

**ФИЗИКО-ХИМИЧЕСКИЕ
ОСНОВЫ
НАНОТЕХНОЛОГИИ**

Профессор Н.Г. Рамбиди



7. Нанотрубки



Структура нанотрубок



Bonds in atoms and molecules

- **Ionic bonds**



Coloumb interaction between oppositely charged ions

- **Covalent bonds**



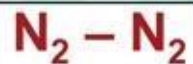
Shared valence electrons
(strength depends on distance)

- **Metallic Bonds**

See HB notes

Delocalised electrons spreading over the entire crystal

- **Van der Waals bond**



Dipole-dipole attraction
(fluctuating dipoles,
1/1000 strength of covalent bonds)

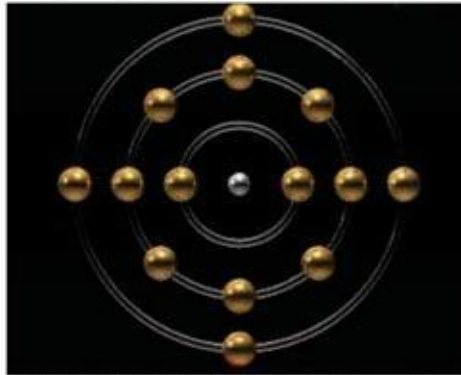


Periodic Table

1 hydrogen 1 H 1.0079	2 helium 2 He 4.0026	3 lithium 3 Li 6.941	4 beryllium 4 Be 9.0122	5 boron 5 B 10.811	6 carbon 6 C 12.011	7 nitrogen 7 N 14.007	8 oxygen 8 O 15.999	9 fluorine 9 F 18.998	10 neon 10 Ne 20.180	11 sodium 11 Na 22.990	12 magnesium 12 Mg 24.305	13 aluminum 13 Al 26.982	14 silicon 14 Si 28.086	15 phosphorus 15 P 30.974	16 sulfur 16 S 32.065	17 chlorine 17 Cl 35.453	18 argon 18 Ar 39.948	
19 potassium 19 K 39.098	20 calcium 20 Ca 40.078	21 scandium 21 Sc 44.956	22 titanium 22 Ti 47.867	23 vanadium 23 V 50.942	24 chromium 24 Cr 51.996	25 manganese 25 Mn 54.938	26 iron 26 Fe 55.845	27 cobalt 27 Co 58.933	28 nickel 28 Ni 58.693	29 copper 29 Cu 63.546	30 zinc 30 Zn 65.39	31 gallium 31 Ga 69.723	32 germanium 32 Ge 72.61	33 arsenic 33 As 74.922	34 selenium 34 Se 78.96	35 bromine 35 Br 79.904	36 krypton 36 Kr 83.80	
37 rubidium 37 Rb 85.468	38 strontium 38 Sr 87.62	39 yttrium 39 Y 88.906	40 zirconium 40 Zr 91.224	41 niobium 41 Nb 92.906	42 molybdenum 42 Mo 95.94	43 technetium 43 Tc [98]	44 ruthenium 44 Ru 101.07	45 rhodium 45 Rh 102.91	46 palladium 46 Pd 106.42	47 silver 47 Ag 107.87	48 cadmium 48 Cd 112.41	49 indium 49 In 114.82	50 tin 50 Sn 118.71	51 antimony 51 Sb 121.76	52 tellurium 52 Te 127.60	53 iodine 53 I 126.90	54 xenon 54 Xe 131.29	
55 caesium 55 Cs 132.91	56 barium 56 Ba 137.33	57-70 lanthanoids *	71 lutetium 71 Lu 174.97	72 hafnium 72 Hf 178.49	73 tantalum 73 Ta 180.95	74 tungsten 74 W 183.84	75 rhenium 75 Re 186.21	76 osmium 76 Os 190.23	77 iridium 77 Ir 192.22	78 platinum 78 Pt 195.08	79 gold 79 Au 196.97	80 mercury 80 Hg 200.59	81 thallium 81 Tl 204.38	82 lead 82 Pb 207.2	83 bismuth 83 Bi 208.98	84 polonium 84 Po [209]	85 astatine 85 At [210]	86 radon 86 Rn [222]
87 francium 87 Fr [223]	88 radium 88 Ra [226]	89-102 actinoids **	103 lawrencium 103 Lr [262]	104 rutherfordium 104 Rf [261]	105 dubnium 105 Db [262]	106 seaborgium 106 Sg [266]	107 bohrium 107 Bh [264]	108 hassium 108 Hs [269]	109 meitnerium 109 Mt [268]	110 ununnilium 110 Uun [271]	111 unununium 111 Uuu [272]	112 ununbium 112 Uub [277]	113 ununtrium 113 Uut [288]	114 ununquadium 114 Uuq [289]	115 ununpentium 115 Uup [290]	116 ununhexium 116 Uuh [291]	117 ununseptium 117 Uus [292]	118 ununoctium 118 Uuo [293]

Key:

element name
atomic number
symbol
atomic weight (mean relative mass)



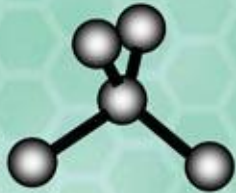
*lanthanoids

**actinoids

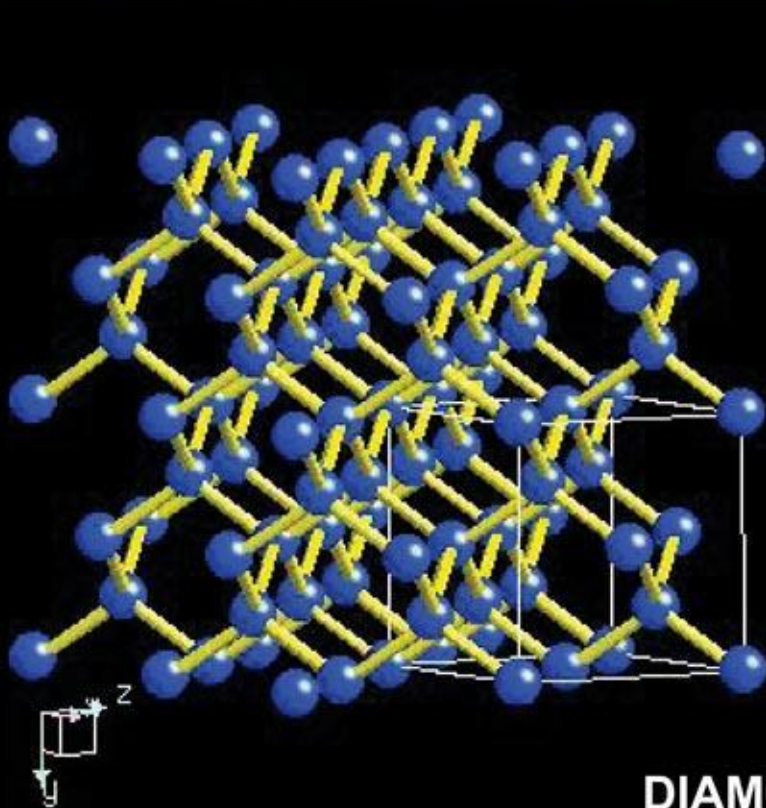
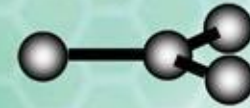
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]



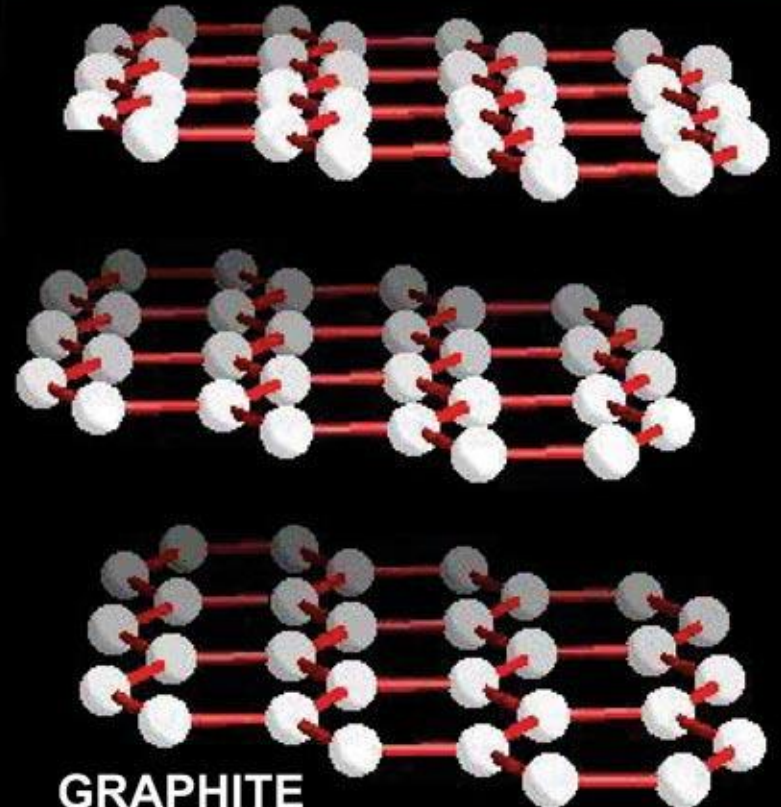
Diamond and graphite



Bond length 1.4 nm
Stacking distance 3.4 nm

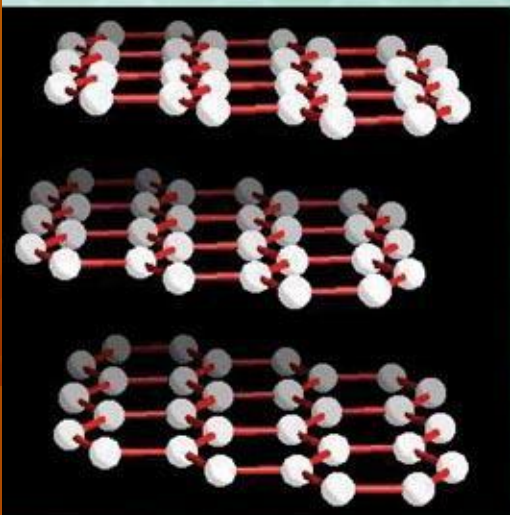


DIAMOND

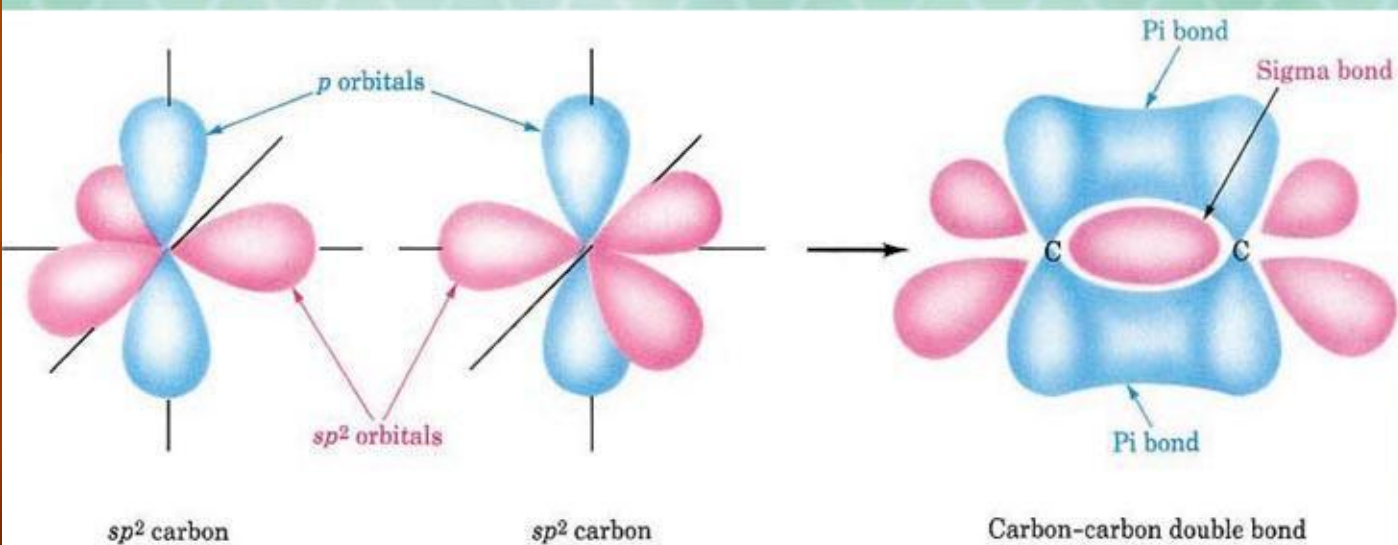


GRAPHITE

sp² hybridisation



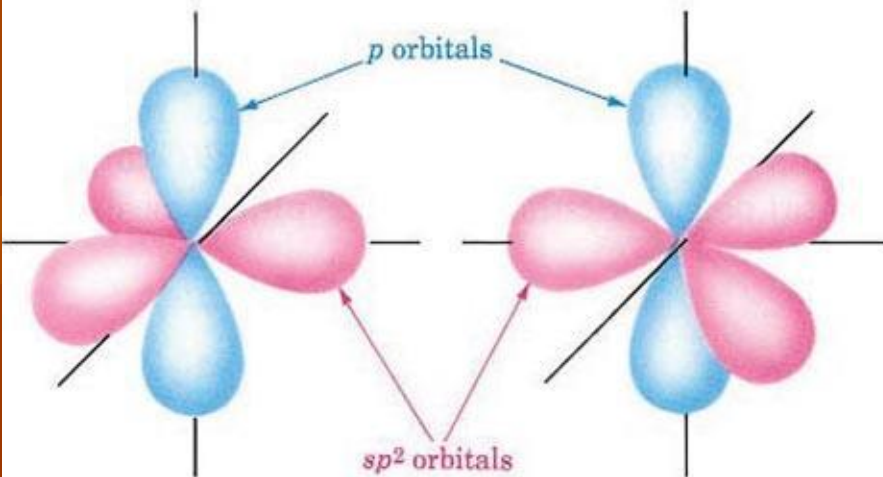
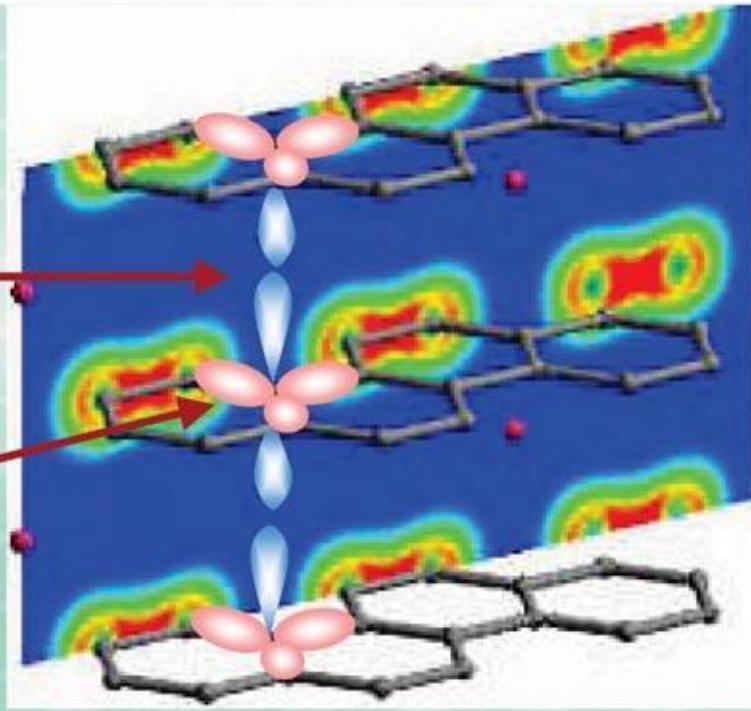
- Graphite is a stack of single "graphene" sheets
- In graphene the electron bonds *hybridize*; they form three identical "sigma" orbitals at 120 degrees to each other.
- Each bond originates from one s and two p orbitals (sp²). The remaining p orbital is perpendicular to the plane, called a π-bond (pi).
- The strength of the π bond (van der Waals bond) is much weaker than the σ bond (covalent)
- Electrons are delocalized in pi-bonds – current can flow in the graphene layer



σ and π -bonds

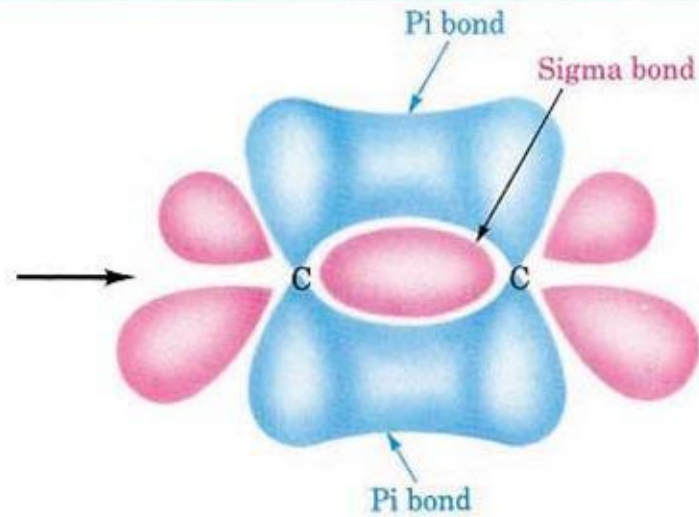
π bonds (weak)

sp^2 hybridised bonds (strong)



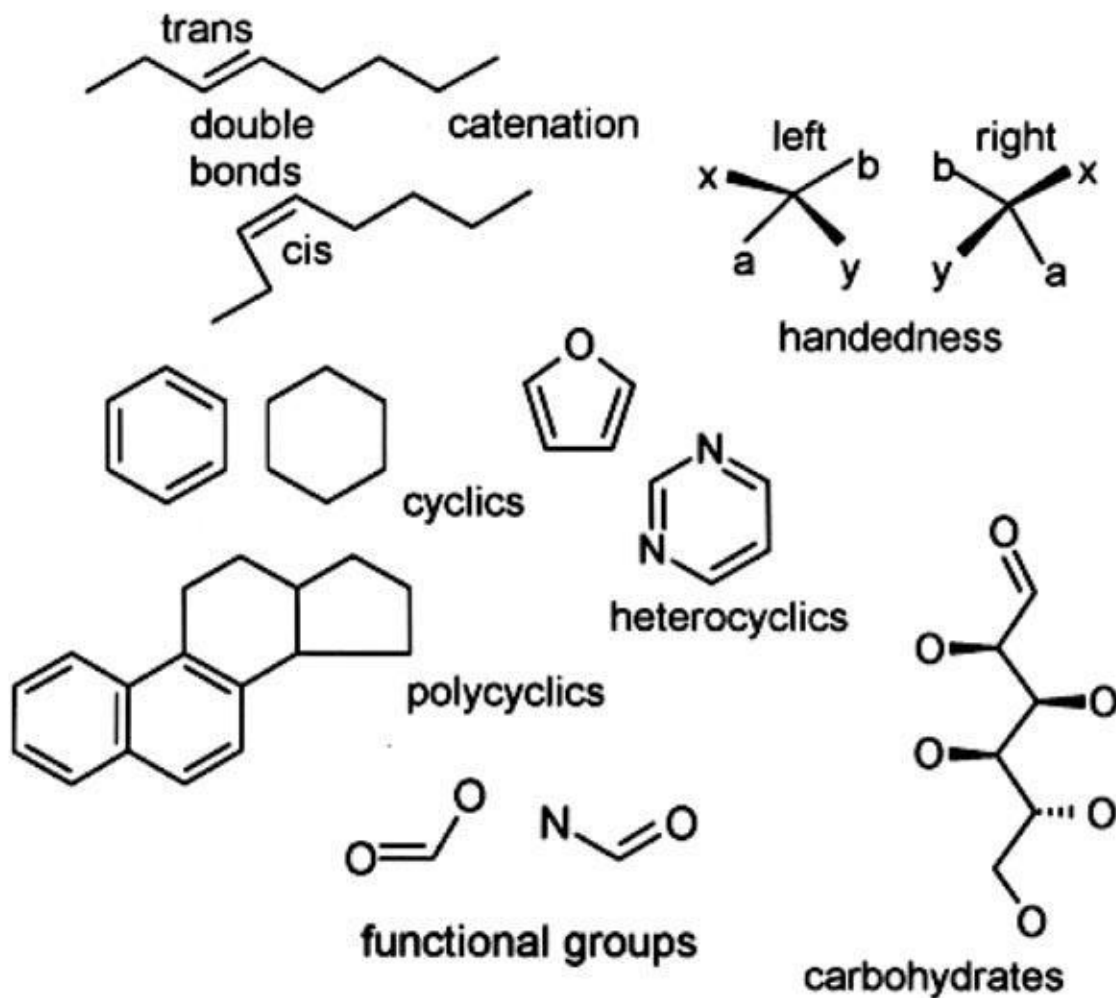
sp^2 carbon

sp^2 carbon



Carbon-carbon double bond

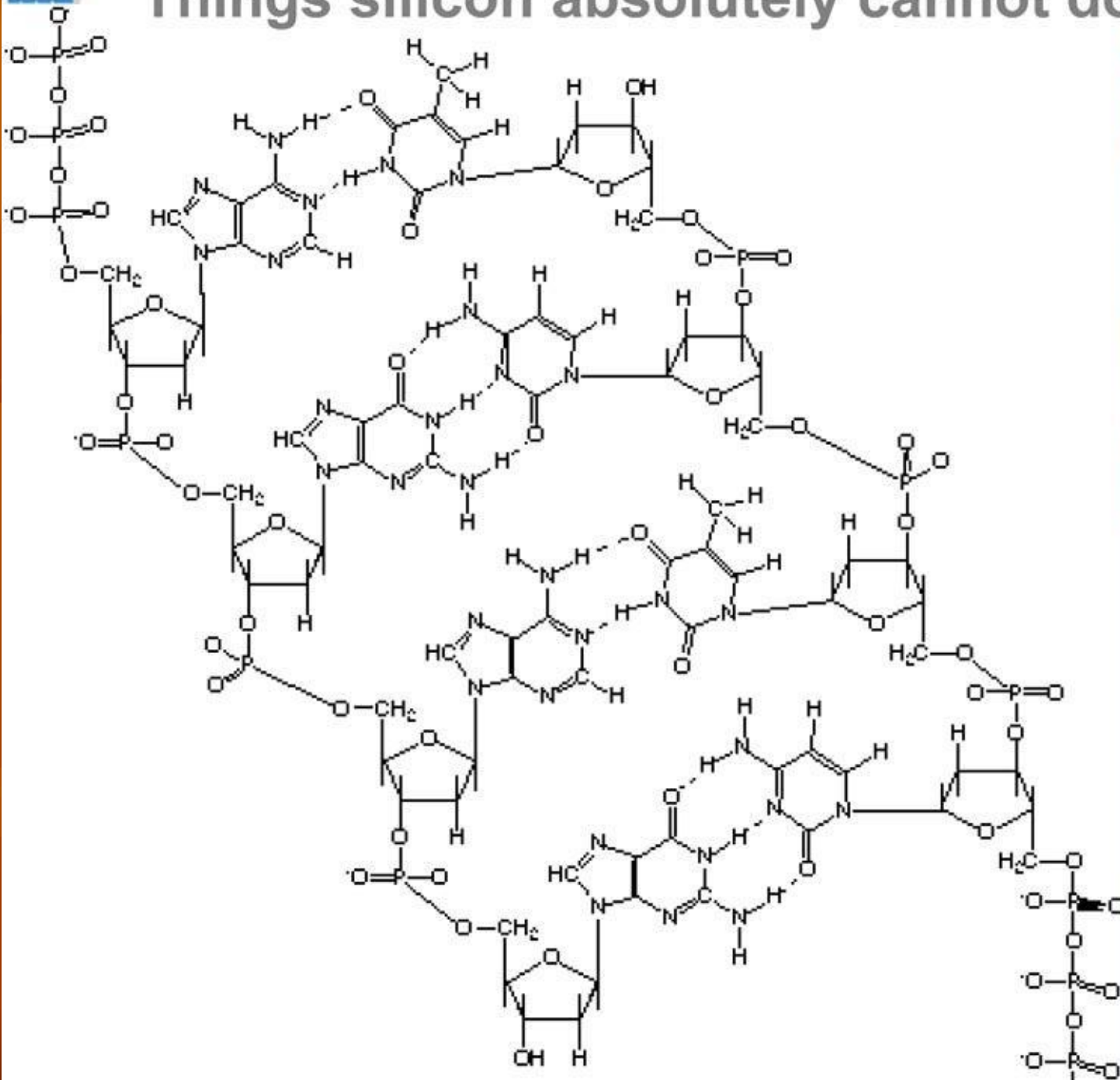
Things silicon cannot do!



WHAT IS SPECIAL ABOUT C

- C can form chains with itself
- C forms stable compounds with many elements (N, O, H) but preferably itself
- C does not bind too strongly to O - does not oxidise, like silicon and many other solids
- ...on the other hand it forms strong bonds with hydrogen (important for terminating "loose ends")

Things silicon absolutely cannot do!



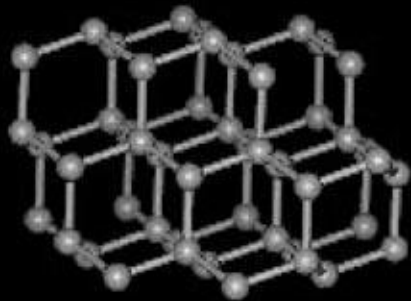


Carbon sooth...?

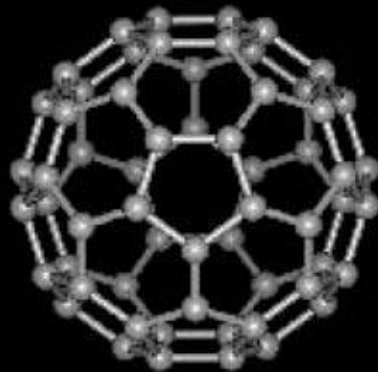




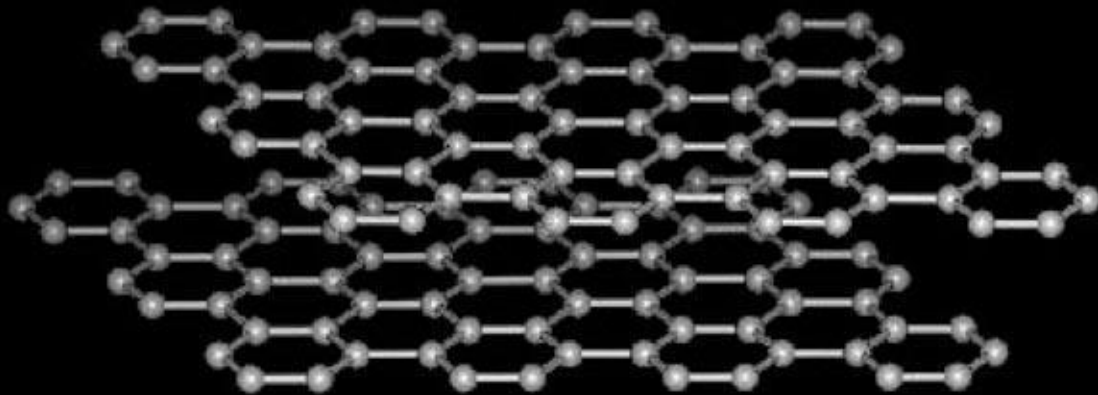
Carbon's allotropic forms



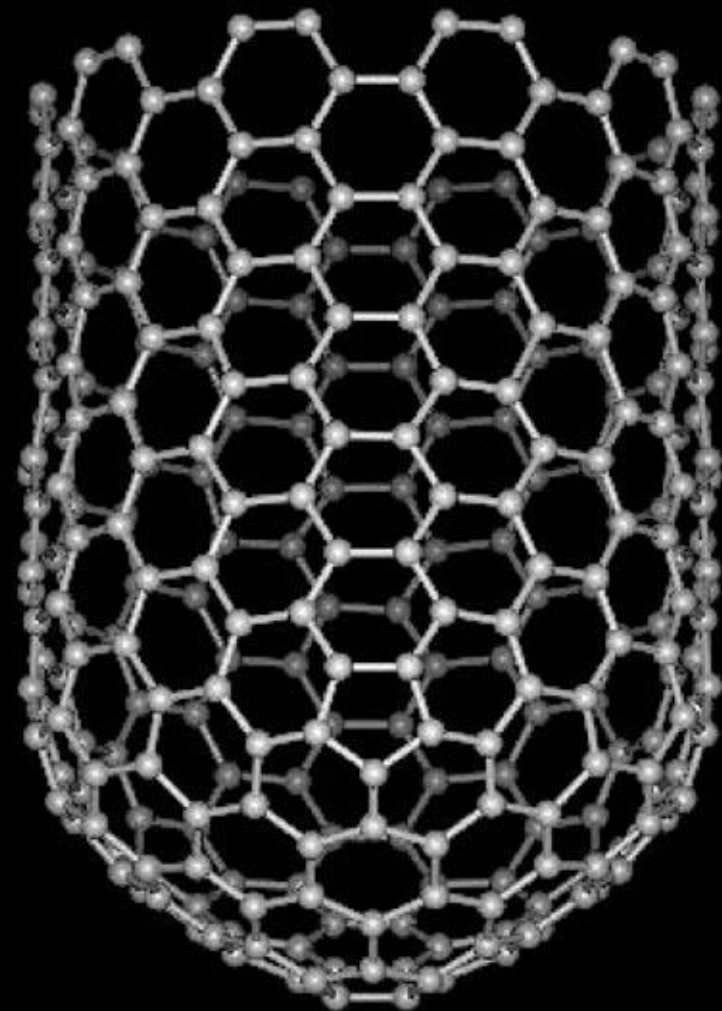
diamond



C_{60}
"buckminsterfullerene"



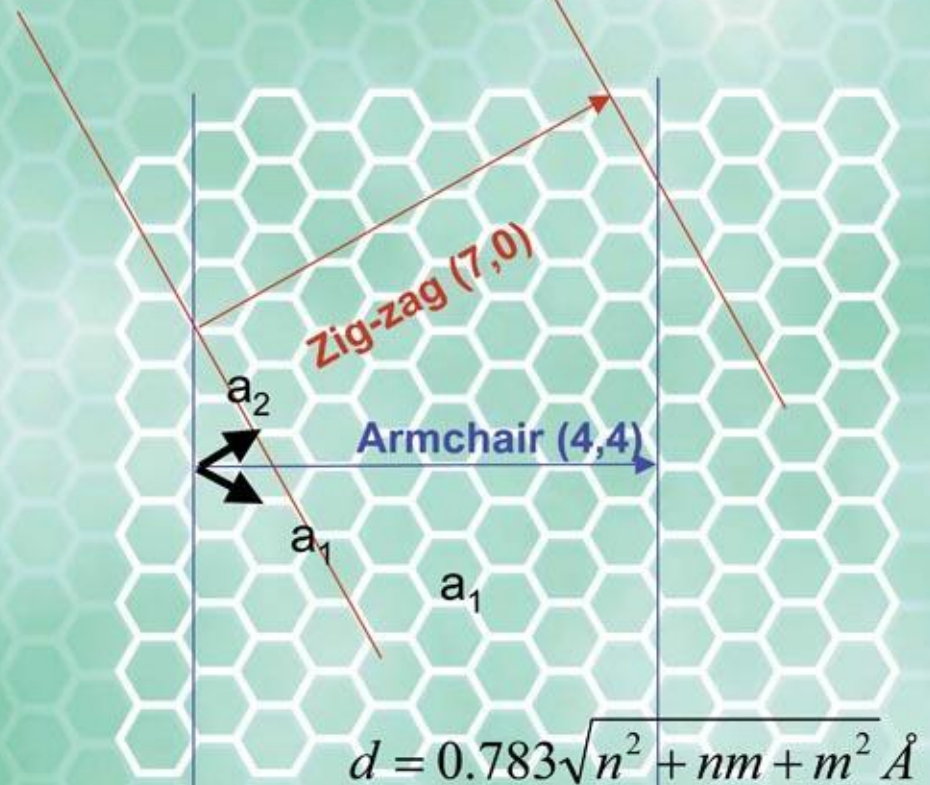
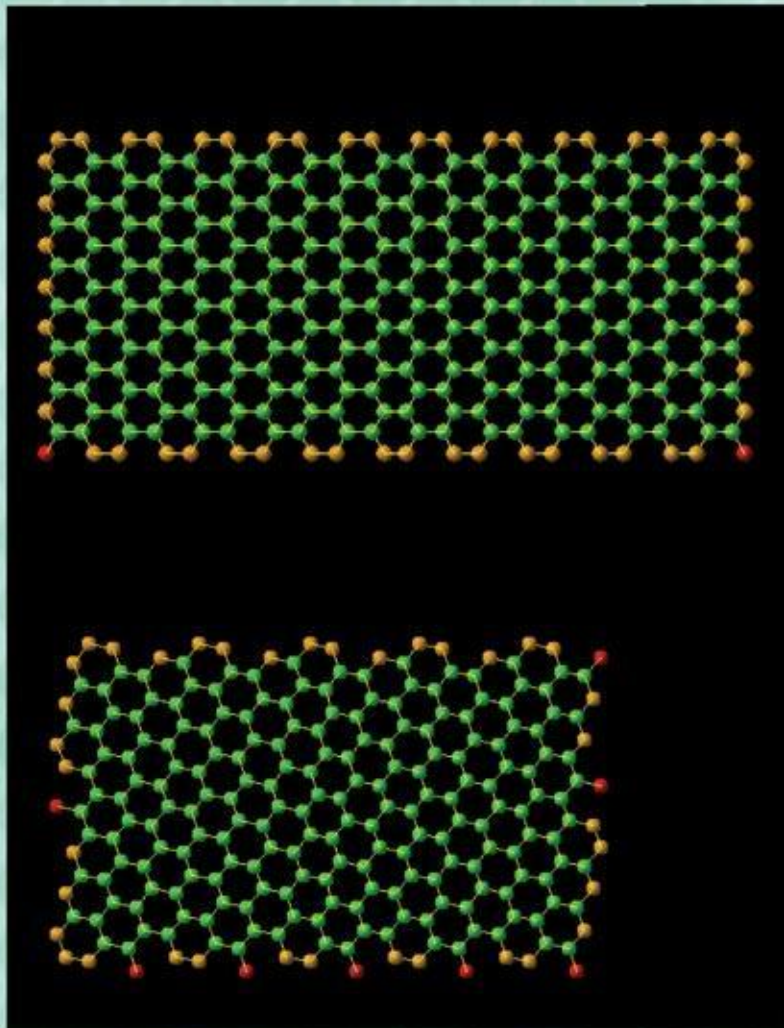
graphite

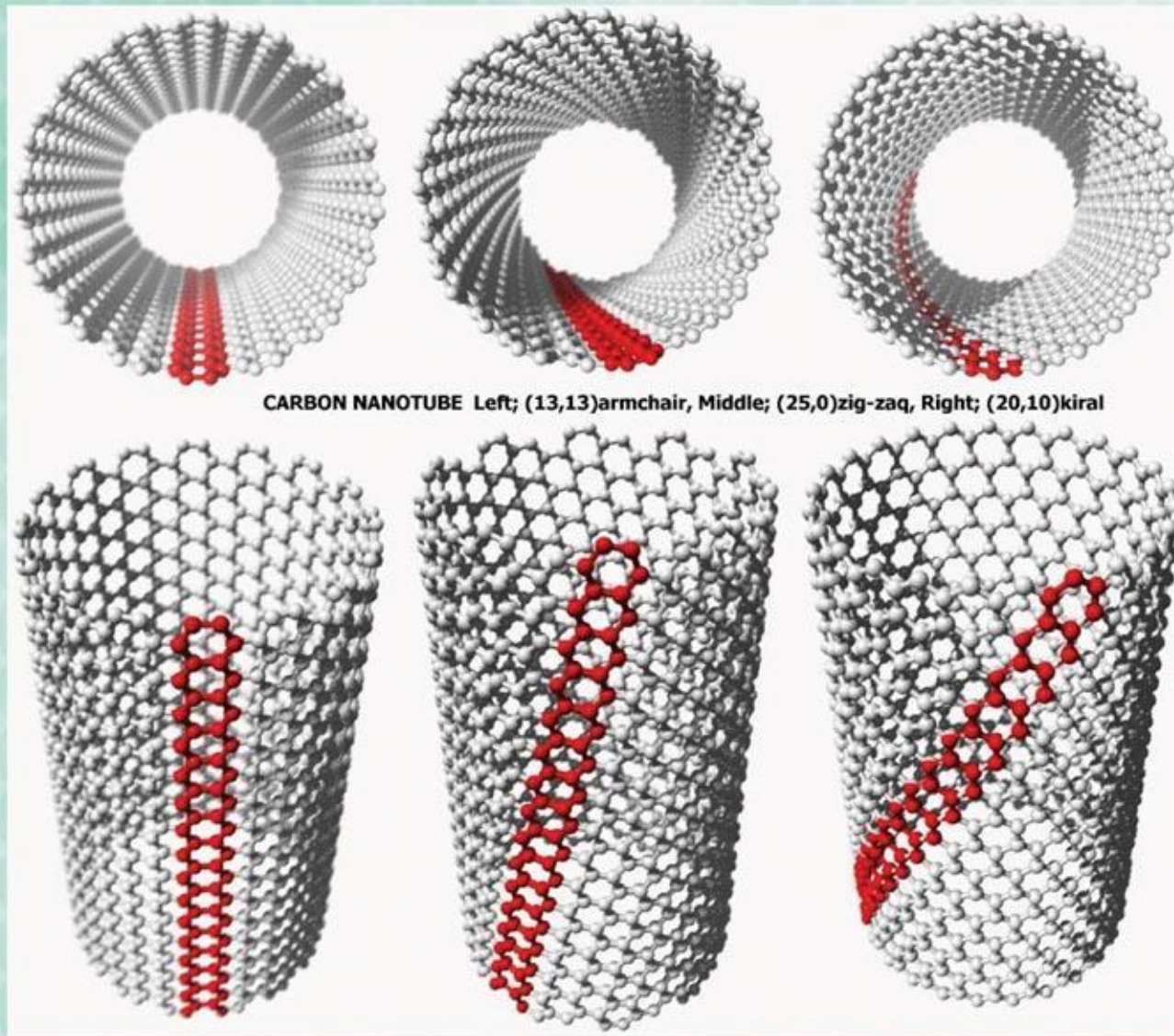


(10,10) tube

Rolling a sheet of graphene

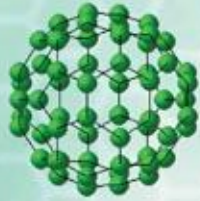
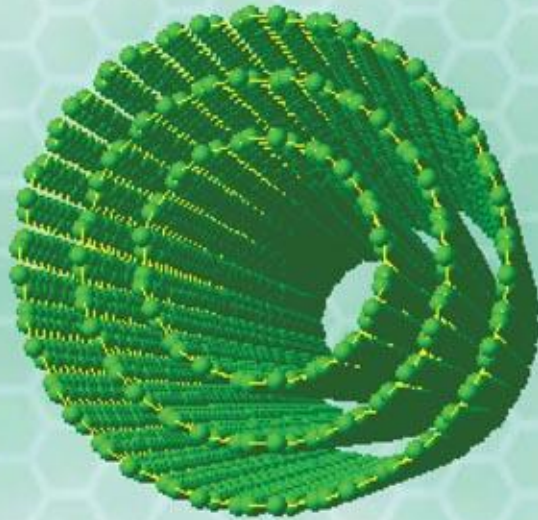
- Nanotubes can be rolled in different angles between 0 and 30 degrees.
- They are classified by the chirality vector given by the base lattice vectors a_1 and a_2 : $C = n a_1 + m a_2$



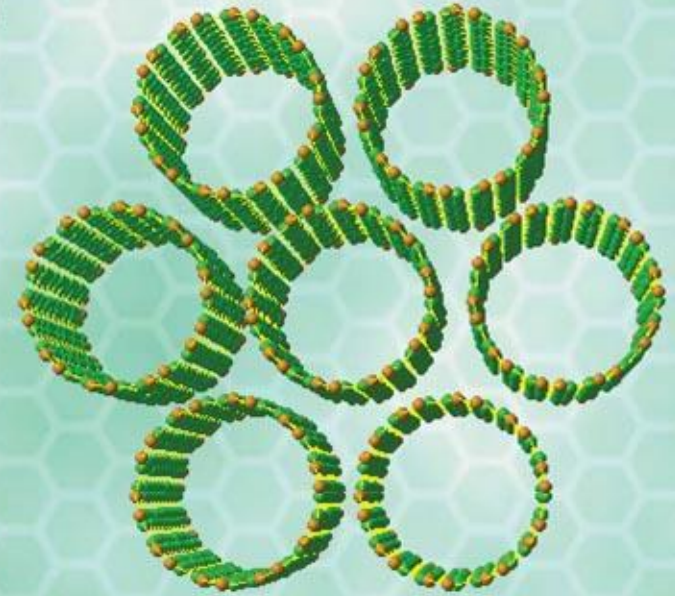




Other types of nanotubes



C60



Multi-walled nanotube (MWNT)

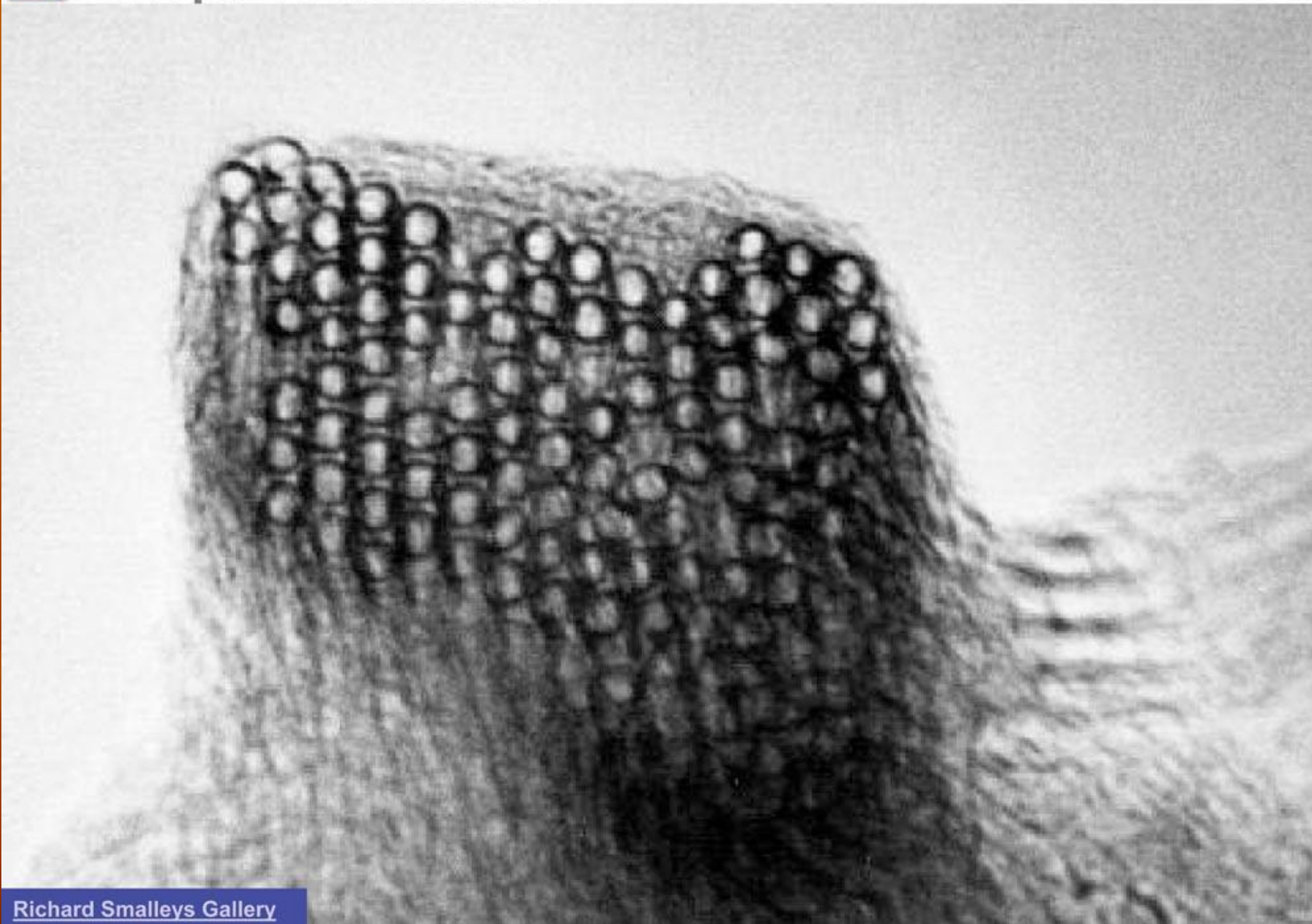
- 5-50 walls interspacing: 3.5 nm (like graphite)
- diameters normally around 10-50 nm (can be up to 200 nm)
- Can be very long, several 100 μm
- Walls slide easily inside each other (like graphite)
- The layers have independent chiralities (one may be armchair, the next zig-zag)

Nanotube rope

- Like graphite, the layers slide easily on each other
- Stick together by van der Waals forces

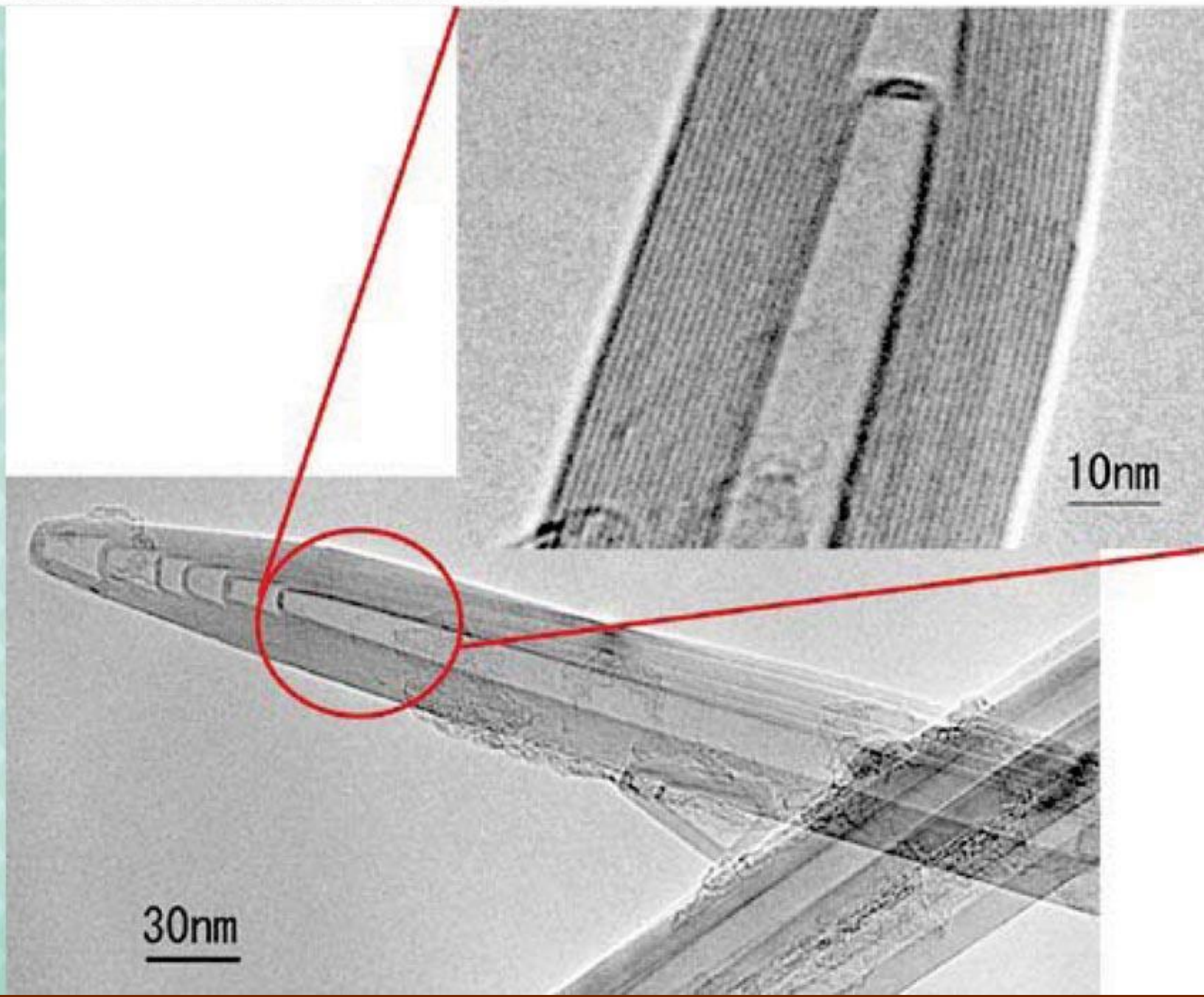


Rope of nanotube





Multiwalled nanotubes





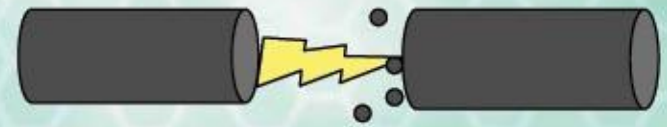
Методы формирования



Methods for fabrication of nanotubes

- **Arc discharge**

- Carbon is evaporated by a plasma of Helium . This is ignited by a high current passing through a graphite anode and cathode



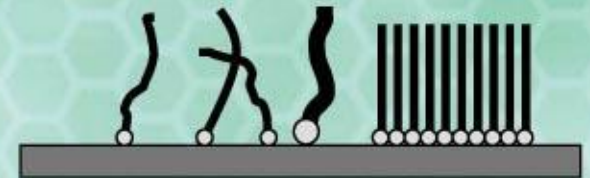
- **Laser evaporation**

- Direct laser vaporization of transitional metal (e.g. Co-Ni,1%) graphite composite electrode targets is done in helium atmosphere at high temperatures (1200°C).

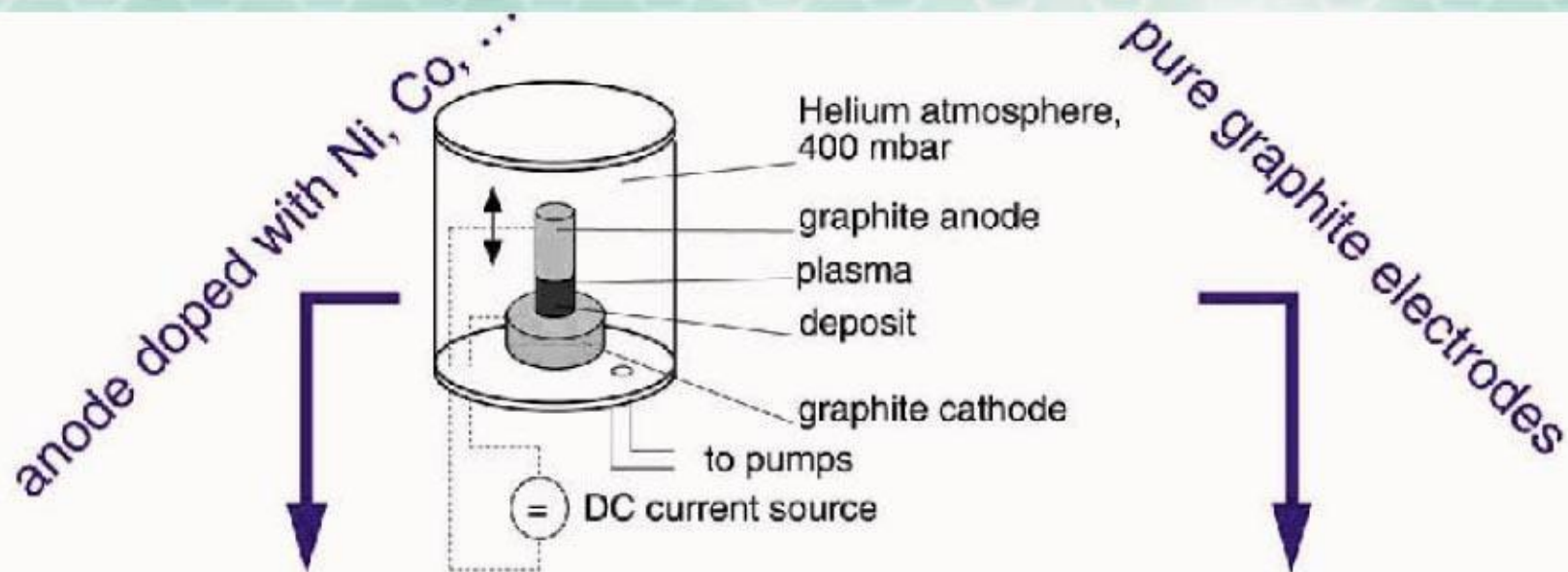


- **Chemical vapor deposition**

- Organic gas is decomposed (e.g. Methane) in an oven containing catalyst particles, at 600-800C. The diameter and type of catalyst particles determine the nanotube diameter and properties.

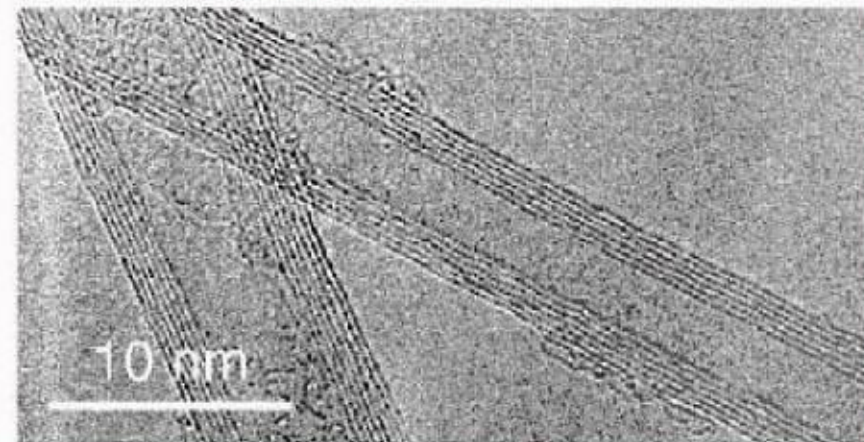
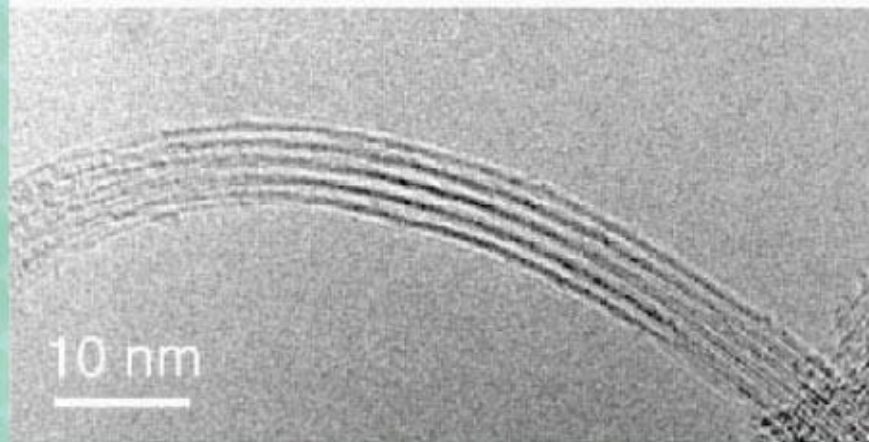


Arc discharge



Single wall nanotubes

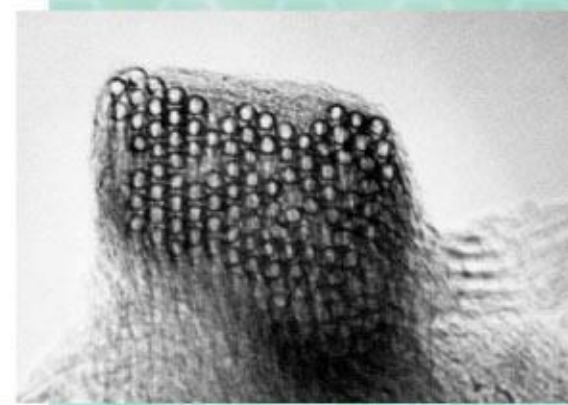
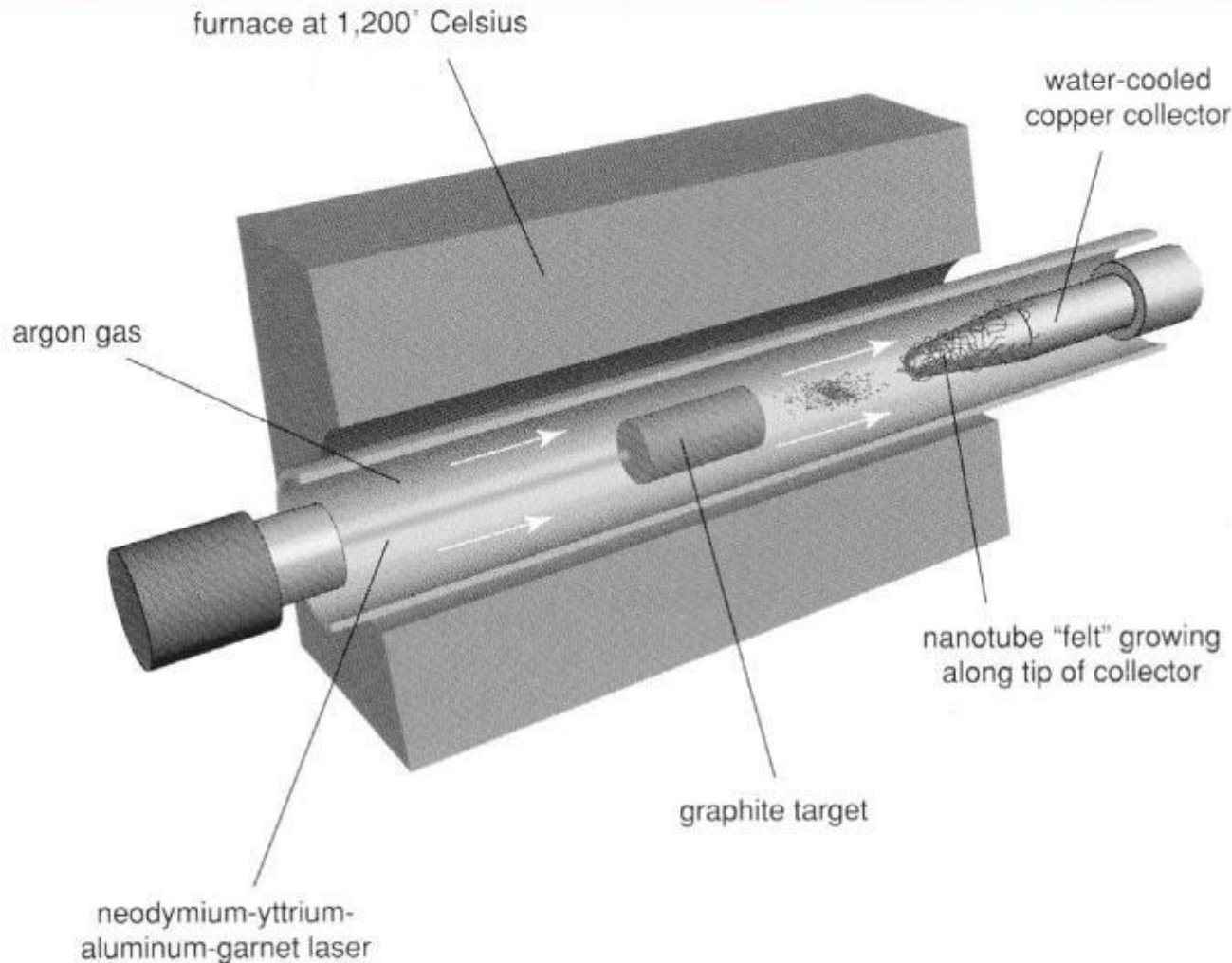
Multiwall nanotubes



Result: Pure SWNT and MWNT of high quality



Laser ablation



Result: Pure SWNT and ropes of high quality



Chemical vapor deposition (CVD)

• CVD

- A hydrocarbon gas is decomposed at a high temperature
- Carbon diffuses into catalyst particle Ni, Fe and is expelled in form of a nanotube

• MWNT:

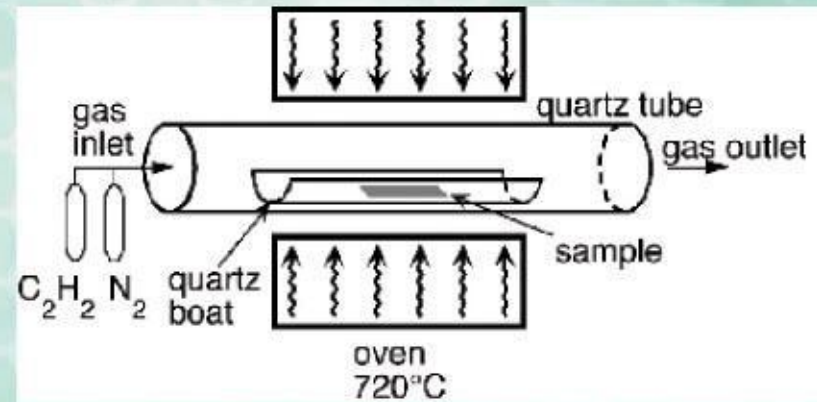
- Acetylene, 600 – 800°C.

• SWNT

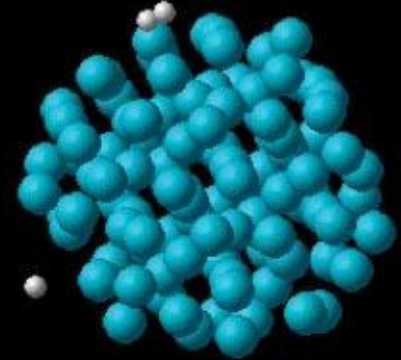
- Carbon monoxide, 900 – 1200°C (SWNT have higher formation energy)

• Result:

- SWNT and MWNT of moderate quality
- Many impurities and defects
- large quantities, can be lithographically positioned

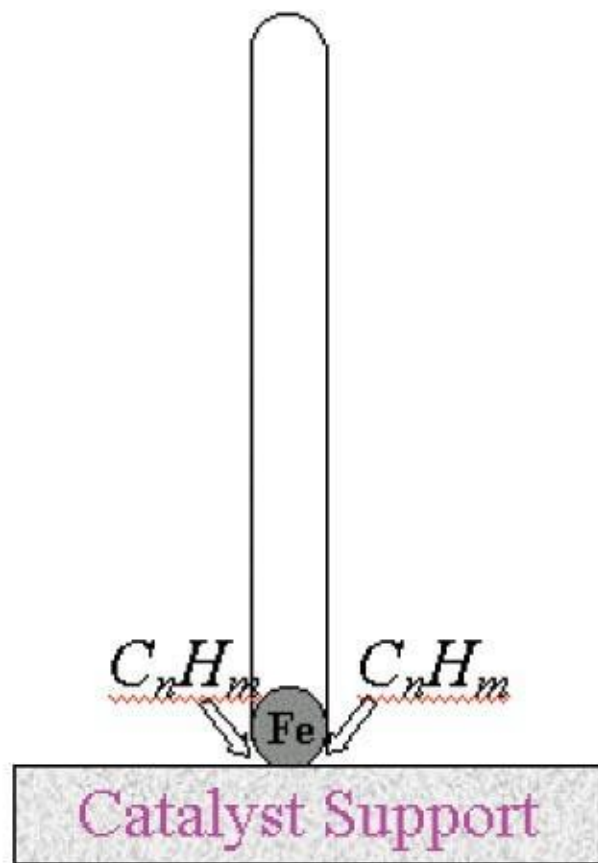


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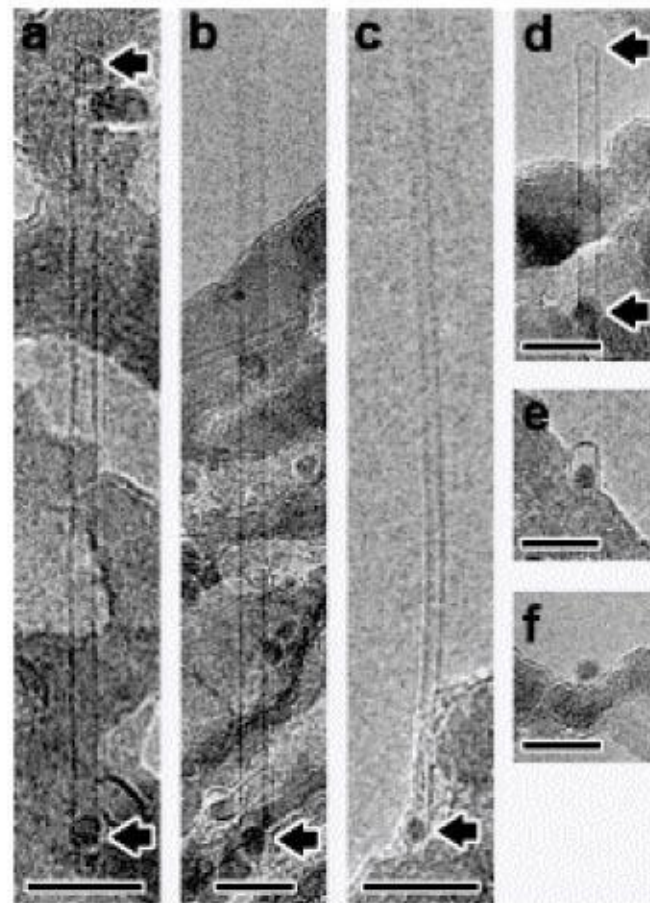




Chemical vapor deposition



'Base' Growth Model



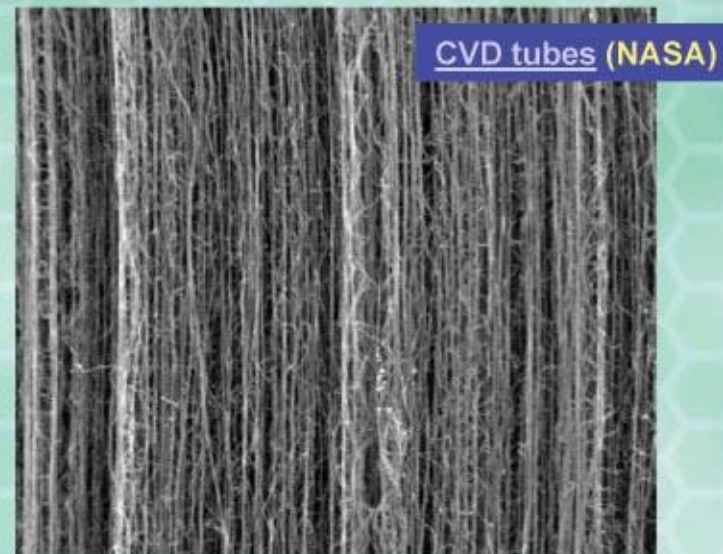
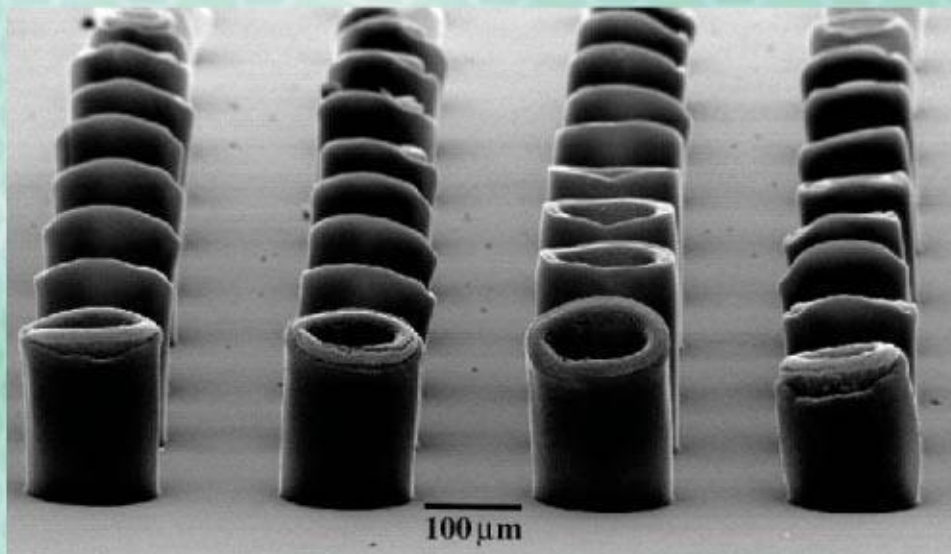
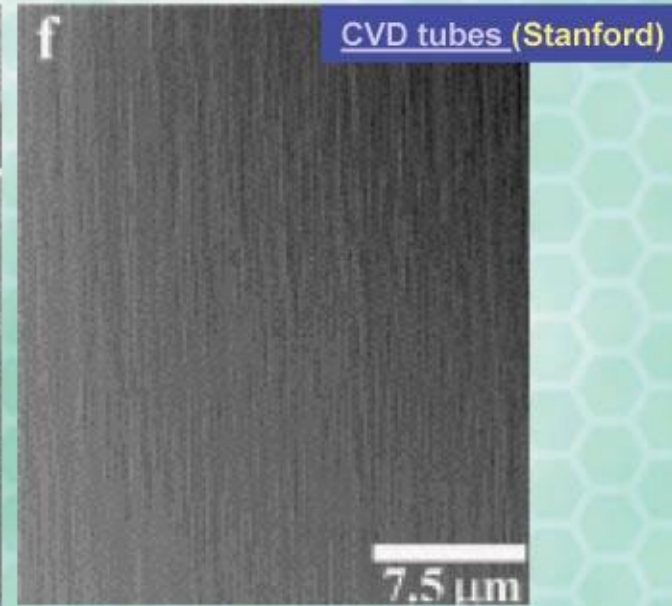
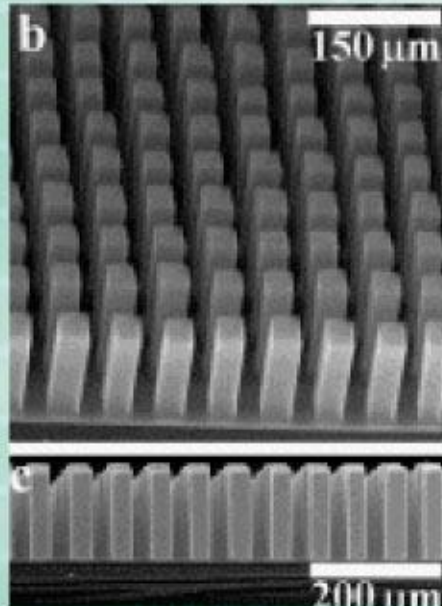
TEM data showing particle-tube relation

The catalyst particles grow from the base, and keep growing as long as the process continues and the catalyst is not encapsulated by carbon soot

Chemical vapor deposition

- **Catalyst printing**

- Catalyst material is lithographically deposited on a surface. The nanotubes grow straight up in thick ropes matching the footprint of the catalyst
- Applications > field emission displays .

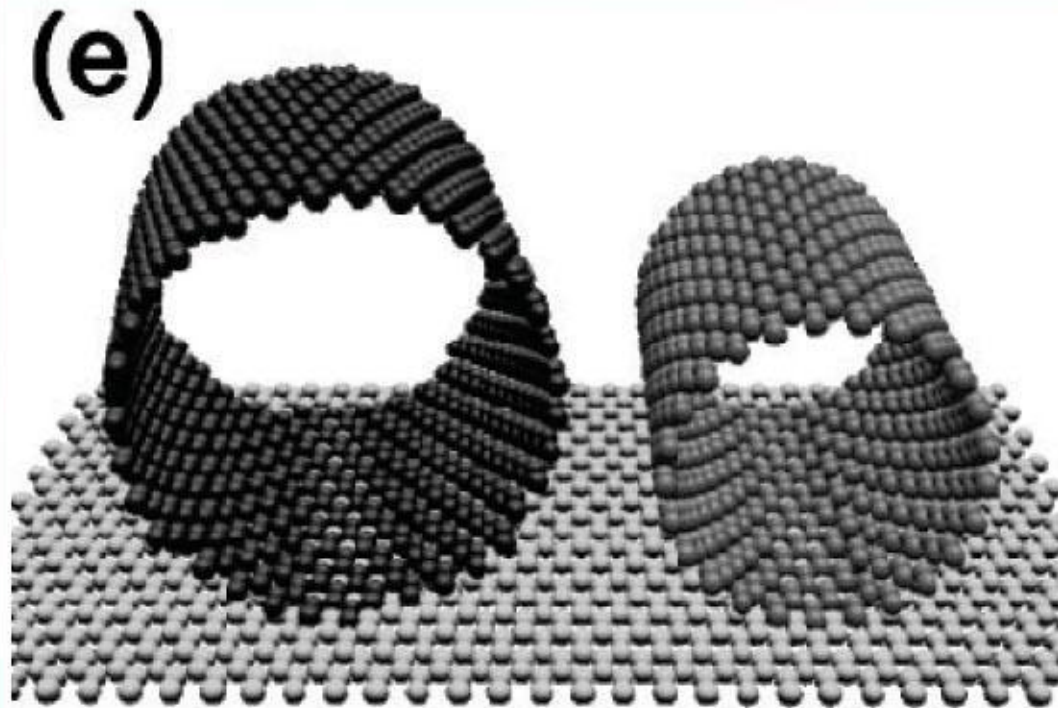
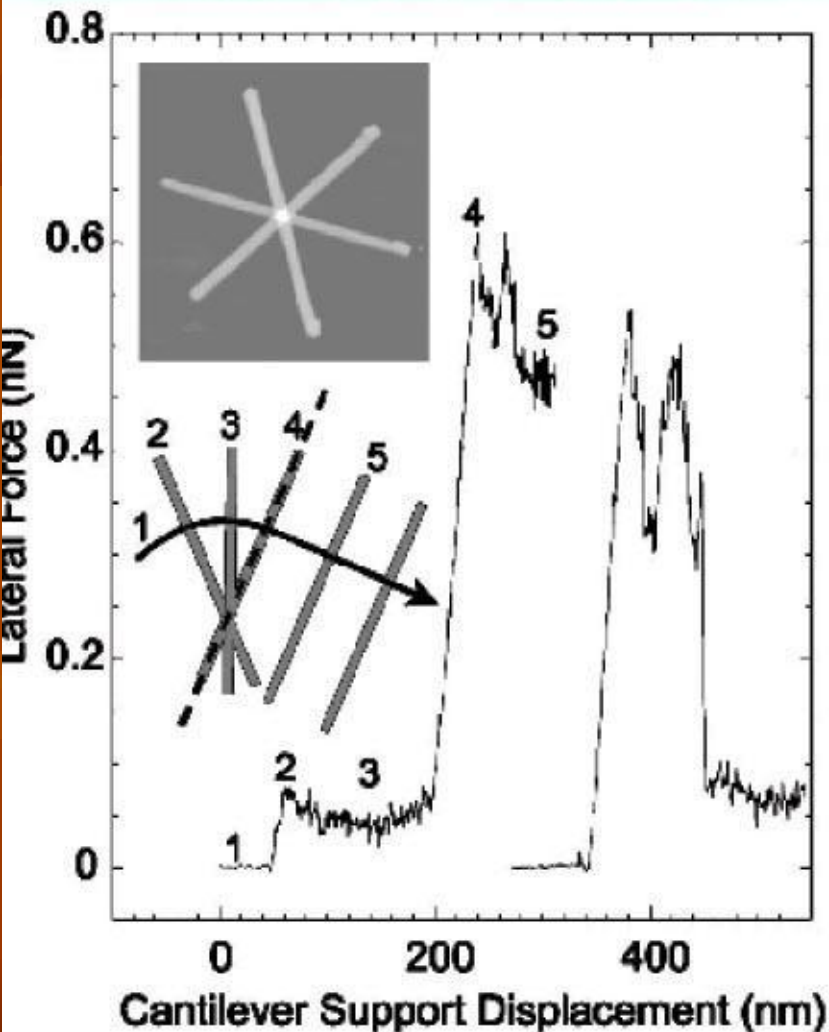




Свойства нанотрубок

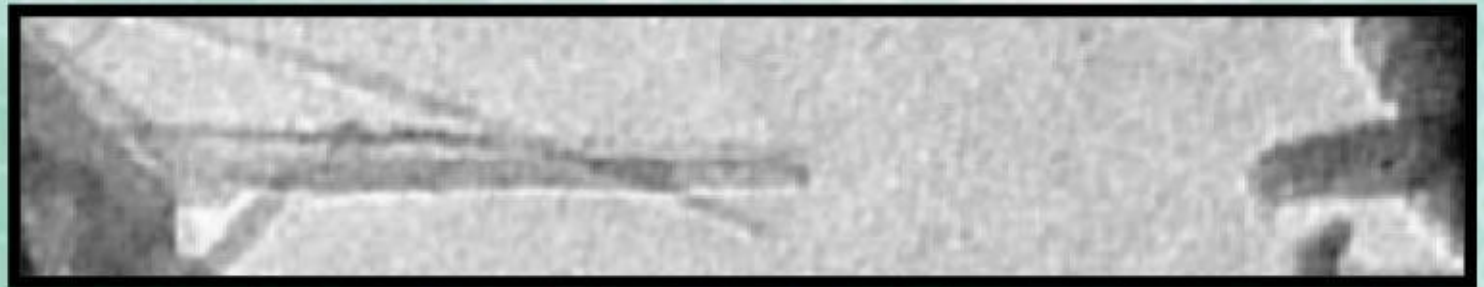
Friction

- The nanotubes were pushed on a graphite surface with an AFM tip.
- Whenever the tubes aligned with the graphite lattice, the friction coefficient went orders of magnitude up...
- Friction due to lattice lock-in
- FRICTION IS DIFFERENT AT NANOSCALE





Mechanical properties: tensile strength



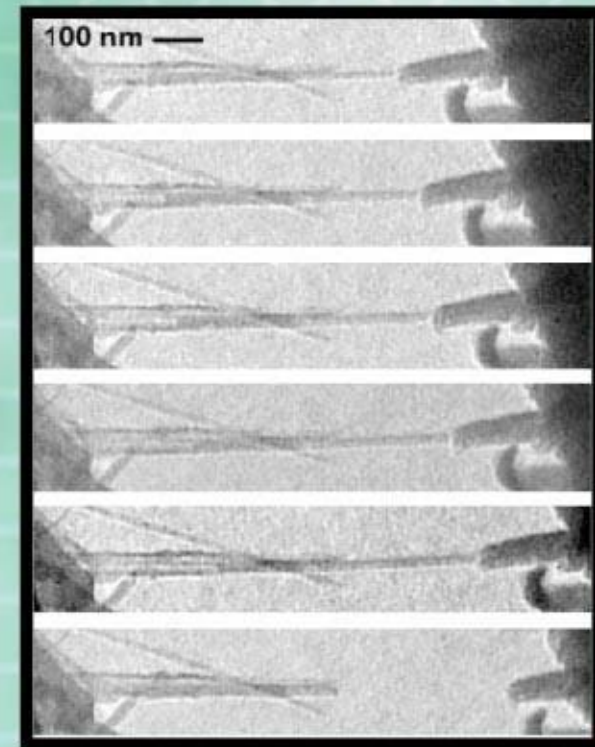
J. Cumings and A. Zettl, Science 289, 602 (2000).

- **Pulling a multiwalled nanotube**

- The inner tube is dragged out of the outer shell – like a **telescope**
- When the tube breaks, the remainder snaps back into its shell
- Difficult to measure tensile strength

- **Defects degrade the strength**

- CVD MWNT much weaker due to high defect densities



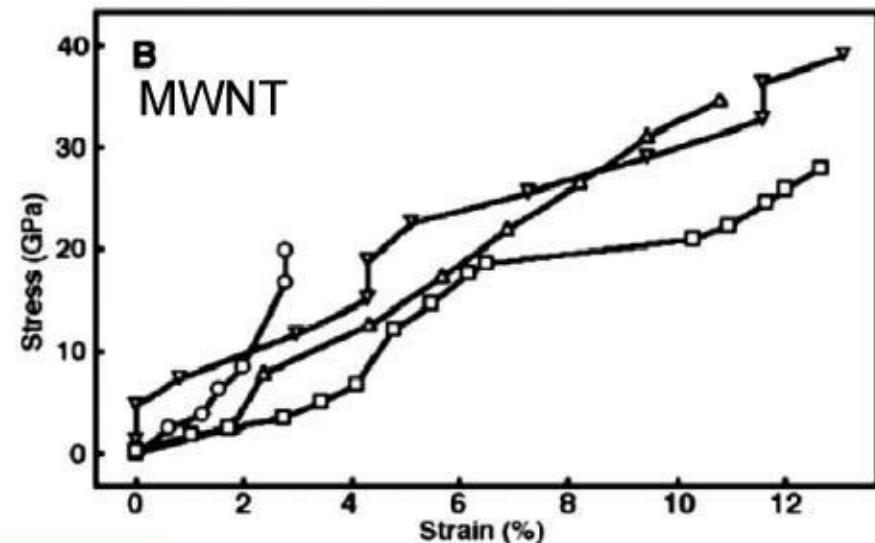
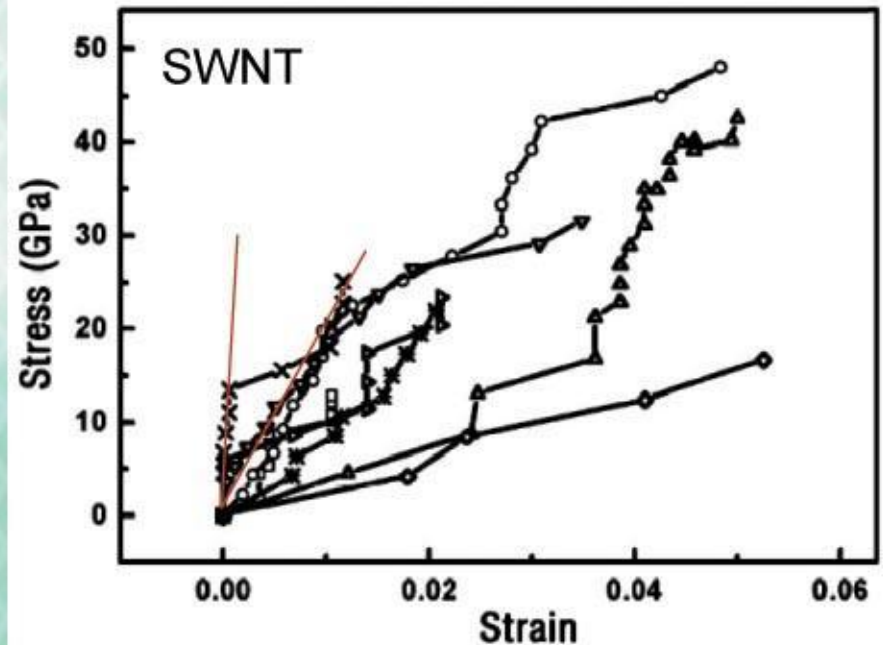
Tensile strength

Youngs modulus

- SWNT: 1.3 TPa
- MWNT: 1 Tpa

Tensile strength

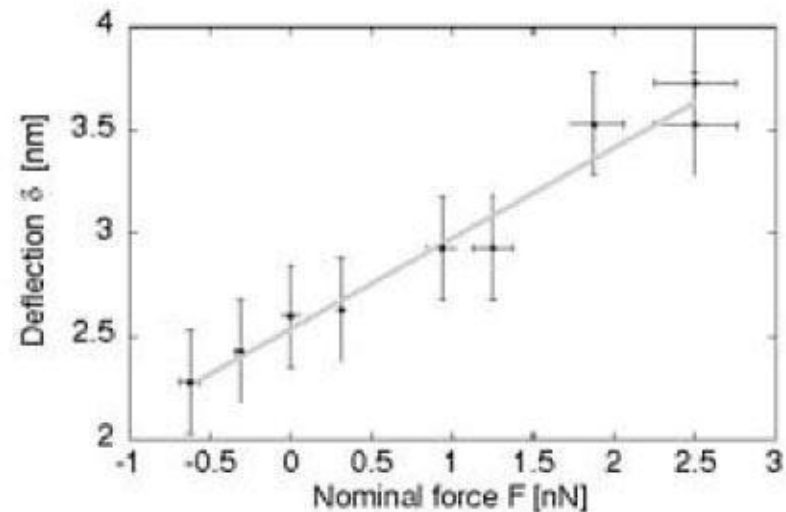
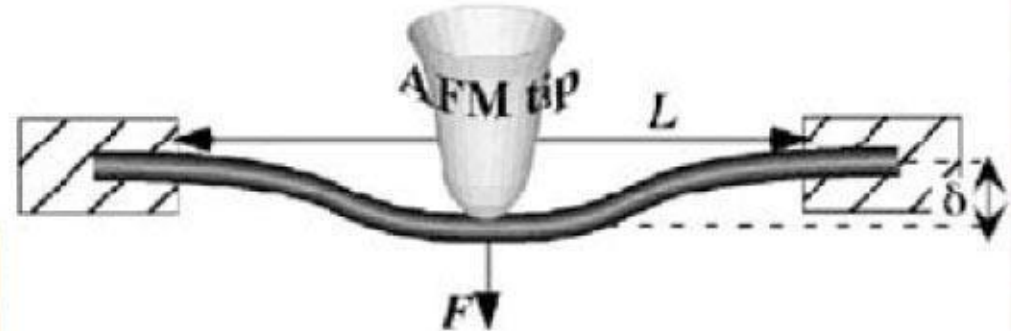
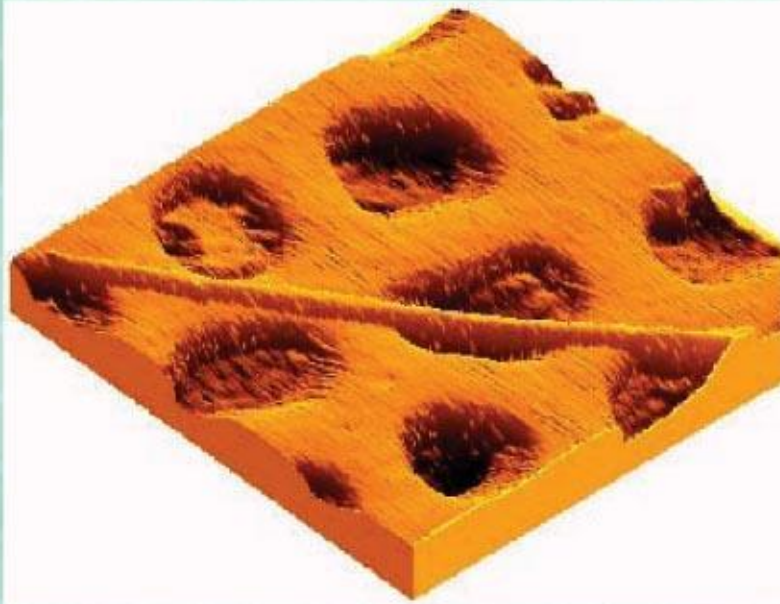
- 30-60 GPa
- Theory: 200 GPa





Mechanical properties

- Youngs modulus: 1 TPa (MWNT, SWNT)



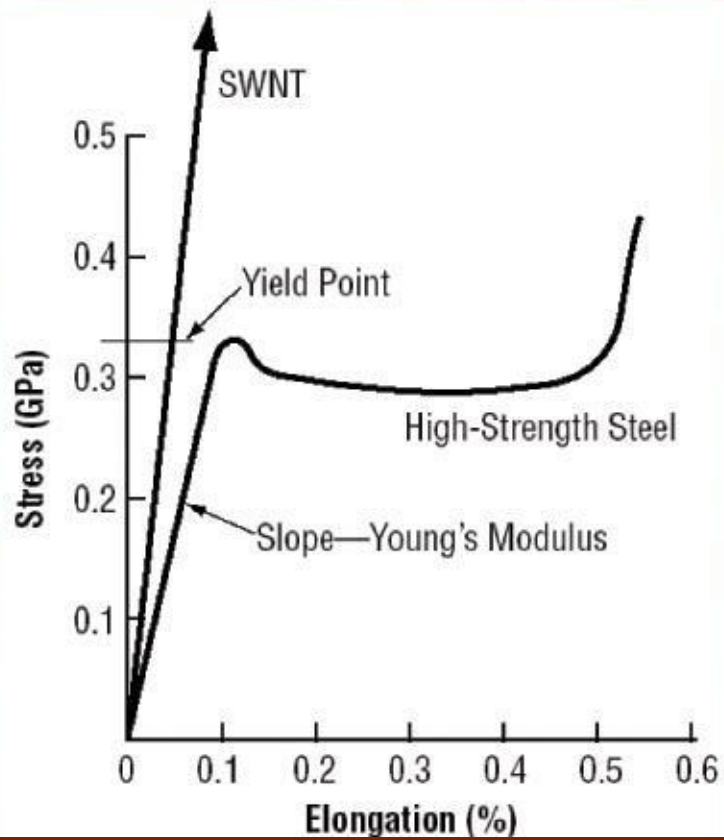
[J. P. Salvetat et al., Adv Mater. \(1999\)](#)



Mechanical properties

Material	Youngs modulus (Gpa)	Tensile Strength (Gpa)	Density (g/cm3)
Silicon	47	1 (brittle!)	2.3
Steel	208	0.4 (ductile)	7.8
Carbon Nanotubes	1000 (MWNT), 1300 (SWNT)	30-60* Theory: 150-200	1.3

* (brittle at low temp, ductile at high, depend on chirality)

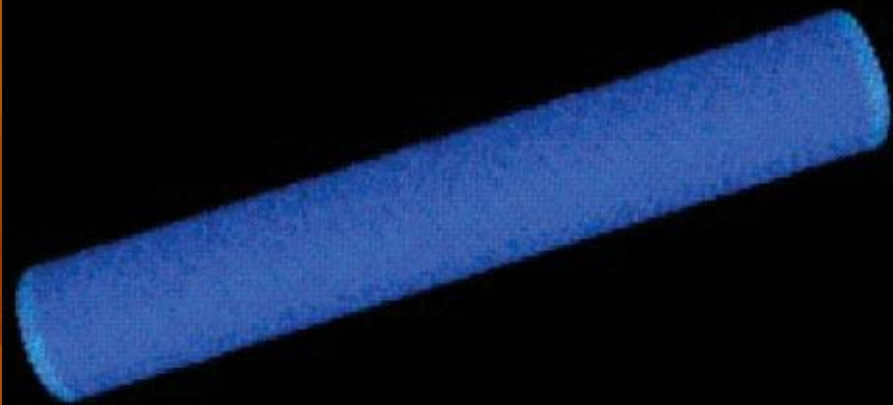


- **Nanotubes 100 times stronger than steel and 6 times lighter**
- **Nanotubes can sustain a large tensile strain:**
 - **5% (SWNT)**
 - **10% (MWNT)**



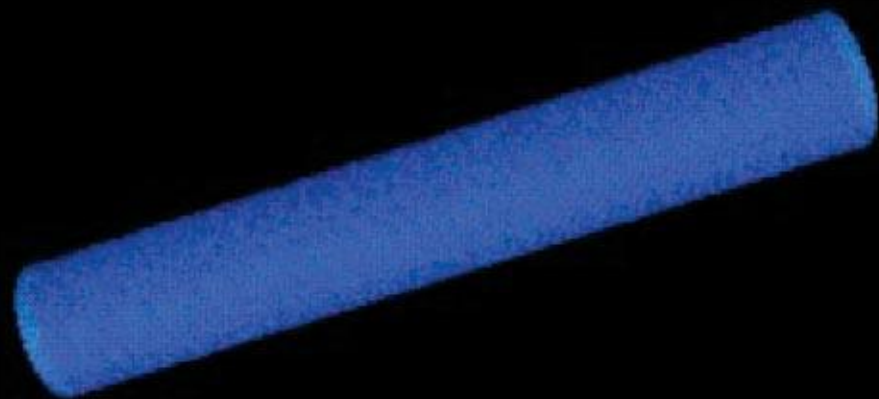
Deformation of nanotubes

MWNT, twisting



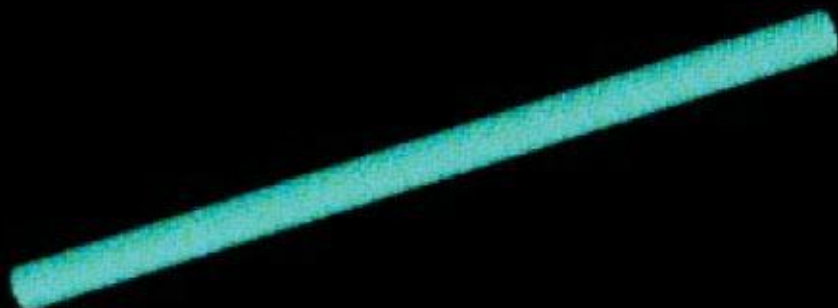
0.00 ps

MWNT, bending



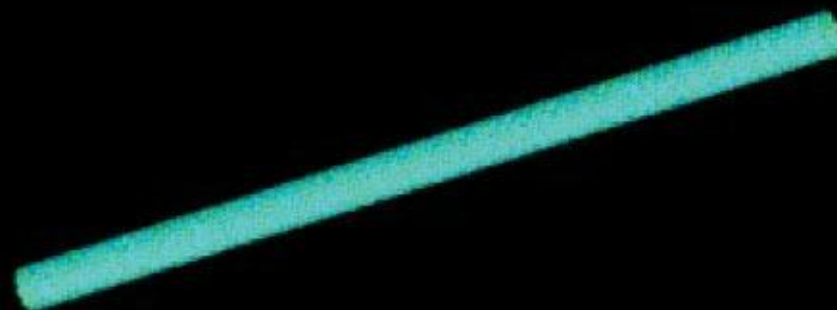
0.00 ps

SWNT, twisting



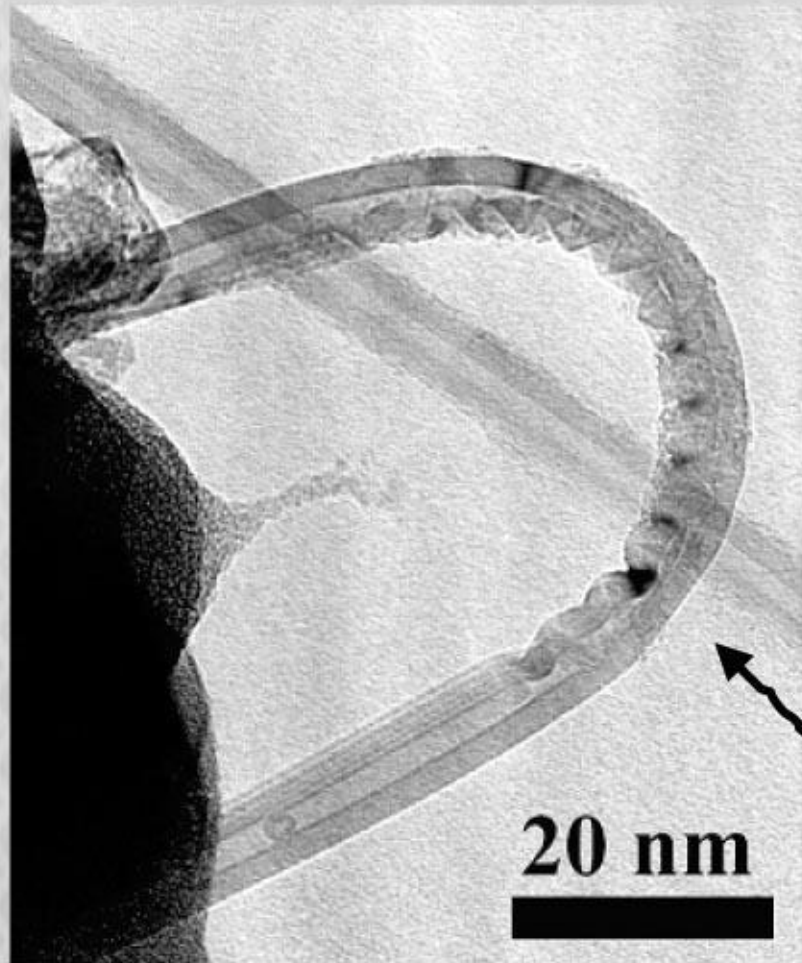
0.00 ps

SWNT, bending

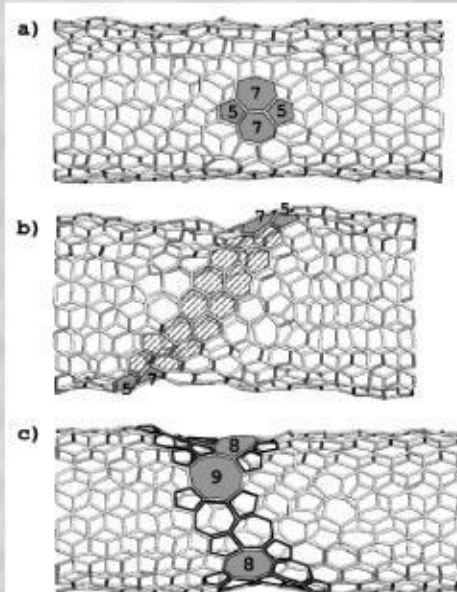


0.00 ps

Deformation of nanotubes



- **Nanotubes can be deform plastically - reversibly**
 - Do not break by bending
 - Deform with little fracturing: stress is compensated by rearrangement of carbon atoms
 - Full recovery upon release



By the way: what happens to the electrical transport???



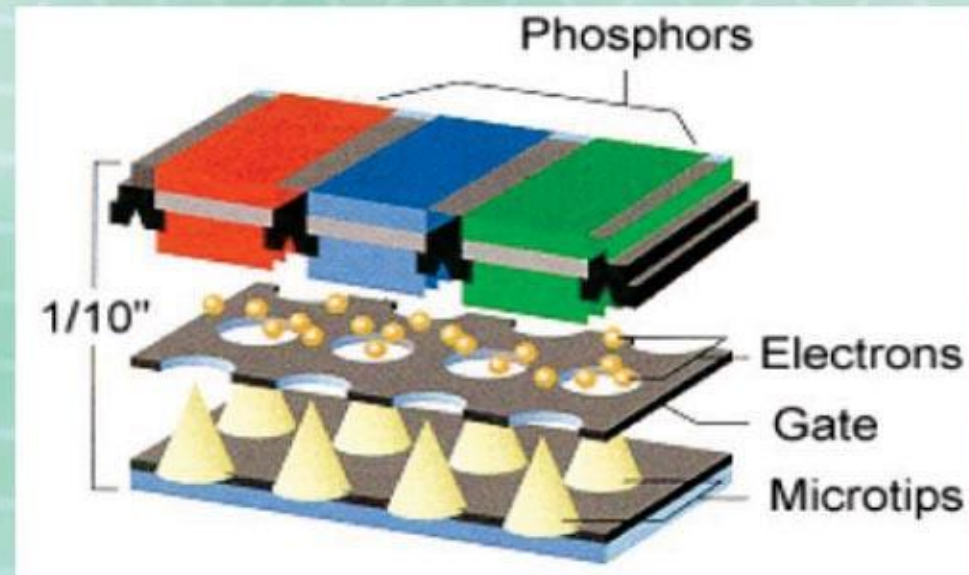
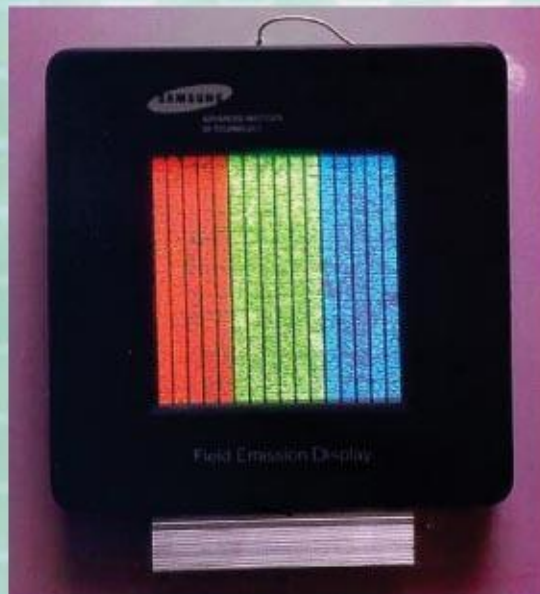
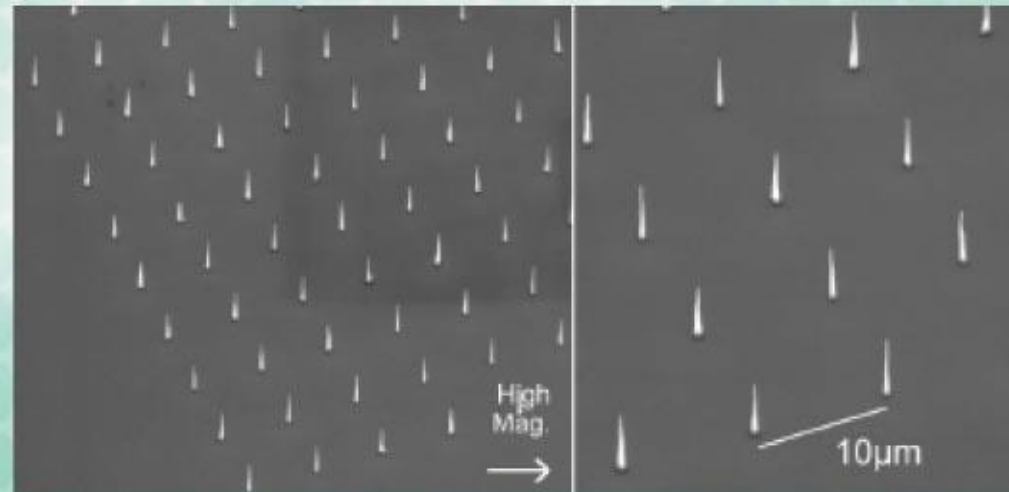
Области применения



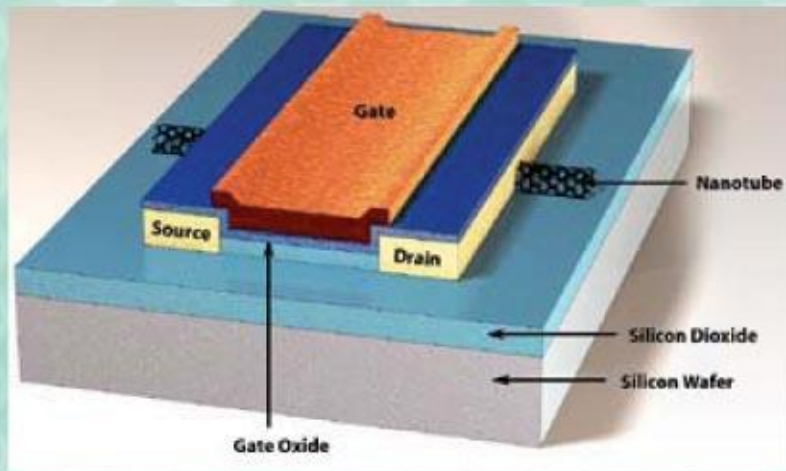
Nanotube display

Carbon nanotube arrays

- Nanotubes can conduct very high current densities
- NT are very sharp (field intensity depends on tip sharpness)
- Ideal properties for field emitters
- Prototypes already made (5 inch color and 14 inch grayscale)



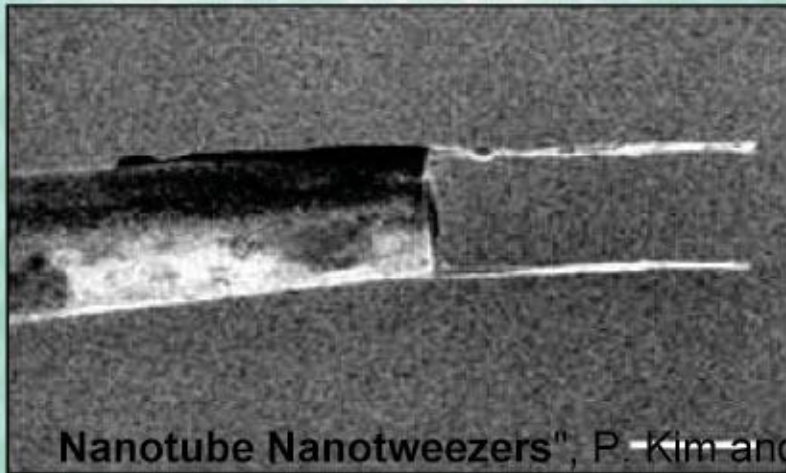
Nanotube transistor



FIELD EFFECT TRANSISTORS

[Nanotubes for Electronics \(Collins and Avouris, Scientific american\)](#)

[Nanotube transistor \(IBM\)](#)



NANO TWEEZERS

"Nanotube Nanotweezers", P. Kim and CM Lieber, Science 286, 2148 - 2150 (1999).

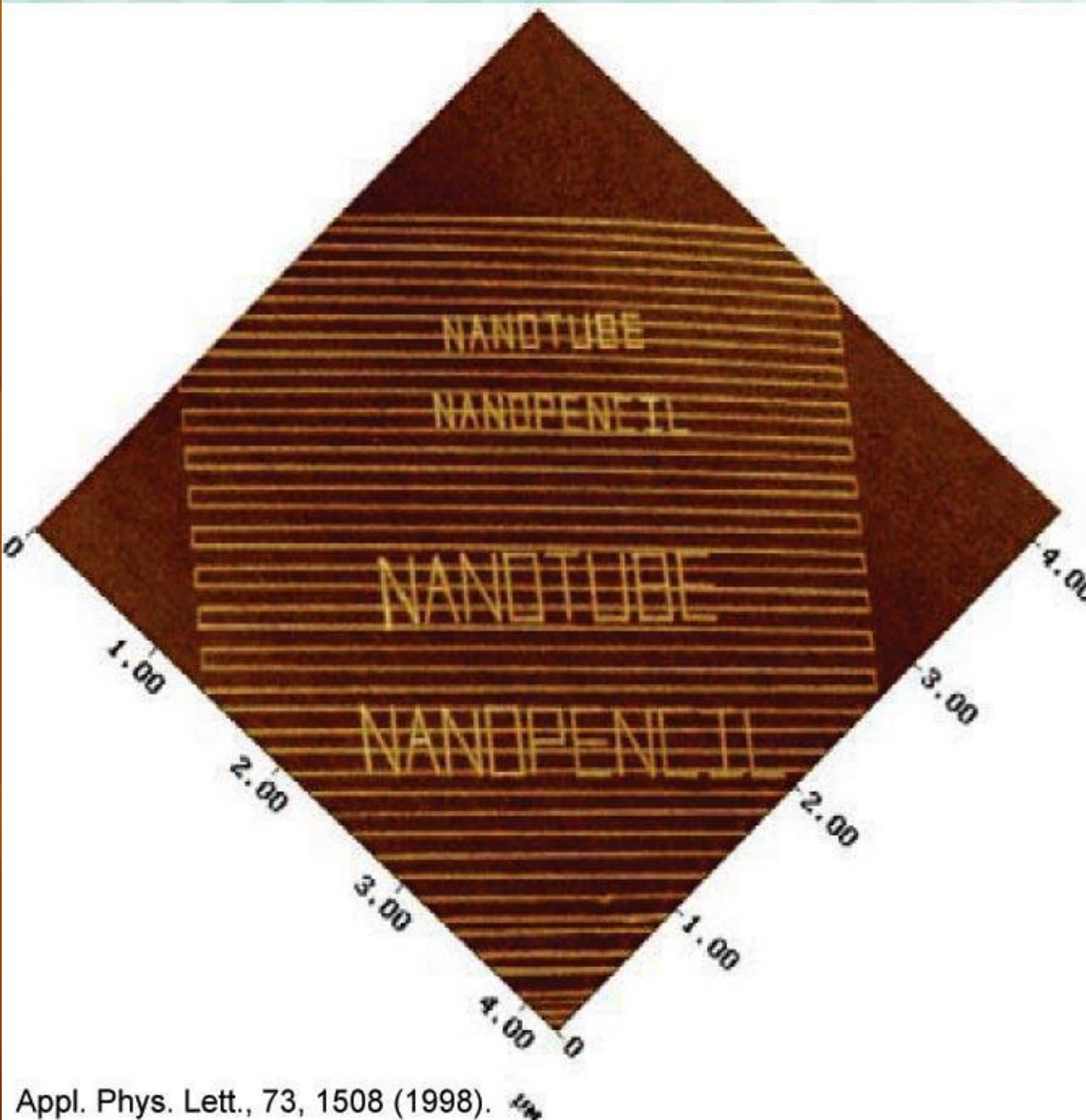
More on this in lecture 4

[Nanotube Nanotweezers \(BBC News article\)](#)

[Nanotweezers grabbing DNA \(Research paper\)](#)

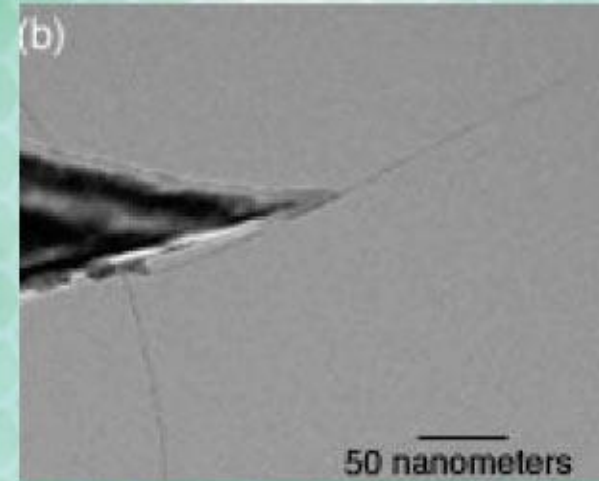


A real nanotube stiftblyant



A nanotube at the end of an AFM:

- High aspect ratio
- Nanolithography
- Conducting AFM/STM



[Nanotube AFM](#) (Popular article)

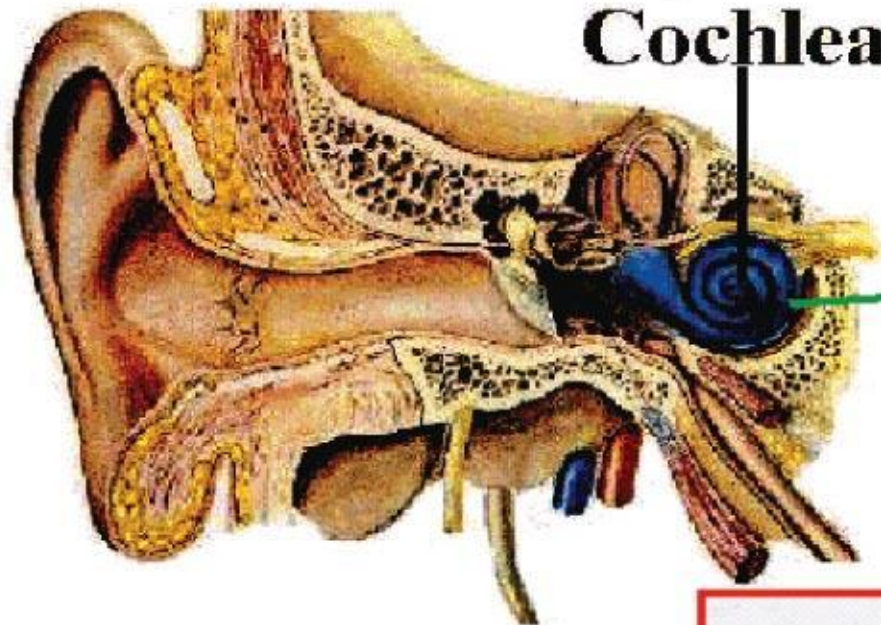
[Nanotube AFM](#) (Lieber, Harvard)

[Nanotube pencil](#) (Dai, Stanford)

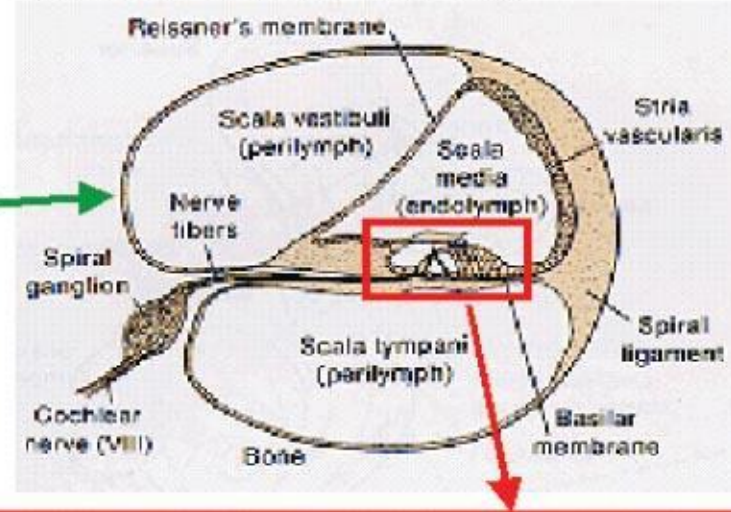


Nanotube hearing aid

Cochlea

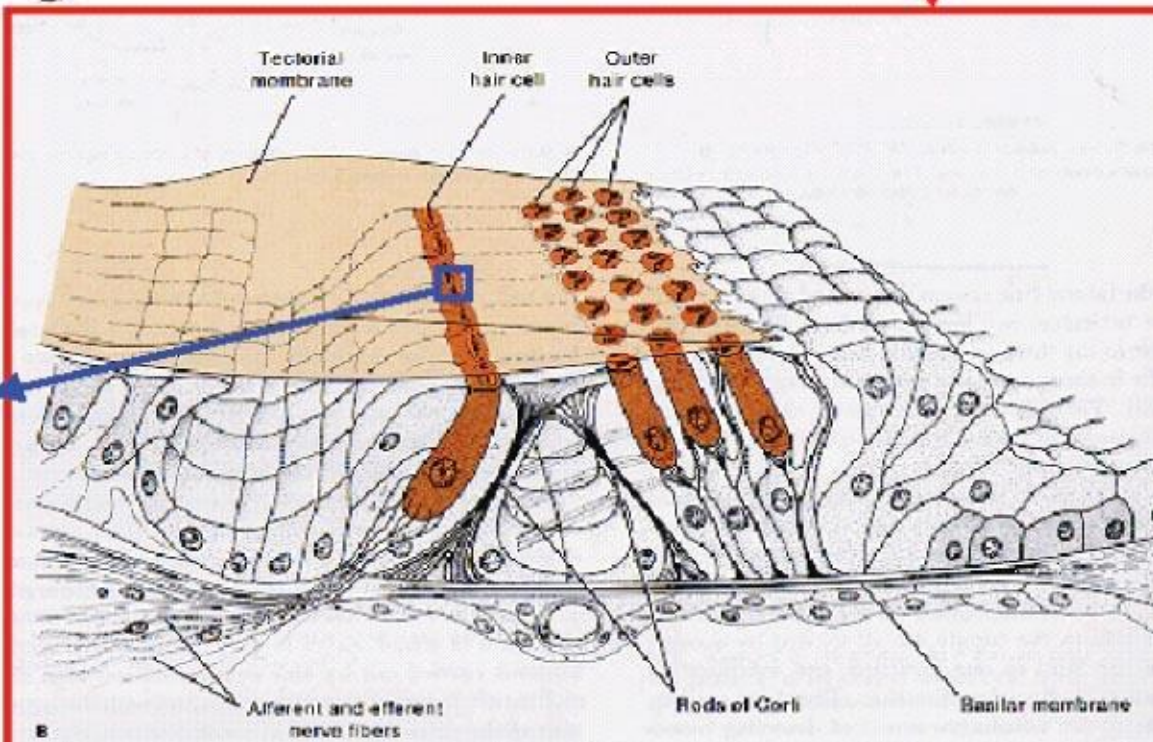
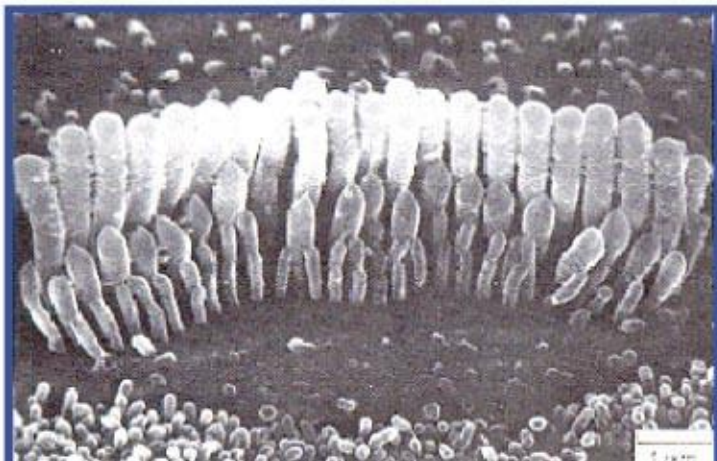


Cross-section through cochlear canal (Eckert 1988)



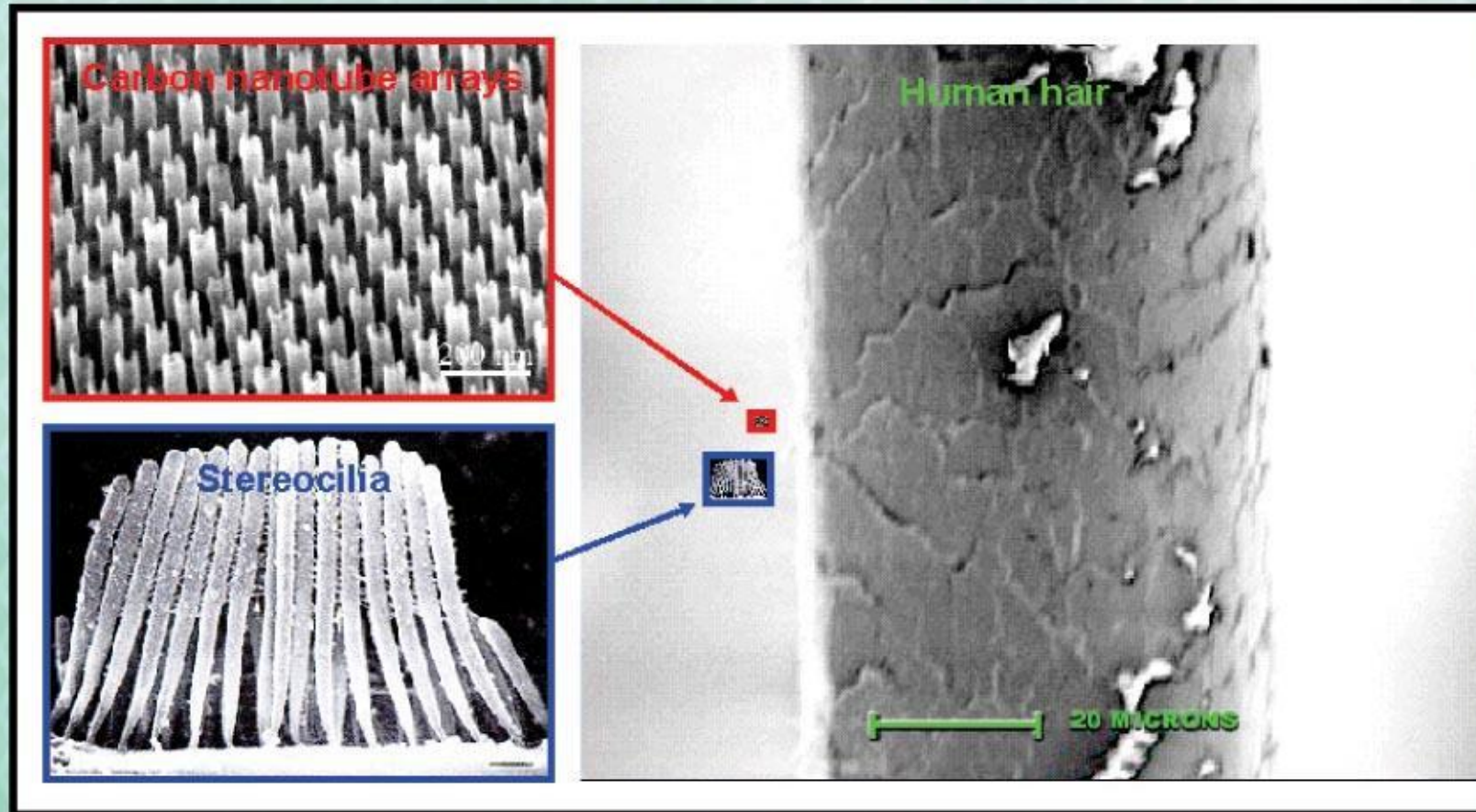
(Alec N. Salt, Washington University)

Stereocilia (Pickles 1988)





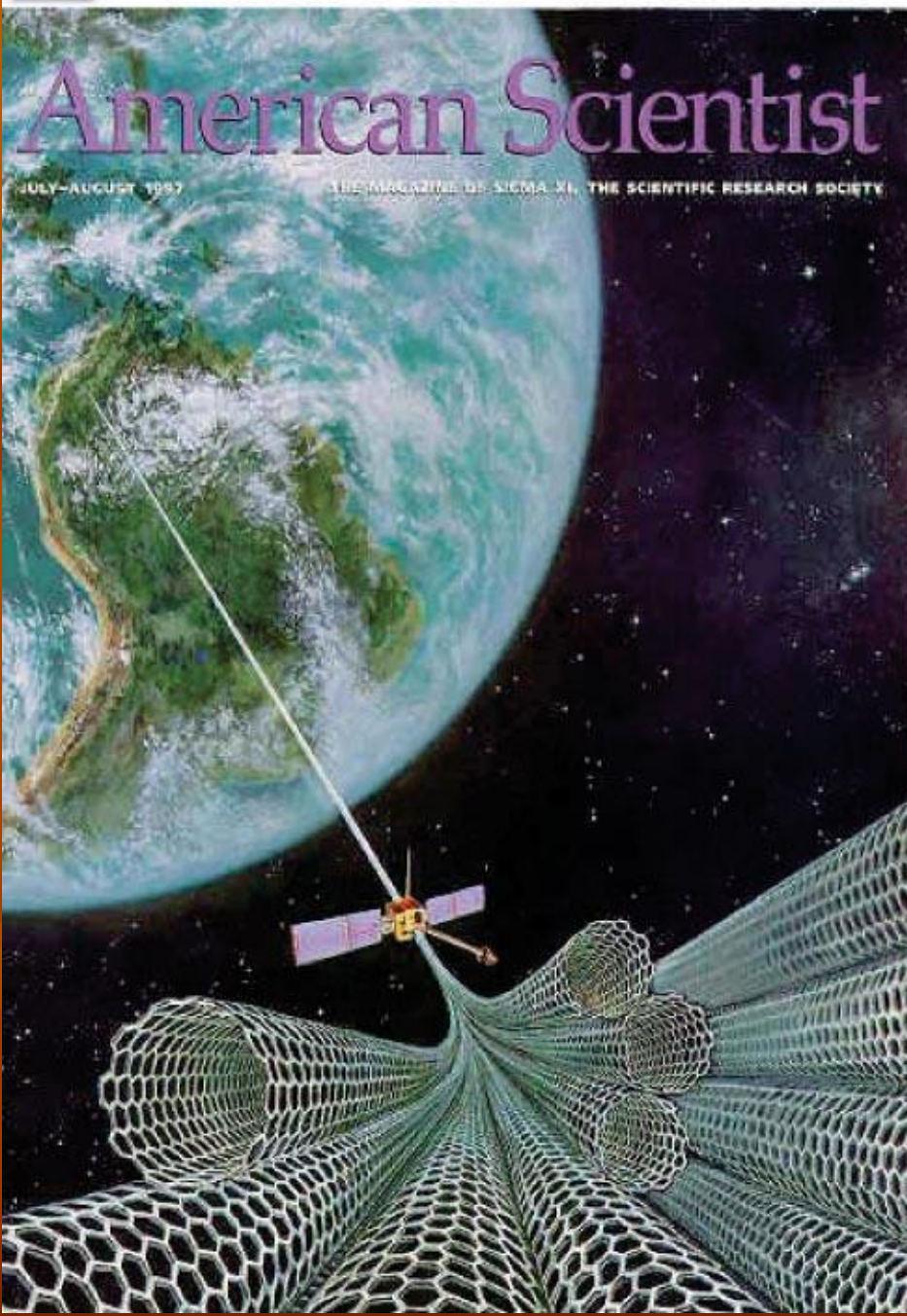
Nanotube hearing aid



- Highly ordered arrays of parallel carbon nanotubes grown by CVD
- Claimed to be sensitive enough to pick up activity level of living cells (how does a cancer cell sound?)



Nanoscale materials: space elevator



A space shuttle uses 1.8 million kg rocket fuel

A space elevator uses none

What is needed

- An extremely tall base tower on Earth
- A heavy weight orbiting the Earth
- A cable that connects the tower to the weight
- A spacecraft that can ride the cable into orbit

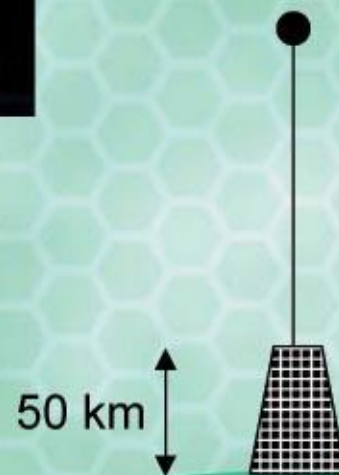


Nanoscale materials: space elevator



NASA REPORT

- **Cable length:** 144000 km
- **Cable material:** 60 GPa tensile strength
- **Base tower (anchor):** 50 km
 - The tower is necessary to hold the cable
 - The cable needs to be strong, and therefore thick, and therefore heavy itself
 - Carbon nanotubes are not only just about strong enough, they are also light!



[Space elevator report \(NASA\)](#)