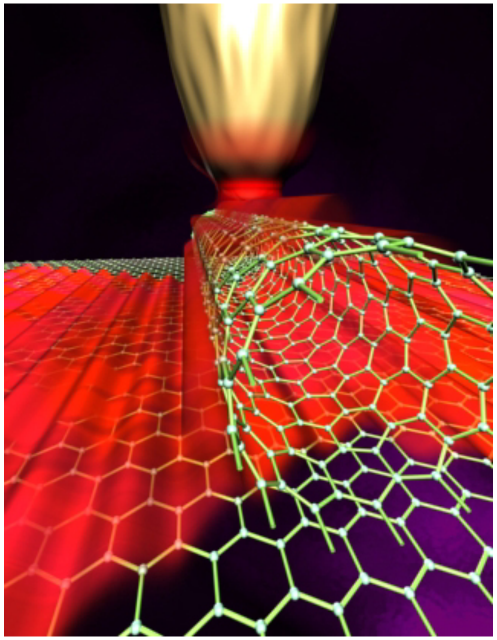
From Nanotechnology to Space: The Physics and Chemistry of Carbon Nanotubes



Marco Buongiorno Nardelli

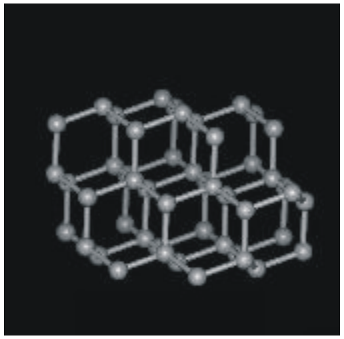
NC State University and

Oak Ridge National Laboratory

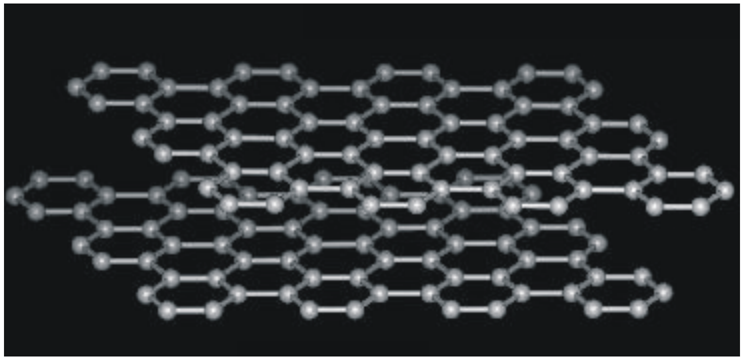
Nanotubes: what are they?

Carbon and dimensionality

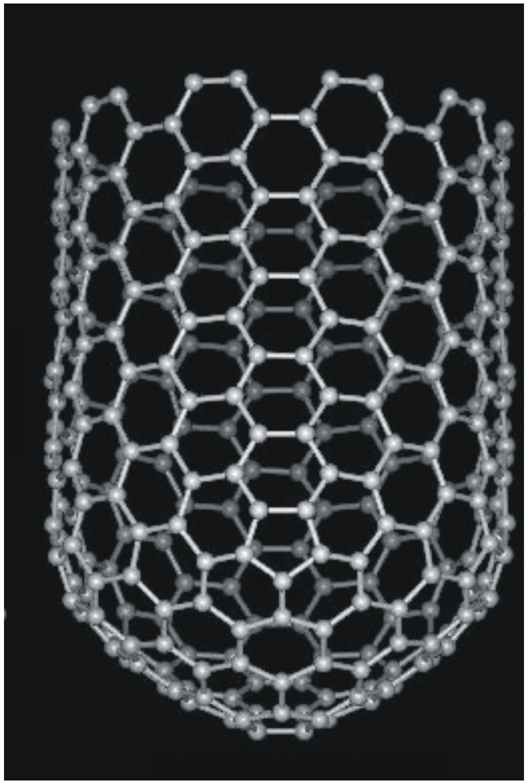
3D



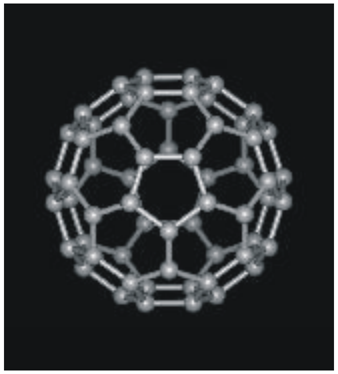
2D

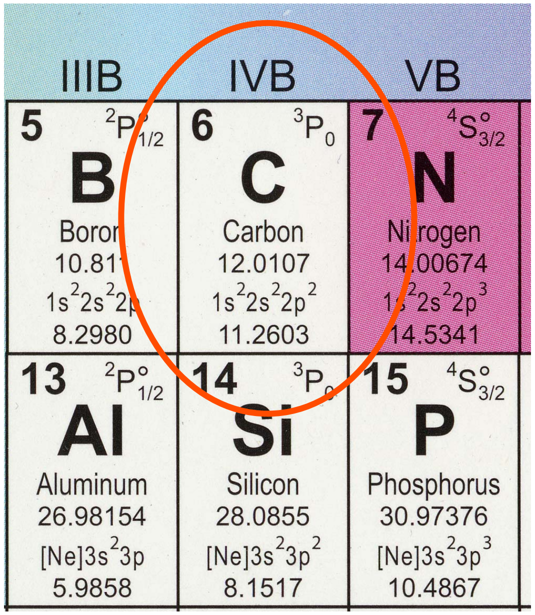


1D



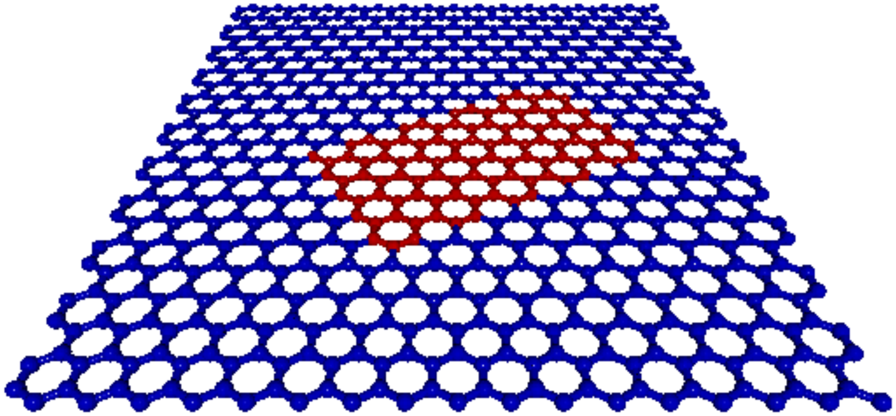
0D

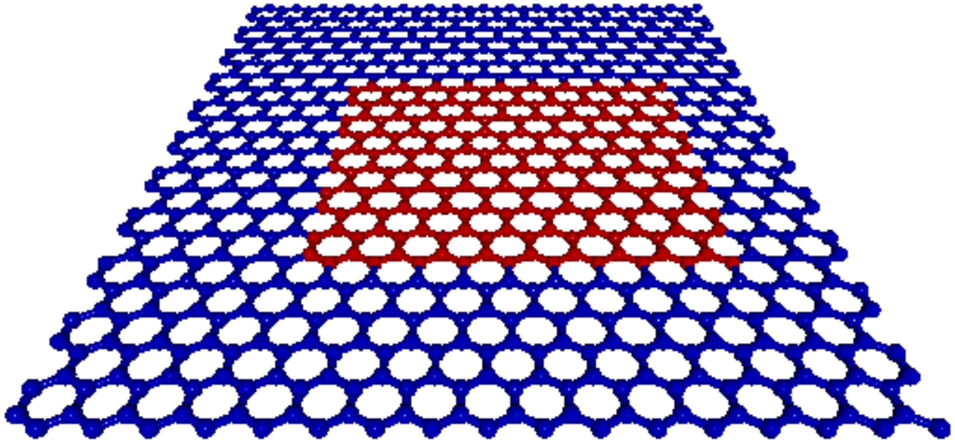


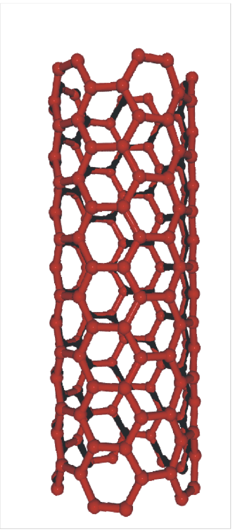


IIIB	IVB	VB
5 $^2P^\circ_{1/2}$ **B** Boron 10.811 $1s^22s^22p$ 8.2980	6 $^3P_0$ **C** Carbon 12.0107 $1s^22s^22p^2$ 11.2603	7 $^4S^\circ_{3/2}$ **N** Nitrogen 14.00674 $1s^22s^22p^3$ 14.5341
13 $^2P^\circ_{1/2}$ **Al** Aluminum 26.98154 $[Ne]3s^23p$ 5.9858	14 $^3P_0$ **Si** Silicon 28.0855 $[Ne]3s^23p^2$ 8.1517	15 $^4S^\circ_{3/2}$ **P** Phosphorus 30.97376 $[Ne]3s^23p^3$ 10.4867

From 2D to 1D

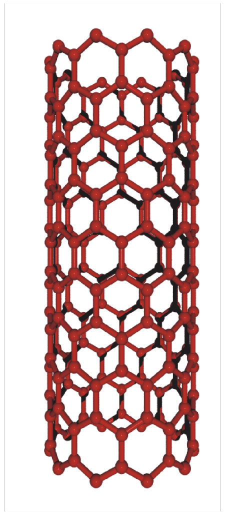




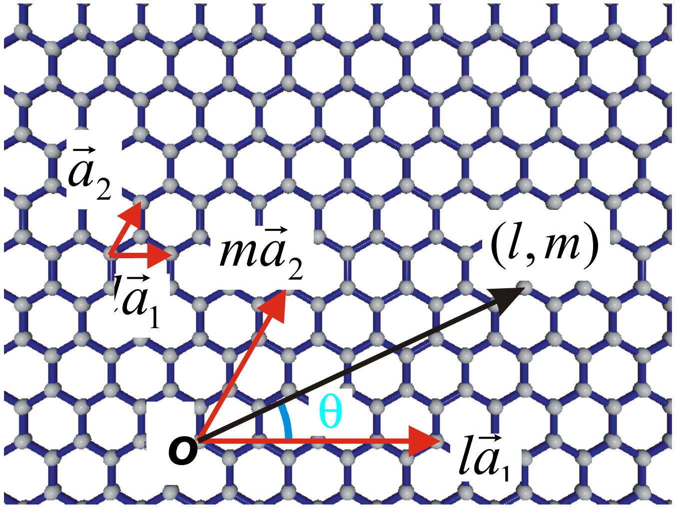


“Armchair”

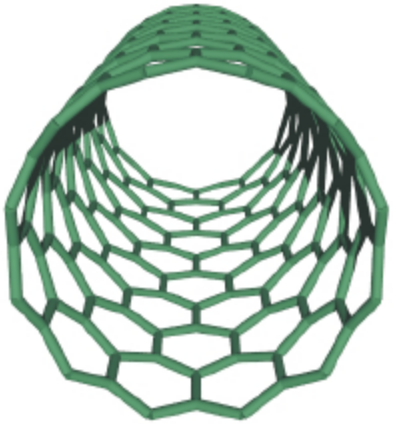
“Zig-zag”



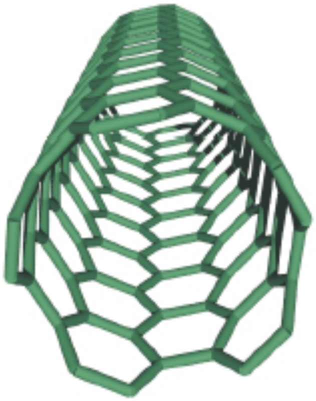
What is a nanotube?



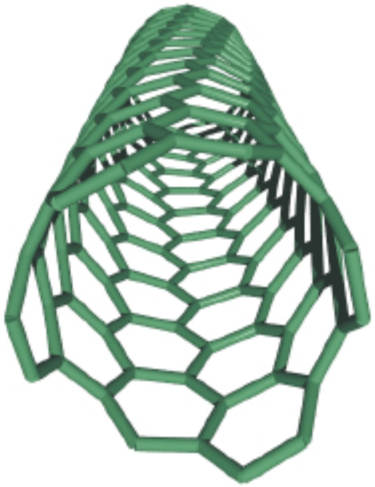
	Properties	*(l,m)* relation
Geometric	**radius**	$R = \frac{\sqrt{3}d\sqrt{l^2+m^2+lm}}{2\pi}$
	chiral angle	$\theta = \arcsin\frac{\sqrt{3}m}{3\sqrt{l^2+m^2+lm}}$
Electronic	**metal**	$\mathrm{mod}(l-m)=3$
	semi-conductor	$\mathrm{mod}(l-m)\neq 3$



(12,0)



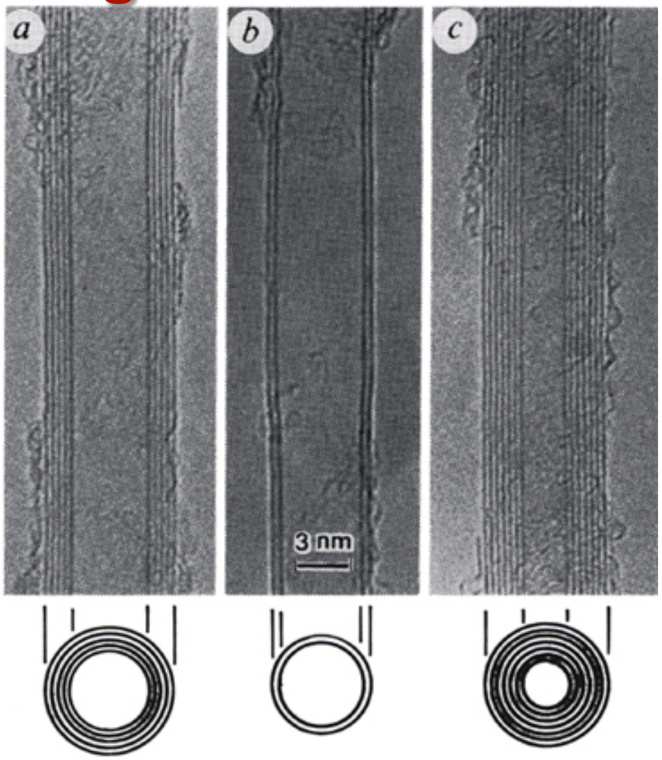
(6,6)



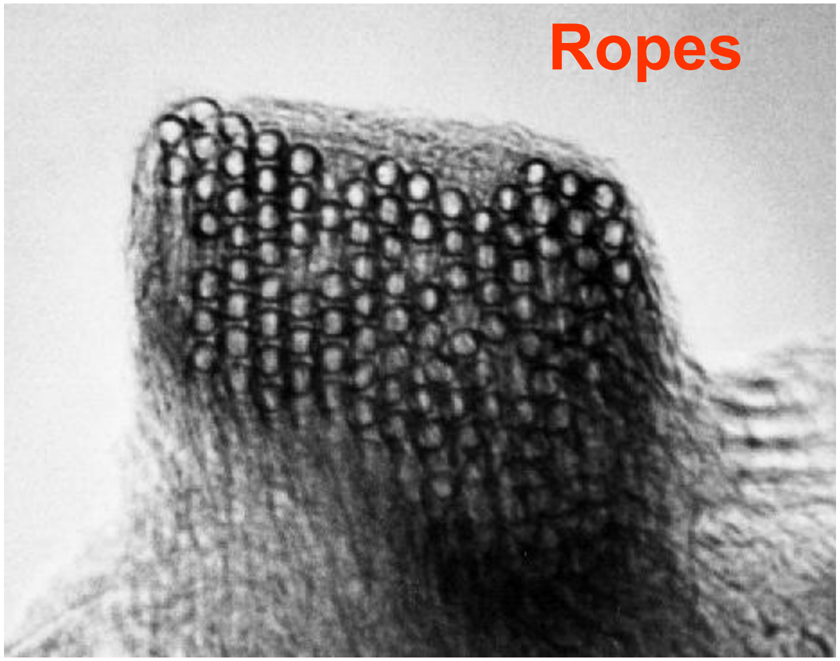
(6,4)

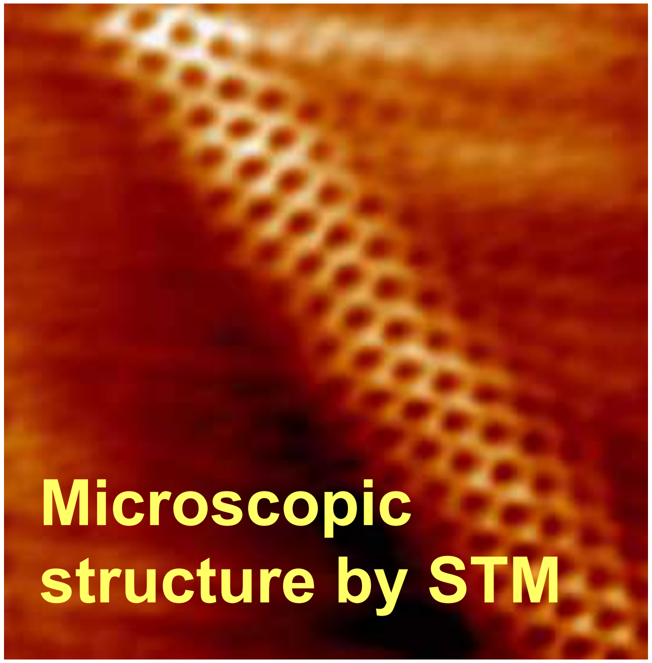
Can be produced by: Carbon-arc discharge, Laser ablation or catalytic growth

Single- and multi-walled

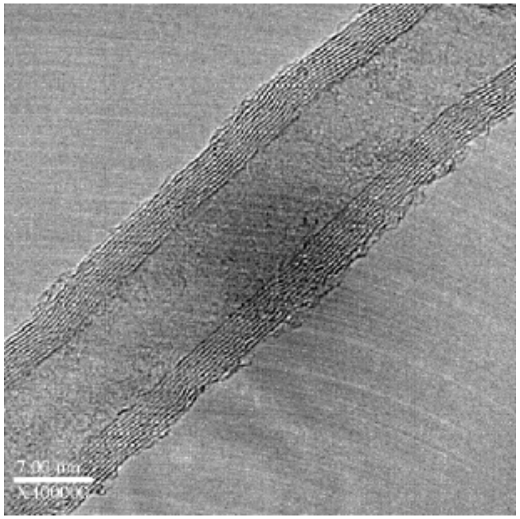


Nano = 10^{-9} meters
1 single human hair = 10^{-5} meters

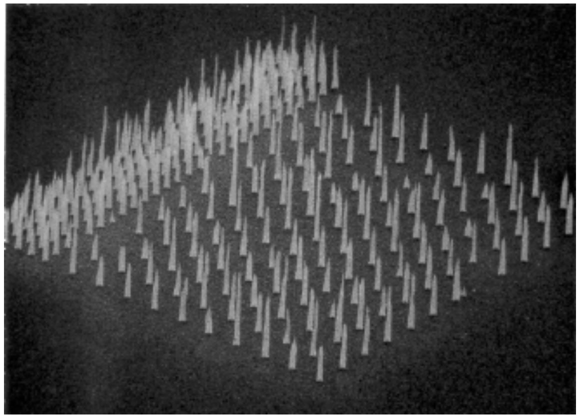

Ropes

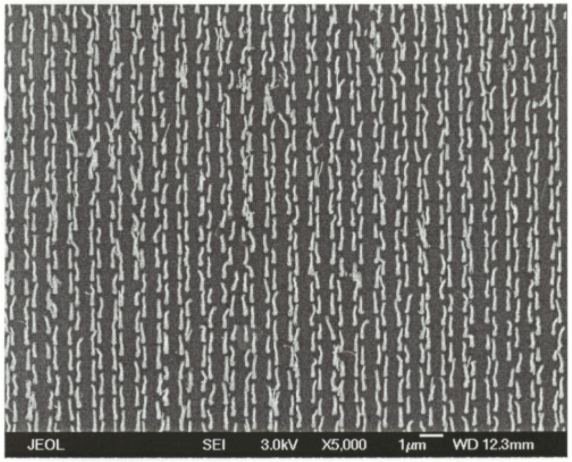

Microscopic structure by STM

Commercial sources

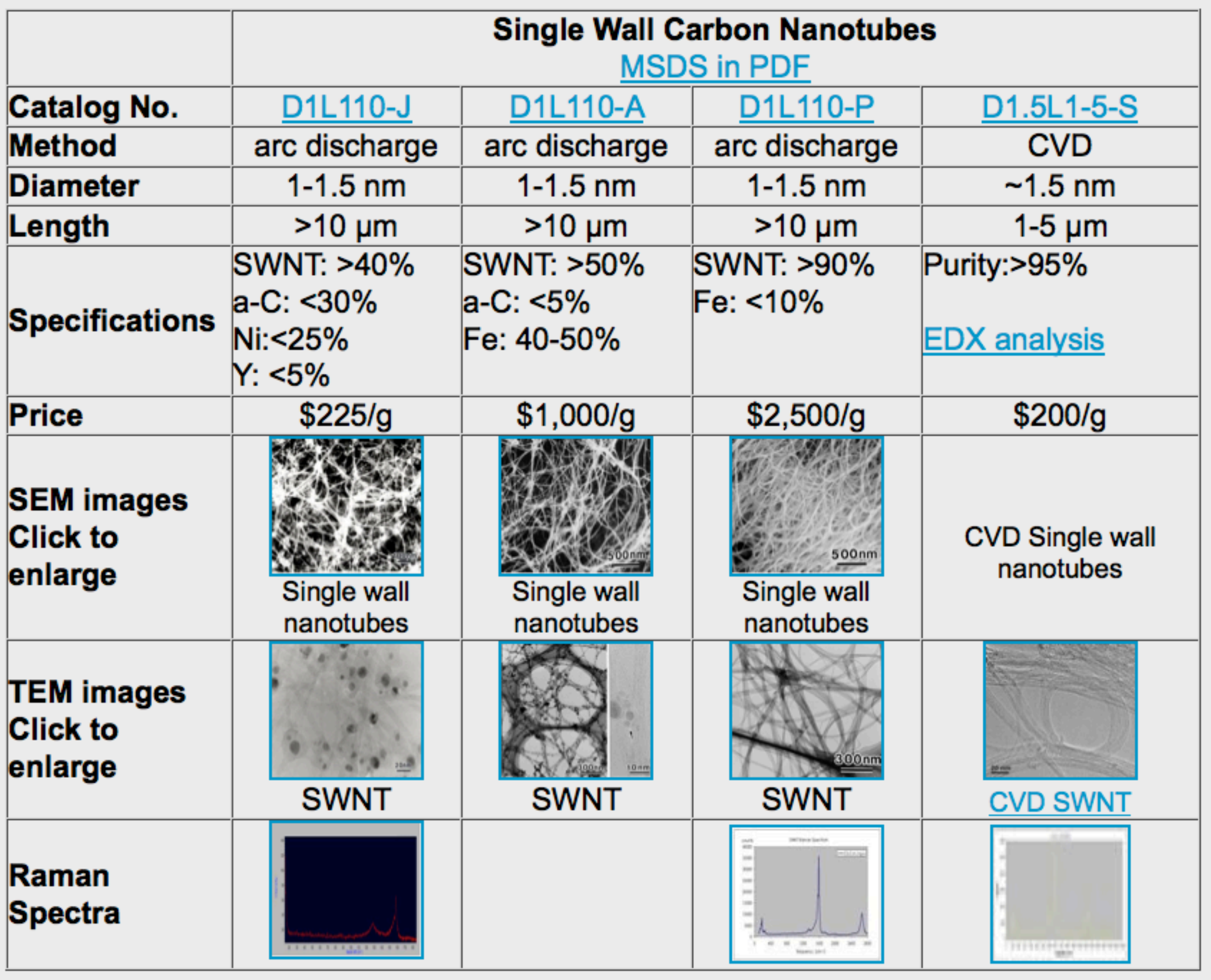


- 60-150/gram for SWNTs
- 100$/gram for MWNTs
- >1000$ for arrays or composites
  - http://www.nano-c.com/
  - http://buckyusa.com/
  - http://www.nano-lab.com/
  - ….many more…





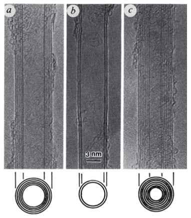
Commercial sources



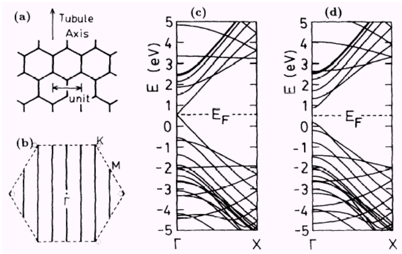
	Single Wall Carbon Nanotubes MSDS in PDF			
Catalog No.	D1L110-J	D1L110-A	D1L110-P	D1.5L1-5-S
Method	arc discharge	arc discharge	arc discharge	CVD
Diameter	1-1.5 nm	1-1.5 nm	1-1.5 nm	~1.5 nm
Length	>10 µm	>10 µm	>10 µm	1-5 µm
Specifications	SWNT: >40% a-C: <30% Ni:<25% Y: <5%	SWNT: >50% a-C: <5% Fe: 40-50%	SWNT: >90% Fe: <10%	Purity:>95% EDX analysis
Price	$225/g	$1,000/g	$2,500/g	$200/g
SEM images Click to enlarge	Single wall nanotubes	Single wall nanotubes	Single wall nanotubes	CVD Single wall nanotubes
TEM images Click to enlarge	SWNT	SWNT	SWNT	CVD SWNT
Raman Spectra				

1991

Discovery of MWNT (Iijima, Nature)



1992

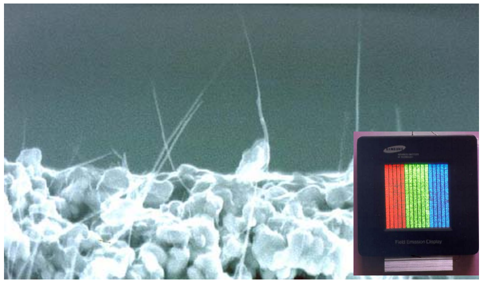


Conductivity (Hamada, PRL)

1993

Strength of CNT (MBN, Lieber, Ruoff)

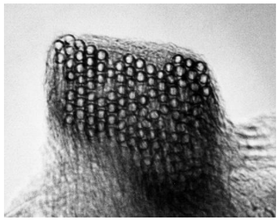
1995



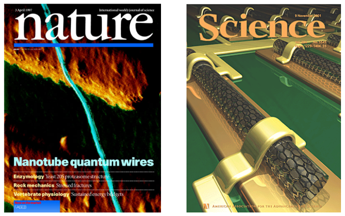
Field Emitter (Choi, APL)

1996

Ropes (Thess Science)



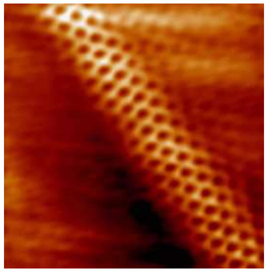
1997



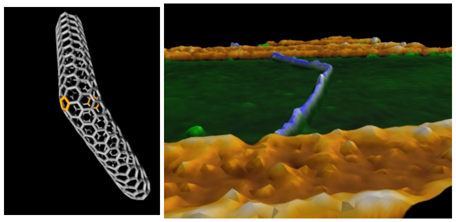
Quantum Conductance (Tans, Nature)

1998

Atomic Resoltuion STM images (Odom, Nature)



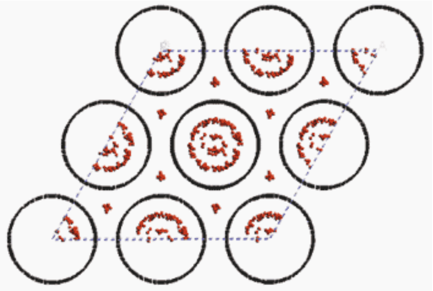
1999



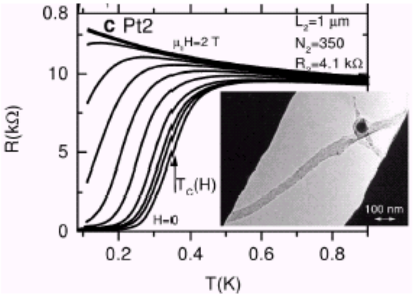
Intramolecular Junction (Zhao, Science)

2000

Energy Storage (Dai, Nature)

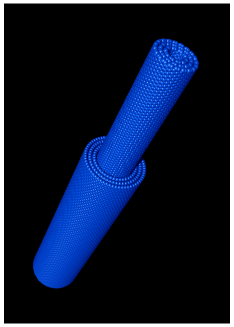


2001



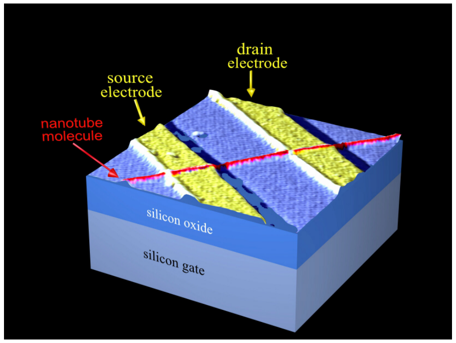
Superconductivity (Kociak, PRL))

2002



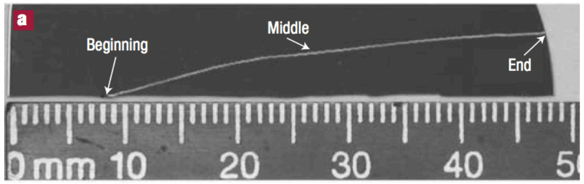
Multi-walled nanotubes demonstrated to be fastest known oscillators

2003



stable fabrication technology of carbon nanotube transistors

2004

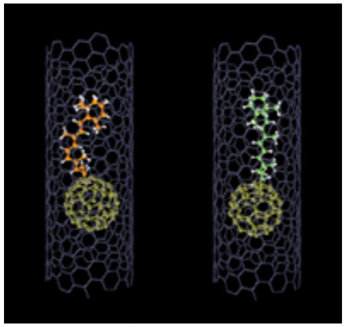


individual 4 cm long single-wall nanotube

2005

prototype high-definition 10-centimetre flat screen

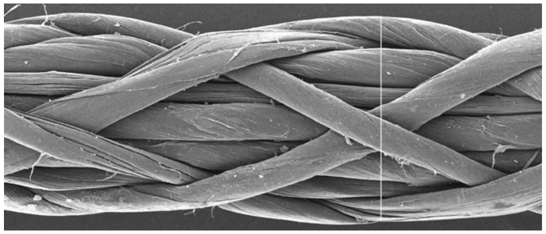
2006



scaffold for damaged nerve regeneration

Nanotubes incorporated in virus battery

2009



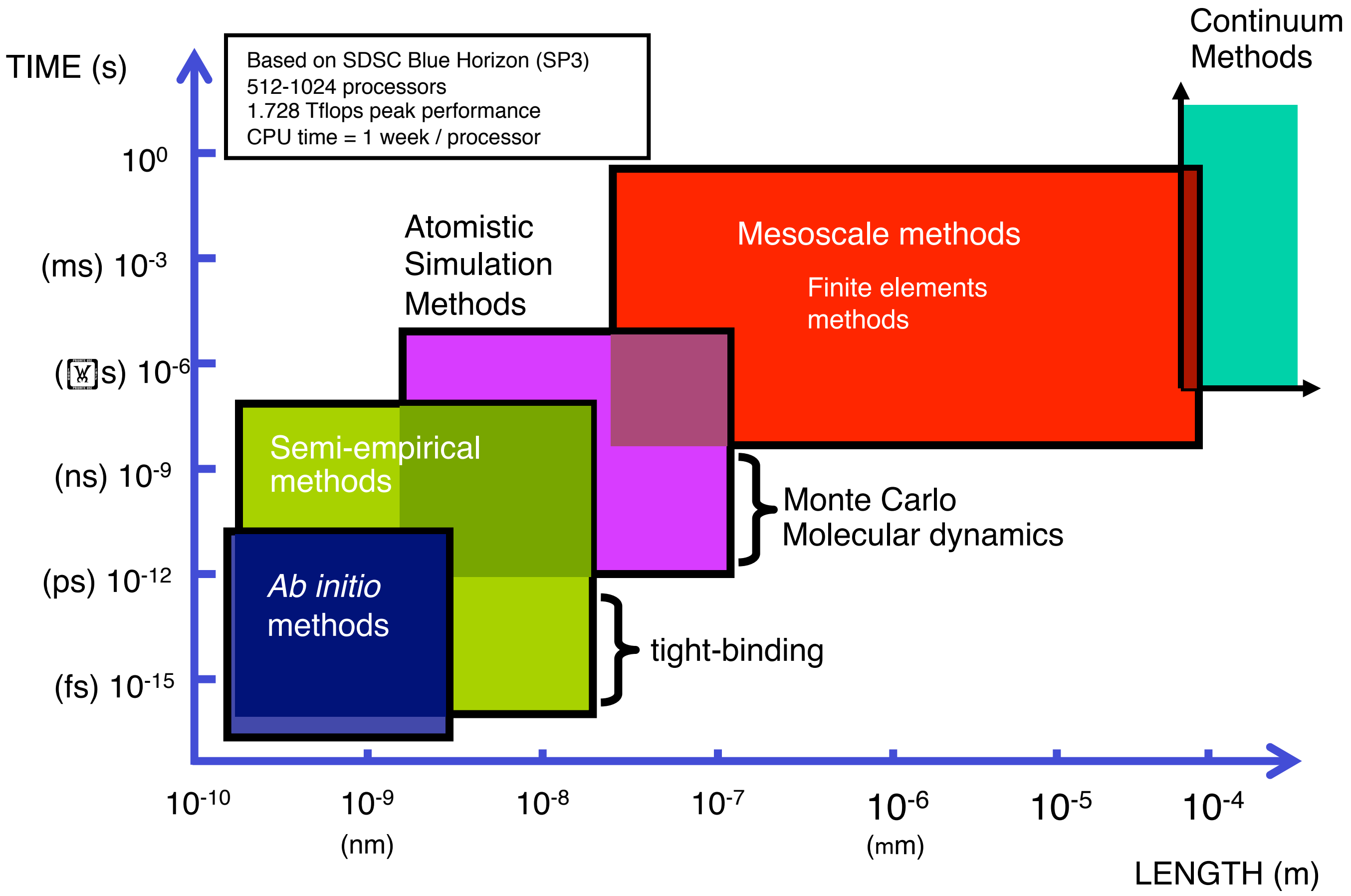
Nano-yarns 1 Km long

Still more to come!

M. Buongiorno Nardelli – IOP VAST 2009

Multi-scale modeling

- Challenge: modeling a physical phenomenon from a broad range of perspectives, from the atomistic to the macroscopic end



Multi-scale modeling

- **Ab initio methods**: calculate materials properties from first principles, solving the quantum-mechanical Schrödinger (or Dirac) equation numerically
- Pros:
  - Give information on both the electronic and structural/mechanical behavior
  - Can handle processes that involve bond breaking/formation, or electronic rearrangement (e.g. chemical reactions).
  - Methods offer ways to systematically improve on the results, making it easy to assess their quality.
  - Can (in principle) obtain essentially exact properties without any input but the atoms conforming the system.
- Cons:
  - Can handle only relatively small systems, about O(10^2) atoms.
  - Can only study fast processes, usually O(10) ps.
  - Numerically expensive!

Multi-scale modeling

- **Semi-empirical methods**: use simplified versions of equations from *ab initio* methods, e.g. only treat valence electrons explicitly; include parameters fitted to experimental data.
- Pros:
  - Can also handle processes that involve bond breaking/formation, or electronic rearrangement.
  - Can handle larger and more complex systems than *ab initio* methods, often of O(10^3) atoms.
  - Can be used to study processes on longer timescales than can be studied with *ab initio* methods, of about O(10) ns.
- Cons:
  - Difficult to assess the quality of the results.
  - Need input from experiments or ab initio calculations and large parameter sets.

Multi-scale modeling

- **Atomistic methods**: use empirical or *ab initio* derived force fields, together with semi-classical statistical mechanics (SM), to determine thermodynamic (MC, MD) and transport (MD) properties of systems. SM solved ‘exactly’.
- Pros:
  - Can be used to determine the microscopic structure of more complex systems, O($10^{4\text{-}6}$) atoms.
  - Can study dynamical processes on longer timescales, up to O(1) [illegible]s
- Cons:
  - Results depend on the quality of the force field used to represent the system.
  - Many physical processes happen on length- and time-scales inaccessible by these methods, e.g. diffusion in solids, many chemical reactions, protein folding, micellization.

Multi-scale modeling

- **Connection between the scales**:

  "Upscaling"

  Using results from a lower-scale calculation to obtain parameters for a higher-scale method. This is relatively easy to do; *deductive* approach. Examples:

  - Calculation of phenomenological coefficients (e.g. elastic tensors, viscosities, diffusivities) from atomistic simulations for later use in a continuum model.
  - Fitting of force-fields using *ab initio* results for later use in atomistic simulations.
  - Deriving potential energy surface for a chemical reaction, to be used in atomistic MD simulations
  - Deriving coarse-grained potentials for 'blobs of matter' from atomistic simulation, to be used in meso-scale simulations

Multi-scale modeling

- **Connection between the scales**:

  “Downscaling”

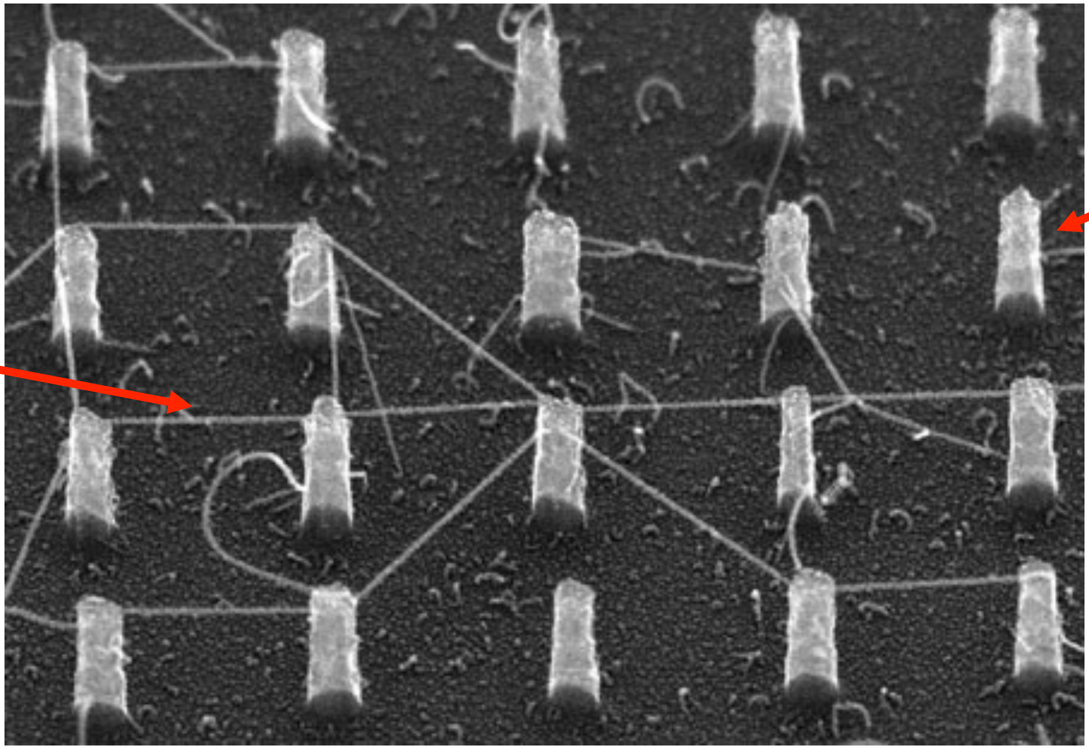
  Using higher-scale information (often experimental) to build parameters for lower-scale methods. This is more difficult, due to the non-uniqueness problem. For example, the results from a meso-scale simulation do not contain atomistic detail, but it would be desirable to be able to use such results to return to the atomistic simulation level. *Inductive* approach. Examples:

- Fitting of two-electron integrals in semiempirical electronic structure methods to experimental data (ionization energies, electron affinities, etc.)
- Fitting of empirical force fields to reproduce experimental thermodynamic properties, e.g. second virial coefficients, saturated liquid density and vapor pressure

Strength of nanotubes

Nanotubes as nanoscale cables

Nanotubes as nanoscale cables



Suspended carbon nanotubes

Si pillars

(Homma et al, APL, 2002)

Nanotubes in space

The Space Elevator

Bradley C. Edwards, Ph.D.: Funded by NIAC

Concept: A cable with one end attached to Earth and the other 100,000 km up in space that can be ascended by mechanical means.

Benefits:

- Reduction of launch costs to <1% of rockets
- Expandable to larger and distributed (Mars) system
- Capable of launching large, fragile payloads
- Large capacity per launch and over time

Basic system consists of:

- Cable - carbon nanotube composite
- Anchor - ocean going platform (*Sealaunch)*
- Counterweight - deployment satellite and climbers
- Power system - laser power beaming (*Compower)*
- Climbers - off-the-shelf components
- Cable deployment requires 7 Shuttles and >200 climbers

Specifications:

- Cable - 100,000 km (3X longest trans-oceanic cable), 30 cm wide, microns thick
- Cable capacity - 20,000 kg
- Destinations - LEO, GEO, other planets
- Schedule - operational in 15 to 30 years
- Cost - ~$40B for construction

Required development:

- Mass production of long carbon nanotubes
- Carbon nanotube composites

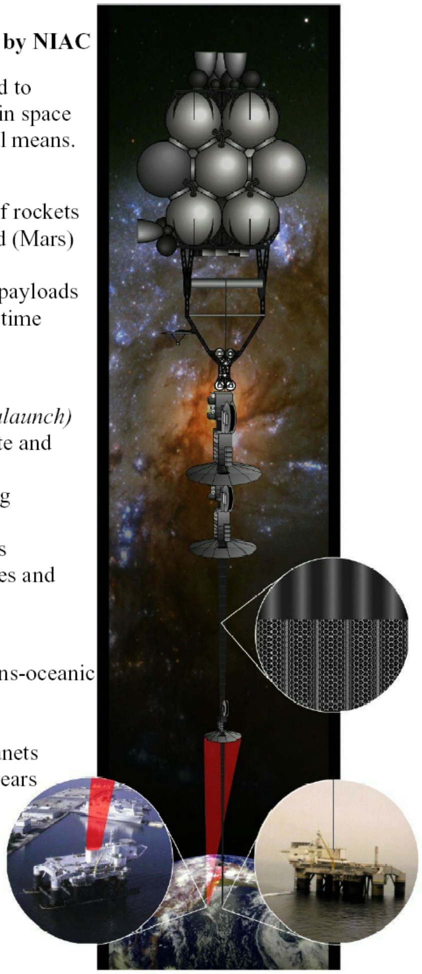
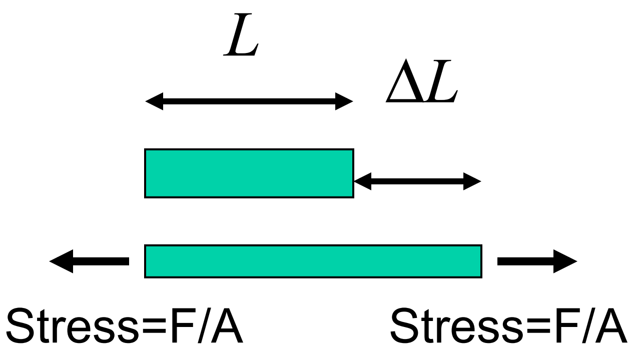


Figure 1: Artists conception of the space elevator developed in our NIAC Phase I work..

Strength of nanotubes

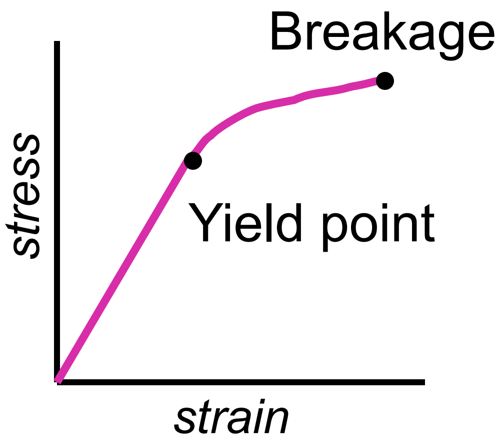


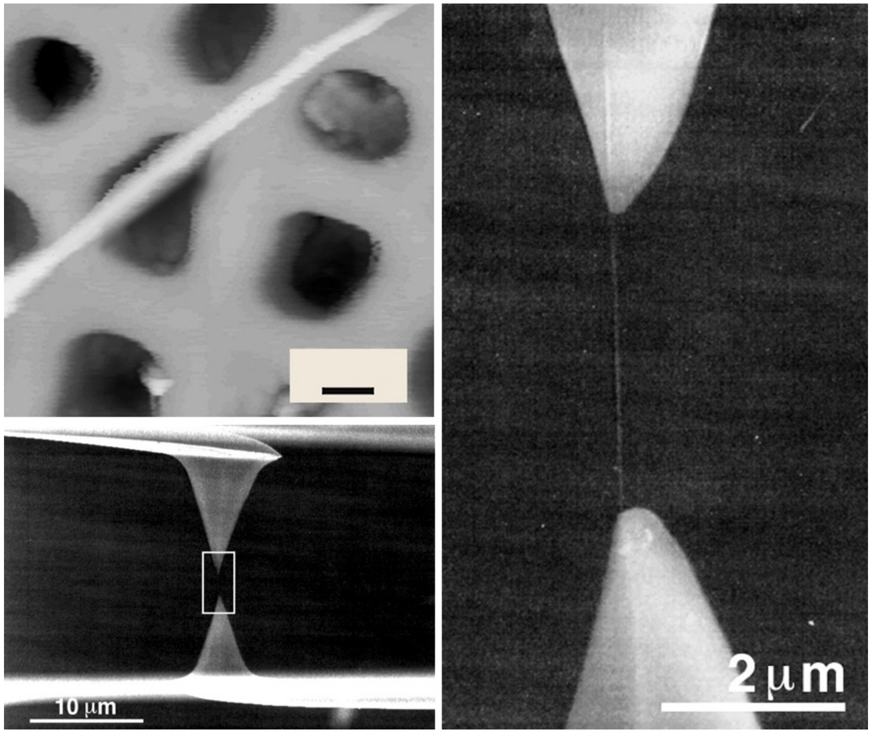
Stress=F/A

Stress=F/A

$$\frac{F}{A}=Y\frac{\Delta L}{L}$$

Young modulus



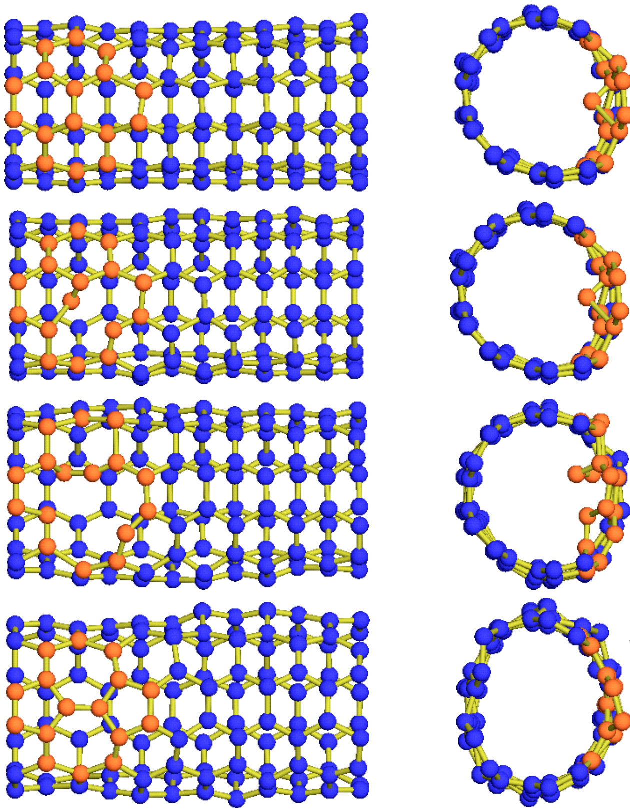


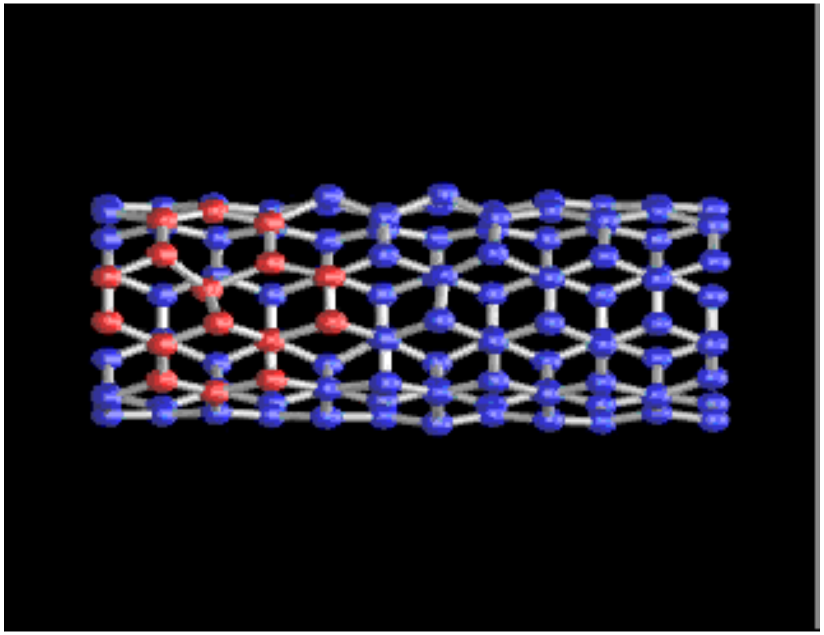
(Ruoff, PRL, 2000)

- High Young modulus =
  - Strong material
  - High mechanical resilience

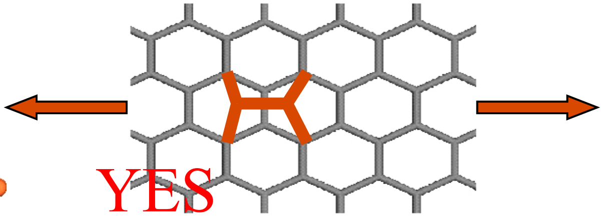
Strength of nanotubes

Nanotubes break by first forming a <u>bond rotation</u> 5-7-7-5 defect.

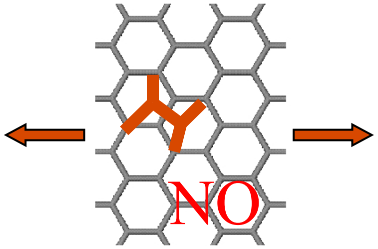




Transverse strain



Longitudinal strain



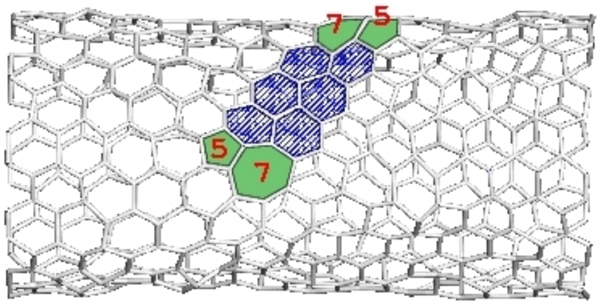
Very strong material!!!

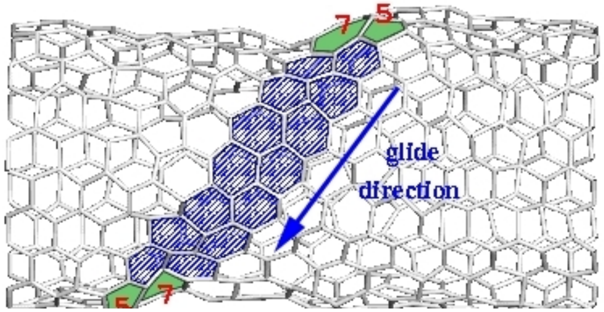
Buongiorno Nardelli, Yakobson, Bernholc PRL 81, 4656 (1998)

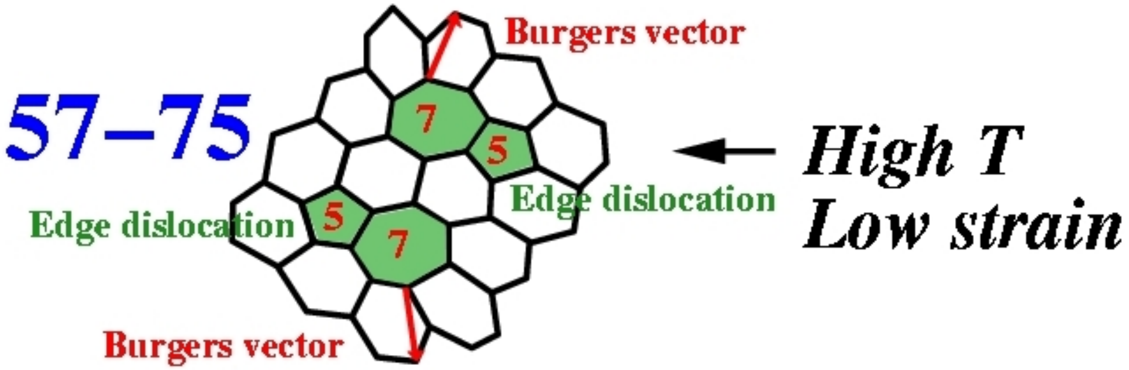
Plastic deformations and electronic devices

For low strain values and high temperatures the (5775) defect behaves as a *dislocation loop* made up of two *edge dislocations*: (57) and (75). The two dislocations can migrate on the nanotube wall through a sequence of bond rotations ➡ *PLASTIC BEHAVIOR*

Edge dislocation





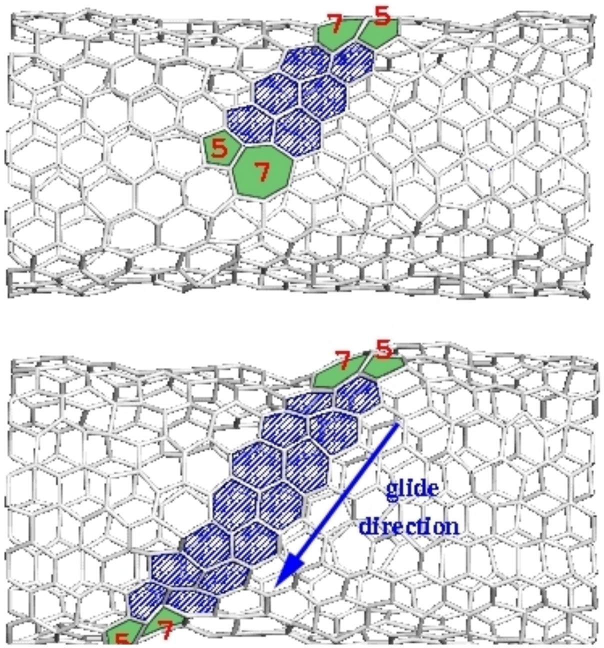


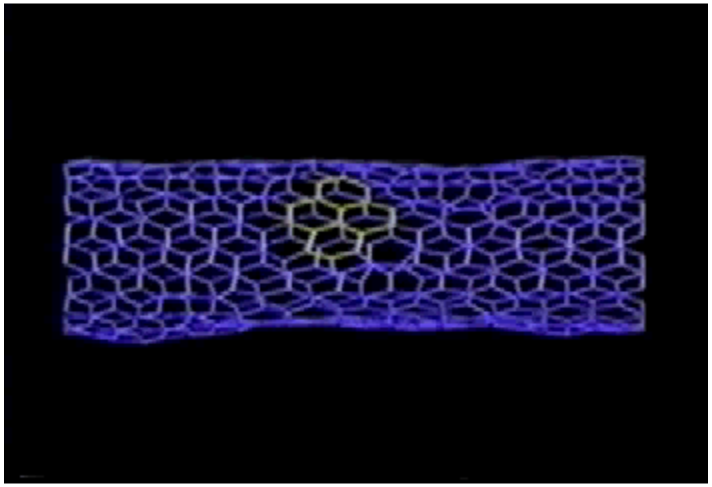
The plastic transformations lead metal-semiconductor junctions
➡ *devices are possible*

Plastic deformations and electronic devices

For low strain values and high temperatures the (5775) defect behaves as a *dislocation loop* made up of two *edge dislocations*: (57) and (75). The two dislocations can migrate on the nanotube wall through a sequence of bond rotations ➡ *PLASTIC BEHAVIOR*

Edge dislocation

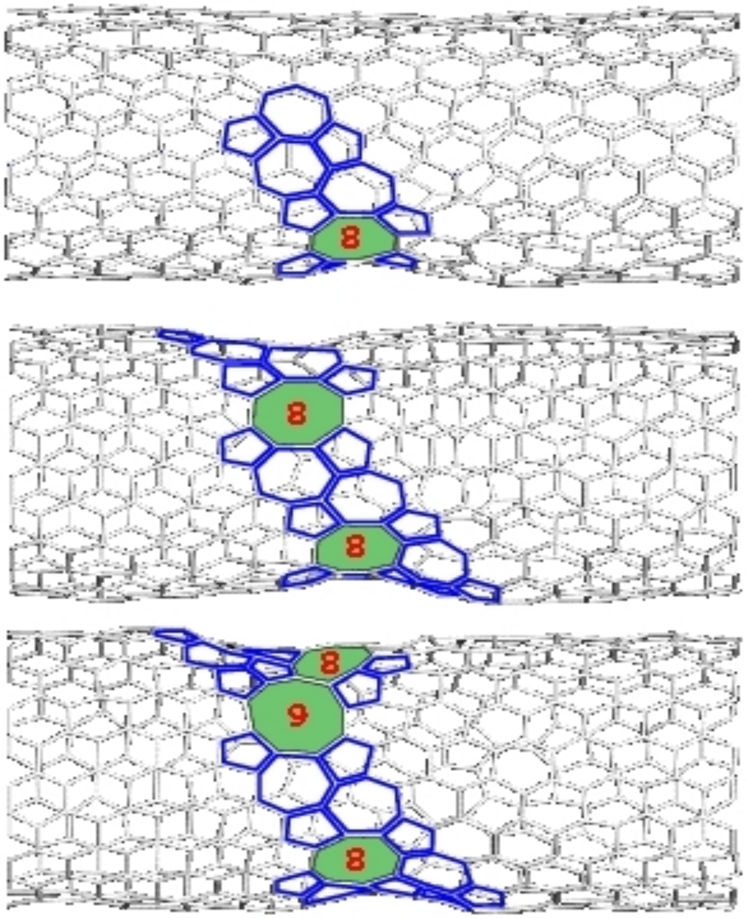


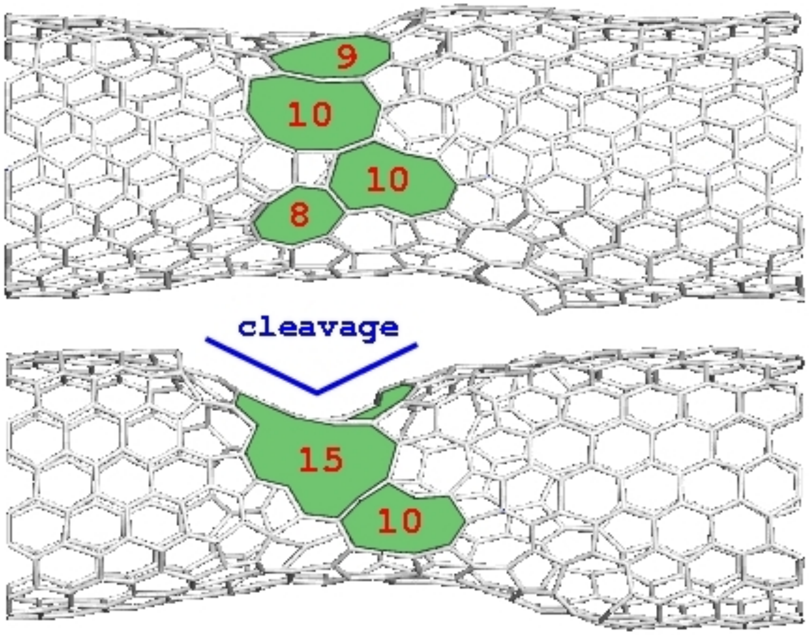


The plastic transformations lead metal-semiconductor junctions
➡ *devices are possible*

Breakage of nanotubes

Additional bond rotations lead to larger defects and cleavage.

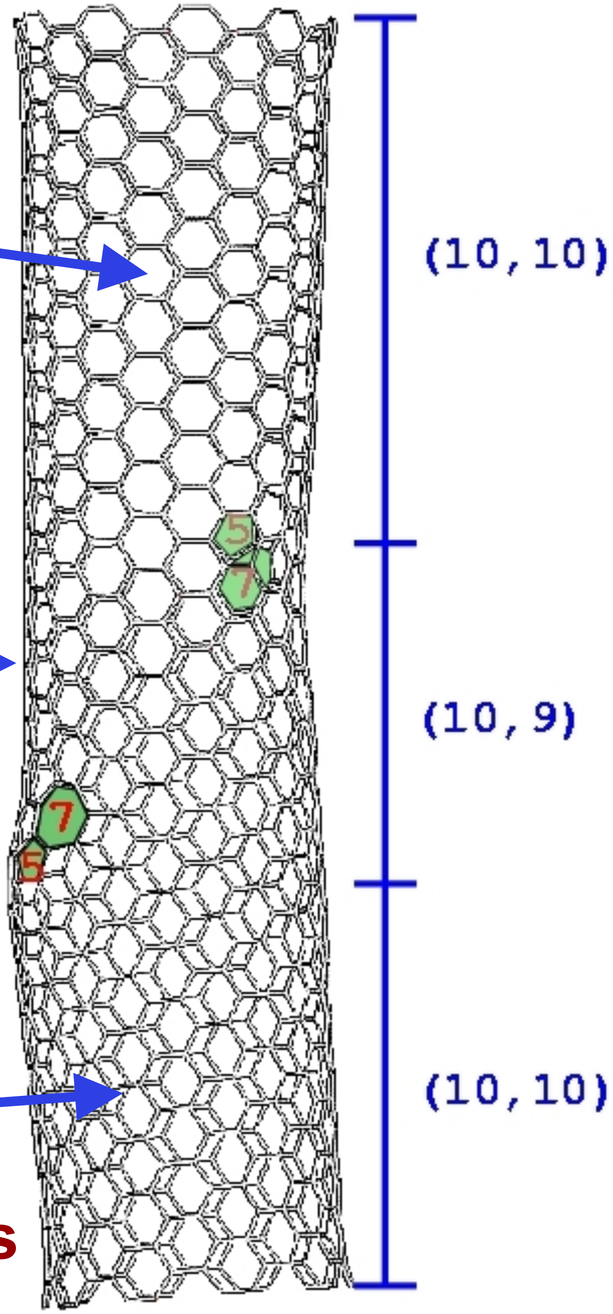




Experimentally tubes are seen to break at around 5% strain, in agreement with our predictions

(Smalley APL, 1999; Ruoff PRL, 1999)

Topological strain transformations



Original symmetry

Topological defects induce a change in the chirality (or index) of a nanotube. The plastic flow of a dislocation leaves behind a region of the tube with changed indices.

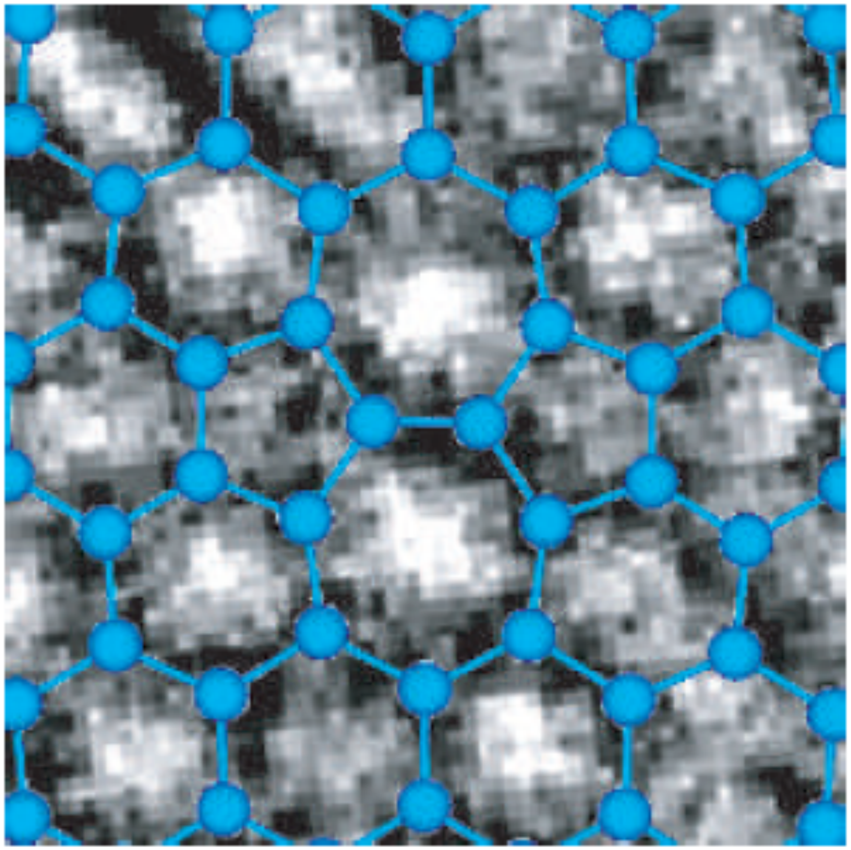
Changed symmetry

This fact has very important implications for the electronic behavior of the nanotube under strain

Original symmetry

Mechanically-induced heterojunctions

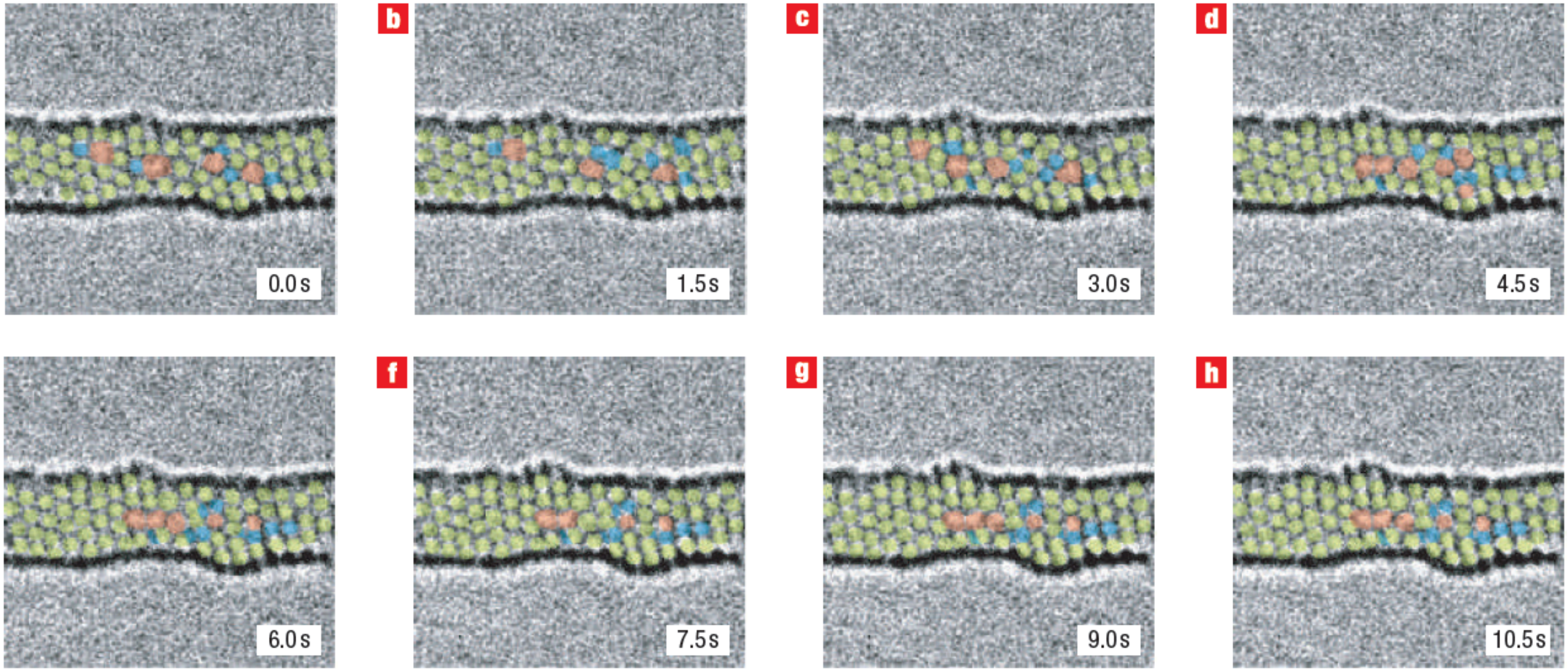
Strain induced plasticity



HR-TEM image of a Stone-Wales defect

(Iijima et al. Nat. Nanotech., 2007)

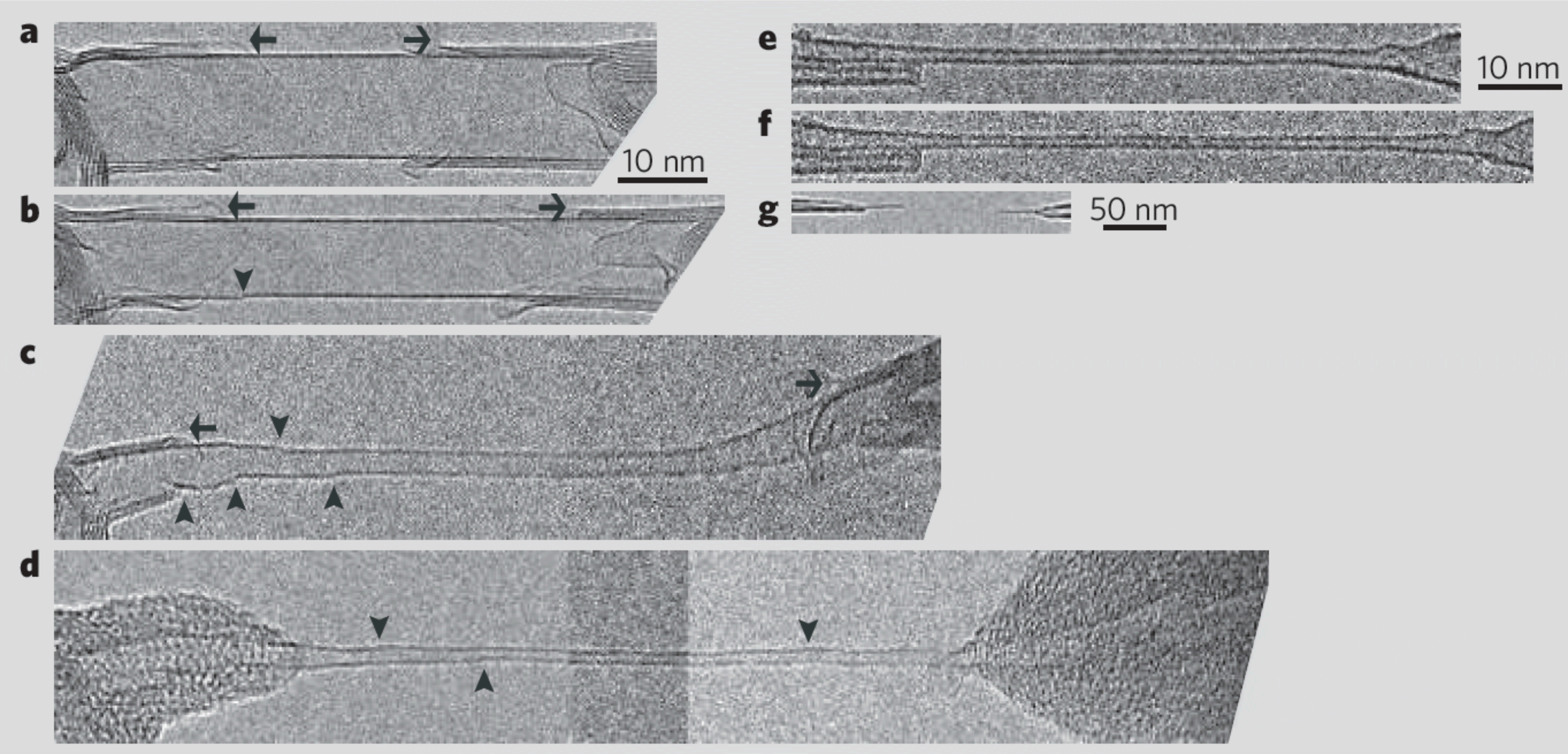
Strain induced defects



HR-TEM image of pentagons (blue) and higher order rings (red) defect

(Iijima et al. Nat. Nanotech., 2007)

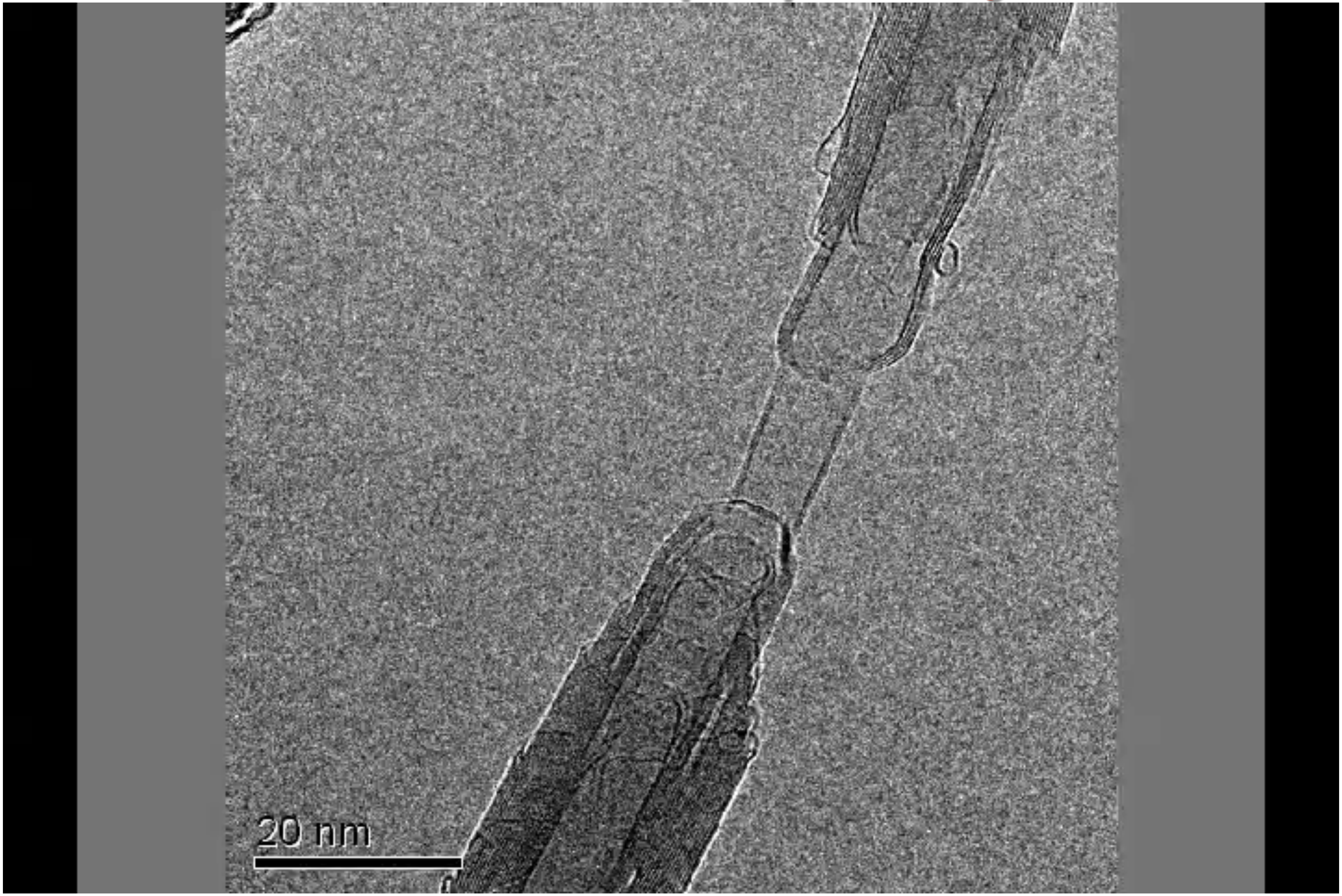
Nanotubes super-plasticity



In situ tensile elongation of individual nanotubes

(Dresselhaus' group, Nature, 2006)

Nanotubes super-plasticity



Carbon nanotubes in the Tour

Floyd Landis en route to winning the Tour de France 2006 (before being stripped of the title for failing a drug test – not a nanotube test!)