

**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



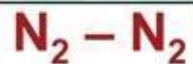
Shared valence electrons  
(strength depends on distance)

- 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)

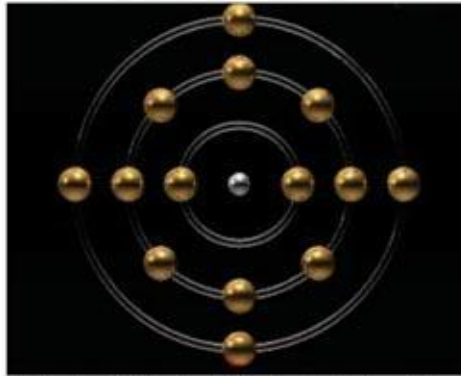


# Periodic Table

1 hydrogen 1 <b>H</b> 1.0079	2 helium 2 <b>He</b> 4.0026	3 lithium 3 <b>Li</b> 6.941	4 beryllium 4 <b>Be</b> 9.0122	5 boron 5 <b>B</b> 10.811	6 carbon 6 <b>C</b> 12.011	7 nitrogen 7 <b>N</b> 14.007	8 oxygen 8 <b>O</b> 15.999	9 fluorine 9 <b>F</b> 18.998	10 neon 10 <b>Ne</b> 20.180	11 sodium 11 <b>Na</b> 22.990	12 magnesium 12 <b>Mg</b> 24.305	13 aluminum 13 <b>Al</b> 26.982	14 silicon 14 <b>Si</b> 28.086	15 phosphorus 15 <b>P</b> 30.974	16 sulfur 16 <b>S</b> 32.065	17 chlorine 17 <b>Cl</b> 35.453	18 argon 18 <b>Ar</b> 39.948	
19 potassium 19 <b>K</b> 39.098	20 calcium 20 <b>Ca</b> 40.078	21 scandium 21 <b>Sc</b> 44.956	22 titanium 22 <b>Ti</b> 47.867	23 vanadium 23 <b>V</b> 50.942	24 chromium 24 <b>Cr</b> 51.996	25 manganese 25 <b>Mn</b> 54.938	26 iron 26 <b>Fe</b> 55.845	27 cobalt 27 <b>Co</b> 58.933	28 nickel 28 <b>Ni</b> 58.693	29 copper 29 <b>Cu</b> 63.546	30 zinc 30 <b>Zn</b> 65.39	31 gallium 31 <b>Ga</b> 69.723	32 germanium 32 <b>Ge</b> 72.61	33 arsenic 33 <b>As</b> 74.922	34 selenium 34 <b>Se</b> 78.96	35 bromine 35 <b>Br</b> 79.904	36 krypton 36 <b>Kr</b> 83.80	
37 rubidium 37 <b>Rb</b> 85.468	38 strontium 38 <b>Sr</b> 87.62	39 yttrium 39 <b>Y</b> 88.906	40 zirconium 40 <b>Zr</b> 91.224	41 niobium 41 <b>Nb</b> 92.906	42 molybdenum 42 <b>Mo</b> 95.94	43 technetium 43 <b>Tc</b> [98]	44 ruthenium 44 <b>Ru</b> 101.07	45 rhodium 45 <b>Rh</b> 102.91	46 palladium 46 <b>Pd</b> 106.42	47 silver 47 <b>Ag</b> 107.87	48 cadmium 48 <b>Cd</b> 112.41	49 indium 49 <b>In</b> 114.82	50 tin 50 <b>Sn</b> 118.71	51 antimony 51 <b>Sb</b> 121.76	52 tellurium 52 <b>Te</b> 127.60	53 iodine 53 <b>I</b> 126.90	54 xenon 54 <b>Xe</b> 131.29	
55 caesium 55 <b>Cs</b> 132.91	56 barium 56 <b>Ba</b> 137.33	57-70 lanthanoids *	71 lutetium 71 <b>Lu</b> 174.97	72 hafnium 72 <b>Hf</b> 178.49	73 tantalum 73 <b>Ta</b> 180.95	74 tungsten 74 <b>W</b> 183.84	75 rhenium 75 <b>Re</b> 186.21	76 osmium 76 <b>Os</b> 190.23	77 iridium 77 <b>Ir</b> 192.22	78 platinum 78 <b>Pt</b> 195.08	79 gold 79 <b>Au</b> 196.97	80 mercury 80 <b>Hg</b> 200.59	81 thallium 81 <b>Tl</b> 204.38	82 lead 82 <b>Pb</b> 207.2	83 bismuth 83 <b>Bi</b> 208.98	84 polonium 84 <b>Po</b> [209]	85 astatine 85 <b>At</b> [210]	86 radon 86 <b>Rn</b> [222]
87 francium 87 <b>Fr</b> [223]	88 radium 88 <b>Ra</b> [226]	89-102 actinoids **	103 lawrencium 103 <b>Lr</b> [262]	104 rutherfordium 104 <b>Rf</b> [261]	105 dubnium 105 <b>Db</b> [262]	106 seaborgium 106 <b>Sg</b> [266]	107 bohrium 107 <b>Bh</b> [264]	108 hassium 108 <b>Hs</b> [269]	109 meitnerium 109 <b>Mt</b> [268]	110 unnilium 110 <b>Uun</b> [271]	111 ununium 111 <b>Uuu</b> [272]	112 unbinium 112 <b>Uub</b> [277]	113 ununium 113 <b>Uuq</b> [289]	114 unquadium 114 <b>Uuq</b> [289]	115 unpentium 115 <b>Uup</b> [288]	116 unhexium 116 <b>Uuh</b> [286]	117 unseptium 117 <b>Uus</b> [284]	118 unoctium 118 <b>Uuo</b> [284]

Key:

element name
atomic number
<b>symbol</b>
atomic weight (mean relative mass)



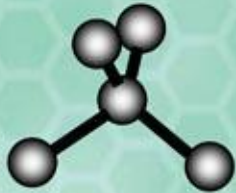
\*lanthanoids

\*\*actinoids

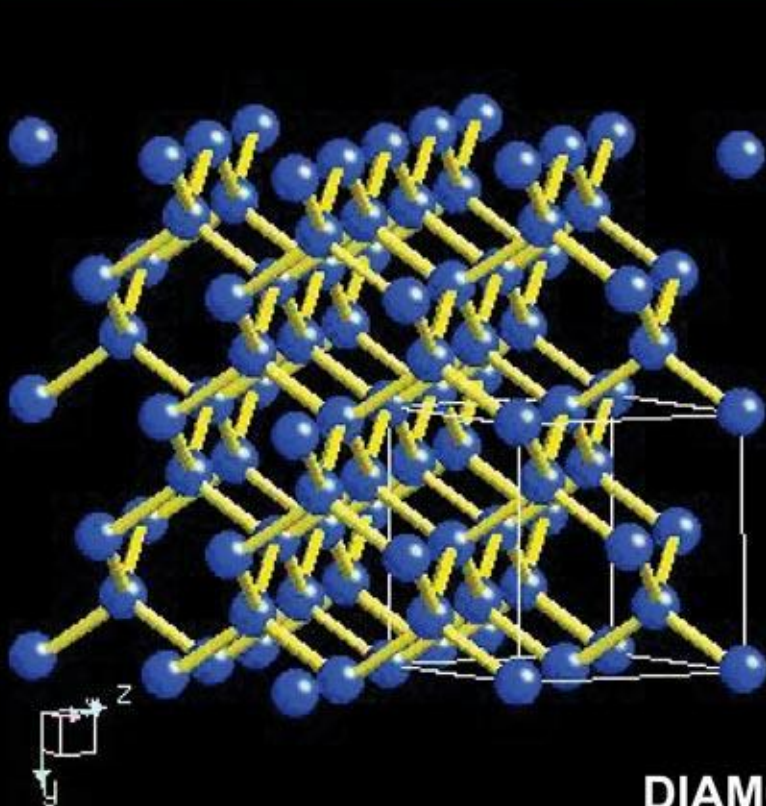
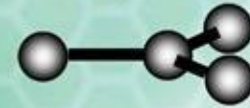
lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium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



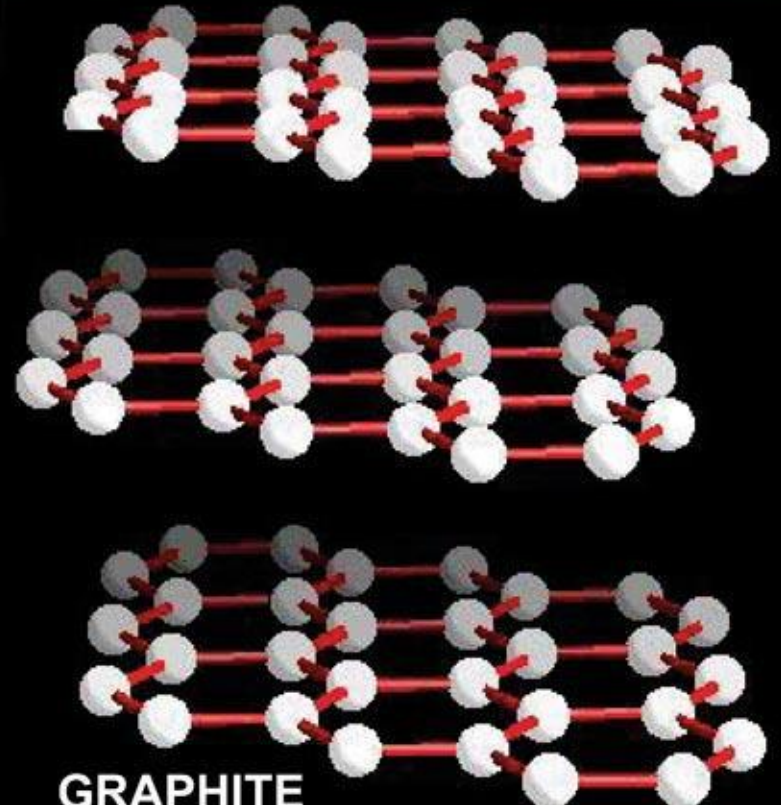
# Diamond and graphite



Bond length 1.4 nm  
Stacking distance 3.4 nm

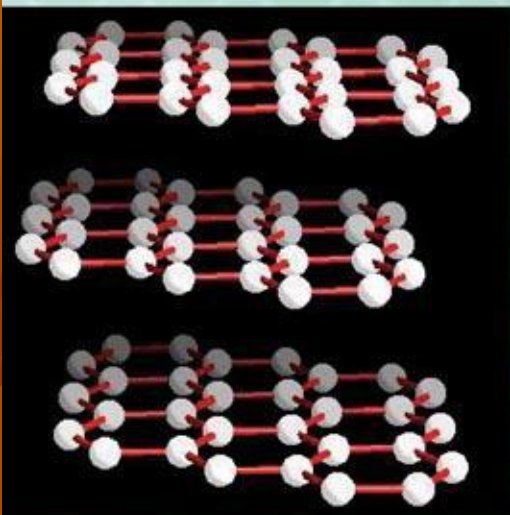


DIAMOND

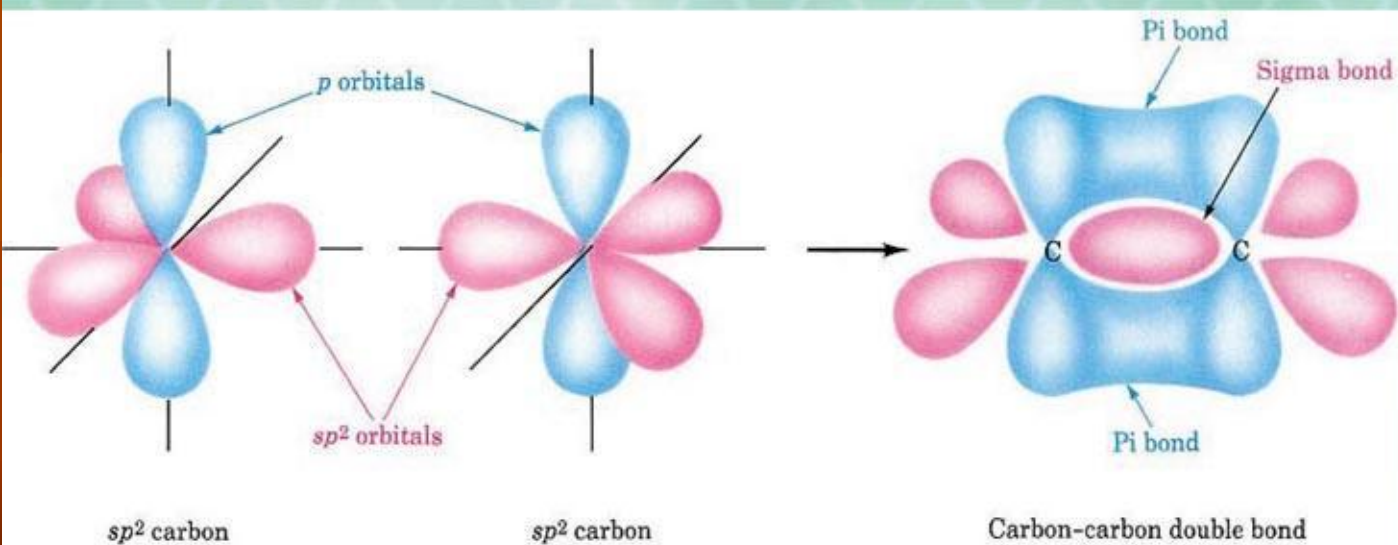


GRAPHITE

# sp<sup>2</sup> hybridisation



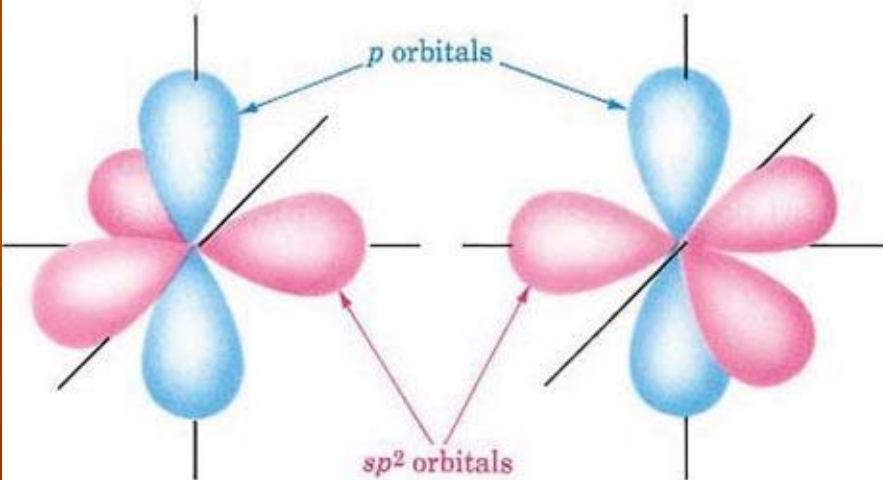
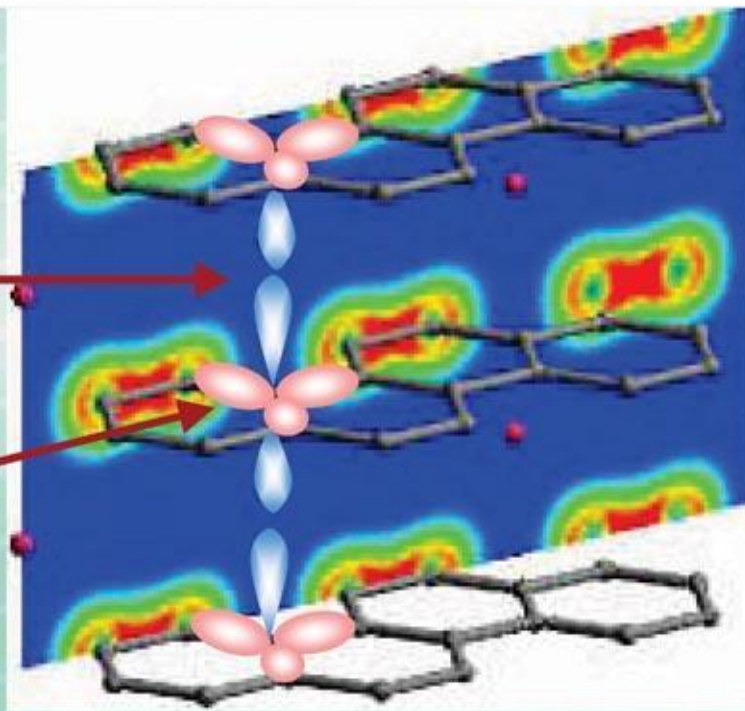
- Graphite is a stack of single "graphene" sheets
- In graphene the electron bonds *hybridize*; they form three identical "sigma" orbitals at 120 degrees to each other.
- Each bond originates from one s and two p orbitals (sp<sup>2</sup>). The remaining p orbital is perpendicular to the plane, called 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



# $\sigma$ and $\pi$ -bonds

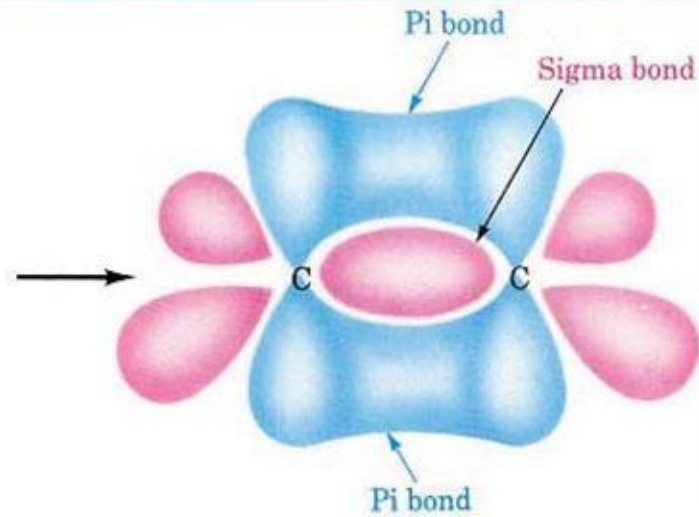
$\pi$  bonds (weak)

$sp^2$  hybridised bonds (strong)



$sp^2$  carbon

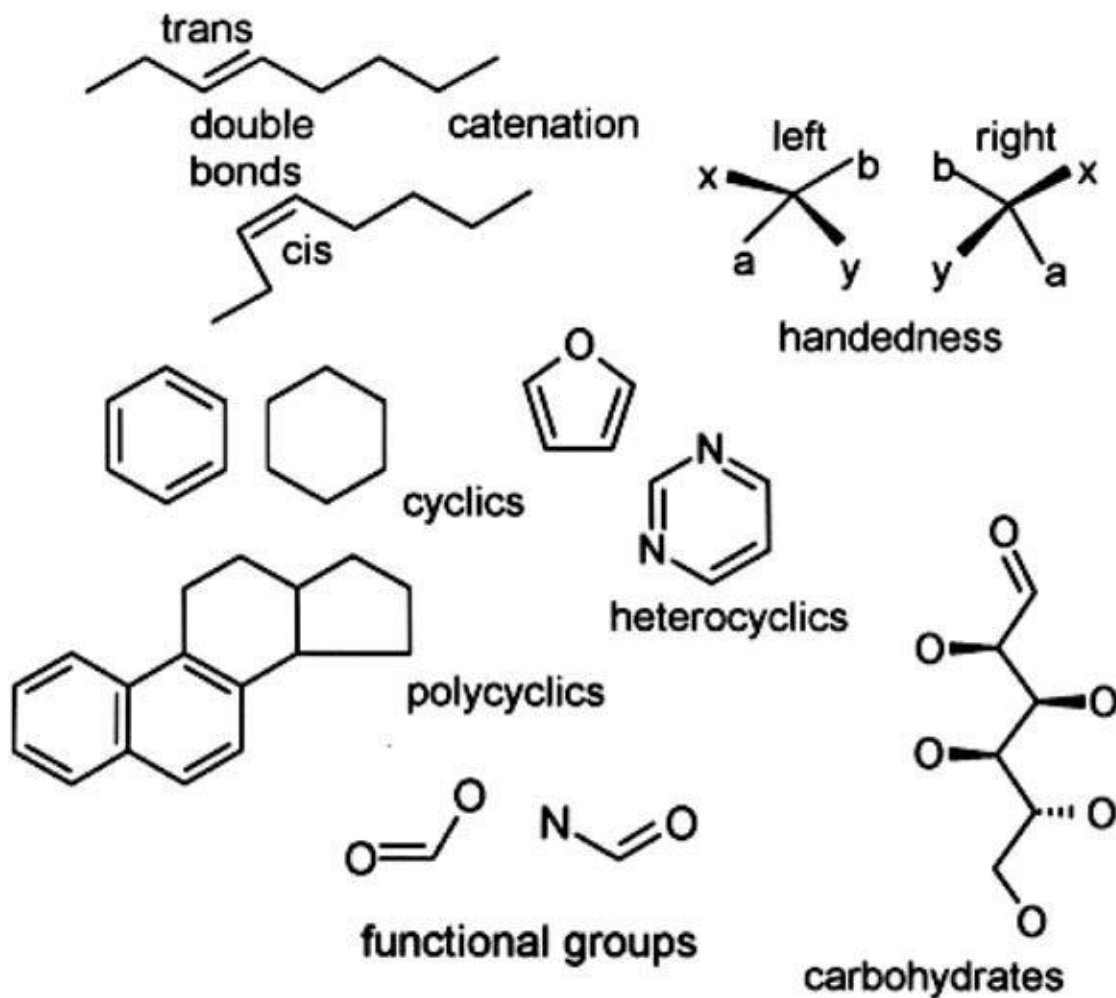
$sp^2$  carbon



Carbon-carbon double bond



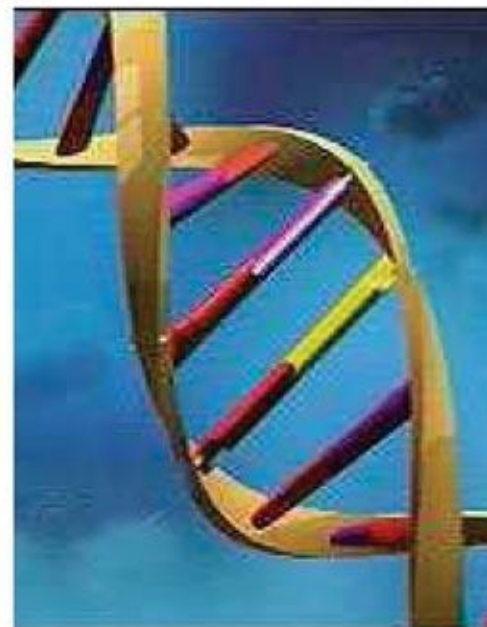
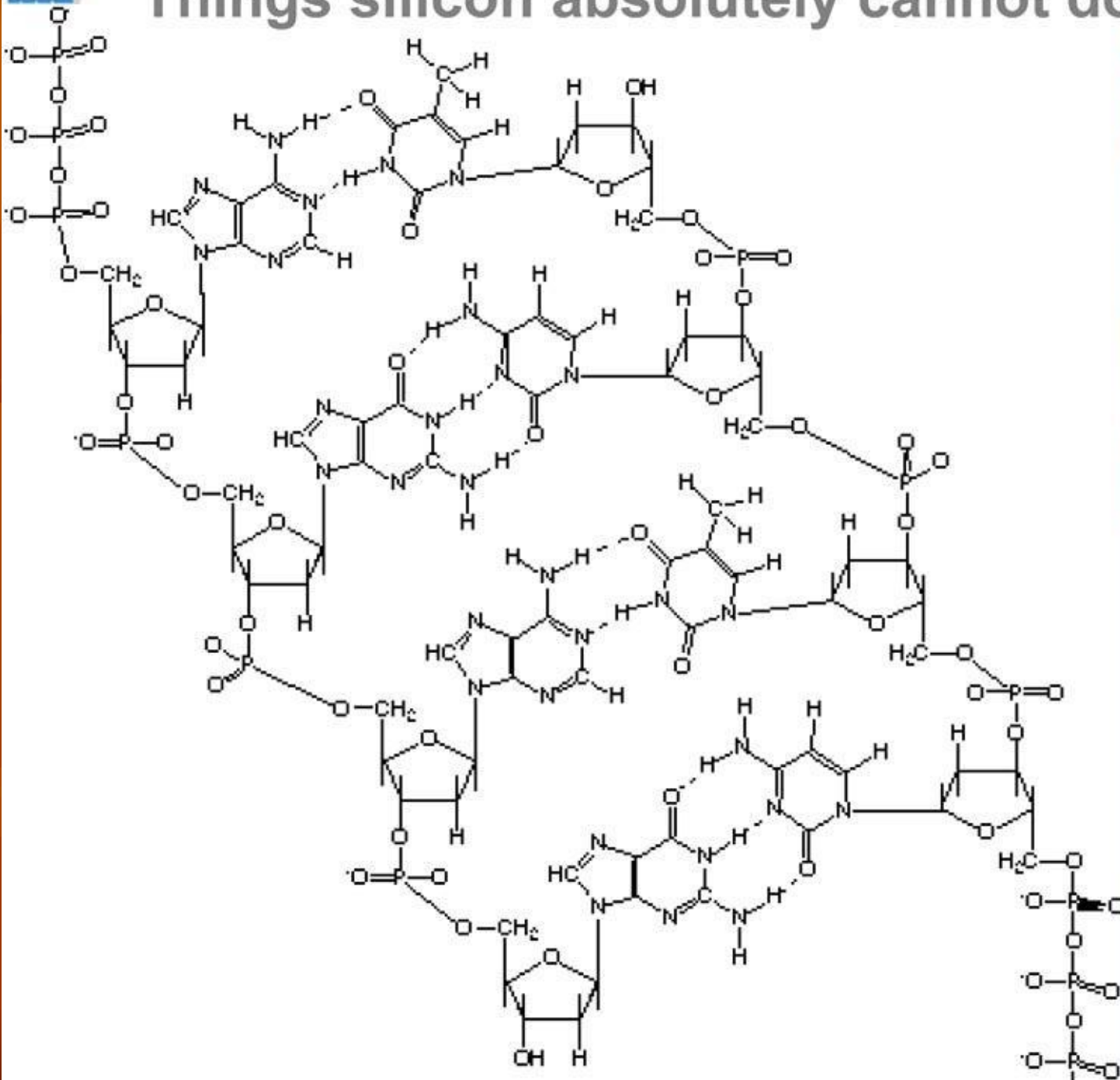
# Things silicon cannot do!



## 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!



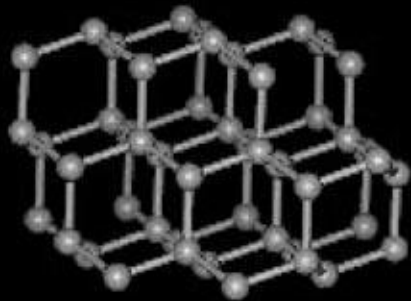


# Carbon sooth...?

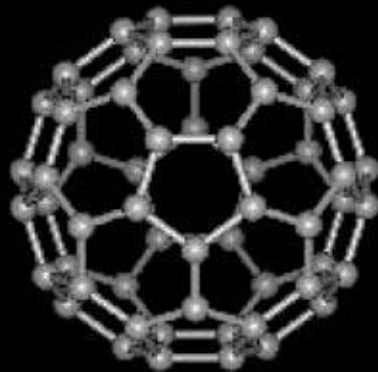




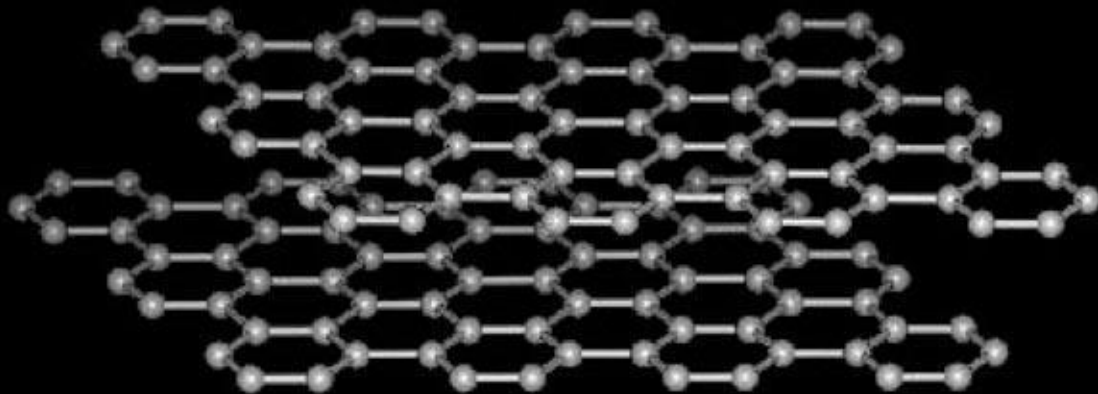
# Carbon's allotropic forms



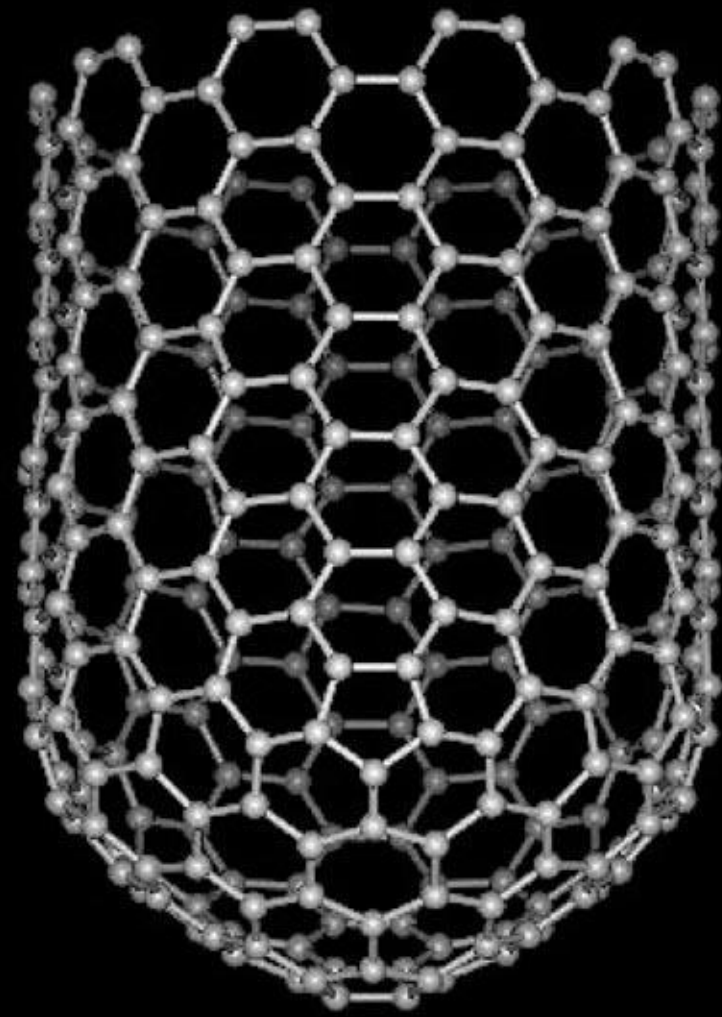
diamond



$C_{60}$   
"buckminsterfullerene"



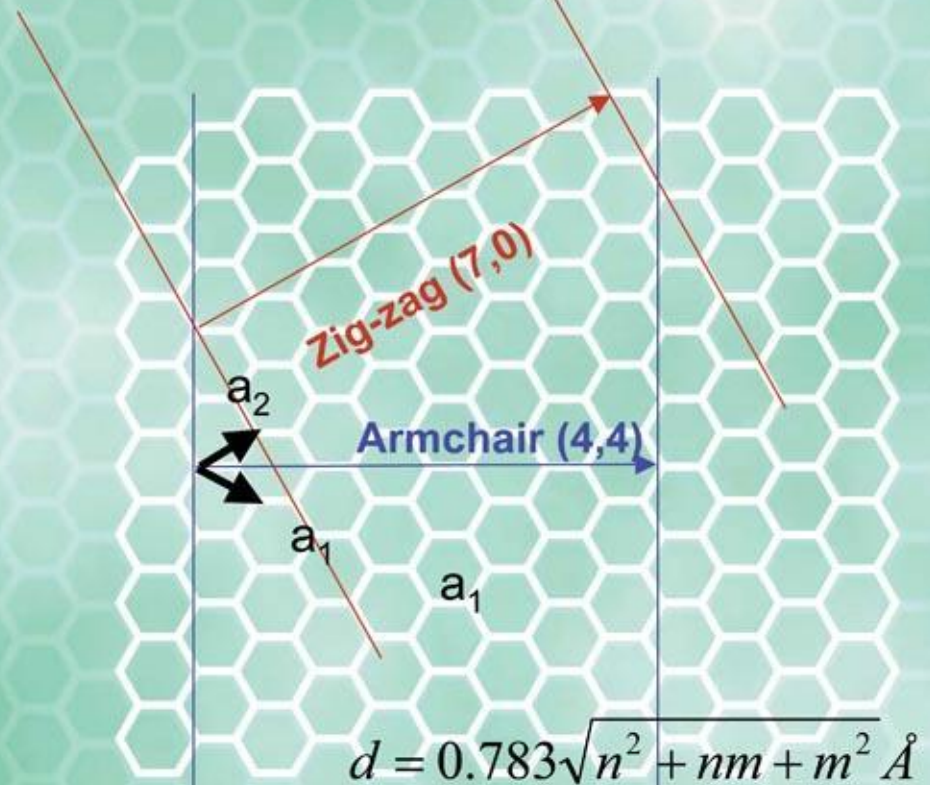
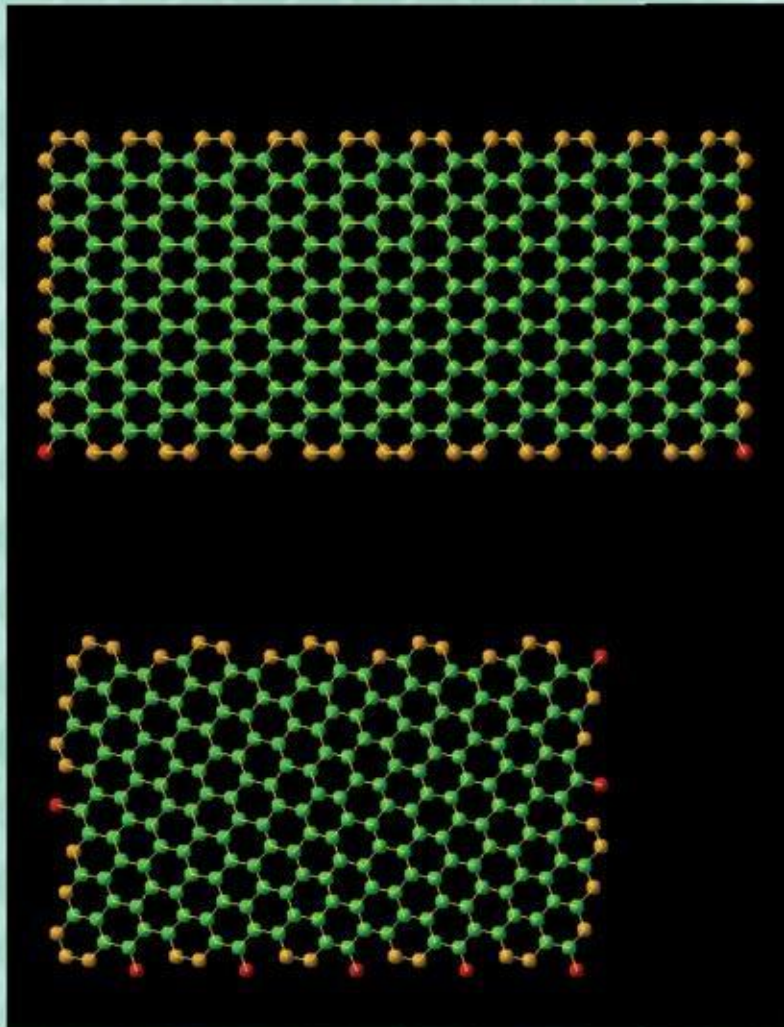
graphite

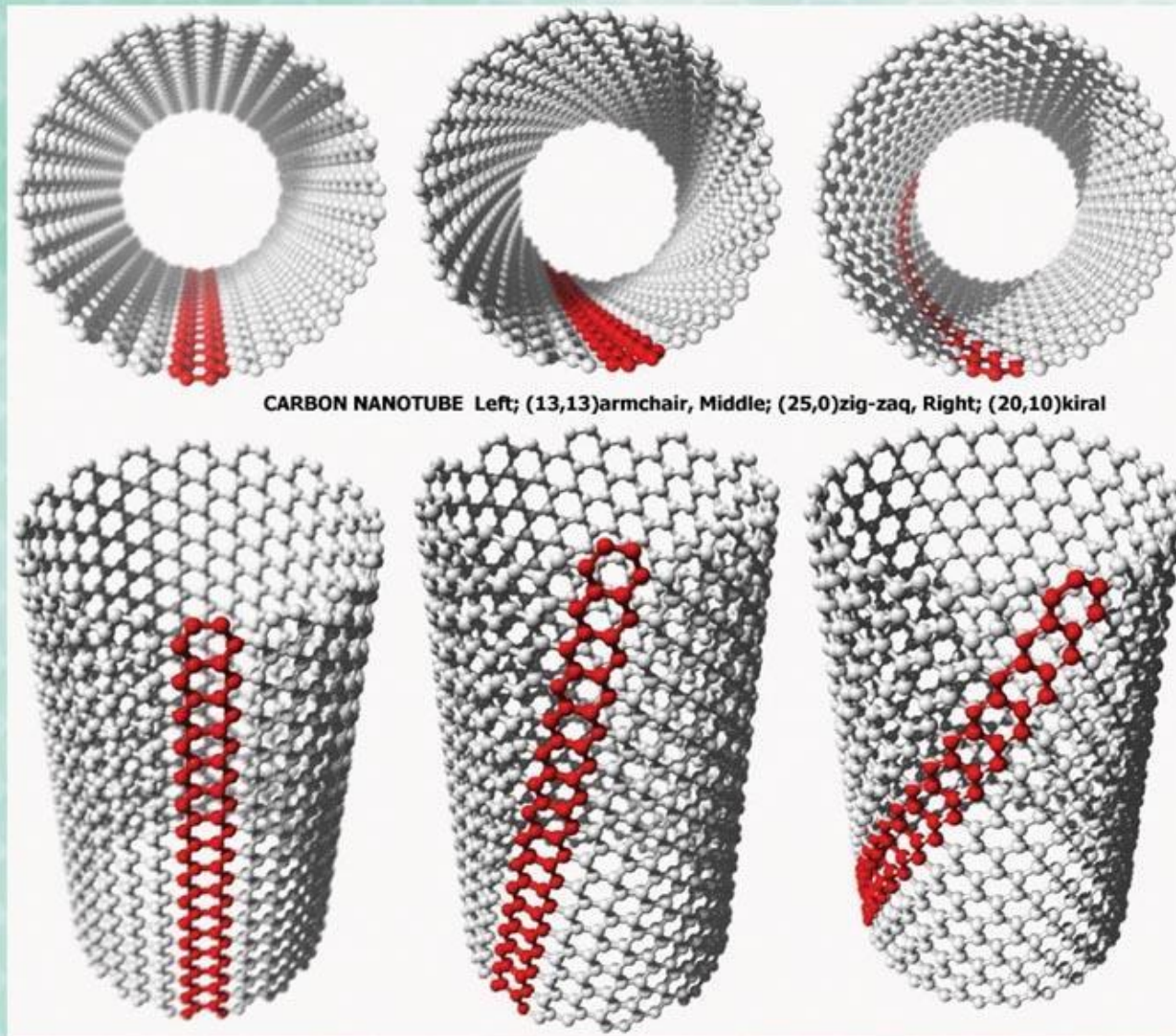


(10,10) tube

# Rolling a sheet of graphene

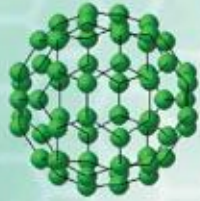
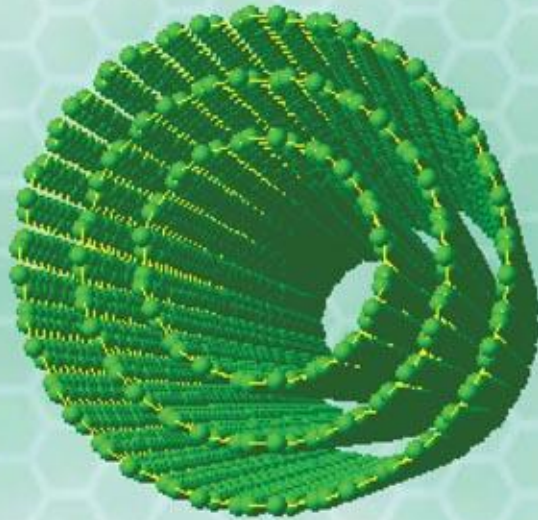
- Nanotubes can be rolled in different angles between 0 and 30 degrees.
- They are classified by the chirality vector given by the base lattice vectors  $a_1$  and  $a_2$ :  $C = n a_1 + m a_2$



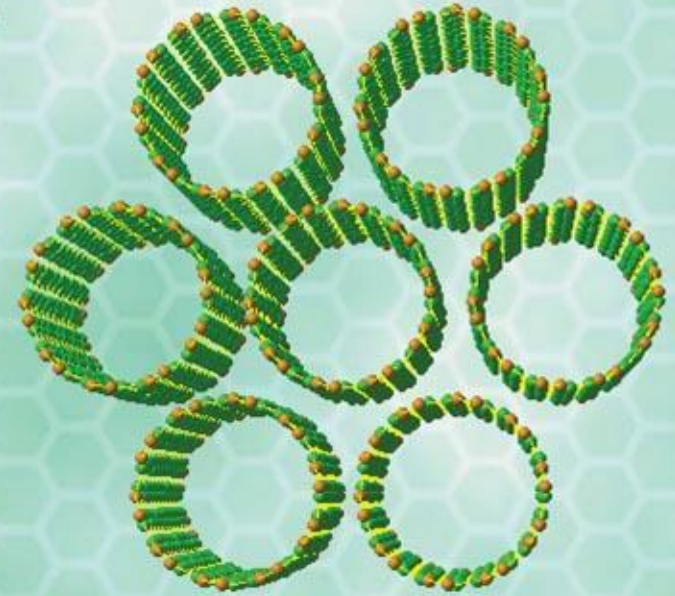




# Other types of nanotubes



C60



## Multi-walled nanotube (MWNT)

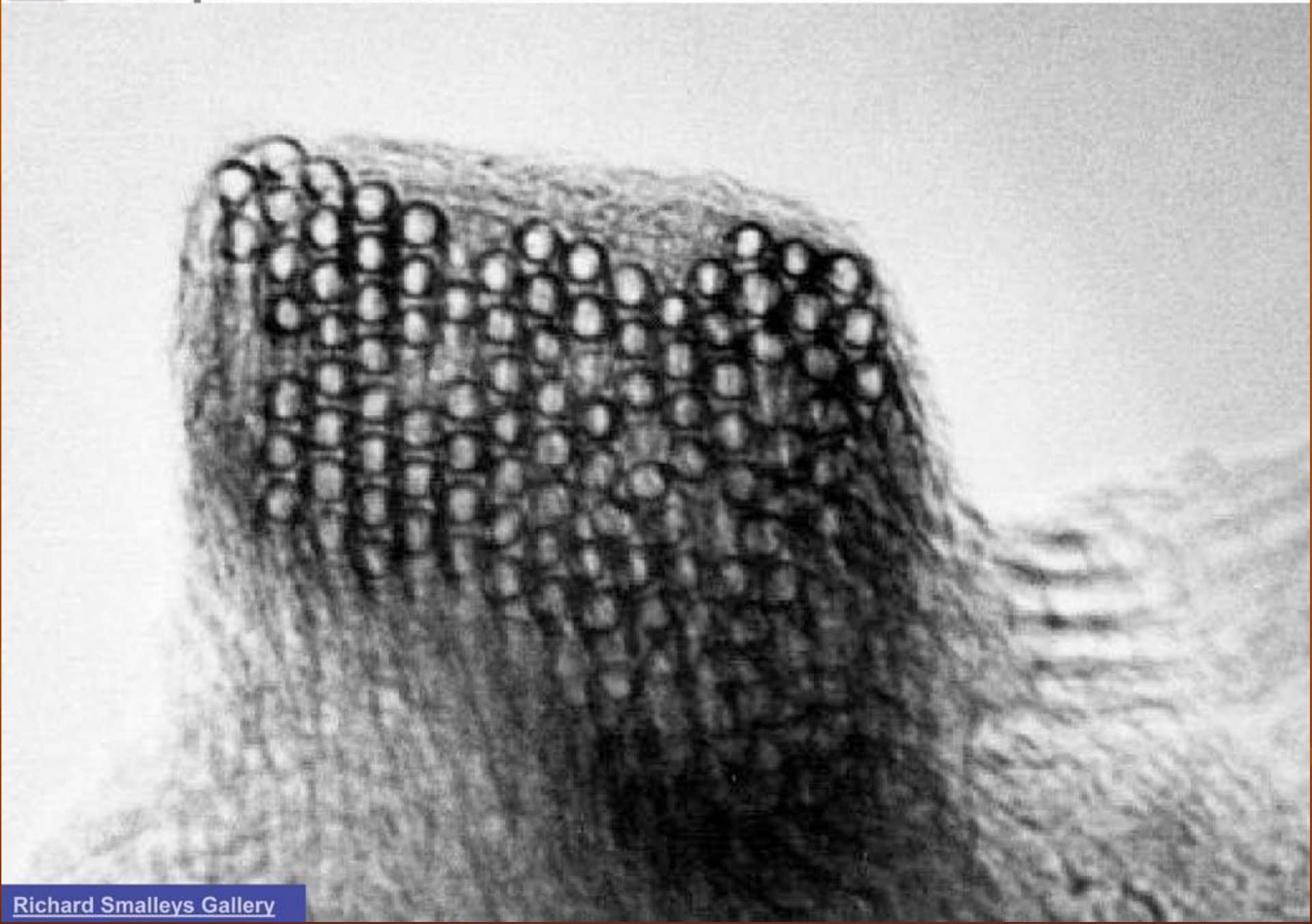
- 5-50 walls interspacing: 3.5 nm (like graphite)
- diameters normally around 10-50 nm (can be up to 200 nm)
- Can be very long, several 100  $\mu\text{m}$
- Walls slide easily inside each other (like graphite)
- The layers have independent chiralities (one may be armchair, the next zig-zag)

## Nanotube rope

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



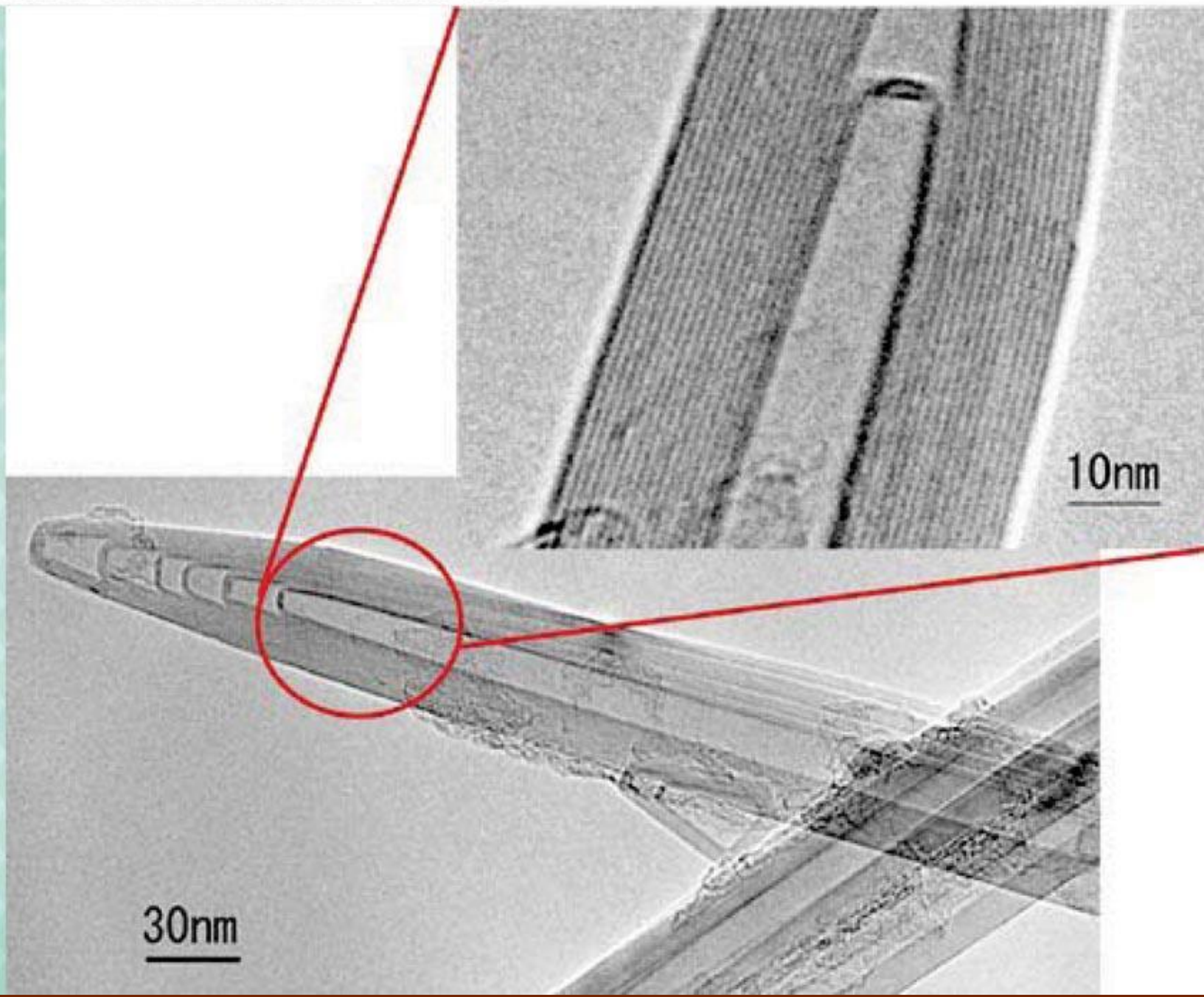
# Rope of nanotube







# Multiwalled nanotubes





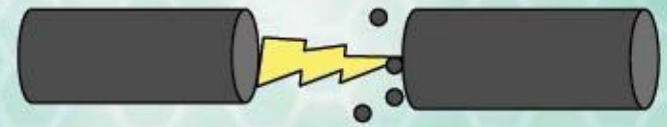
# **Методы формирования**



# 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



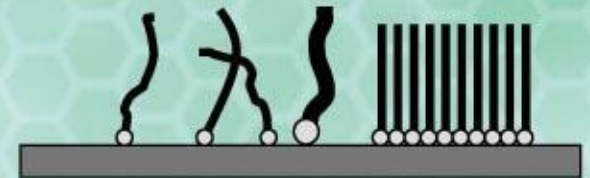
- **Laser evaporation**

- 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).

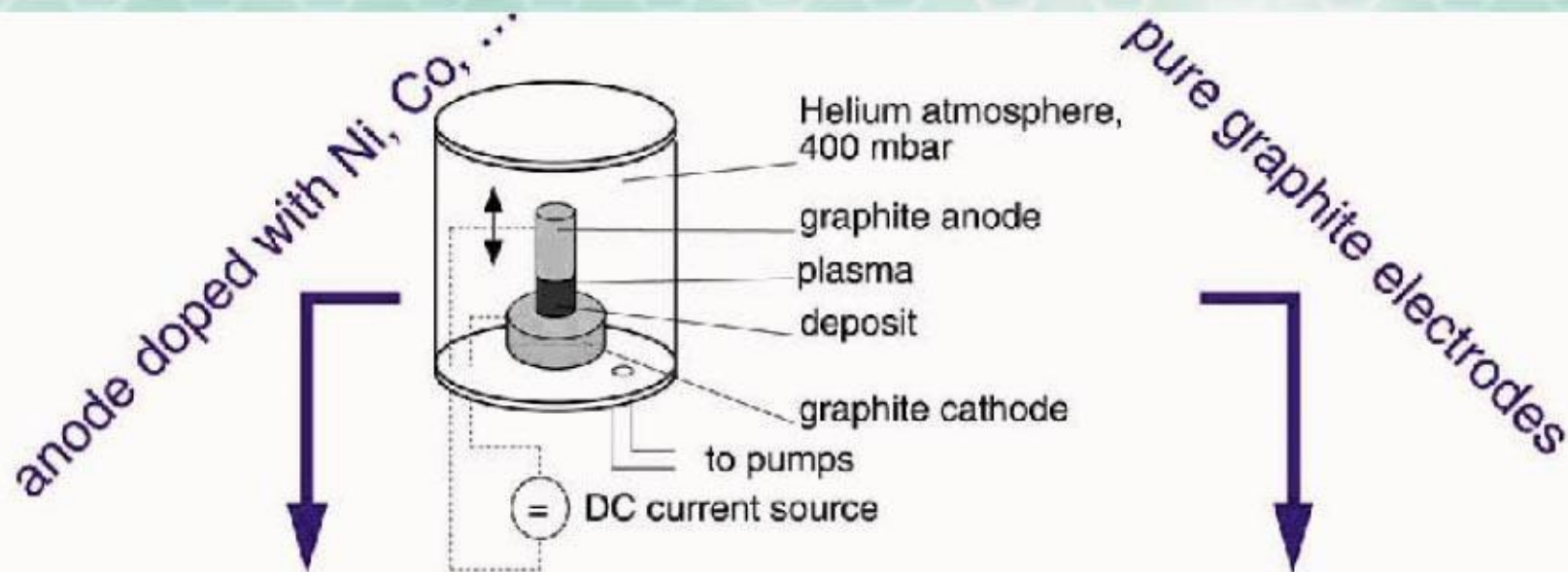


- **Chemical vapor deposition**

- 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.

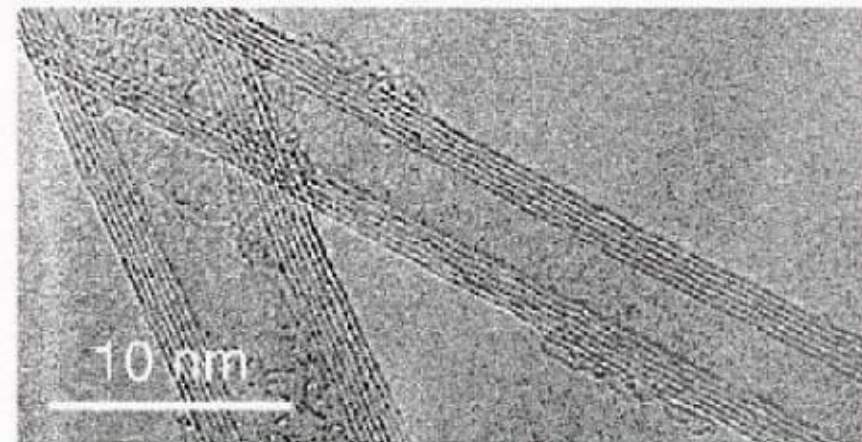
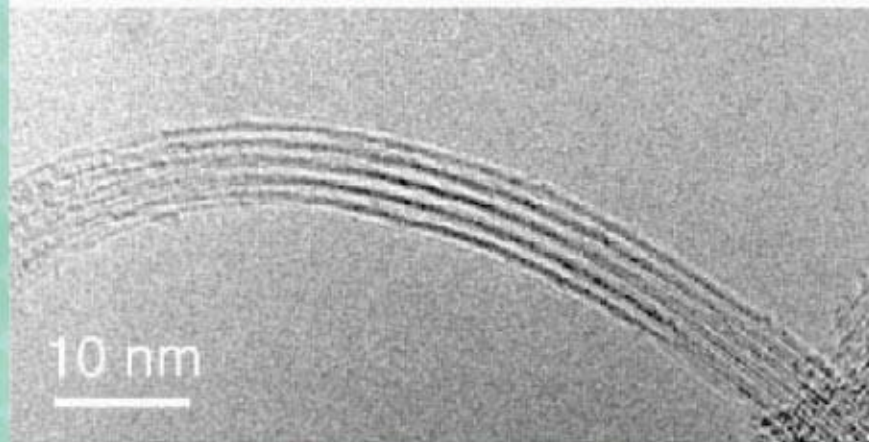


# Arc discharge



Single wall nanotubes

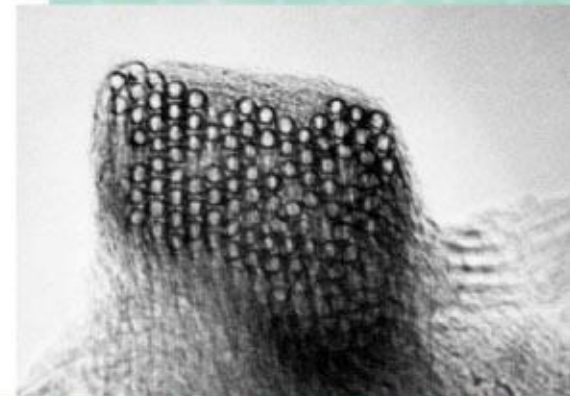
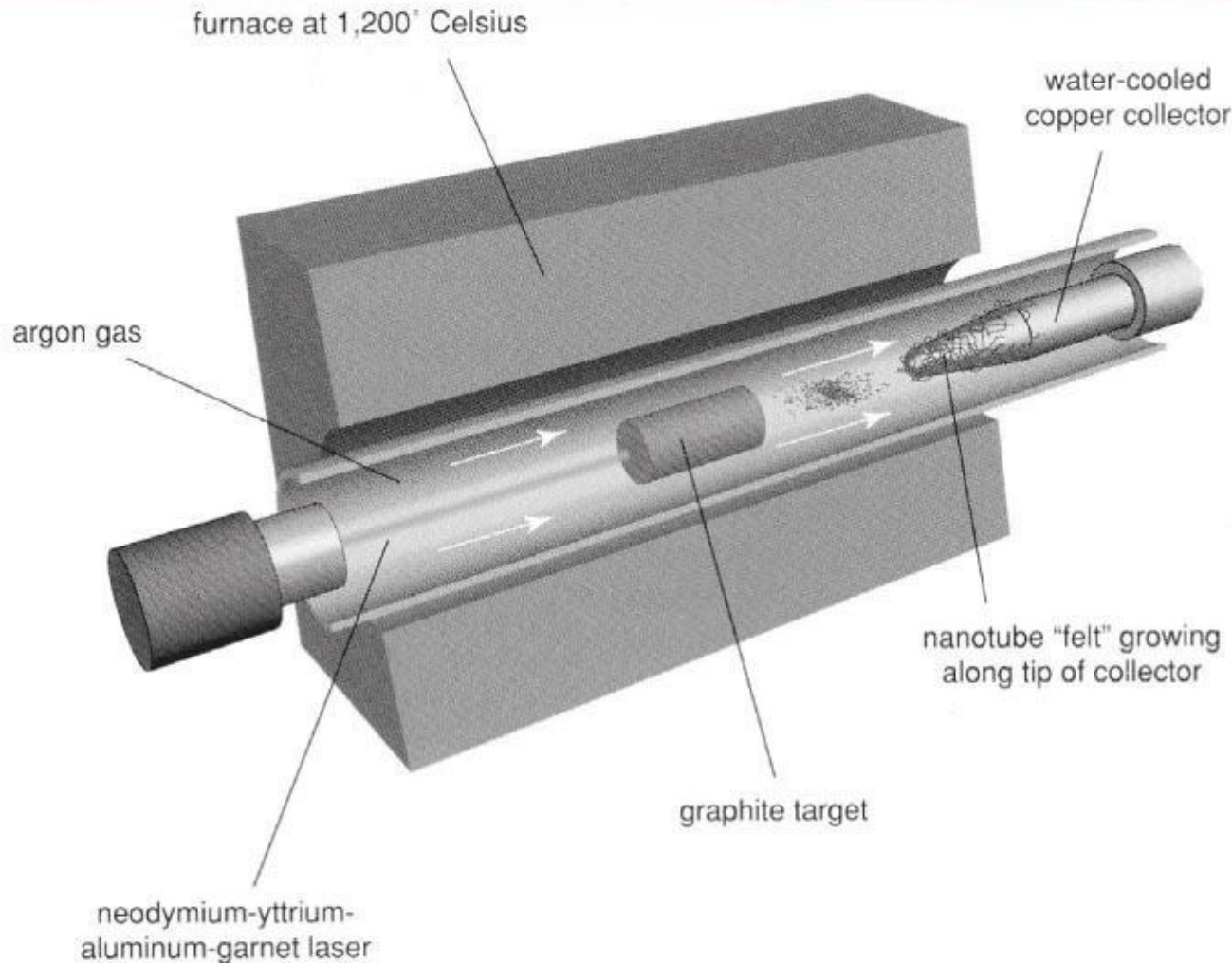
Multiwall nanotubes



**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:**

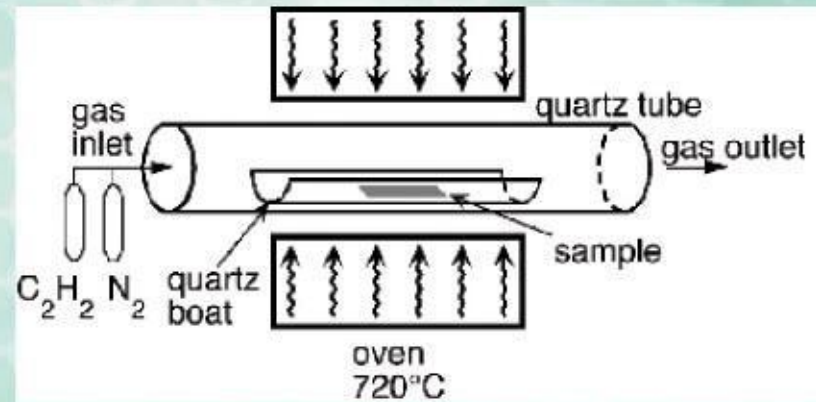
- Acetylene, 600 – 800°C.

- **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

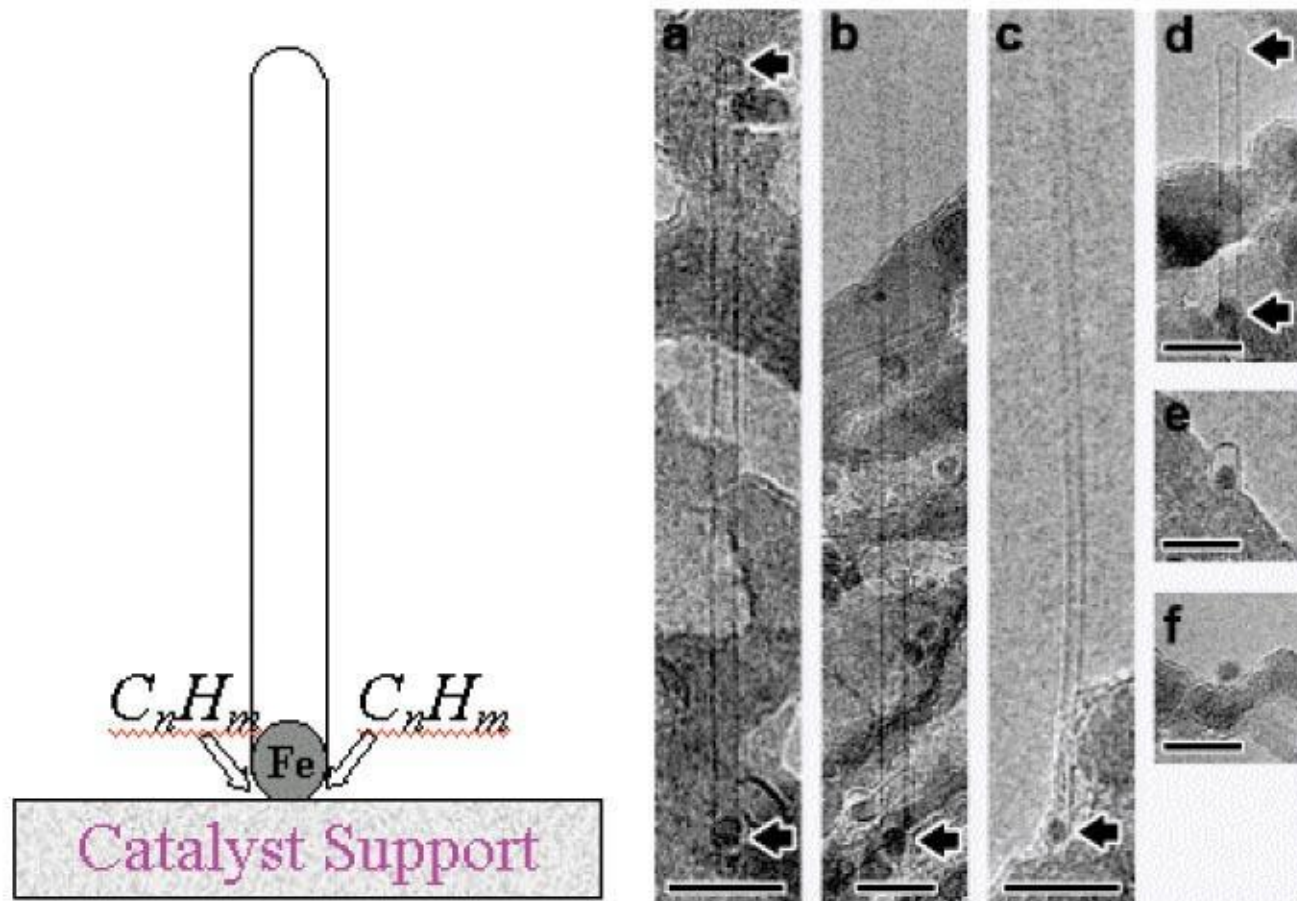


0.0ns





# Chemical vapor deposition



'Base' Growth Model

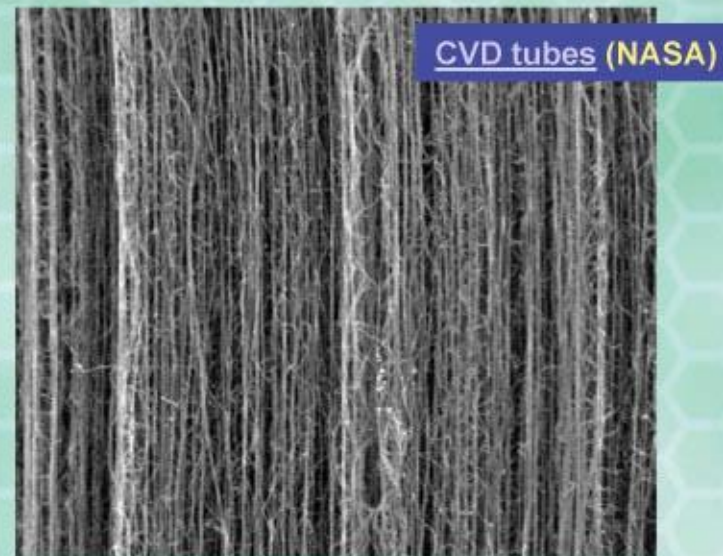
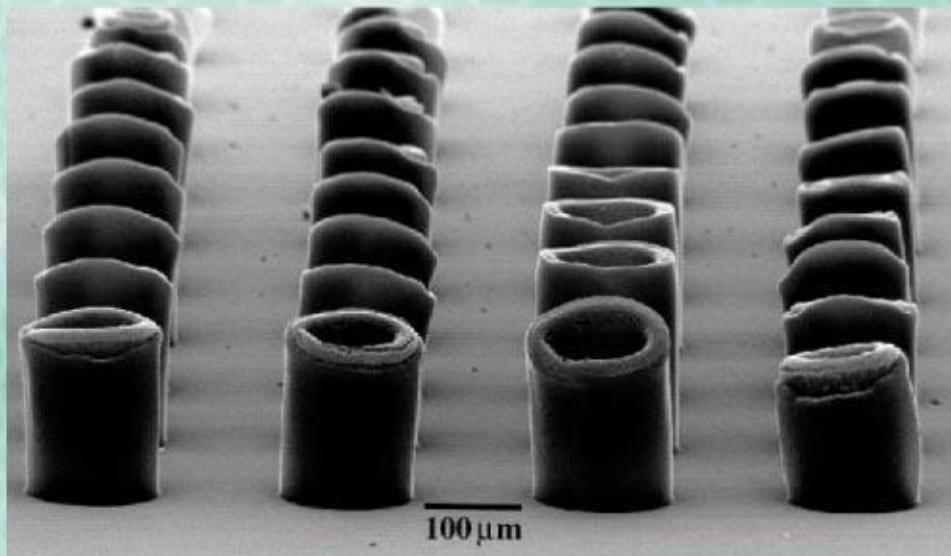
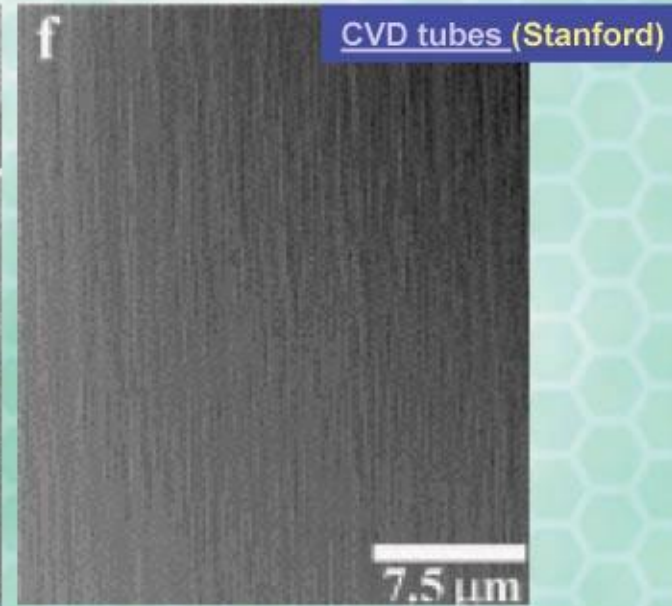
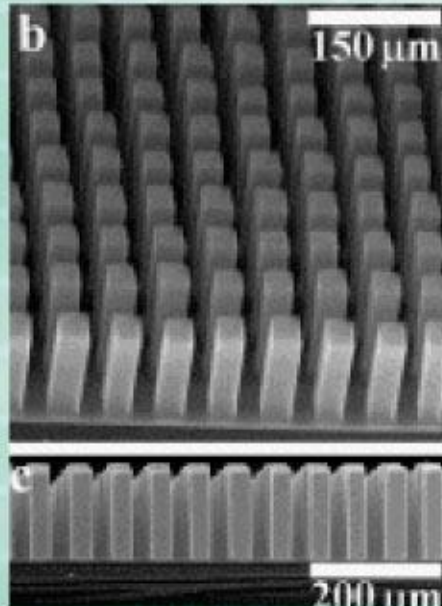
TEM data showing particle-tube relation

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 .





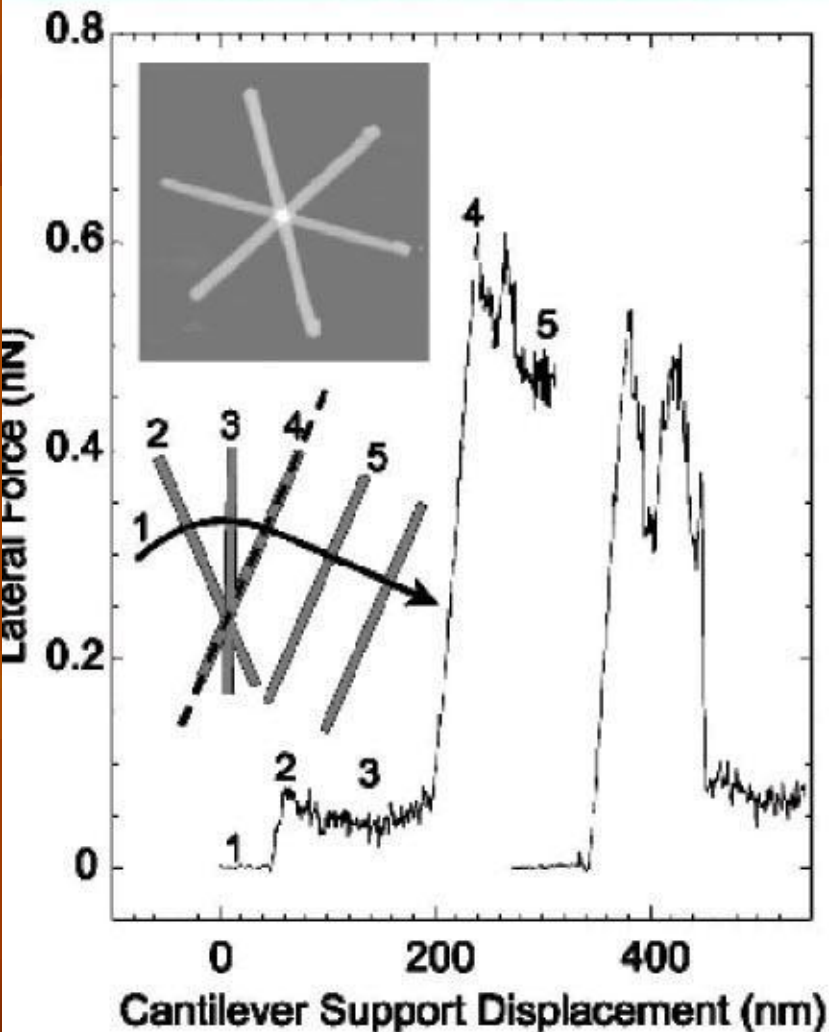


# *Свойства нанотрубок*

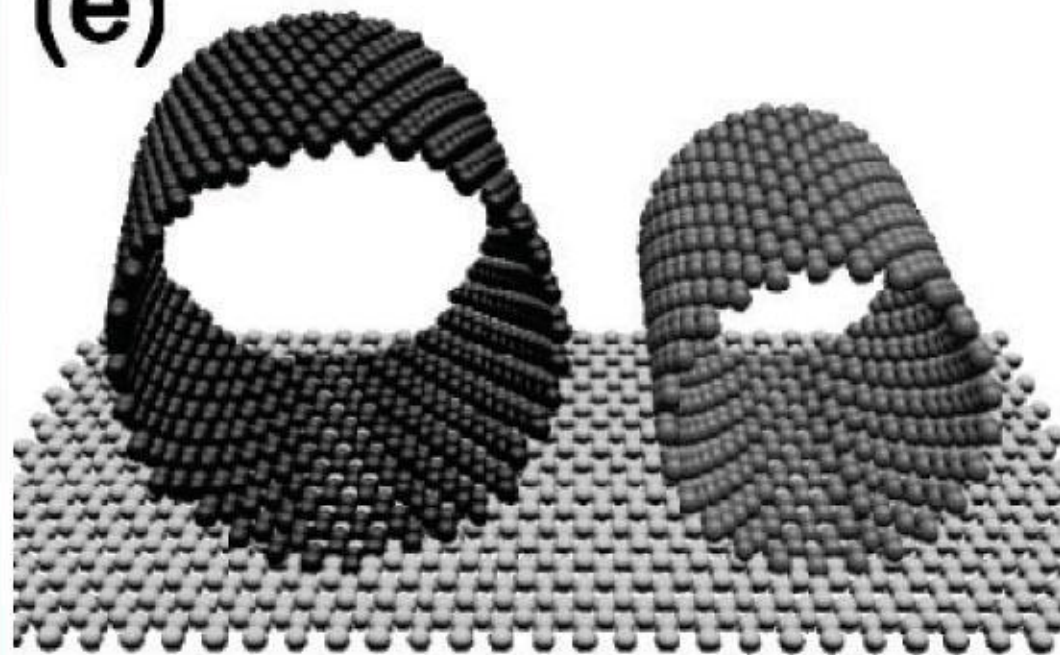


# Friction

- 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

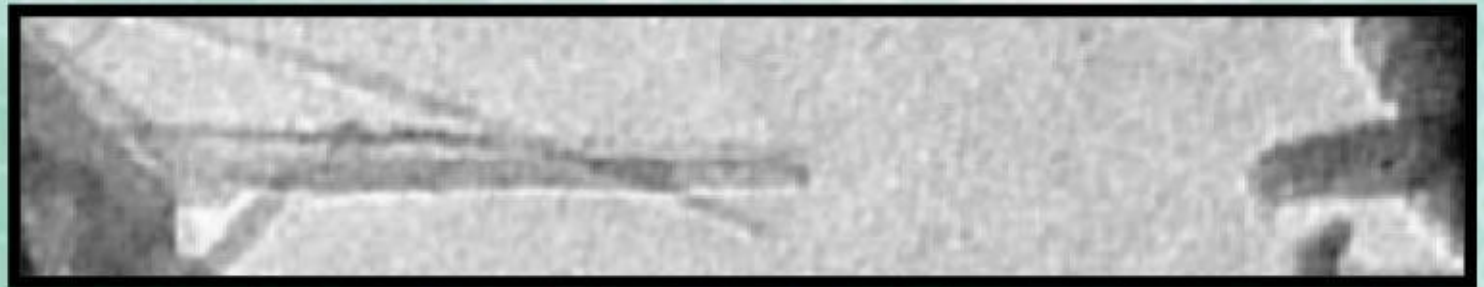


(e)





# Mechanical properties: tensile strength



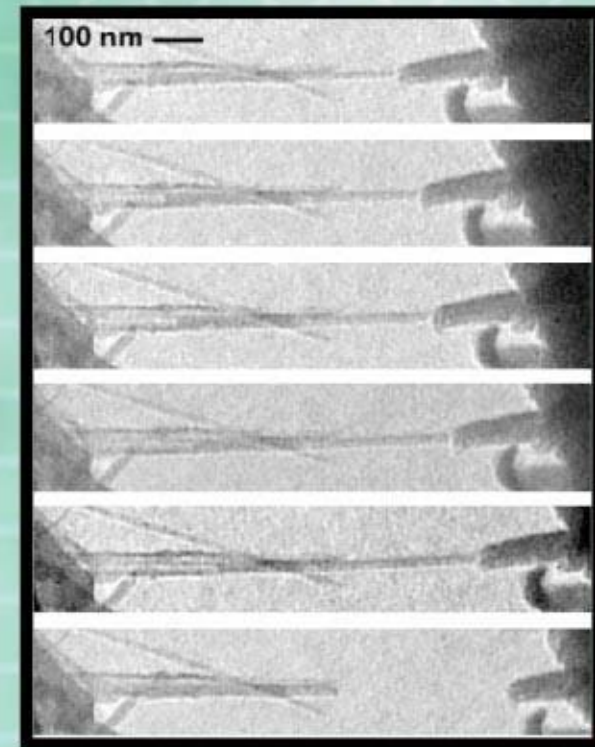
J. Cumings and A. Zettl, Science 289, 602 (2000).

- **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



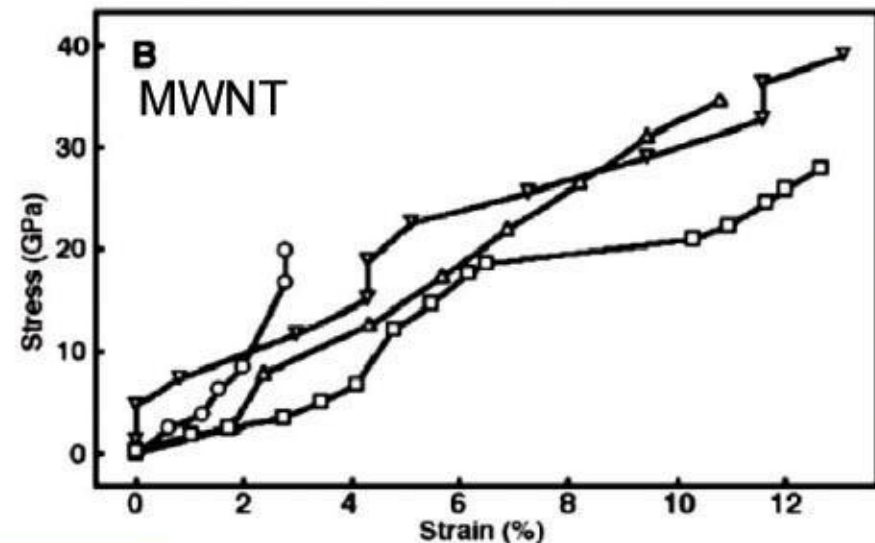
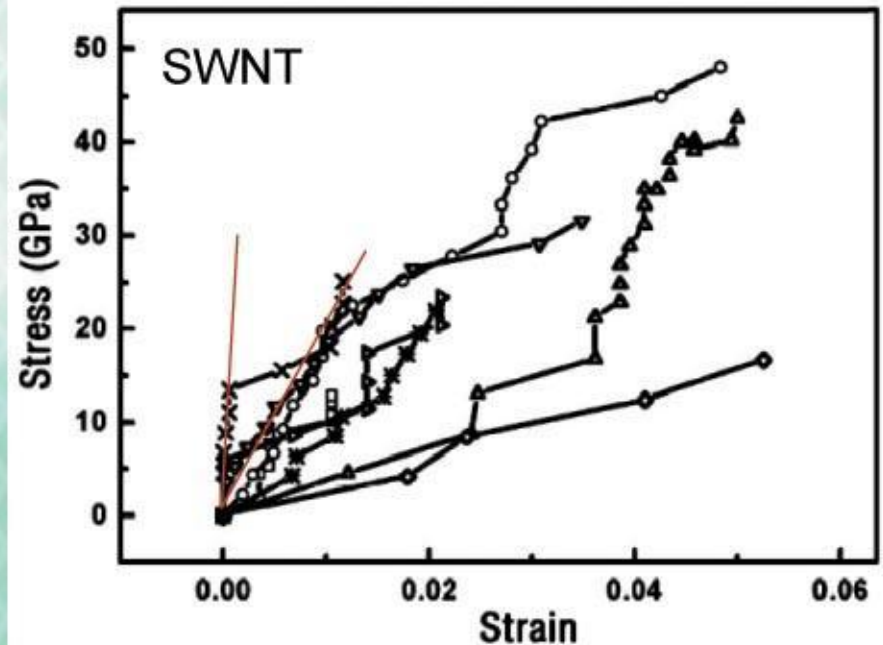
# Tensile strength

## Youngs modulus

- SWNT: 1.3 TPa
- MWNT: 1 Tpa

## Tensile strength

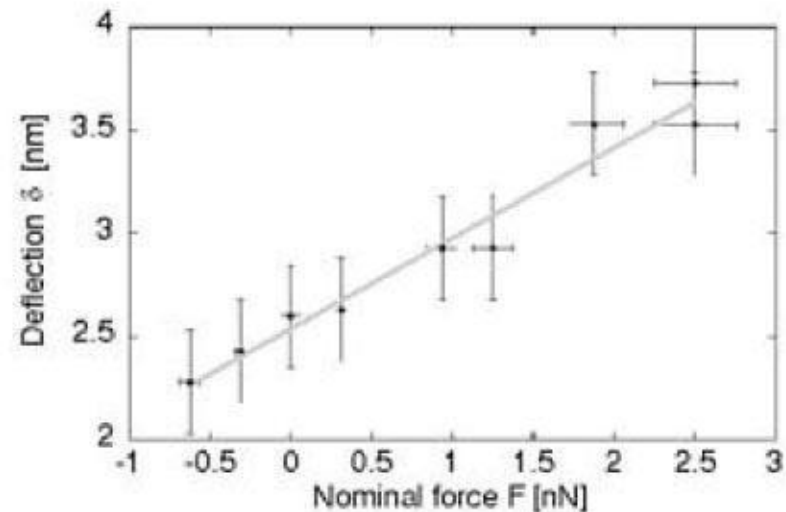
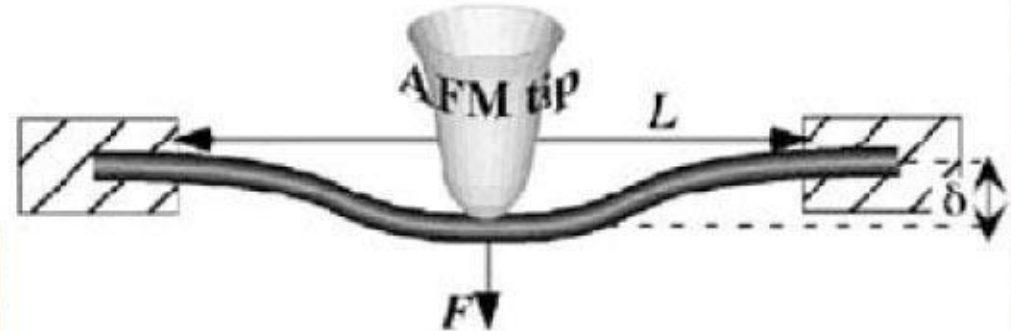
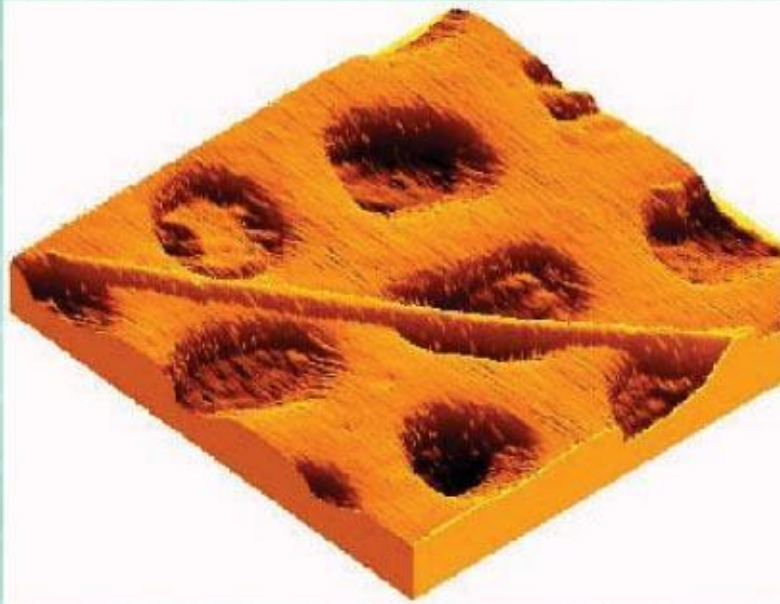
- 30-60 GPa
- Theory: 200 GPa





# Mechanical properties

- Youngs modulus: 1 TPa (MWNT, SWNT)



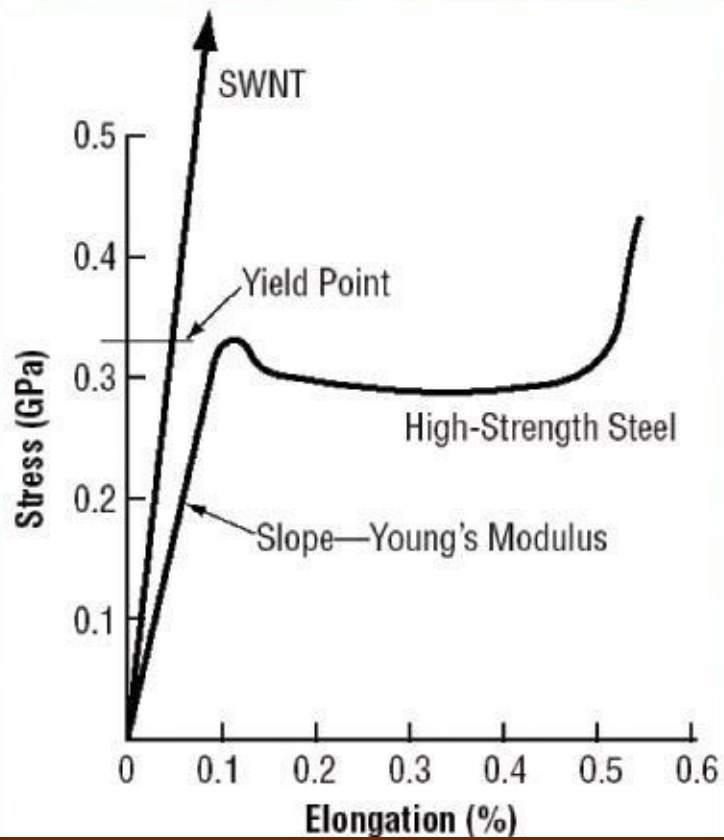
[J. P. Salvetat et al., Adv Mater. \(1999\)](#)



# 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)

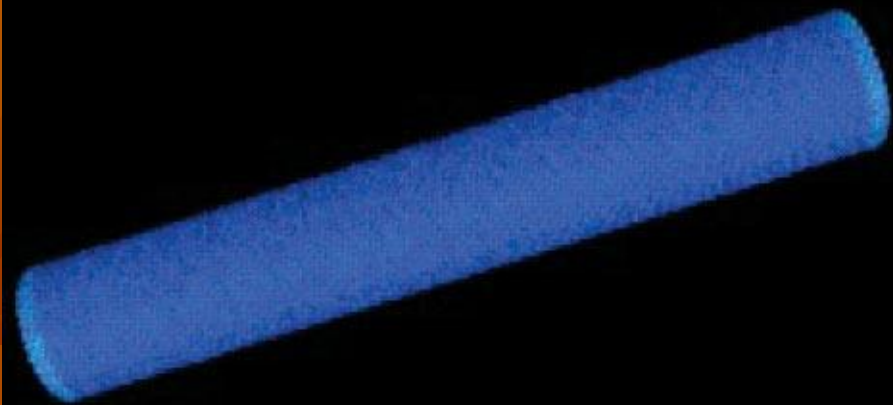


- Nanotubes 100 times stronger than steel and 6 times lighter
- Nanotubes can sustain a large tensile strain:
  - 5% (SWNT)
  - 10% (MWNT)



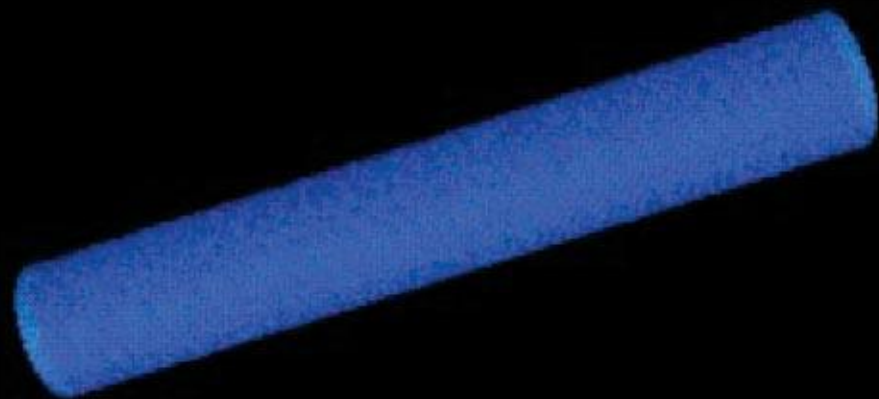
# Deformation of nanotubes

MWNT, twisting



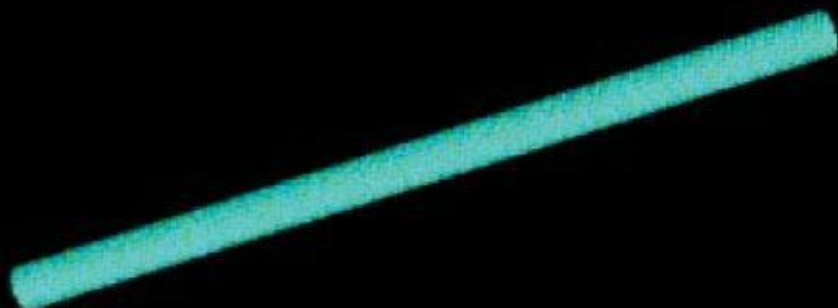
0.00 ps

MWNT, bending



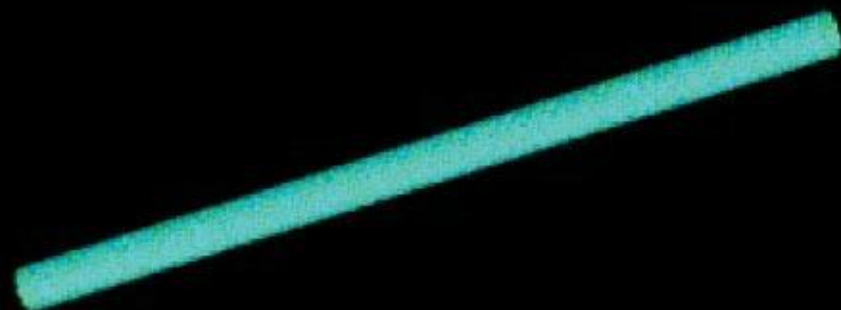
0.00 ps

SWNT, twisting



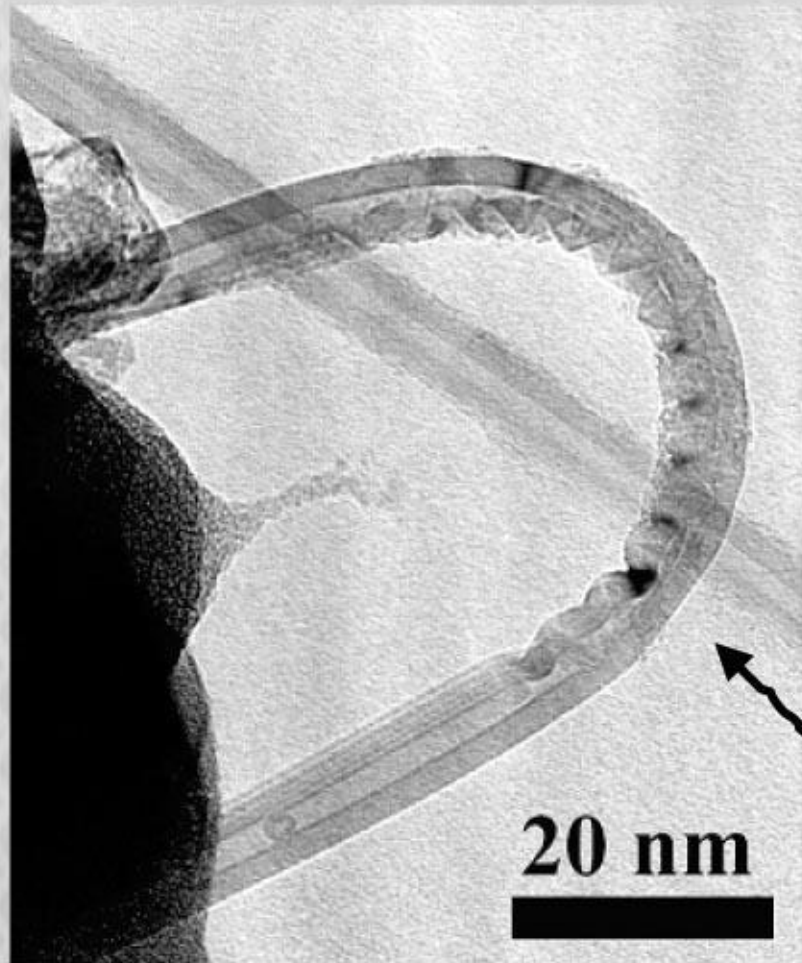
0.00 ps

SWNT, bending

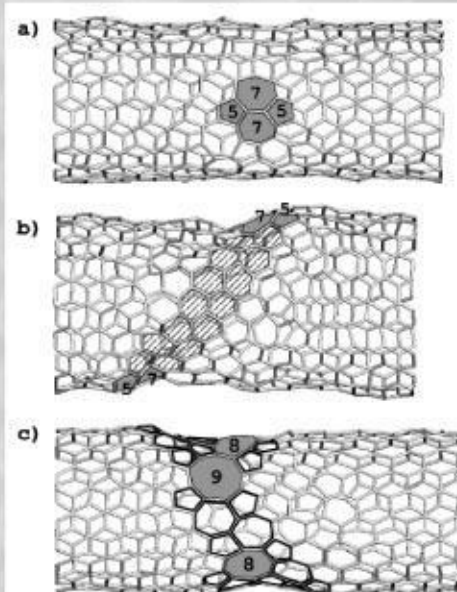


0.00 ps

# 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???





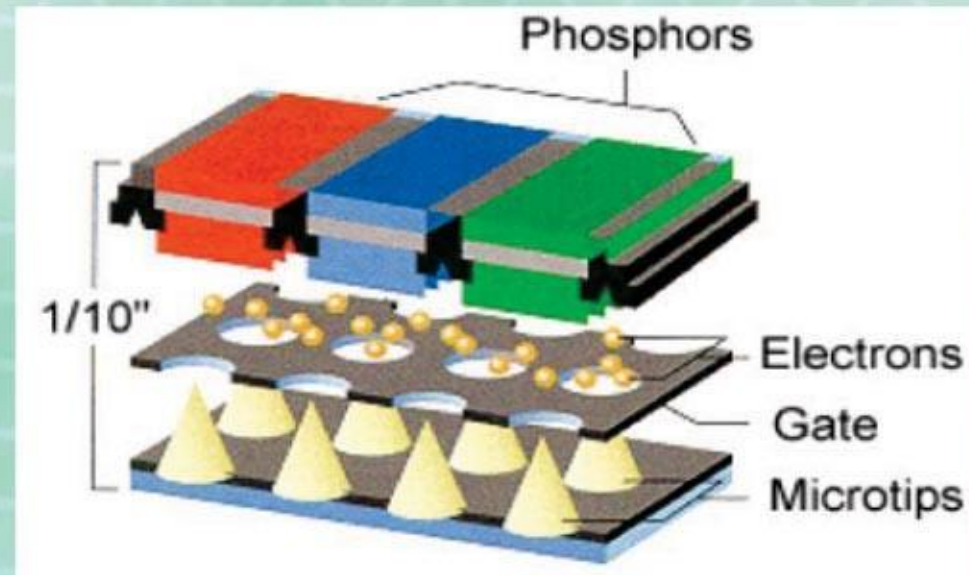
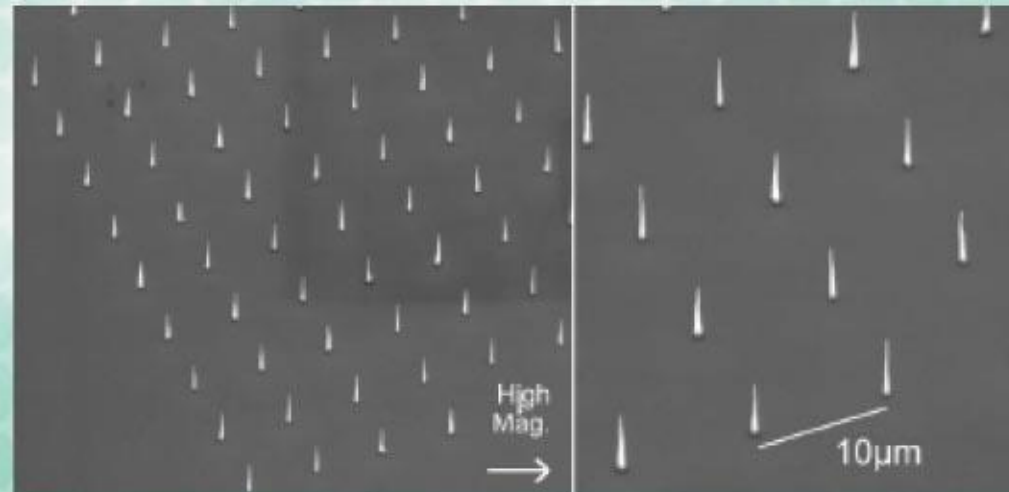
# **Области применения**



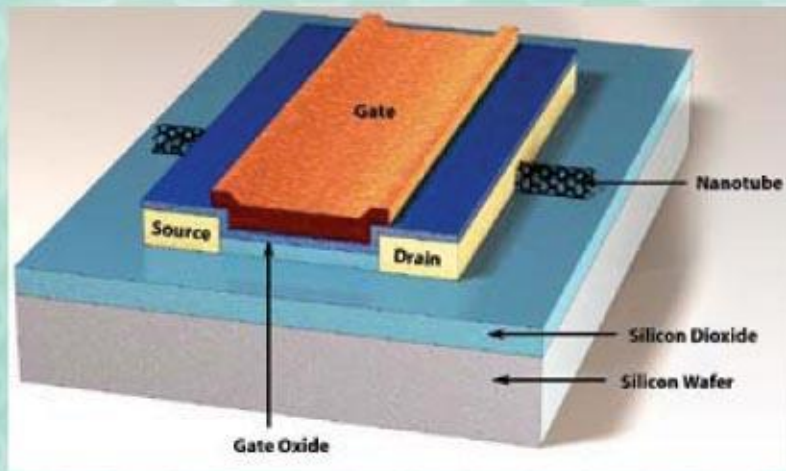
# Nanotube display

## 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)



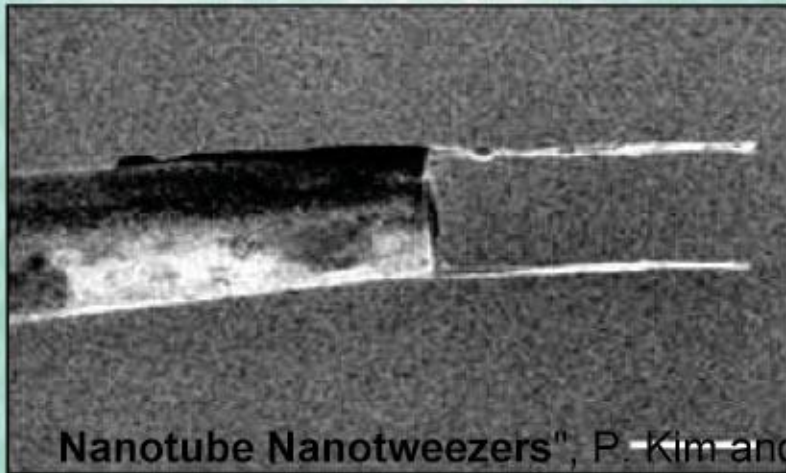
# Nanotube transistor



## 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).

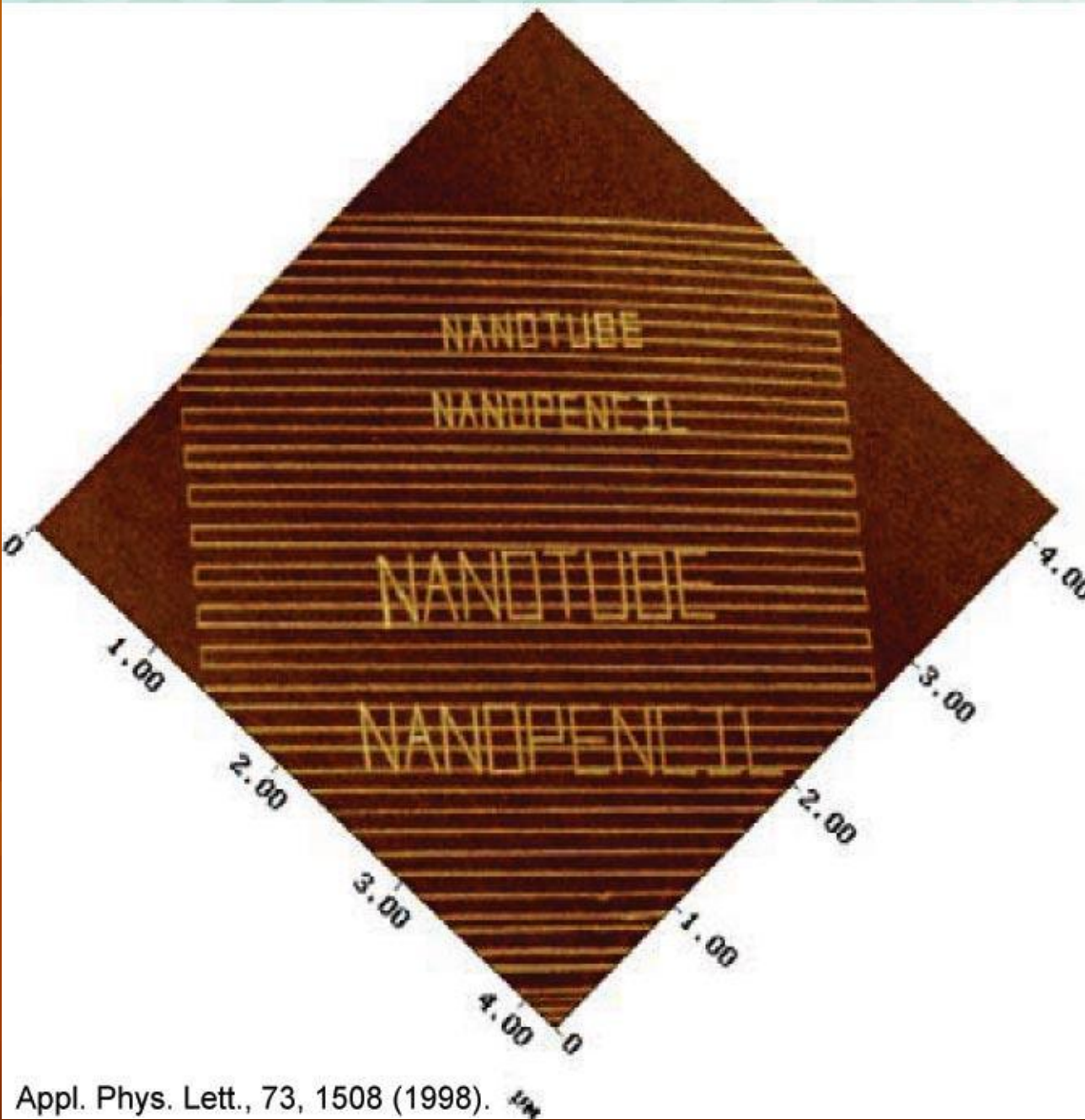
**More on this in lecture 4**

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

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

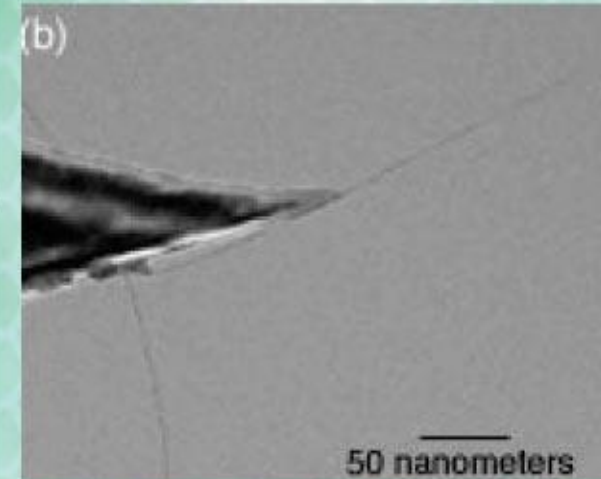


# A real nanotube stiftblyant



A nanotube at the end of an AFM:

- High aspect ratio
- Nanolithography
- Conducting AFM/STM



[Nanotube AFM](#) (Popular article)

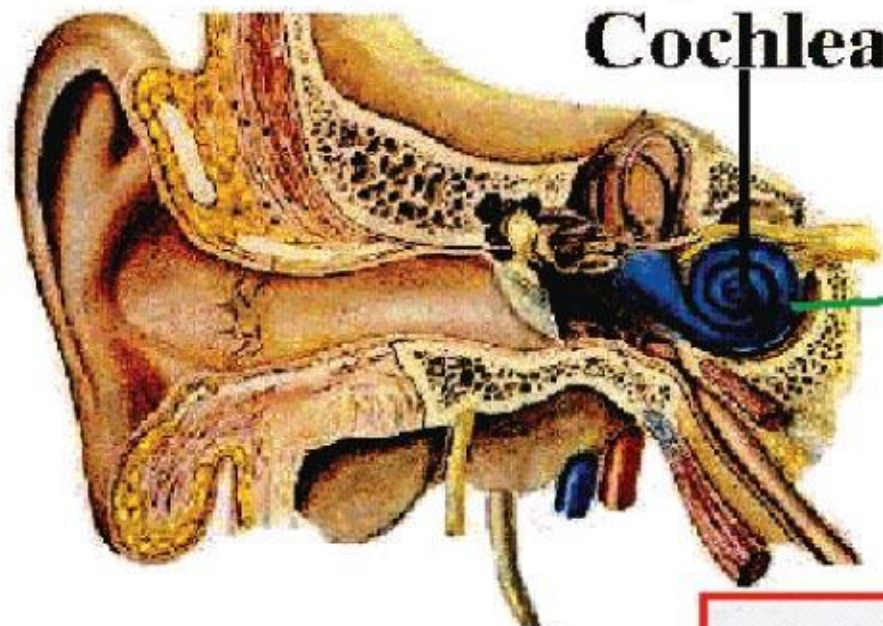
[Nanotube AFM](#) (Lieber, Harvard)

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

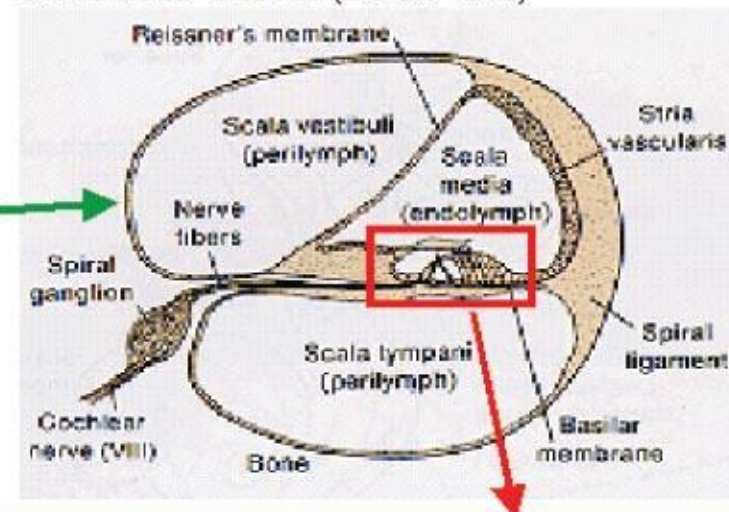


# Nanotube hearing aid

## Cochlea

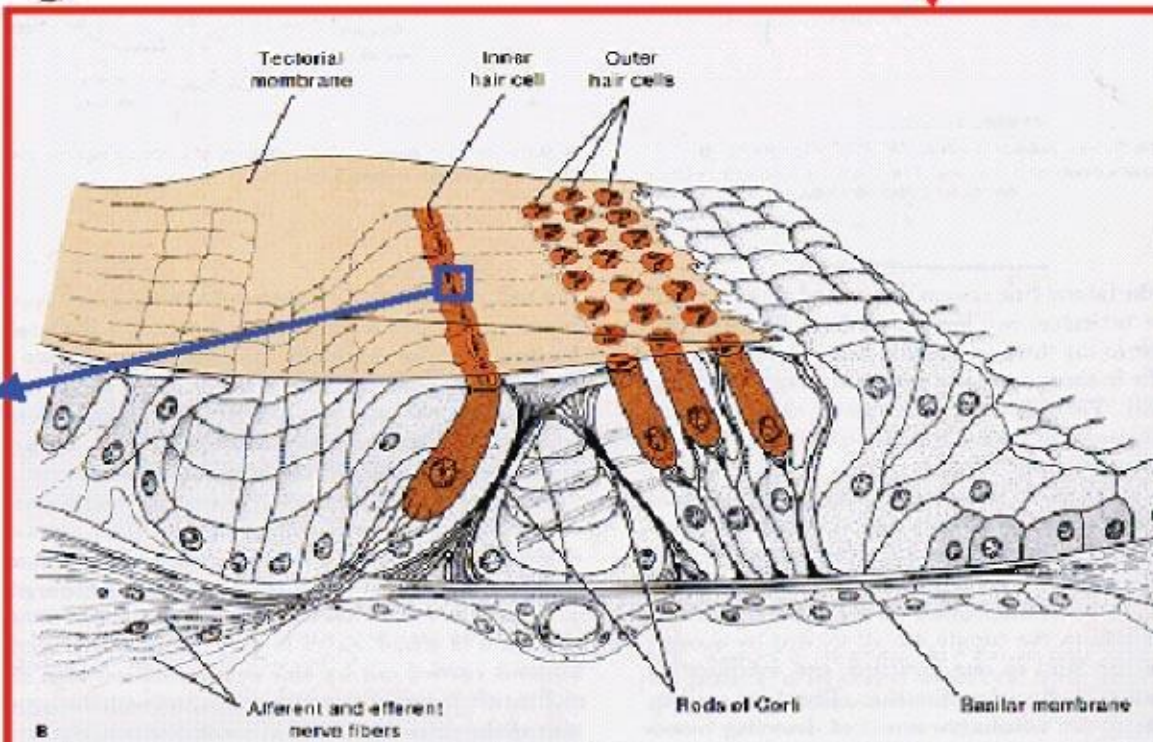
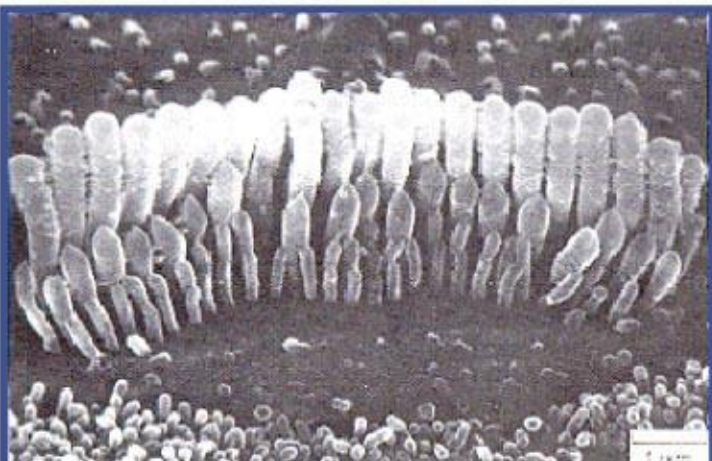


## Cross-section through cochlear canal (Eckert 1988)



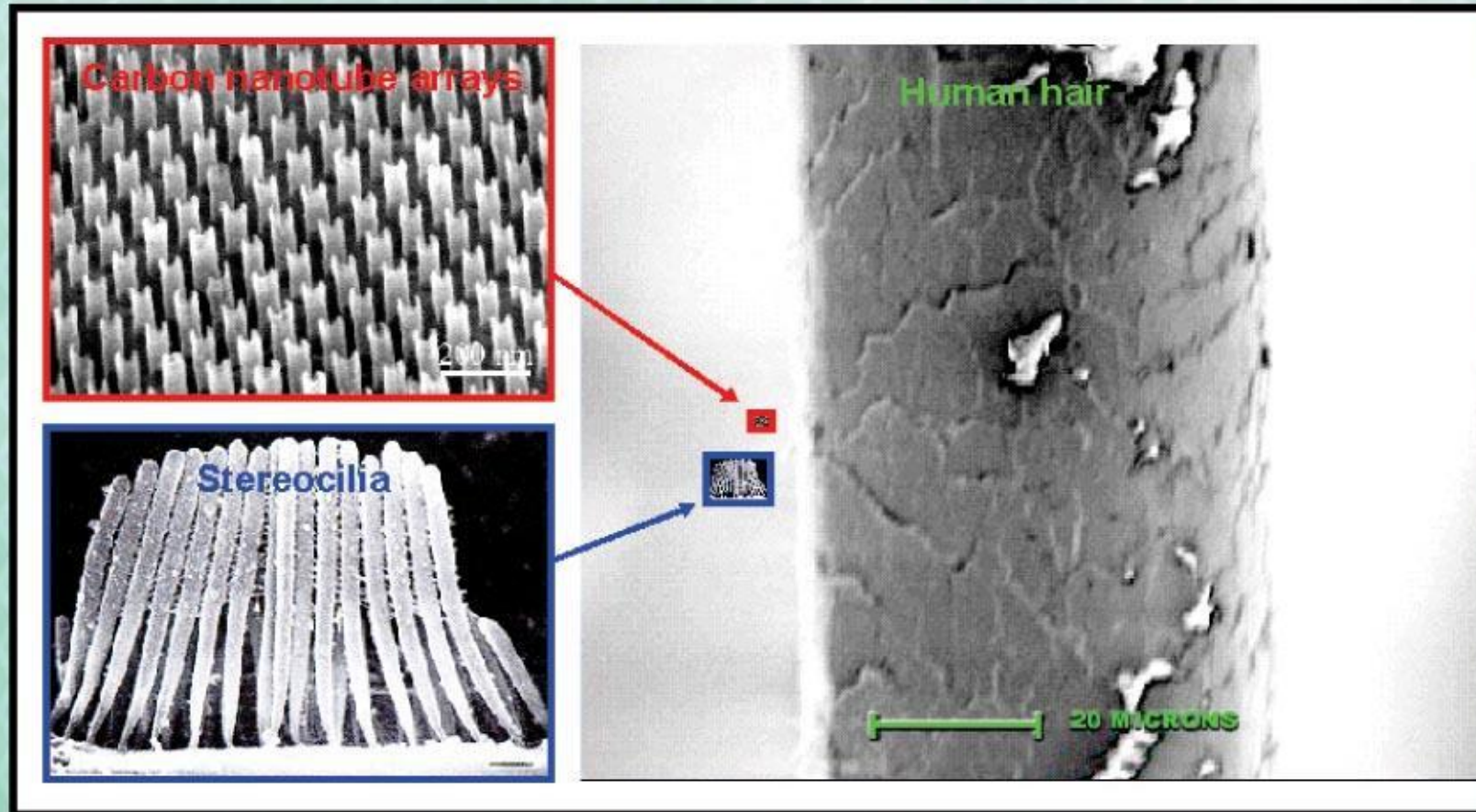
(Alec N. Salt, Washington University)

## 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

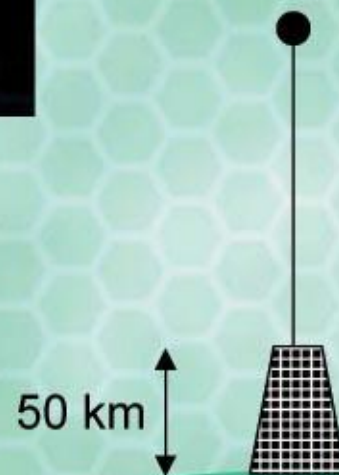


# Nanoscale materials: space elevator



## 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 \(NASA\)](#)