Carbon Nanotubes

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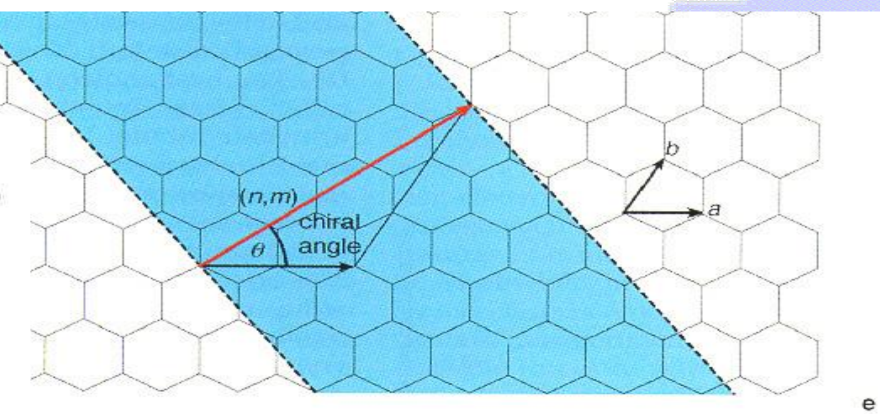
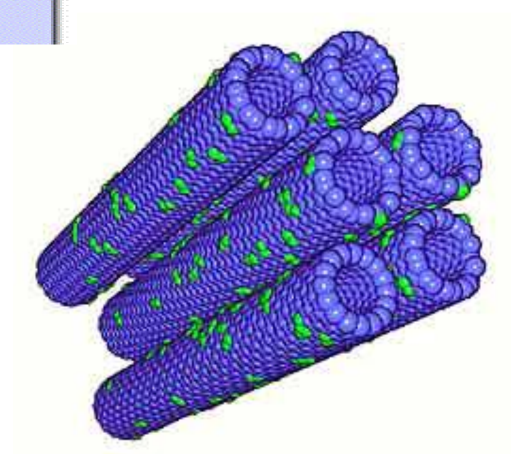
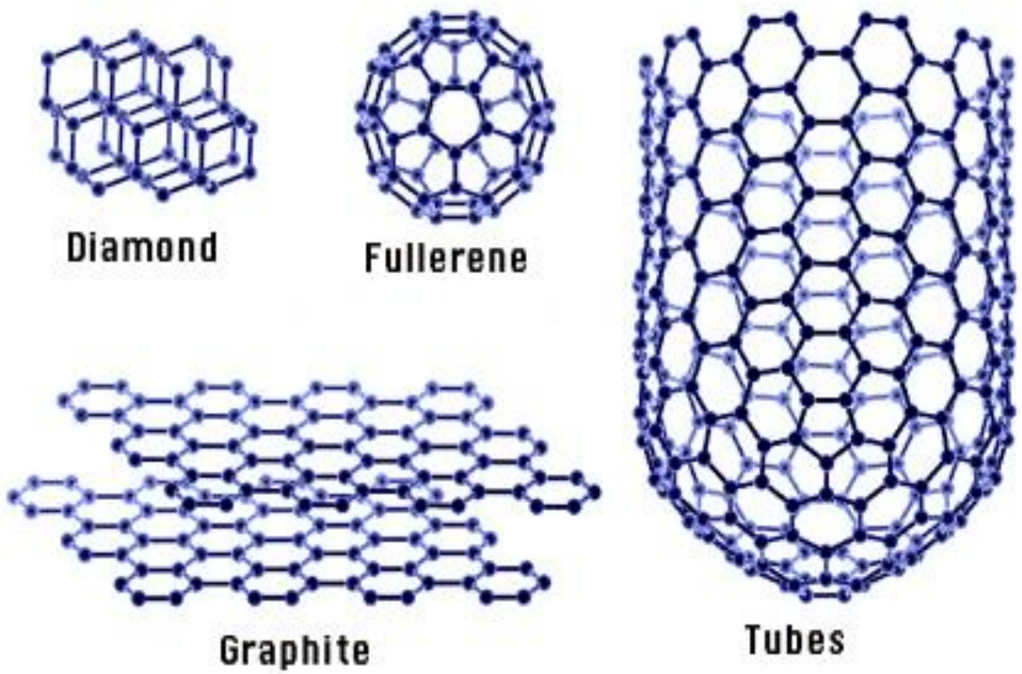
Elettra Synchrotron Light Source





Carbon Allotropes



Up to 1985 the only two allotropic form of carbon were known: graphite and diamond.

1985 - discovery of C_{60} (Smalley, Kroto and Curl) and then of higher fullerenes and nanotubes (lijima 1991).

Very promising systems:

A wide range of transport properties, from insulators to high-temperature superconductors.

Nanotubes can be used for novel electronic devices.

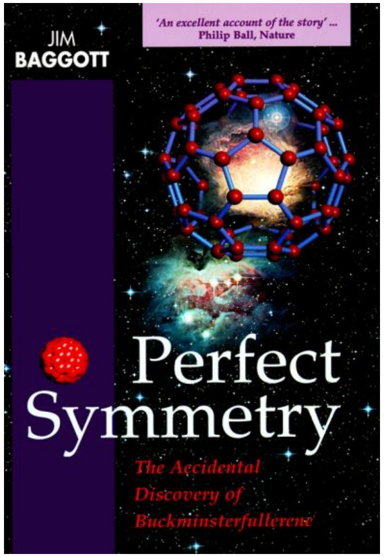
Their marked mechanical properties make fullerenes and nanotubes serious competitors to composite materials.

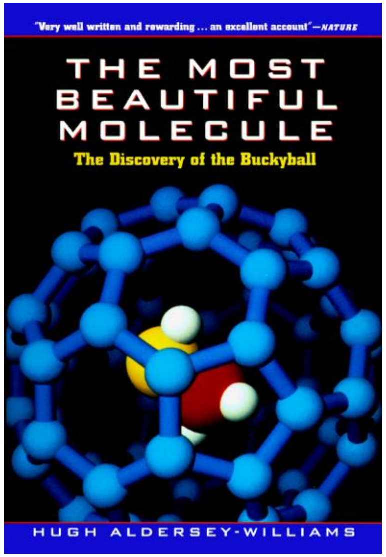
Nanotechnology: **A new mantra of the 21st century, the next industrial revolution**

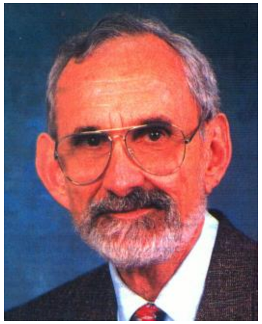
Fullerenes and Nanotubes are Fundamental Building Blocks

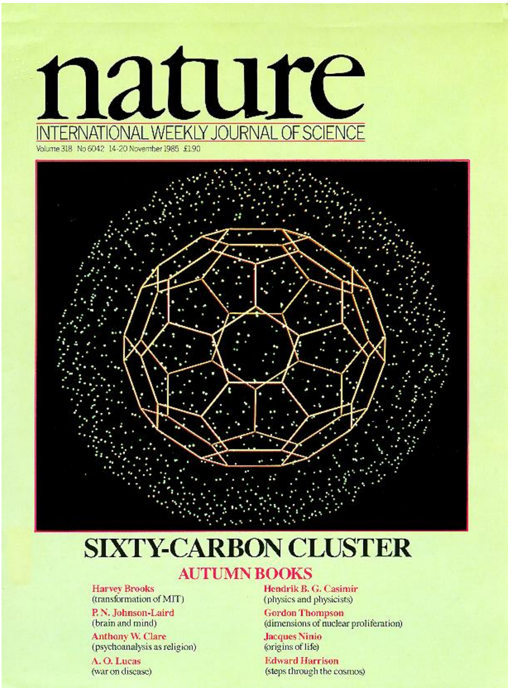
Buckminsterfullerene - C_{60}

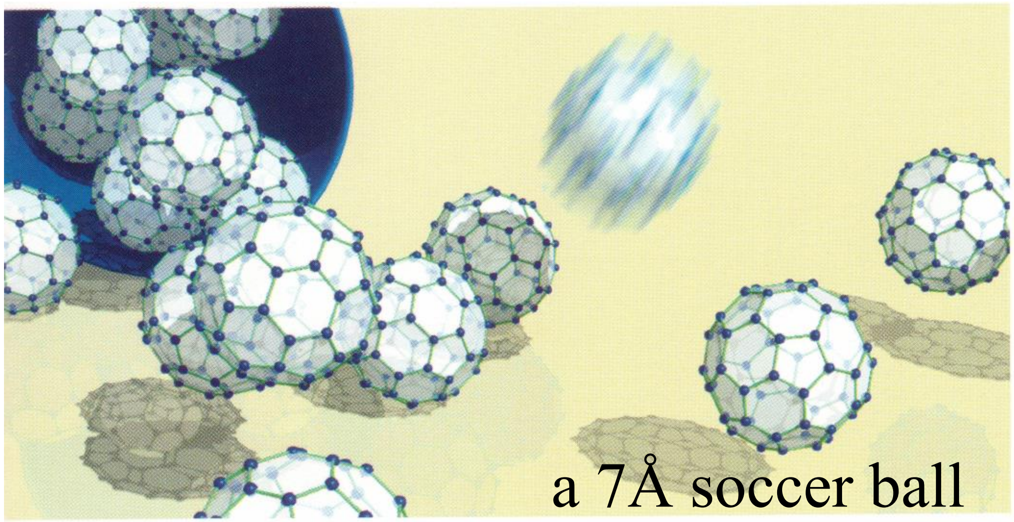
The 1996 Nobel Prize for Chemistry

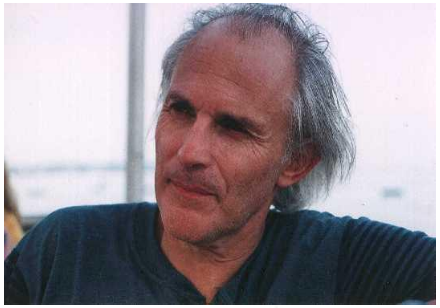






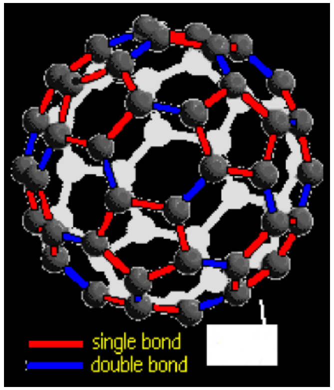




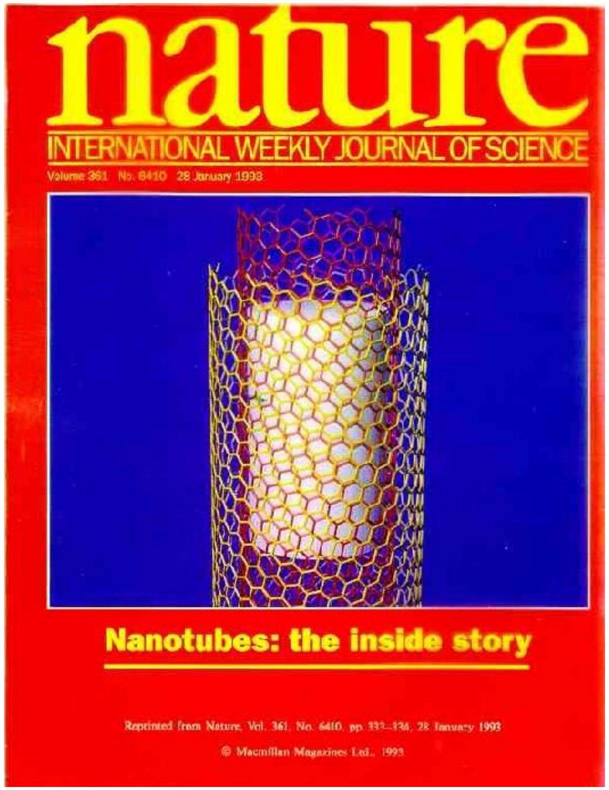


A fascinating new group of carbon molecules

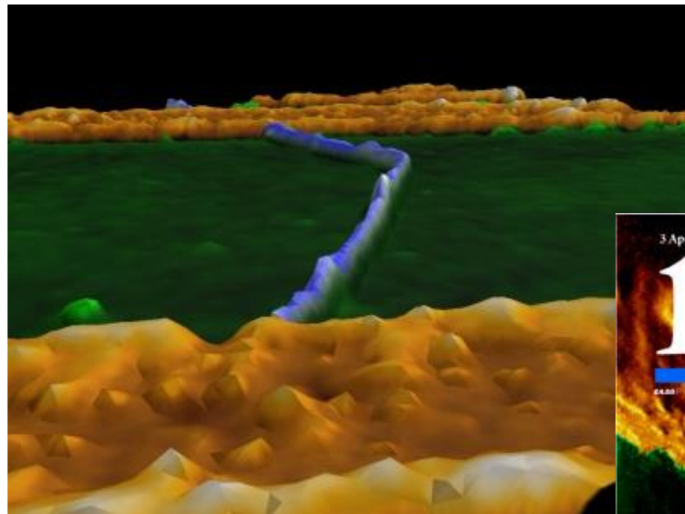
Fullerenes: a whole new ball game



Why are nanotube important?



They are a new and fascinating physical system at the nanoscale

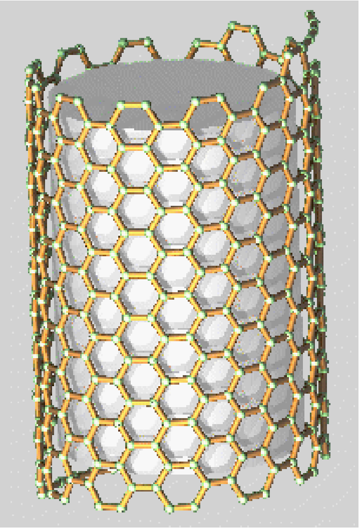


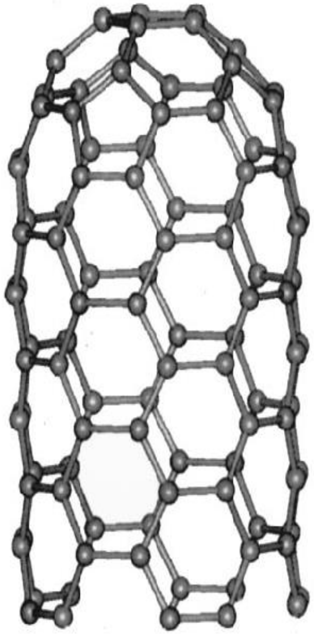
They hold substantial promise for applications as super-strong fibers and in novel electronic devices

Carbon Nanotubes (CNTs)

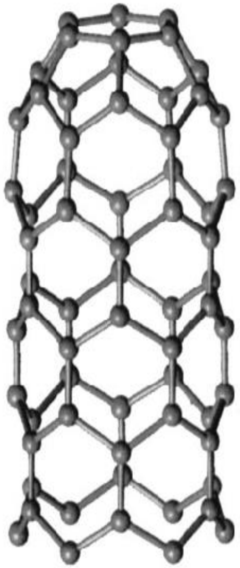
CNT is a tubular form of carbon with diameter as small as < 1 nm.
Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.





C_{60}



C_{36}

C_{20}

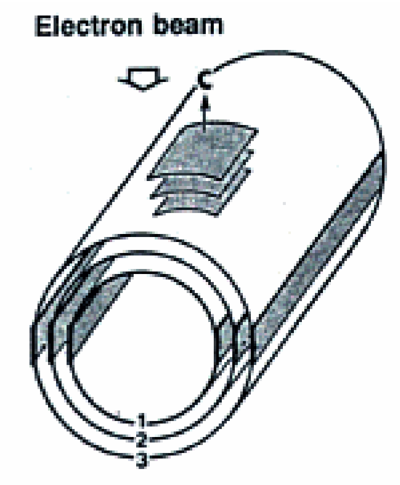
CNTs can be single-wall or multi-walls.
Open-end or Close-end.

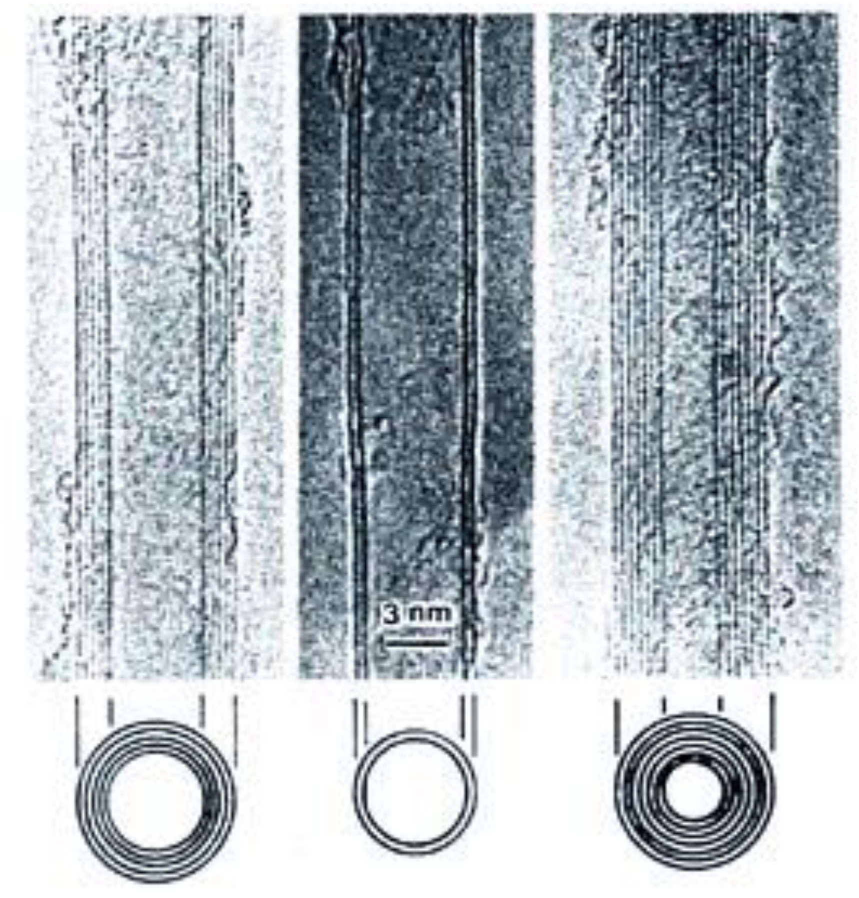
CNTs exhibit extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.

CNTs can be metallic or semiconducting depending on the way the graphene sheet is rolled-up.

Carbon Nanotubes (CNTs)

TEM images of a variety of MWCNTs



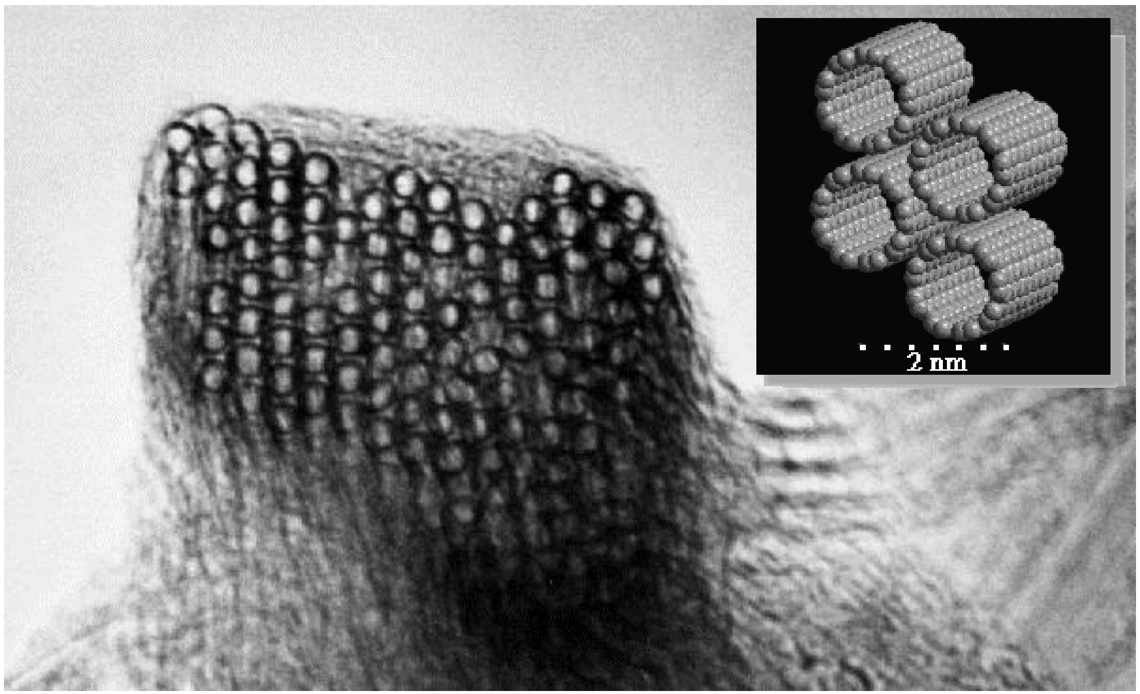


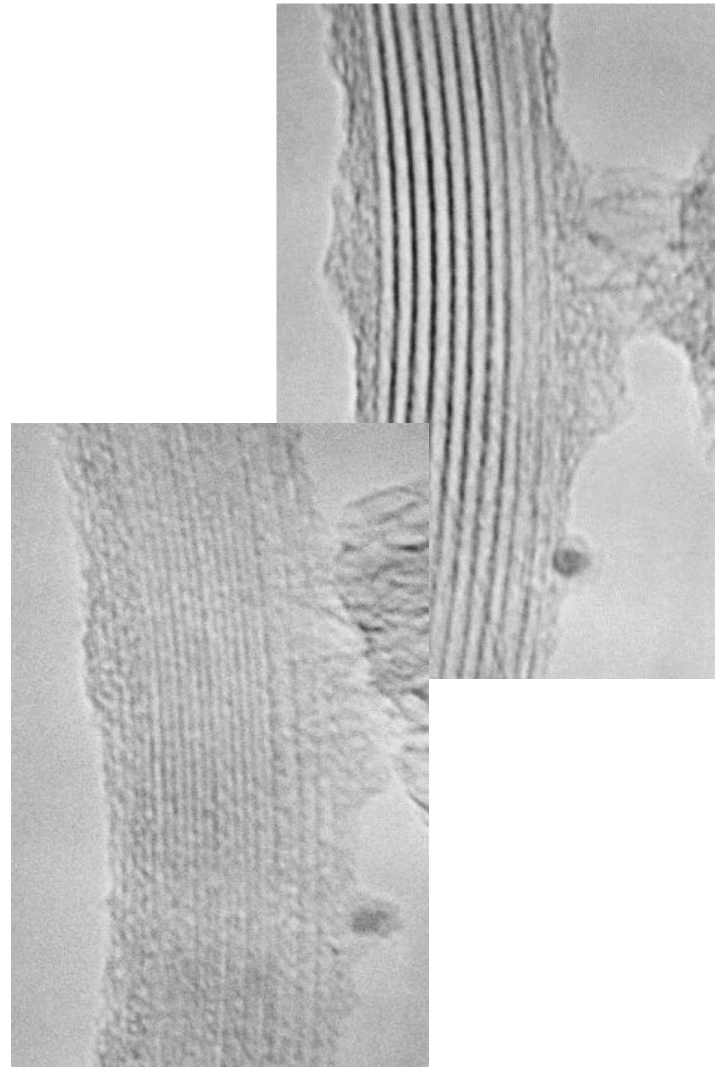
S. Iijima, Nature **354**, 56 (1991)

Carbon Nanotubes (CNTs)

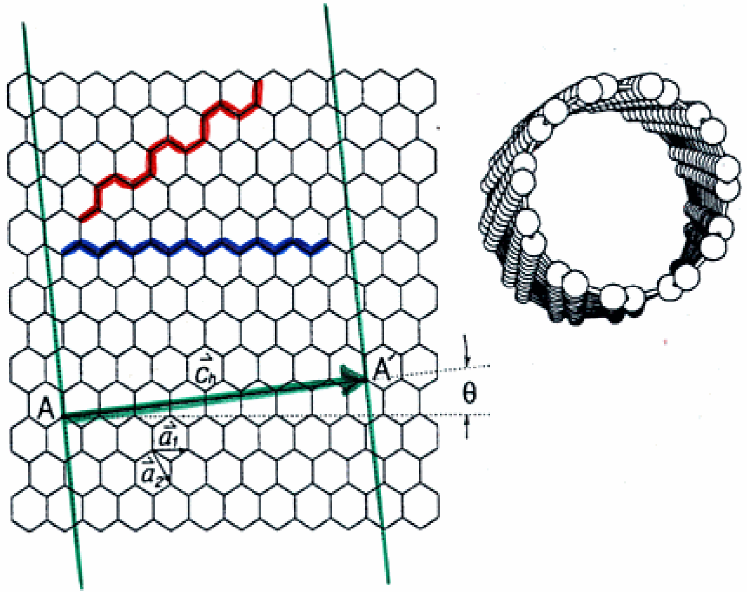
SWCNTs are typically aligned in triangular lattices forming bundles (lattice constant ≈ 1.7 nm; intertube separation ≈ 0.32 nm)

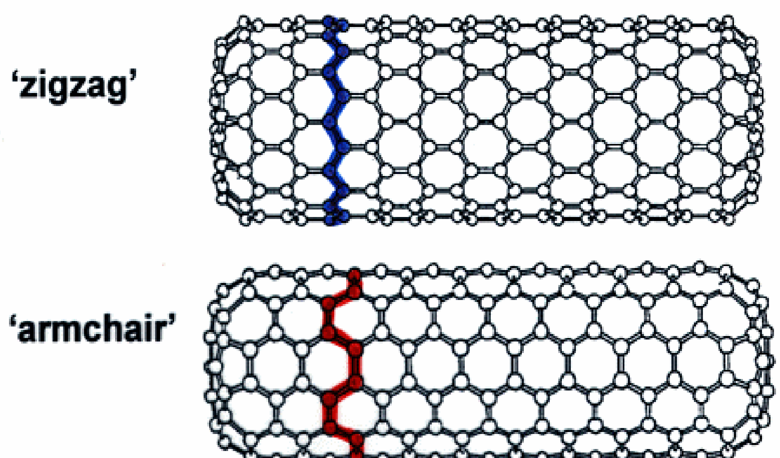
Sets of bundles form ropes

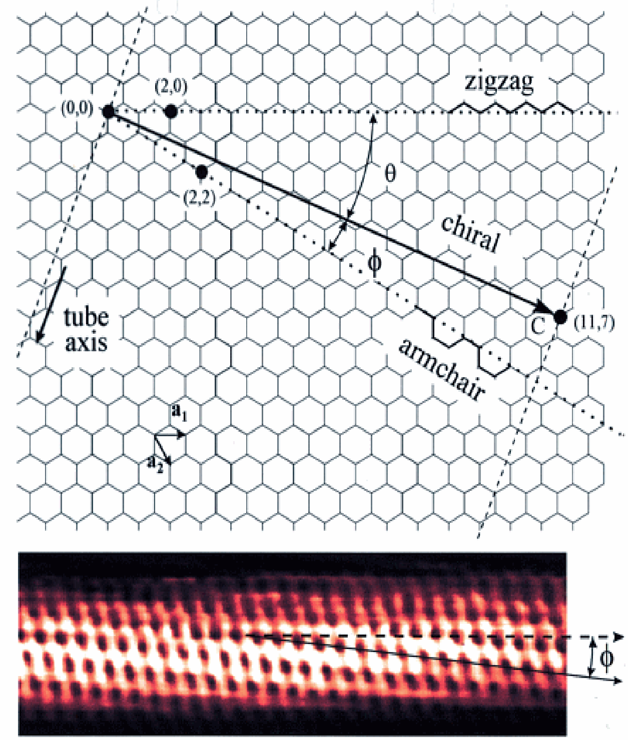




Various types of nanotubes



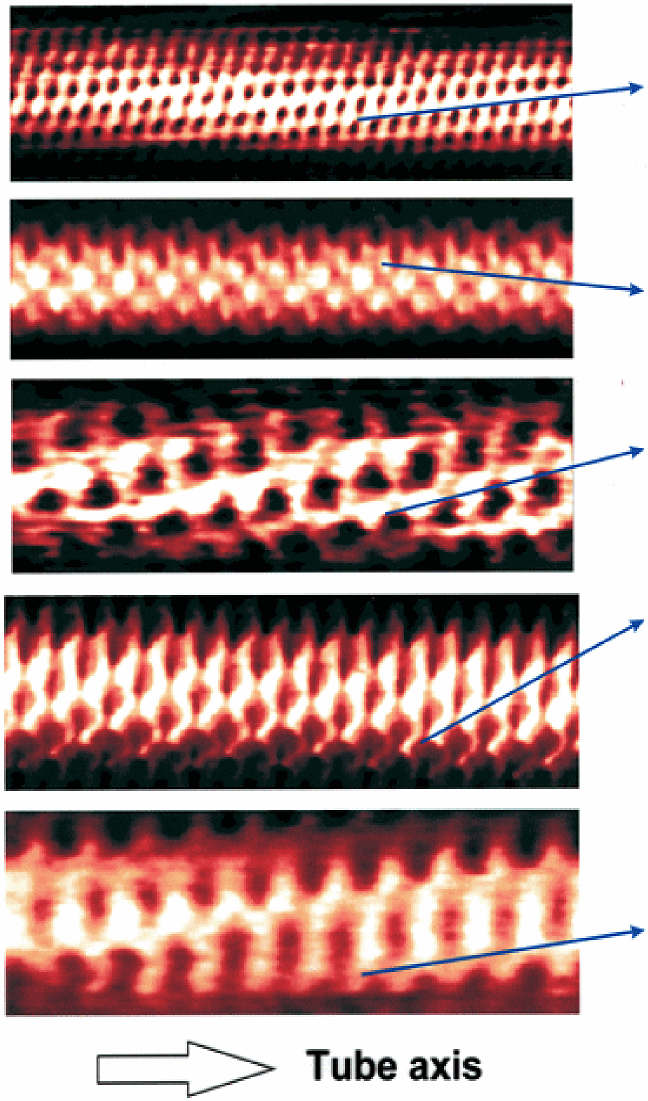




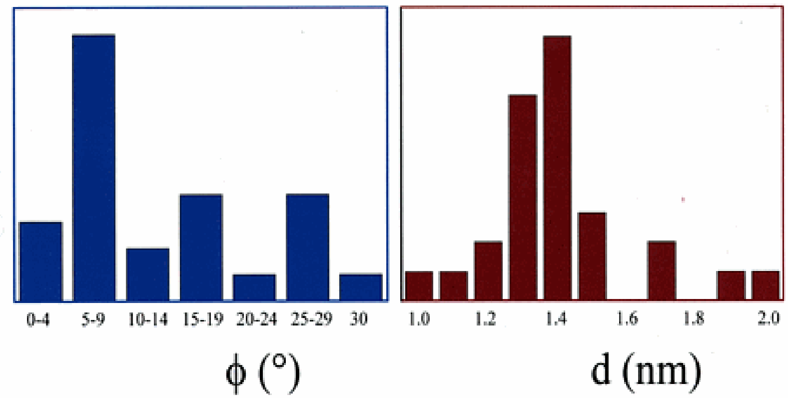
CNT diameter and chirality are defined by a vector perpendicular to the tube axis.

All possible tubes are obtained by spanning the vector between the armchair and zigzag directions.

large variety of chiral angles



Distribution chiral angles / diameters



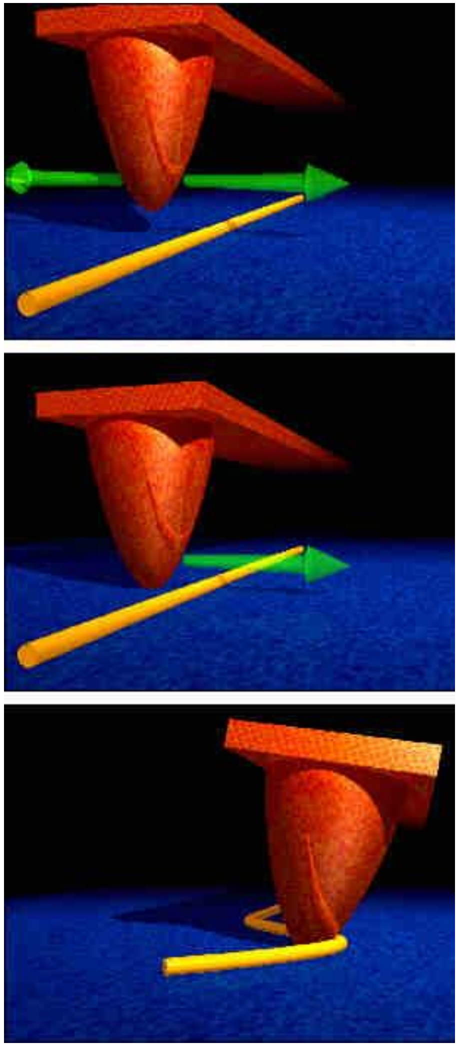
Large variety in chiral angle:

$0° < \phi < 30°$

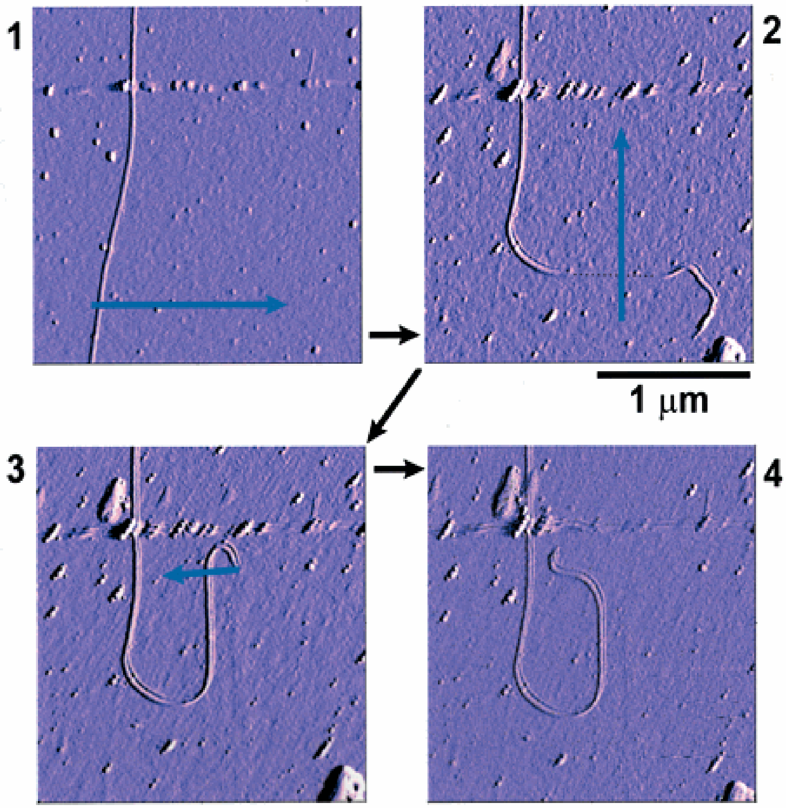
Diameter d around 1.2-1.5 nm

Scanning Tunneling Microscope (STM) allows the visualization of CNT at the atomic scale.

Nanotube manipulation

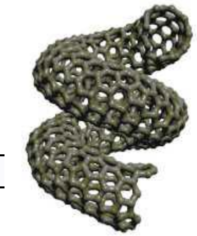


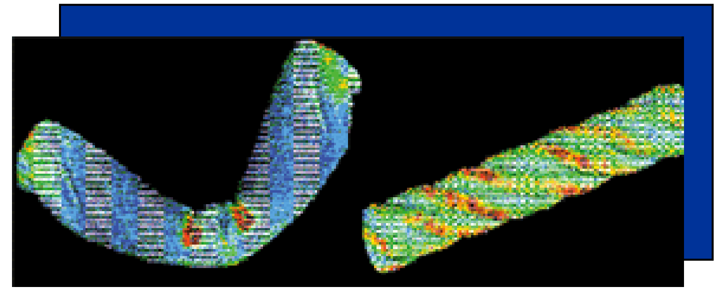
single-wall carbon nanotubes on SiO_2



The AFM and STM tips can move, bend, shift and collect nanotubes, like the fork does with spaghetti

CNT Properties



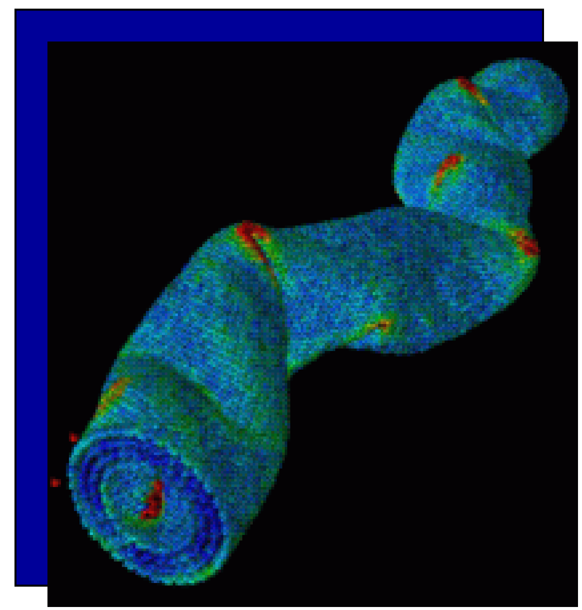


- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture

- Young's modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPA for C-fiber
  - strength to weight ratio 500 time > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy

- Maximum strain 10-30% much higher than any material

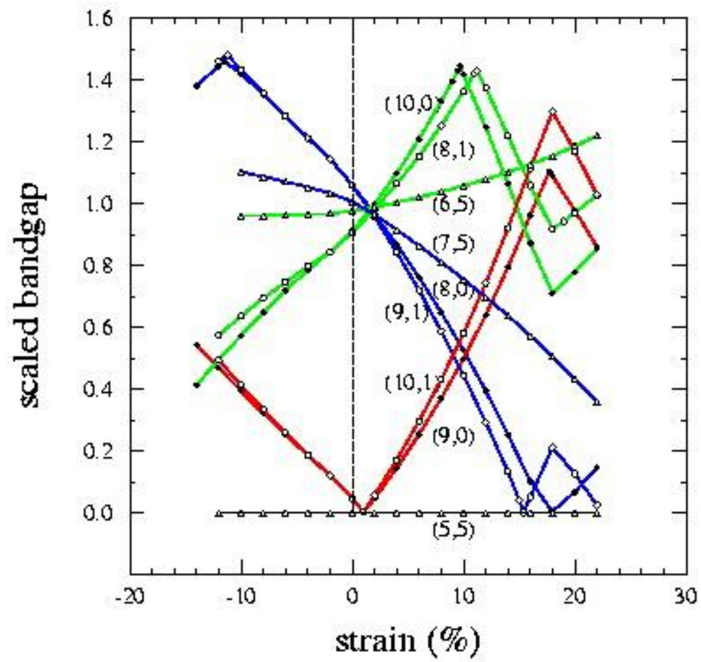
- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction



CNT (electronic) Properties

- Electrical conductivity six orders of magnitude higher than copper

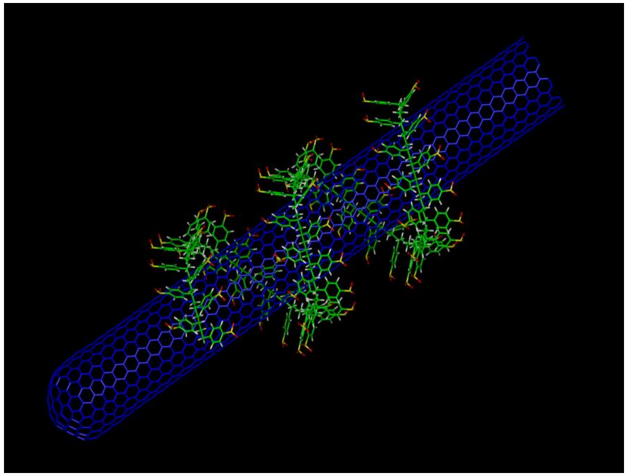
- CNT can be metallic or semiconducting depending on chirality and diameter
  - ‘tunable’ bandgap
  - electronic properties can be tailored through application of external magnetic field, mechanical deformation, absorption of gases, doping …



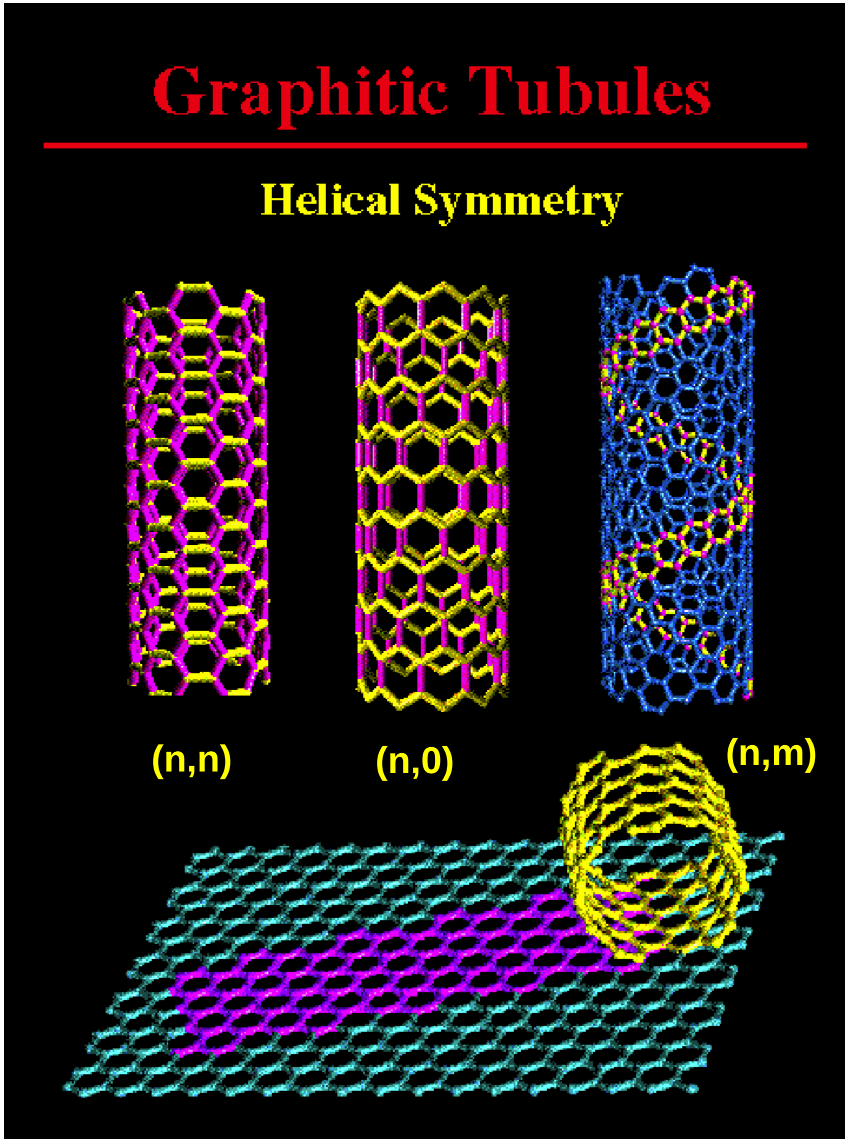
- Very high current carrying capacity

- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission

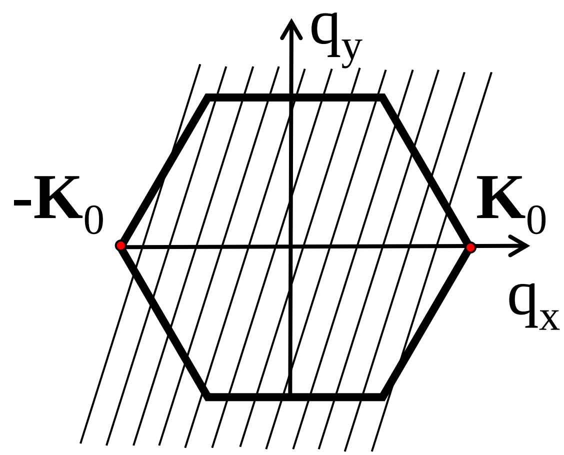
- Can be functionalized

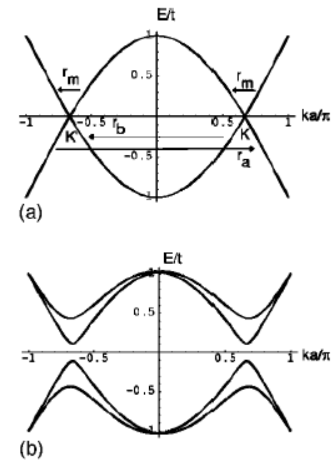


SWCNTs electronic structure: summary



- **Armchair** (n,n) – metals
- **Zig-Zag** (n,0) – mostly semiconductors
- **Chiral** (n,m) n≠m – mostly semiconductors and insulators

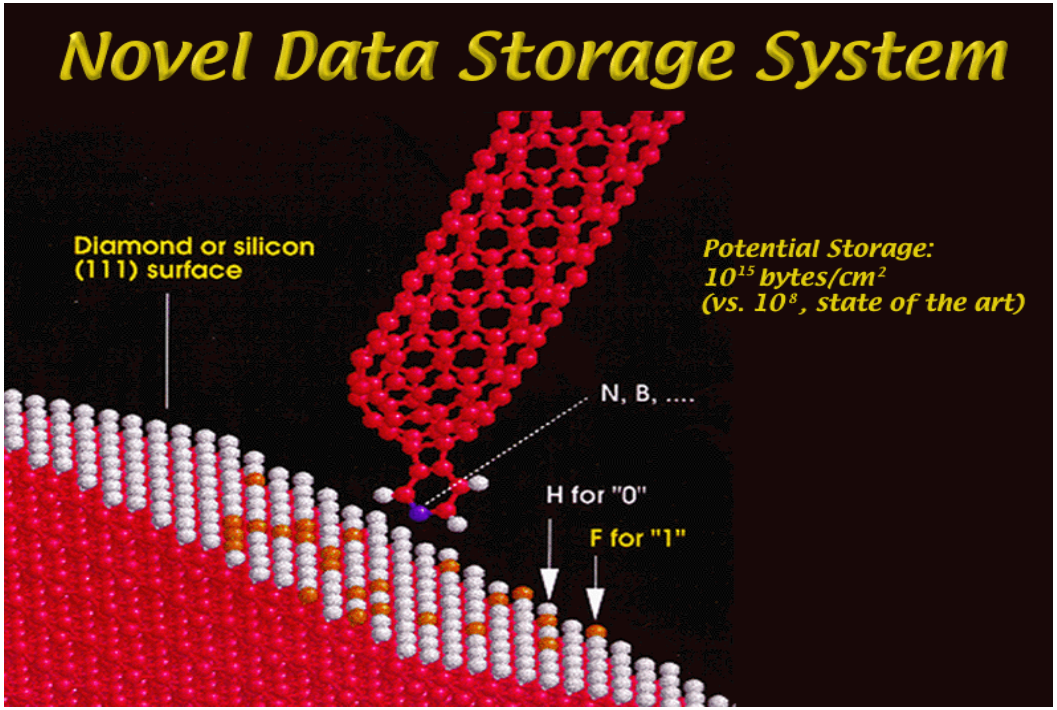




- **mod(3) rule**: if (n-m)=3l the tube might be metallic

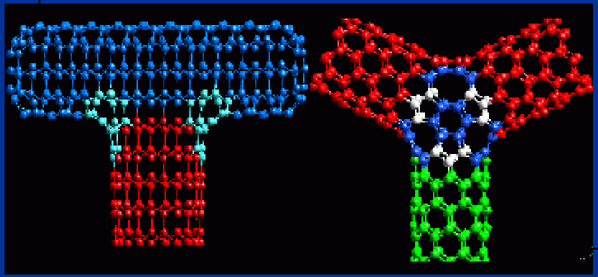
CNT Applications: Electronics

- CNT quantum wire interconnects
- Diodes, transistors and flip-flop for computing
- Capacitors
- Data Storage
- Field emitters for instrumentation
- Flat panel displays
- THz oscillators



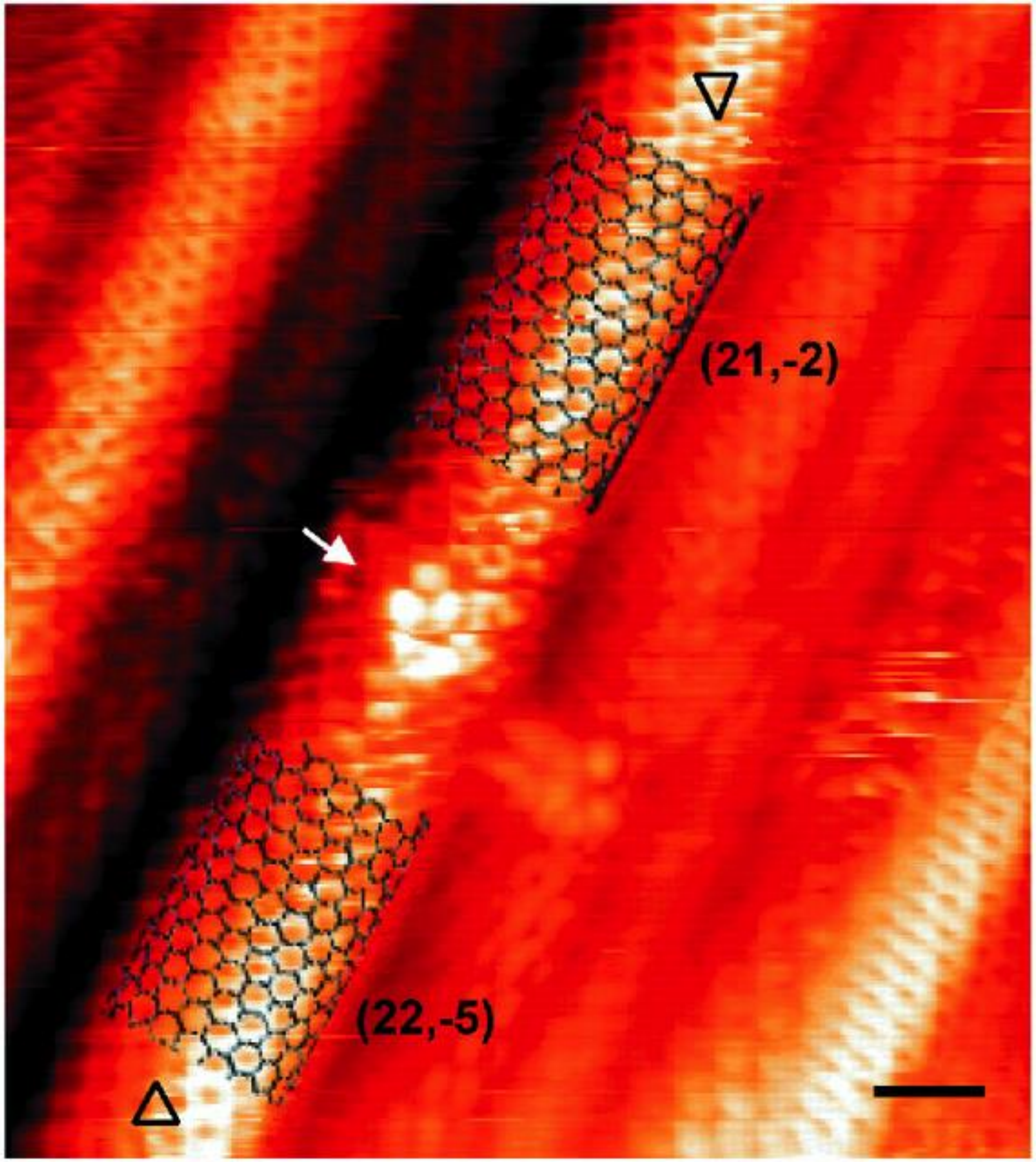
Challenges

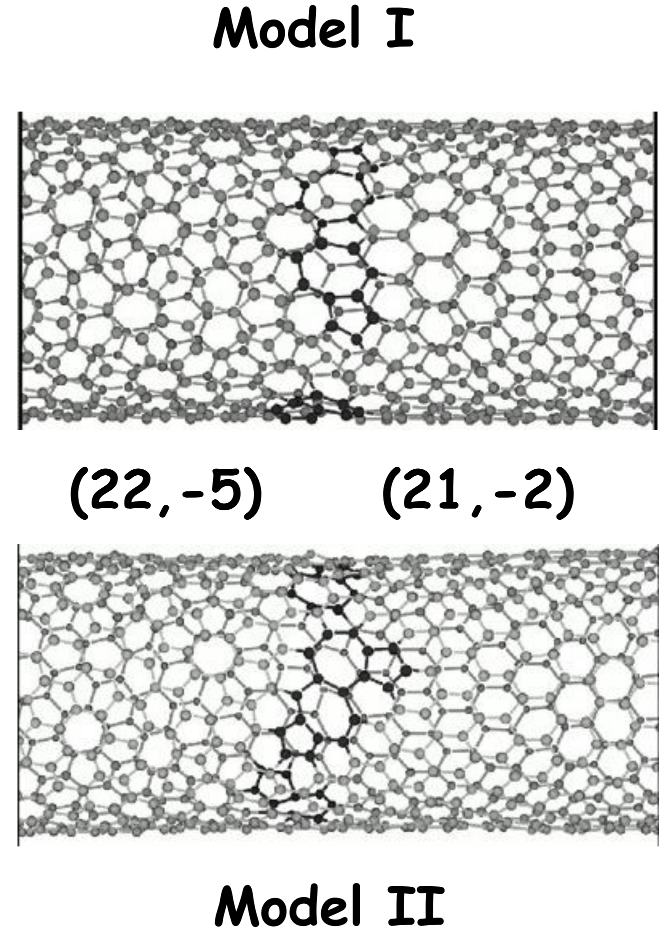
- Control of diameter, chirality
- Doping, contacts
- Novel architectures (not CMOS based!)
- Development of inexpensive manufacturing processes



CNT "T" and "Y" Junctions

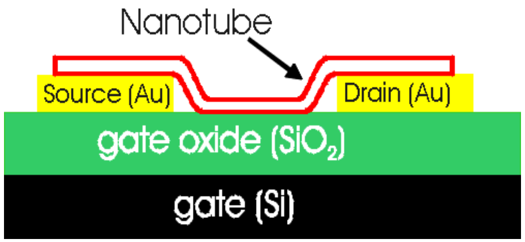
CNT welding: wire connections, diodes ...

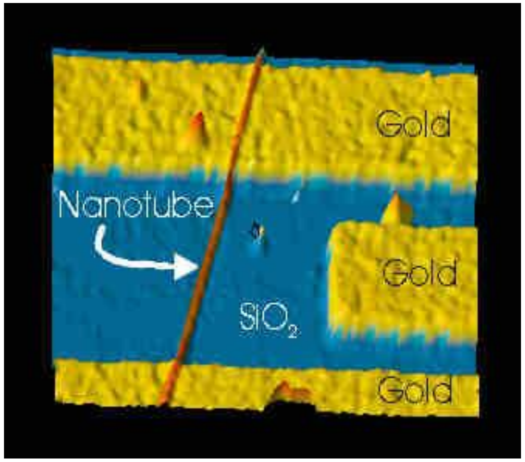


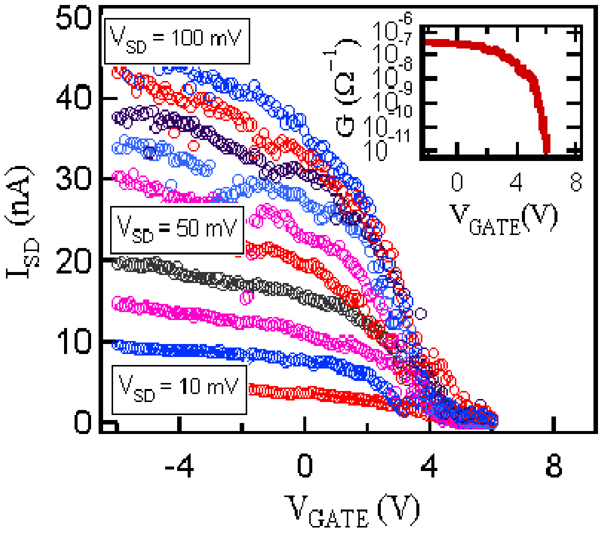


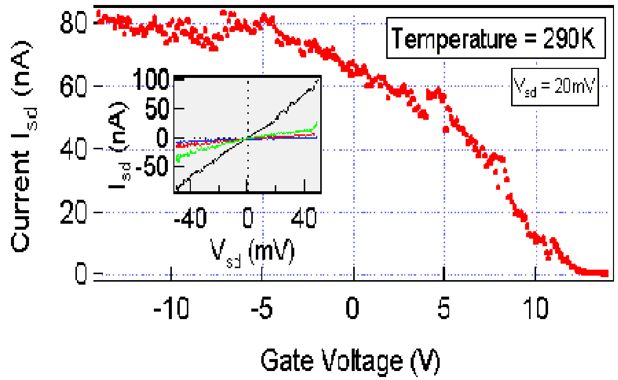
Min Ouyang *et al.*,
Science **291**, 97 (2001)

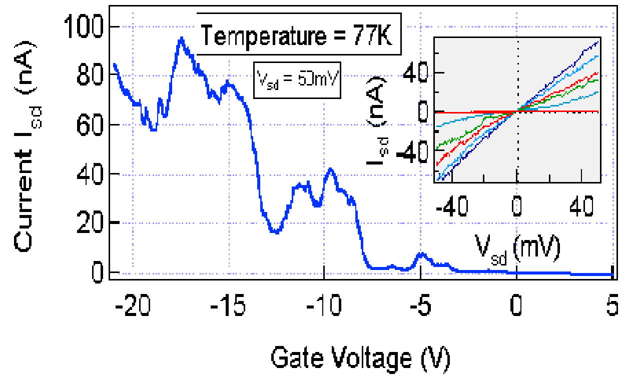
CNT transistor

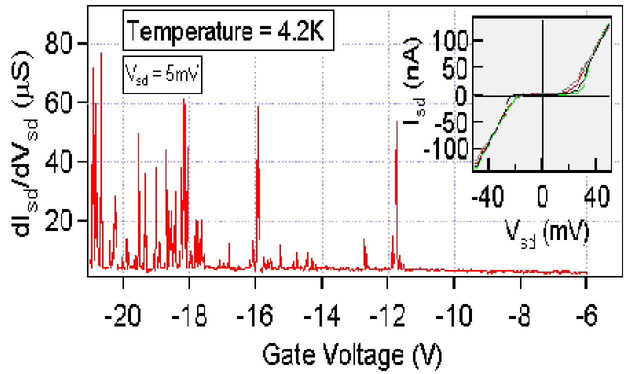




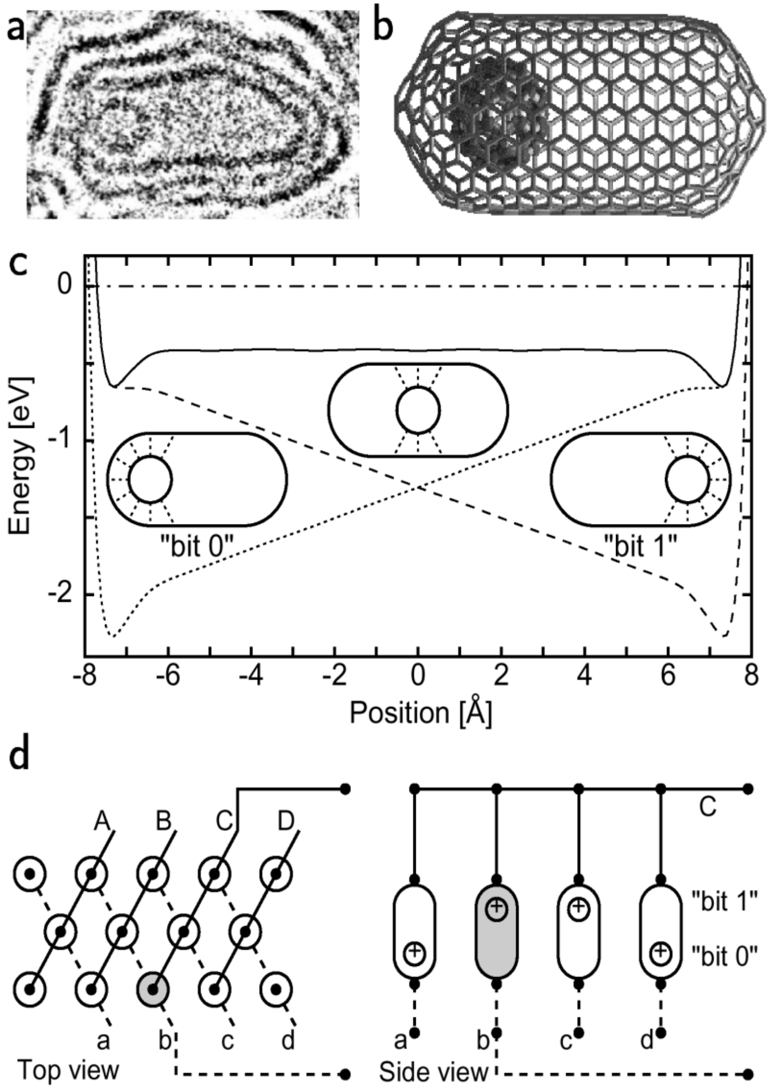






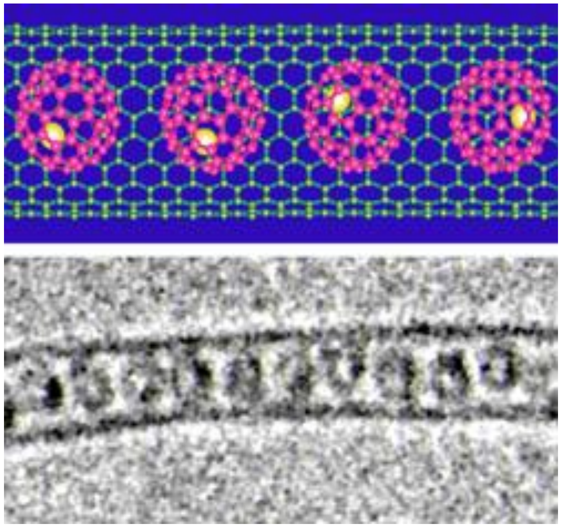


A memory element: the bucky shuttle

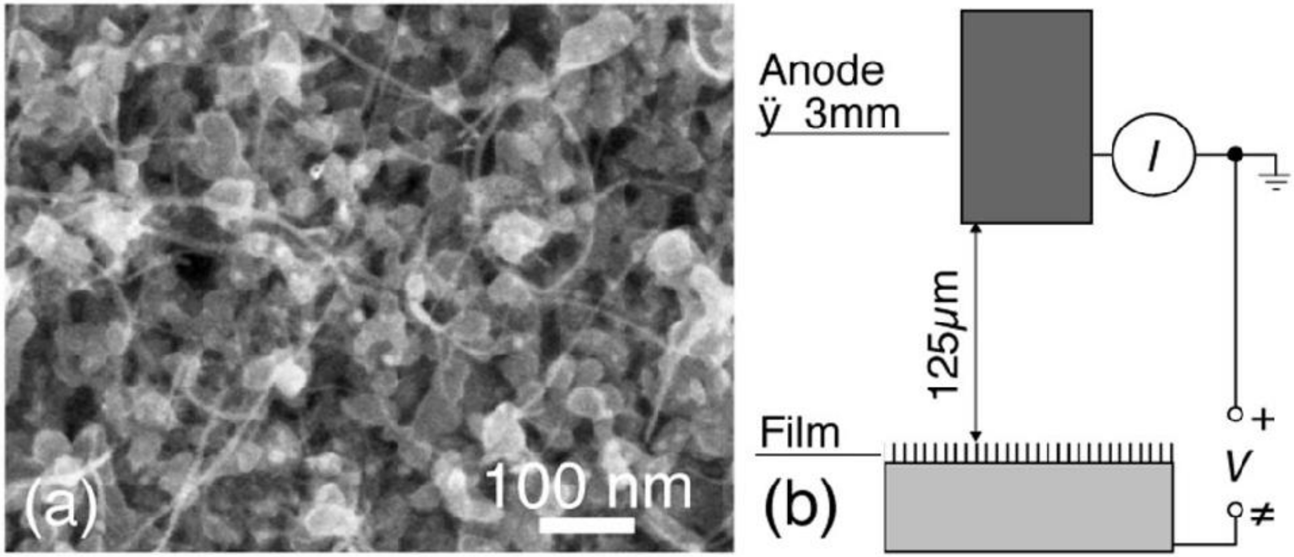


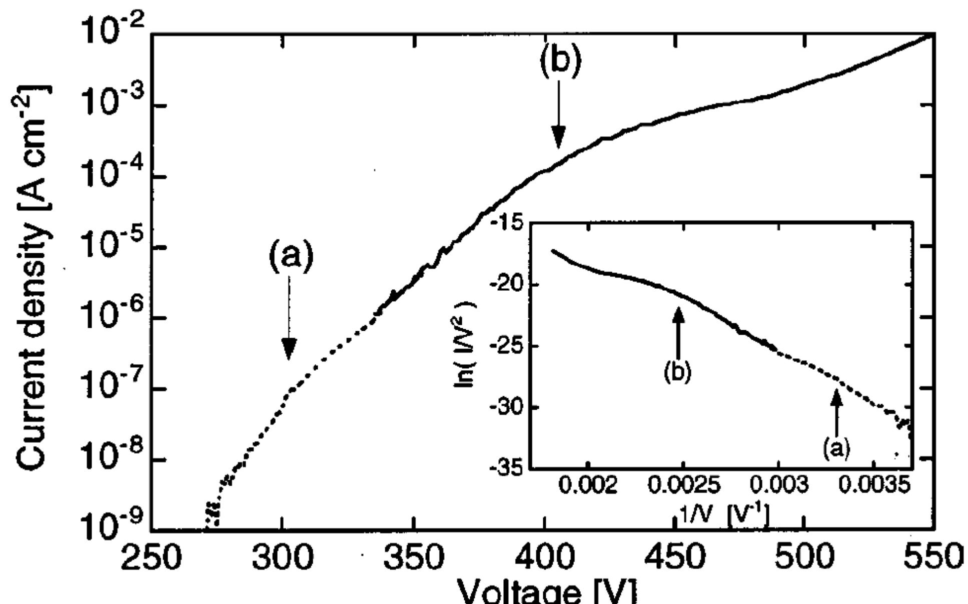
20 ps switching

A dream? No, CNT can be filled with fullerenes: the CNT-peapods



CNT field emission

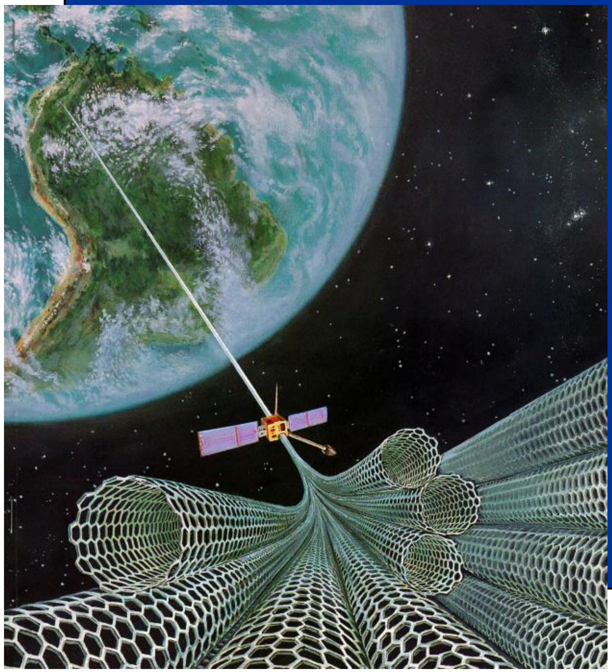




J-M. Bonard *et al.*,
Applied Phys. Lett. **73**, 918 (1998)

CNT Applications: Structural, Mechanical

- High strength composites
- Cables, tethers, beams
- Multifunctional materials
- Functionalize and use as polymer back bone
  - plastics with enhanced properties like ‘blow molded steel’
- Heat exchangers, radiators, thermal barriers, cryo-tanks
- Radiation shielding
- Filter membranes, supports
- Body armor, space suits

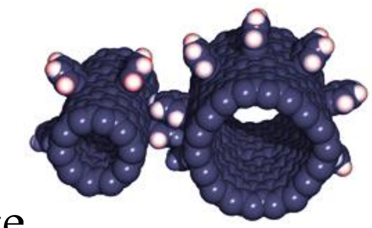


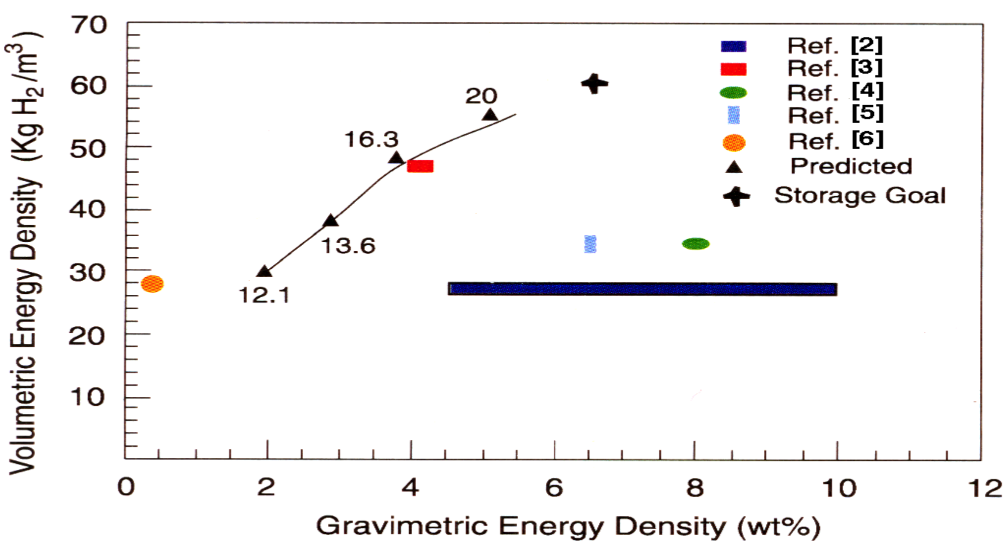
Challenges

- Control of properties, characterization
- Dispersion of CNT homogeneously in host materials
- Large scale production
- Application development

CNT Applications:
Sensors, Mol. Mechanics, Biology

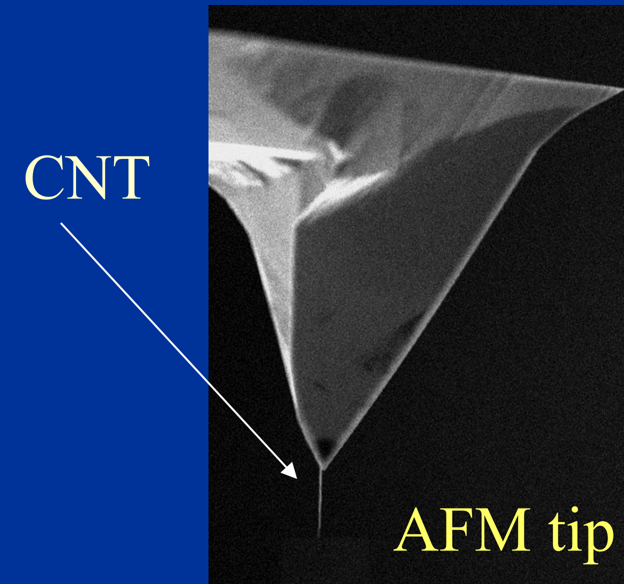
- CNT based microscopy: AFM, STM…
- Nanotube sensors: force, pressure, chemical…
- Biosensors for Astrobiology
- Molecular gears, motors, actuators
- Batteries, Fuel Cells: H_2, Li storage
- Nanoscale reactors, ion channels





Challenges

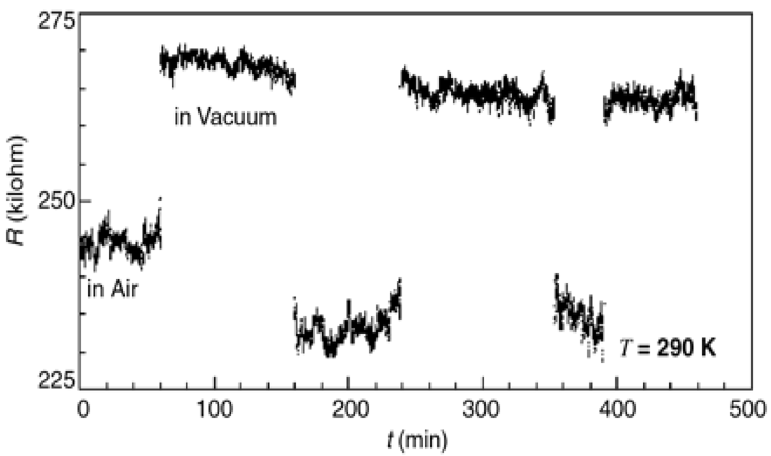
- Controlled growth
- Functionalization with probe molecules, robustness
- Integration, signal processing
- Fabrication techniques



CNT as chemical sensors

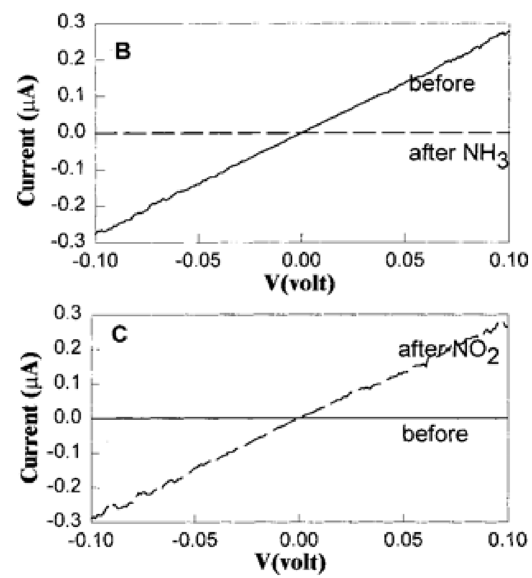
- **Advantages**
  - **High adsorption surface area**
  - **Changing electrical properties at room temp.**
  - **Detect very small concentrations (ppm) of O_2, NO_2, NH_3**

- **Semiconducting nanotube**
- **Depletion or accumulation of carriers depending on species**



Change of electrical resistance of SWNT with exposure to O_2

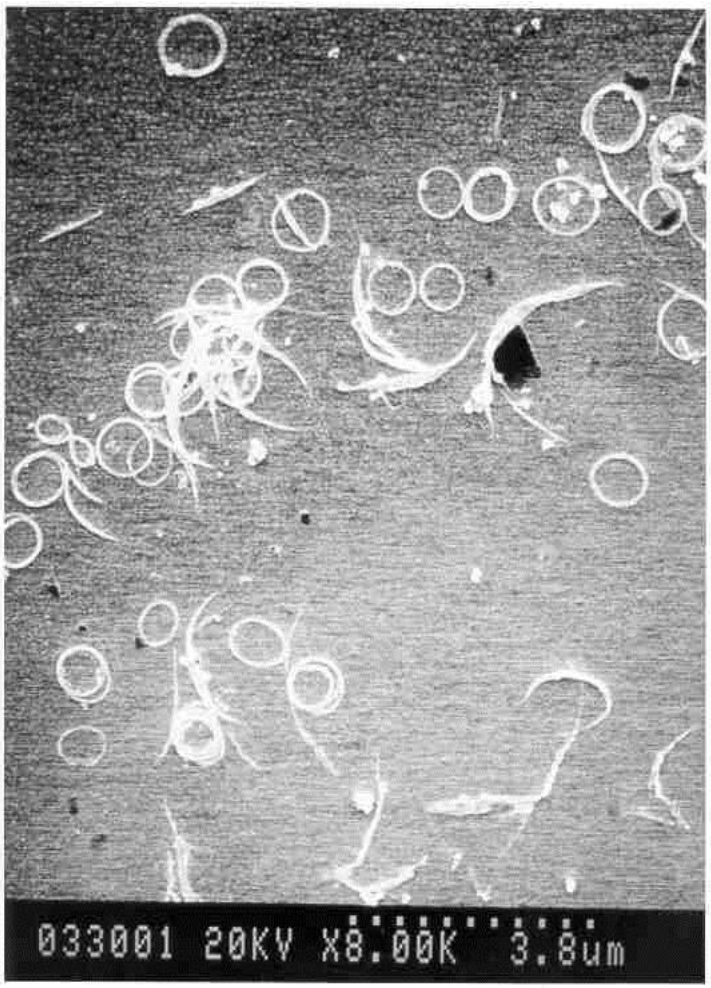
Collins *et al., Science (2000)*

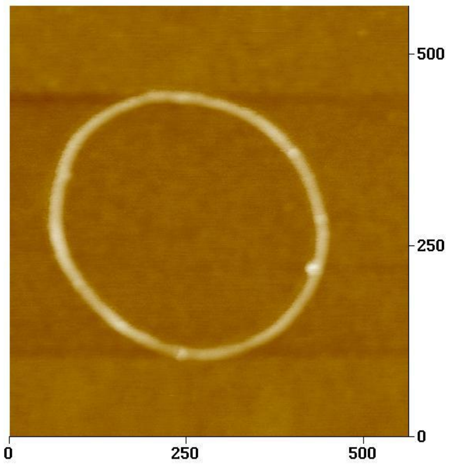


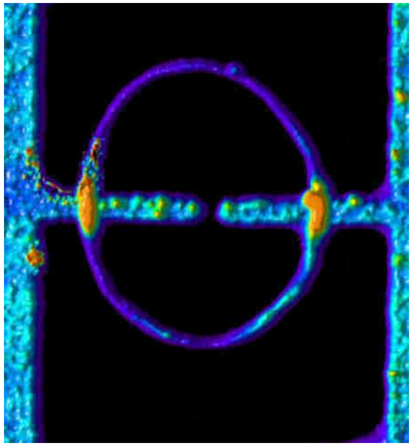
V-I curves for NH_3 and NO_2 exposure

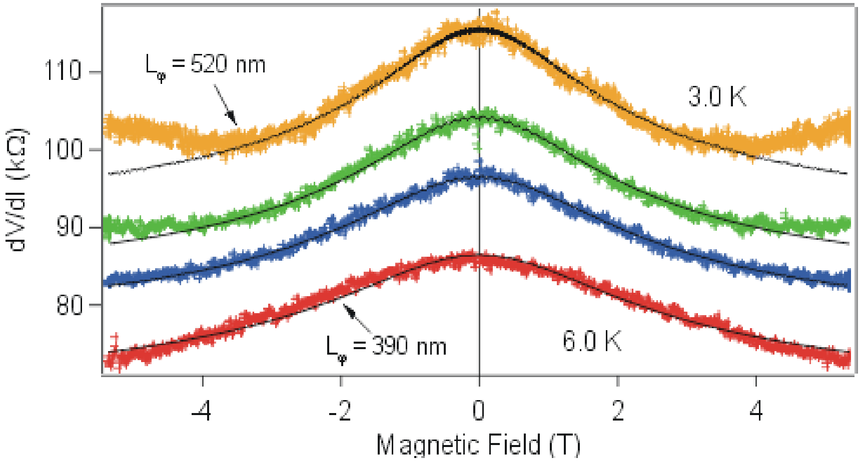
Kong *et al., Science (2000)*

Nano sensors: CNT coil



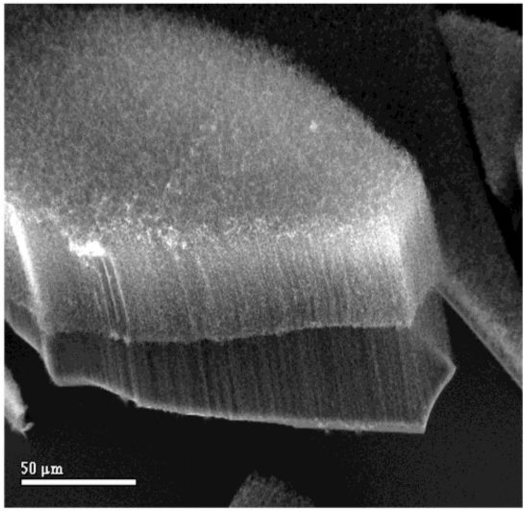


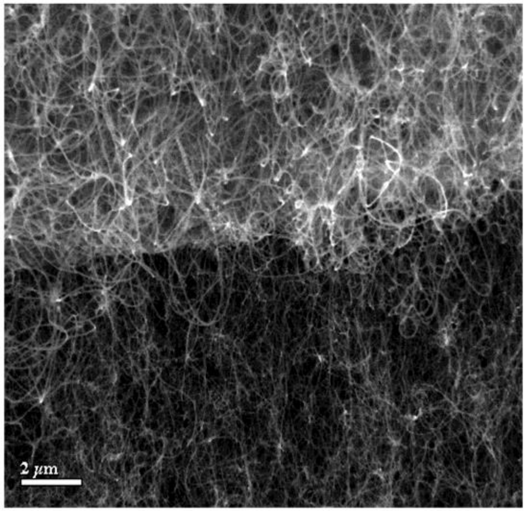




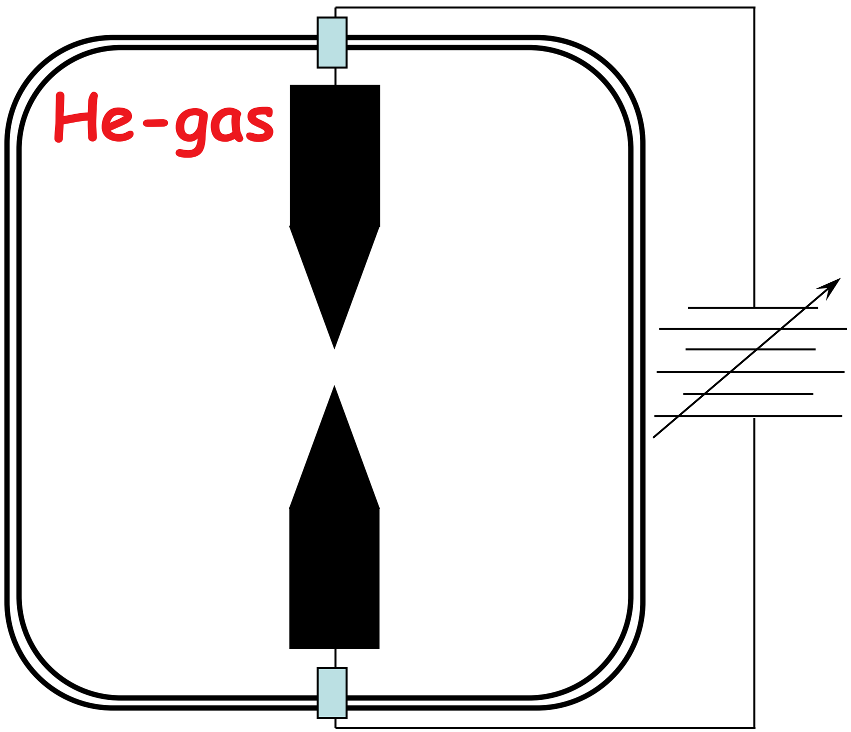
CNT Synthesis

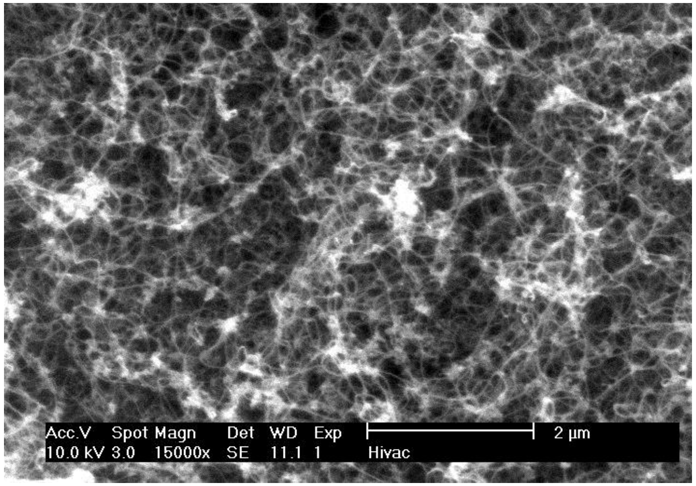
- CNT has been grown by laser ablation (pioneering at Rice) and carbon arc process (NEC, Japan) - early 90s.
  - SWNT, high purity, purification methods
- CVD is ideal for patterned growth (electronics, sensor applications)
  - Well known technique from microelectronics
  - Hydrocarbon feedstock
  - Growth needs catalyst (transition metal)
  - Multiwall tubes at 500-800° deg. C.
  - Numerous parameters influence CNT growth





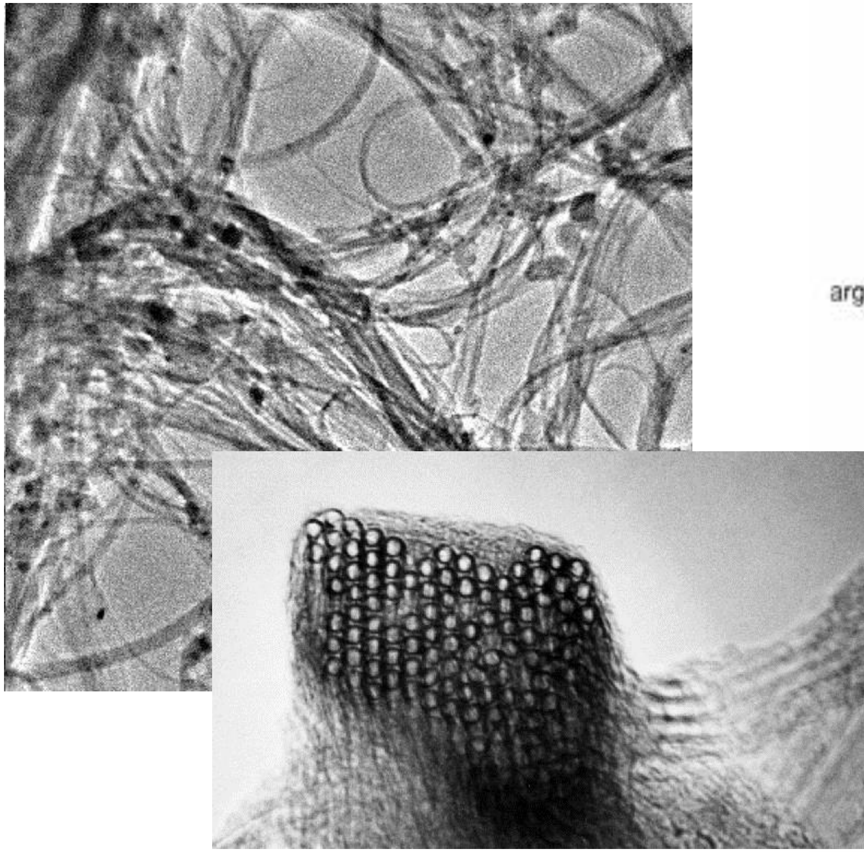
CNT growth by arc-discharge

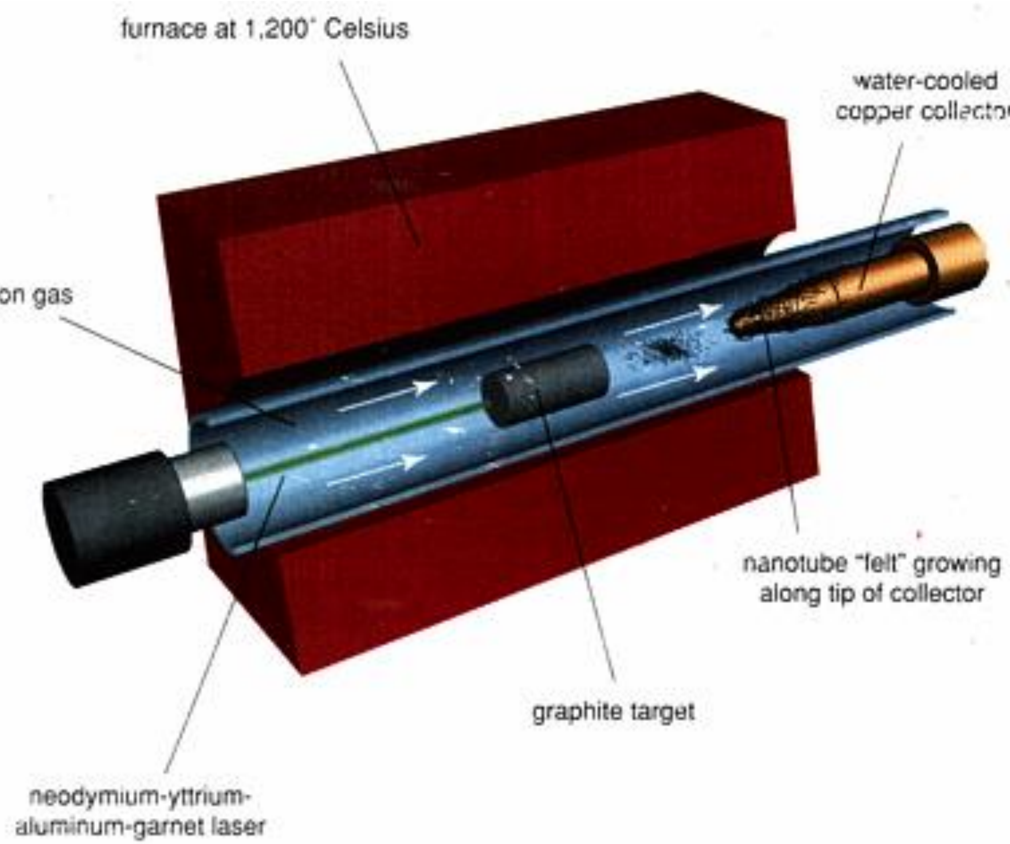




- Carbon atoms from graphite electrodes are sublimated in a plasma.
- High-quality SWCNTs and MWCNTs in gram quantities.
- Need of a metal (Ni, Co,Fe,…) catalyst and purification.
- Disordered CNT tangles, amorphous carbon (a-C), fullerenes, etc…

CNT growth by laser-ablation

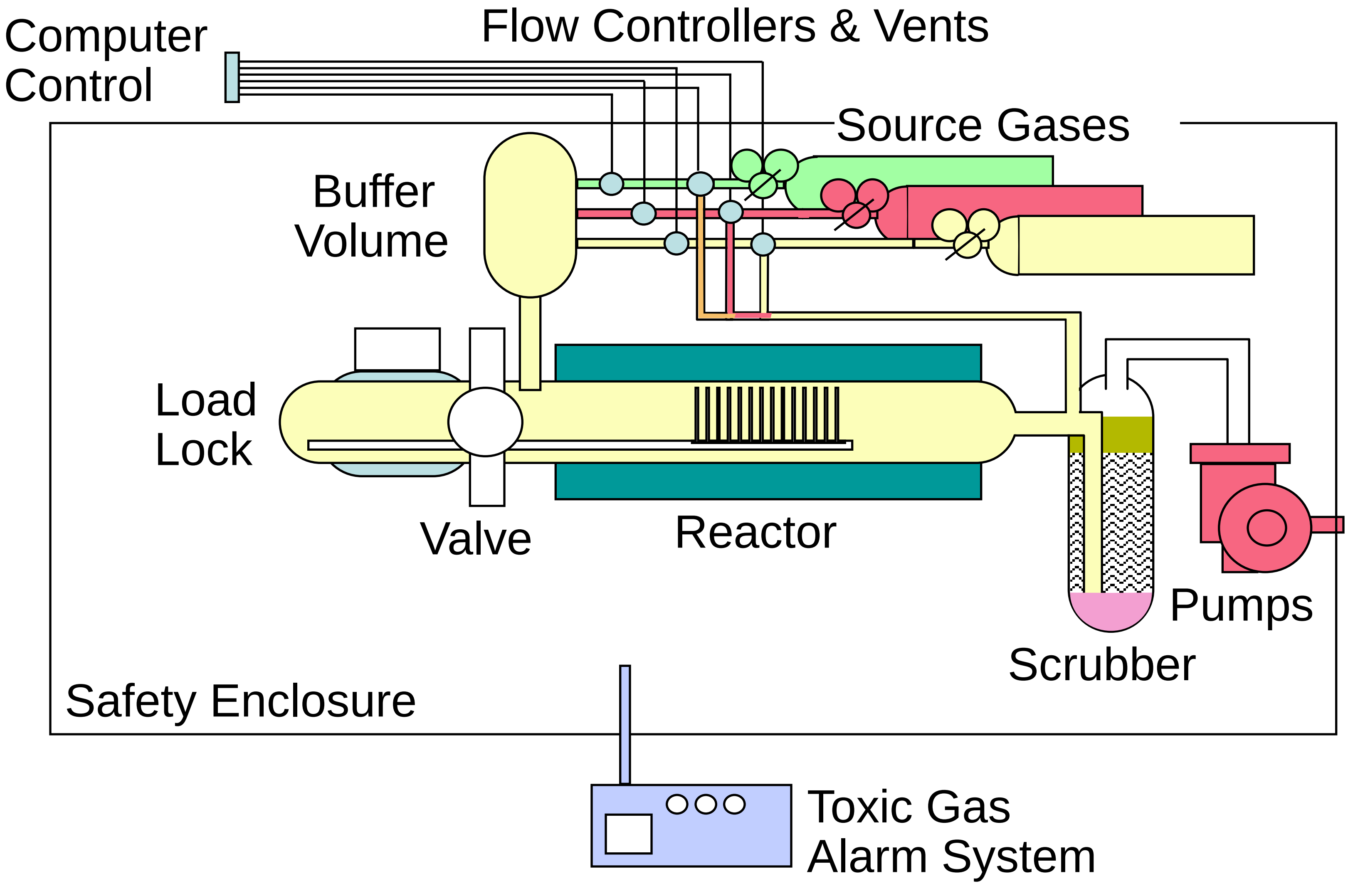




- Massive production (gr scale) of high-quality SWCNTs assembled in bundles: disordered material, a-C
- Metal catalysts (Ni, Co, Fe…) in the graphite target

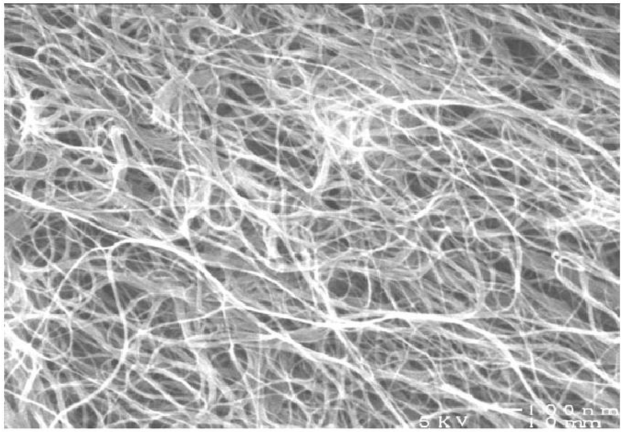
Purification needed

CNT growth by (PE)CVD

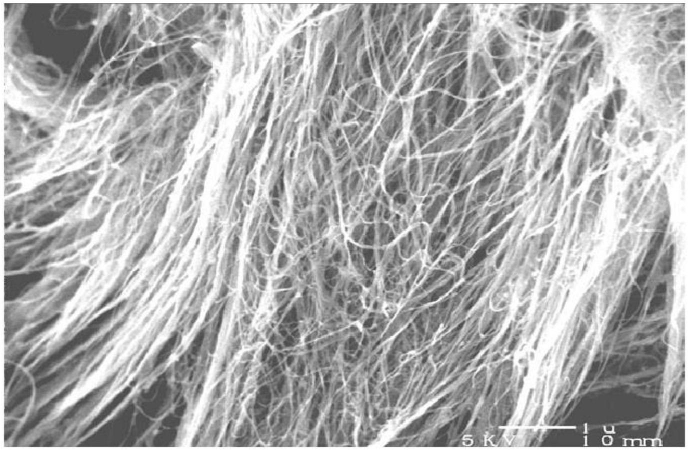


Purification Method for SWCNTs

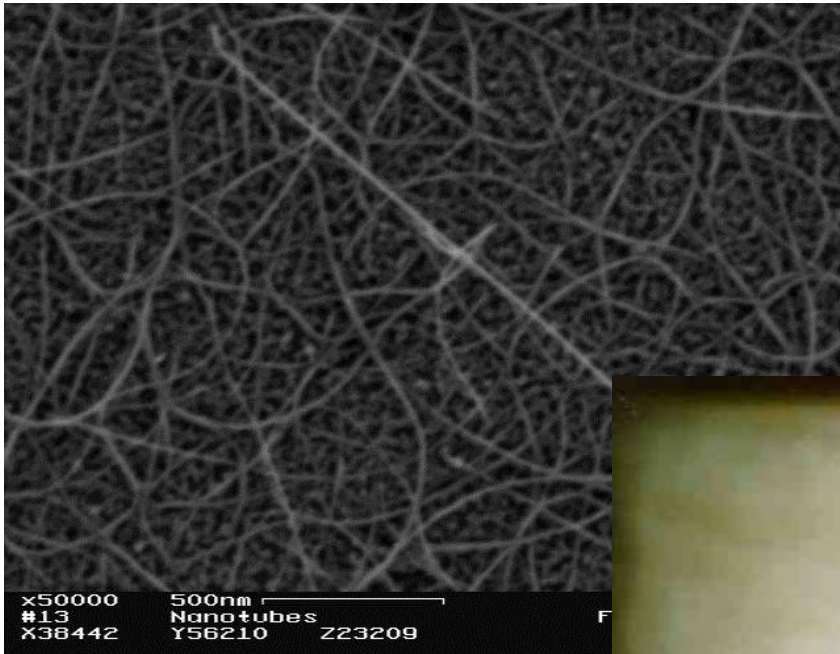
After removing fullerenes via appropriate solvents (typically Toluene), several treatments of the as-grown material in a nitric/sulfuric acid solution to remove the metal catalyst species. Washing in de-ionized water and methanol refluxes. Oxidation in a mixture of sulfuric acid and hydrogen peroxide. Washing in NaOH reflux. SWCNTs can be dissolved/dispersed in NaOH aqueous solutions containing sodium-laureth-sulfate (Triton X-100 surfactant): filtration gives SWCNT bucky-papers



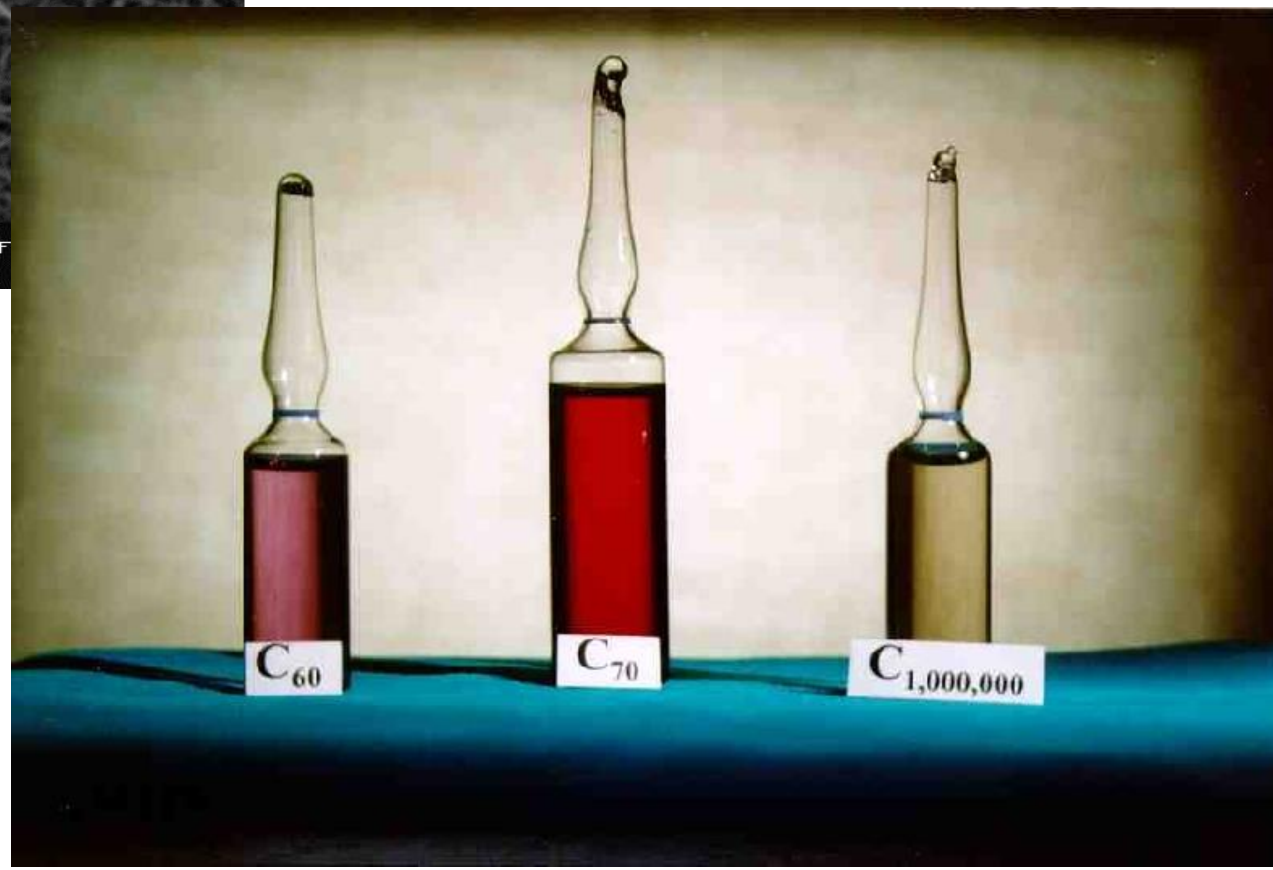
Jie Liu *et al.*,
Science **280**, 1253 (1998)



Purified material

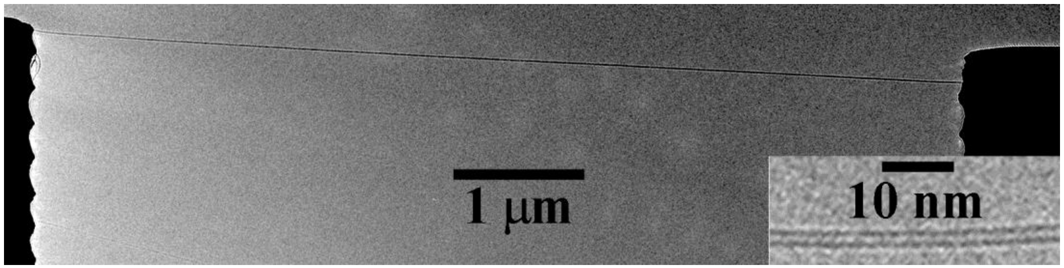


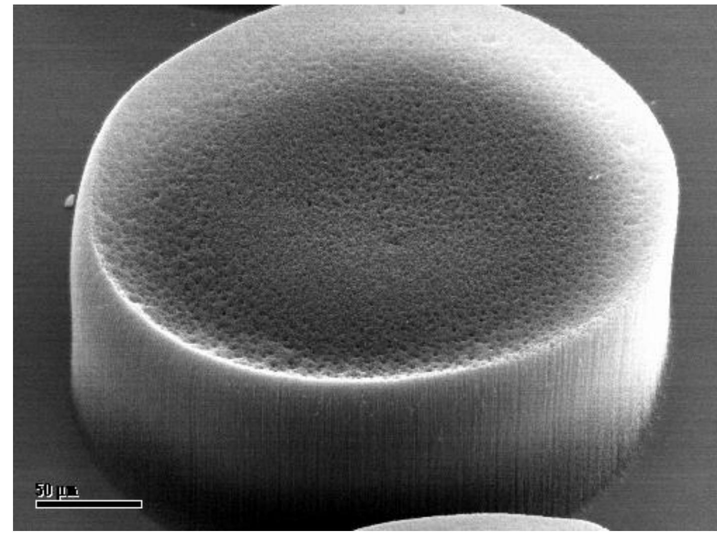
SWCNTs bundles
in a bucky-paper

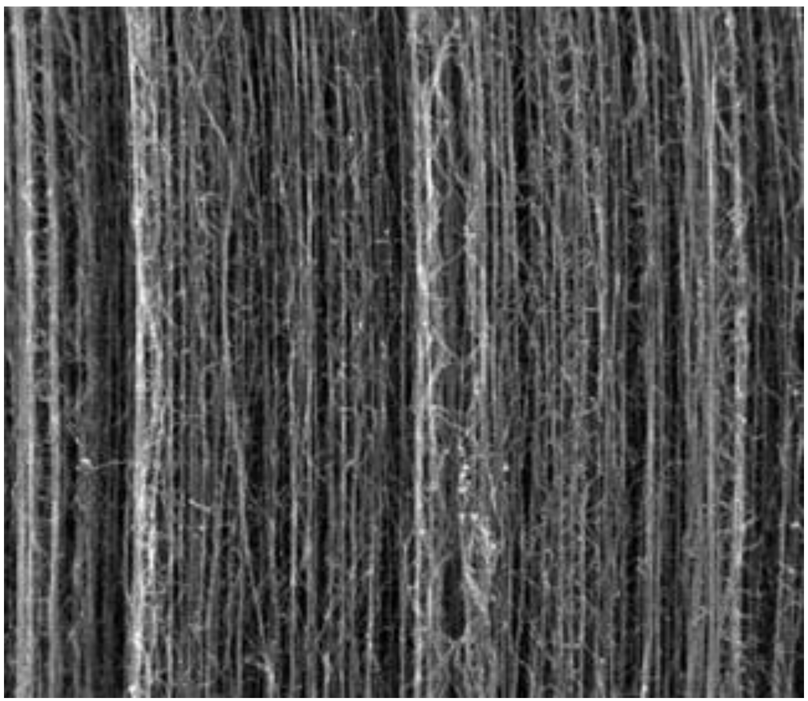


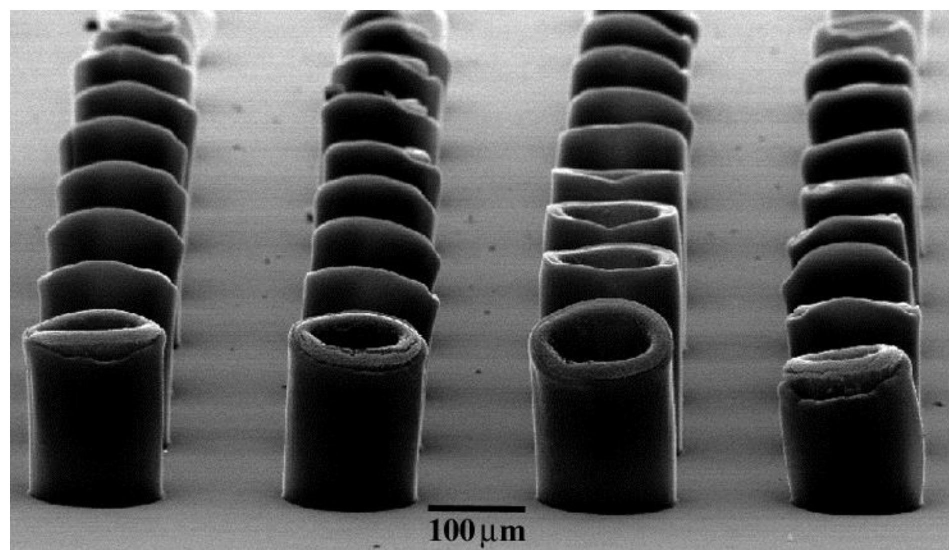
Fullerenes and SWCNTs in solution

CNT patterned & controlled growth

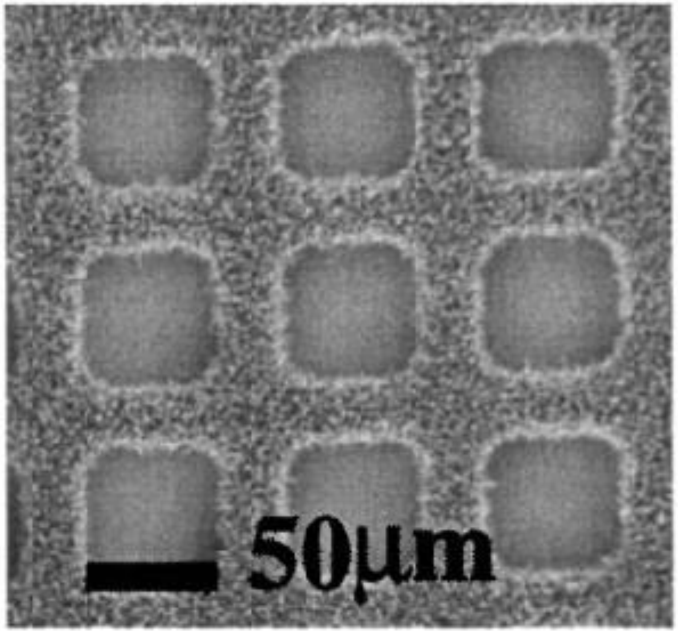


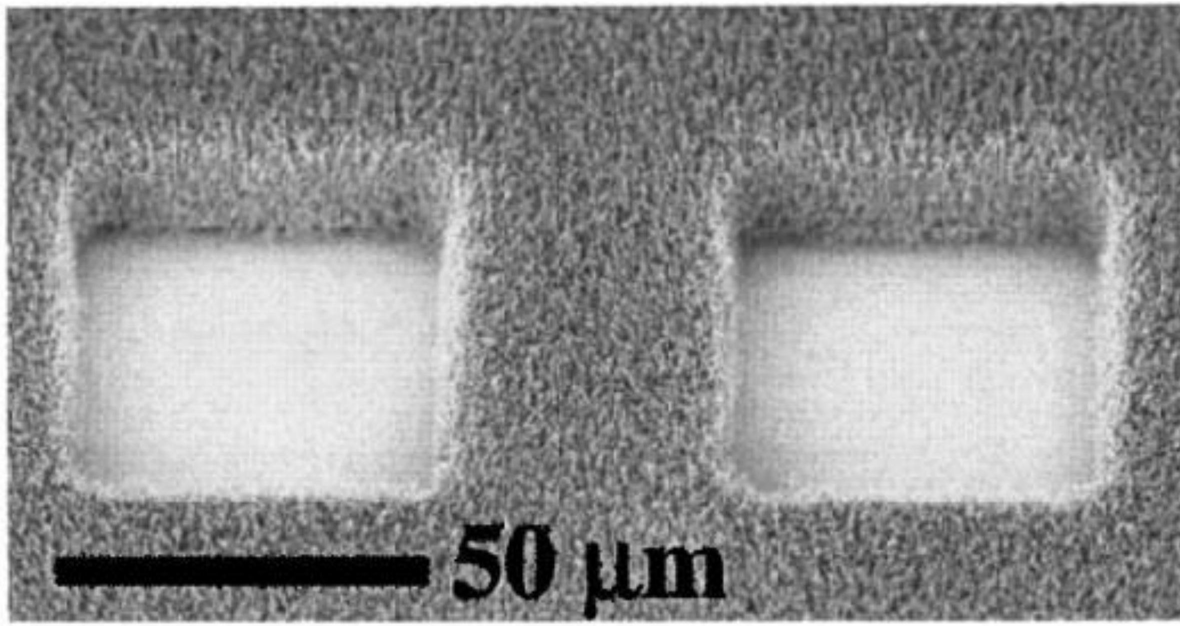


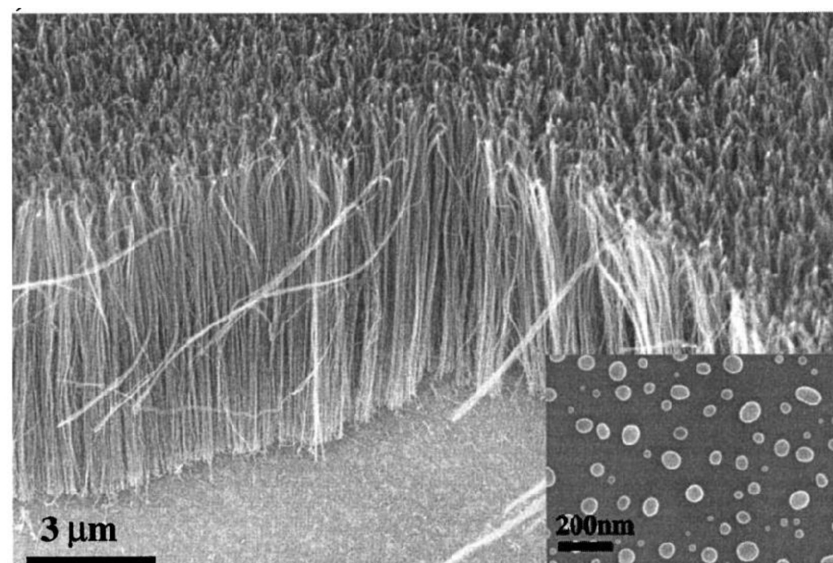




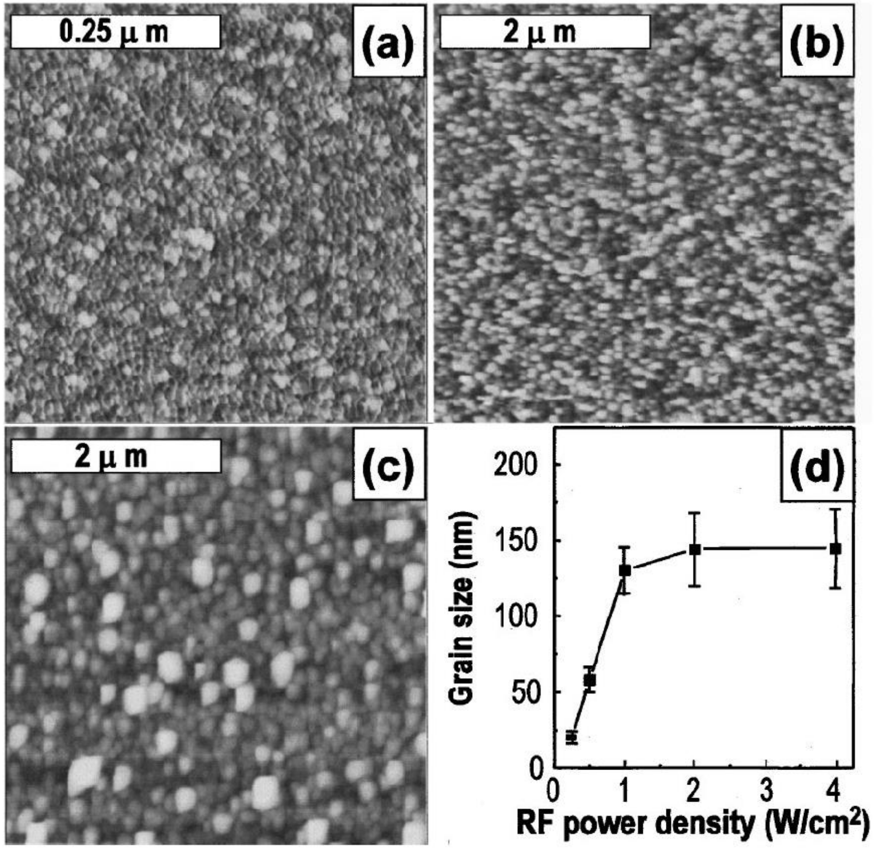
Nano-Patterning of Aligned MWCNTs

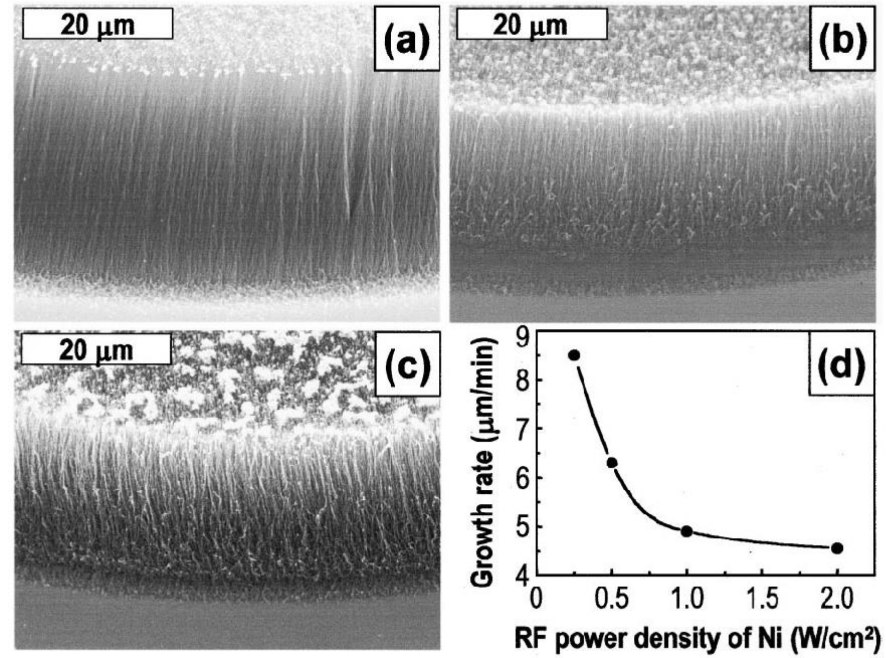


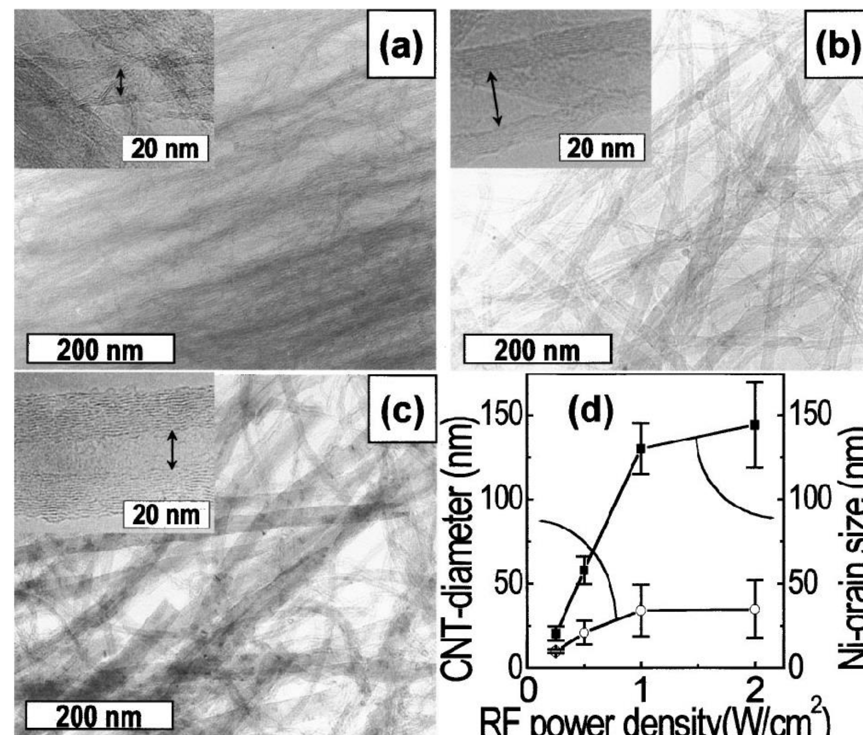




C. Bower *et al.*, Appl. Phys. Lett. **77**, 830 (2000)



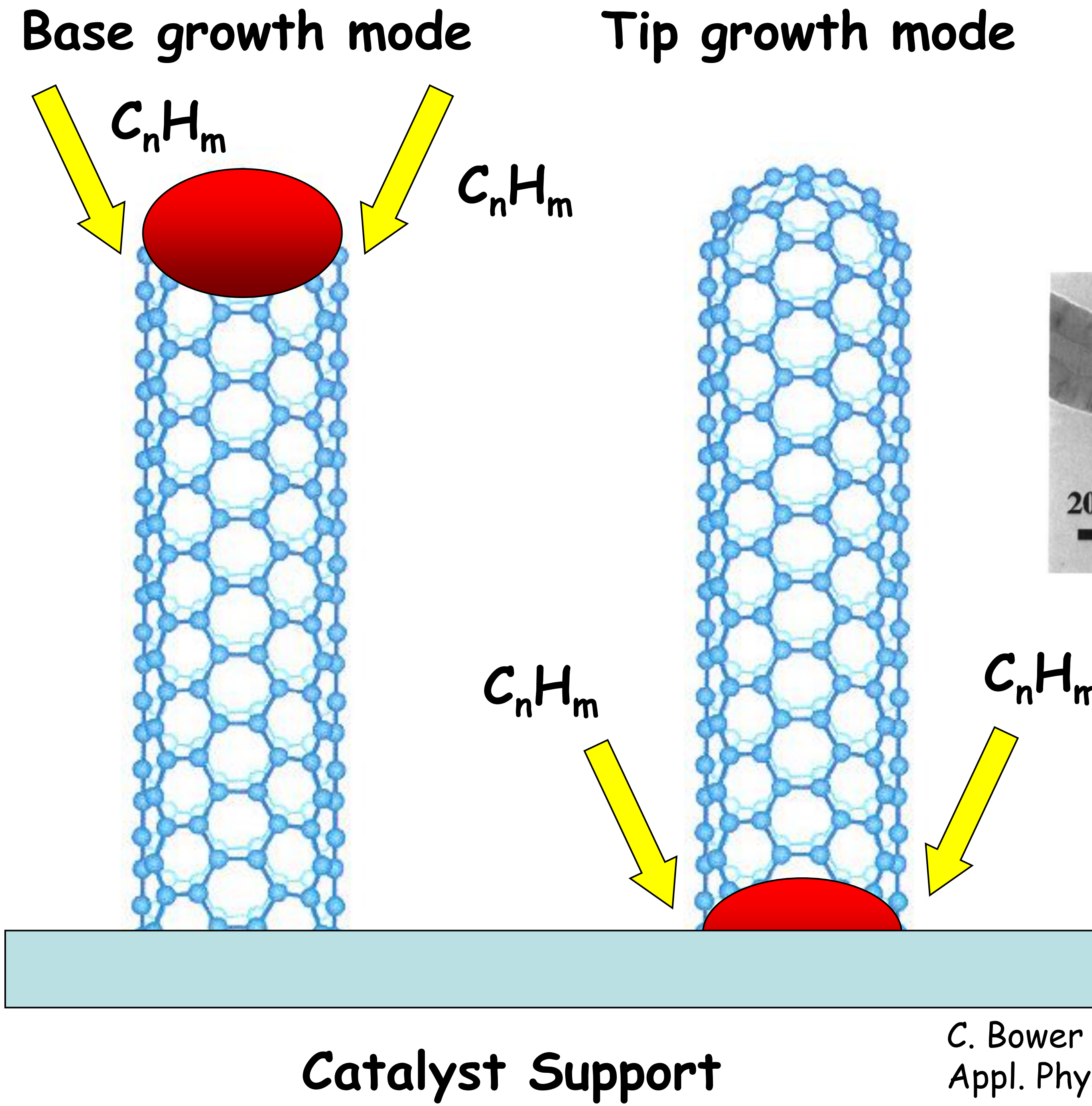


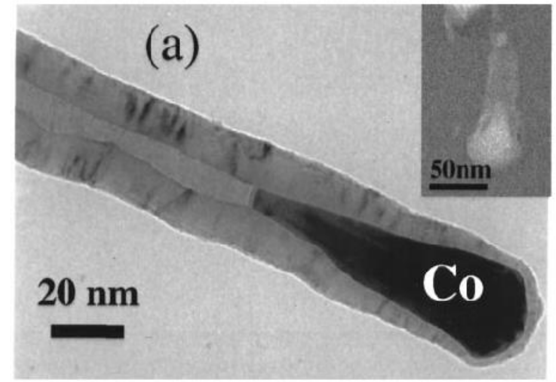


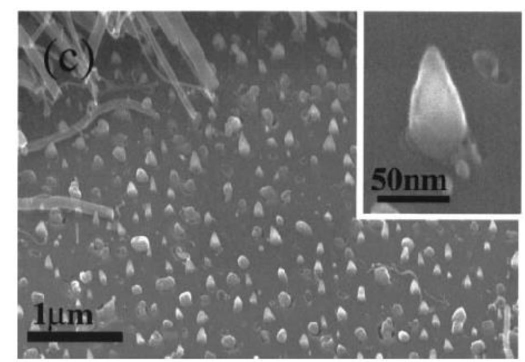
Controlling the diameter, growth rate, and density of vertically aligned CNTs sythesized via PECVD

Young Chul Choi *et al.*,
Appl. Phys. Lett. **76**, 2367 (2000)

Chemical Vapor Deposition

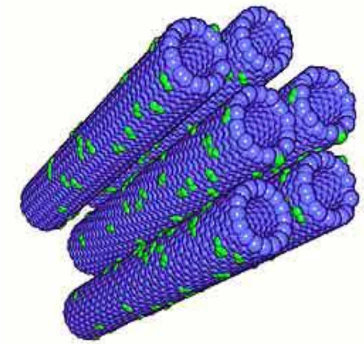






C. Bower *et al.*,
Appl. Phys. Lett. **77**, 2767 (2000)

Nanotubes @ ELETTRA: Research Focus



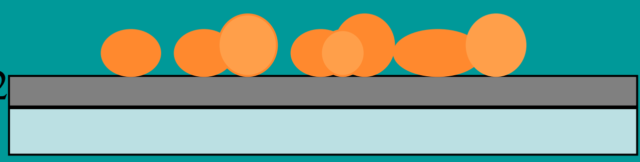
Nanotubes	*Who*
- *In situ* growth of CNT (with and without catalyst)	ENEA, ELETTRA & TASC-INFM
- Controlled, patterned growth of CNT	Lilit (INFM, ELETTRA) & TASC-INFM
- Interaction/storage of gases in nanotubes bundles (oxygen, hydrogen, NO_2,HNO_3…)	ELETTRA (SuperESCA)
- Real time and nano-spectroscopy studies of growth and electronic properties	ELETTRA(SuperESCA & ESCAmicroscopy)

From C nano-particles to single wall nanotubes

Bundles of SWCNTs

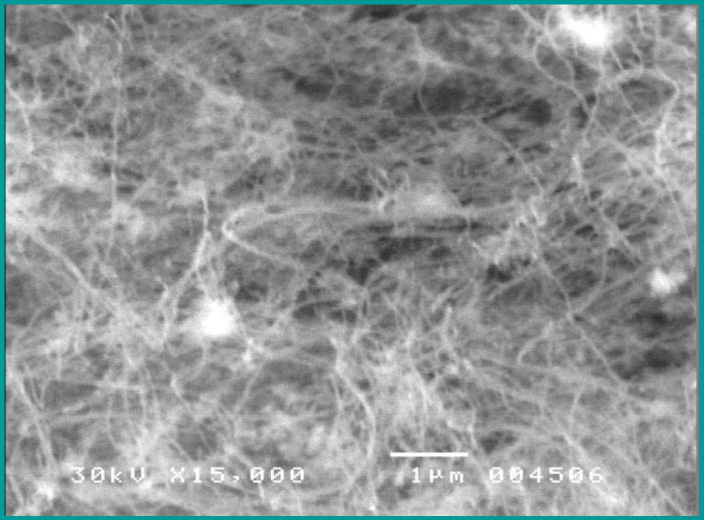
S. Botti et al., Appl. Phys. Lett. 80, 1441 (2002)

SiO_2



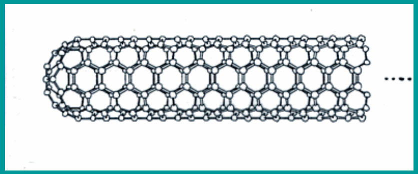
Si

annealing to ~ 1000 °C



● C nano-particles

↔ 50 nm



~ 1.4 nm

- What we can learn about the carbon nano-particles?
- How does the C atom reorganization work?
- Does the Si substrate play any role?

What is ahead?

NASA news

NASA Nanotechnology Roadmap

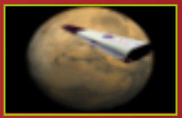
C A P A B I L I T Y

Multi-Functional Materials

High Strength Materials (>10 GPa)

Reusable Launch Vehicle (20% less mass, 20% less noise)

Revolutionary Aircraft Concepts (30% less mass, 20% less emission, 25% increased range)



Autonomous Spacecraft (40% less mass)

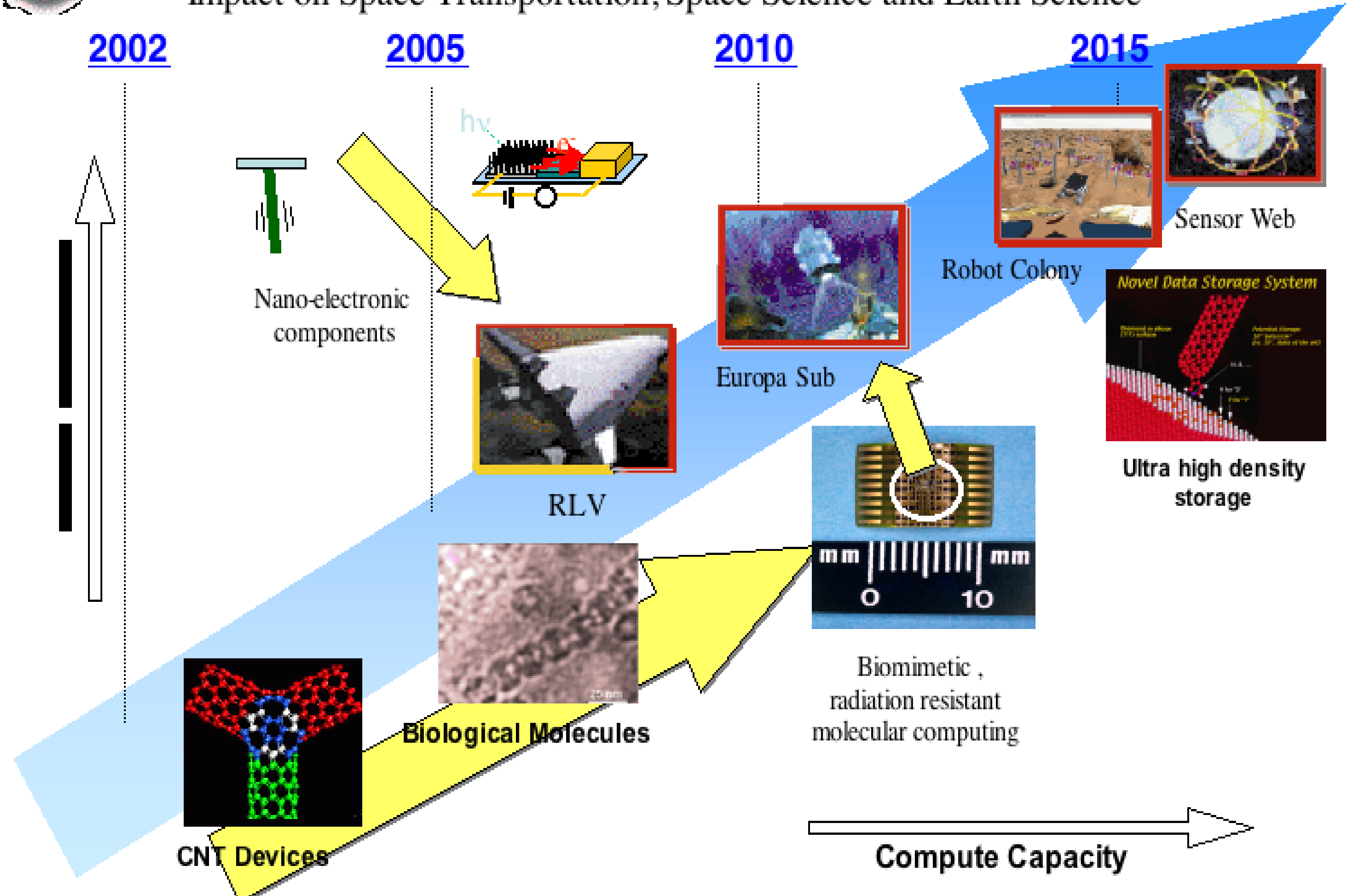
Bio-Inspired Materials and Processes

Adaptive Self-Repairing Space Missions

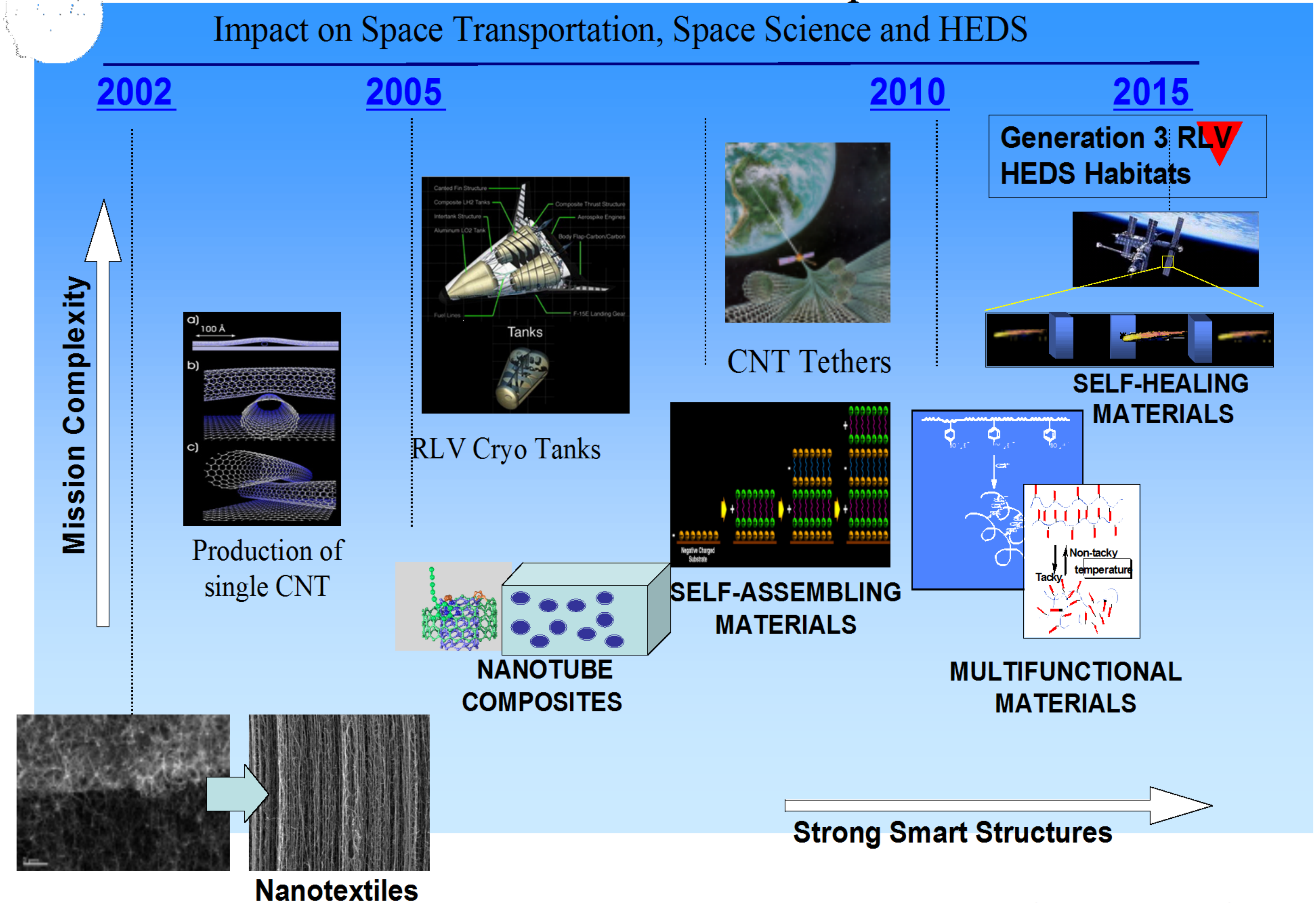
	2002	2004	2006	2011	2016
Materials	• Single-walled nanotube fibers	• Nanotube composites	• Integral thermal/shape control	• Smart "skin" materials	• Biomimetic material systems
Electronics/ computing	• Low-Power CNT electronic components	• Molecular computing/data storage	• Fault/radiation tolerant electronics	• Nano electronic "brain" for space Exploration	• Biological computing
Sensors, s/c components	• In-space nanoprobes	• Nano flight system components	• Quantum navigation sensors	• Integrated nanosensor systems	• NEMS flight systems @ 1 μW

Nanoelectronics and Computing Roadmap

Impact on Space Transportation, Space Science and Earth Science



Nano-Materials Roadmap



CNT = Carbon Nanotubes

The audacious space elevator