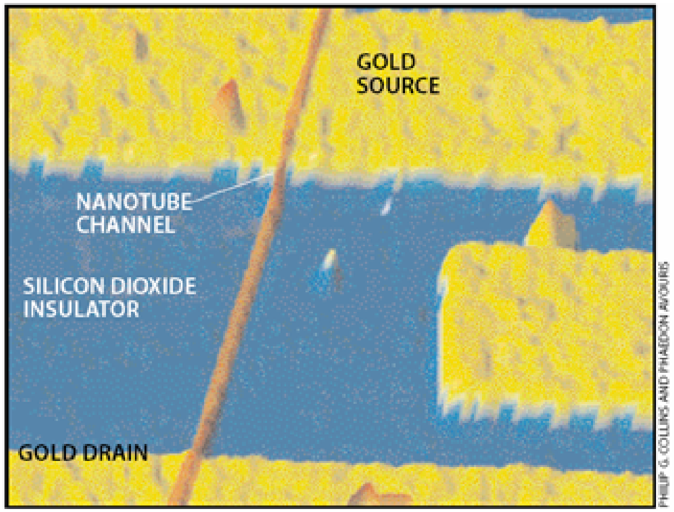
Beyond Electronics

Feasibility Ratings
0 = Science Fiction
2 = Demonstrated
4 = Ready for Market

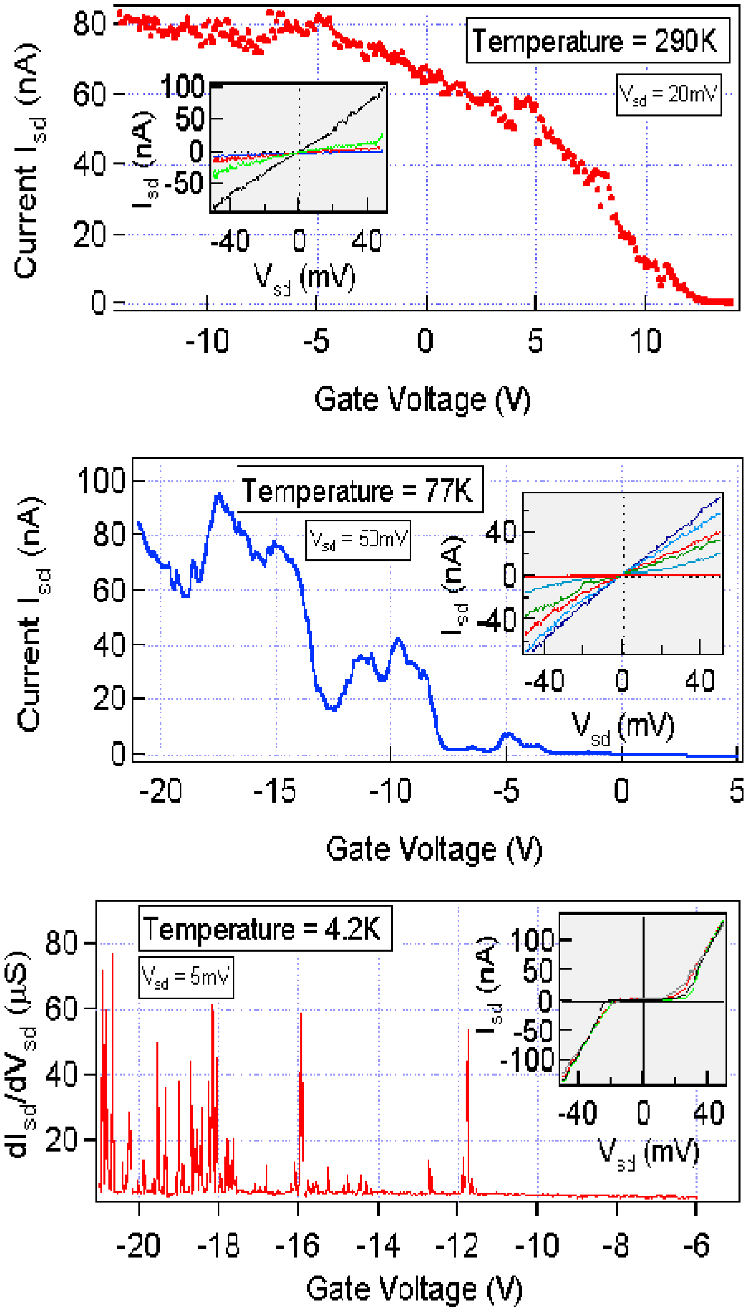
	THE IDEA	OBSTACLES	FEASIBILITY
Chemical and Genetic Probes Tagged strand of DNA	A nanotube-tipped atomic force microscope can trace a strand of DNA and identify chemical markers that reveal which of several possible variants of a gene is present in the strand.	This is the only method yet invented for imaging the chemistry of a surface, but it is not yet used widely. So far it has been used only on relatively short pieces of DNA.	3
Mechanical Memory Nonvolatile RAM	A screen of nanotubes laid on support blocks has been tested as a binary memory device, with voltages forcing some tubes to contact (the "on" state) and others to separate (the "off" state).	The switching speed of the device was not measured, but the speed limit for a mechanical memory is probably around one megahertz, which is much slower than conventional memory chips.	2
Nanotweezers Pincers five microns long	Two nanotubes, attached to electrodes on a glass rod, can be opened and closed by changing voltage. Such tweezers have been used to pick up and move objects that are 500 nanometers in size.	Although the tweezers can pick up objects that are large compared with their width, nanotubes are so sticky that most objects can't be released. And there are simpler ways to move such tiny objects.	2
Supersensitive Sensors Oxygen sticks to tubes	Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkalis, halogens and other gases at room temperature, raising hopes for better chemical sensors.	Nanotubes are exquisitely sensitive to so many things (including oxygen and water) that they may not be able to distinguish one chemical or gas from another.	3
Hydrogen and Ion Storage Atoms in hollow core	Nanotubes might store hydrogen in their hollow centers and release it gradually in efficient and inexpensive fuel cells. They can also hold lithium ions, which could lead to longer-lived batteries.	So far the best reports indicate 6.5 percent hydrogen uptake, which is not quite dense enough to make fuel cells economical. The work with lithium ions is still preliminary.	1
Sharper Scanning Microscope Individual IgM antibodies	Attached to the tip of a scanning probe microscope, nanotubes can boost the instruments' lateral resolution by a factor of 10 or more, allowing clearer views of proteins and other large molecules.	Although commercially available, each tip is still made individually. The nanotube tips don't improve vertical resolution, but they do allow imaging deep pits in nanostructures that were previously hidden.	4
Superstrong Materials Nanotube stress test	Embedded into a composite, nanotubes have enormous resilience and tensile strength and could be used to make cars that bounce in a wreck or buildings that sway rather than crack in an earthquake.	Nanotubes still cost 10 to 1,000 times more than the carbon fibers currently used in composites. And nanotubes are so smooth that they slip out of the matrix, allowing it to fracture easily.	0

Compiled by W. Wayt Gibbs, staff writer

Transition from FET to SET



As we cool the FET down from room temperature to 4 degree Kelvin, we see the device behavior change dramatically. While the device acts like a field-effect transistor at room temperature, at 4K it behaves like a single-electron transistor (SET).



http://www.research.ibm.com/nanoscience/fet.html