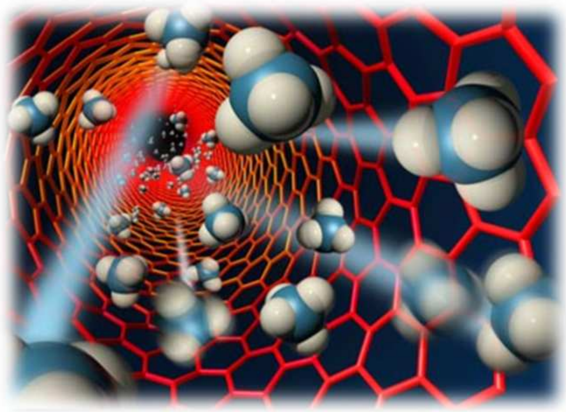
2a Nanomaterials

- nanomaterials and nanostructures – overview
- carbon – nanotubes, graphene
-
- metal-based nanostructures - nanowires, gold nanoparticles (nanorods, nanocages, nanoshells)
- magnetic nanoparticles
-
- polymer nanostructures (dendrimers)
-
- protein-based nanostructures - nanomotors from microbes and mammalian cells (myosin).
- nanomachines based on nucleic acids

Definition

- **a** **nanomaterial** **is a material made up of** **nanostructures** **between 1 and 100** ***nanometres*** **in size**
- **nanostructures can include nanoparticles, nanotubes or nanocrystals, etc.**
- **properties of nanomaterials are different to those of ordinary materials because of the small size of the structures that make them up**
- **principal parameters of nanoparticles are**
  - shape
  - size
  - morphological sub-structure of the substance

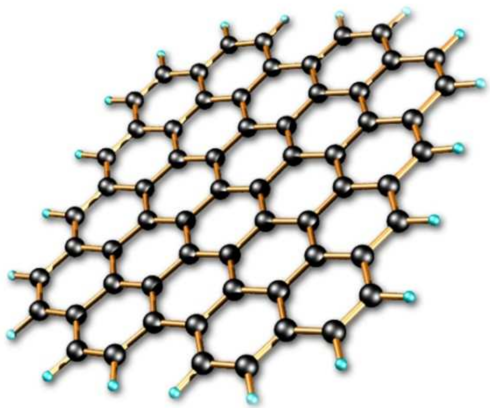
- Nanomaterial
  - Nano-object
  - Nanostructured material



- Nano-object (one or more external dimensions in the nanoscale)
  - Nanoparticle (3 external dimensions in the nanoscale)
  - Nanofiber (2 external dimensions in the nanoscale)
    - Nanowire (electrically conducting nanofiber)
    - Nanotube (hollow nanofiber)
    - Nanorod (rigid nanofiber)
  - Nanoplate (1 external dimension in the nanoscale)

Overview

- **nanomaterials are manufactured for a wide variety of applications**
- **a typical example might be carbon nanotube-based nanomaterials, with applications anticipated in**
  - nanoelectronics (components)
  - medicine (transport of drugs in the body)
  - information technology (computer memory) ....
- **composite nanomaterial (combinations of materials that are normally immiscible) are also being produced**
- **the idea is to introduce nanostructures - nanoparticles, for instance into a matrix (metal, organic material, etc.) to obtain specific properties of hardness, mechanical strength, conductivity or electrical insulation**



Biomed

Biopharmaceutics

- Drug Delivery
  - Drug Encapsulation
  - Functional Drug Carriers
- Drug Discovery

Implantable Materials

- Tissue Repair and Replacement
  - Implant Coatings
  - Tissue Regeneration Scaffolds
- Structural Implant Materials
  - Bone Repair
  - Bioresorbable Materials
  - Smart Materials

Implantable Devices

- Assessment and Treatment Devices
  - Implantable Sensors
  - Implantible Medical Devices
- Sensory Aids
  - Retina Implants
  - Cochlear Implants
  - Surgical Aids
- Operating Tools
  - Smart Instruments
  - Surgical Robots

Diagnostic Tools

- Genetic Testing
  - Ultra-sensitive Labeling and Detection Technologies
  - High Throughput Arrays and Multiple Analyses
- Imaging
  - Nanoparticle Labels

Properties vary with size of the material

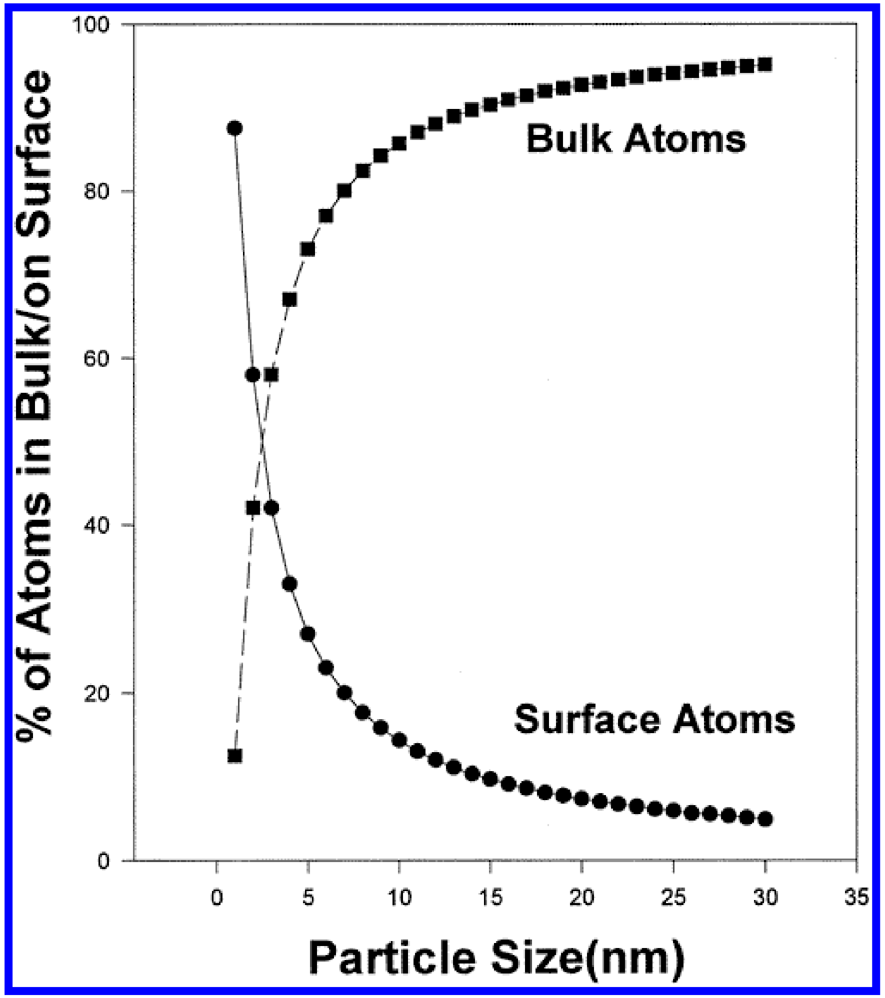
- **(bulk) gold is a shiny yellow metal**
- **nanoscopic gold, *i.e.* clusters of gold atoms measuring 1 nm across, appears red**
- **bulk gold does not exhibit catalytic properties**
- **Au nanocrystal is an excellent low temperature catalyst**
- **therefore, if we can control the processes that make a nanoscopic material, then we can control the material's properties**

Physical properties of nanomaterials

- significantly lower melting point or phase transition temperature
  - due to a huge fraction of surface atoms in the total amount of atoms
- mechanical properties may reach the theoretical strength
  - 1 or 2 orders of magnitude higher than that of single crystals in the bulk form
  - enhancement in mechanical strength - reduced probability of defects
- optical properties can be significantly different from bulk crystals
  - e.g. the optical absorption peak of a semiconductor nanoparticle shifts to short wavelength, due to an increased band gap
  - color of metallic nanoparticles may change with their sizes due to surface plasmon resonance
- electrical conductivity decreases with a reduced dimension
  - due to increased surface scattering;
  - however, electrical conductivity of nanomaterials could also be enhanced appreciably due to the better ordering in microstructure, e.g. fibrils
- magnetic properties are distinctively different from that of bulk materials
  - ferromagnetism of bulk materials disappears and transfers to superparamagnetism in the nanometer scale due to the huge surface energy
- self-purification is an intrinsic thermodynamic property of nanostructures and nanomaterials
  - any heat treatment increases the diffusion of impurities, intrinsic structural defects and dislocations, pushing them to the nearby surface
  - increased perfection would have appreciable impact on the chemical and physical properties – enhanced chemical stability

Special properties of nanomaterials

- high surface / bulk ratio
  - catalysis
  - nanoparticle reagents
  - heat dissipation
  - laminar flow
- finite size effects
  - quantum confinement
  - inter-particle tunneling
  - proximity effects
  - high probability of defect-free crystals

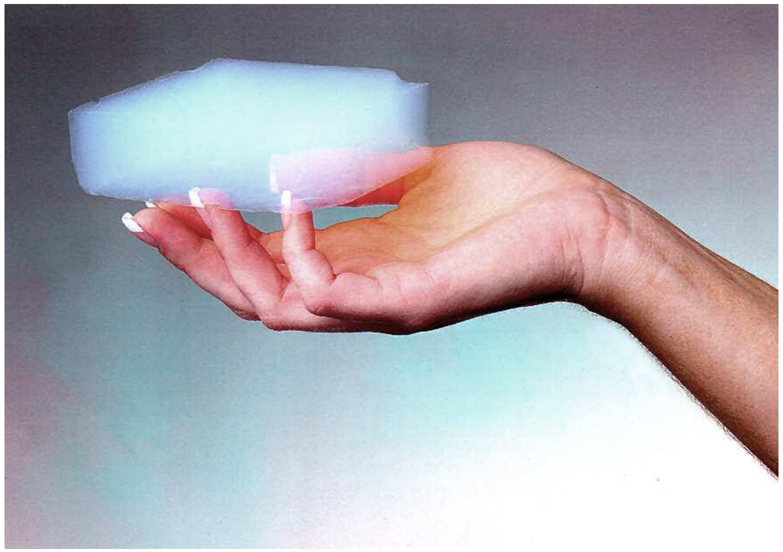


Nanostructures

- aerogels
- biomolecules
- nanocarbon
- composites
- dendrimers
- glasses / ceramics
- hydrogels
- metals and alloys
- nanomagnets
- nanoparticles / catalysts
- nanostrings
- nanowires
- quantum dots
- self assembled monolayers (SAMs)
- silicon structures and MEMS devices
- thin films

Aerogels

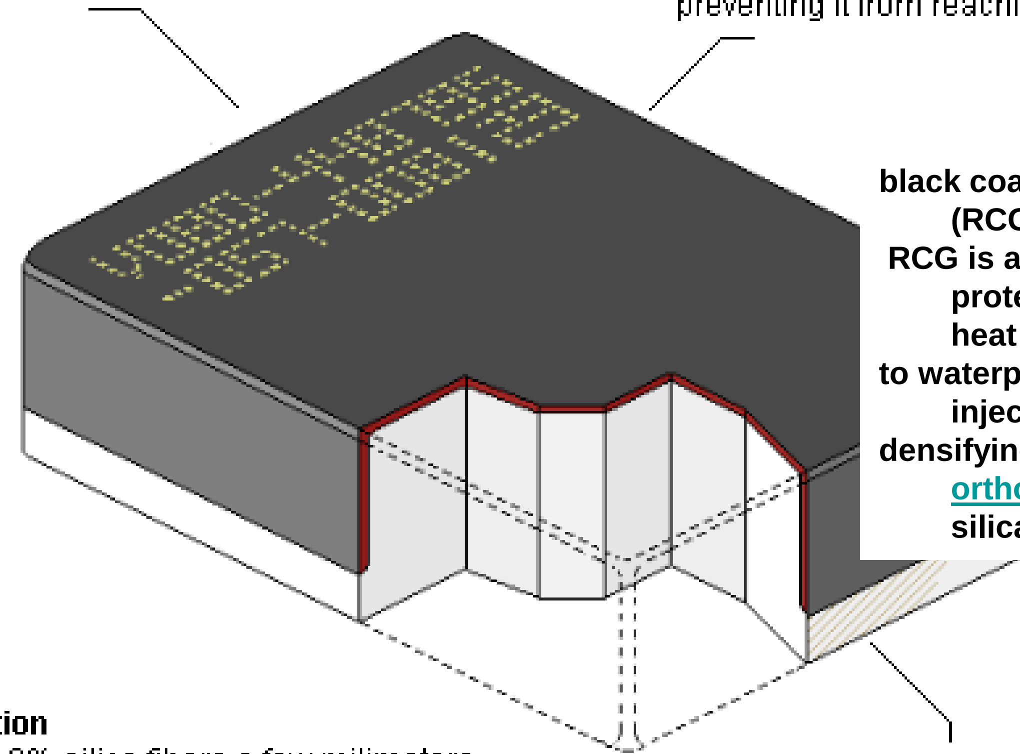
- manufactured material with the lowest bulk density of any known porous solid
- derived from a gel in which the liquid component of the gel has been replaced with a gas
- produced by extracting the liquid component of a gel through supercritical drying
- this allows the liquid to be slowly drawn off without causing the solid matrix in the gel to collapse from capillary action, as would happen with conventional evaporation



Space Shuttle tile - alumina-silicate aerogel

Coating
The outer portion of a tile is covered with a black-glazed coating of borosilicate.
These tiles do most of the coating job by shedding about 95% of the heat encountered.
The remaining 5% is absorbed by the tile's interior, preventing it from reaching the orbiter's aluminum skir

Identification number
ach tile has an identification number which tells atch and location. This number can be fed into a omputer to produce an identical tile.



black coating on the tiles is Reaction Cured Glass (RCG, tetrasilicide and borosilicate)
RCG is applied to all but one side of the tile to protect the porous silica and to increase the heat sink properties
to waterproof the tile, dimethylethoxysilane is injected into the tiles by syringe.
densifying the tile with tetraethyl orthosilicate (TEOS) also helps to protect the silica and waterproof

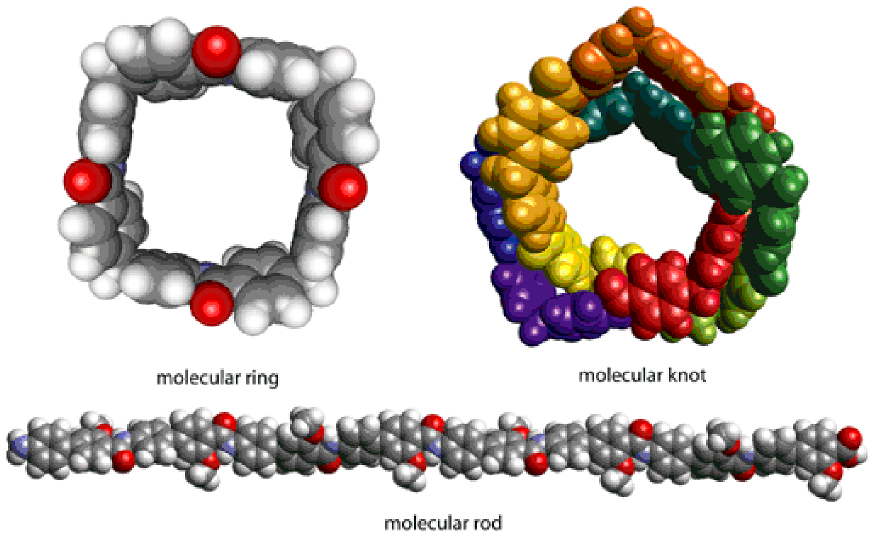
Composition
90% air, 10% silica fibers a few milimeters thick. The tiles feels similar to plastic foam.
The silica fibers are derived from high-quality sand.

Glue
A silicon-rubber glue similar to common bathtub caulking, bonds a tile to a felt pad, that is in turn bonded to the orbiter's skin. The felt absorbs the stresses of airframe bending that could damage the tiles.

Biomolecular nanotechnology

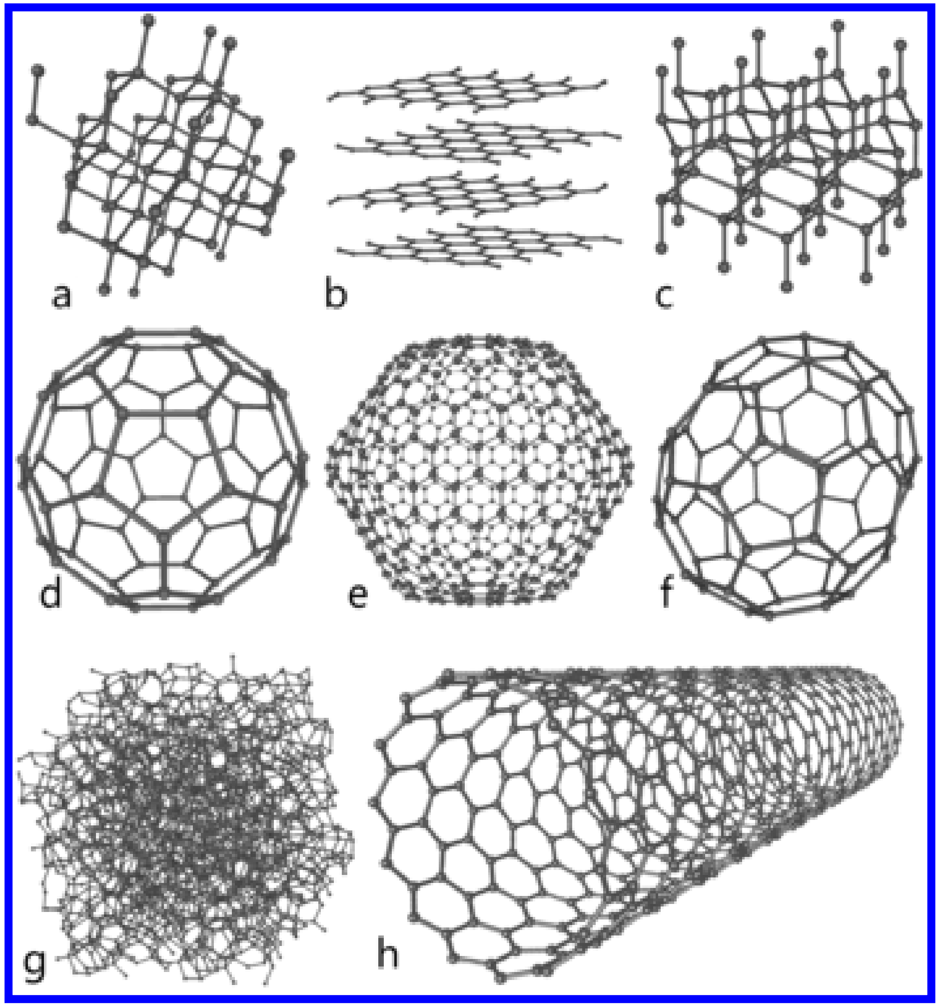
- molecular structures and functional complexes
- DNA templating
- synthetic biology – synthetic biomacromolecules
- liposomes and novel cellular structures

- … not exactly our field (bionanotechnology)



Nanocarbon

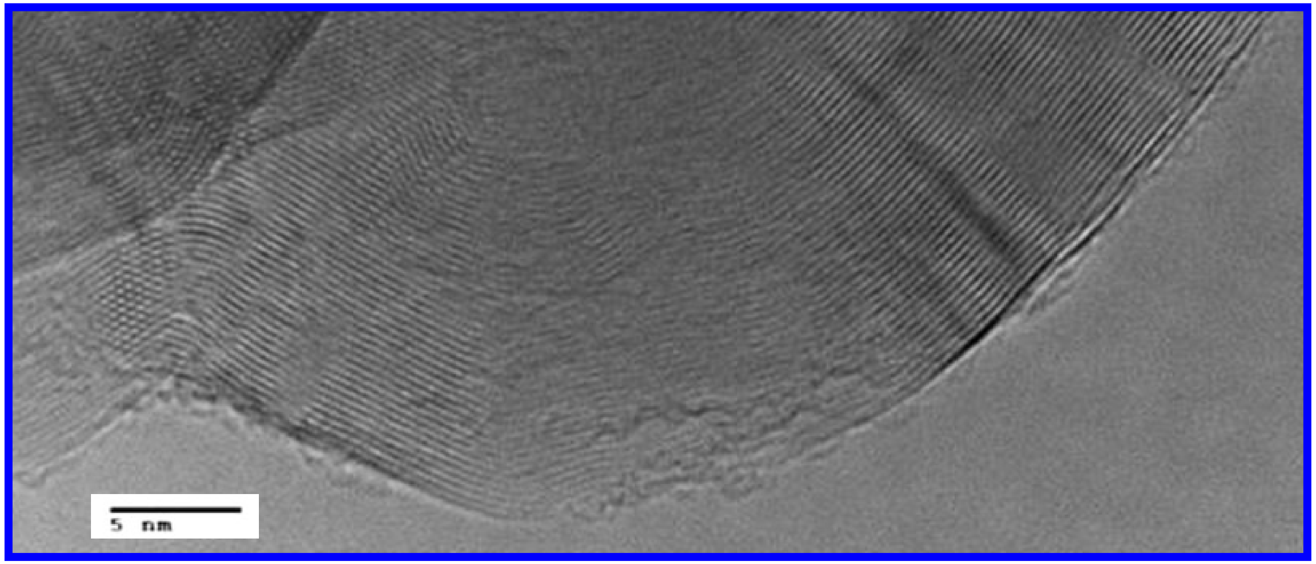
- **carbon nanotubes - single (SWNT) and multiwalled (MWNT)**
- **graphene**
- **carbon nanospheres**
- **nanodiamonds**



Composite materials

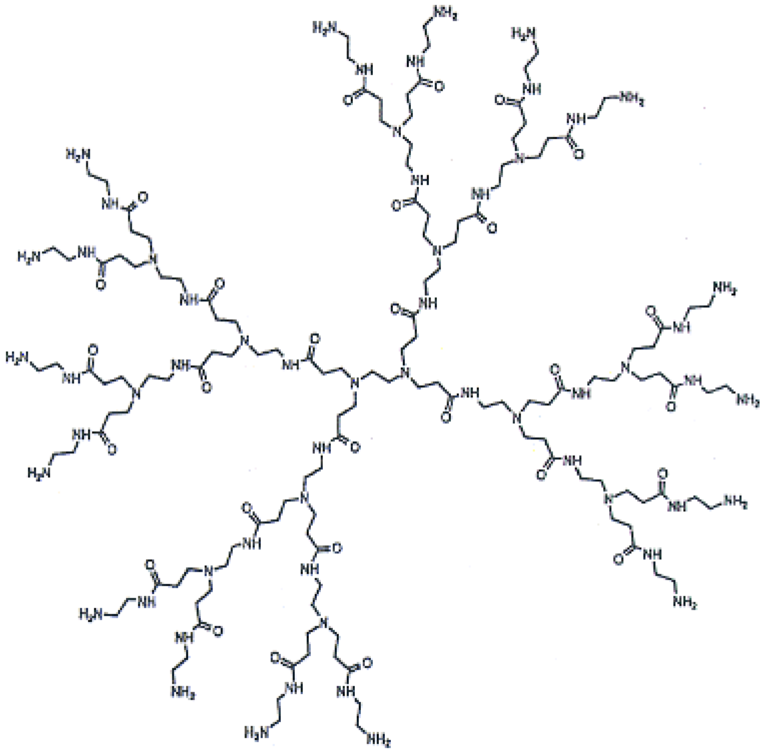
- **carbon nanofibers (CNFs) - vapor grown carbon fibers (VGCFs) or nanofibers (VGCNFs) are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates**

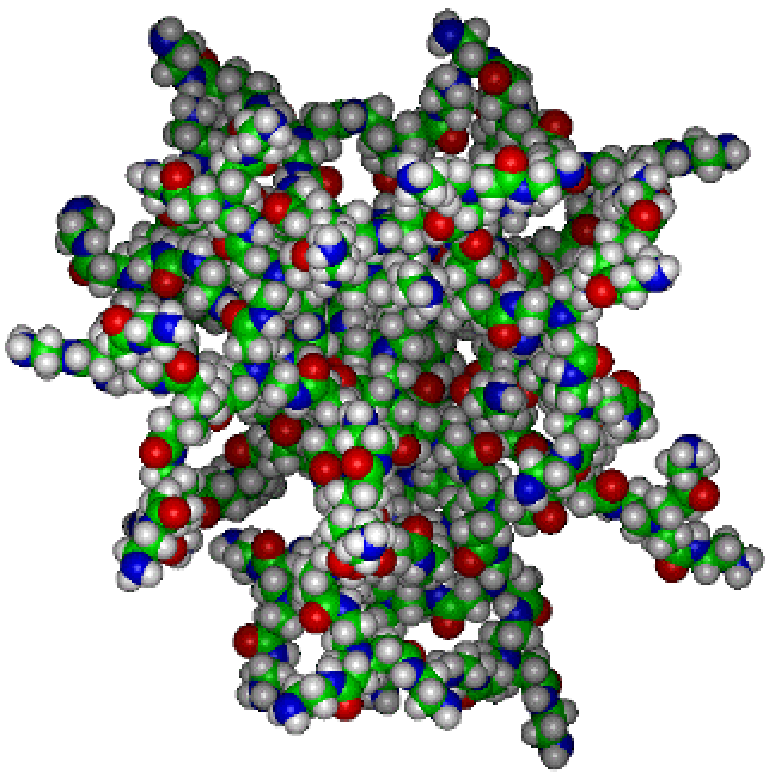
- **nano-onion structure observed in nanospheres, and annealed carbon black (soot)**
- **it is thought that the extended nanostructure forms by wrapping of graphene over a fullerene seed-like nanostructure**



Dendrimers

- **repetitively branched molecules**
  - also known as arborols and cascade molecules
- **typically symmetric around the core**
  - often adopts a spherical three-dimensional morphology





Glasses and ceramics

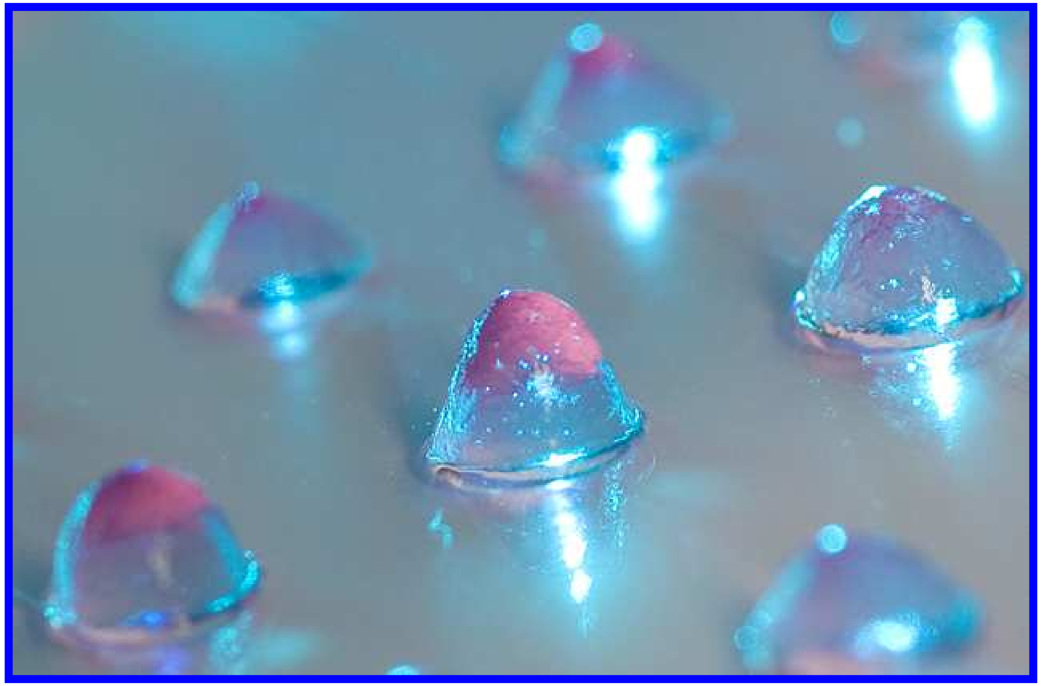
- **glasses are similar to polymers - long chains and almost a liquid**
- **ceramics are metal - nonmetal compounds with typically ionic bonding**
  - high melting points, can be brittle, and typically are non-conductive
  - electroceramics can be conductive
  - have high temperature properties

Nanoglass coatings

- hydrophobic coatings on glass help water to bead up - increased visibility, easier cleaning
- added mechanical / abrasion resistance, by promoting surfaces that are also scratch resistant
- made from fluoropolymers, or methylated siloxane materials, both deposited as plasma polymerized coatings

Hydrogels

- hydrogel (also aquagel) is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium
- highly absorbent (can contain up to 99.9% water) natural or synthetic polymers
- possess a degree of flexibility very similar to natural tissue, due to their significant water content
- highly cross-linked polymers, water insoluble but soak up water, can be ‘mechanically interactive’

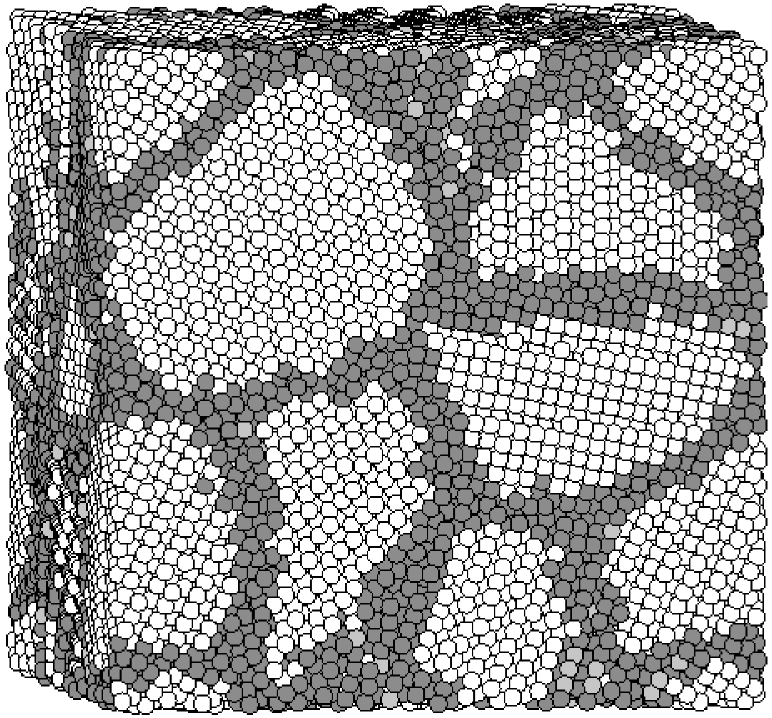


- novel biomaterial with surprising antibacterial properties that can be injected as a low-viscosity gel into a wound where it rigidifies nearly on contact
- delivering a targeted payload of cells and antibiotics to repair the damaged tissue
- (Univ. Delaware)

Metals and alloys

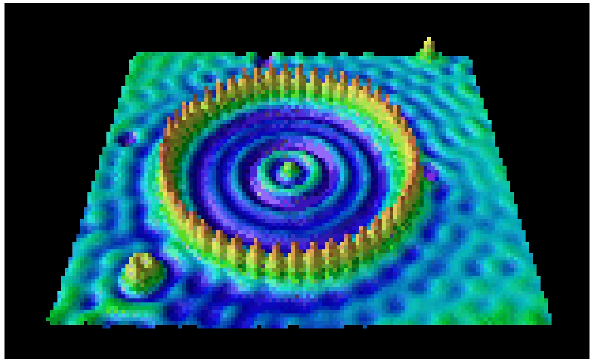
- **grain boundary engineering - high performance alloys**
- **careful control chemistry / processing**
- **increase strength / stiffness, fatigue**

- **grain boundary** is the interface between two grains, or crystallites, in a polycrystalline material; defects in the crystal structure tend to decrease the electrical and thermal conductivity of the material
- high interfacial energy and relatively weak bonding in most grain boundaries often makes them preferred sites for the onset of corrosion and for the precipitation of new phases
- important to many of the mechanisms of creep
- disrupt the motion of dislocations through a material, so reducing crystallite size is a common way to improve strength

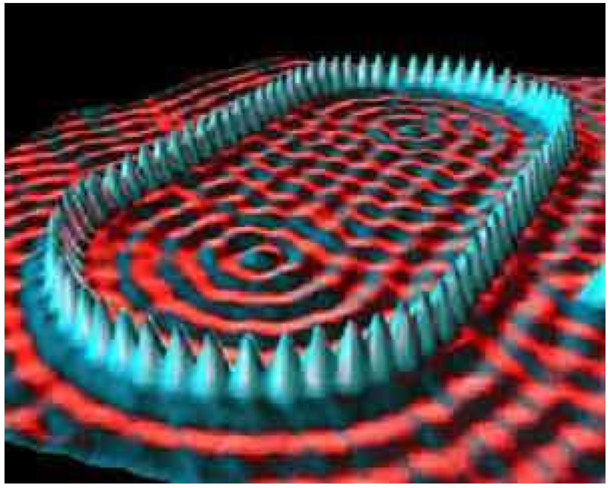


Nanomagnetic materials

- **nanotechnology used to ‘freeze’ the positions of atoms in an orientation that aligns the weak magnetic polarization**
- **nanomagnetic structures are formed by careful control of material composition and processing parameters**
- **applications in magnetic / data storage**

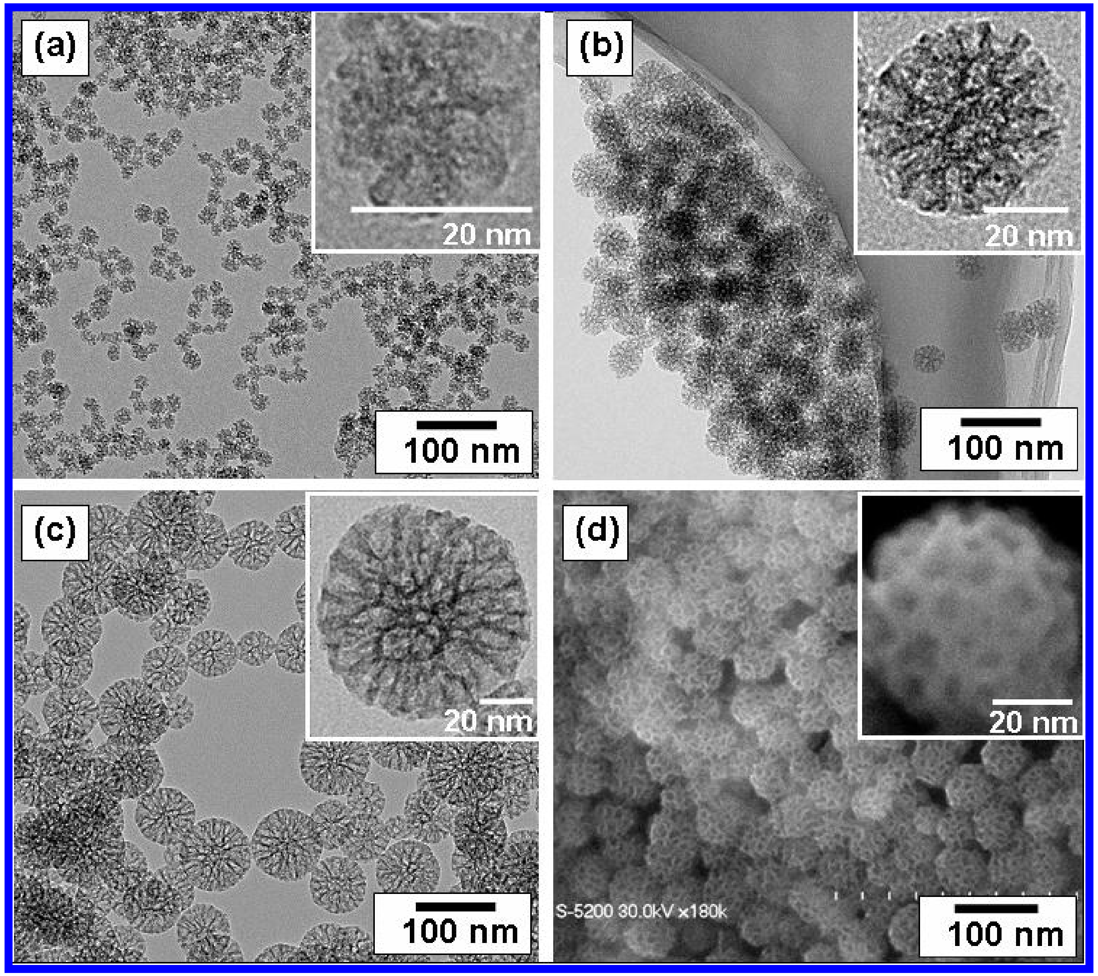


- magnetic force microscopy (MFM) imaging of novel nanomaterials
- magnetic structure of a quantum “corral”, which consists of magnetic iron atoms deposited on a copper surface that "corral" copper electrons



Nanoparticles

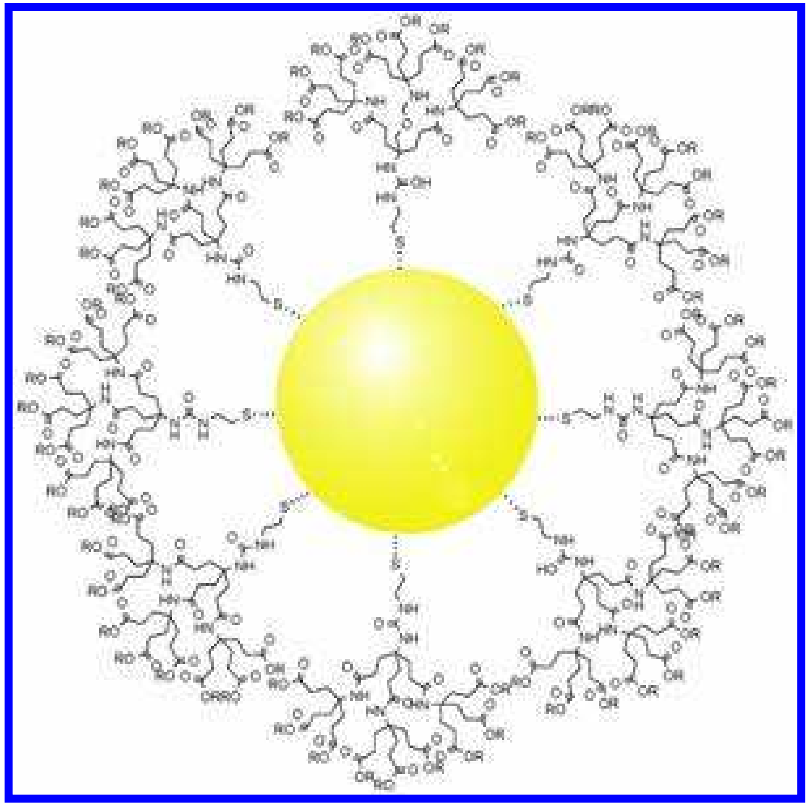
- in nanotech, particle is defined as a small object that behaves as a whole unit in terms of its transport and properties
- particles are further classified according to size
- coarse - between 10,000 and 2,500 nm
- fine - 2,500 to 100 nm
- ultrafine particles, or nanoparticles 100 to 1 nn



TEM (a, b, c) and SEM (d) images of mesoporous silica nanoparticles, mean diameter: (a) 20 nm, (b) 45 nm, (c) 80 nm.
SEM (d) image corresponding to (b)

Nanoparticles and catalysts

- high surface area
- tailored surface chemistry
- added to bulk / composite materials
- metal, ceramic, or polymer
- can also be ‘powder-like’



- dendron conjugated gold nanoparticle

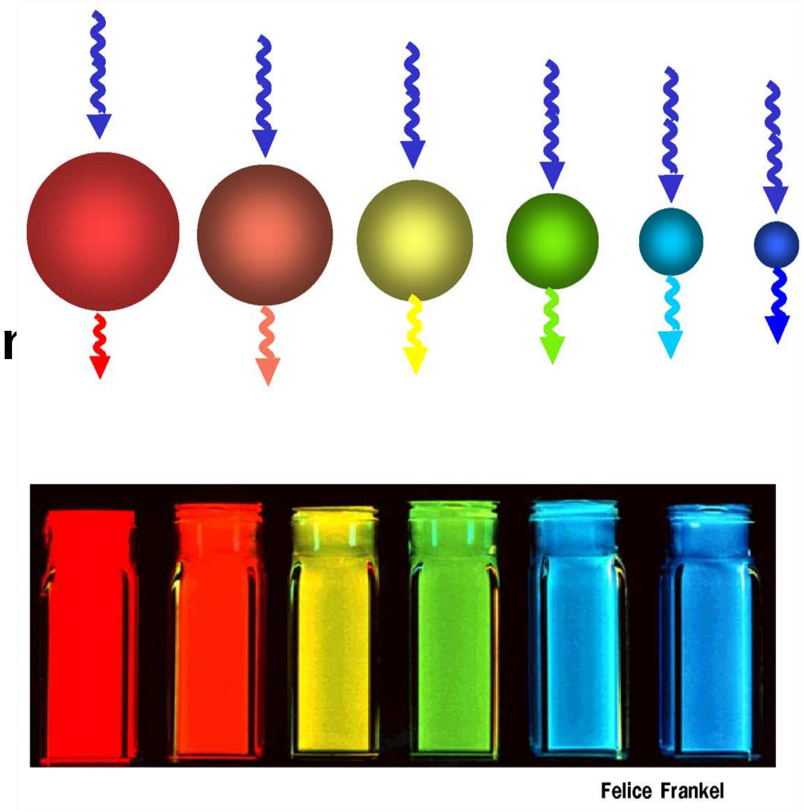
Nanowires

- nanowire is a nanostructure, with the diameter of the order of a nanometer
- alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length
- at these scales, quantum mechanical effects are important - "quantum wires“

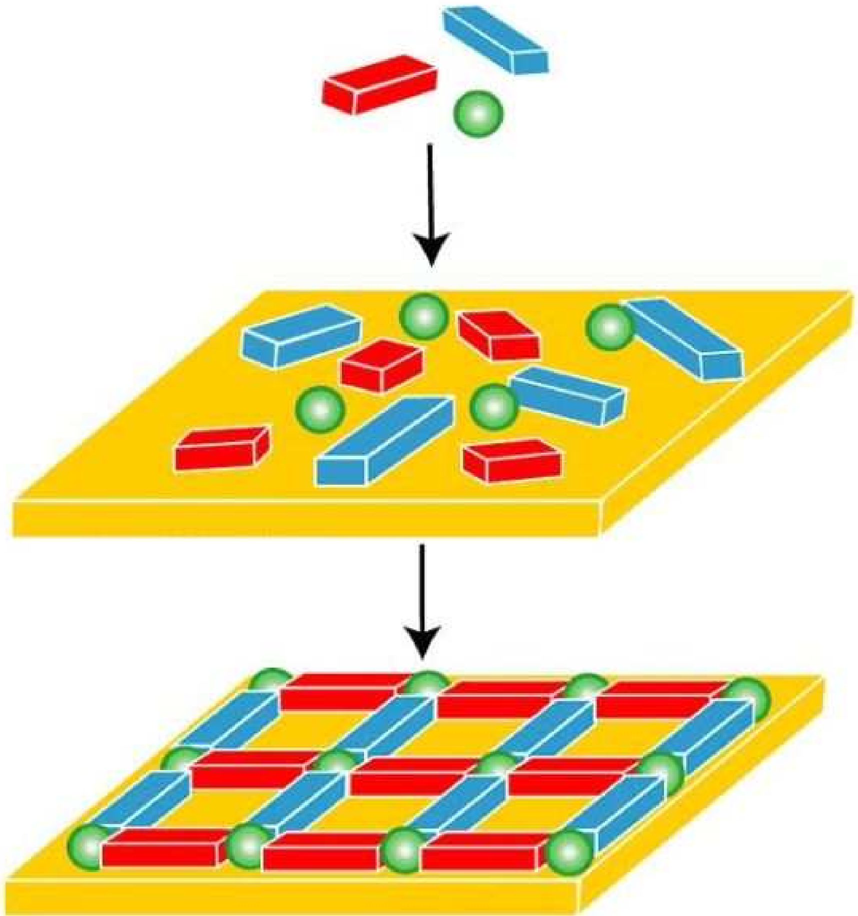
- image width, 5 um

Quantum dots (QD)

- QD is a portion of matter (e.g. semiconductor) whose excitons are confined in all three spatial dimensions
- electronic properties intermediate between bulk semiconductors and discrete molecules
- QD are semiconductors whose electronic properties are closely related to the size and shape of the individual crystal
- the smaller the size of the crystal, the larger the band gap, the greater the difference in energy between the highest valence band and the lowest conduction band
- more energy is needed to excite the dot, and more energy is released when the crystal returns to its resting state

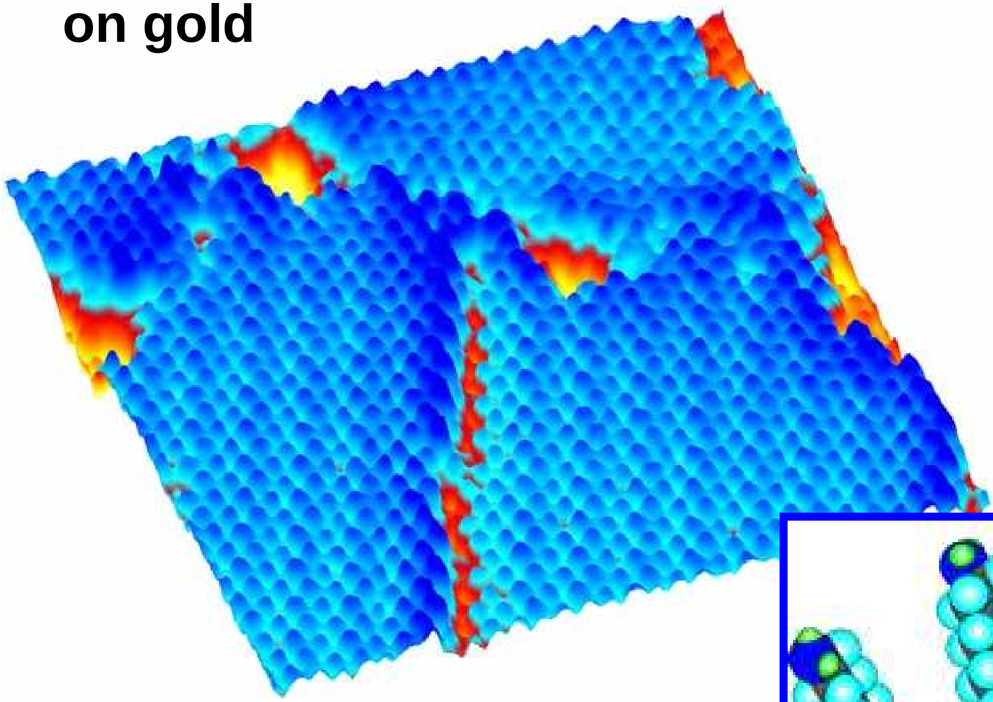


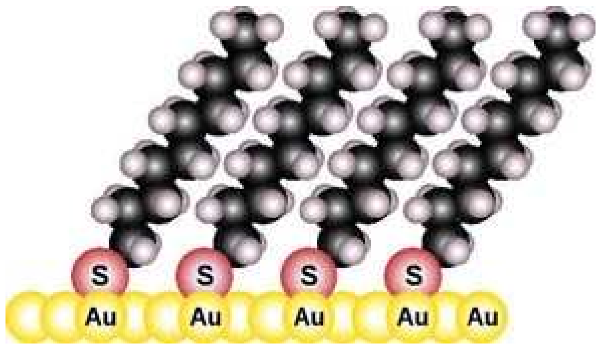
Smart approach – self-assembling

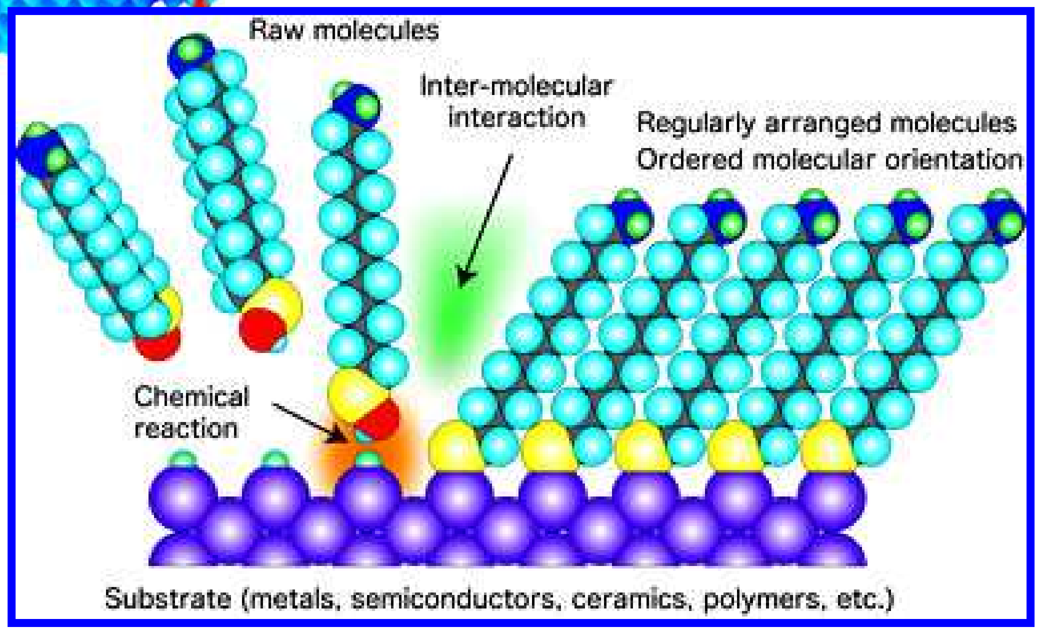


Self assembled monolayers (SAMs)

- **most typical – spontaneous adsorption of thiols on gold**

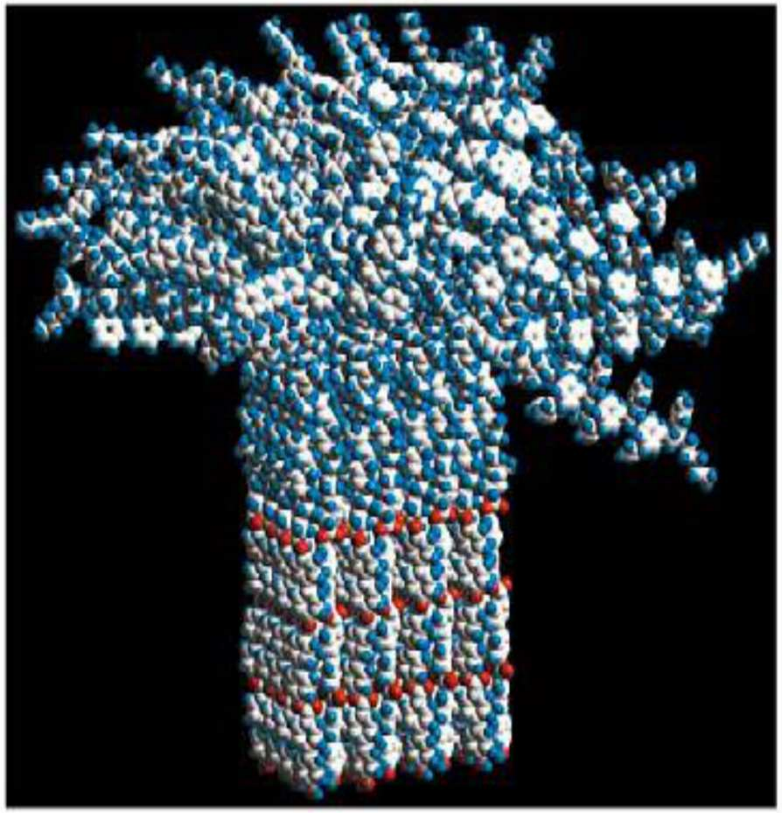


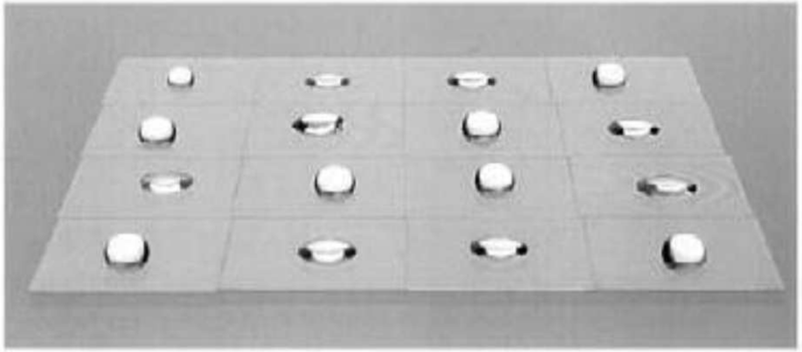




Self-assembly

- **making nanostructures by letting the molecules sort themselves out**
- **molecules will always seek the lowest energy available to them**
- **molecules will align themselves into particular positions**
- **use for large nanoscale arrays, different length scales, low cost, generality**
- **electronic applications, coatings**



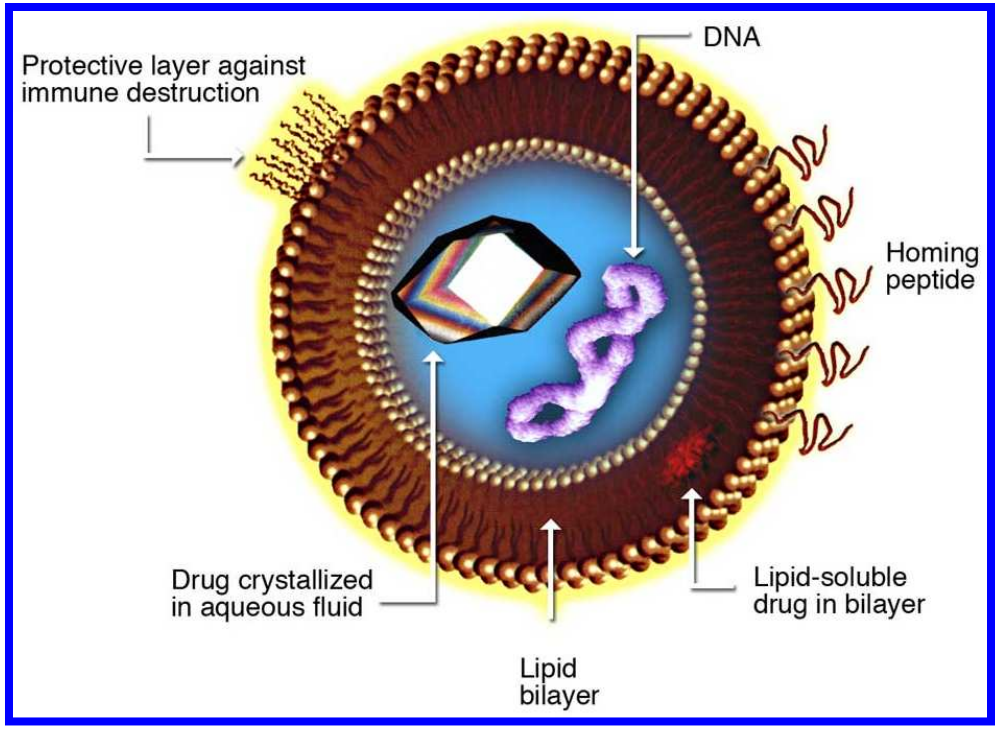


molecular model (top) of a self-assembled "mushroom"
photograph (bottom) shows control of surface wetting by a layer of these mushrooms

Liposomes

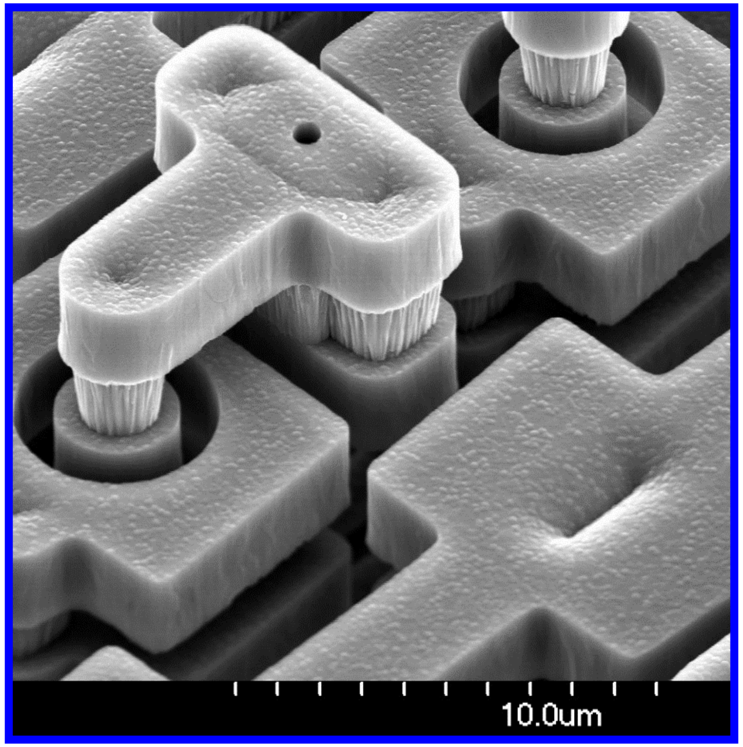
- artificial composite structures made of phospholipid bilayer and may contain small amounts of other molecules
- vary in size from low micrometer range to tens of micrometers
- unilamellar liposomes (shown) are typically in the lower size range with various targeting ligands attached to their surface allowing for their surface-attachment and accumulation in pathological areas for treatment of disease
- can be filled with drugs and used to deliver drugs

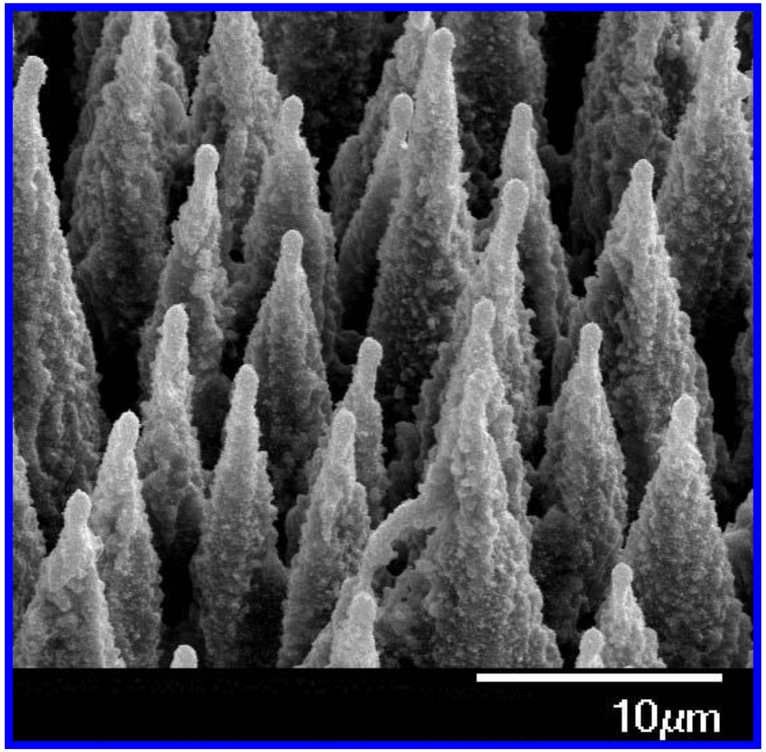
- disrupting biological membranes – sonication
- from natural phospholipids with mixed lipid chains (e.g. egg phosphatidylethanolamine) or other synthetic surfactants
- should not be confused with micelles and reverse micelles composed of monolayers



Silicon structures / materials

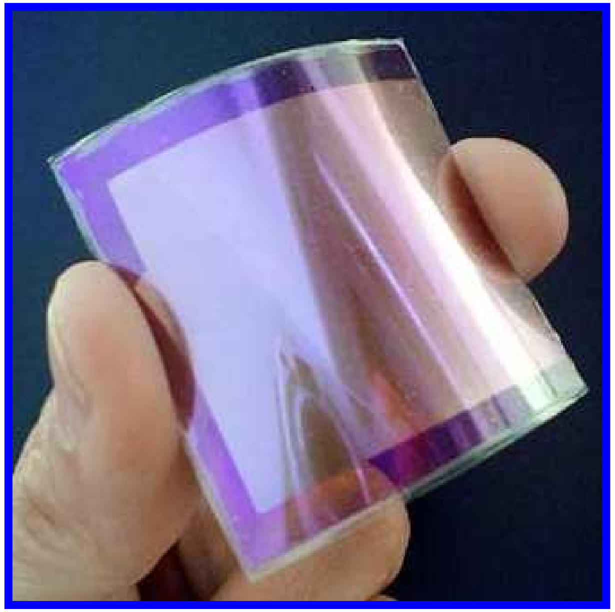
- **wafers**
- **MEMS (microelectromechanical systems)**
- **LOC (lab-on-chip)**
- **biomimetic structures - learning from nature**
  - using shape as well as chemistry
  - some similar function (light gathering, sensing / detection

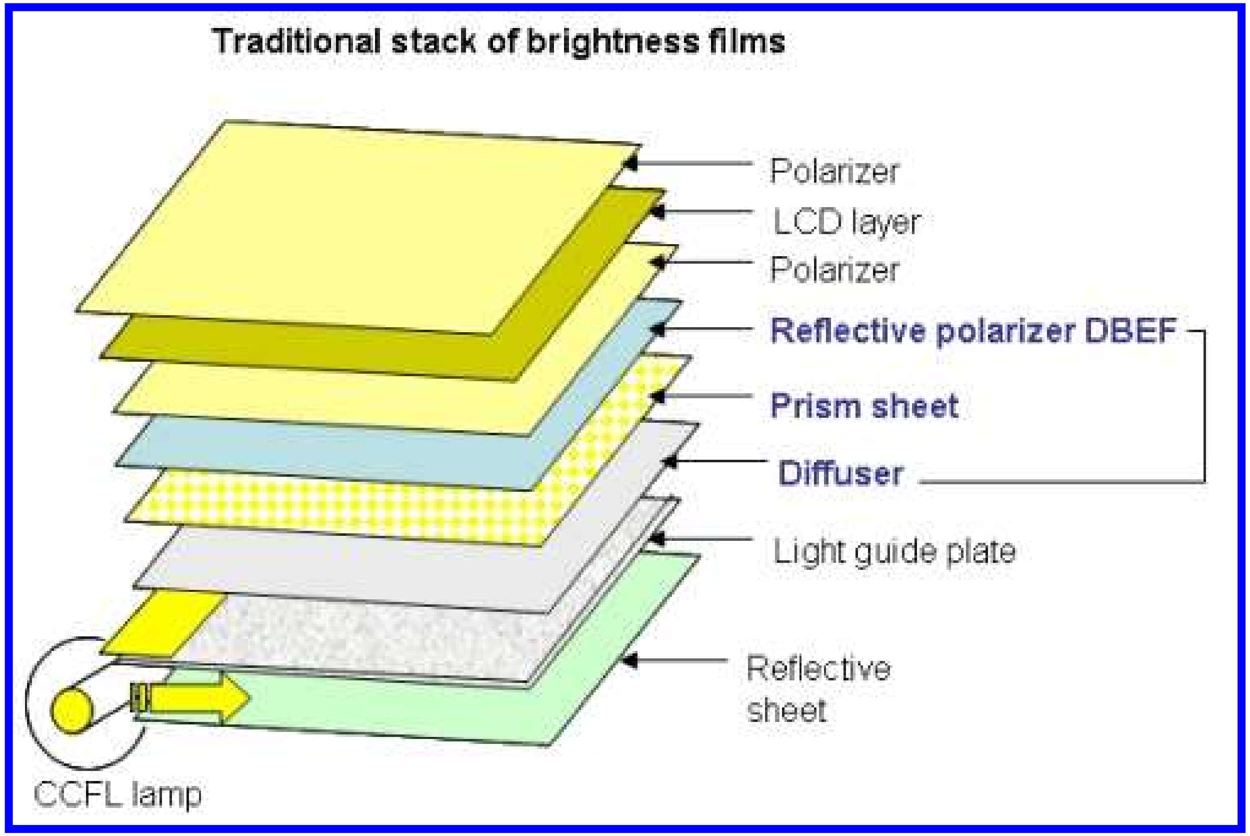




Thin films

- physical coatings
- layered stacks
- deposited films
- functionalized (SAMs)
- magnetic and optical applications
- metallization in silicon semiconductors





Nanofabrication techniques

- nanoparticles
  - colloidal processing
  - flame combustion
  - phase segregation
- nanorods or nanowires
  - template-based electroplating
  - solution-liquid-solid growth (SLS)
- thin films
  - chemical vapour deposition
  - molecular beam epitaxy
  - atomic layer deposition
- nanostructured bulk material
  - photonic bandgap crystals by self-assembly of nanosized particles

grouped according to the form of products

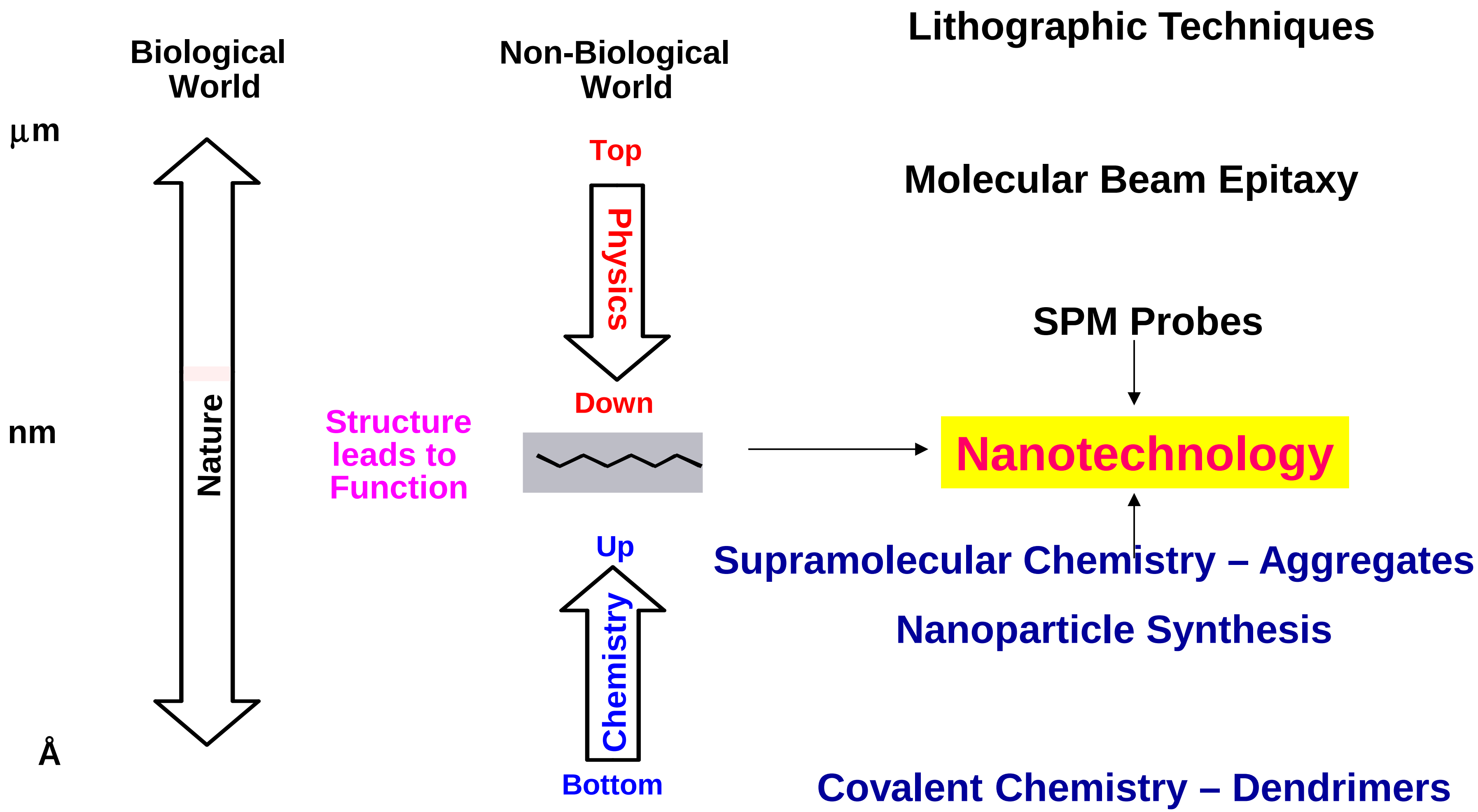
Making of nanostructures

- ***the bottom-up approach*: whereby structures are made atom-by-atom and molecule-by-molecule, harnessing covalent, ionic, metallic or non-covalent bonds**
  - this approach represents how nature self-assembles functioning nanostructures, such as enzymes and viruses

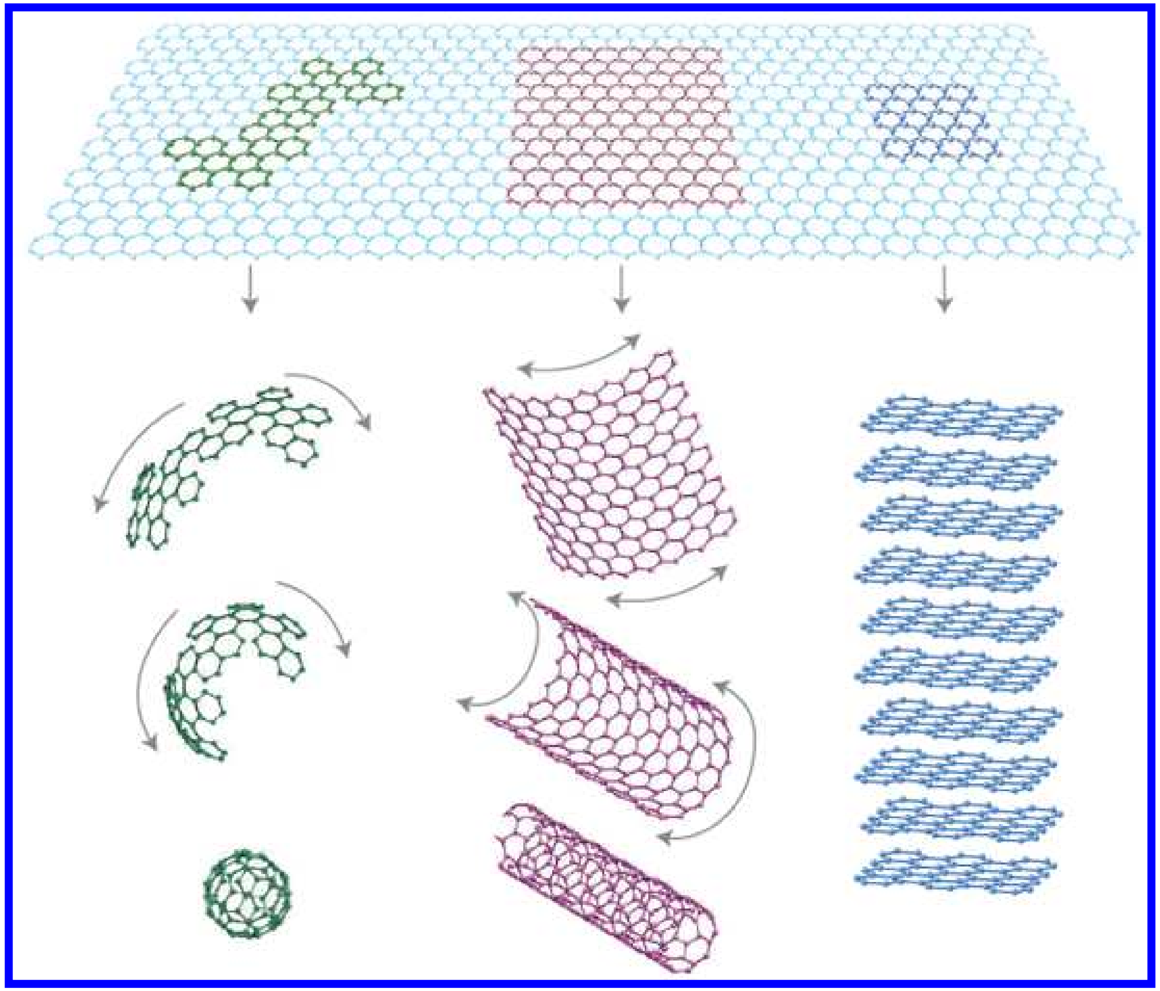
- ***the top-down approach*: whereby structures are etched into bulk materials such as silicon**
  - this approach represents how silicon chips are fabricated

- **thus, nanoscale science is more than creating structures on the length scale of 1-100 nm; it is about making nanostructures which also function in some way**

How to make things small?

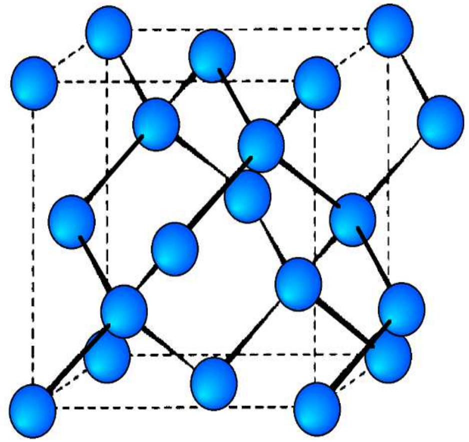


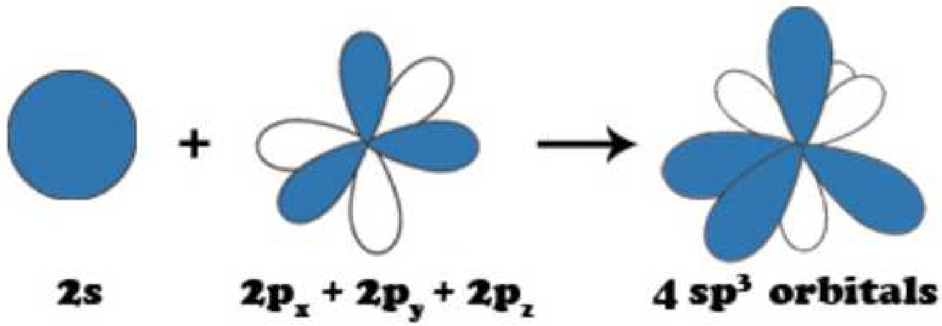
Carbon-based nanomaterials



Carbon atoms

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

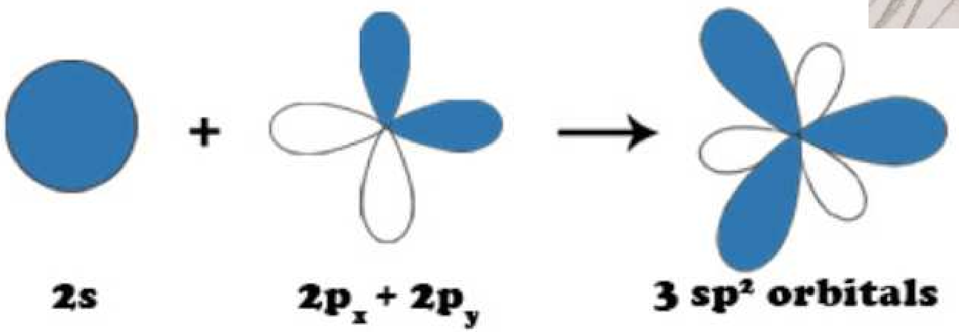


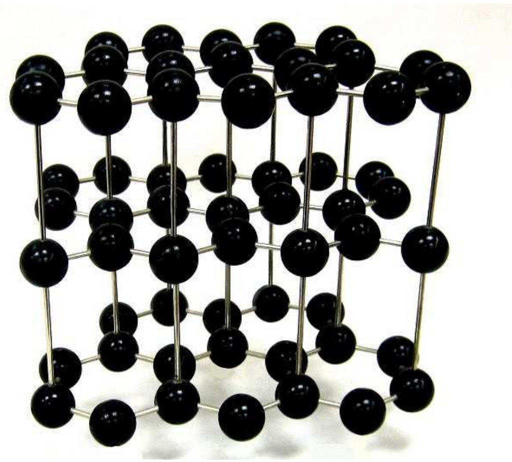


hard, transparent, insulator, expensive

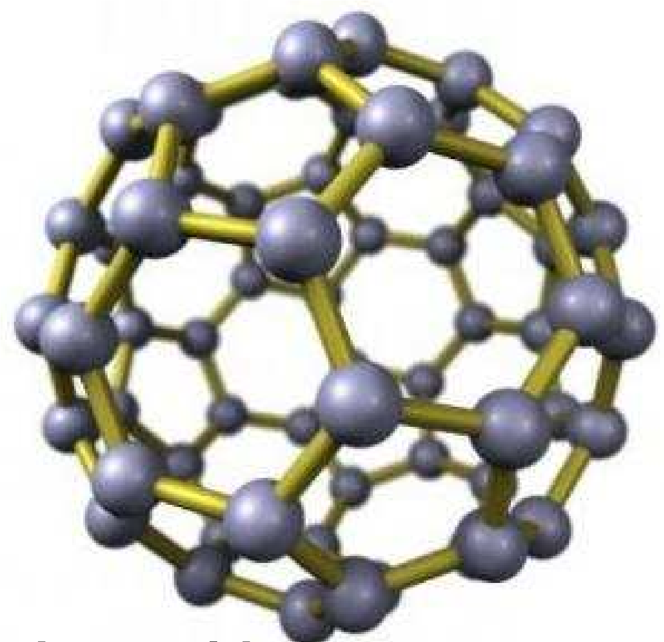
- **graphite**

soft, opaque, conductor, cheap



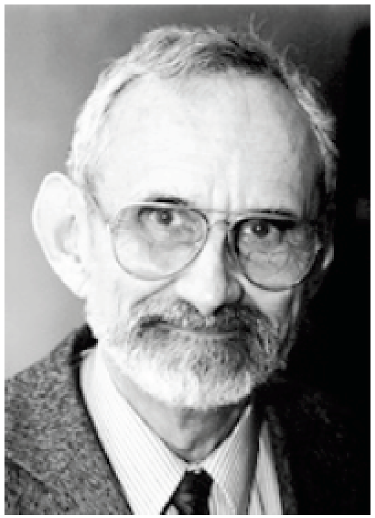


Buckminsterfullerene

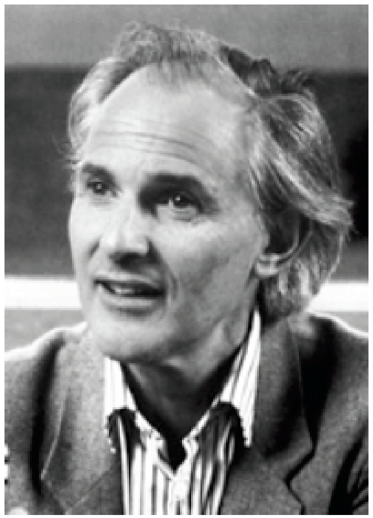


- molecule consisting of 60 C atoms
- sp^2 hybridized bonds
- has 20 hexagons, 12 pentagons
- other related structures have 70 or 84 C atoms

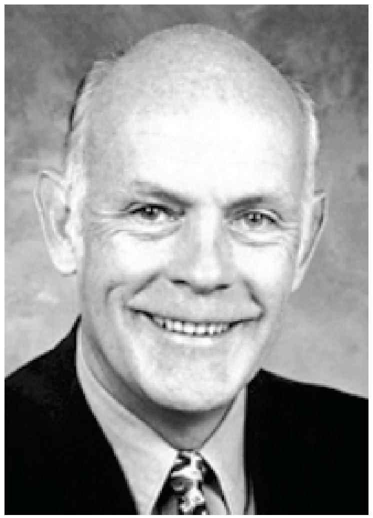
- Nobel Prize in Chemistry 1996: Robert Curl, Sir Harold Kroto, Richard Smalley “for their discovery of fullerenes”.



Robert F. Curl Jr.

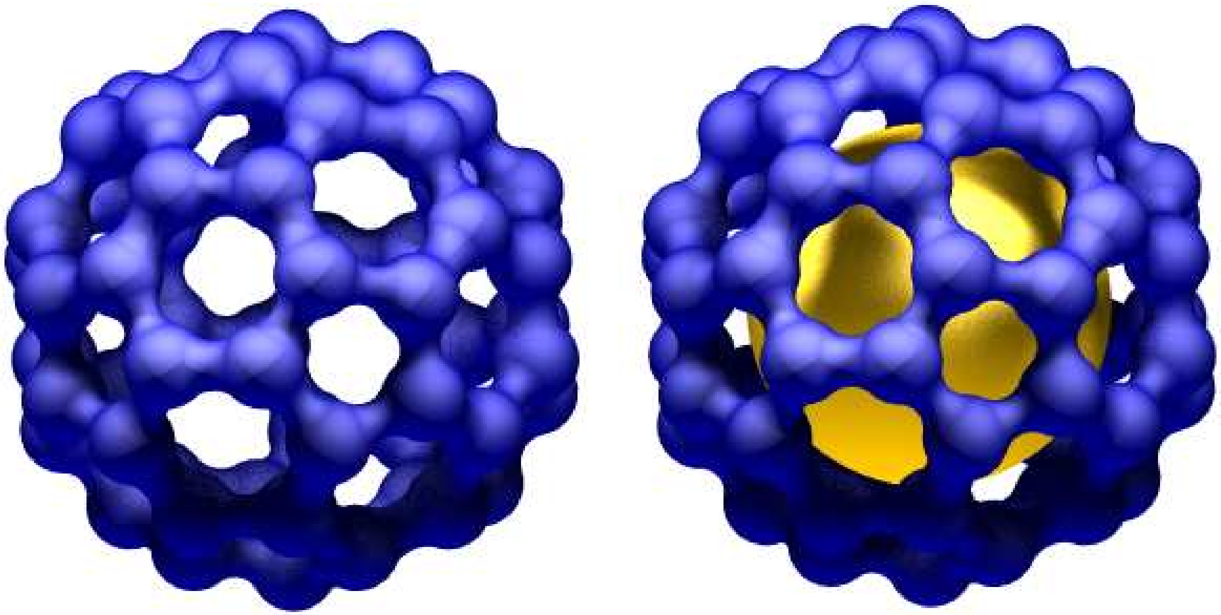


Sir Harold W. Kroto



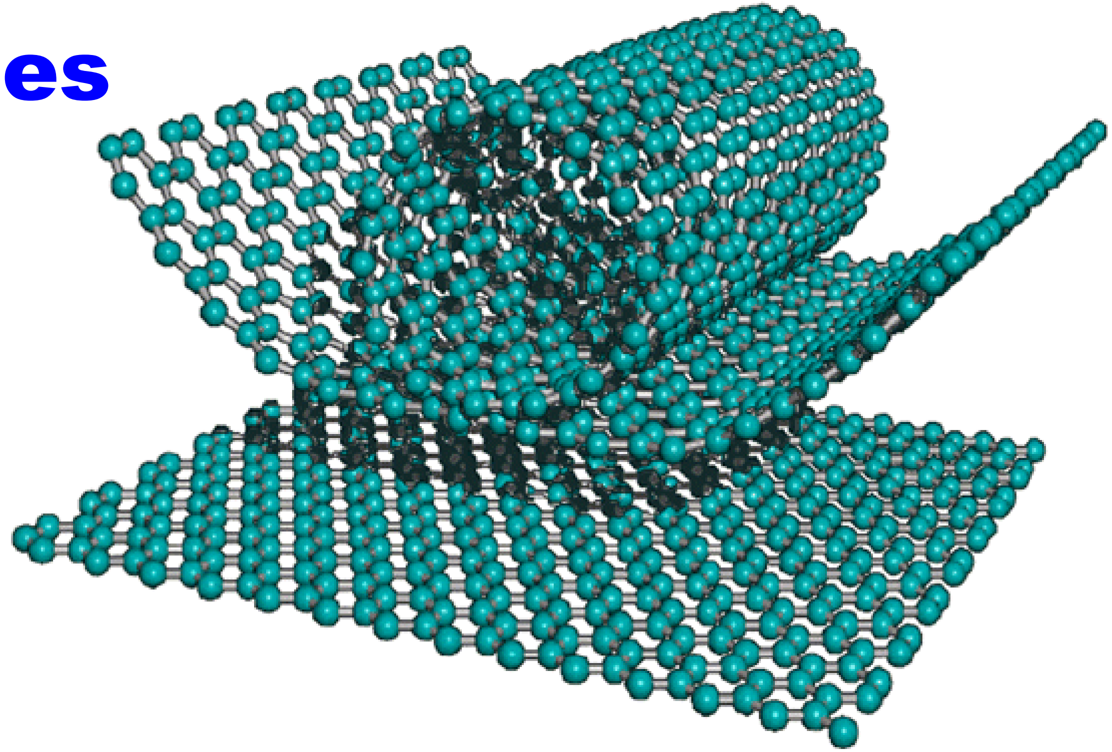
Richard E. Smalley

Fullerene

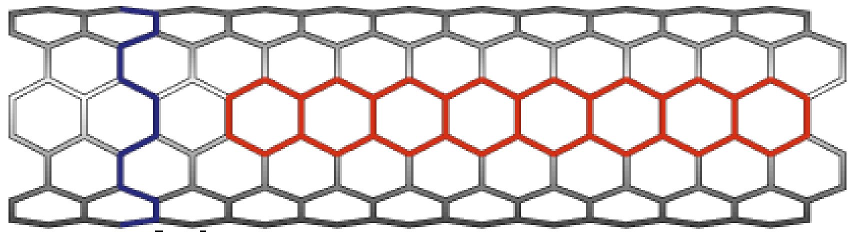


- empty and enclosing other atom(s)
- $RbCs_2C_{60}$ is the highest temperature carbon based super conductor yet discovered, T_c = 33 K
- subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology

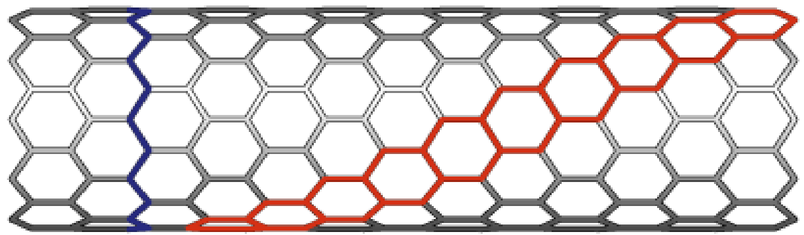
Carbon nanotubes



- 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

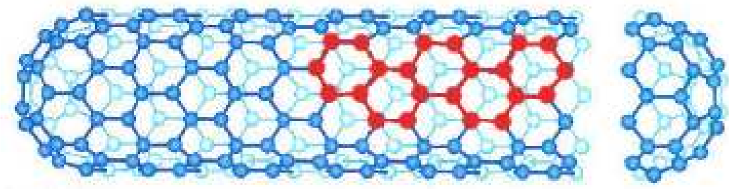


- electrical insulator

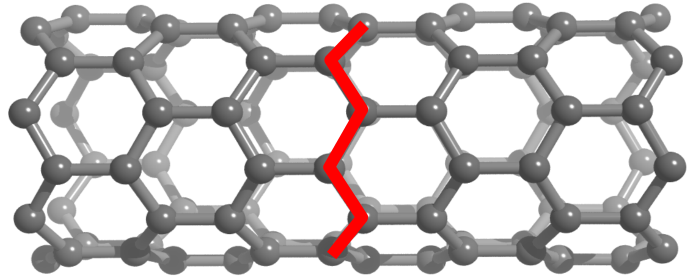


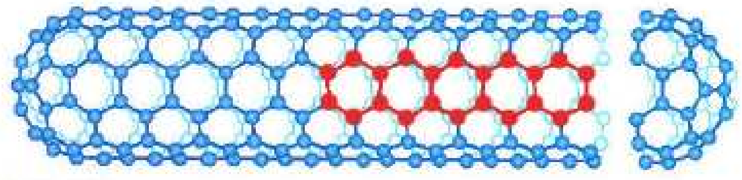
- efficient thermal conductors

Types of SWNCTs

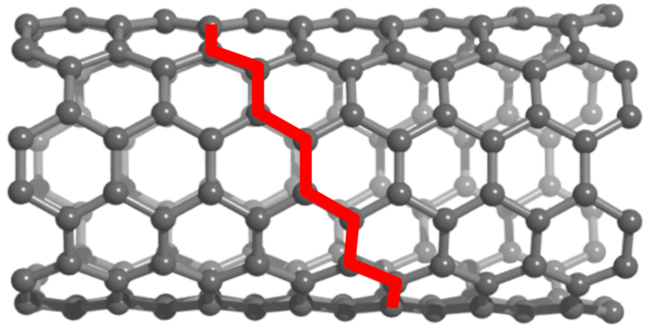


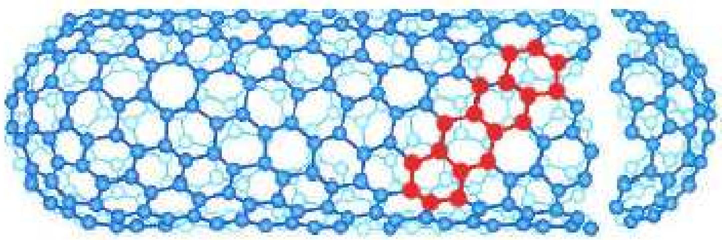
- **zig-zag**



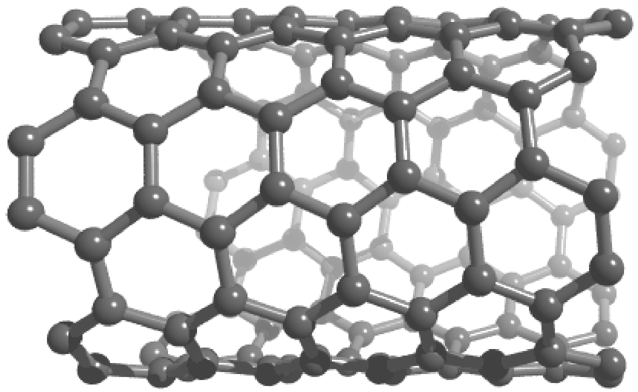


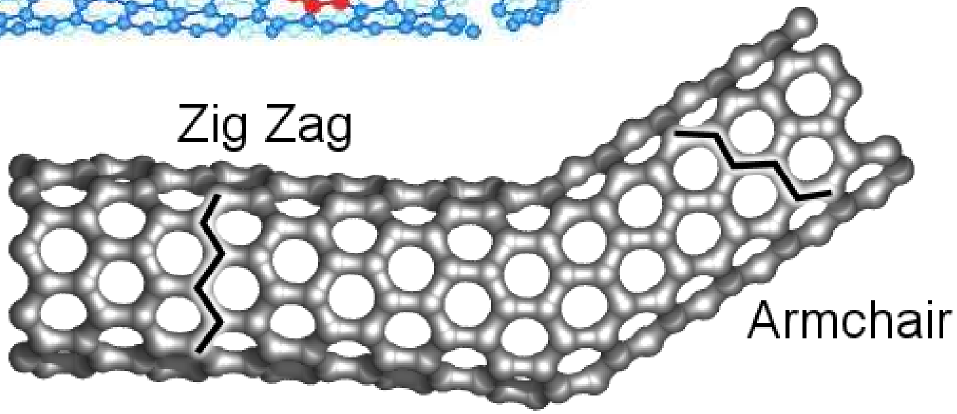
- **arm-chair**



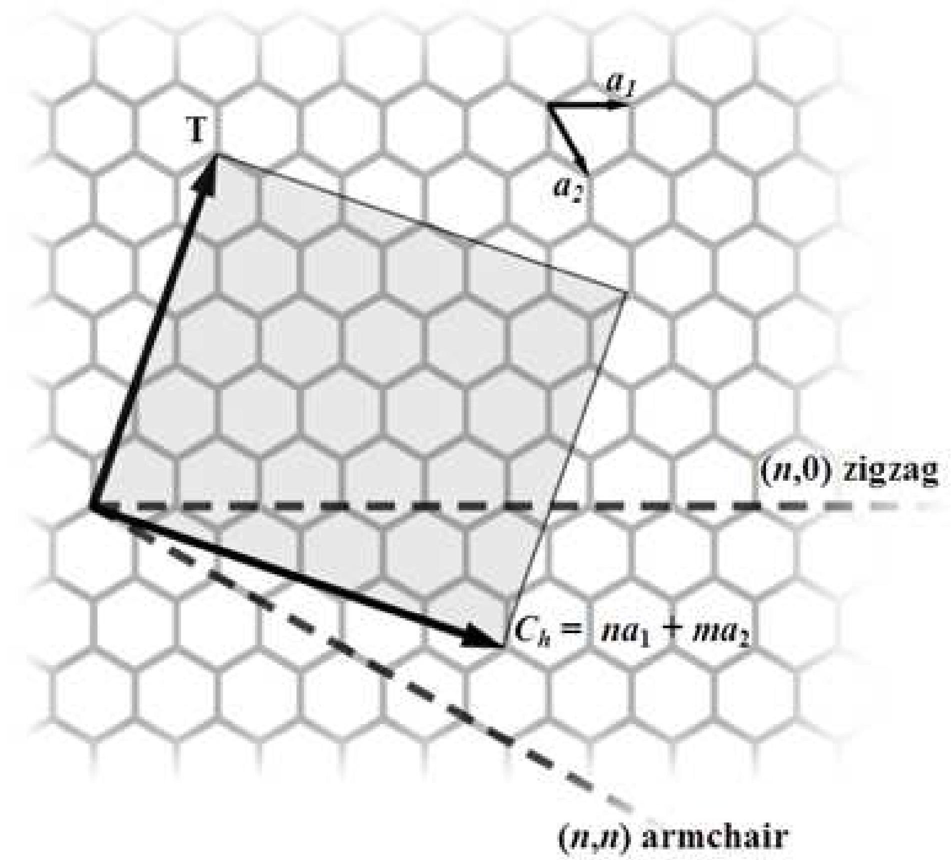


- **chiral**



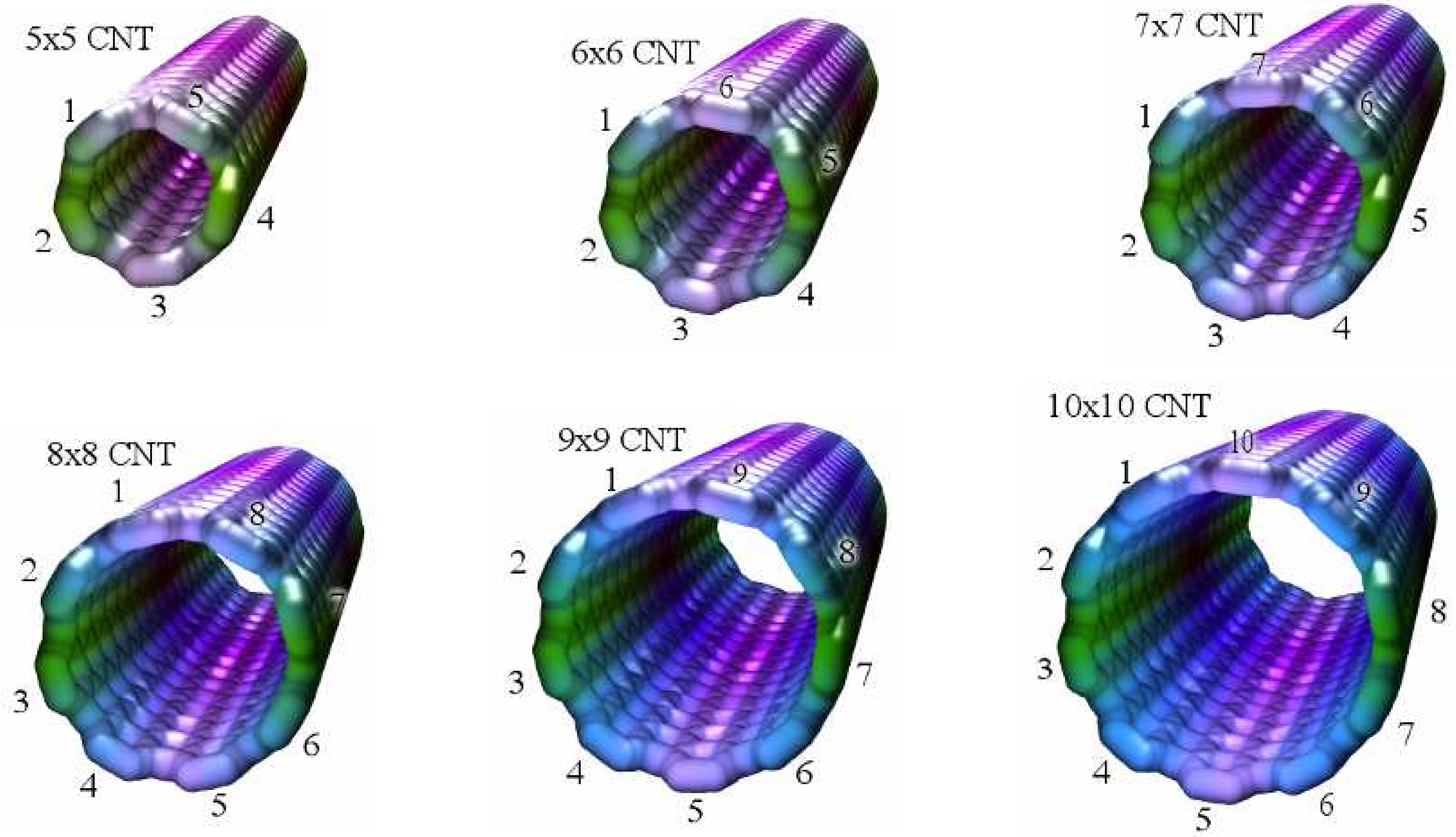


SWCNT
n,*m* numbers

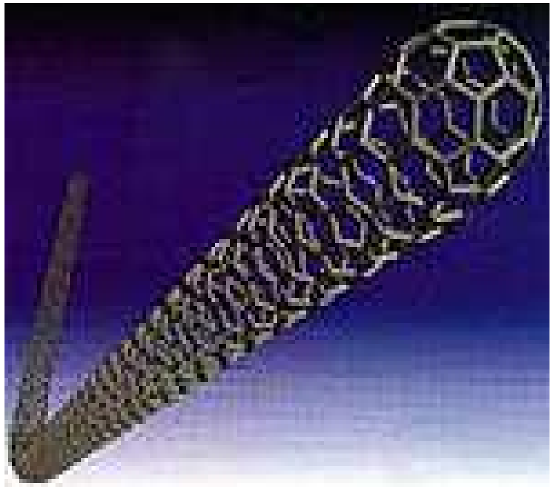


(n,m) nanotube naming scheme can be thought of as a vector C_h in an infinite graphene sheet that describes how to "roll up" the graphene sheet to make the nanotube
T denotes the tube axis, a_1 and a_2 are the unit vectors of graphene in real space

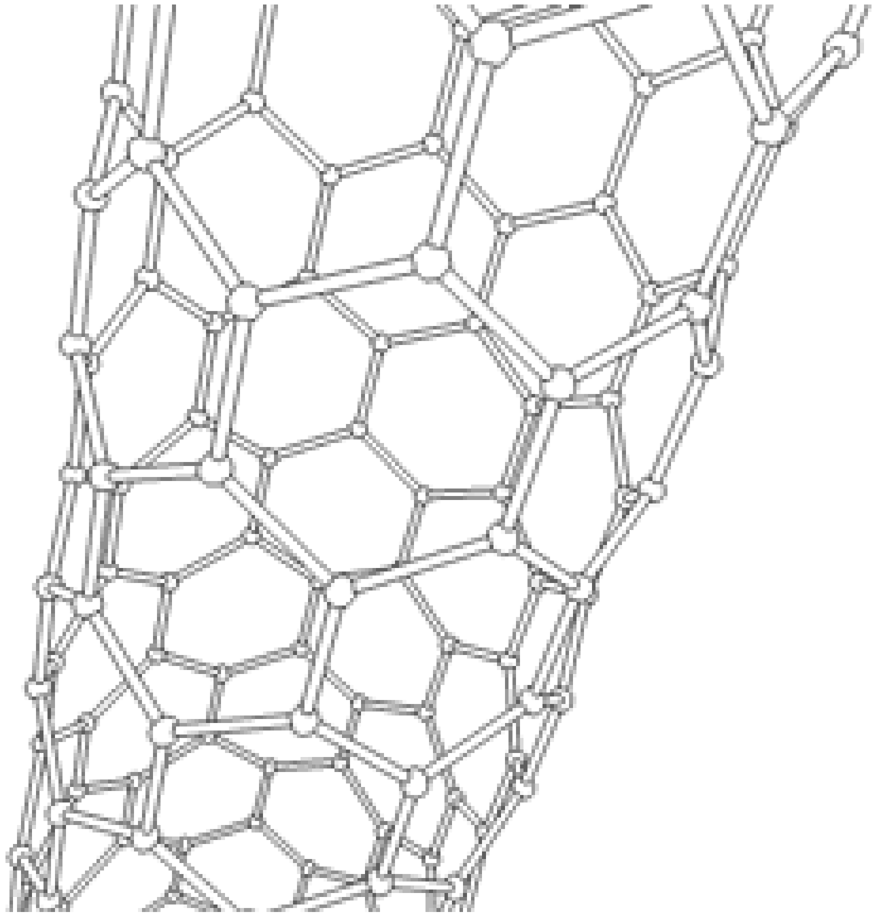
n x *n*, *n* = *m* SWCNTs



Single- and multi-walled CNTs



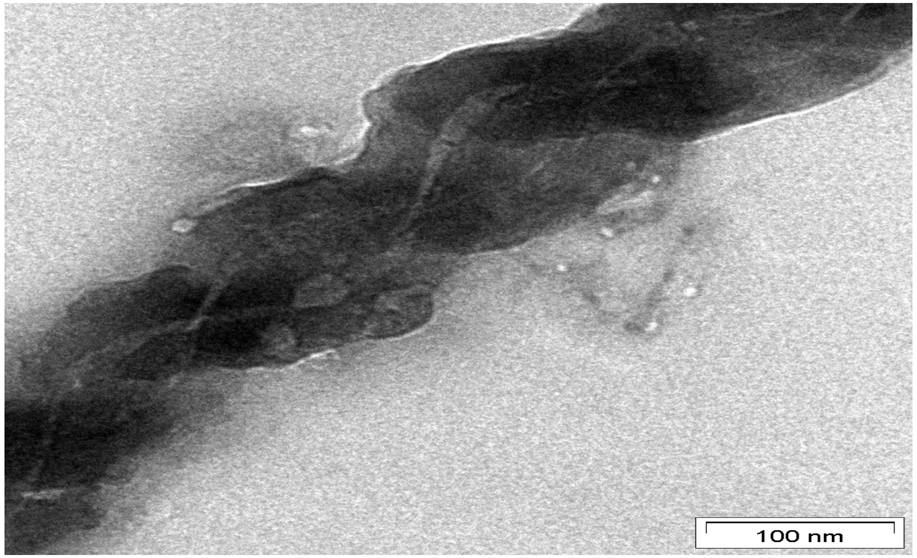
- SWCNT



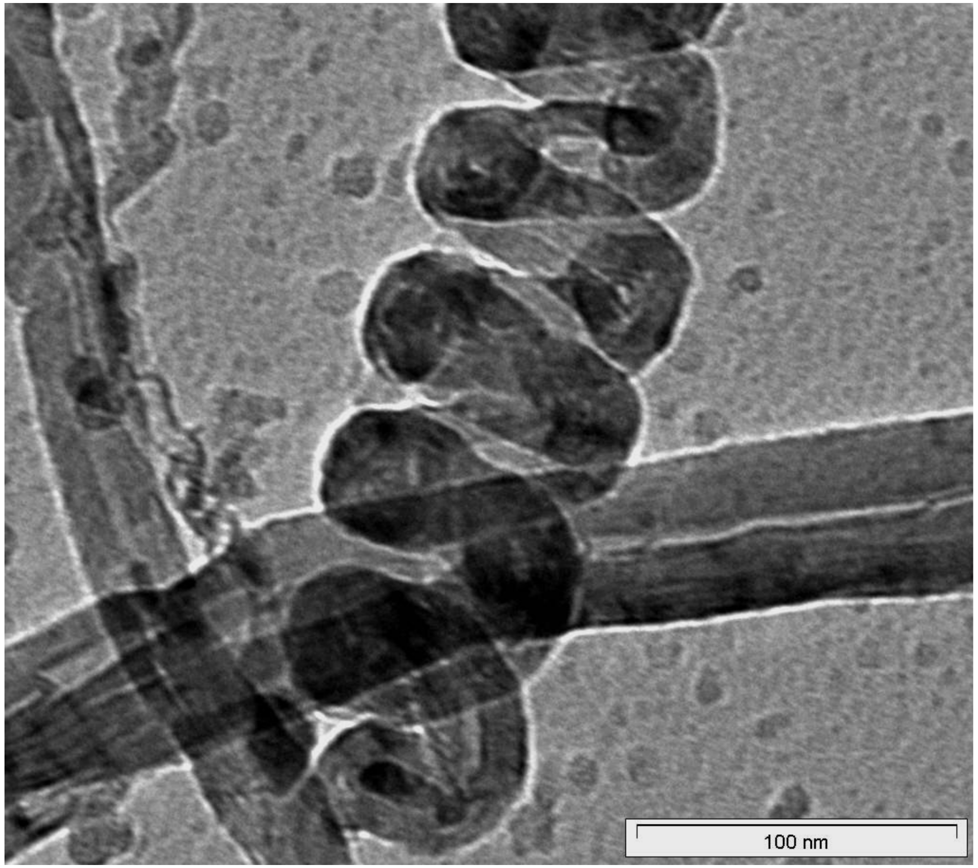
- MWCNT

interlayers spaced 0.34 nm

Flexibility of CNTs



- twisted and spiral CNTs



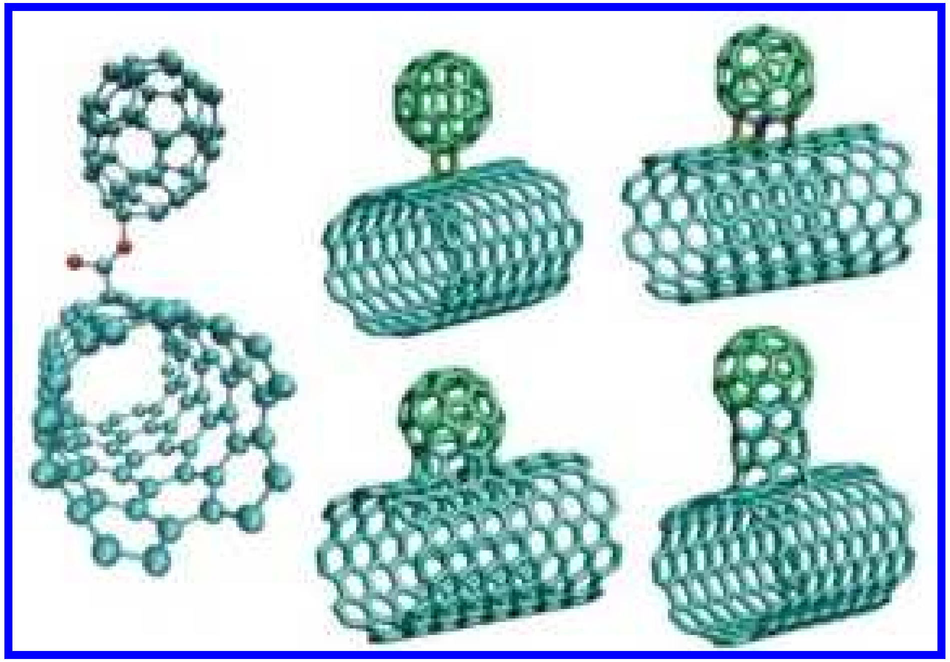
Properties of CNTs

- **strength - strongest and stiffest materials known, in terms of tensile strength and elastic modulus**
  - 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 48 462 kN·m/kg is the best (high-carbon steel154 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
- **AFM tips**
- **nanotweezers**
- **composite materials**
- **nano structures**
- **potential for extremely strong light weight cables / space elevator (** http://www.youtube.com/watch?v=pnwZmWoymeI)
- **physical memory**

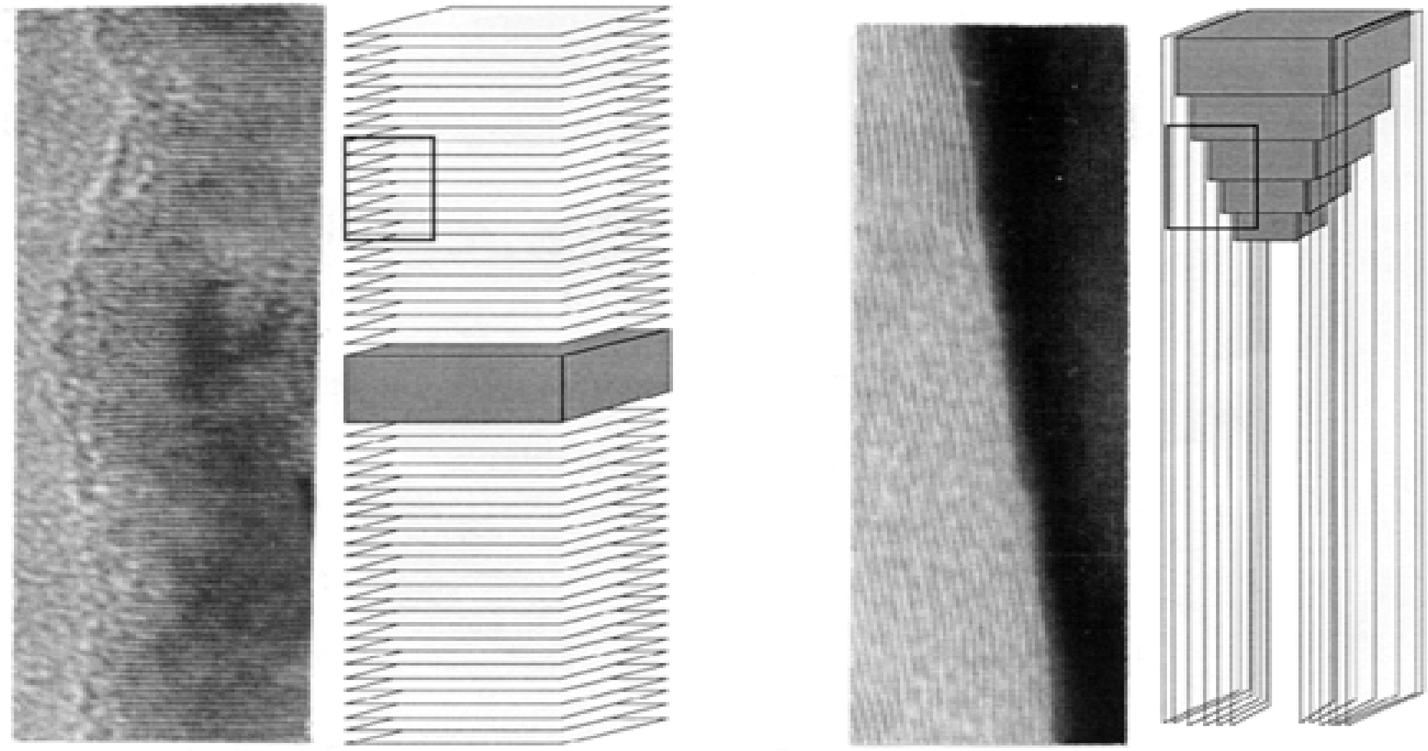
NanoBuds



- 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

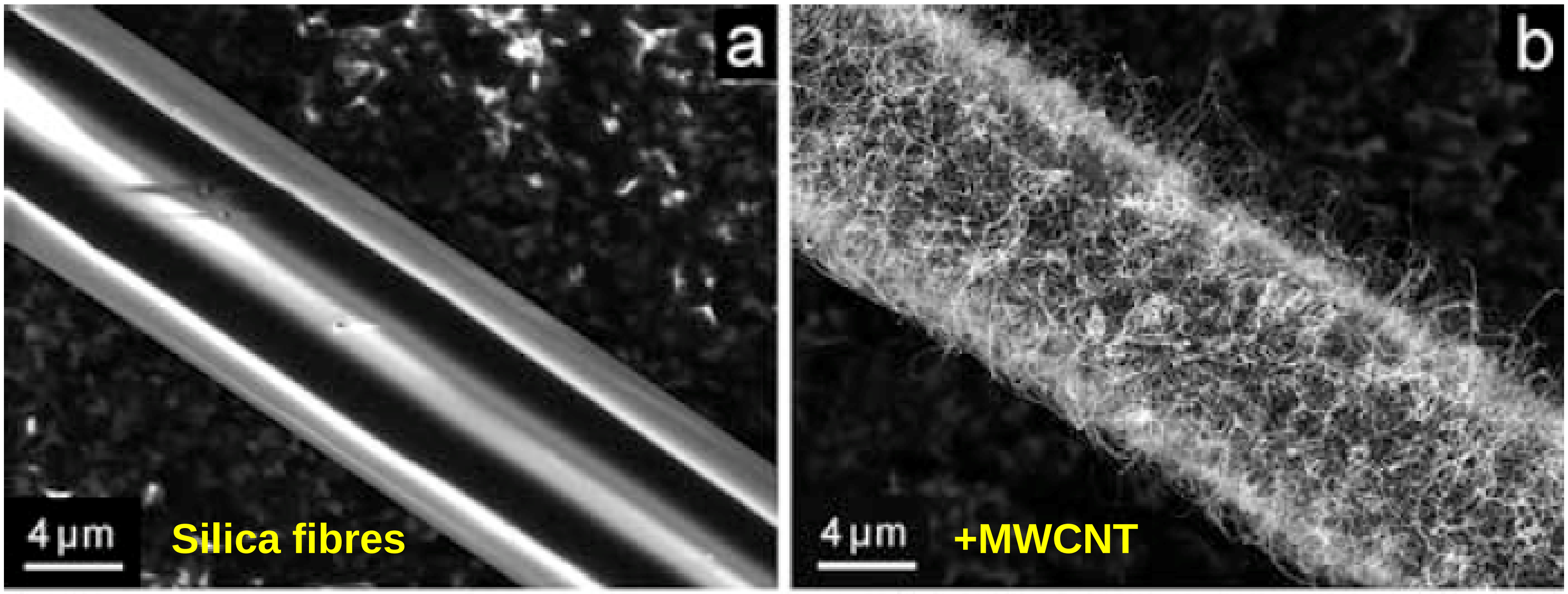
Carbon nanofibers

- 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



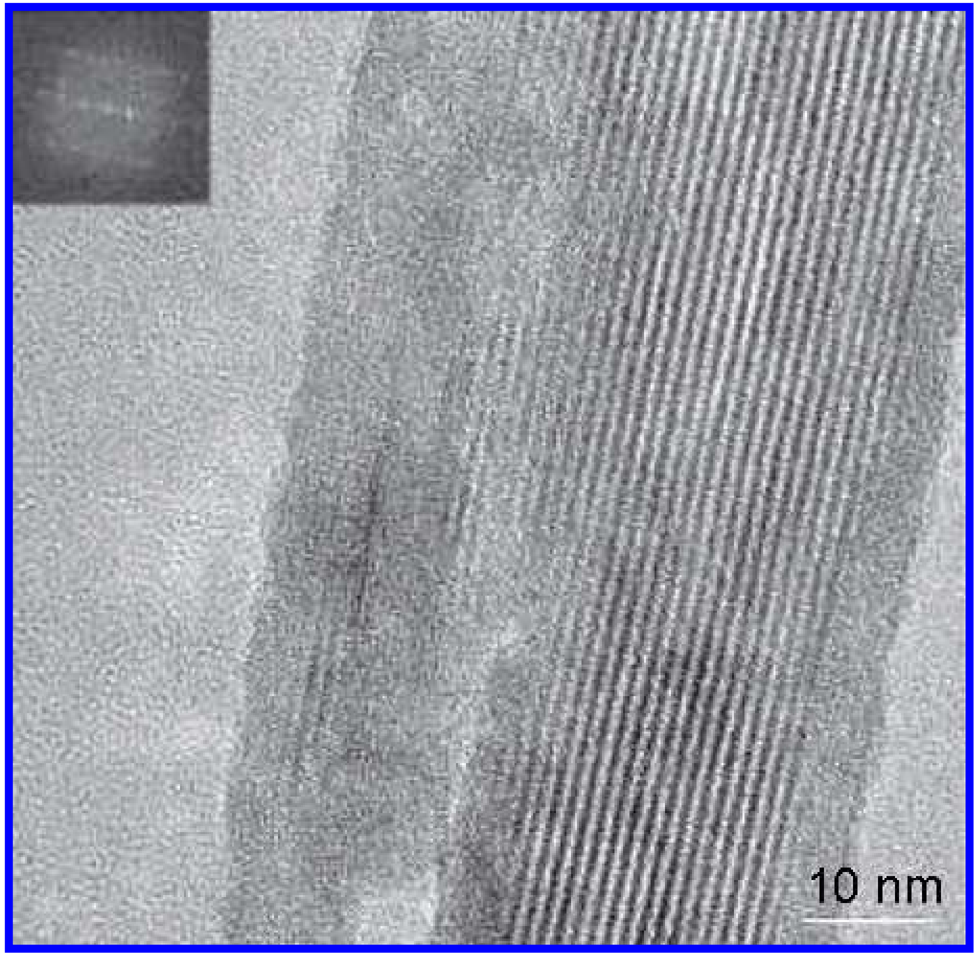
CNTs are strong

- 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



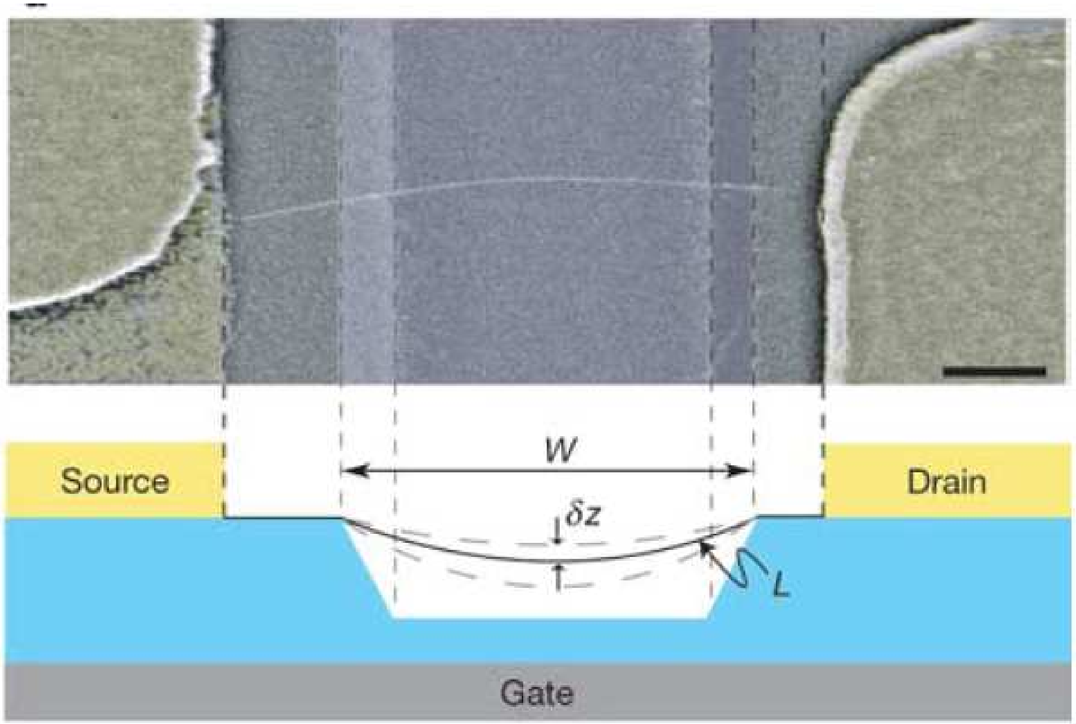
Damascus sabre steel contains CNTs

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



Carbon nanotube mechanical oscillator

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



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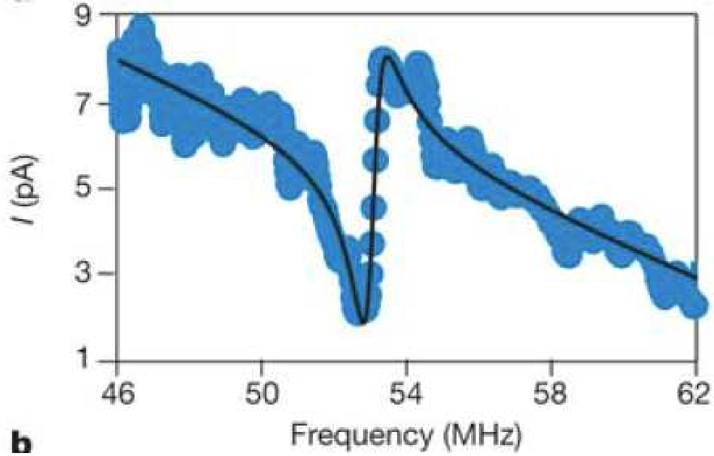

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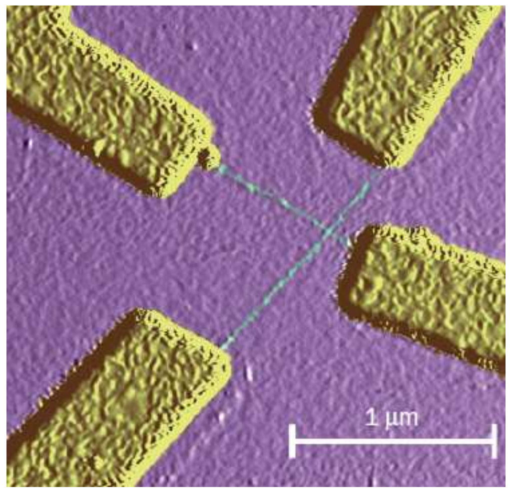
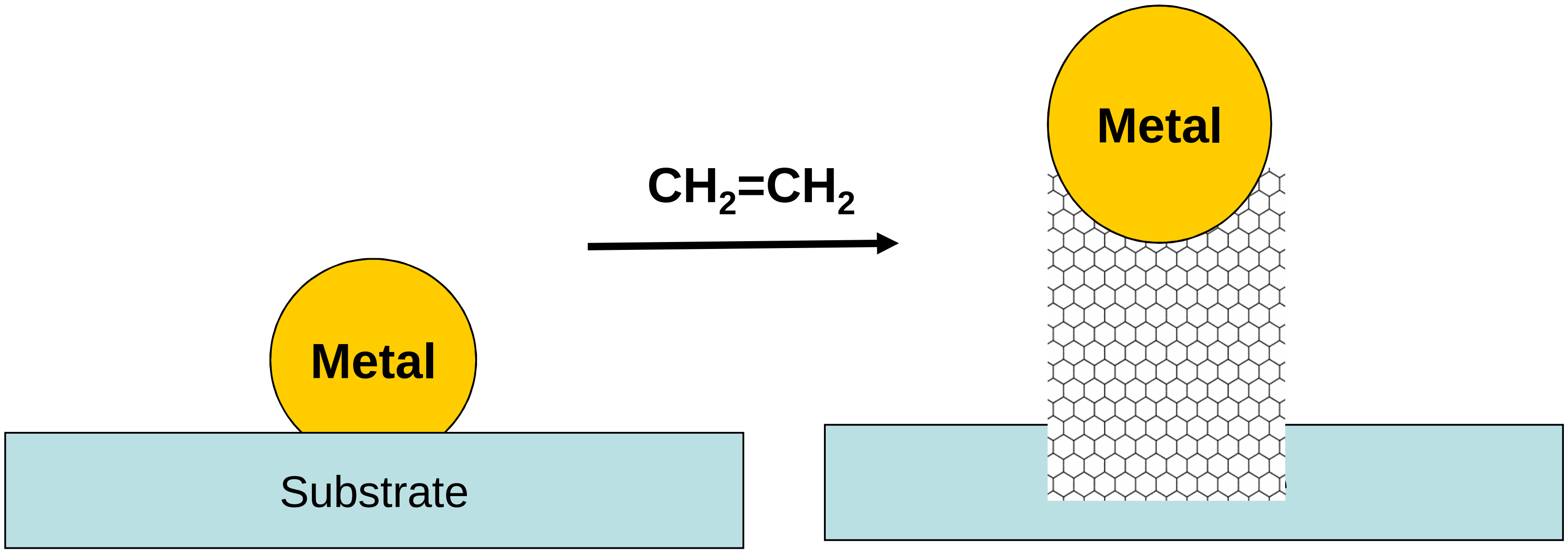


Preparation of CNTs

- **Carbon arc discharge**. Hold two carbon (graphite) electrodes at some potential difference in a Helium 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 is 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

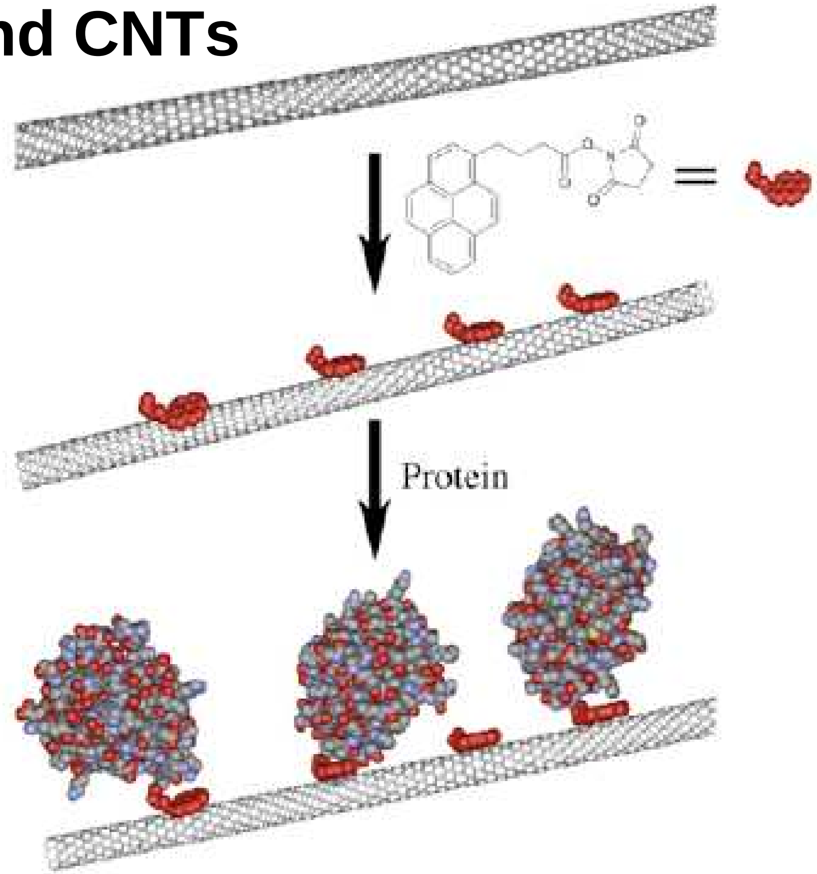


CNTs purification

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

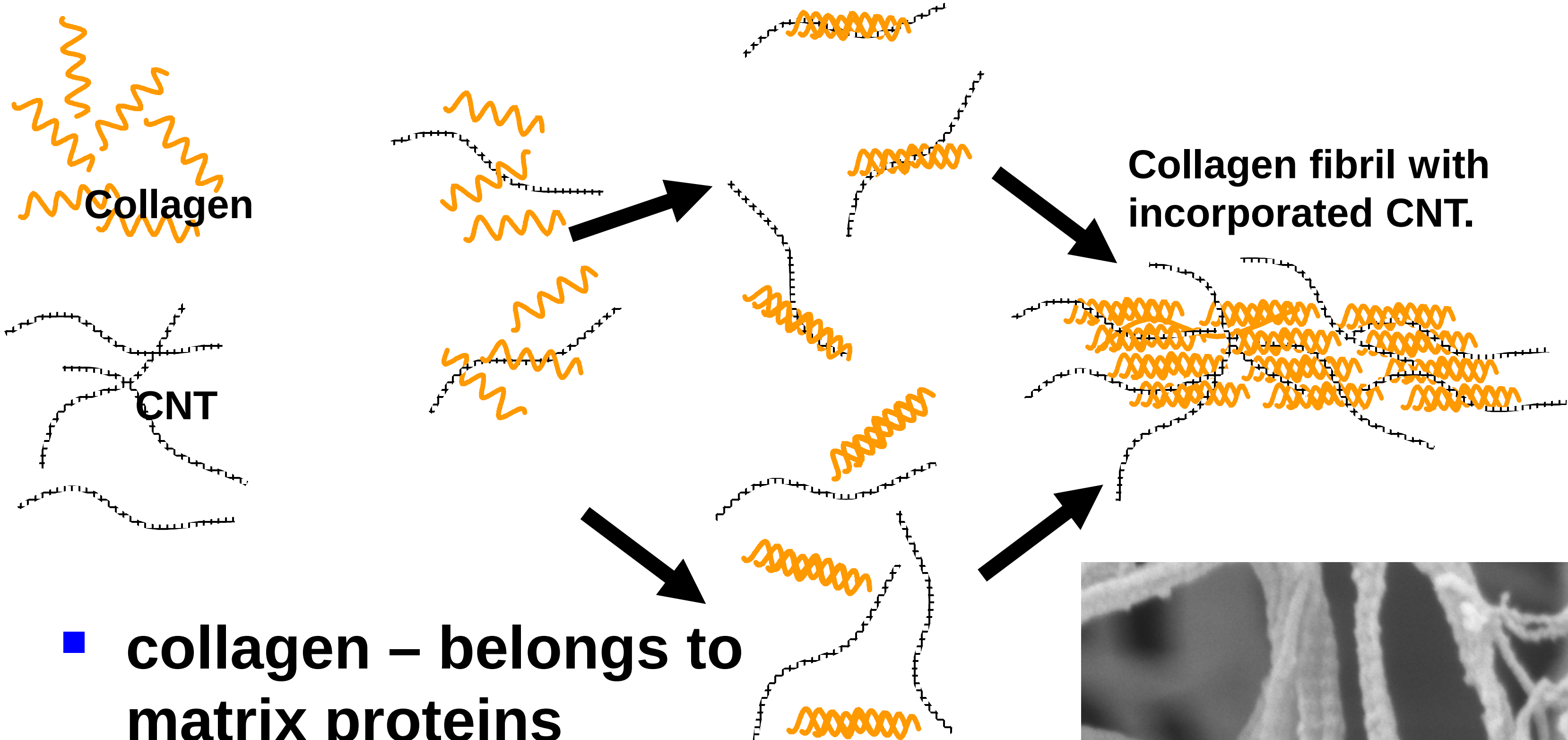
Functionalization

- **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.**

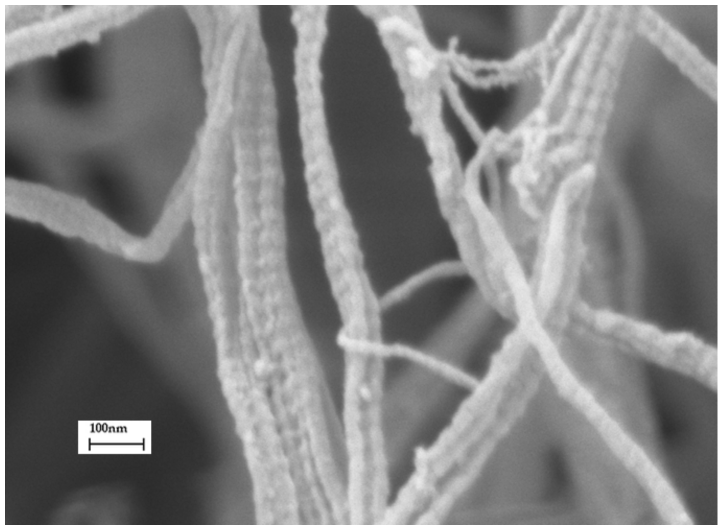


Biocompatible CNTs

- collagen – CNTs composite material



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



Open problems

- to be useful for devices, these carbon nanomaterials need to be prepared on and/or connected reliably to electrodes.

- since the properties of these nanomaterials 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/
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