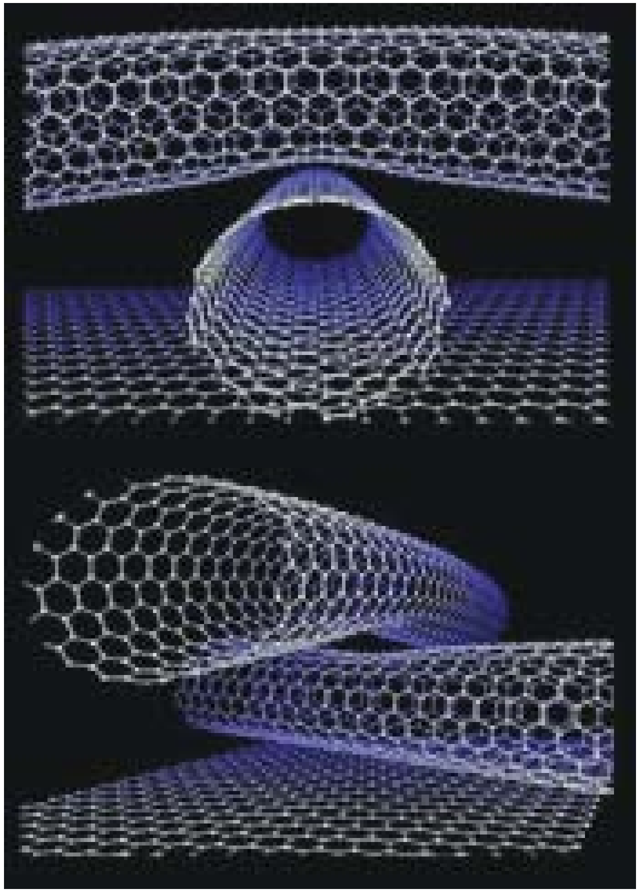
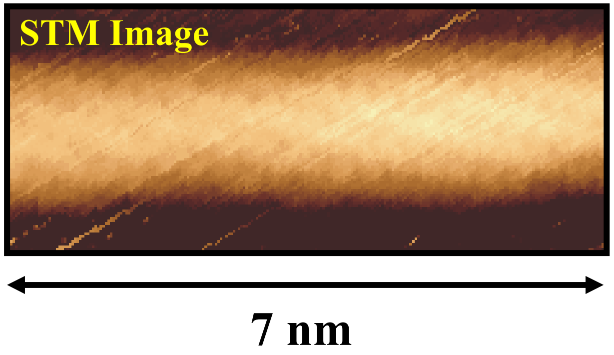
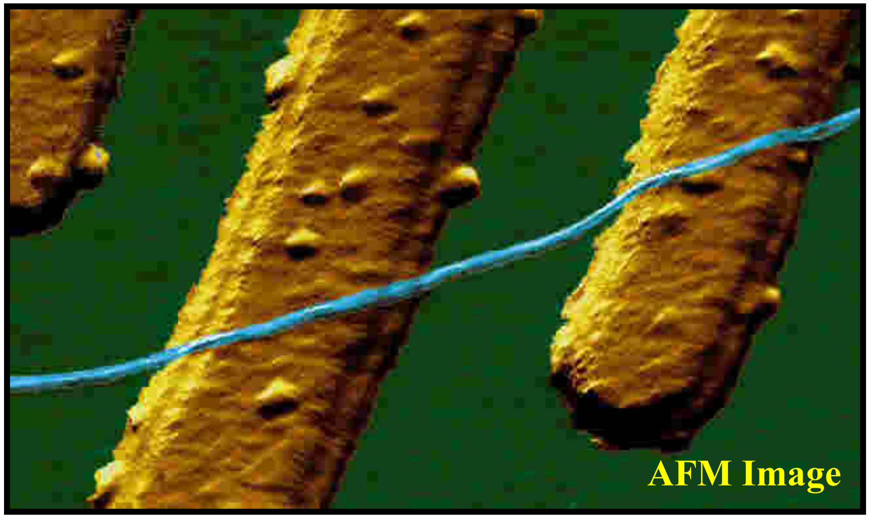
Nanomaterials

Lecture 6: Carbon Nanomaterials

Carbon Nanomaterials







Fullerenes

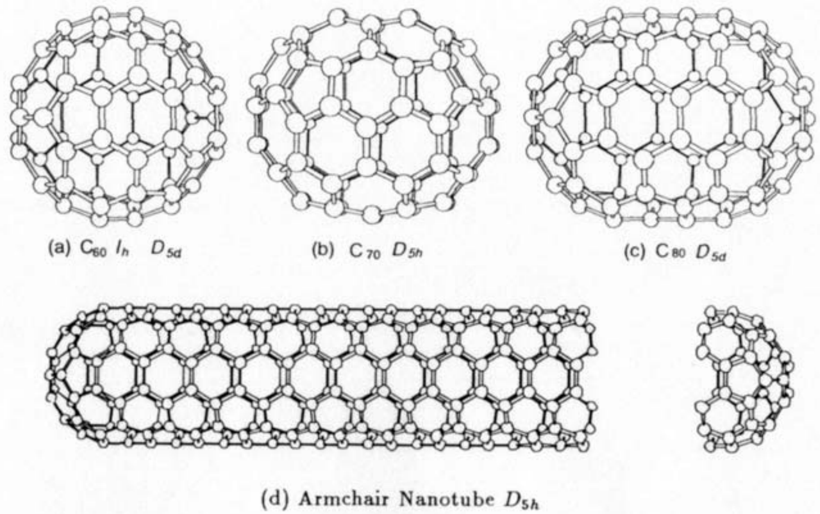


FIGURE 1. Examples of closed shell fullerene configurations which avoid dangling bonds: (a) C_{60}, (b) C_{70}, (c) C_{80} and (d) an armchair carbon nanotube. Also indicated on the figure are the point group symmetries of the various structures. We note that D_{5d} is a subgroup of the icosahedral group I_h, exhibiting inversion symmetry.

- **C_{60} was established by mass spectrographic analysis by Kroto and Smalley in 1985**
- **C_{60} is called a buckminsterfullerene or buckyball due to resemblance to geodesic domes designed and built by R. Buckminster Fuller**

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Endofullerenes

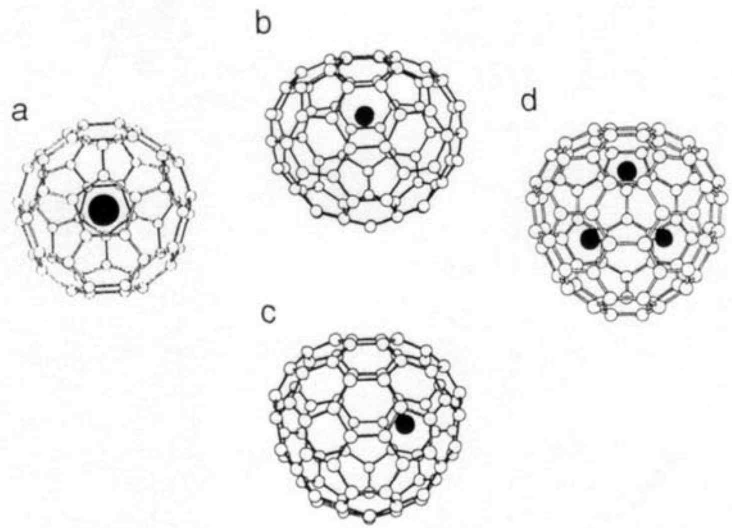

FIGURE 2. Structural models for various endofullerenes. (a) One possible structural model for $M@C_{60}$, with M at the center of the C_{60} cage[73]. (b, c) Two different structural models for $La@C_{82}$, with the La at two different off-center positions within the C_{82} cage[74]. (d) A structural model for $Sc_3@C_{82}$ (assuming C_{3v} symmetry of the C_{82} cage), where black balls represent the three equivalent Sc^{3+} ions, which rapidly reorient within the C_{82} cage as an equilateral triangle[64].

- **Endohedral doping of fullerenes leads to the formation of a dipole moment that influences solubility and other properties.**

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Electronic Structure of Molecular and Solid C_{60}

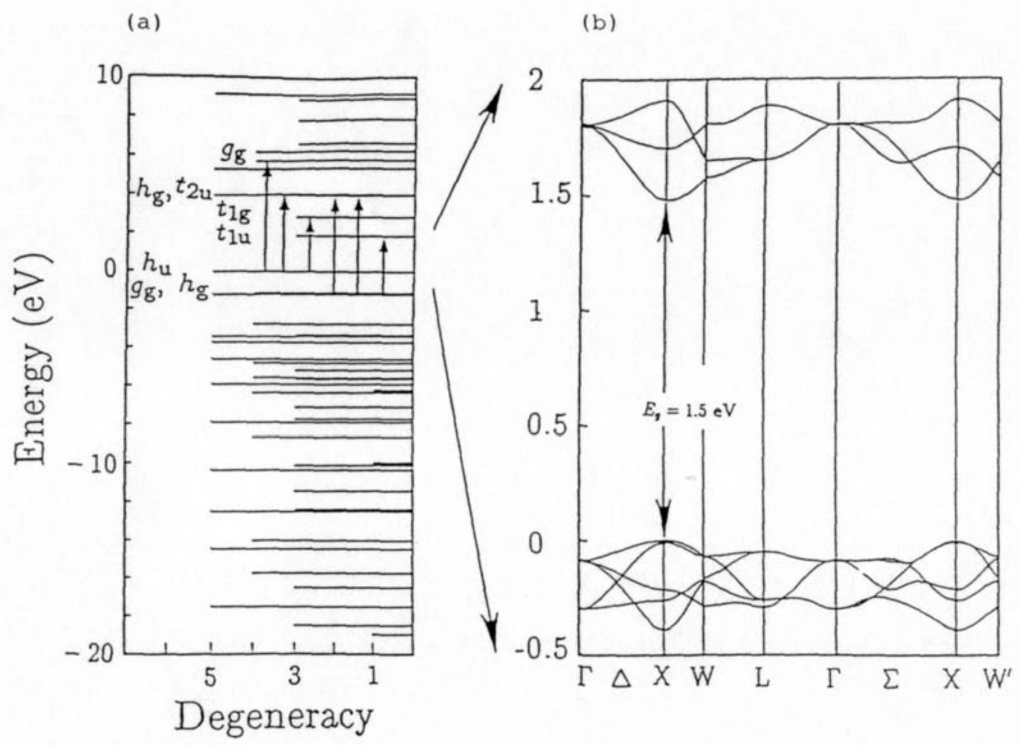

FIGURE 7. Calculated electronic structure of (a) an isolated C_{60} molecule and (b) FCC solid C_{60} where the direct band gap at the X-point is 1.5 eV[106].

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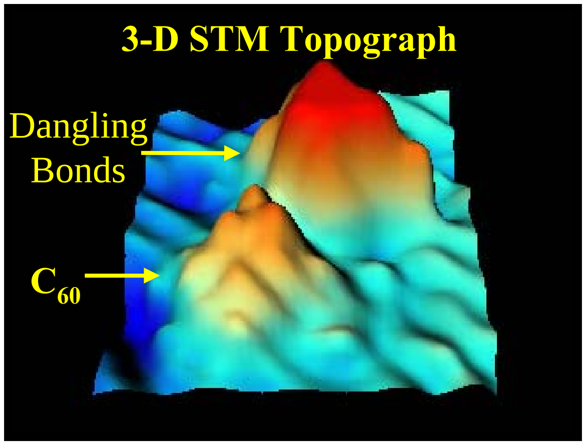
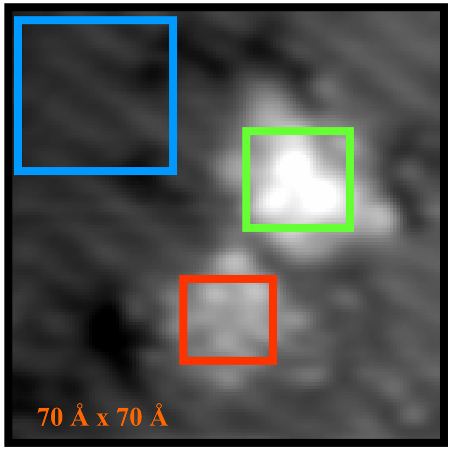
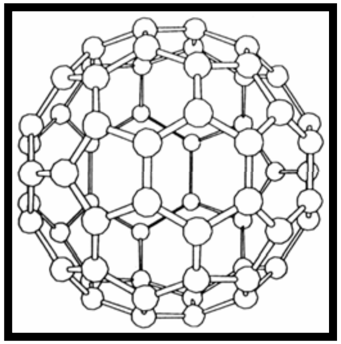
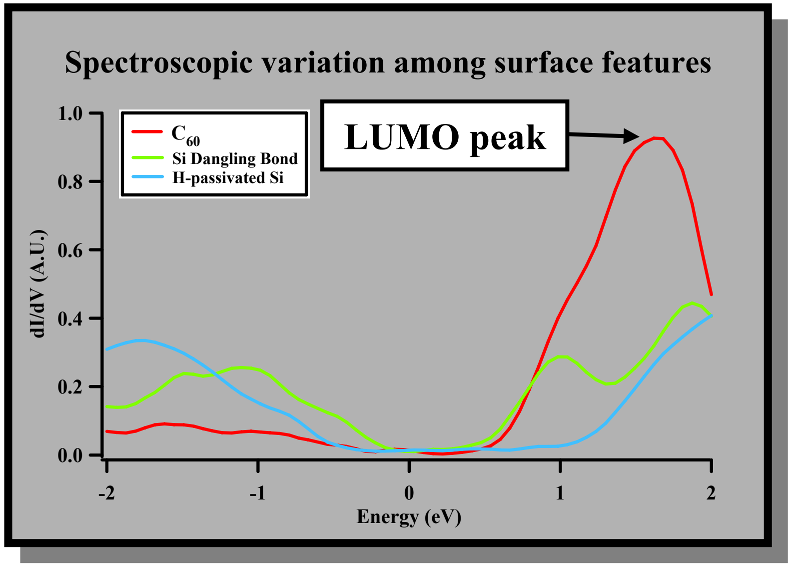
Single Molecule STM Spectroscopy of C_{60}

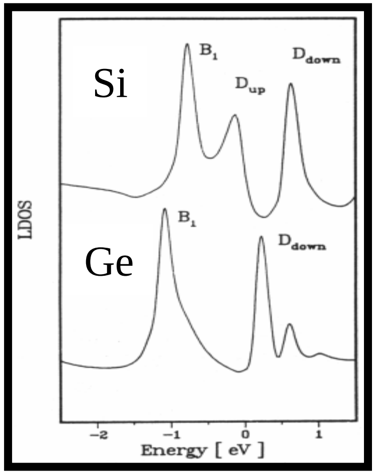






Structure of C_{60}





Calculated local density of states for Si(100)

Rolled Up From Graphene Sheets: Carbon Nanotubes

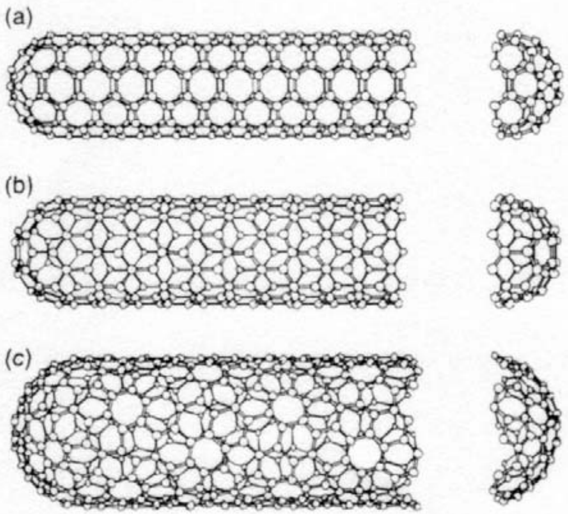


FIGURE 11. By rolling a graphene sheet (a single layer from a 3D graphite crystal) as a cylinder and then capping each end of the cylinder with half of a C_{60} molecule, a "C_{60} tubule" one layer in thickness is formed. Shown here is a schematic model for a tubule arising from (a) an armchair cap with a 5-fold axis, (b) a zigzag cap with a 3-fold axis, and (c) a chiral (10,5) nanotube with caps associated with C_{140}[115].

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Carbon Nanotube Synthesis: Carbon Arc Discharge

A BIG SPARK

In 1992 Thomas Ebbesen and Pulickel M. Ajayan of the NEC Fundamental Research Laboratory in Tsukuba, Japan, published the first method for making macroscopic quantities of nanotubes. It is almost Frankensteinian in its design: wire two graphite rods to a power supply, place them millimeters apart and throw the switch. As 100 amps of juice spark between the rods, carbon vaporizes into a hot plasma (*right*). Some of it recondenses in the form of nanotubes.

Typical yield: Up to 30 percent by weight
Advantages: High temperatures and metal catalysts added to the rods can produce both single-walled and multiwalled nanotubes with few or no structural defects.
Limitations: Tubes tend to be short (50 microns or less) and deposited in random sizes and directions.

OAK RIDGE NATIONAL LABORATORY

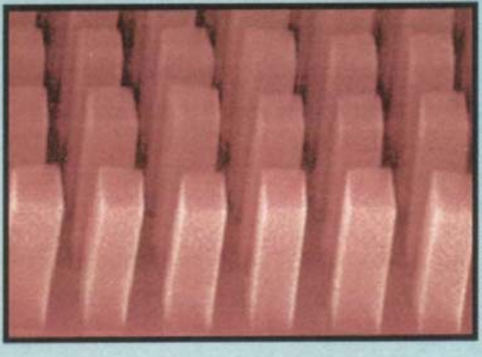
P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Carbon Nanotube Synthesis: Chemical Vapor Deposition

A HOT GAS

Morinubo Endo of Shinshu University in Nagano, Japan, was the first to make nanotubes with this method, which is called chemical vapor deposition (CVD). This recipe is also fairly simple. Place a substrate in an oven, heat to 600 degrees Celsius and slowly add a carbon-bearing gas such as methane. As the gas decomposes, it frees up carbon atoms, which can recombine in the form of nanotubes.

Jie Liu and his colleagues at Duke University recently invented a porous catalyst that they claim can convert almost all the carbon in a feed gas to nanotubes. By printing patterns of catalyst particles on the substrate, Hongjie Dai and his colleagues at Stanford University have been able to control where the tubes form (*left*) and have been working to combine this controlled growth with standard silicon technology.



HONGJIE DAI *Stanford University*

Typical yield: 20 to nearly 100 percent

Advantages: CVD is the easiest of the three methods to scale up to industrial production. It may be able to make nanotubes of great length, which is necessary for fibers to be used in composites.

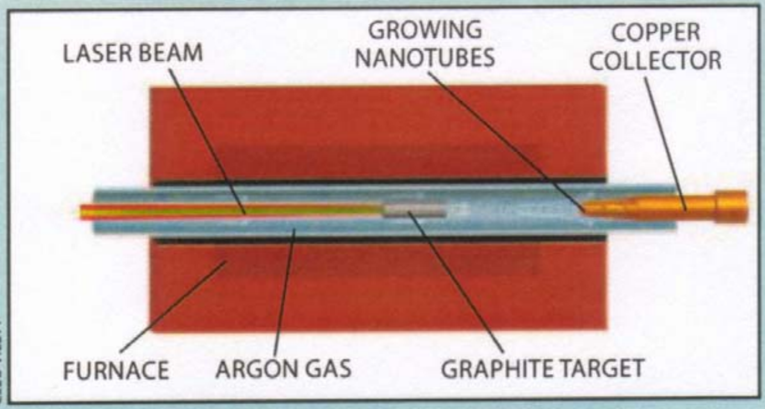
Limitations: Nanotubes made this way are usually multiwalled and are often riddled with defects. As a result, the tubes have only one tenth the tensile strength of those made by arc discharge.

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Carbon Nanotube Synthesis: Laser Ablation

A LASER BLAST

Richard Smalley and his co-workers at Rice University were blasting metal with intense laser pulses to produce fancier metal molecules when the news broke about the discovery of nanotubes. They swapped the metal in their setup for graphite rods and soon produced carbon nanotubes by using laser pulses instead of electricity to generate the hot carbon gas from which nanotubes form (*left*). Trying various catalysts, the group hit on conditions that produce prodigious amounts of single-walled nanotubes.



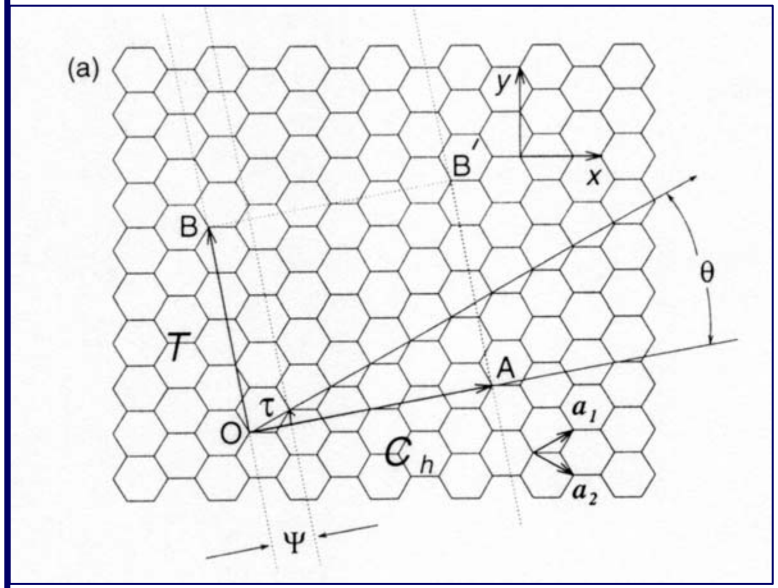
Typical yield: Up to 70 percent

Advantages: Produces primarily single-walled nanotubes, with a diameter range that can be controlled by varying the reaction temperature.

Limitations: This method is by far the most costly, because it requires very expensive lasers. —*P.G.C. and P.A.*

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Chirality of Carbon Nanotubes



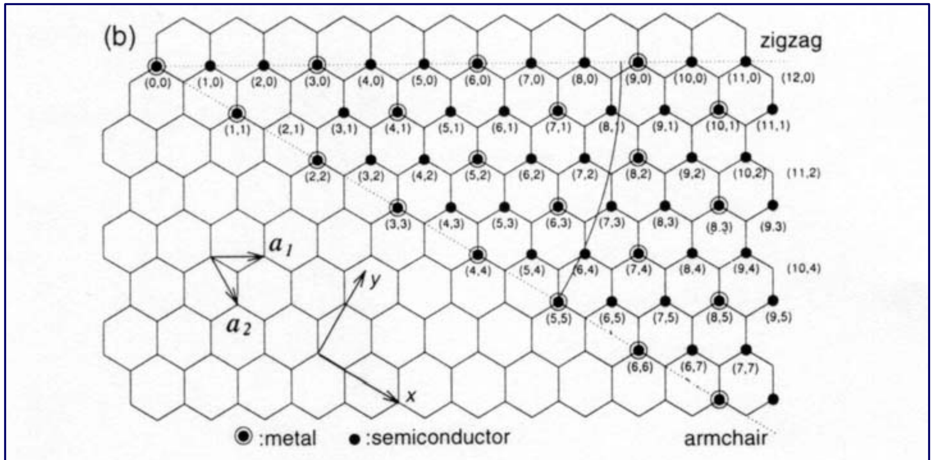


FIGURE 10. (a) The chiral vector $\vec{OA}$ or $\vec{C}_h = n\hat{a}_1 + m\hat{a}2$ is defined on the honeycomb lattice of carbon atoms by unit vectors $\hat{a}_1$ and $\hat{a}_2$ and the chiral angle θ with respect to the zigzag axis. Along the zigzag axis $\theta = 0°$. Also shown are the lattice vector $0\vec{B} = \vec{T}$ of the 1D tubule unit cell and the rotation angle ψ and the translation τ which constitute the basic symmetry operation $R = (\psi|\tau)$ for the carbon nanotube. The diagram is constructed for $(n,m) = (4,2)$. (b) Possible vectors specified by the pairs of integers (n,m) for general carbon tubules, including zigzag, armchair, and chiral tubules. The encircled dots denote metallic tubules while the small dots are for semiconducting tubules[115].

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Energy Band Diagrams of Carbon Nanotubes

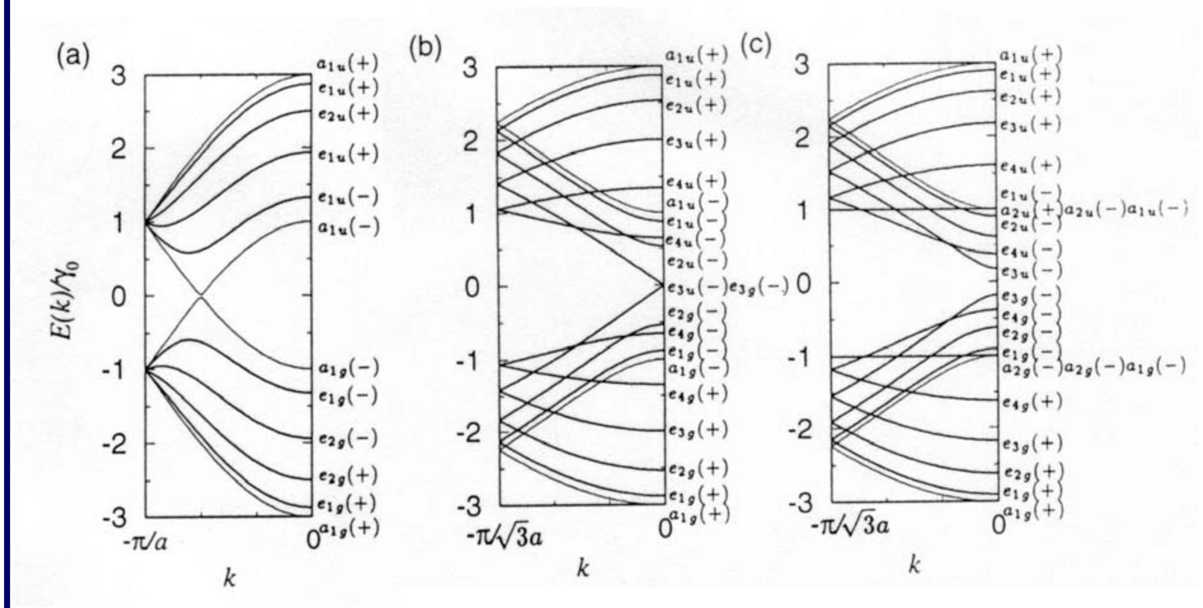

FIGURE 12. One-dimensional energy dispersion relations for (a) armchair (5,5) tubules, (b) zigzag (9,0) tubules, and (c) zigzag (10,0) tubules labeled by the irreducible representations of the point group $D_{(2n+1)d}$ at $k=0$. The A-bands are non-degenerate and the E-bands are doubly degenerate at a general k-point[128,134,135].

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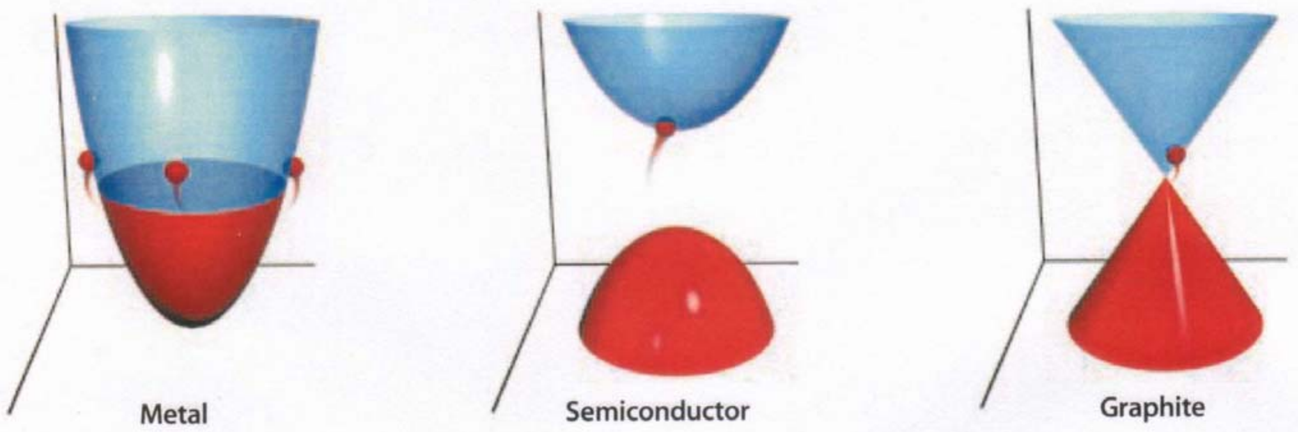
Electrical Properties of Graphite

The Electrical Behavior of Nanotubes

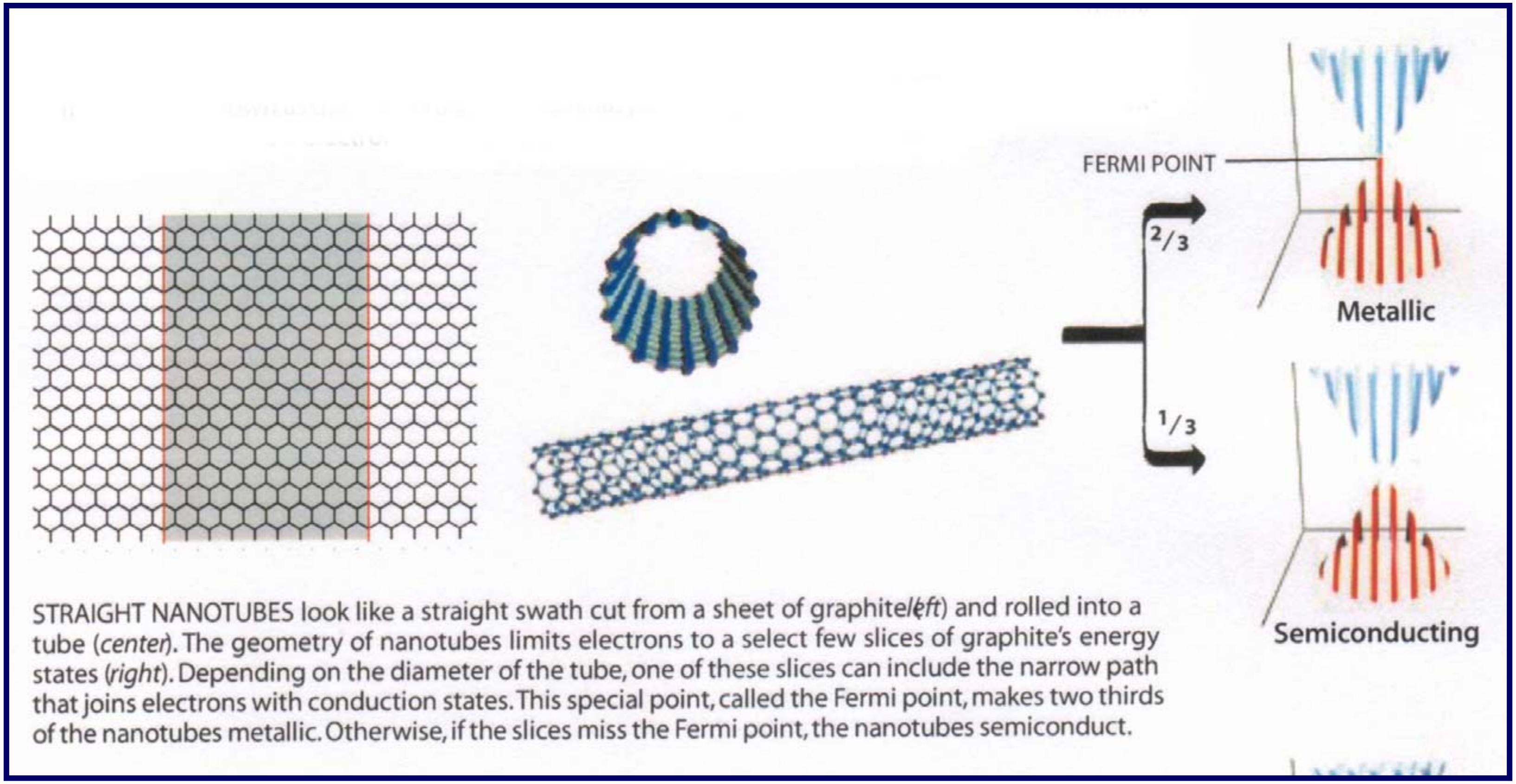
A Split Personality



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.

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

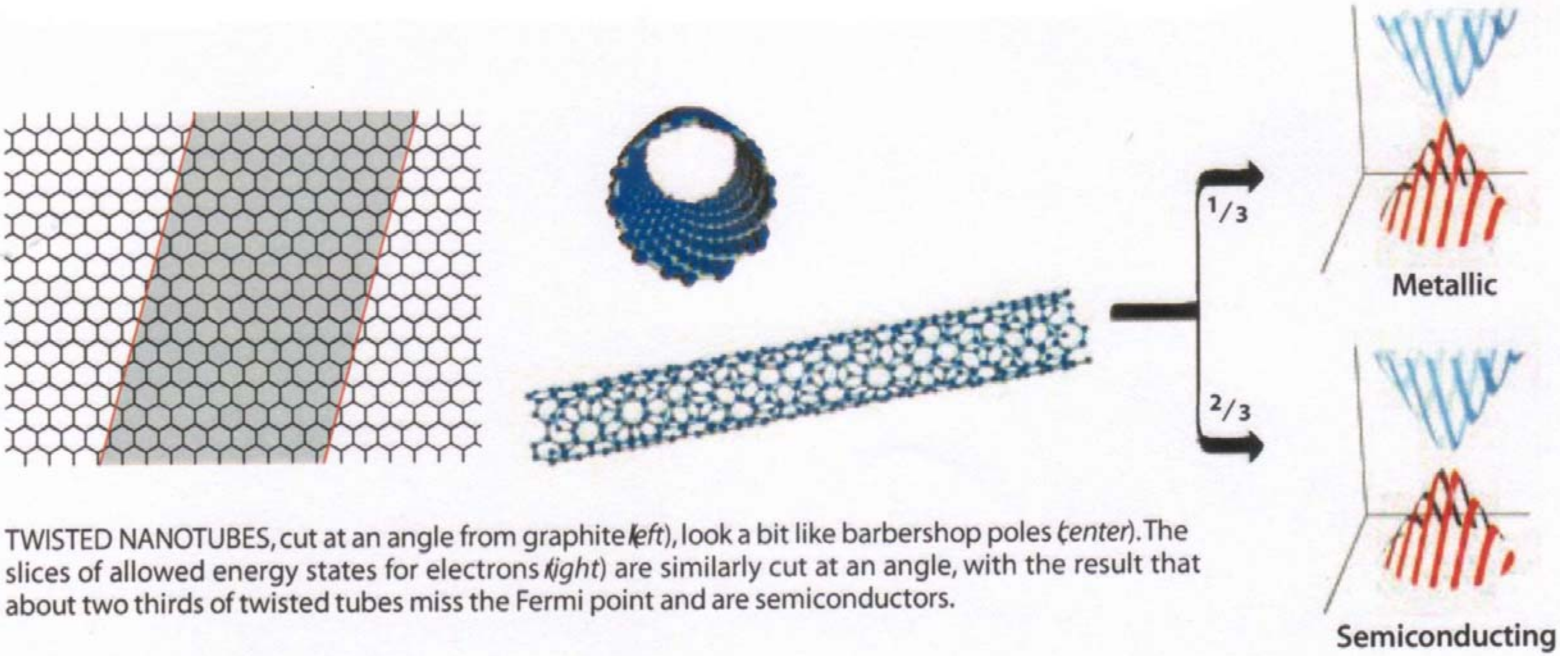
Electrical Properties of Straight Nanotubes



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.

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Electrical Properties of Twisted Nanotubes



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.

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Bandgap of Semiconducting Nanotubes

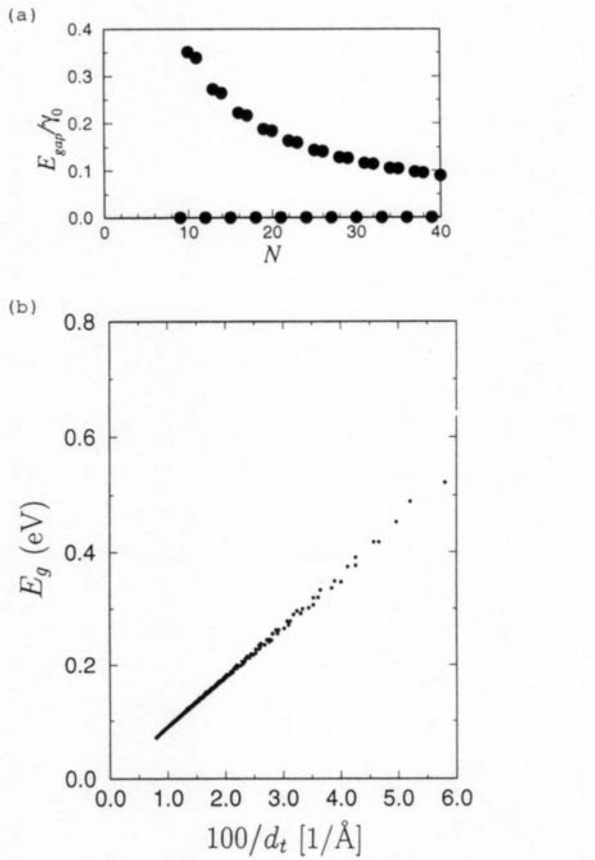


FIGURE 13. The dependence of the energy gap (normalized to the nearest neighbor overlap energy) on tubule diameter. (a) The dependence of the energy gap on the number of carbon atoms N along the circumference of zig-zag tubules[137]. (b) The energy gap E_g for a general chiral carbon nanotube as a function of 100 Å $/d_t$, where d_t is the tubule diameter in Å.

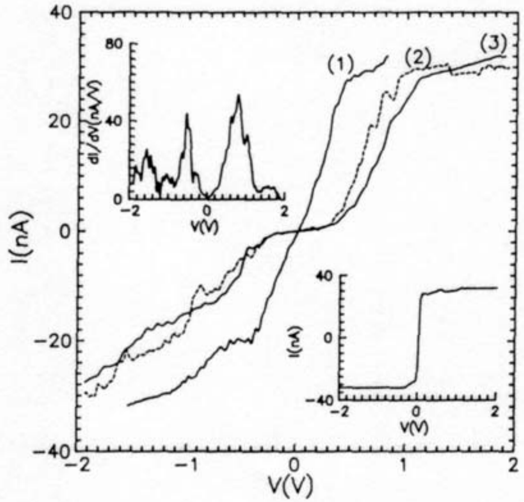


FIGURE 15. Current–voltage I vs. V traces taken with scanning tunneling spectroscopy (STS) on individual nanotubes of various diameters: (1) $d_t = 8.7$ nm, (2) $d_t = 4.0$ nm, and (3) $d_t = 1.7$ nm. The top inset shows the conductance vs. voltage plot for data taken on the 1.7 nm nanotube. The bottom inset shows an I–V trace taken on a gold surface under the same conditions[145].

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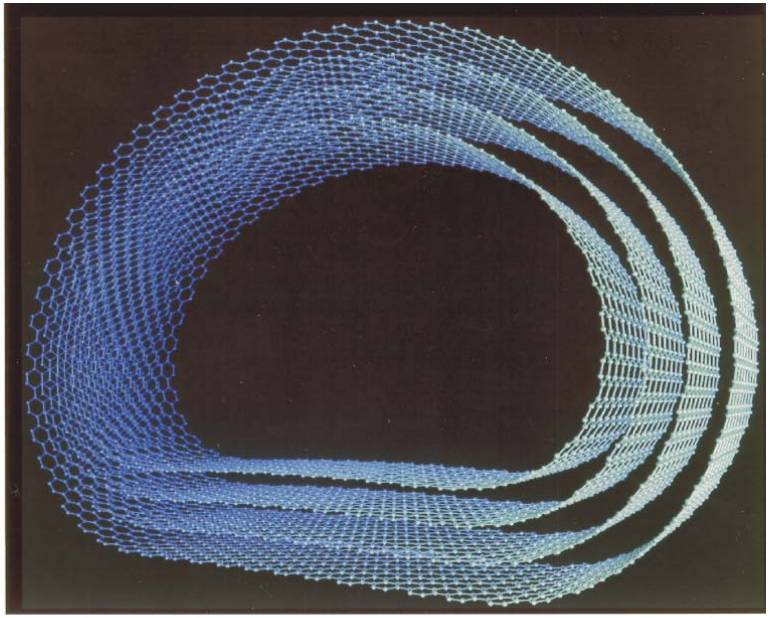
Electrical Properties of MWNTs



- MWNT bandgap is proportional to 1/d → At room temperature, MWNTs behave like metals since d ~ 10 nm
- Only the outermost shell carries current in an undamaged MWNT

Other Properties of SWNTs

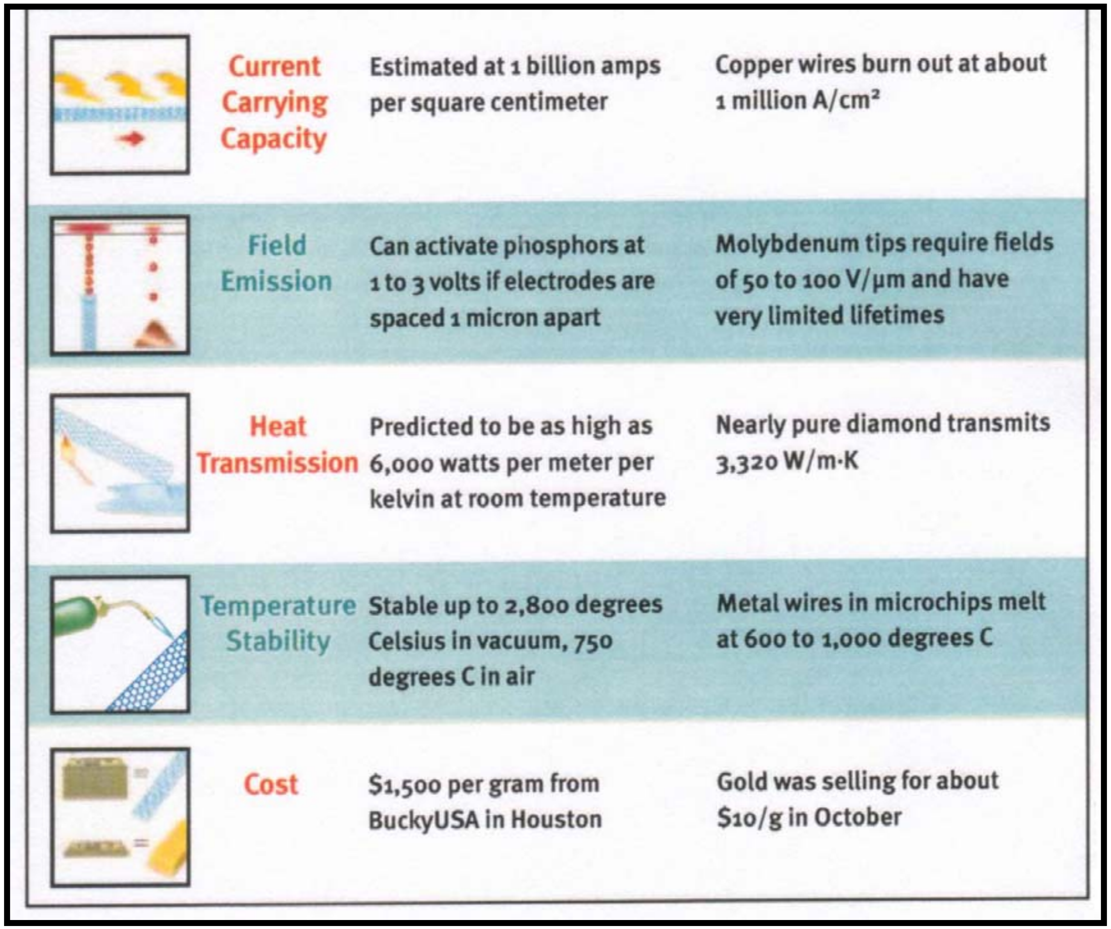
Properties of Carbon Nanotubes

Going to Extremes

	PROPERTY	SINGLE-WALLED NANOTUBES	BY COMPARISON
	Size	0.6 to 1.8 nanometer in diameter	Electron beam lithography can create lines 50 nm wide, a few nm thick
	Density	1.33 to 1.40 grams per cubic centimeter	Aluminum has a density of 2.7 g/cm^3
	Tensile Strength	45 billion pascals	High-strength steel alloys break at about 2 billion Pa
	Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries

P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

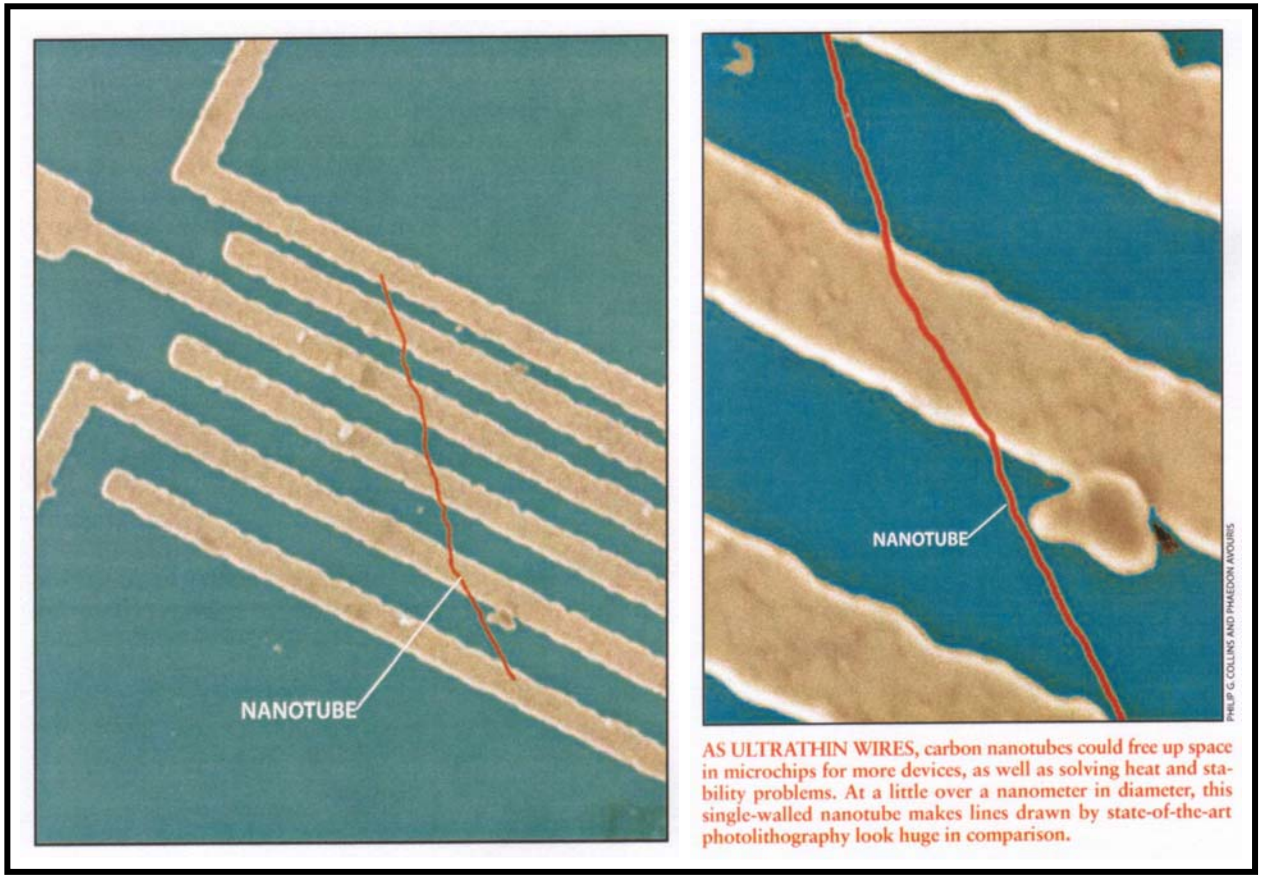
Other Properties of SWNTs



Current Carrying Capacity	Estimated at 1 billion amps per square centimeter	Copper wires burn out at about 1 million A/cm²
Field Emission	Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart	Molybdenum tips require fields of 50 to 100 V/μm and have very limited lifetimes
Heat Transmission	Predicted to be as high as 6,000 watts per meter per kelvin at room temperature	Nearly pure diamond transmits 3,320 W/m·K
Temperature Stability	Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air	Metal wires in microchips melt at 600 to 1,000 degrees C
Cost	$1,500 per gram from BuckyUSA in Houston	Gold was selling for about $10/g in October

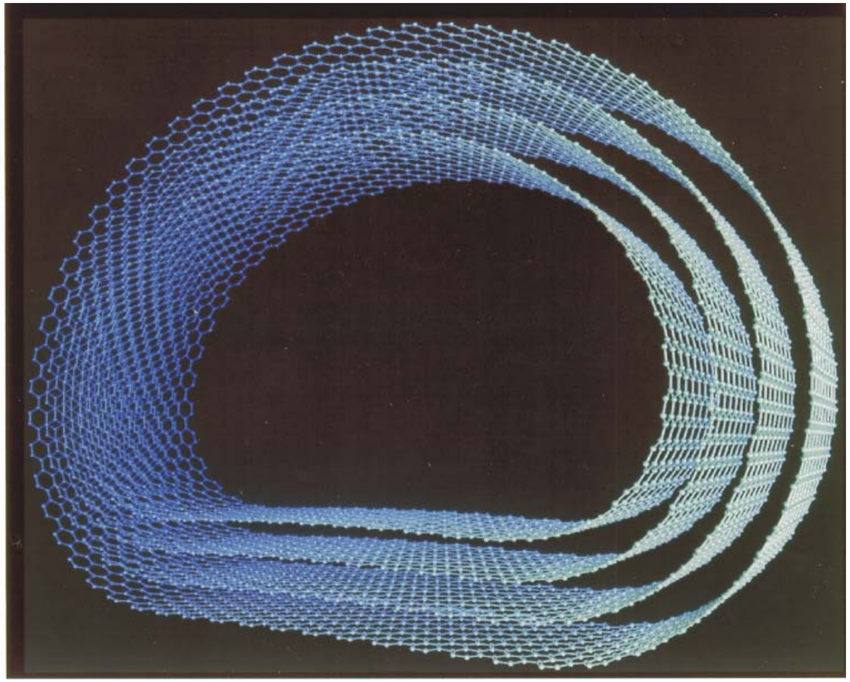
P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Nanotubes as Interconnects



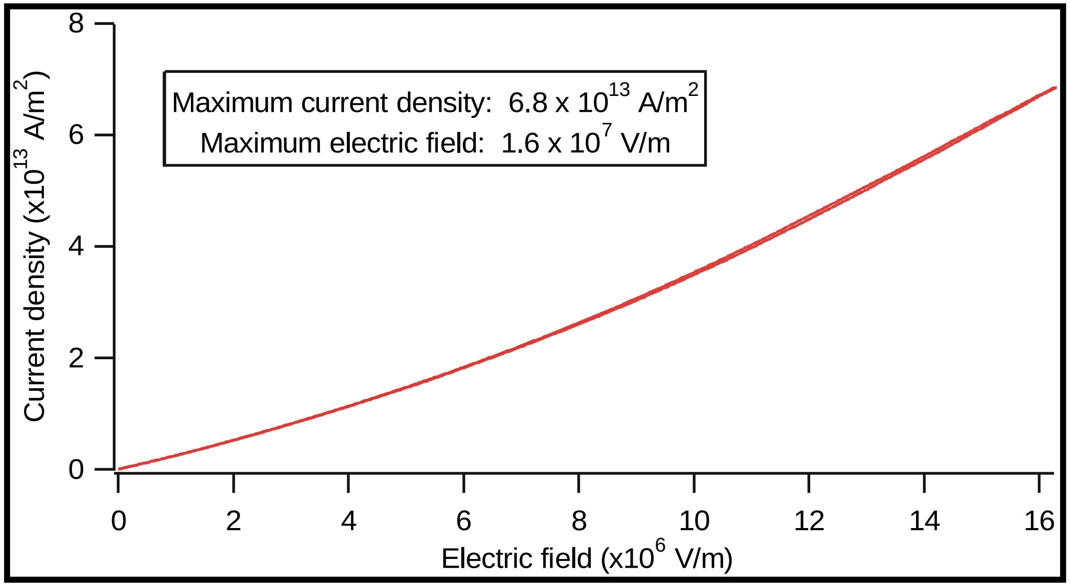
P. G. Collins and Ph. Avouris, *Scientific American*, **283**, 62 (2000).

Current Carrying Capacity of MWNTs



Although a cross-sectional view of a MWNT shows several cylindrical shells, only the outermost shell carries current in an undamaged MWNT.

Representative MWNT I-V Curve:

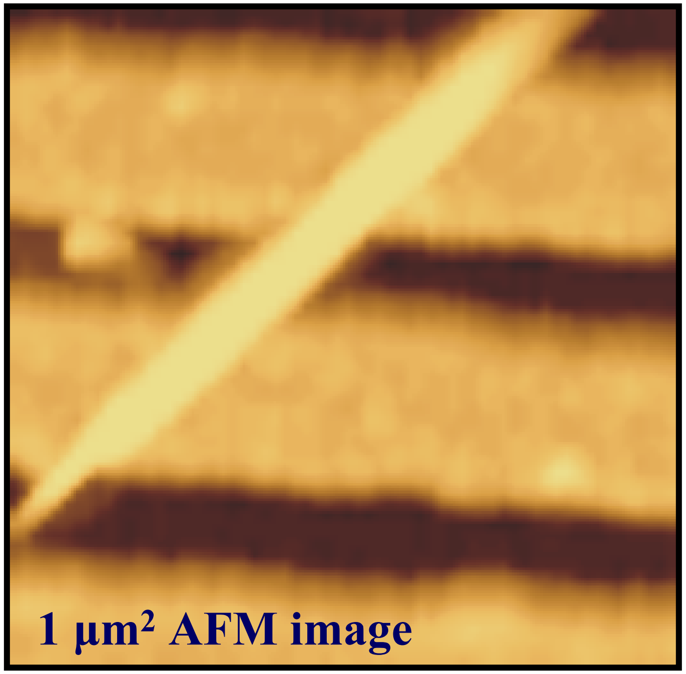


Maximum current densities of potential interconnect materials:

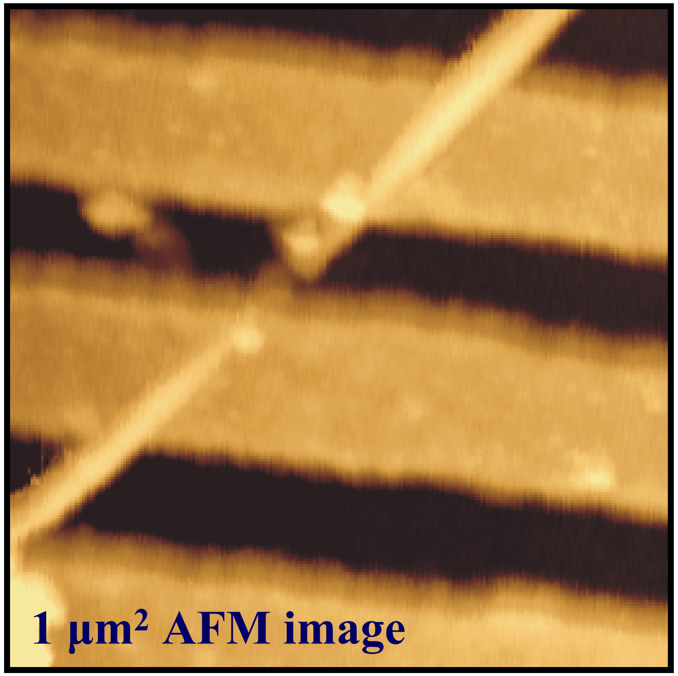
- Metals: $10^{10} – 10^{12}$ A/m^2
- Superconductors: $J_c \sim 10^{12}$ A/m^2
- MWNTs: $>5\times10^{13}$ A/m^2

Electrically Stressed MWNTs

Before Electrical Stress

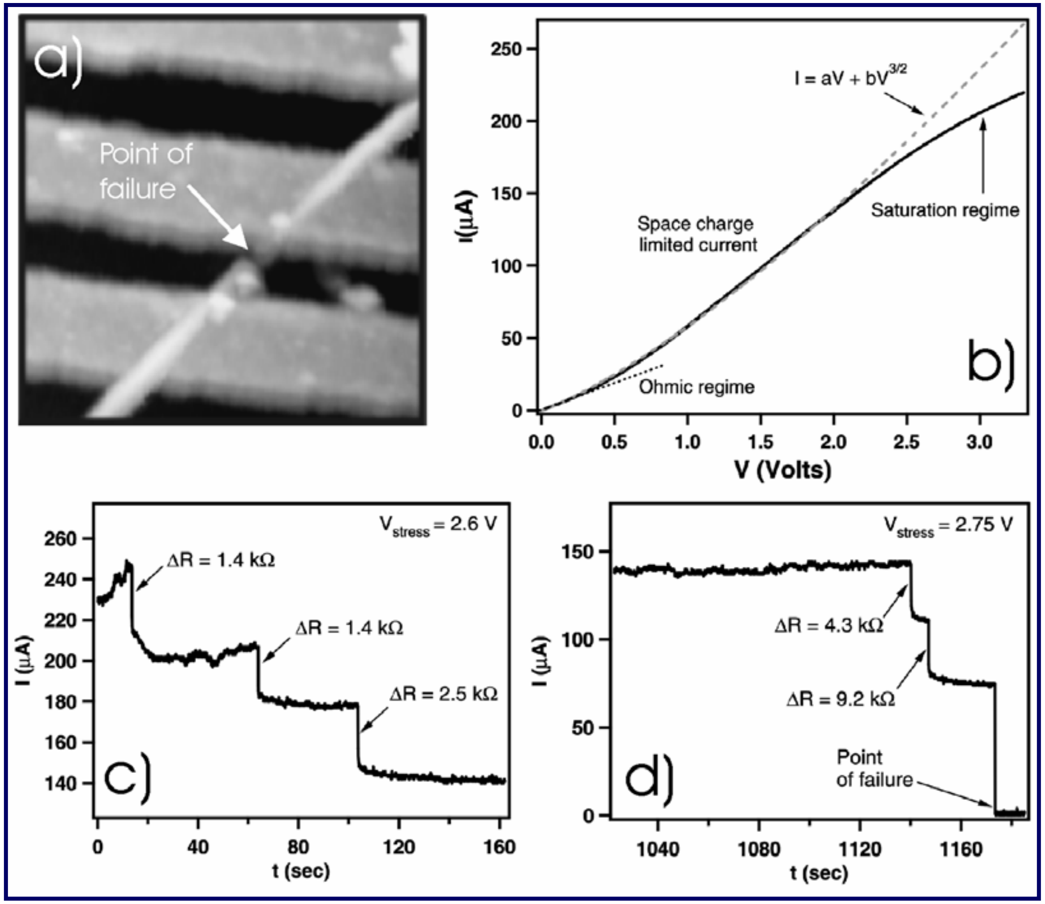


After Failure



Experimental method: Monitor the current as a function of time while stressing the MWNT at a fixed voltage.

Multiwalled Carbon Nanotube Failure



P. G. Collins, *et al.*, *Phys. Rev. Lett.*, **86**, 3128 (2001).

Device Applications of Nanotube Junctions

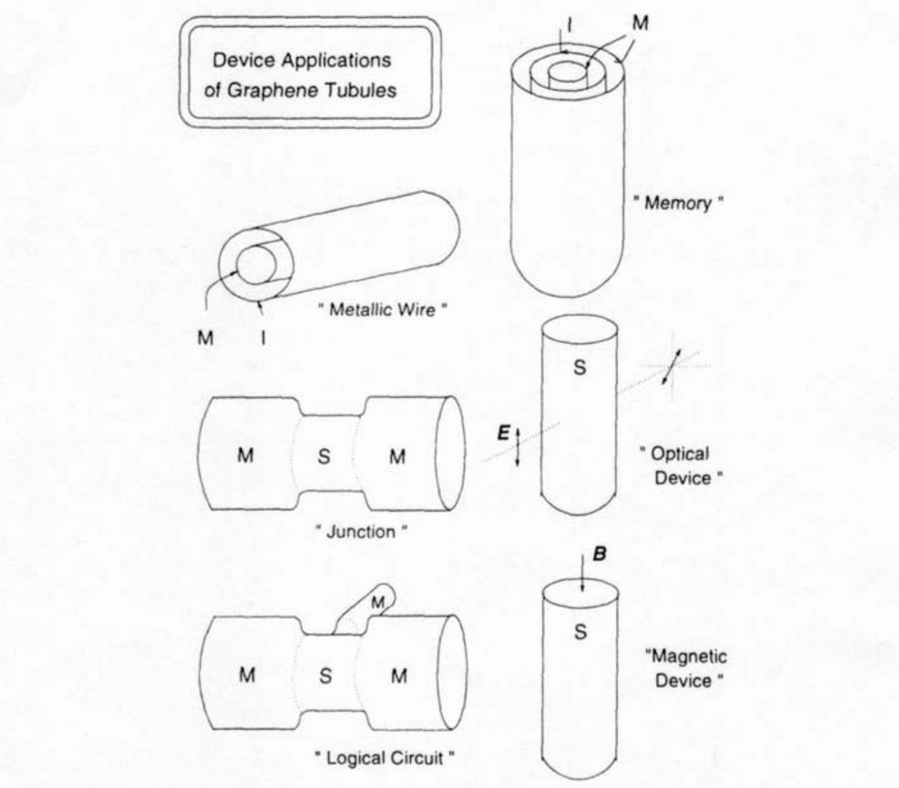


FIGURE 18. Schematic presentation of several proposed electronic device applications for carbon nanotubes[163].

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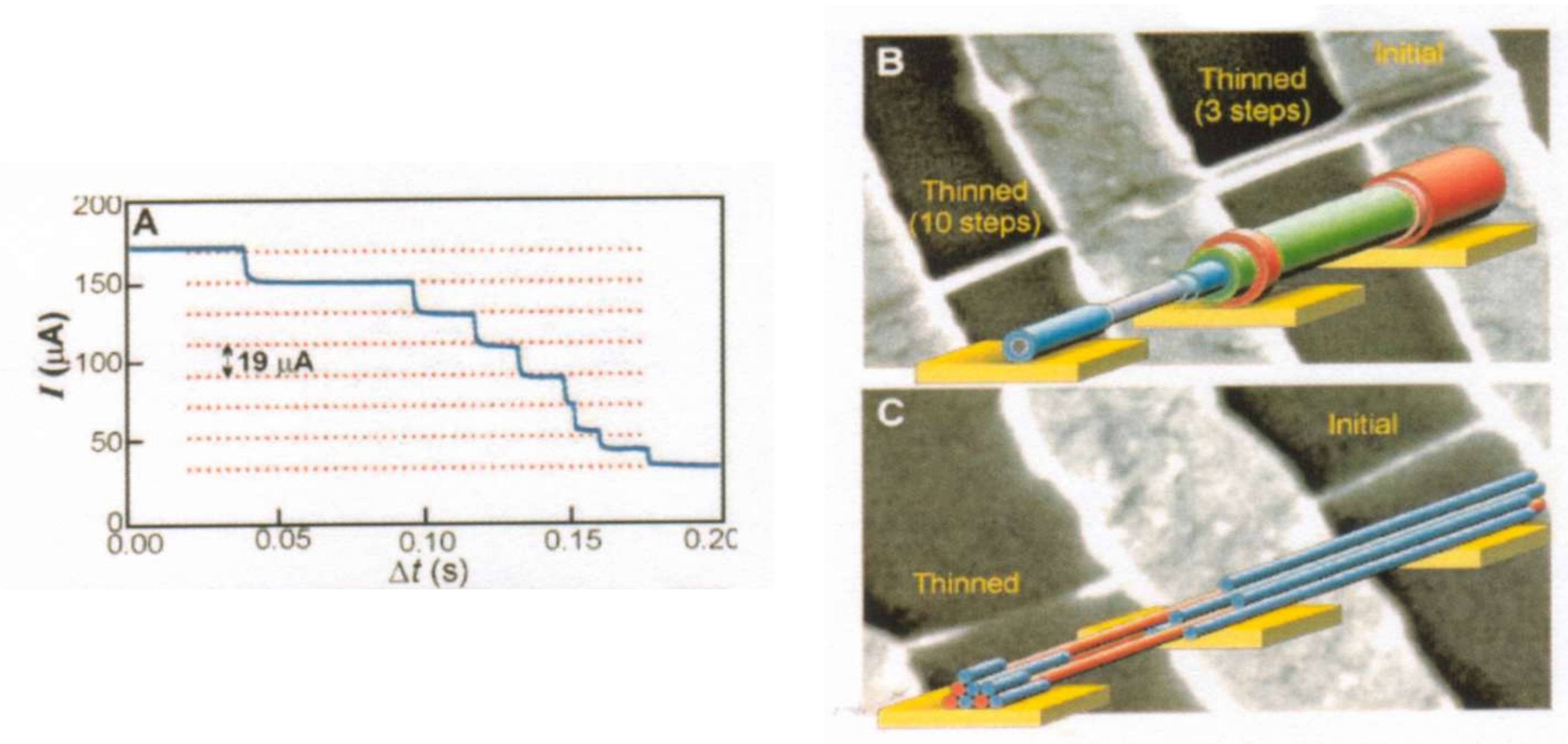
Engineering Carbon Nanotubes Using Electrical Breakdown



P. G. Collins, *et al.*, *Science*, **292**, 706 (2001).

Engineering Carbon Nanotubes Using Electrical Breakdown

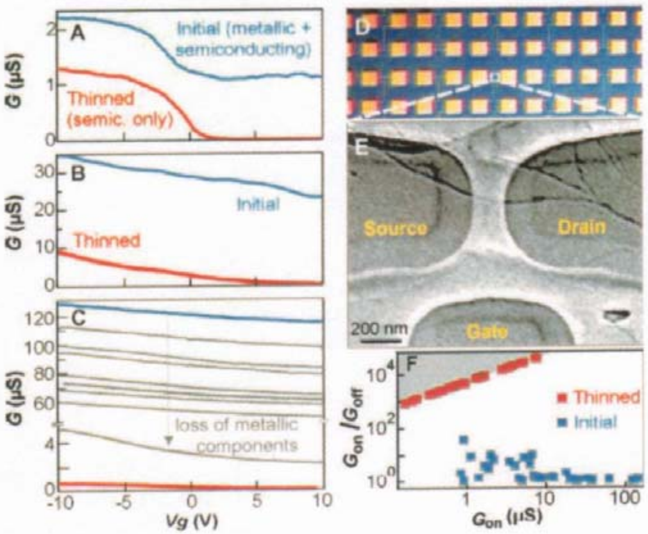


Fig. 4. (**A** and **B**) Stressing a mixture of s- and m-SWNTs while simultaneously gating the bundle to deplete the semiconductors of carriers resulted in the selective breakdown of the m-SWNTs. The $G(V_g)$ curve rigidly shifted downward as the m-SWNTs were destroyed. The remaining current modulation is wholly due to the remaining s-SWNTs. (**C**) In very thick ropes, some s-SWNTs must also be sacrificed to remove the innermost m-SWNTs. By combining this technique with standard lithography, arrays of three-terminal, nanotube-based FETs were created (**D** and **E**) out of disordered bundles containing both m- and s-SWNTs. Although these bundles initially show little or no switching because of their metallic constituents, final devices with good FET characteristics were reliably achieved (**F**).

Table 1. Comparison of relative band gaps from experiments (Fig. 2B) with calculations based on the expected diameter dependence. The only parameters are the initial diameter of the tube and the 0.34 nm spacing between adjacent shells. Calc., calculated; Meas., measured.

Shell	Diameter (nm)	Relative band gap (eV)	
		Calc.	Meas.
n	9.5		
~	~		
n-10	2.7	0.24	0.22
n-11	2.0	0.33	
n-12	1.3	0.49	0.48
n-13	0.7	1.00	1.00

P. G. Collins, *et al.*, *Science*, **292**, 706 (2001).