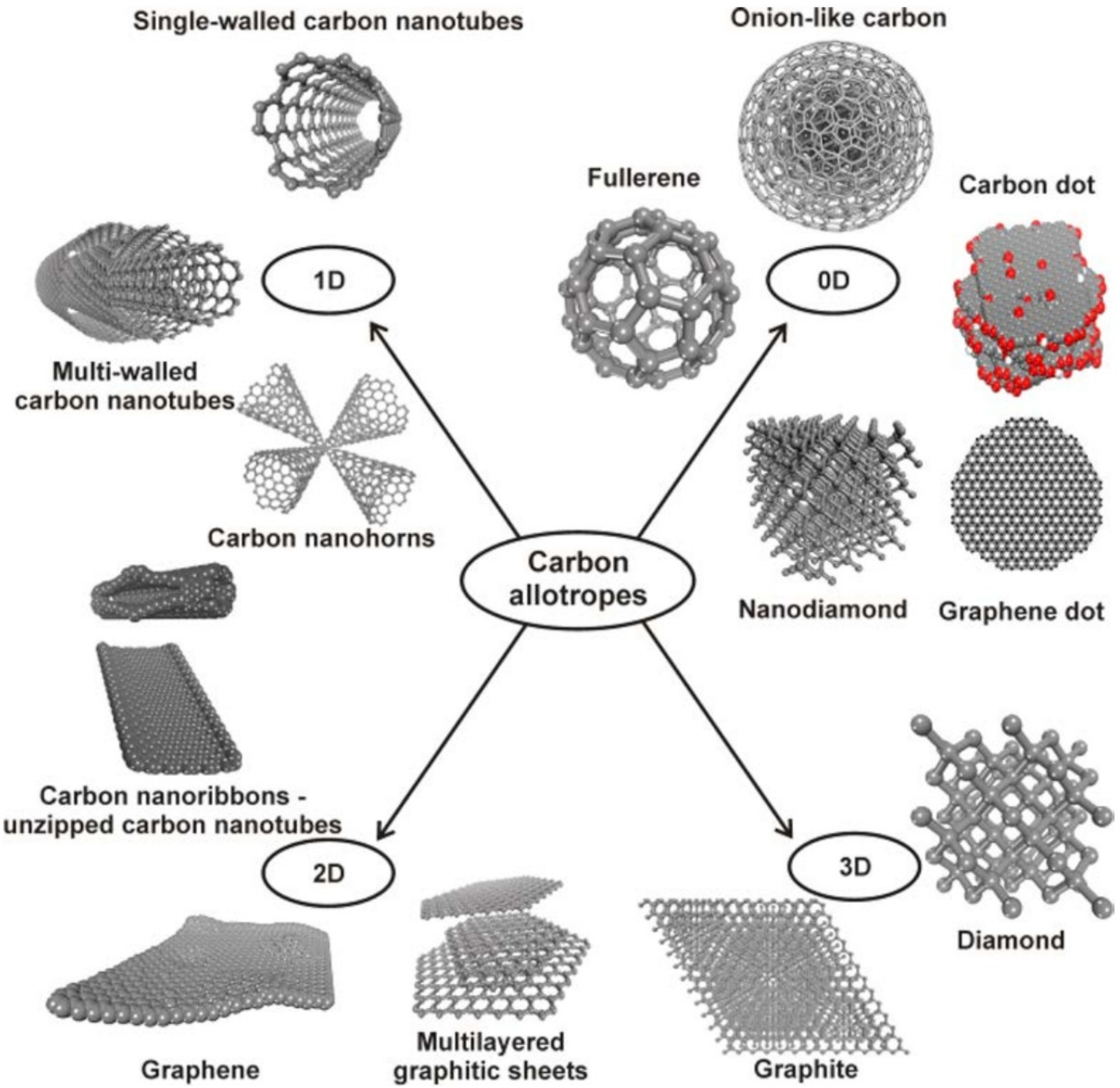
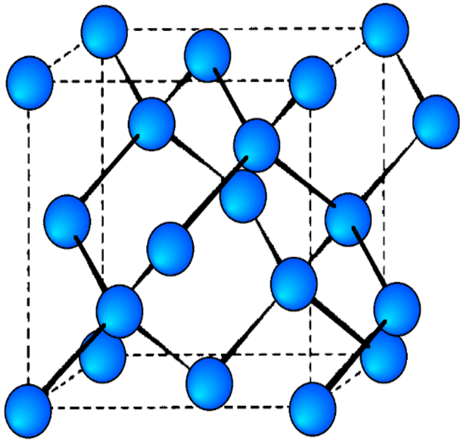
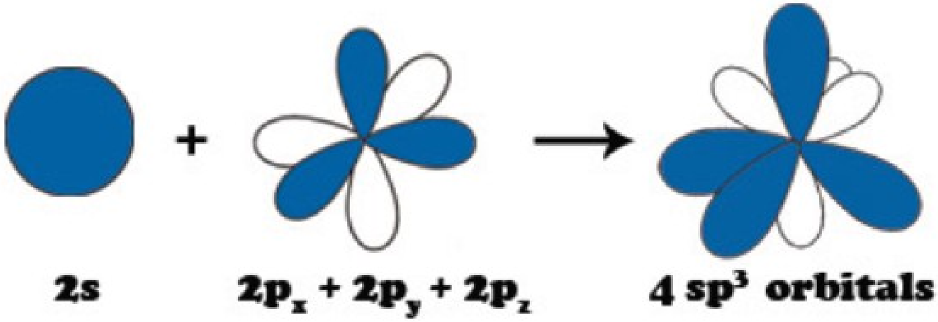
Carbon-based nanomaterials



Carbon atoms

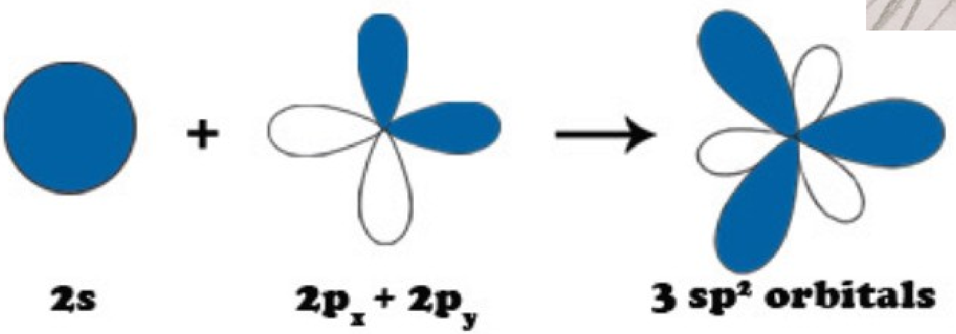
- sp^3 and sp^2 hybridization states
- diamond and graphite

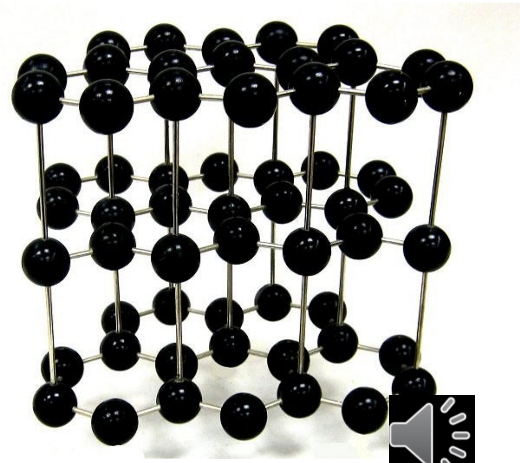




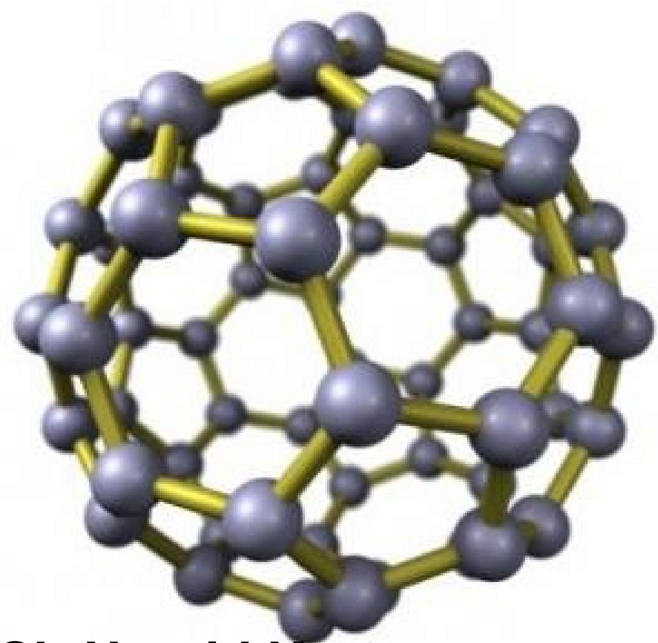
hard, transparent, insulator, expensive

soft, opaque, conductor, cheap



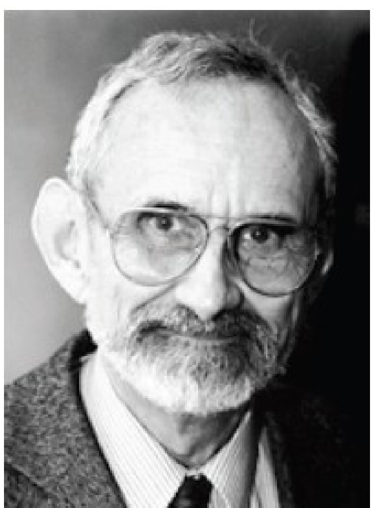


Buckminsterfullerene

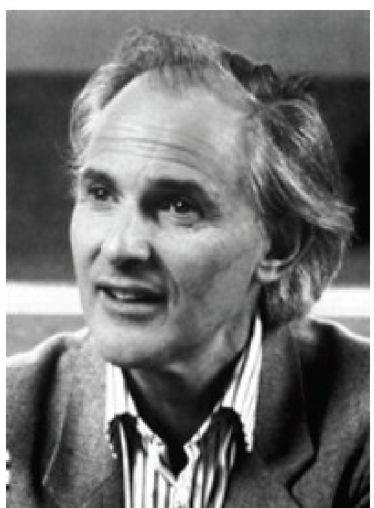


- molecule consisting of 60 C atoms
- sp^2 hybridized bonds
- has 20 hexagons, 12 pentagons
- other related structures have 70 or 84 C atoms

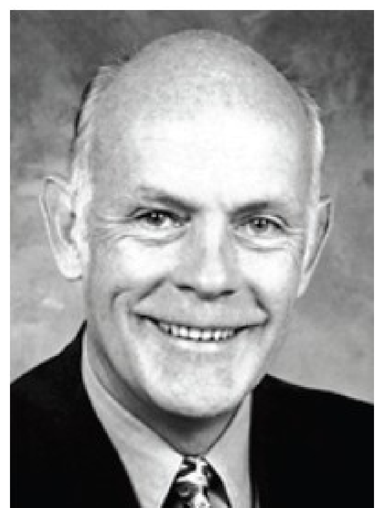
- Nobel Prize in Chemistry 1996: Robert Curl, Sir Harold Kroto, Richard Smalley "for their discovery of fullerenes".



Robert F. Curl Jr.

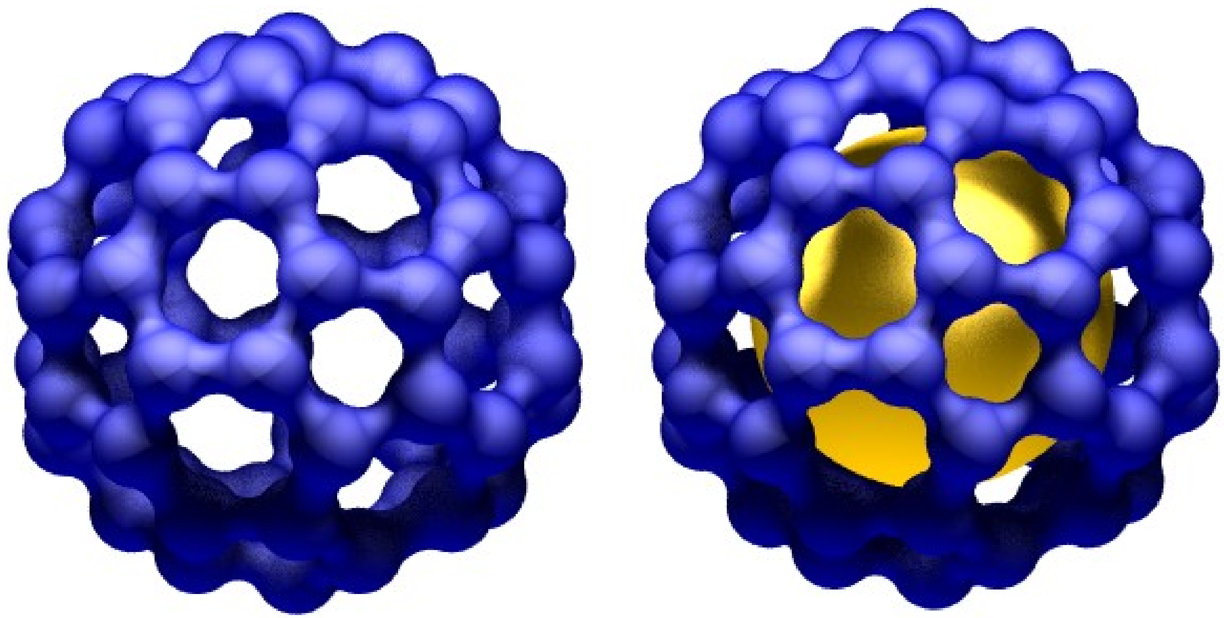


Sir Harold W. Kroto



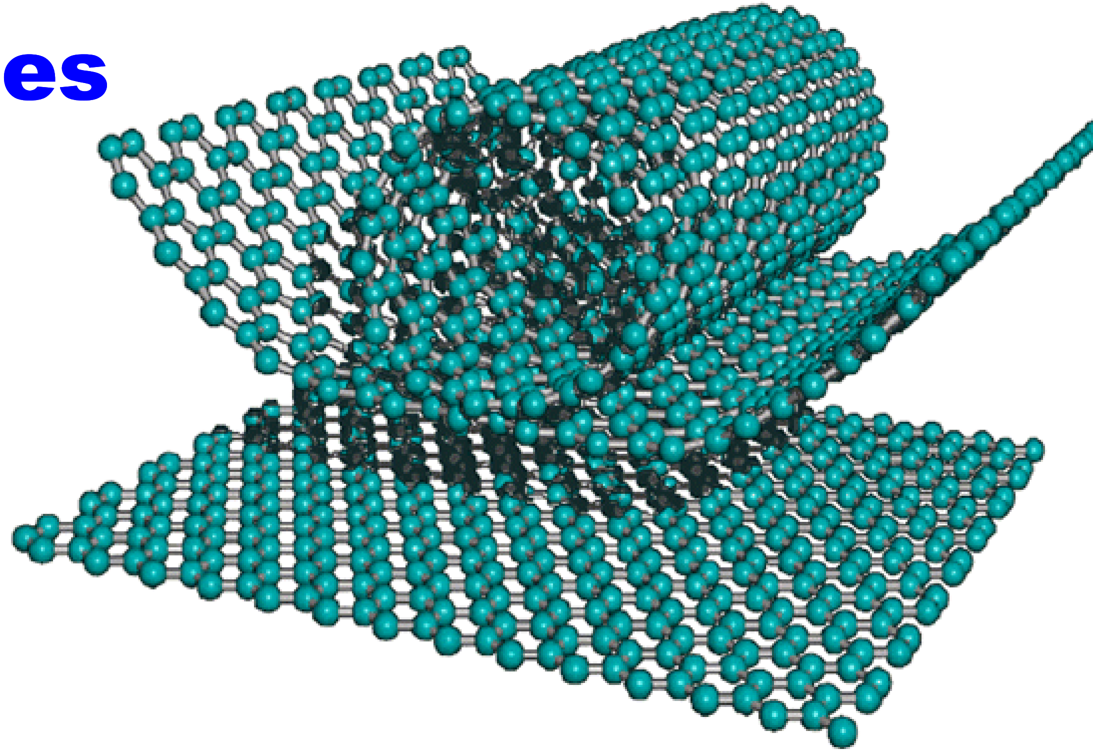
Richard E. Smalley

Fullerene

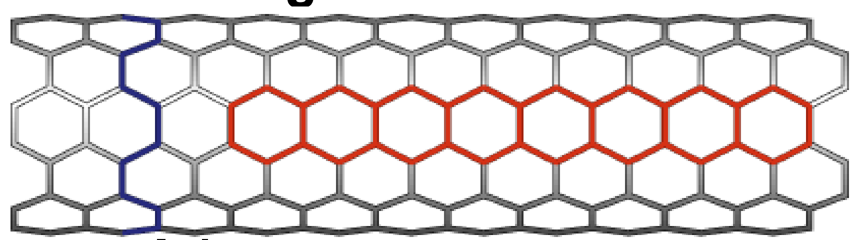


- empty and enclosing other atom(s)
- $RbCs_2C_{60}$ is the highest temperature carbon based super conductor yet discovered T_c = 33 K

Carbon nanotubes

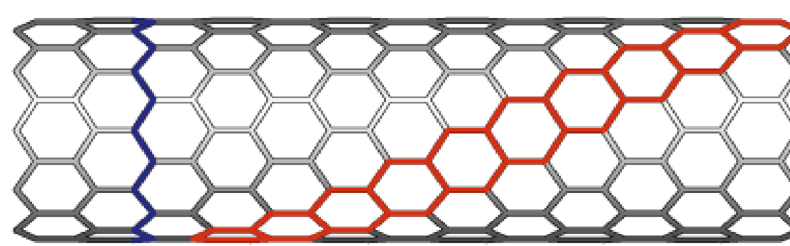


- rolled up sheet of sp^2 bonded C atoms
- can be formed from a single sheet of C atoms or several sheets
- SWCNT / MWCNT
- properties depend on how they are rolled up
- 100 times stronger than steel at 1/6 the weight
- electrical conductor



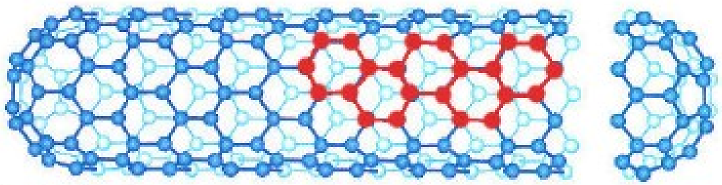
Armchair

- electrical insulator

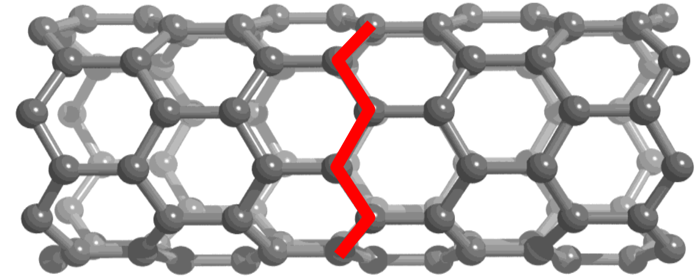


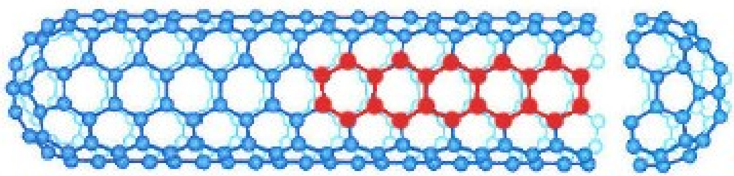
Zig-zag

Types of SWNCTs

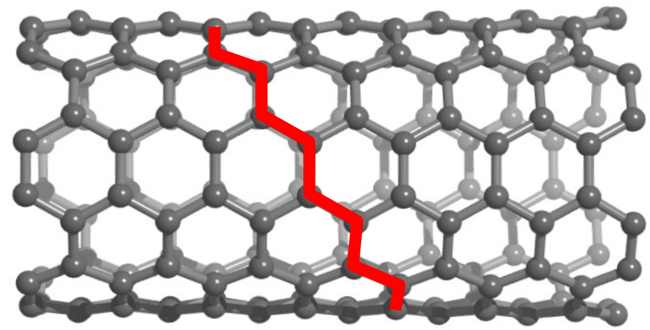


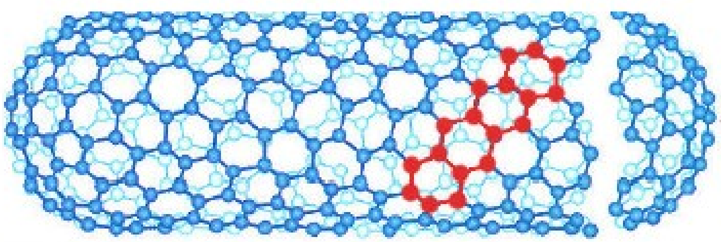
- **zig-zag**



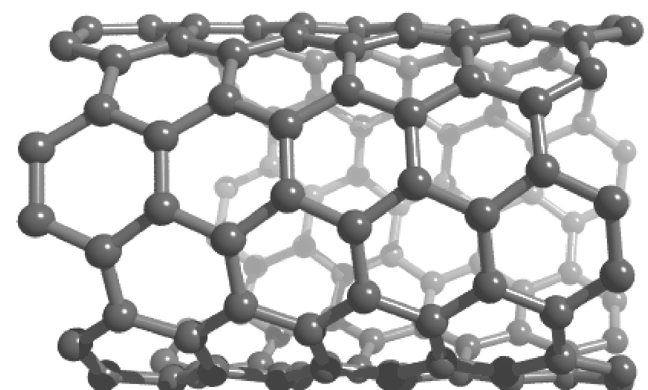


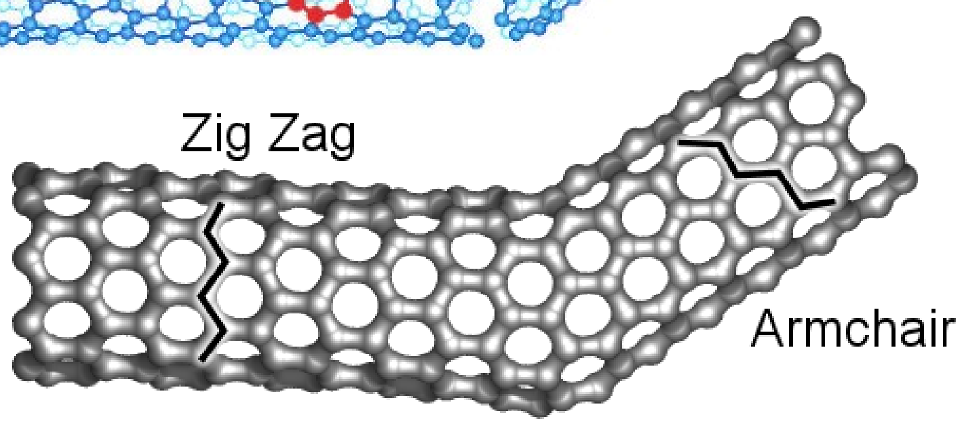
- **arm-chair**



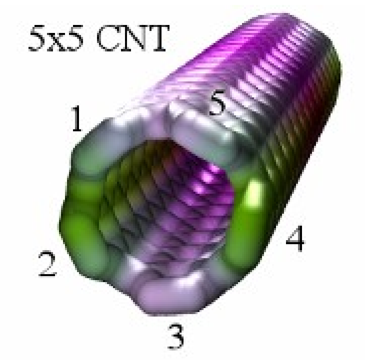


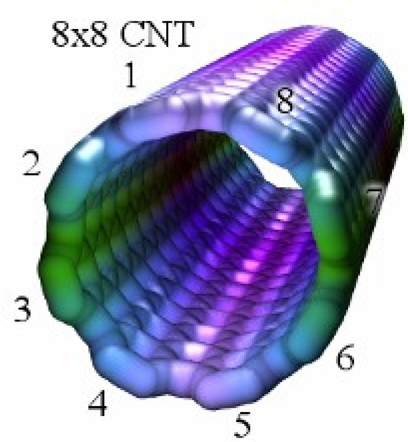
- **chiral**

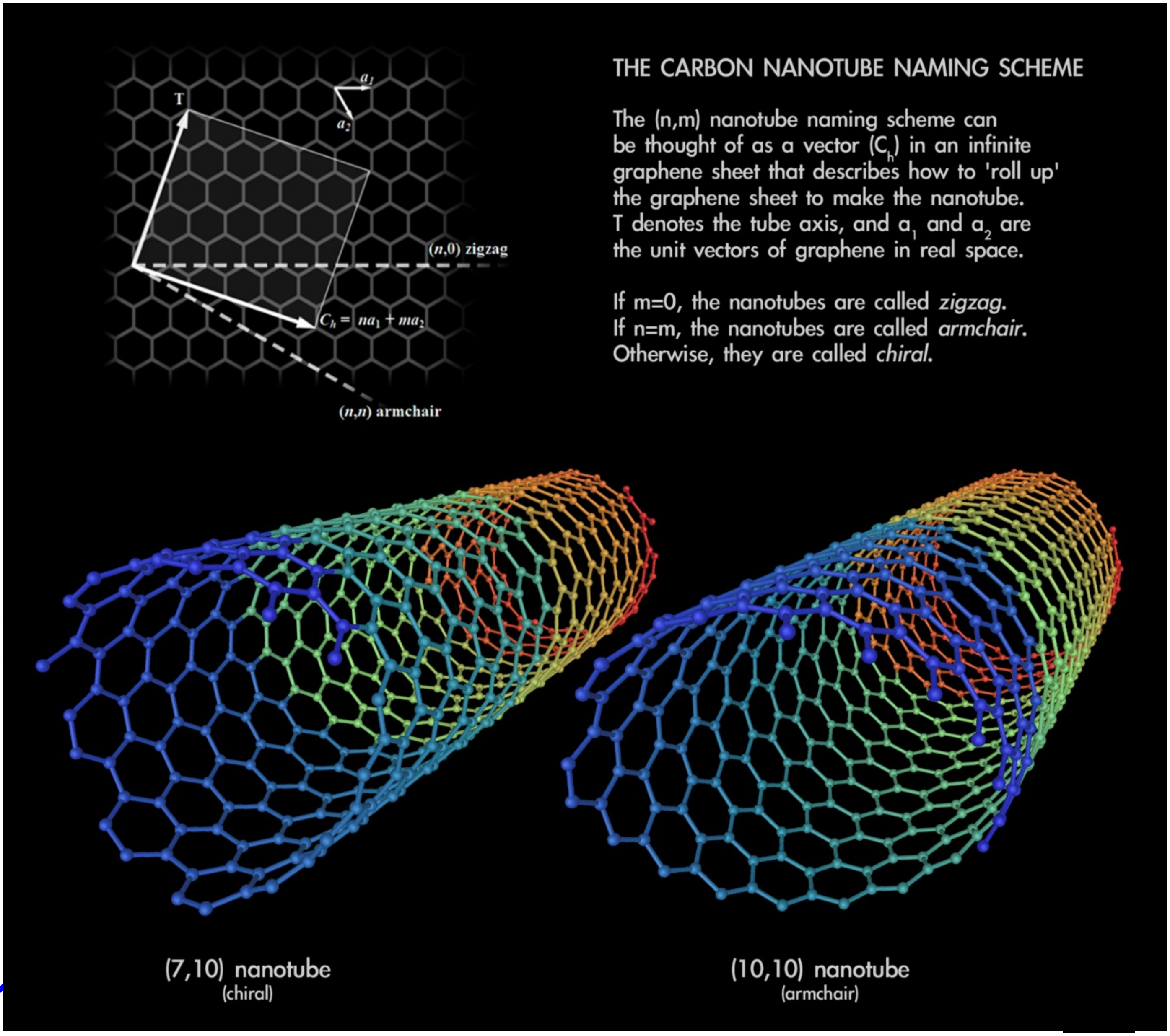




n x m SWCNTs

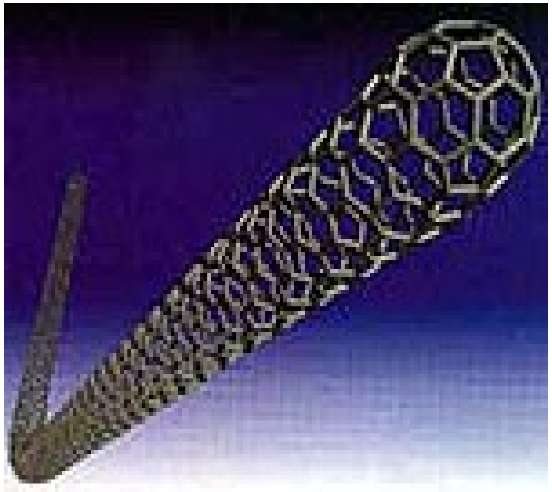




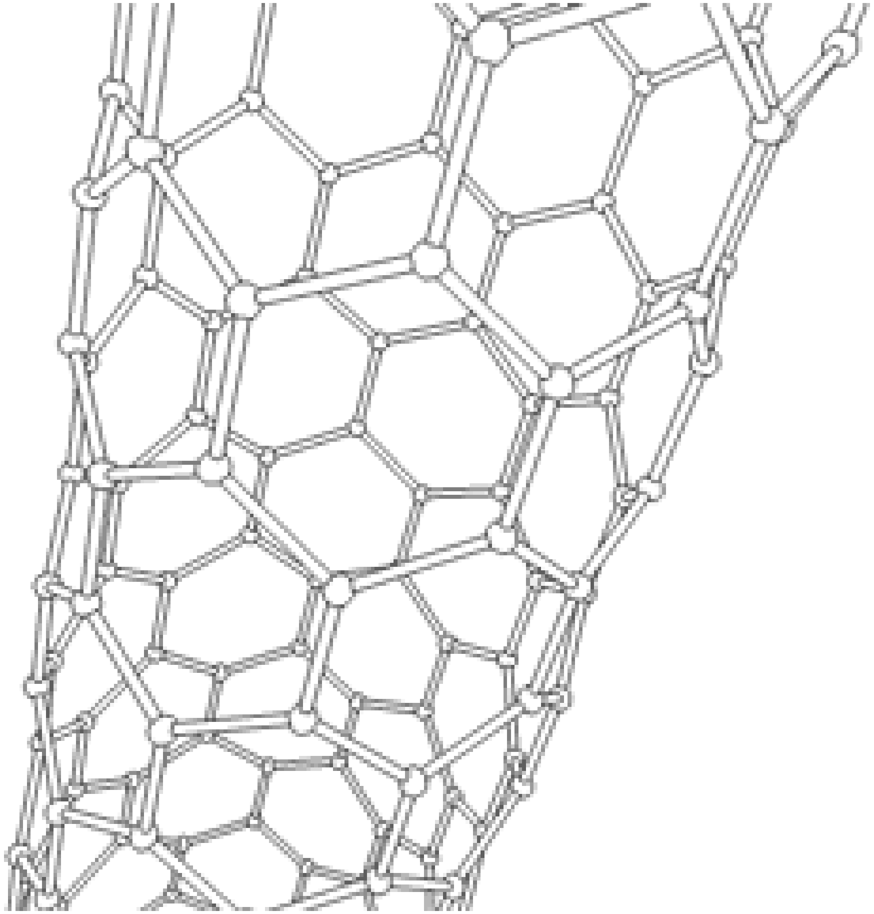


en.wikipedia.org/wik

Single- and multi-walled CNTs



- **SWCNT**

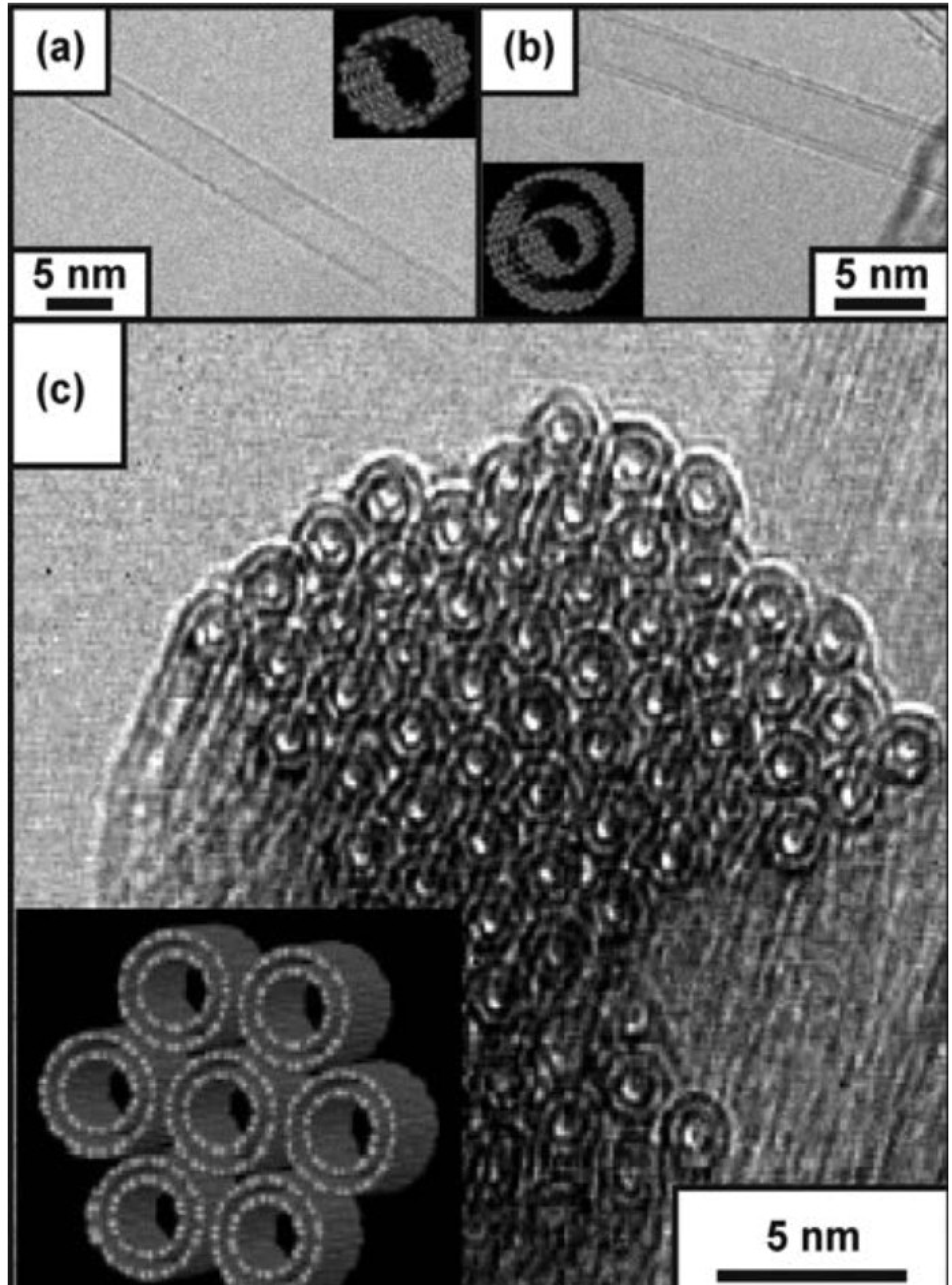


- **MWCNT**

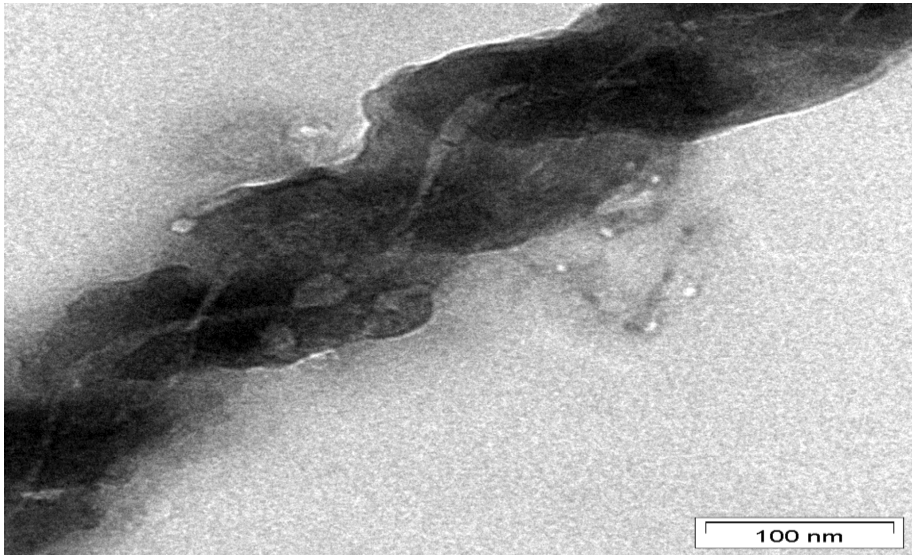
interlayers spaced 0.34 nm

TEMs of CNTs

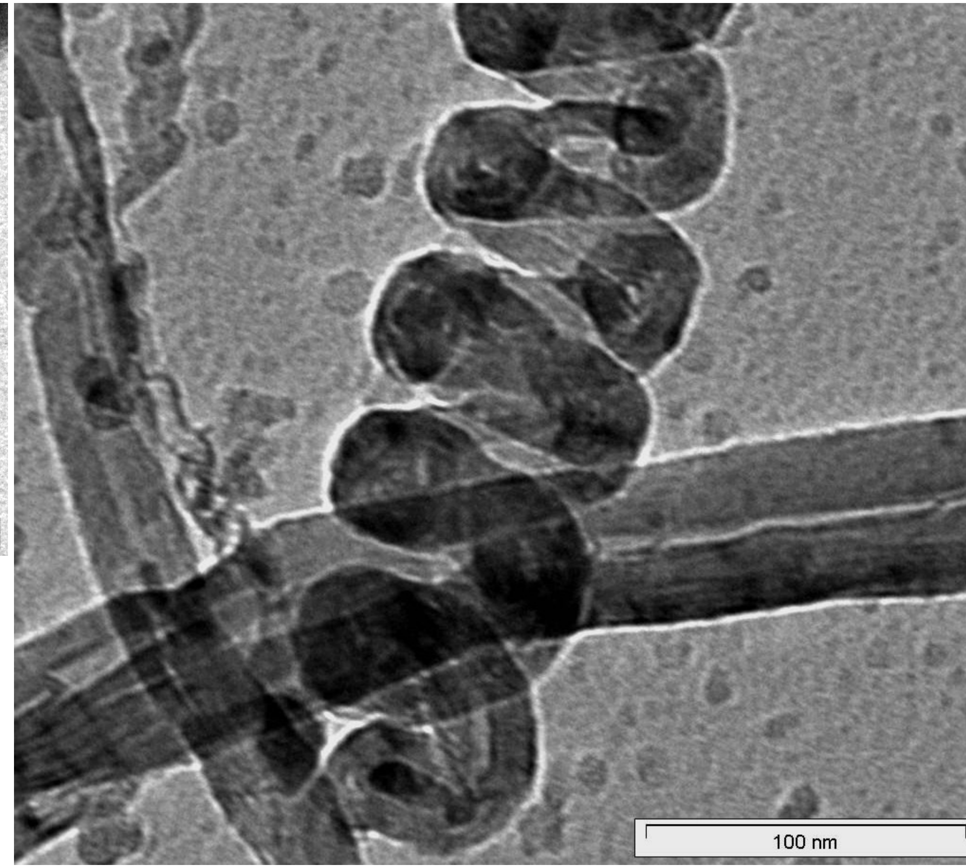
- a SWCNTs
- b double-wall CNTs
- c bundle



Flexibility of CNTs



- twisted and spiral CNTs



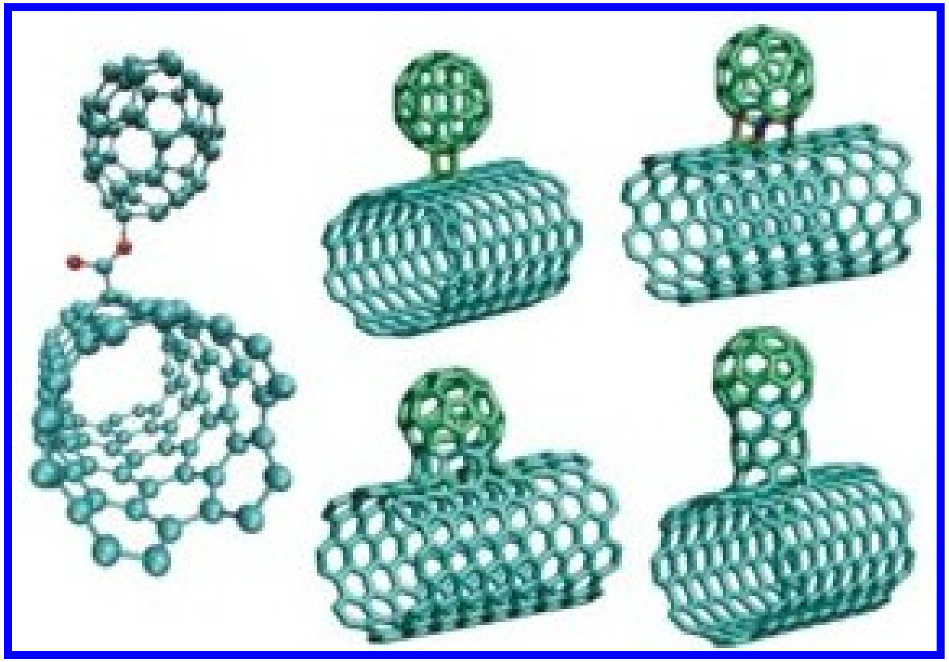
Properties of CNTs

- **strength - strongest and stiffest materials known, in terms of tensile strength and elastic modulus respectively**
  - a multi-walled carbon nanotube was tested to have a tensile strength of 63 Gpa (high-carbon steel 1.2 Gpa)
  - very high elastic moduli ~1 Tpa
  - CNTs have a low density for a solid of 1.3-1.4 g/cm³, its specific strength of up to 48 500 kN·m/kg is the best (high-carbon steel 154 kN·m/kg)
- **electrical - structure of a nanotube strongly affects its electrical properties**
  - for a given (n,m) nanotube, if n - m is a multiple of 3, then the nanotube is metallic, otherwise semiconductor
  - thus all armchair (n=m) nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting
  - metallic CMTs can have an electrical current density more than 1000 times greater than Cu and Ag
- **thermal - very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction,"**
  - but good insulators laterally to the tube axis
  - it is predicted that carbon nanotubes will be able to transmit up to 6 kW per meter per kelvin at RT (Cu only transmits 385 W/m/K)

Potential applications of CNTs

- **energy storage**
  - hydrogen storage, 6.5% by weight is needed
  - Li intercalation, electrochemical supercapacitors
- **field emission devices**
- **transistors**
  - CNTs are p-type; can be doped with K to make them n-type
- **AFN tips**
- **nanotweezers**
- **composite materials**
- **nano structures**
- **potential for extremely strong light weight cables / space elevator** (http://www.youtube.com/watch?v=pnwZmWoymeI)
- **physical memory**

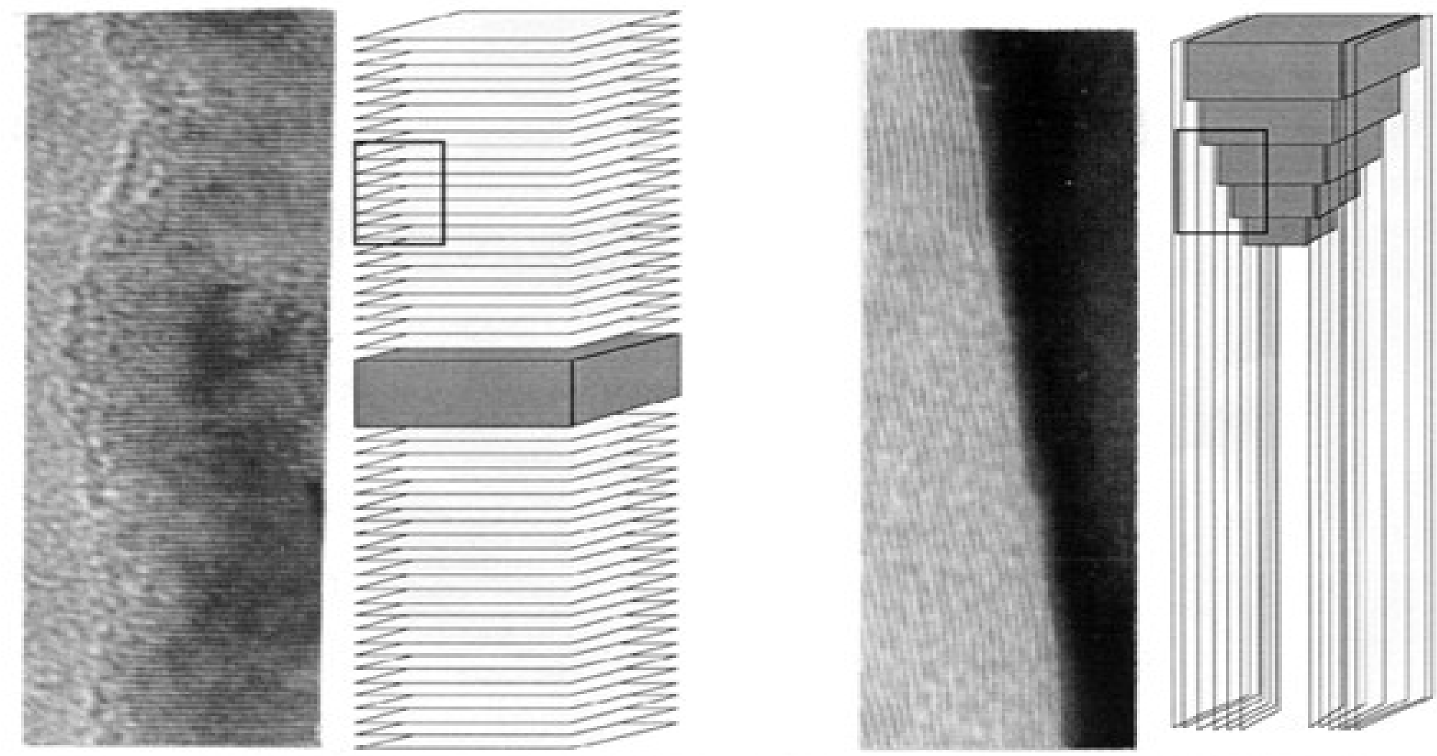
NanoBuds



- fullerenes covalently bonded to outer sidewalls of underlying nanotube.
- exhibit properties of both CNTs and fullerenes.
- mechanical properties and electrical conductivity are similar to CNTs
- however, because of the higher reactivity of the attached fullerene molecules, the hybrid can be further functionalized through known fullerene chemistry
- the attached fullerenes can be used as molecular anchors to prevent slipping of the nanotubes in various composite materials, thus improving mechanical properties

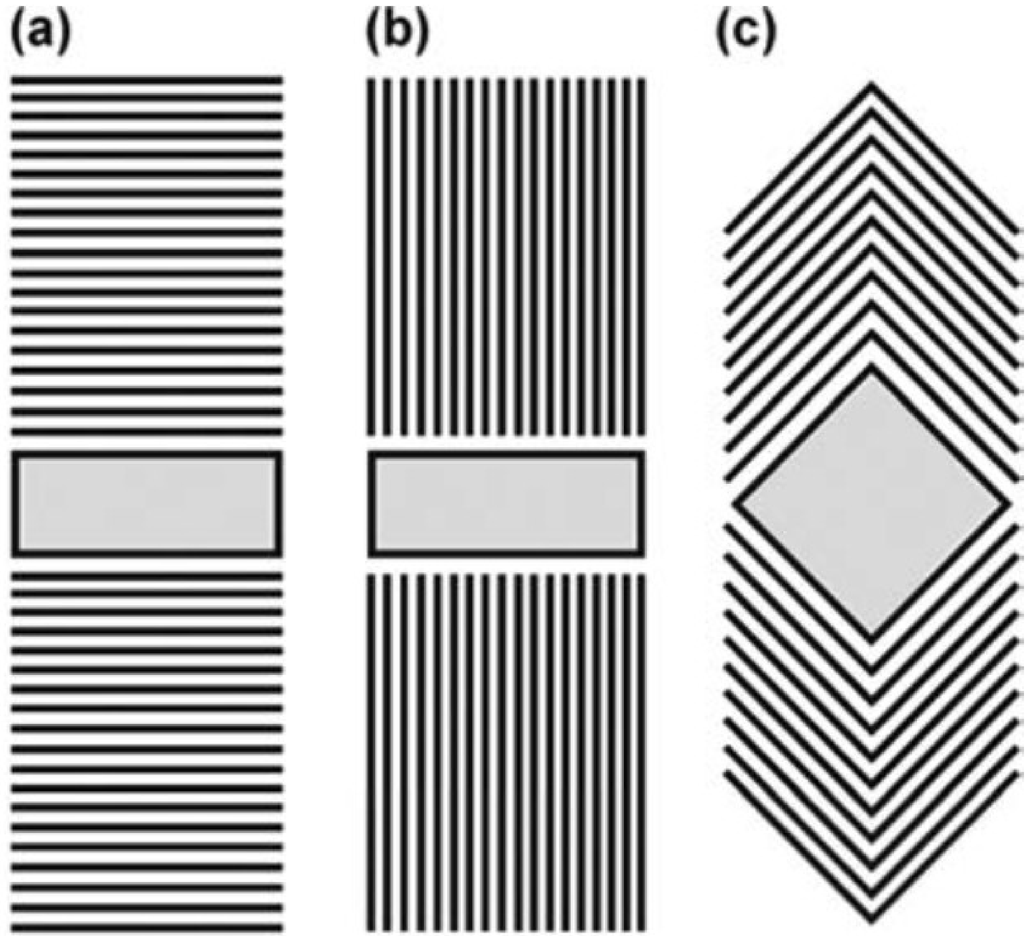
Carbon nanofibers

- consist of the graphite sheet completely arranged in various orientations
- outstanding feature - presence of a plenty of sides which in turn make sites accessible to chemical or physical adsorption
- lenght from 5 to several hundred um, 100- 300 nm in diameter
- graphite platelets "perpendicular" and "parallel" to the fiber axis



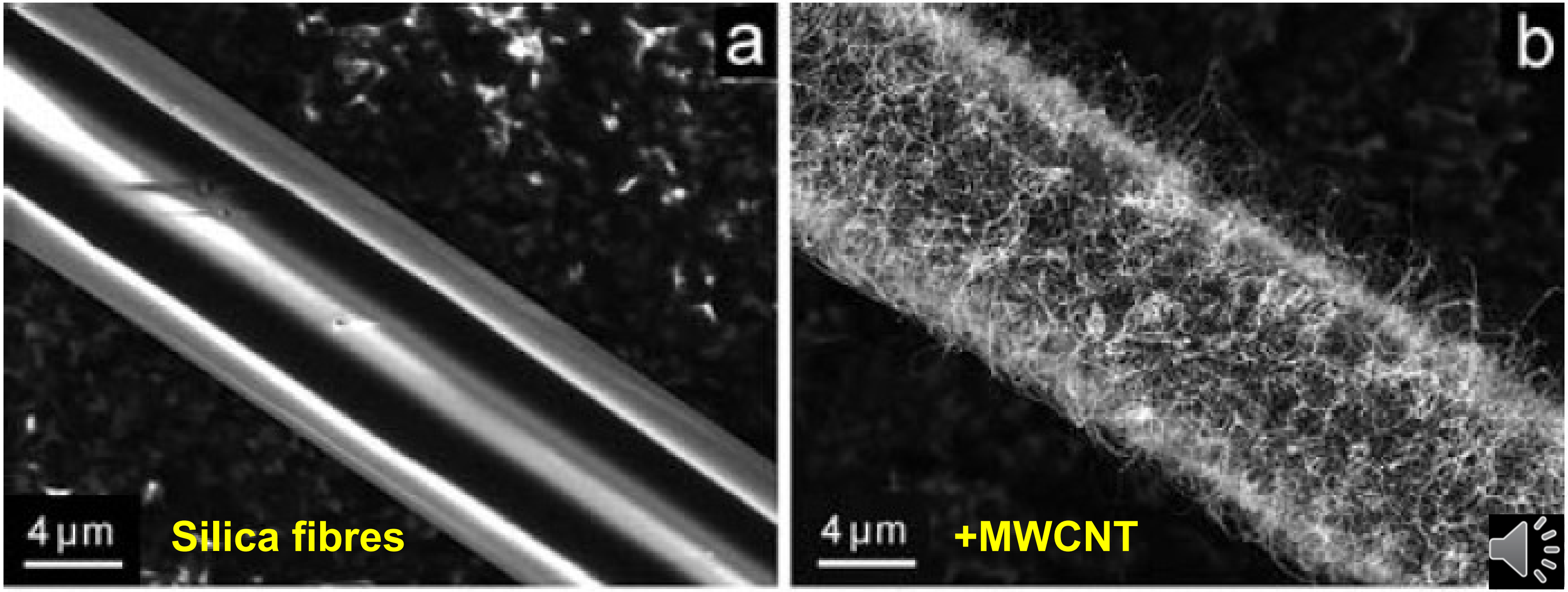
Orientation of layers

- a) platelet carbon nanofibers, perpendicular graphene layers
- b) ribbon nanofibers, layers forming a stack parallel to the fiber axis
- c) herringbone – graphene sheets tilted to the fiber axis



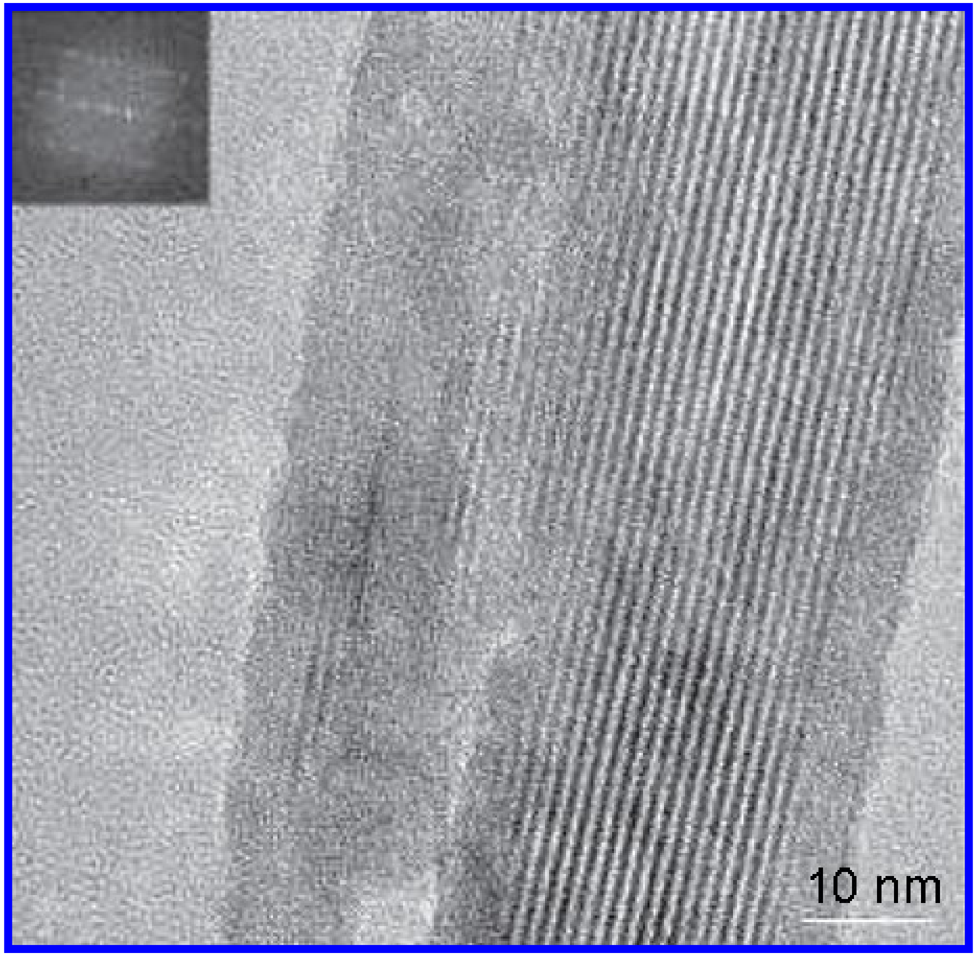
CNTs are strong

- large length (up to several microns) and small diameter (a few nanometres) result in a large aspect ratio
- mechanical properties can improve by 50% or more by adding carbon nanotubes



Damascus sabre steel contains CNTs

- MWCNTs found in the 17th century sword
- formed during the synthesis and may have produced the very good mechanical properties.

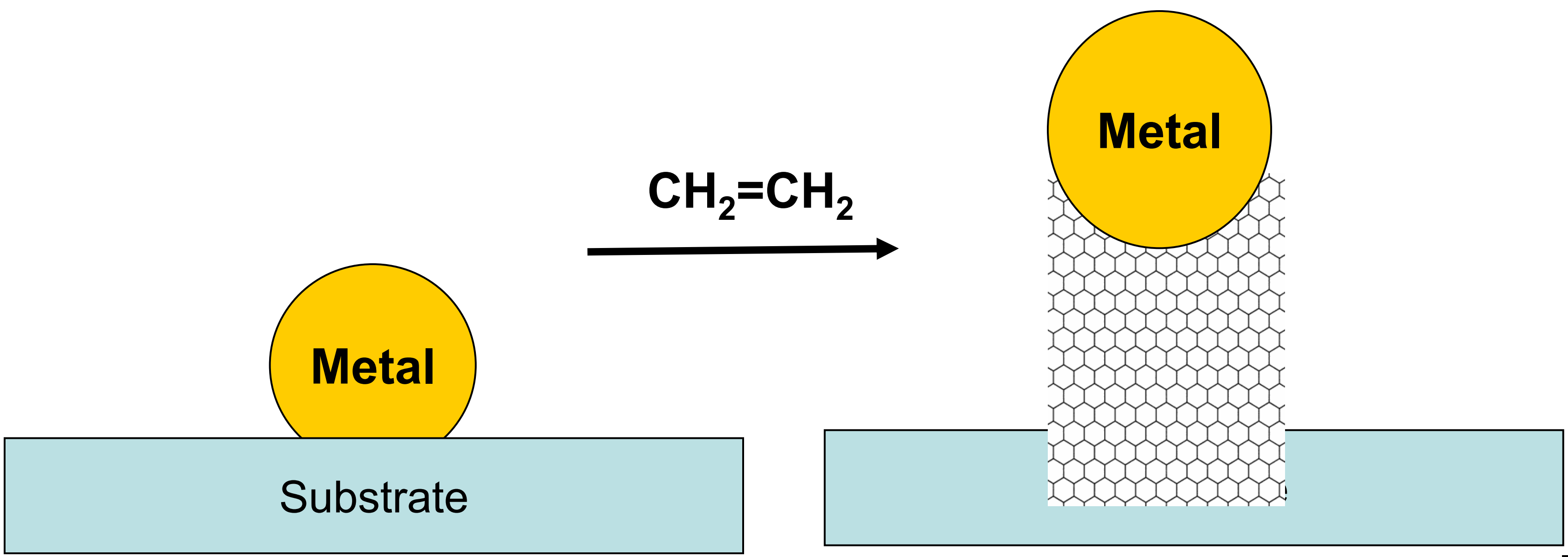


Preparation of CNTs

- **Carbon arc discharge.** Hold two carbon (graphite) electrodes at some potential difference in a He atmosphere and bring the electrodes together. At some separation and arc will be produced, and carbon nanotubes will grow on the cathode. These will normally be multiwalled nanotubes, but single walled nanotubes can be grown by adding Ni, Fe, or Co to the cathode
- **Laser ablation.** Heat up a lump of graphite to ~1200 C in an Ar atmosphere, and then blast it with a laser. This can make single walled nanotubes if the graphite has a catalyst like Co or Ni included.
- **Catalytic growth.** Heat up hydrocarbons (e.g. acetylene) to high temperatures and then let them settle on a substrate coated with a catalyst (Fe, Co, Ni). This will form either multiwalled nanotubes or single walled nanotubes depending on the growth conditions.

CNT synthesis

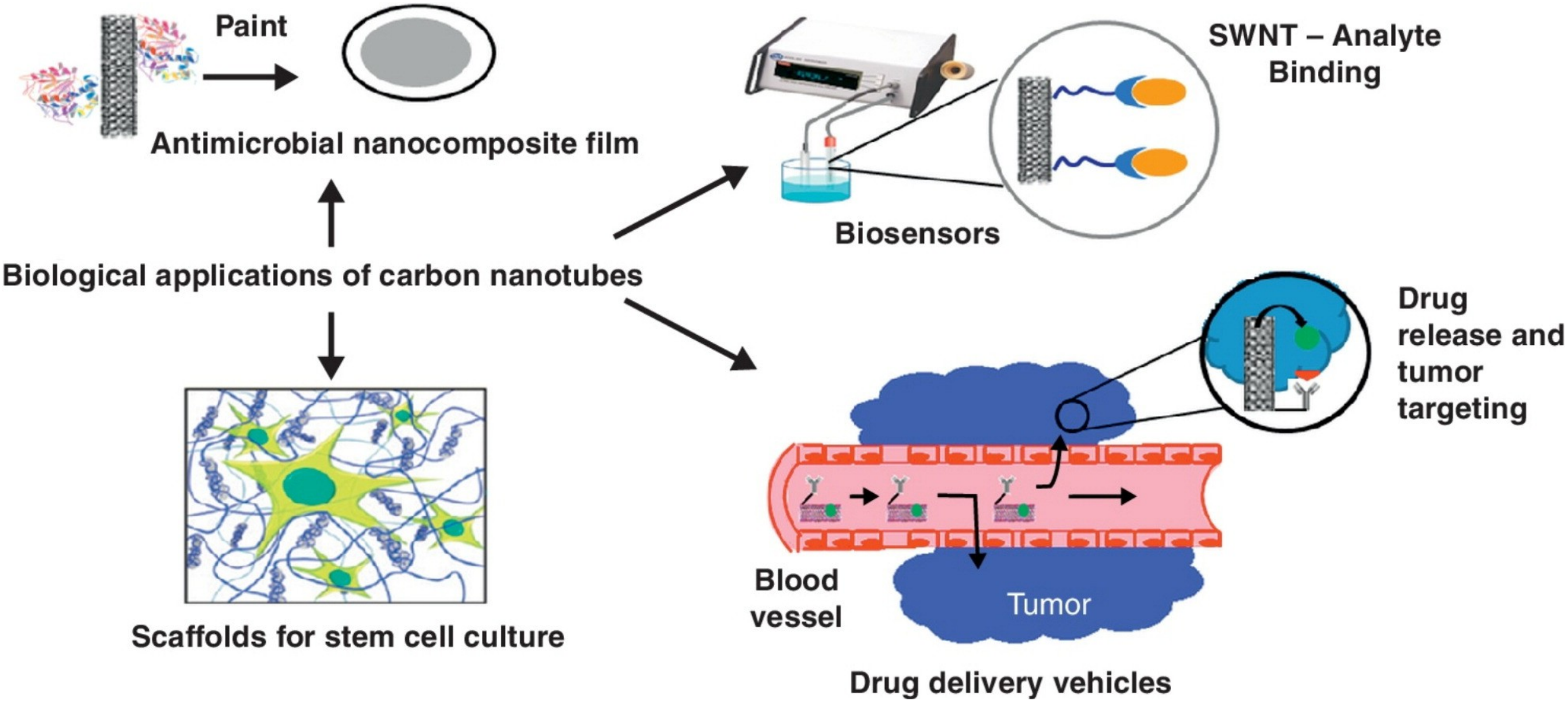
- a metal particle acts as a catalyst for carbon nanotube growth
- growth takes place in an inert atmosphere, often He
- a source of carbon and energy are needed



CNTs purification

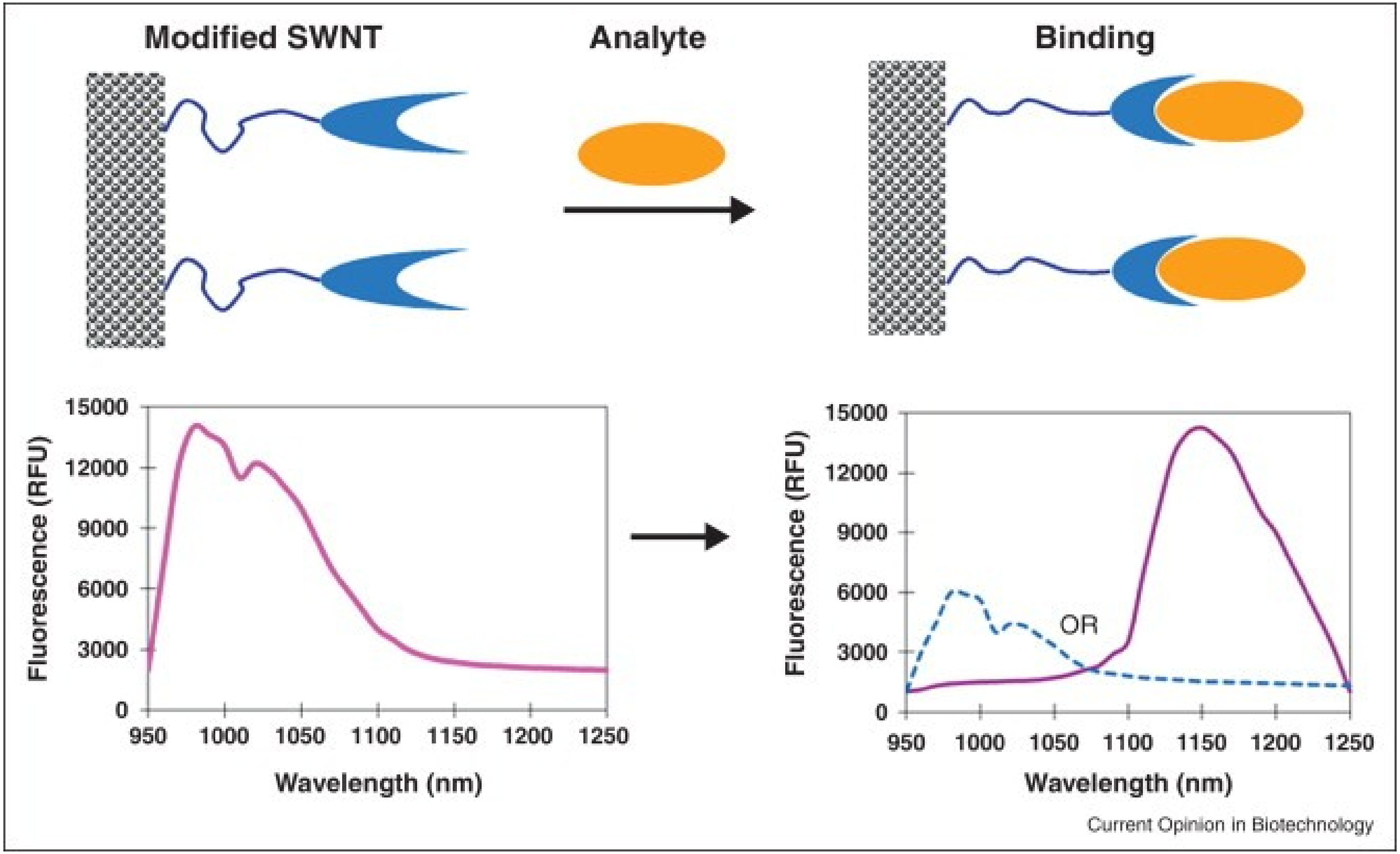
- carbon nanotubes must usually be purified in some way to remove the catalyst
- oxidation
- acid treatment
- annealing
- ultrasound
- magnetic purification
- micro-filtration
- chromatography

CNTs bioapplications?

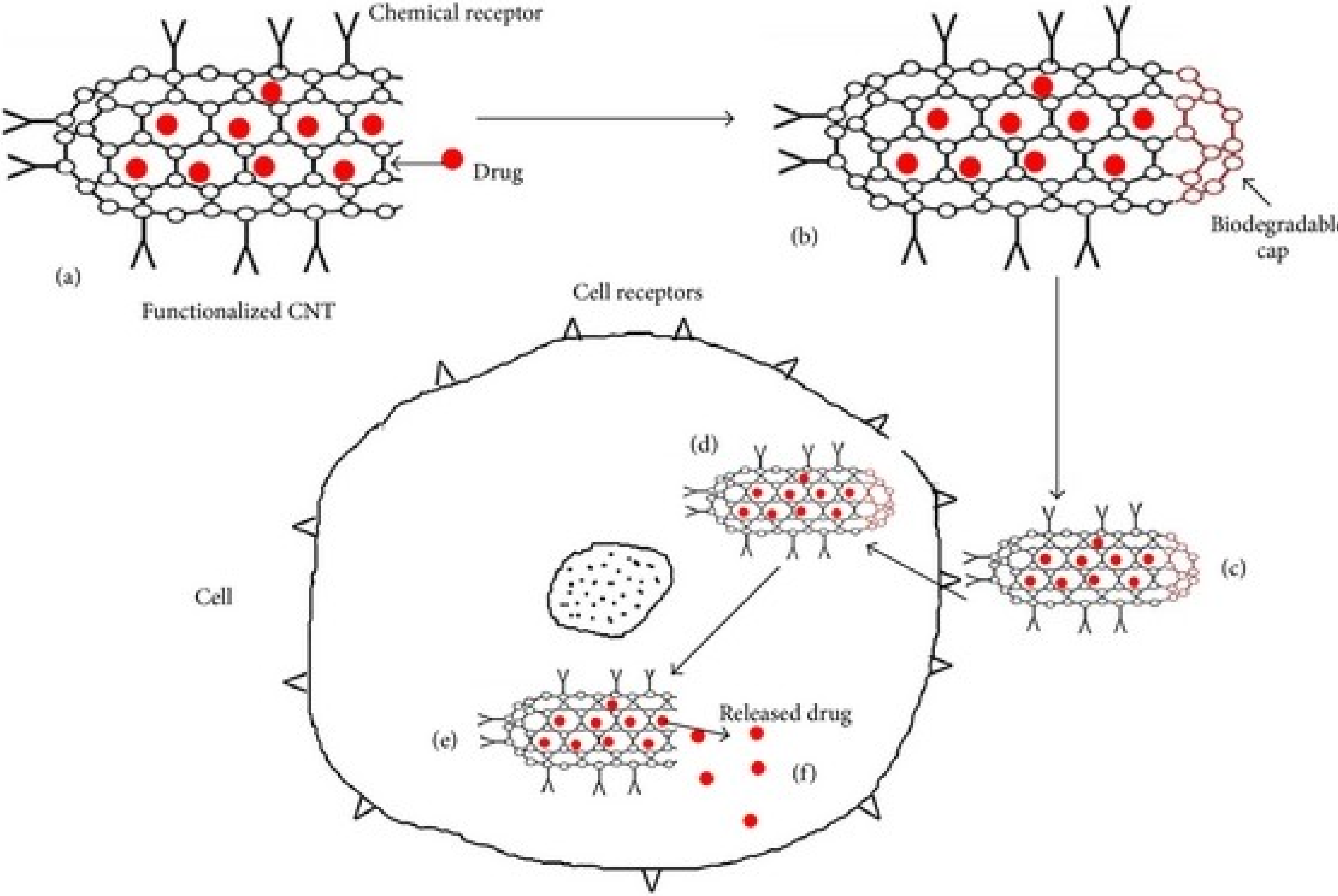


Biosensing - optical

- modified SWNTs used in fluorescent sensing of molecules
- upon binding of the analyte, there is either a shift in the emission wavelength or a change in fluorescence intensity

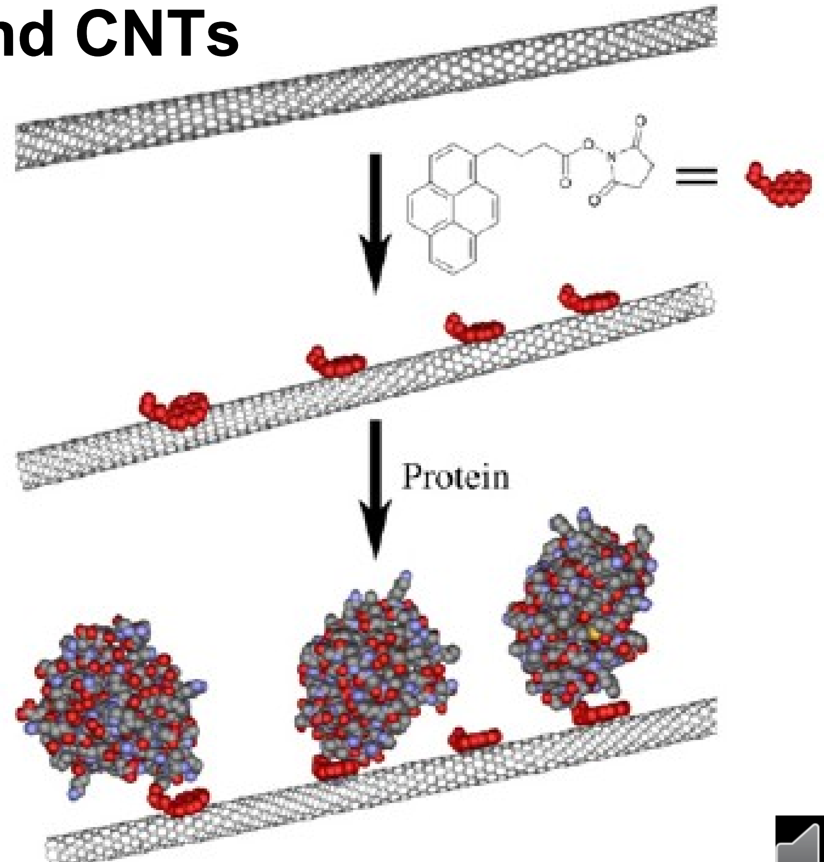


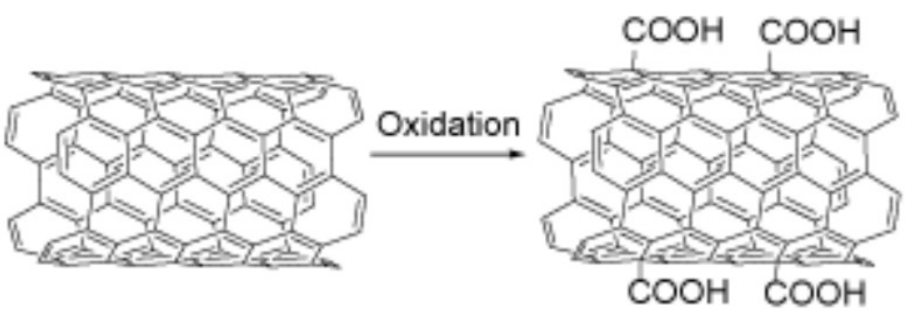
Target delivery



Functionalization

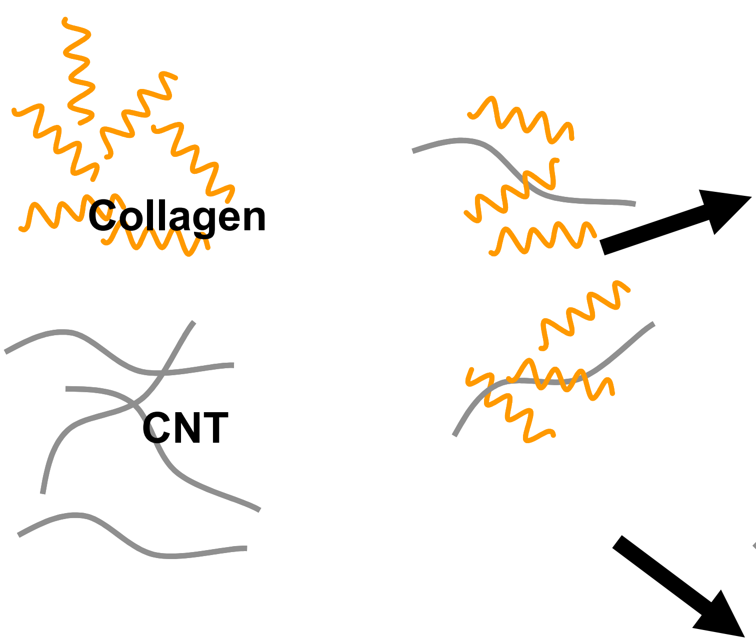
- **CNTs can react chemically with different molecules**
- **they can be made soluble in water**
  - Aldrich sells CNTs with polyaminobenzene sulfonic acid (PABS) a water soluble conducting polymer covalently bonded directly to the nanotube.
- **lipids can be organized around CNTs**
- **benzene can be attached to carbon nanotubes**
- **CNTs can be opened, filled with a metal and closed**
- **oxidation provides -COOH**

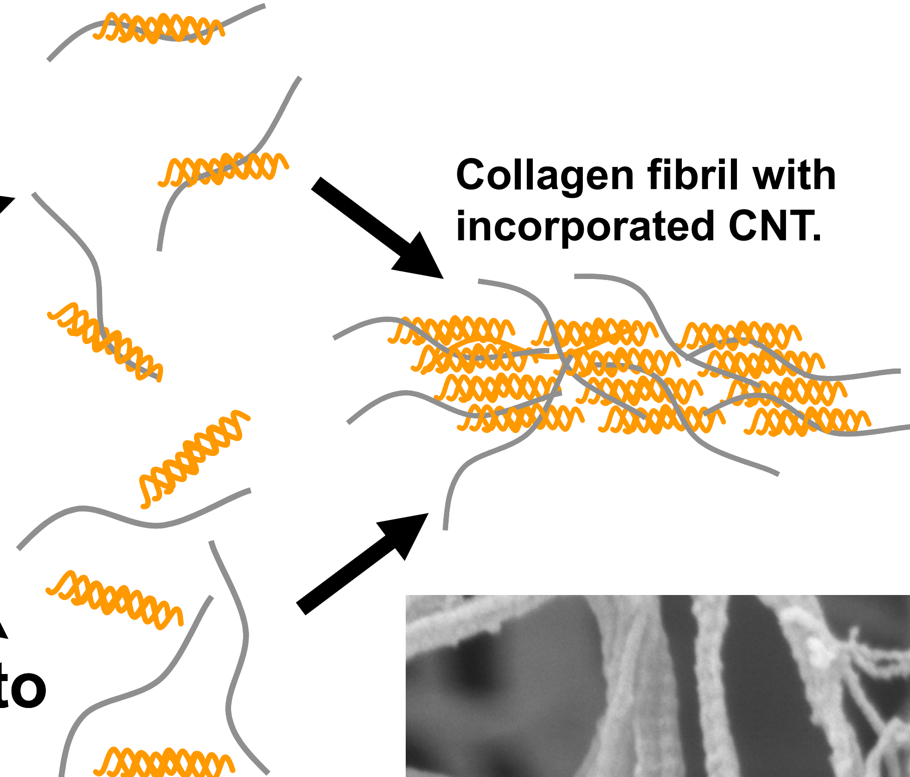




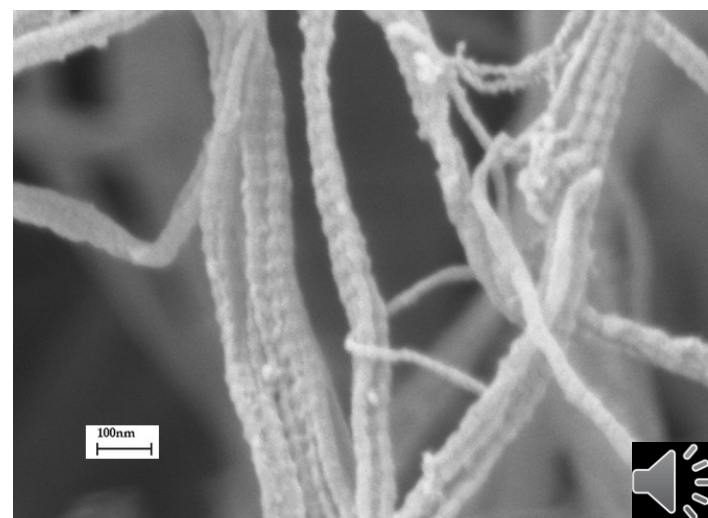
Biocompatible CNTs

- collagen – CNTs composite material



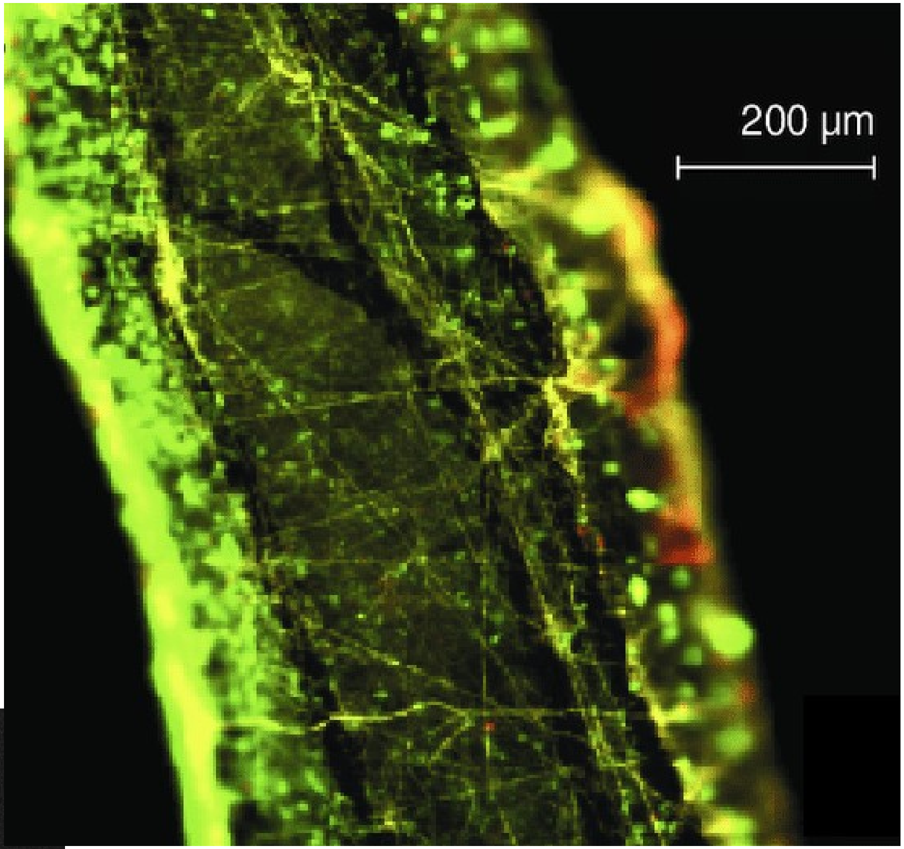


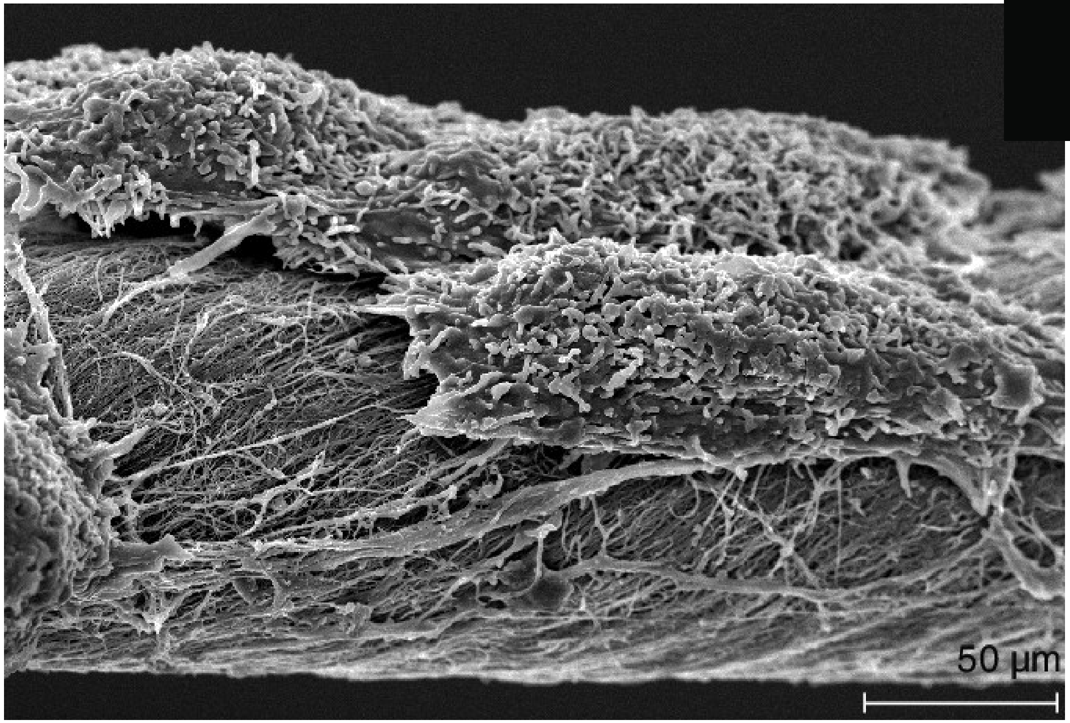
- collagen – belongs to matrix proteins
- surface more compatible for attachment of cells



Scaffolds for cells

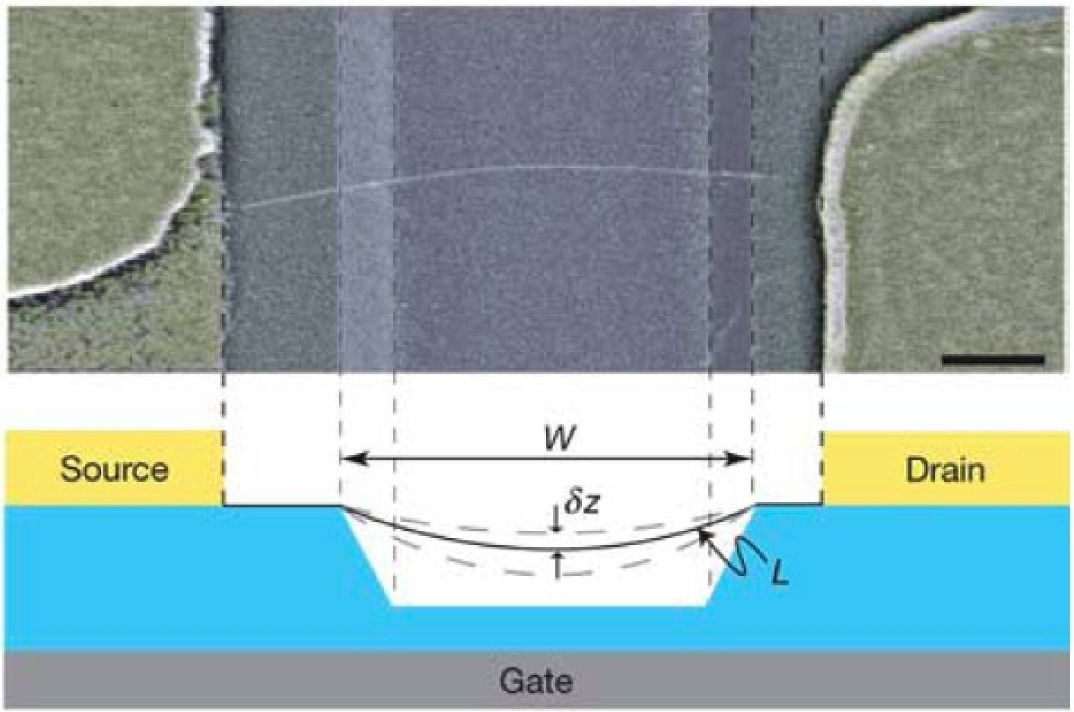
- fibroblasts on multiwalled carbon nanotube
- cell attachment on MWCNT poly(lactic-co-glycolic acid) scaffold
- fluorescent / SEM images

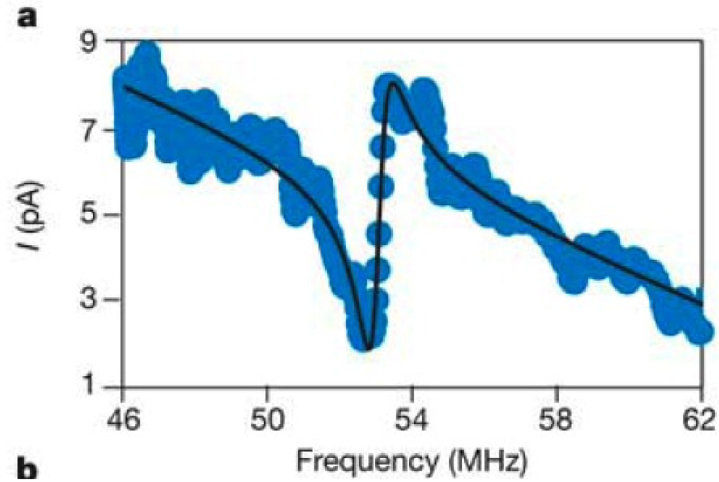




CNT as mechanical oscillator

Force sensitivity of 1 fN $Hz^{-1/2}$





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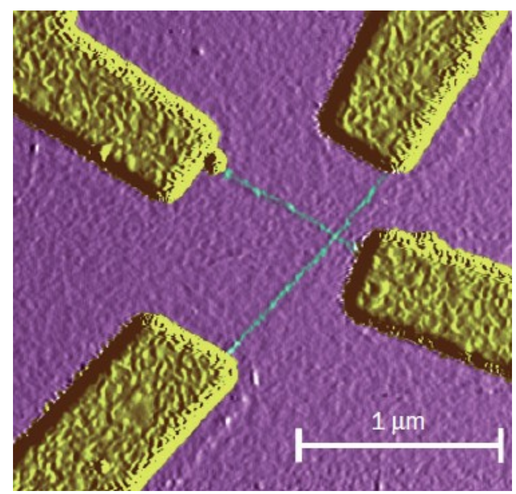


Open problems

- to be useful for devices, these carbon nanomaterials need to be prepared on and/or connected reliably to electrodes
- since the properties depend strongly on structure (e.g. armchair vs zig-zag nanotubes), we need to have good control over these structural details
- many unanswered physics questions remain, including the magnetism, superconductivity, and optical properties of these materials

Manufacturers

- home.flash.net/~buckyusa/
- carbolex.com/
- cnanotech.com/
- www.fibrils.com/
- www.pa.msu.edu/cmp/csc/nanotube.html
- www.nano-lab.com/
- carbonsolution.com/
- www.mercorp.com/mercorp/
- www.nanocarblab.com/
- www.nanocs.com/
- www.nanocyl.com/
- www.nanoledge.com/
- www.e-nanoscience.com/
- www.sesres.com/Nanotubes.asp
- www.sunnano.com/
- www.rsphysse.anu.edu.au/nanotube/
- www.thomas-swan.co.uk/pages/nmframeset.html
- www.apexnanomaterials.com/
- www.timesnano.com/default.html
- www.seocal.com/products_pdflist.html
- www.simagis.com/nanotubes.htm
- www.xintek.com/products/overview.html
- www.helixmaterial.com/
- store.nanoscience.com/index.asp?PageAction=VIEWPROD&ProdID=168

Graphene history

- **1859 - the first example of chemical exfoliation of graphite**
- **B.C. Brodie treated flakes of graphite with potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3) at 60 oC for 3–4 days**
- **product washed by water to remove acid**
- **the entire procedure repeated several times until no further change was observed**
- **Brodie managed to isolate material that was "extremely thin and perfectly transparent"**
  - resulting material consisted of carbon, oxygen and hydrogen
  - which explained the increased total mass from the starting flakes of graphite
- **"graphic acid" (Brodie's term) or " graphitic acid"**
  - since it was dispersible in neutral and basic media, but not in acids

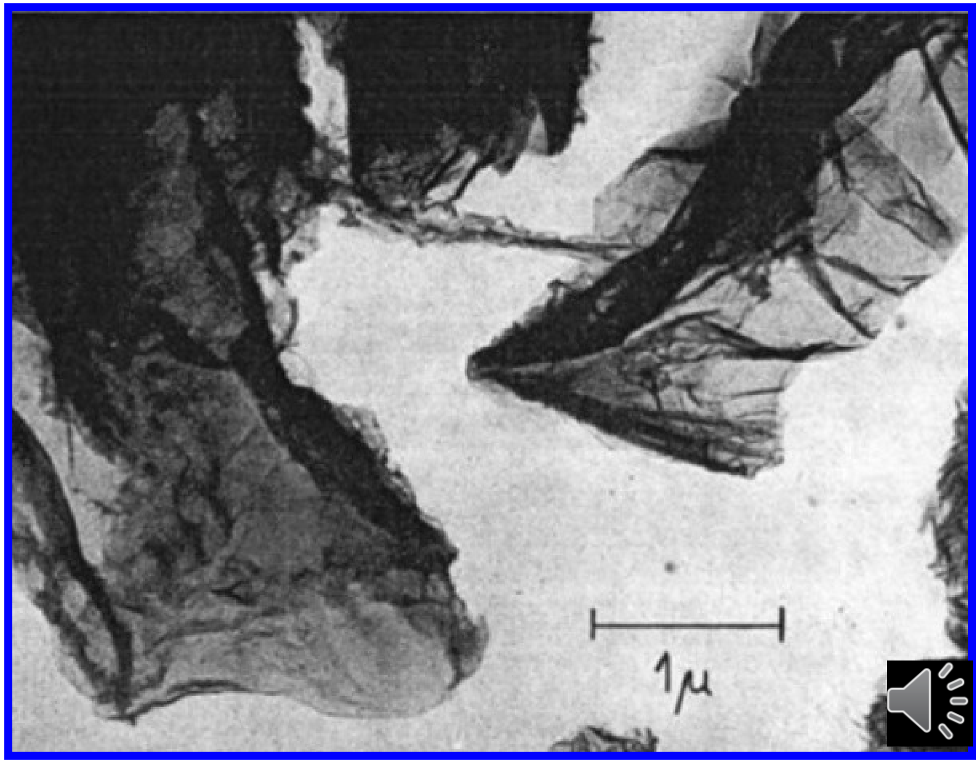
- **now typically named "graphite oxide"**
  - preserves the layered structure of graphite, layers are heavily oxidized
  - can be relatively easily separated in water or other polar solvents by mild sonication or stirring, resulting in a solution of
- **graphene oxide (GO)**
  - majority of the flakes are either mono- or few-layer stacks
  - can be reduced - hydrazine, hydroxylamine, sodium borohydride, sodium hydride, …
  - resulting in "chemically converted"

- **graphene**

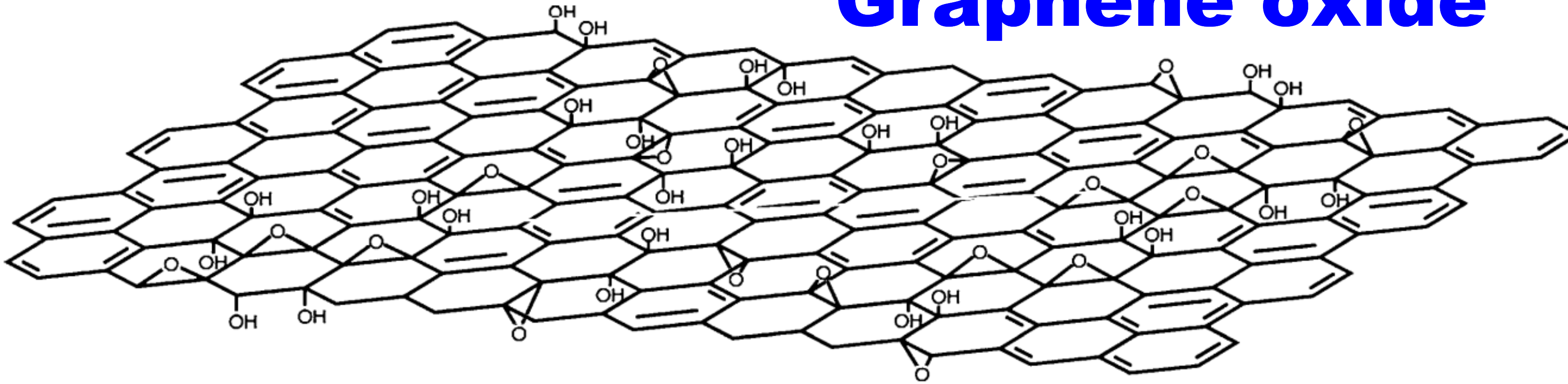
Hummer’s method

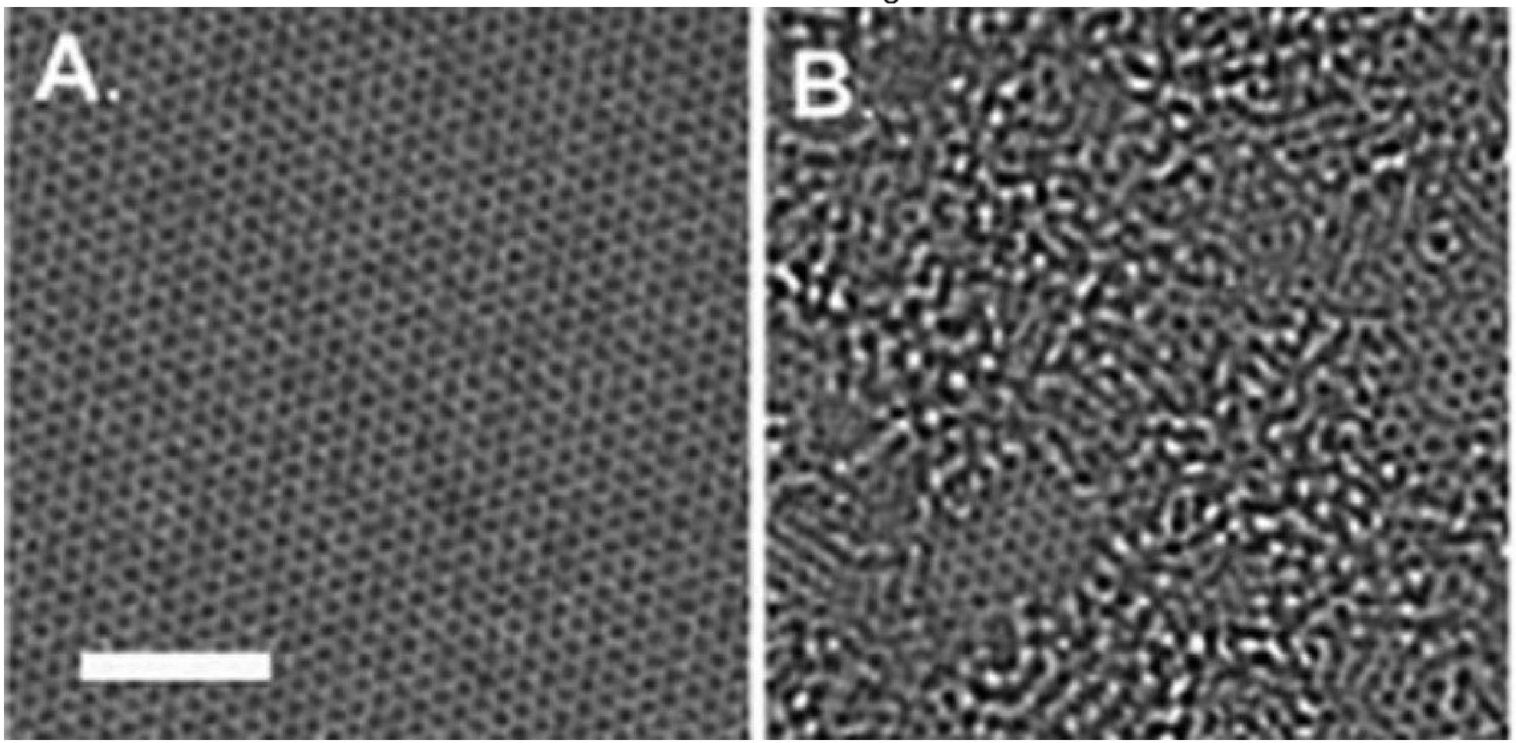
- synthesis of graphite oxide can be accomplished by treating graphite with a mixture of concentrated sulfuric acid, sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$)
- much faster (few hours for completion)
- no explosive gases evolve (… but toxic, caution!)

- after reduction with hydrazine TEM image



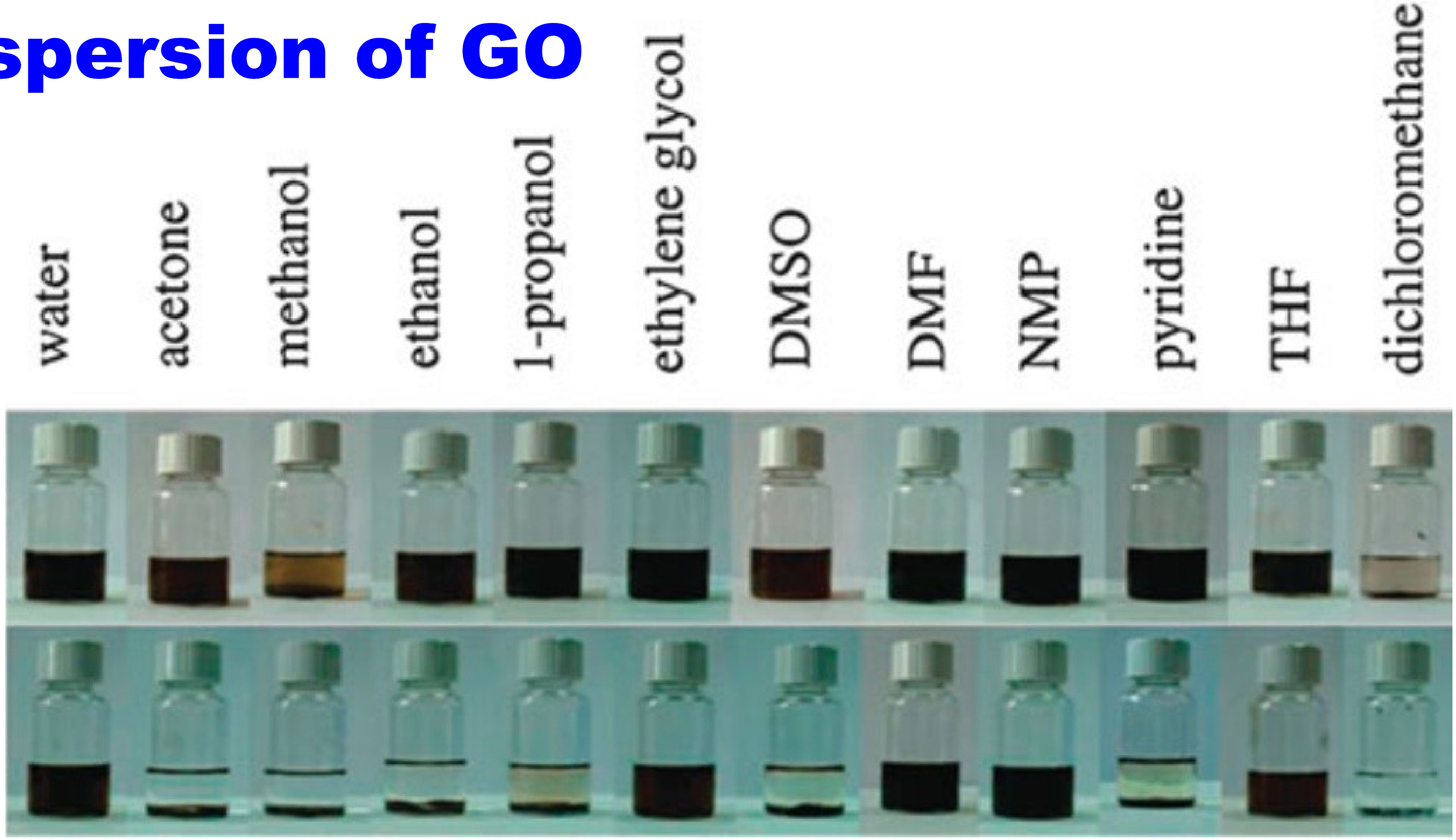
Graphene oxide





- TEM images of graphene (A) and graphene oxide (B); scale bar 2 nm
- GO is not conductive

Dispersion of GO



- **1 h (top) and 3 weeks (bottom) after sonication**

Graphene

- **single sp² bonded carbon sheet, C atoms in hexagonal array**

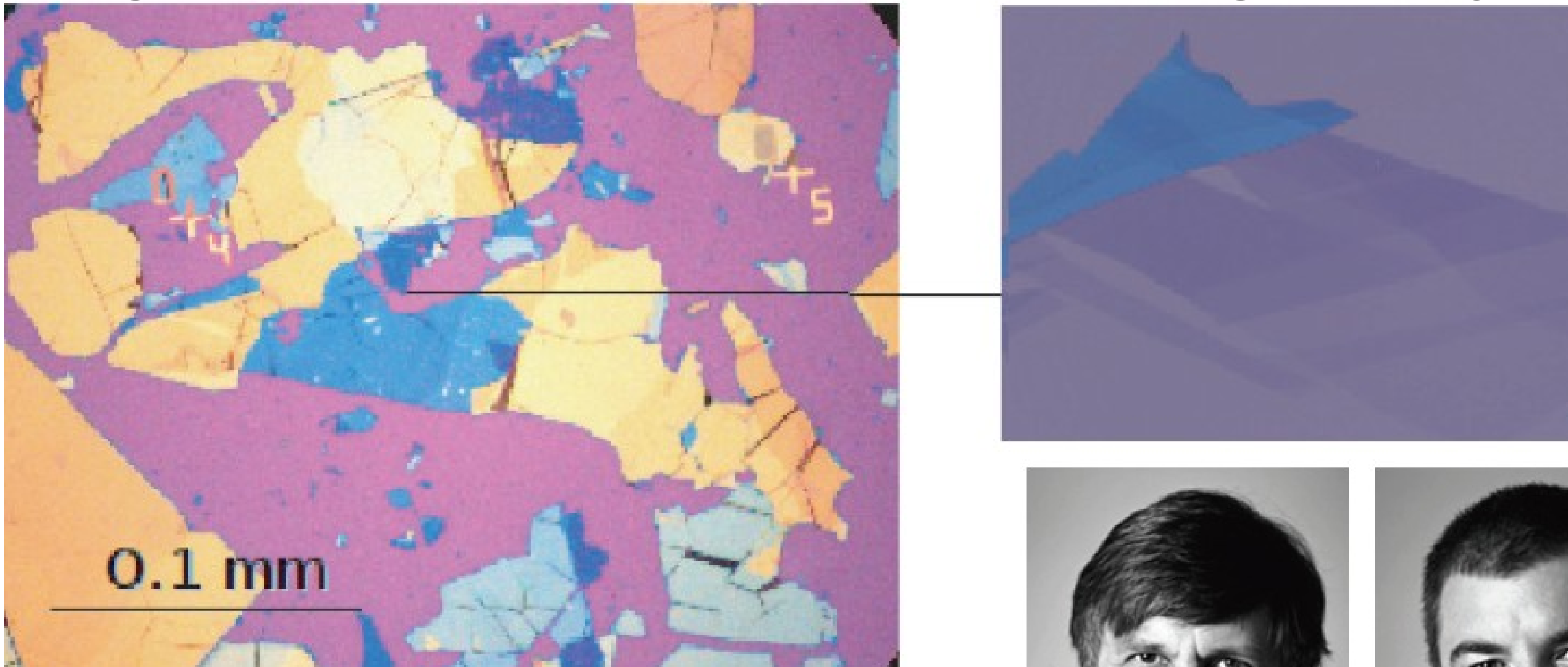


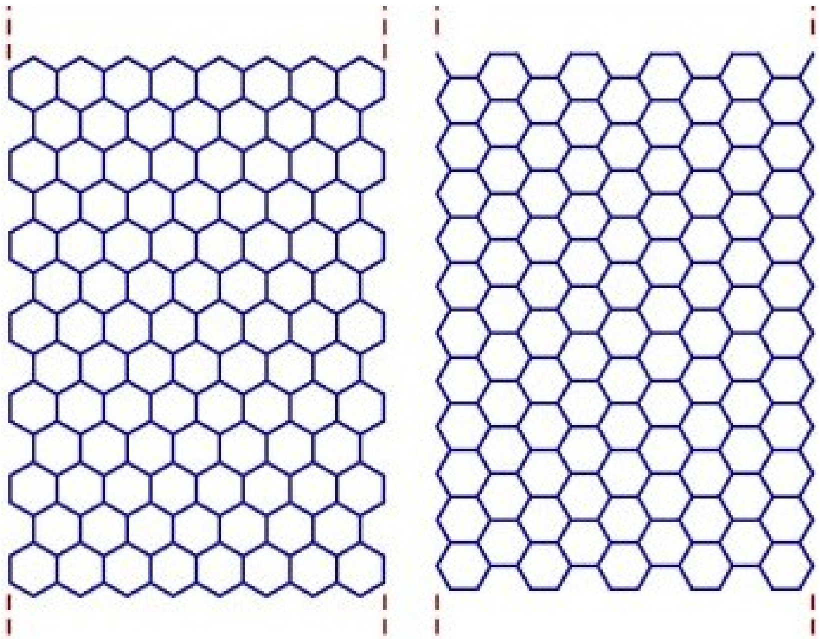

Photo: U. Montan
Andre Geim

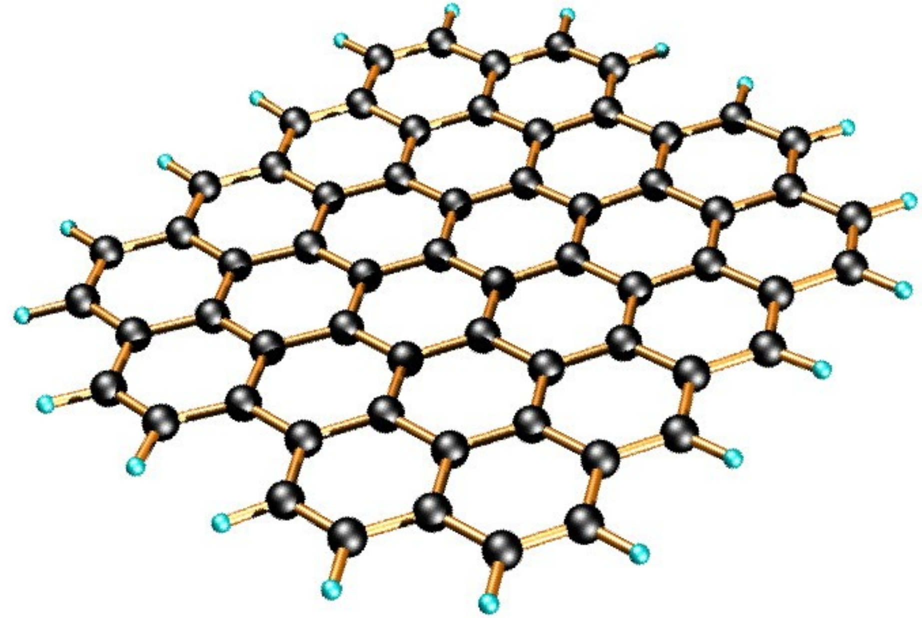

Photo: U. Montan
Konstantin Novoselov

- Nobel Prize in Physics 2010: Andre Geim and Konstantin Novoselov “for groundbreaking experiments regarding the two-dimensional material graphene”

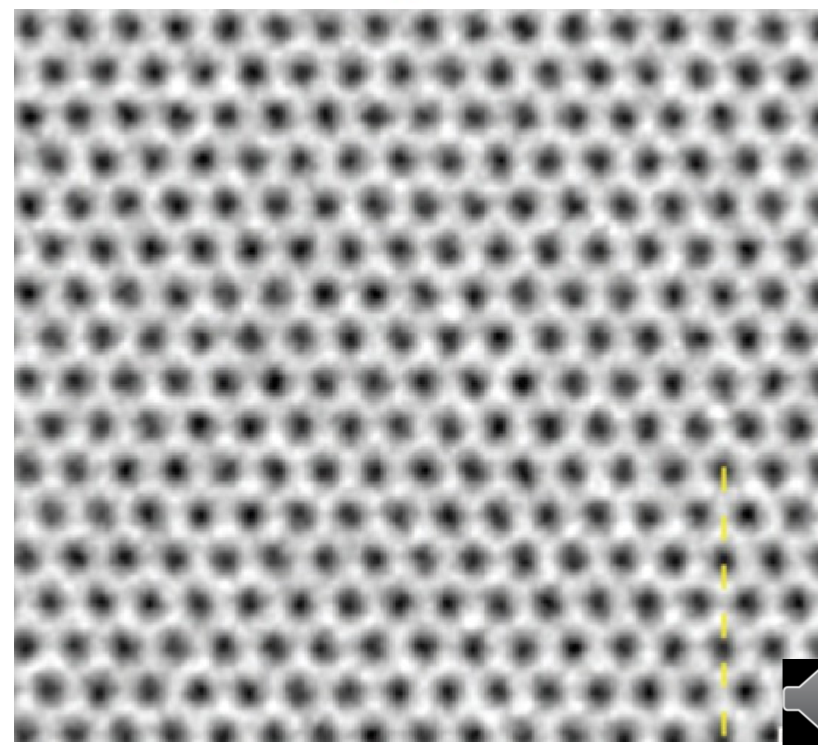
Graphene

- **sp2 hexagonal sheet**
- **orientation**
  arm-chair / zig-zag



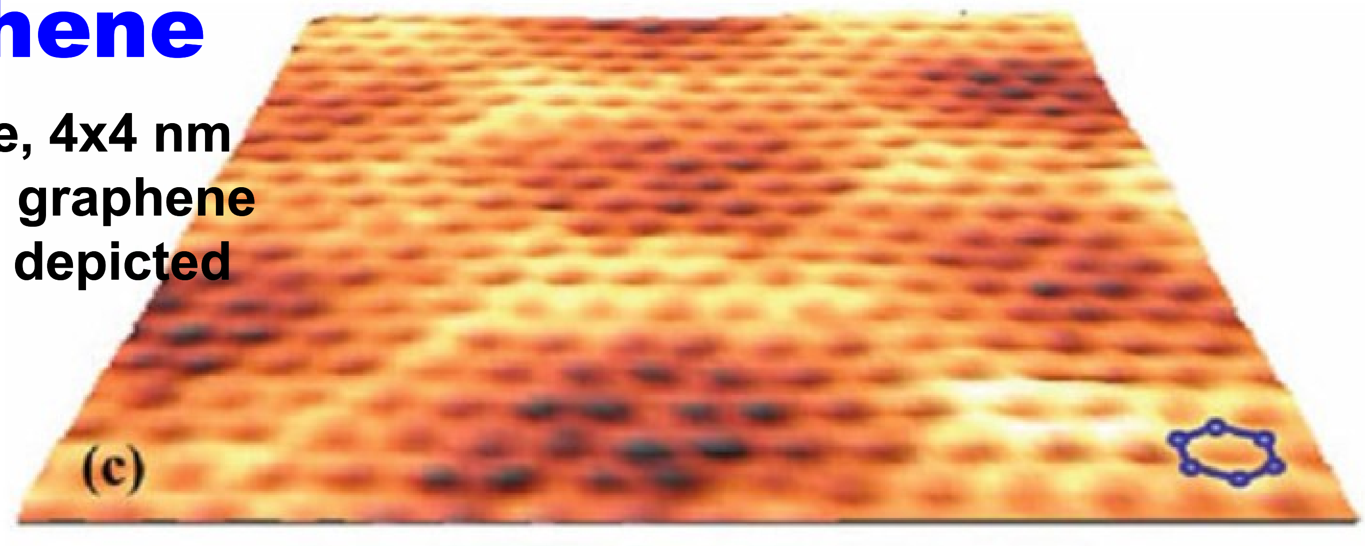


scale bar 0.2 nm

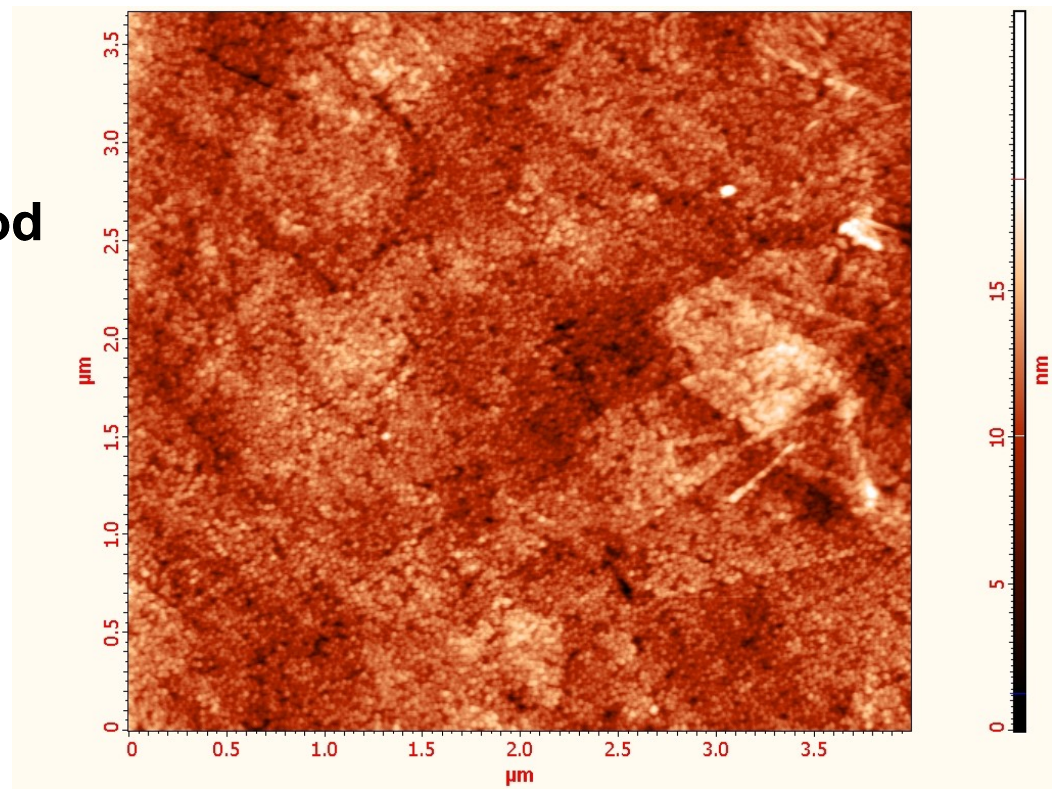


Graphene

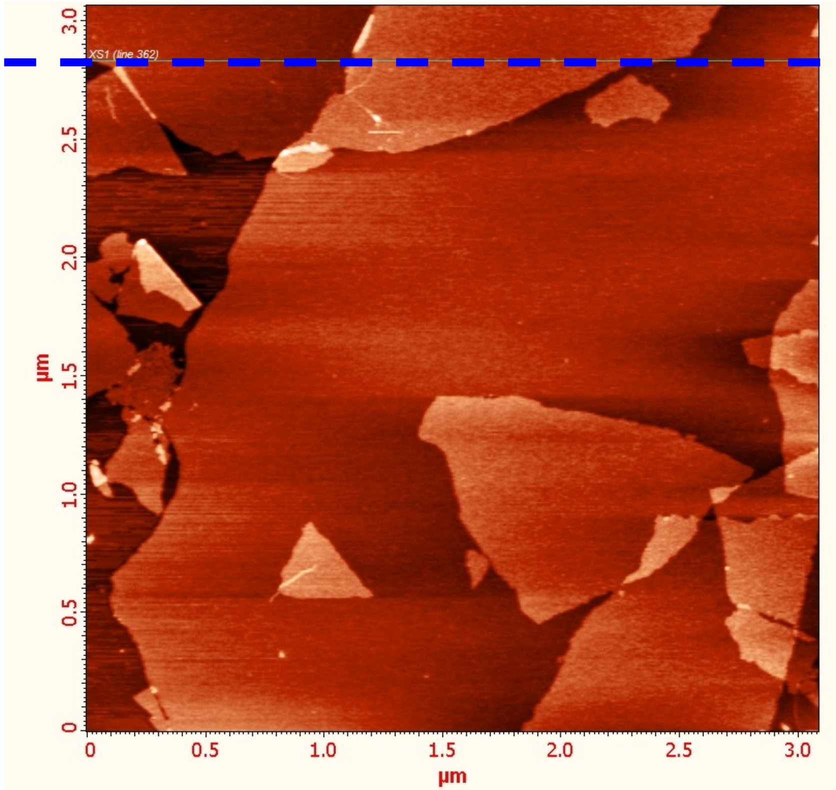
- **STM image, 4x4 nm hexagonal graphene unit cell is depicted**

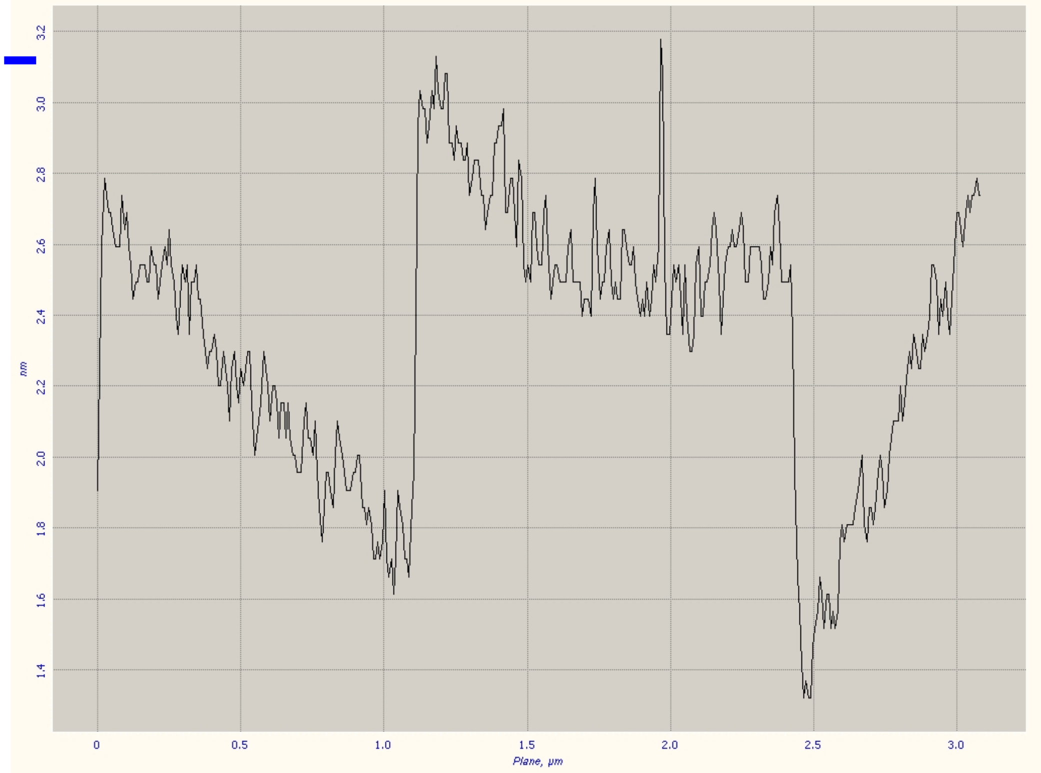


- **AFM image of graphene from the Hunter's method**



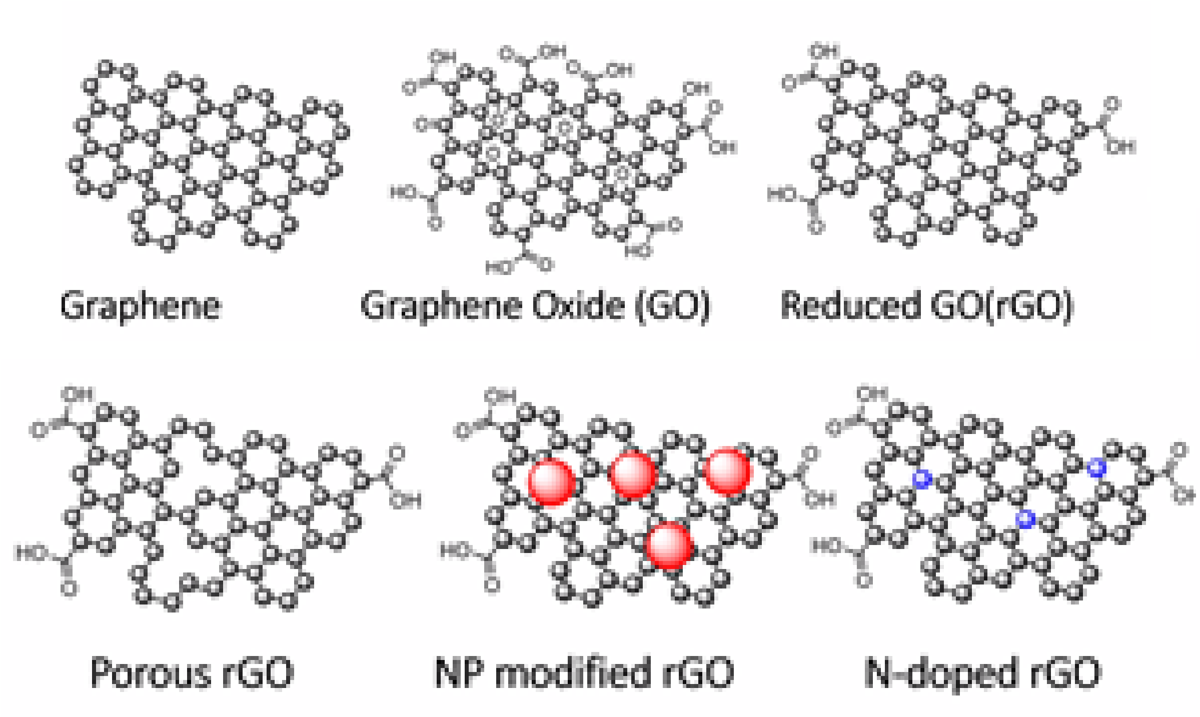
AFM of graphene



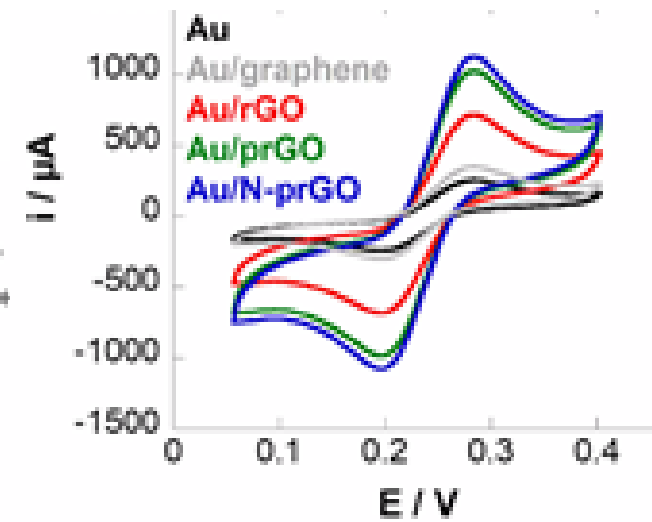


- **left, topography, right, height profile in the indicated line**
  - observed roughness depends on the supporting material, on mica it could be around 0.07 nm for a monolayer

Graphene variants

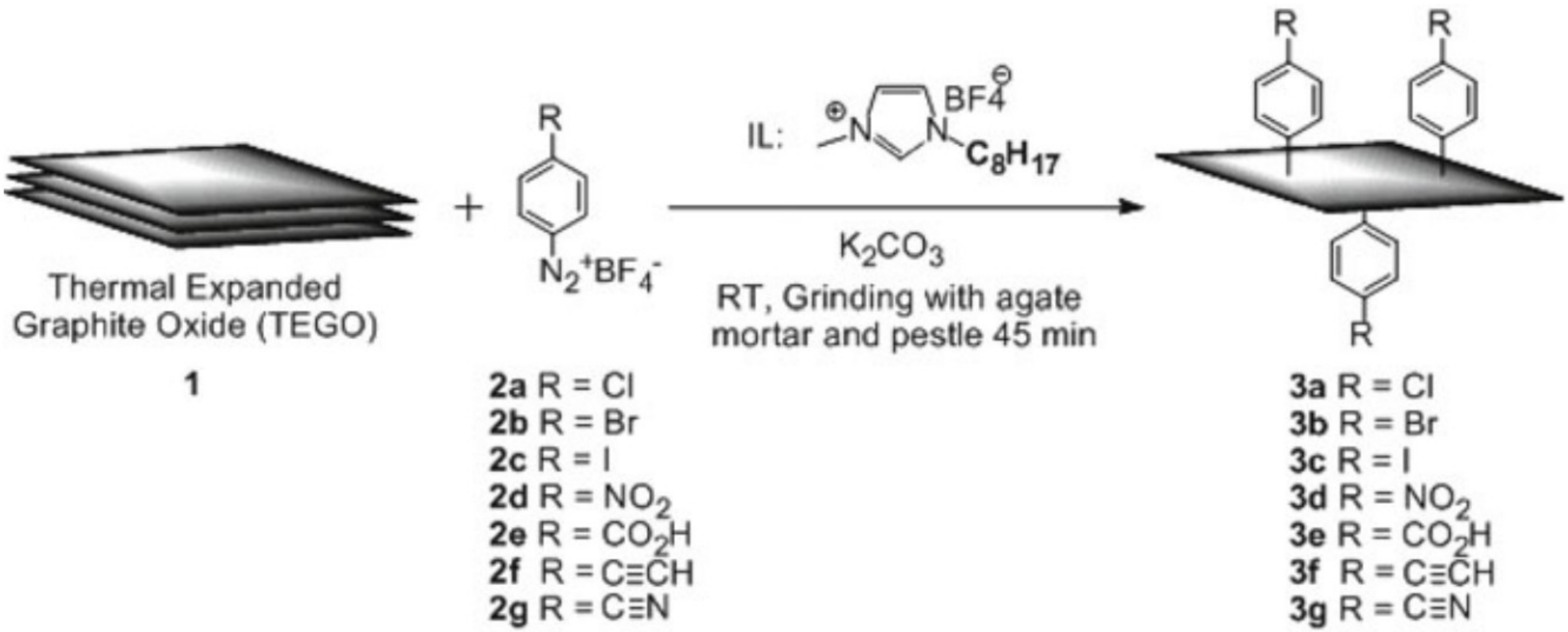


CVs of ferri/ferrocyanide



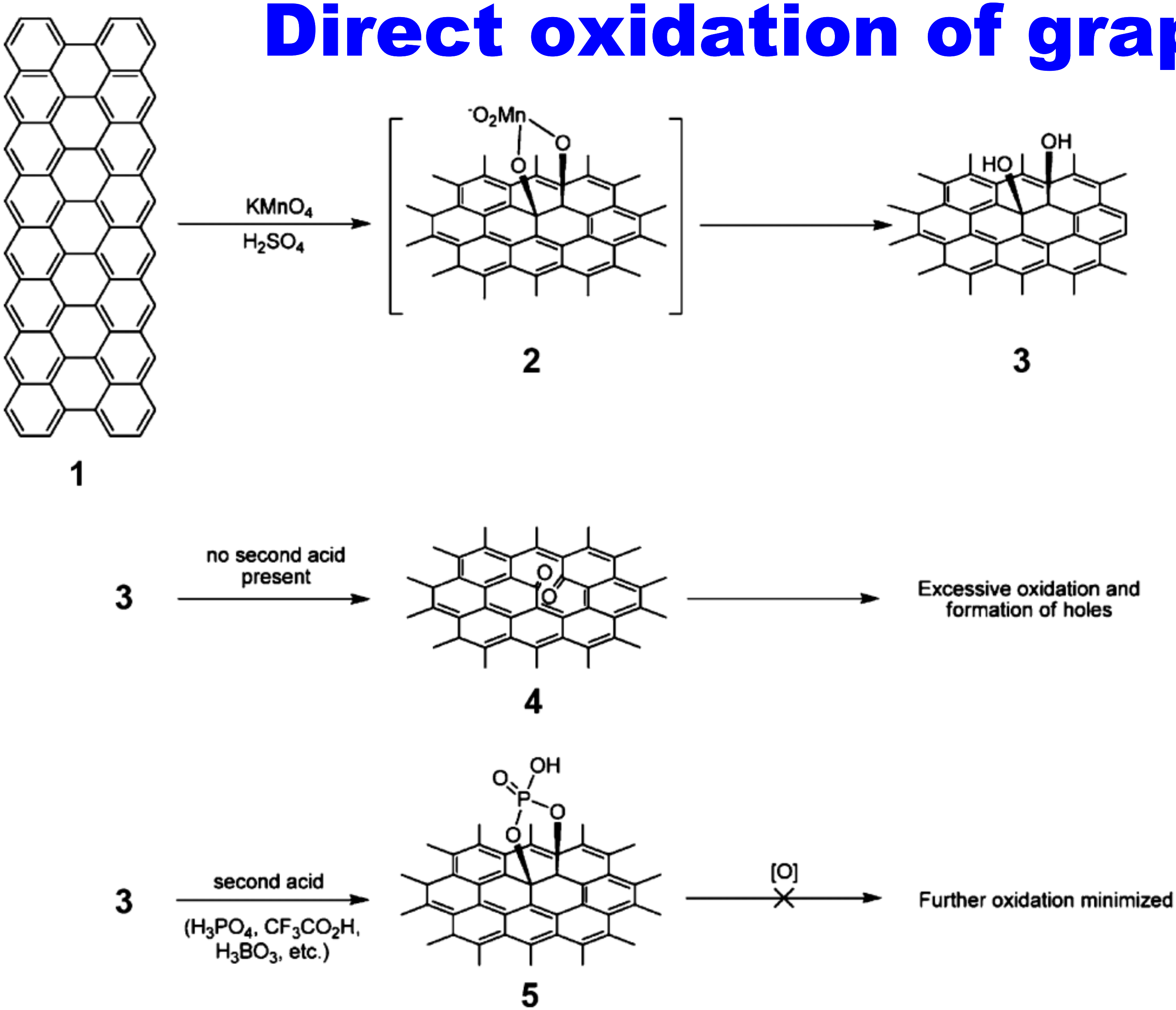
- **electrical / electrochemical conductivity**
- **flexible (not stretchable), transferable, biocompatible**

Chemically modified graphene



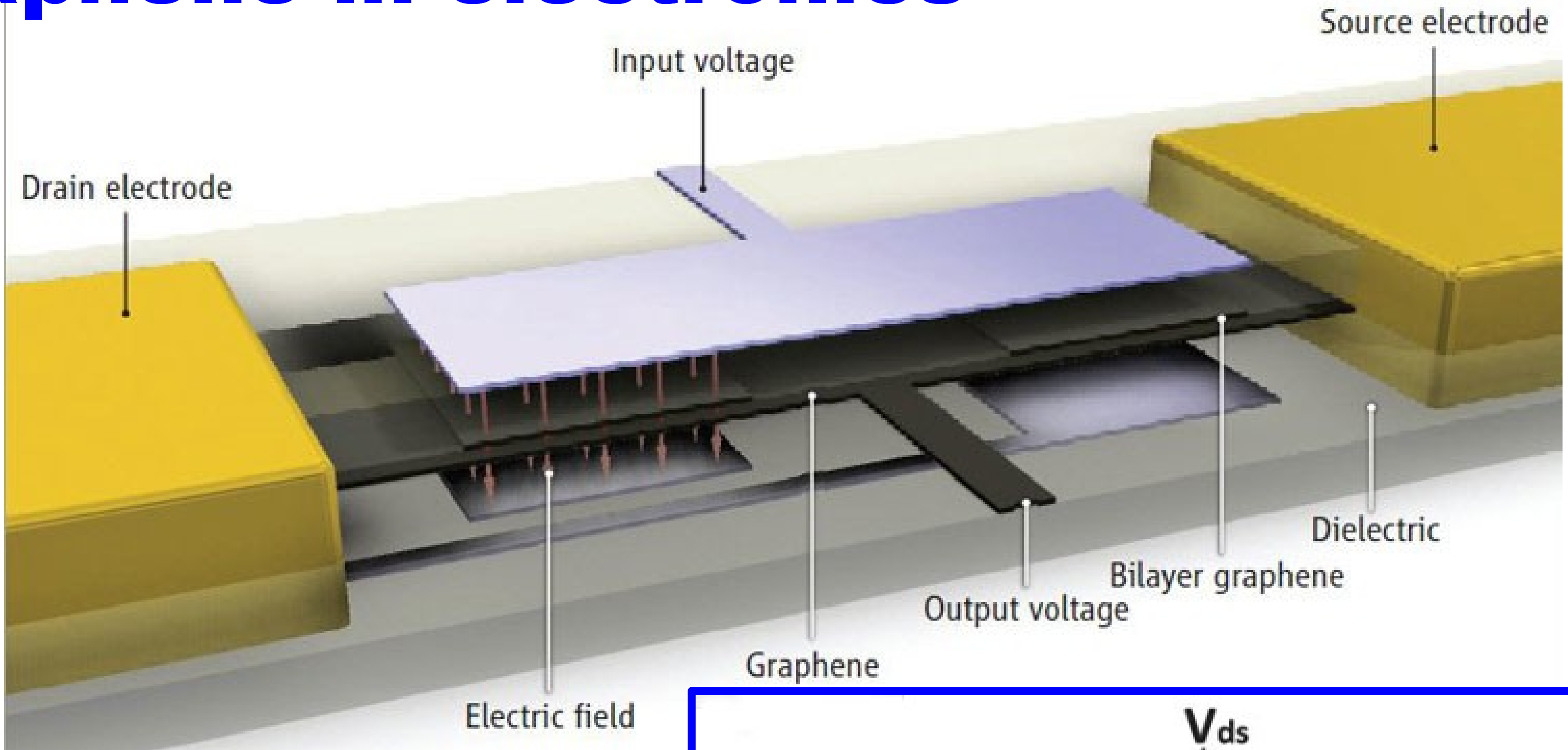
- **example of modification with the help of diazonium salts in the presence of ionic liquid**
- **for covalent binding of biomolecules (enzymes), the carboxy group is particularly useful**

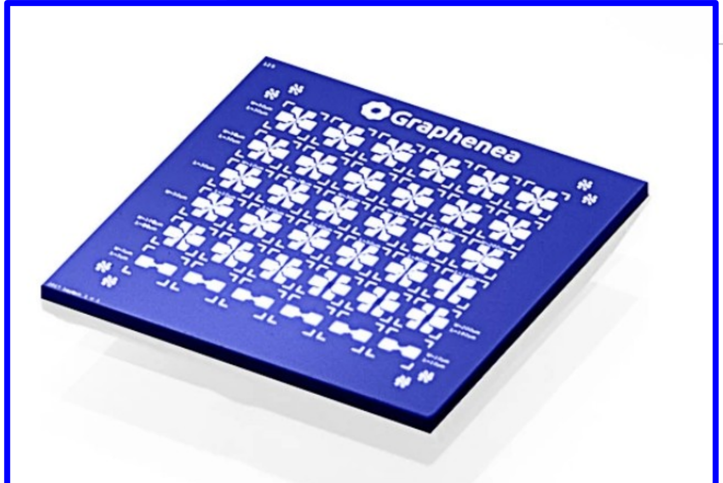
Direct oxidation of graphene

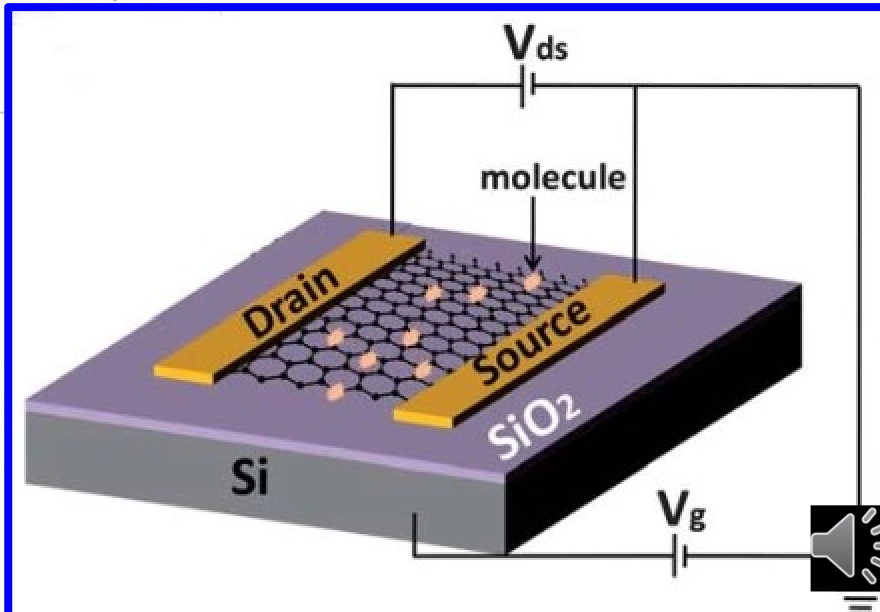


- **should be very careful …**

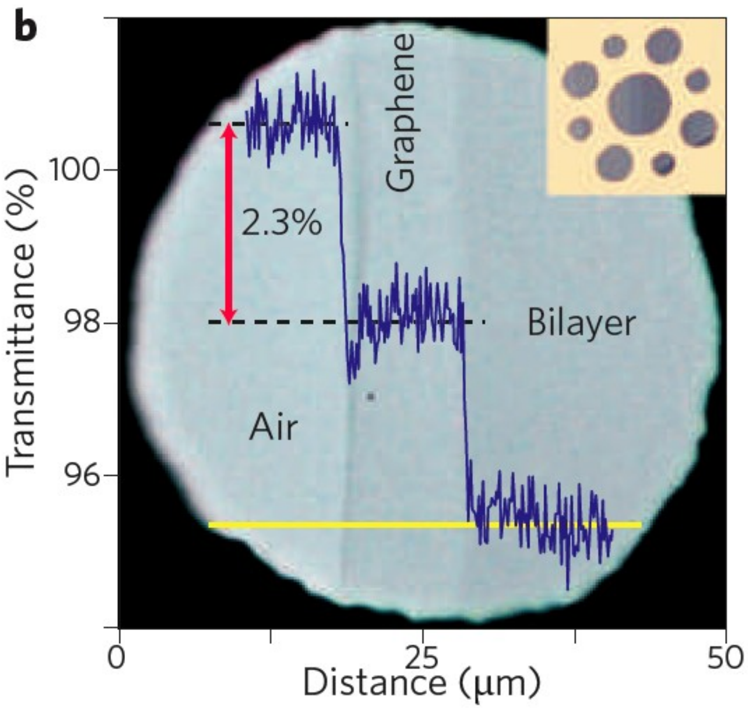
Graphene in electronics

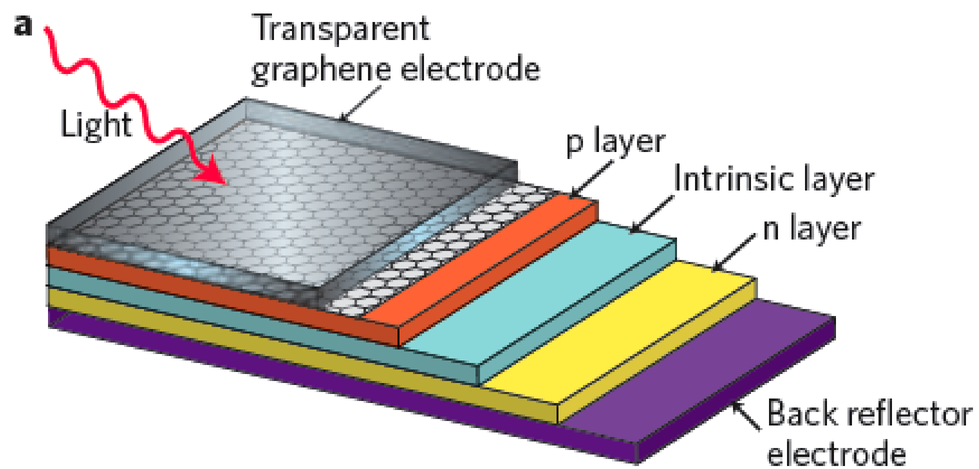




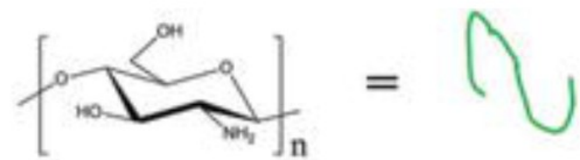


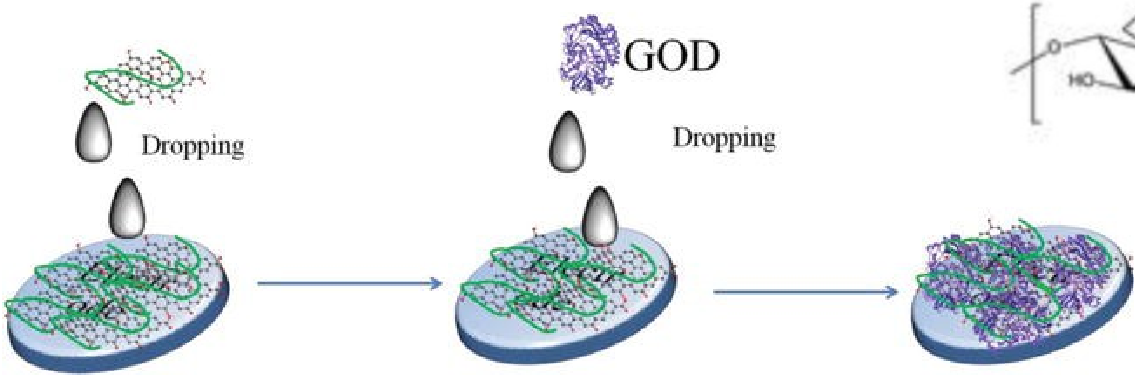
Graphene as a transparent conductor

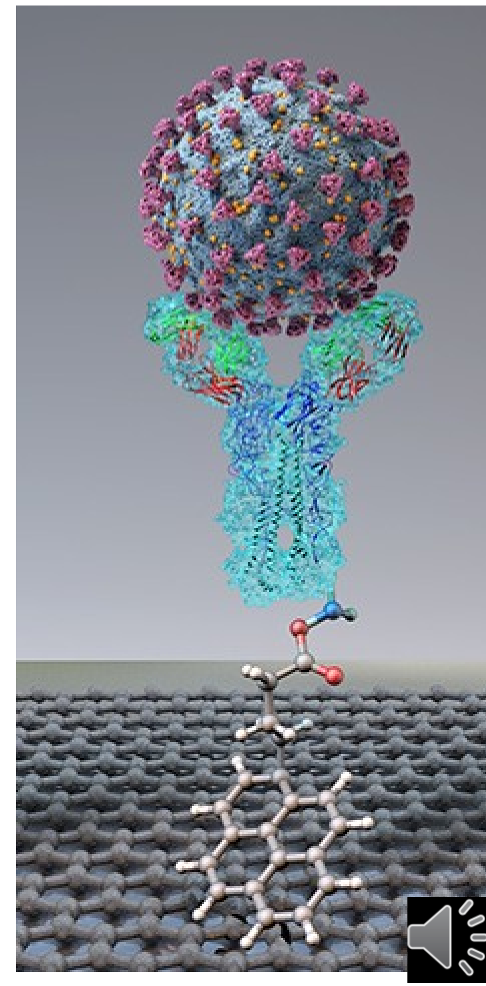




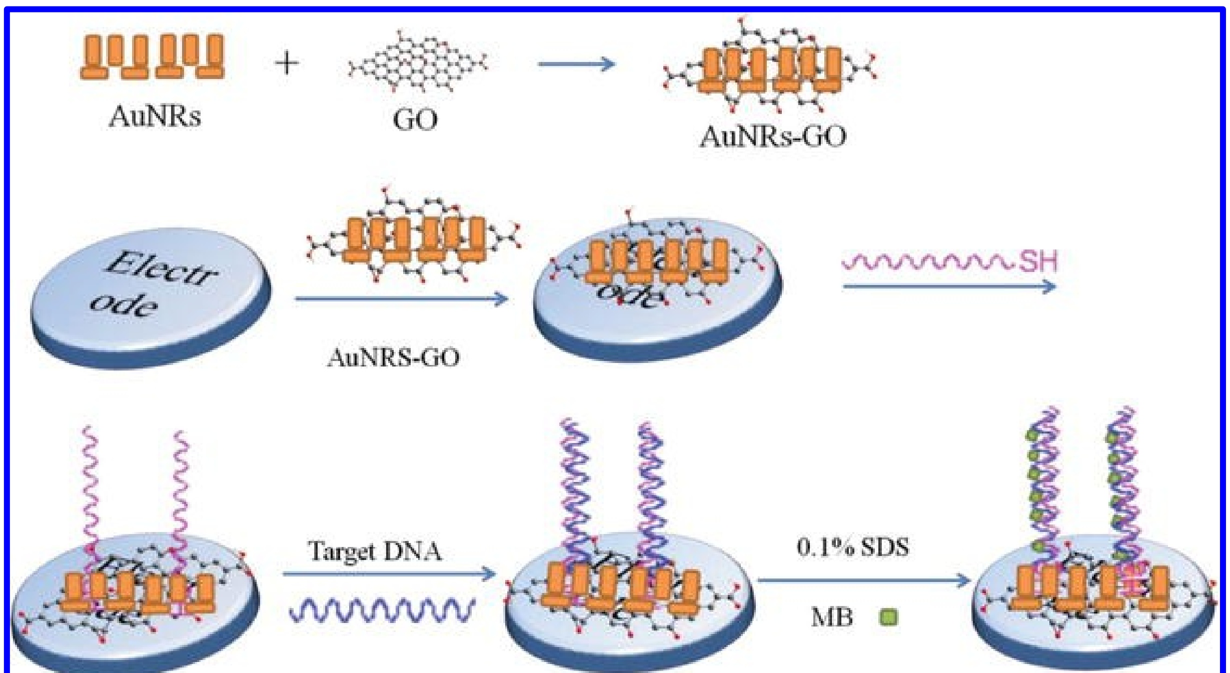
Graphene in biosensors





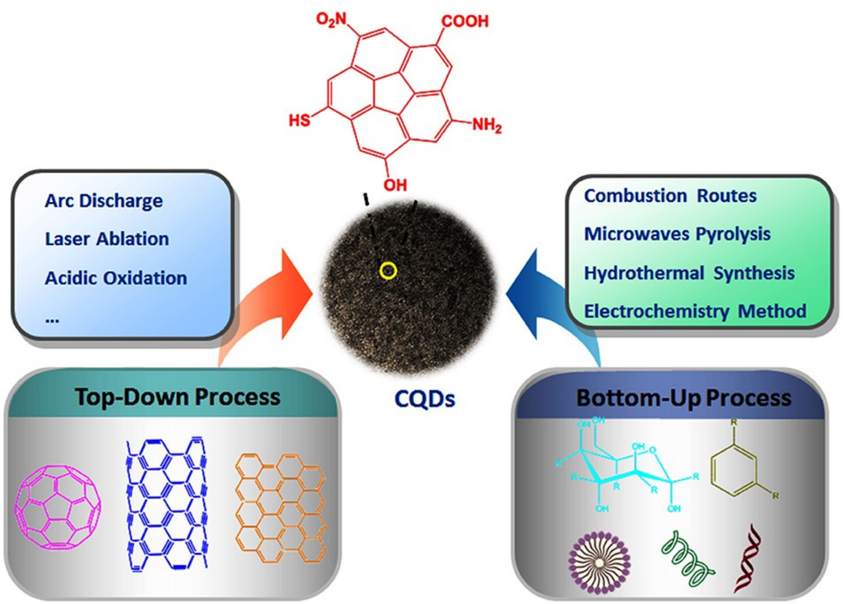


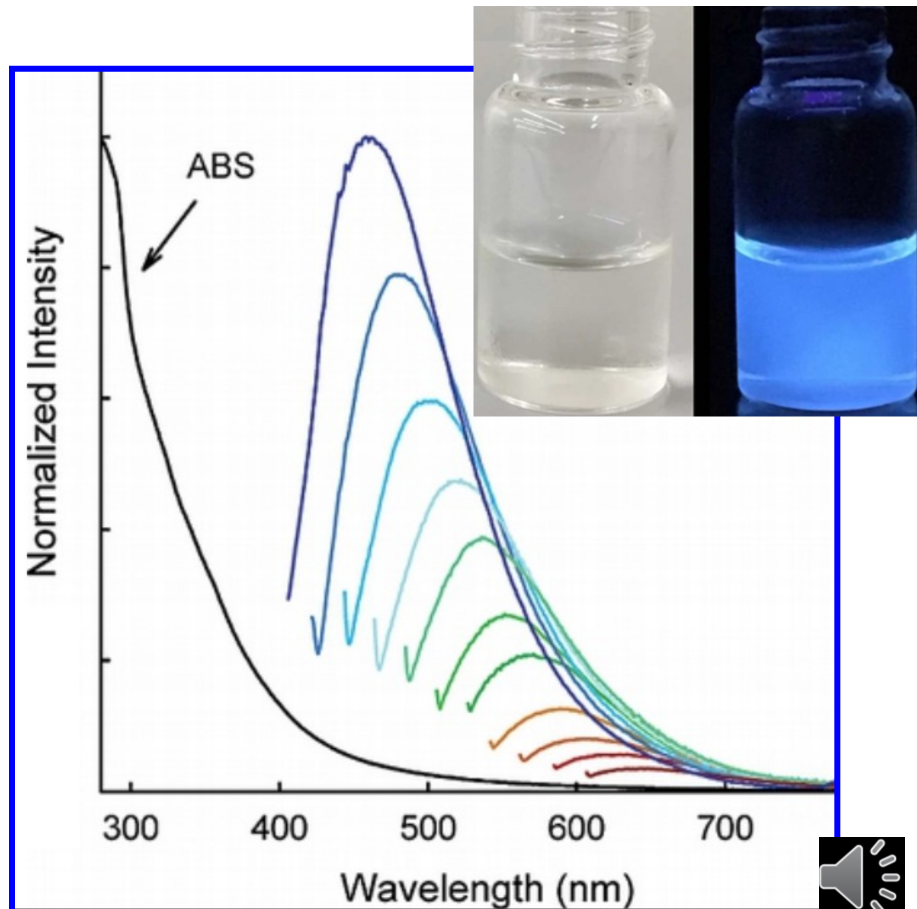
- **enzymes / nucleic acids / antibodies**

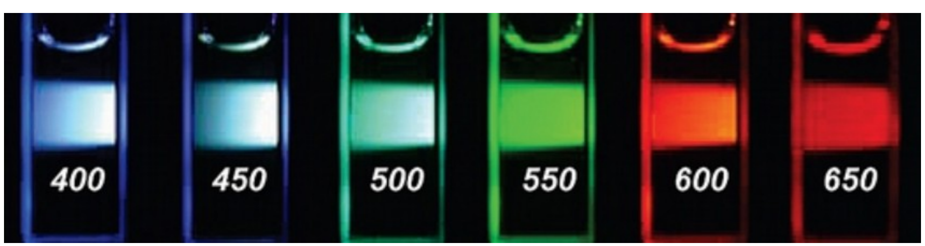


Carbon-based quantum dots

- C-dots – non-toxic fluorescent labels (also CDs or CQDs, < 10 nm)
- produced by thermal decomposition of organic materials including carbon black, paraffin wax
- spectral properties depend on the size and excitation wavelenght

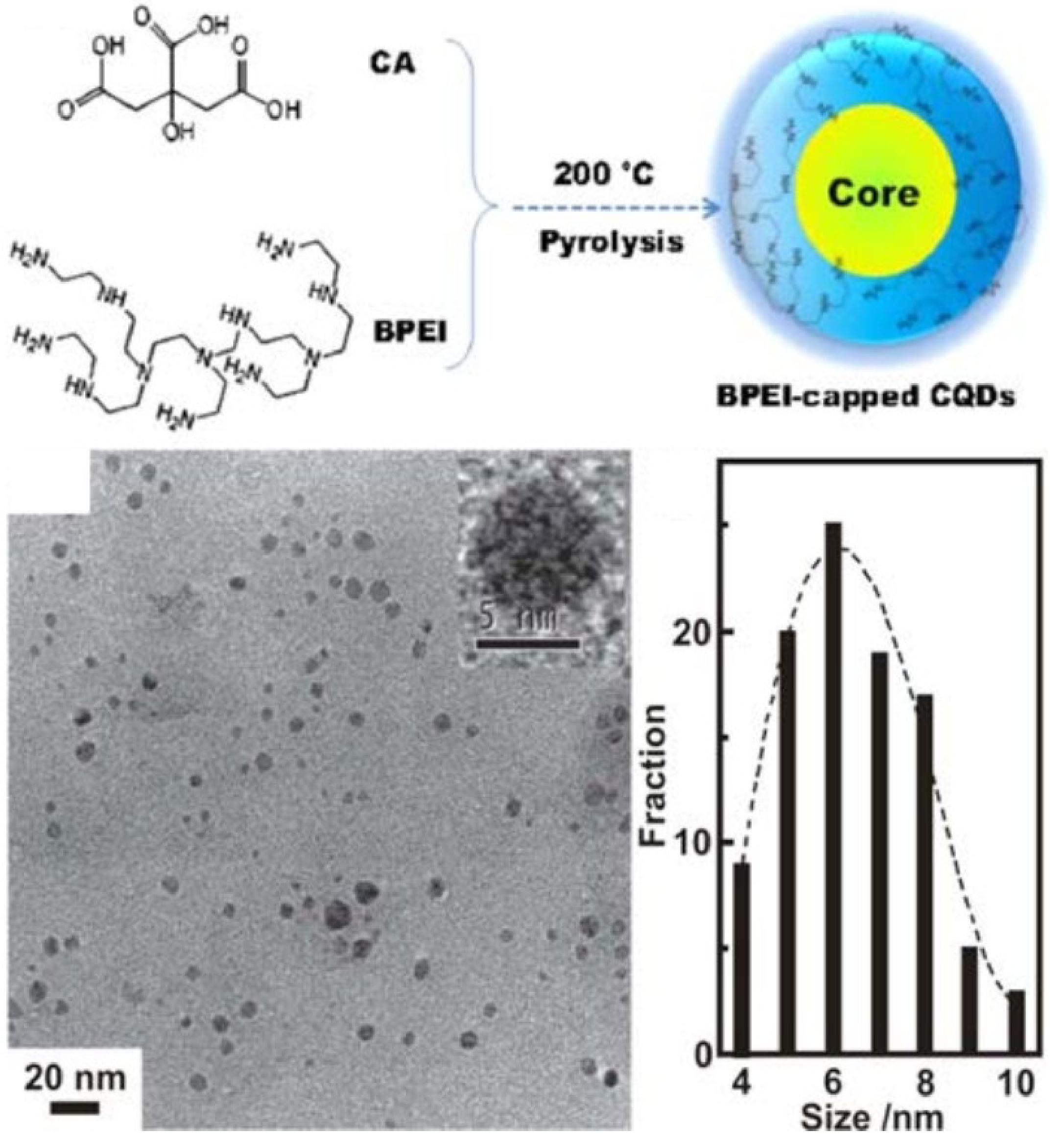






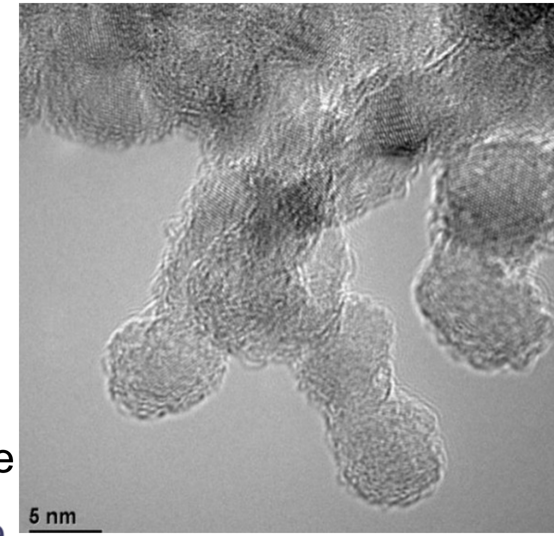
Preparation

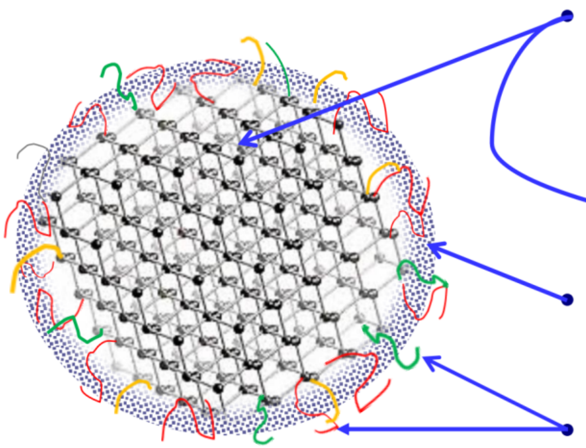
- citric acid is one the most widely used carbon sources in C-dot preparation due to its low carbonization temperature
- solutions of branched poly(ethylenimine) (BPEI) and citric acid in water are carbonized at low temperatures (<200 C)



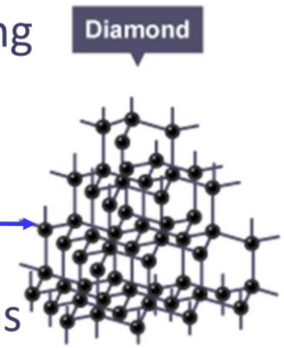
Nanodiamonds

- **carbon-based – non-toxic nanomaterial (NDs)**
- **made by impact methods (explosions)**
  - hydrothermal synthesis, ion / laser bombardment, microwave plasma chemical vapor deposition, ultrasound
  - decompose graphitic C_3N_4 under high pressure / temperature



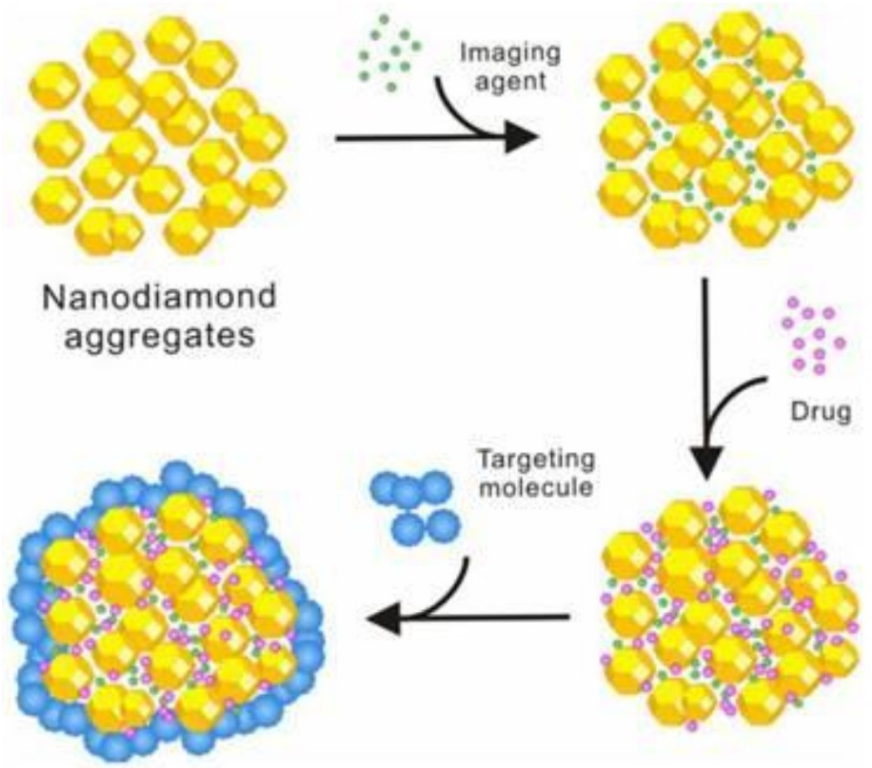


- Diamond core (sp3) with average size of ~4 nano-meters having unique diamond properties
- Hybrid surface structure (sp2) with unpaired electrons
- Active surface shell of various functional groups containing O, H and N



- **strong affinity towards proteins and antibodies – conjugates**

NDs in biomed



- **stability of ND nucleus / chemical activity of its functional cover**
  - interactions with bio-molecules and drugs
- **large specific surface area and high adsorption potential**
  - can trap 5x more than existing drug delivery
  - slow (months) release of drugs
  - gene therapy applications
- **mechanical hardness**
- **can be turned into a semiconductor**
- **photoluminescence – imaging applications; MRI contrast agent**
- **high sound propagation velocity**
- **biocompatibility and non-cytotoxicity – medical implants / devices**