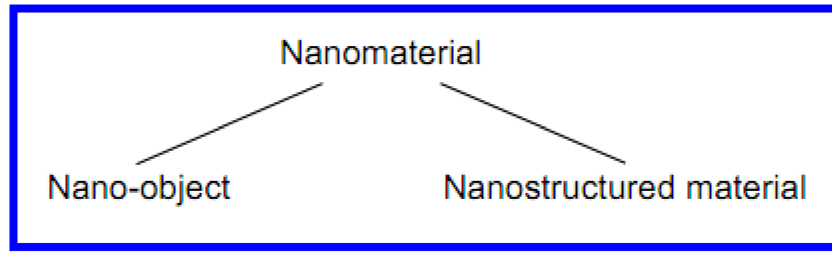
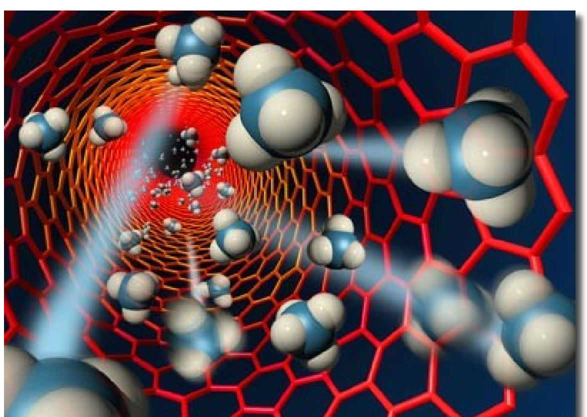
2 Nanomaterials

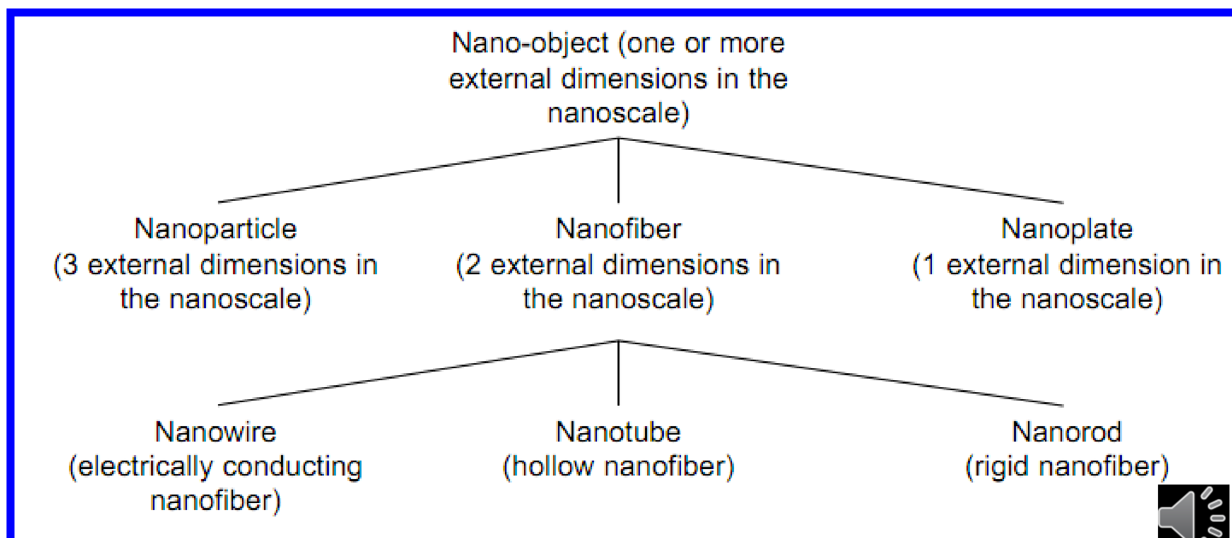
- nanomaterials and nanostructures – overview
- carbon – nanotubes, graphene
- metal-based nanostructures - nanowires, gold nanoparticles (nanorods, nanocages, nanoshells)
- magnetic nanoparticles
- polymer nanostructures (dendrimers)
- protein-based nanostructures - nanomotors from microbes and mammalian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

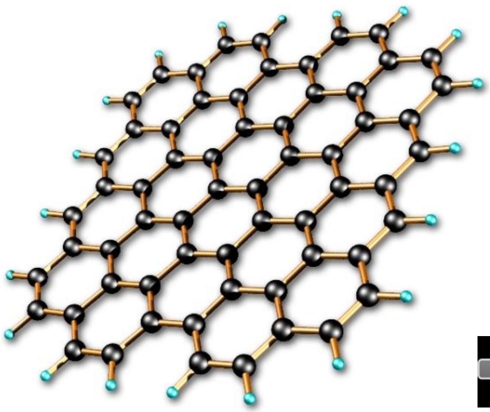






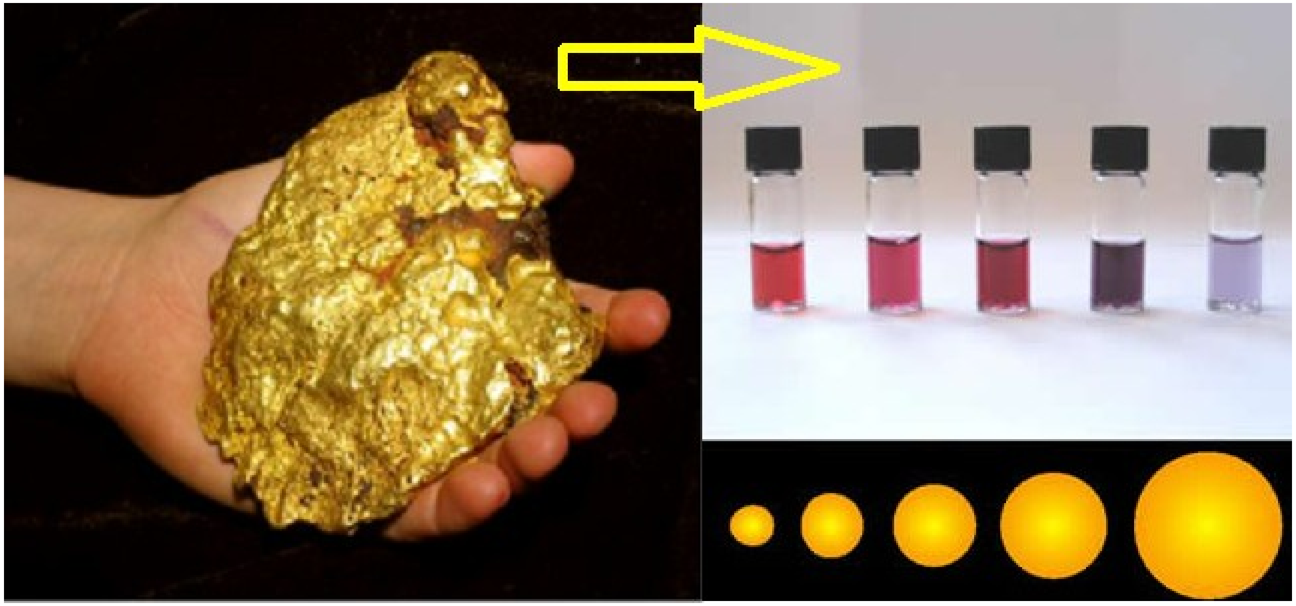
Overview

- 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



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



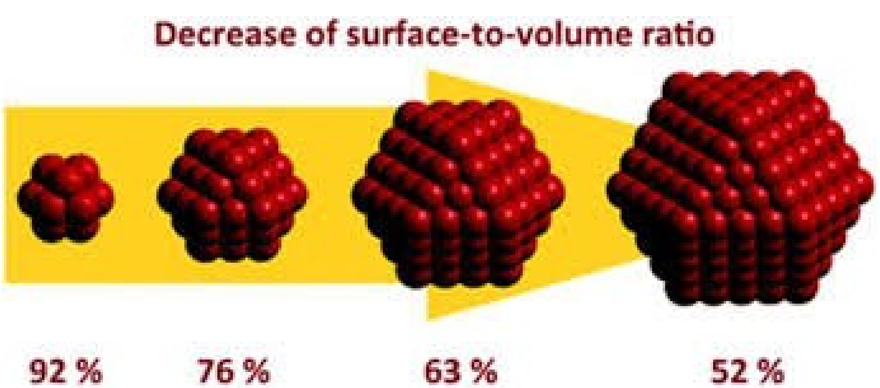
Physical properties of nanomaterials

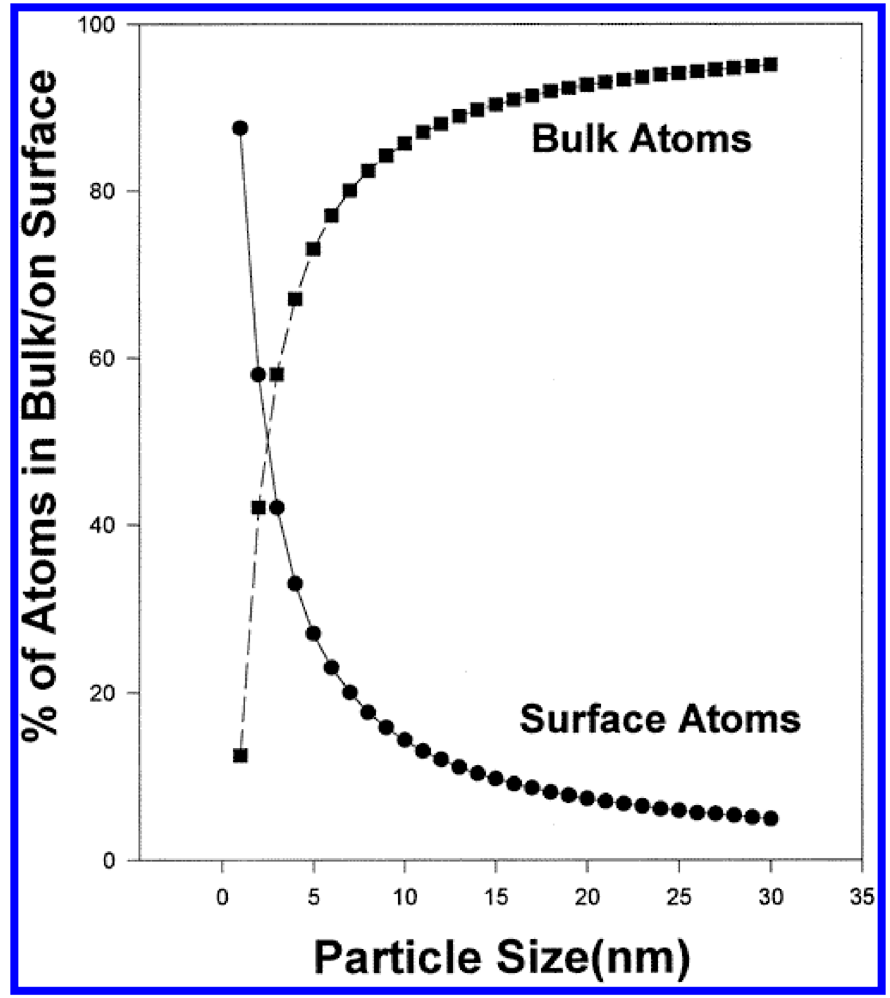
- significantly lower melting point or phase transition temperature
  - due to a huge fraction of surface atoms in the total amount of atoms
- mechanical properties may reach the theoretical strength
  - 1 or 2 orders of magnitude higher than that of single crystals in the bulk form
  - enhancement in 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
  - interparticle tunneling
  - proximity effects
  - high probability of defect-free crystals



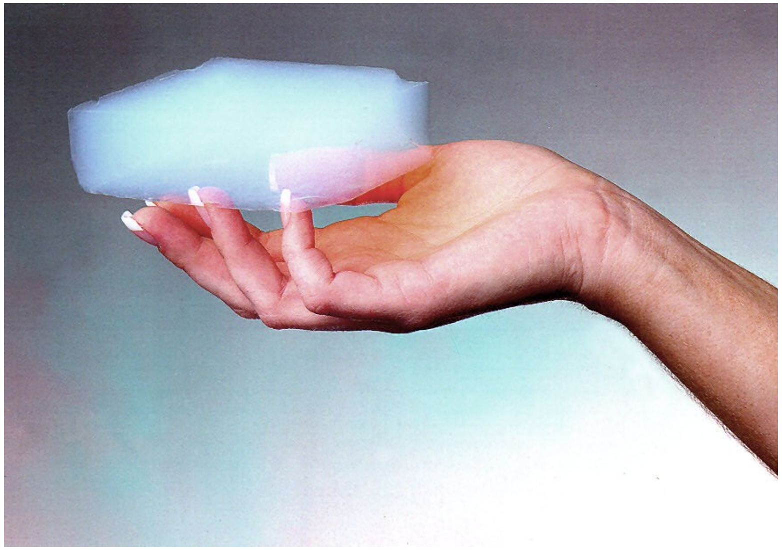


Nanostructures

- 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

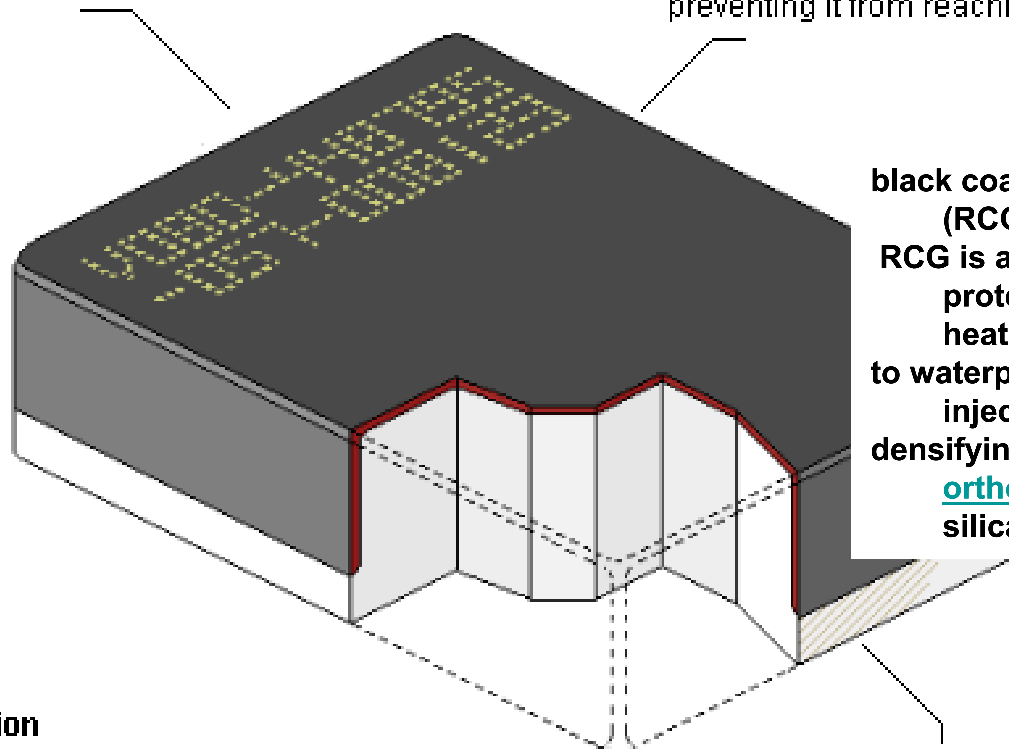
- manufactured material with the lowest bulk density of any known porous solid
- derived from a gel in which the liquid component of the gel has been replaced with a gas
- produced by extracting the liquid component of a gel through supercritical drying
- this allows the liquid to be slowly drawn off 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

dentification 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.

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



- 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

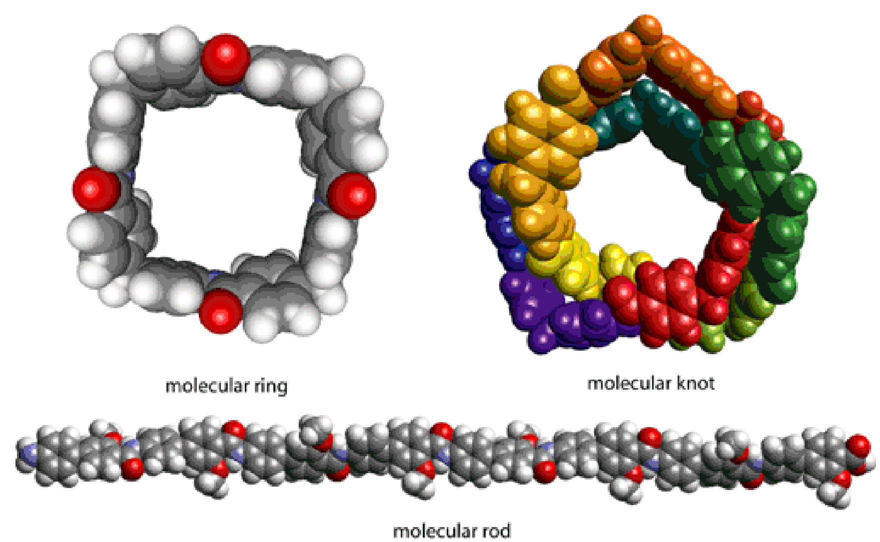
Composition
90% air, 10% silica fibers a few milimeters thick. The tiles feels similar to plastic foam.
The silica fibers are derived from high-quality sand.

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

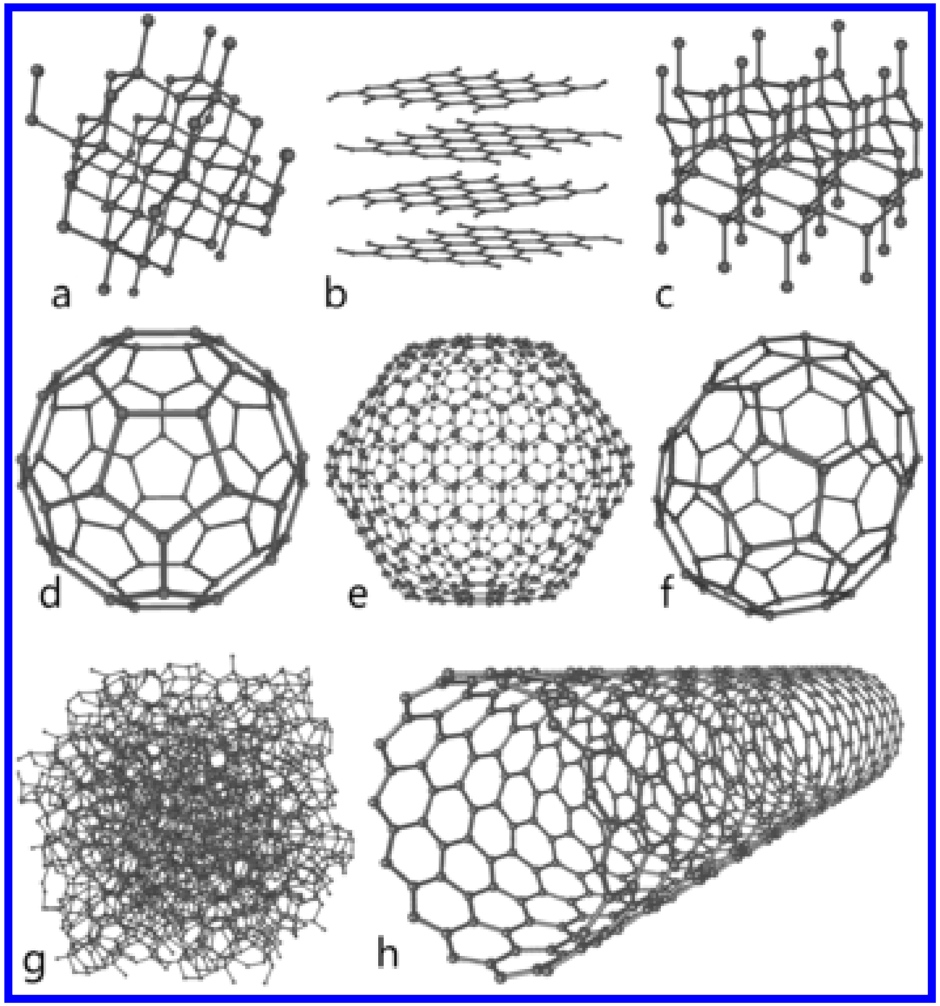
- molecular structures and functional complexes
- DNA templating
- synthetic biology – synthetic biomacromolecules
- liposomes and novel cellular structures

- … not exactly our field



Nanocarbon

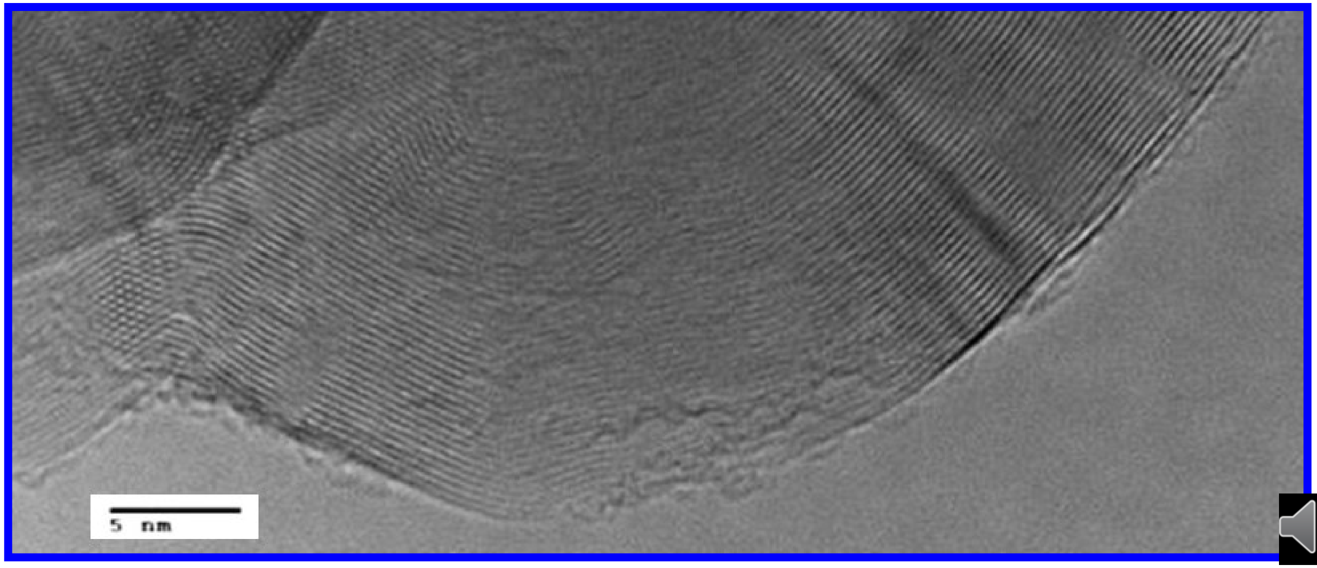
- carbon nanotubes - single (SWNT) and multiwalled (MWNT)
- graphene
- carbon nanospheres
- nanodiamonds



Composite materials

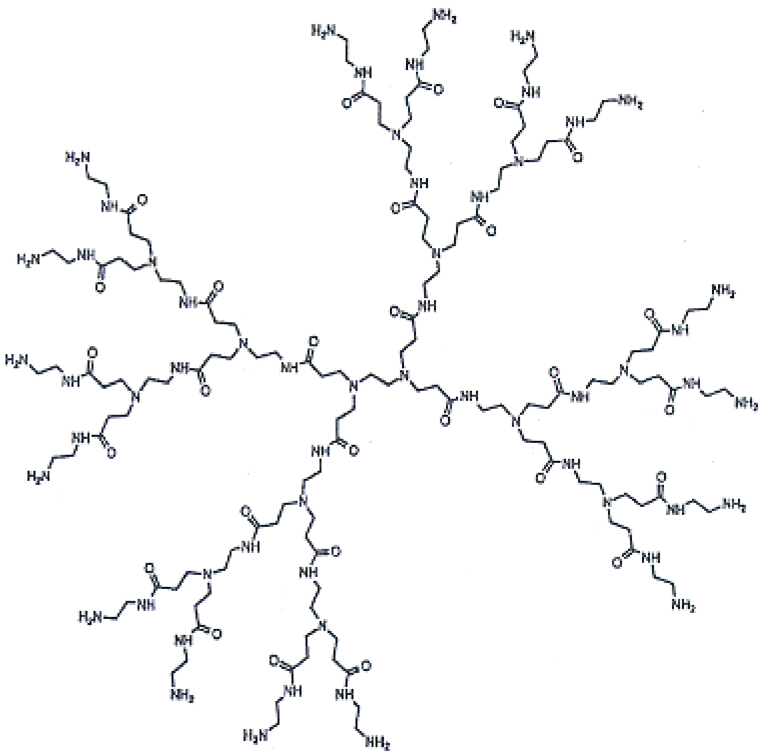
- **carbon nanofibers (CNFs) - vapor grown carbon fibers (VGCFs) or nanofibers (VGCNFs) are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates**

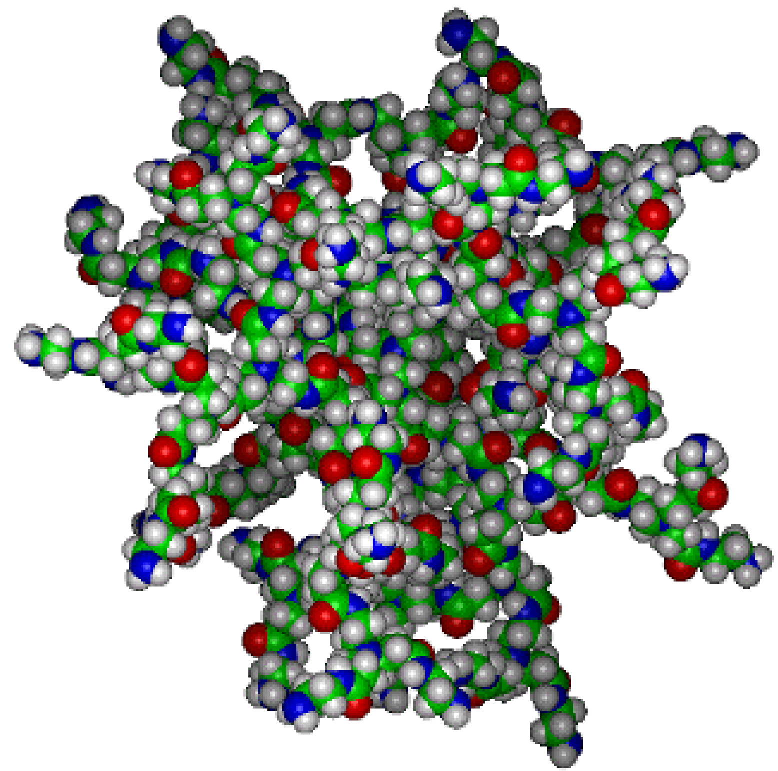
- **nano-onion structure observed in nanospheres, and annealed carbon black (soot)**
- **it is thought that the extended nanostructure forms by wrapping of graphene over a fullerene seed-like nanostructure**



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

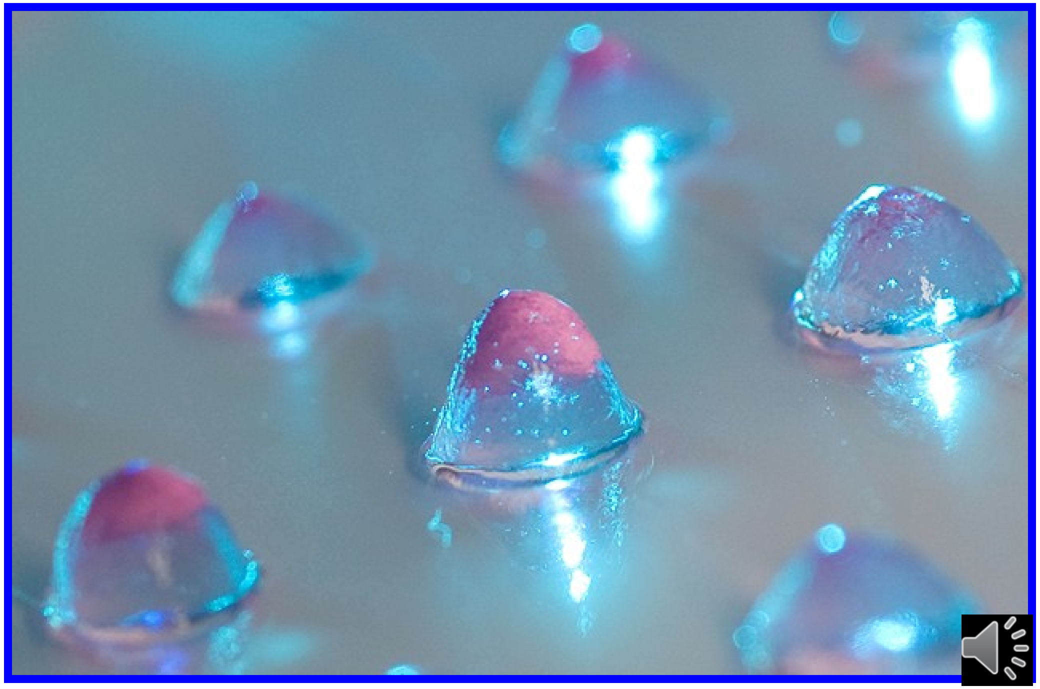
Nanoglass coatings

- 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’

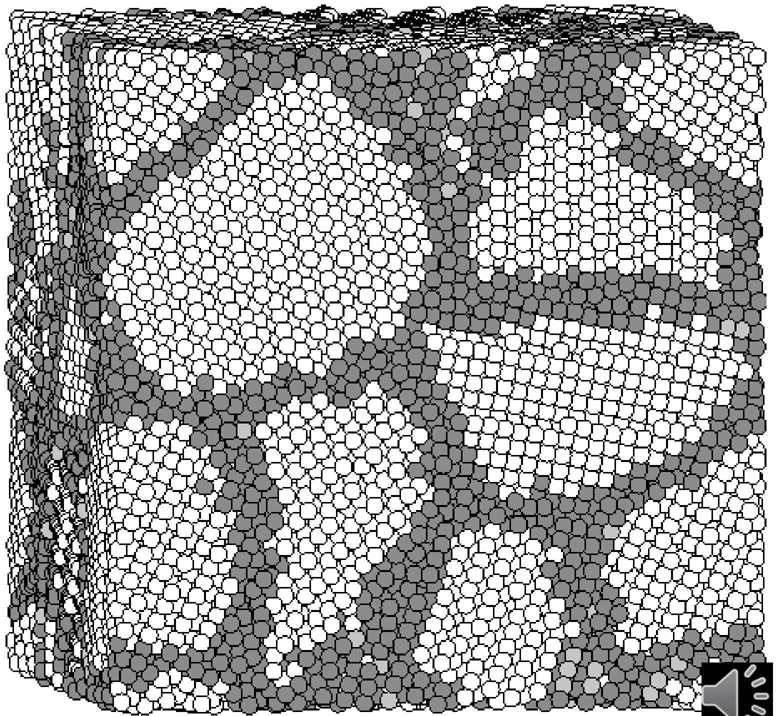
- novel biomaterial with surprising antibacterial properties that can be injected as a low-viscosity gel into a wound where it rigidifies nearly on contact
- delivering a targeted payload of cells and antibiotics to repair the damaged tissue
- (Univ. Delaware)



Metals and alloys

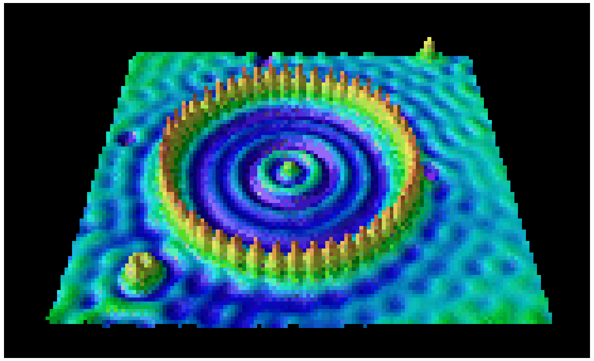
- **grain boundary engineering - high performance alloys**
- **careful control chemistry / processing**
- **increase strength / stiffness, fatigue**

- **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

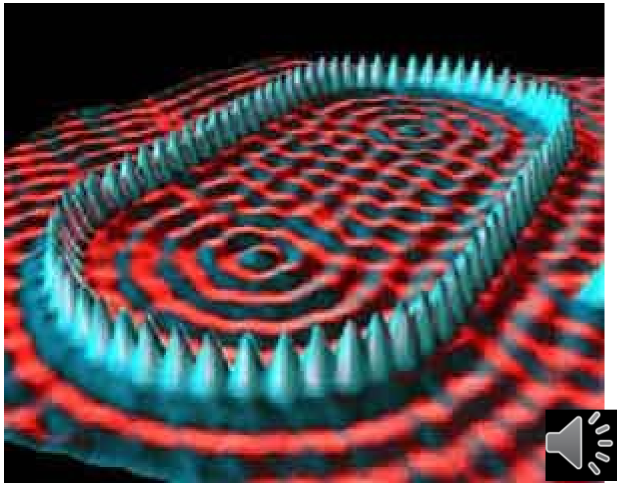


Nanomagnetic materials

- **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**

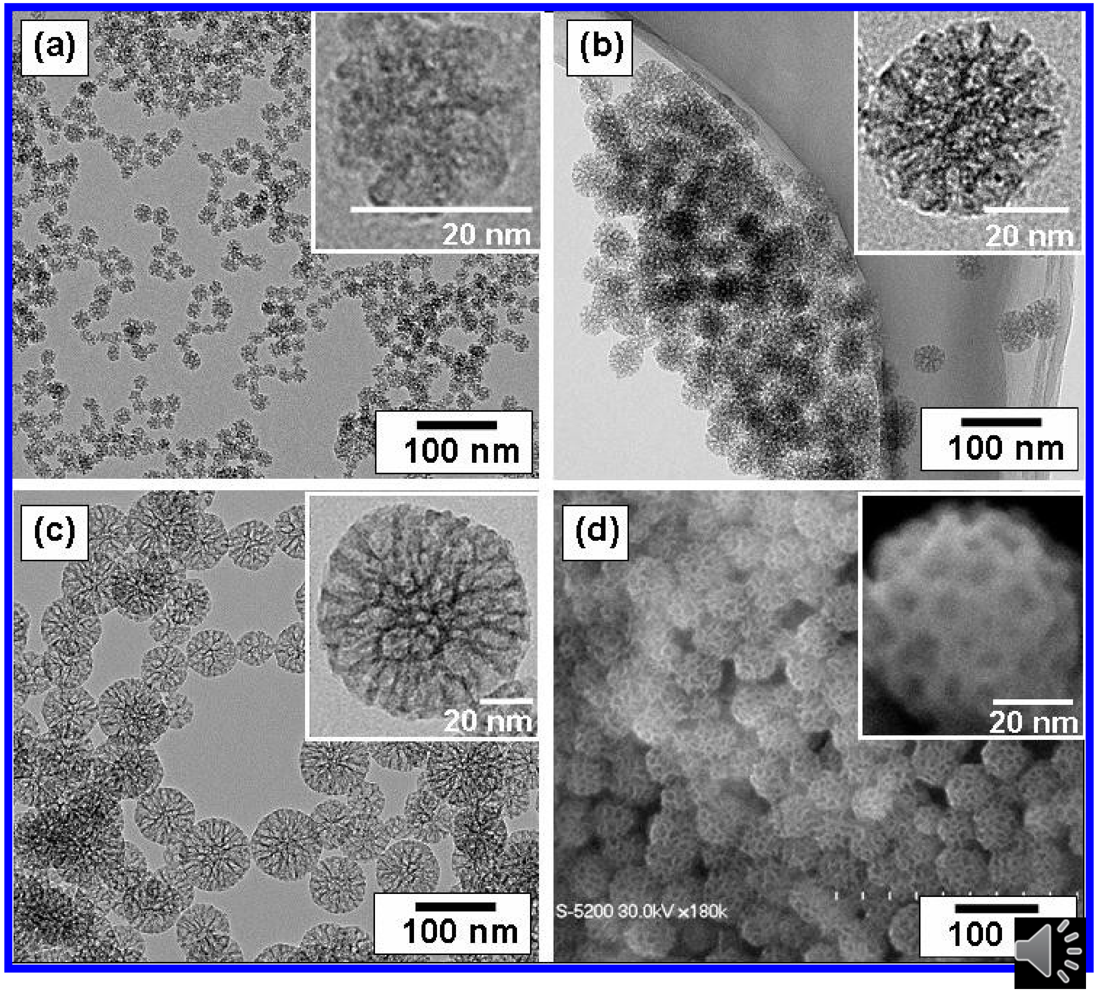


- magnetic force microscopy (MFM) imaging of novel nanomaterials
- magnetic structure of a quantum “corral”, which consists of magnetic iron atoms deposited on a copper surface that "corral" copper electrons



Nanoparticles

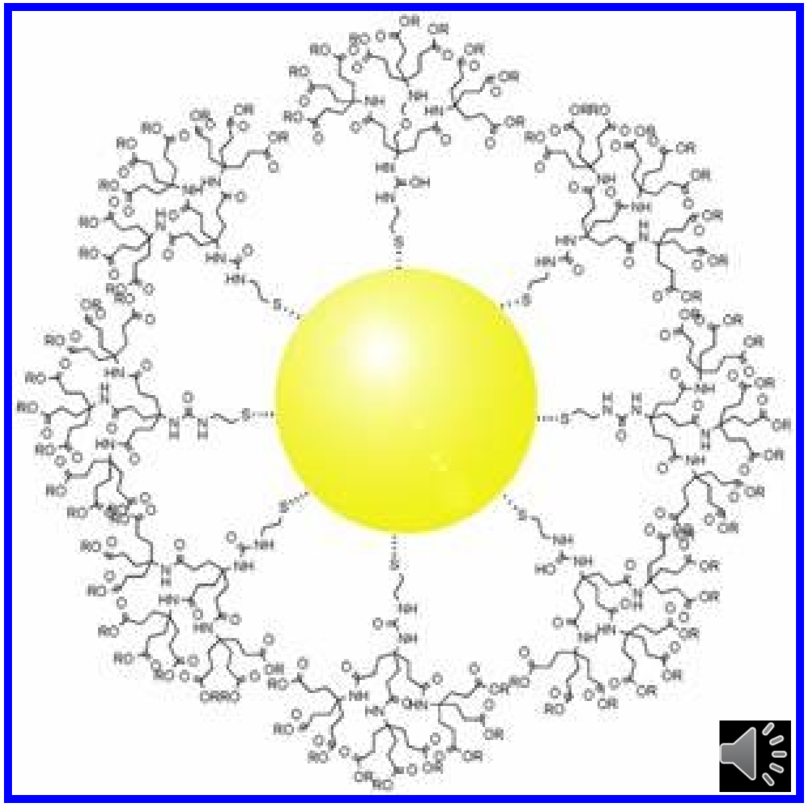
- in nanotech, particle is defined as a small object that behaves as a whole unit in terms of its transport and properties
- particles are further classified according to size
- coarse - between 10,000 and 2,500 nm
- fine - 2,500 to 100 nm
- ultrafine particles, or nanoparticles 100 to 1 nn



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

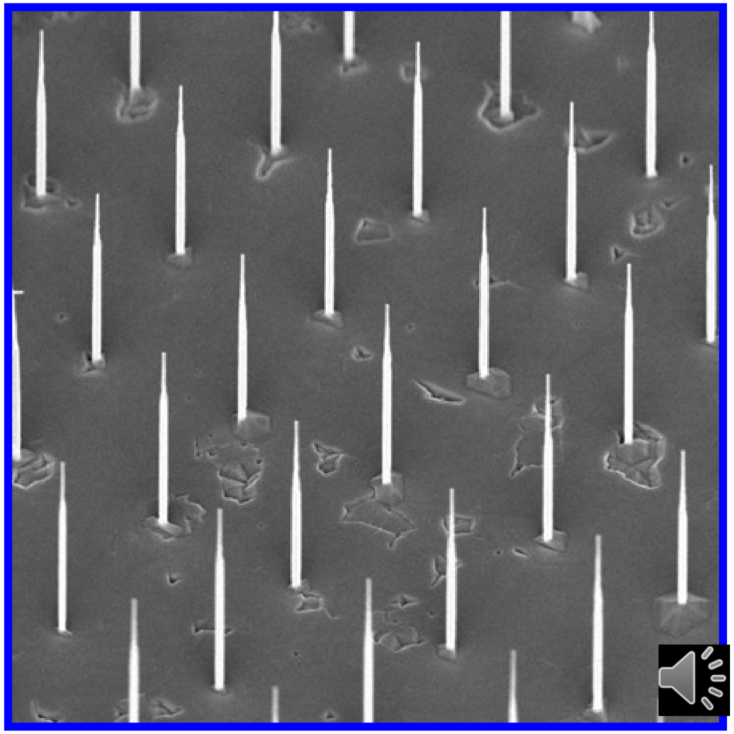
- **high surface area**
- **tailored surface chemistry**
- **added to bulk / composite materials**
- **metal, ceramic, or polymer**
- **can also be ‘powder-like’**



- **dendron conjugated gold nanoparticle**

Nanowires

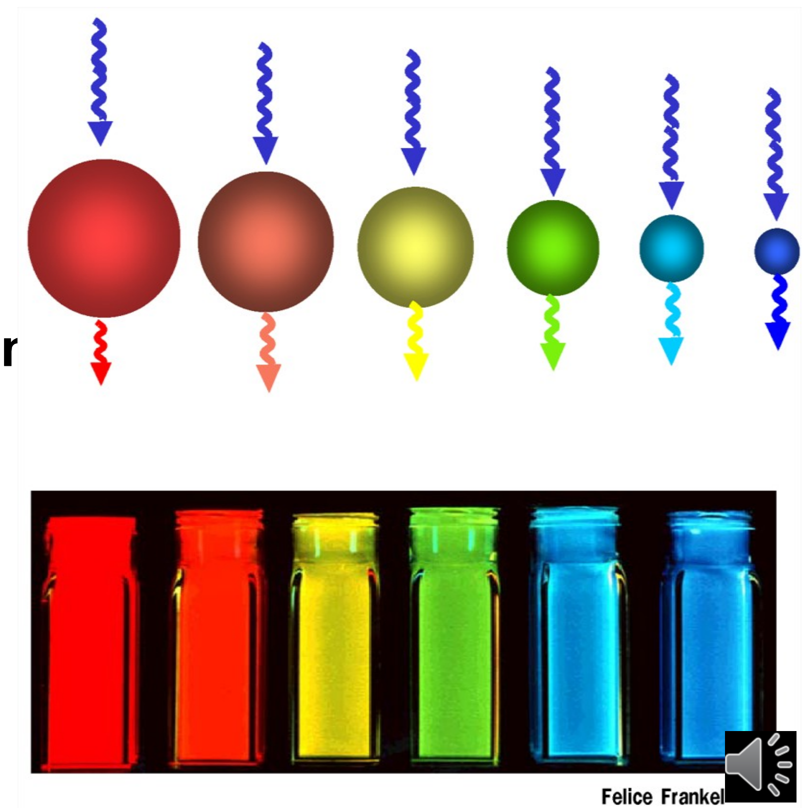
- nanowire is a nanostructure, with the diameter of the order of a nanometer
- alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length
- at these scales, quantum mechanical effects are important - "quantum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



- image width, 5 um

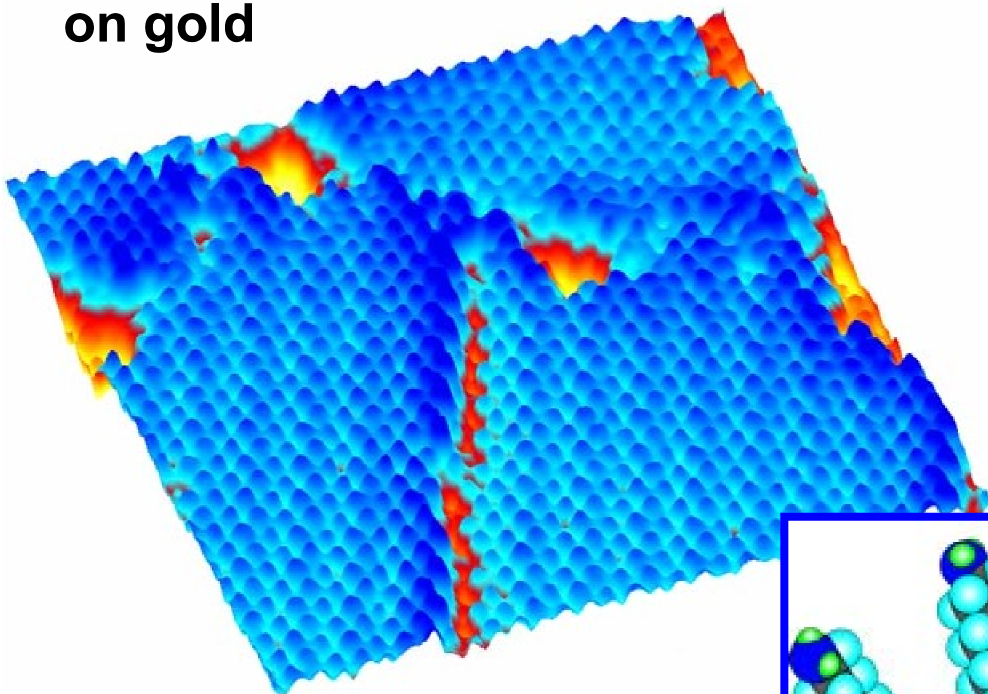
Quantum dots (QD)

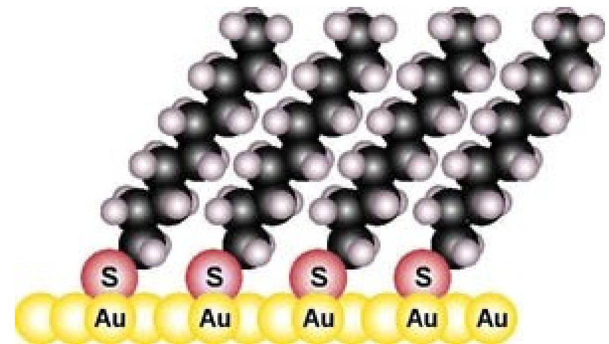
- QD is a portion of matter (e.g. semiconductor) whose excitons are confined in all three spatial dimensions
- electronic properties intermediate between bulk semiconductors and discrete molecules
- QD are semiconductors whose electronic properties are closely related to the size and shape of the individual 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

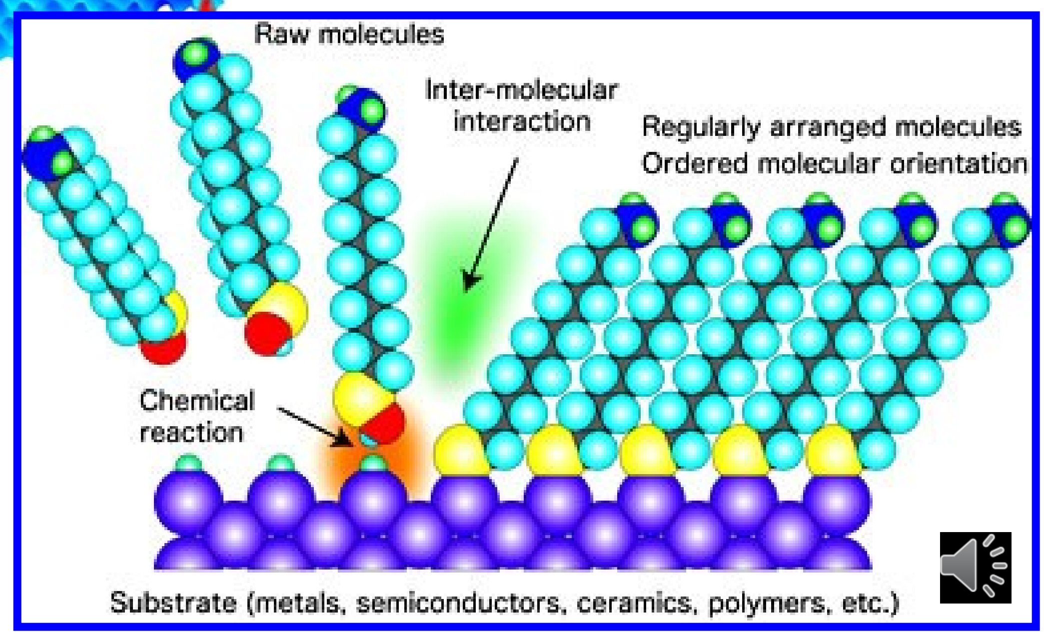


Self assembled monolayers (SAMs)

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

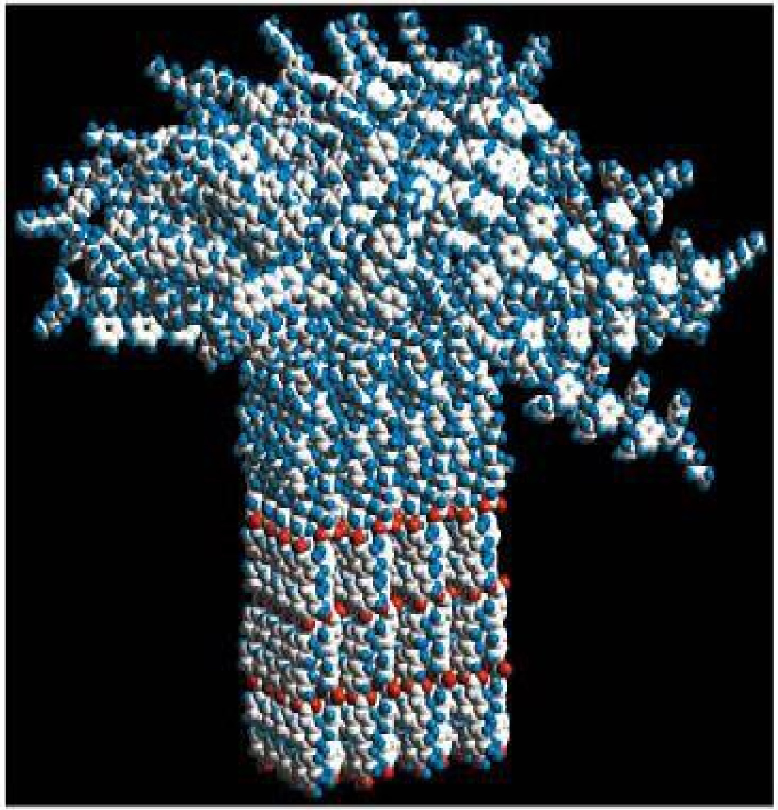


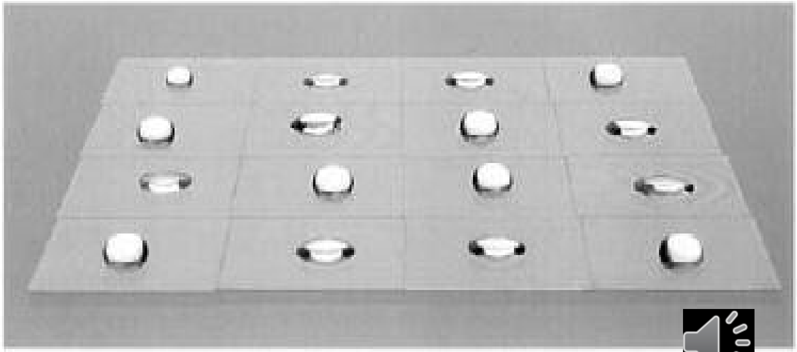




Self-assembly

- **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**



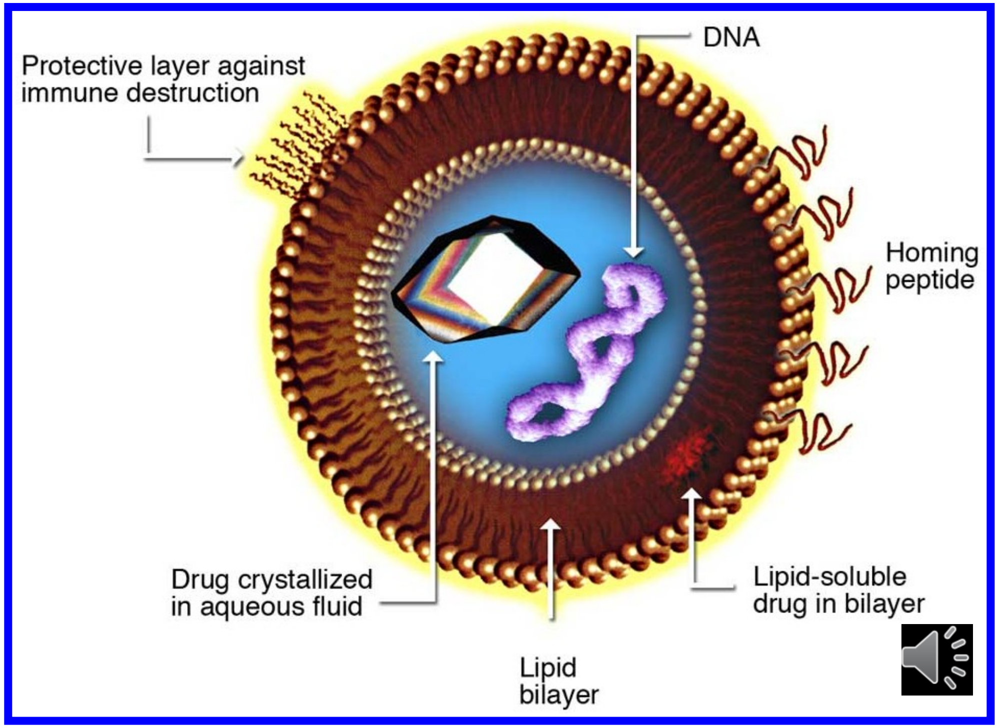


molecular model (top) of a self-assembled "mushroom"
photograph (bottom) shows control of surface wetting by a layer of these mushrooms

Liposomes

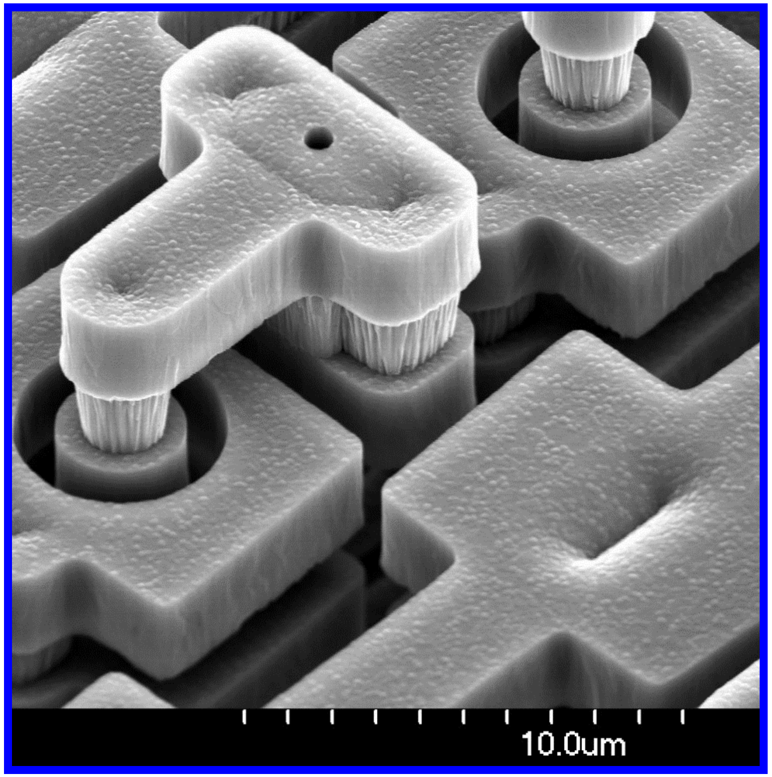
- artificial composite structures made of phospholipid bilayer and may contain small amounts of other molecules
- vary in size from low micrometer range to tens of micrometers
- unilamellar liposomes (shown) are typically in the lower size range with various targeting ligands attached to their surface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

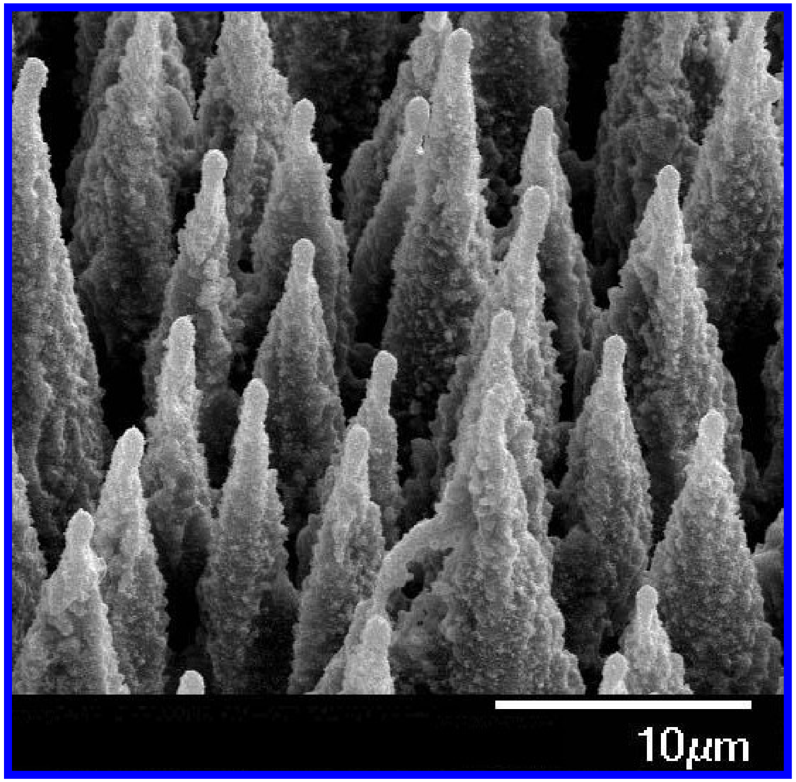
- disrupting biological membranes – sonication
- from natural phospholipids with mixed lipid chains (e.g. egg phosphatidylethanolamine) or other synthetic surfactants
- should not be confused with micelles and reverse micelles composed of monolayers



Silicon structures / materials

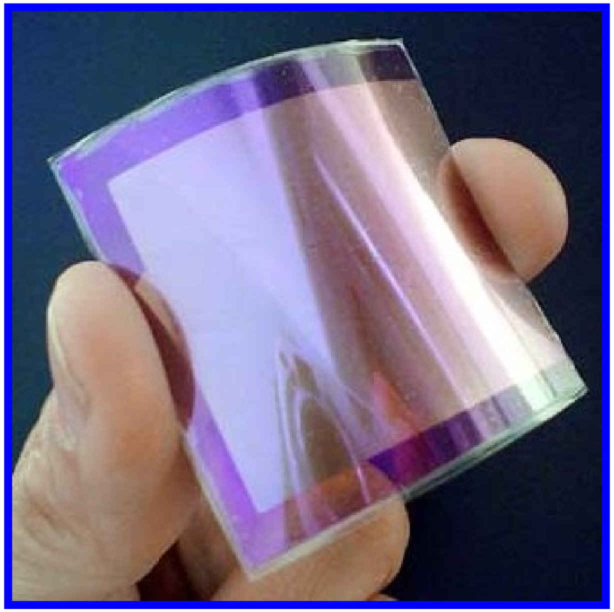
- wafers
- MEMS
- LOC
- biomimetic structures

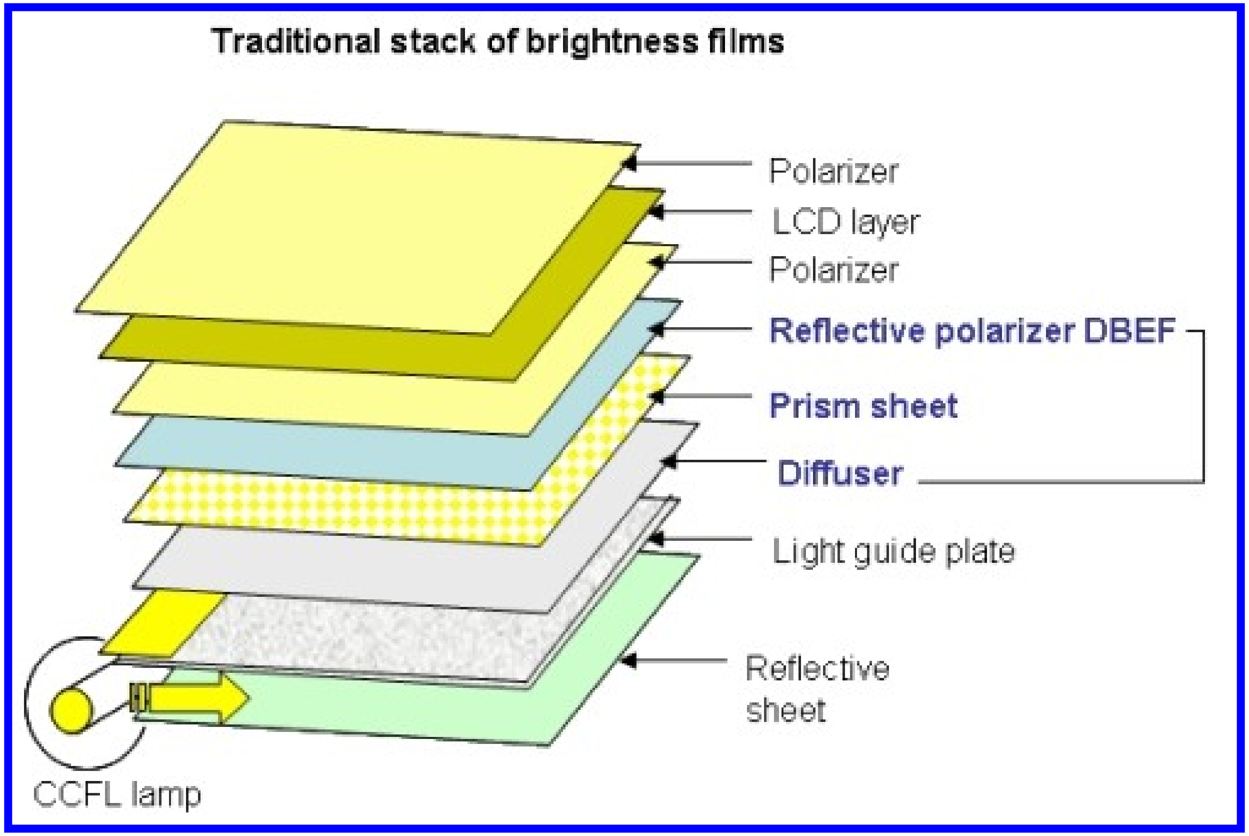




Thin films

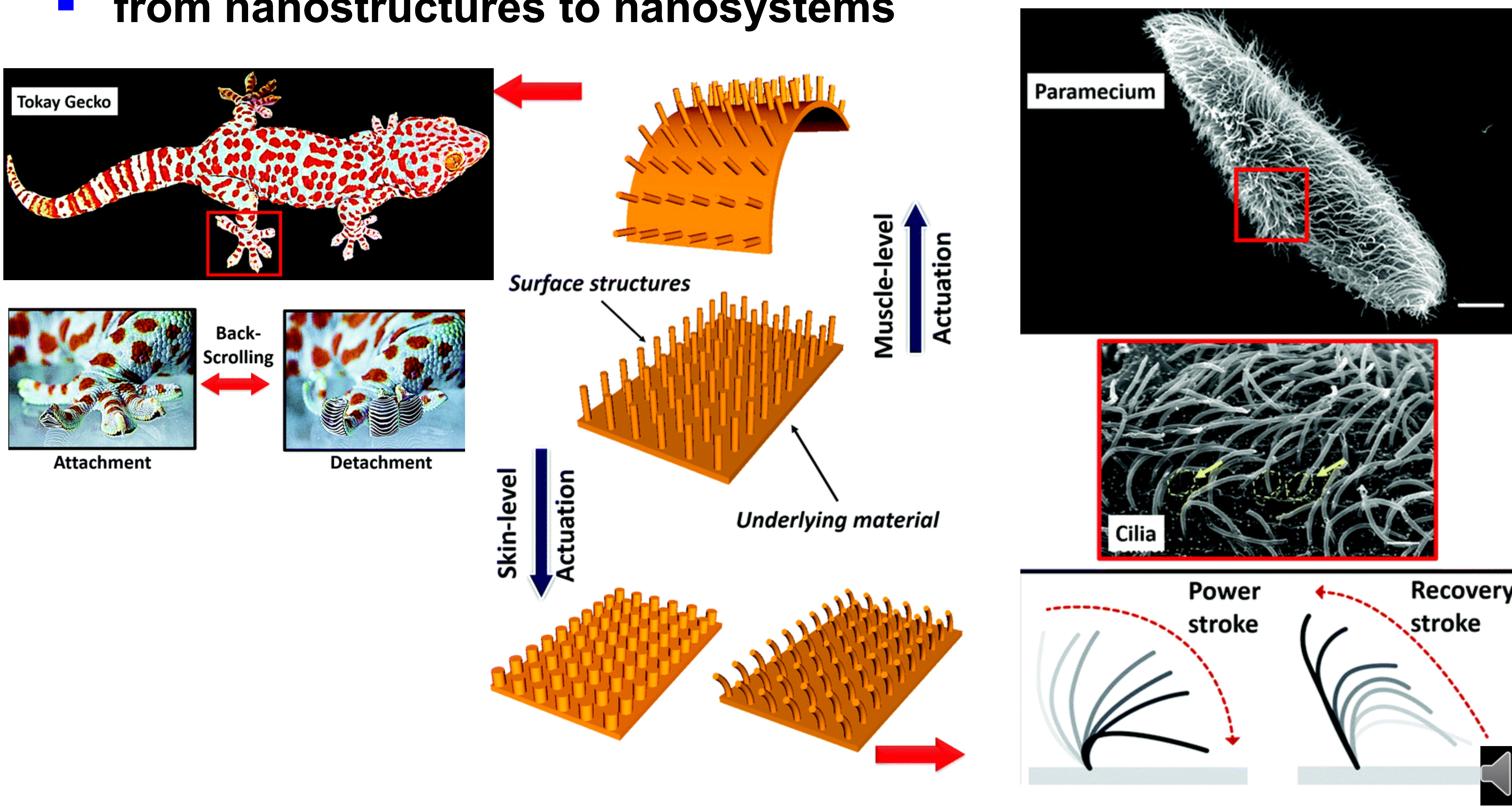
- physical coatings
- layered stacks
- deposited films
- functionalized (SAMs)
- magnetic and optical applications
- metallization in silicon semiconductors





Biomimetic structures

- learning from nature
- using shape as well as chemistry
- some similar function (light gathering, sensing/detection, etc.
- from nanostructures to nanosystems



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 (CBD and MOCVD)
  - 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, or**
- ***the top-down approach*: whereby structures are etched into bulk materials such as silicon. This approach represents how silicon chips are fabricated**

- **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?