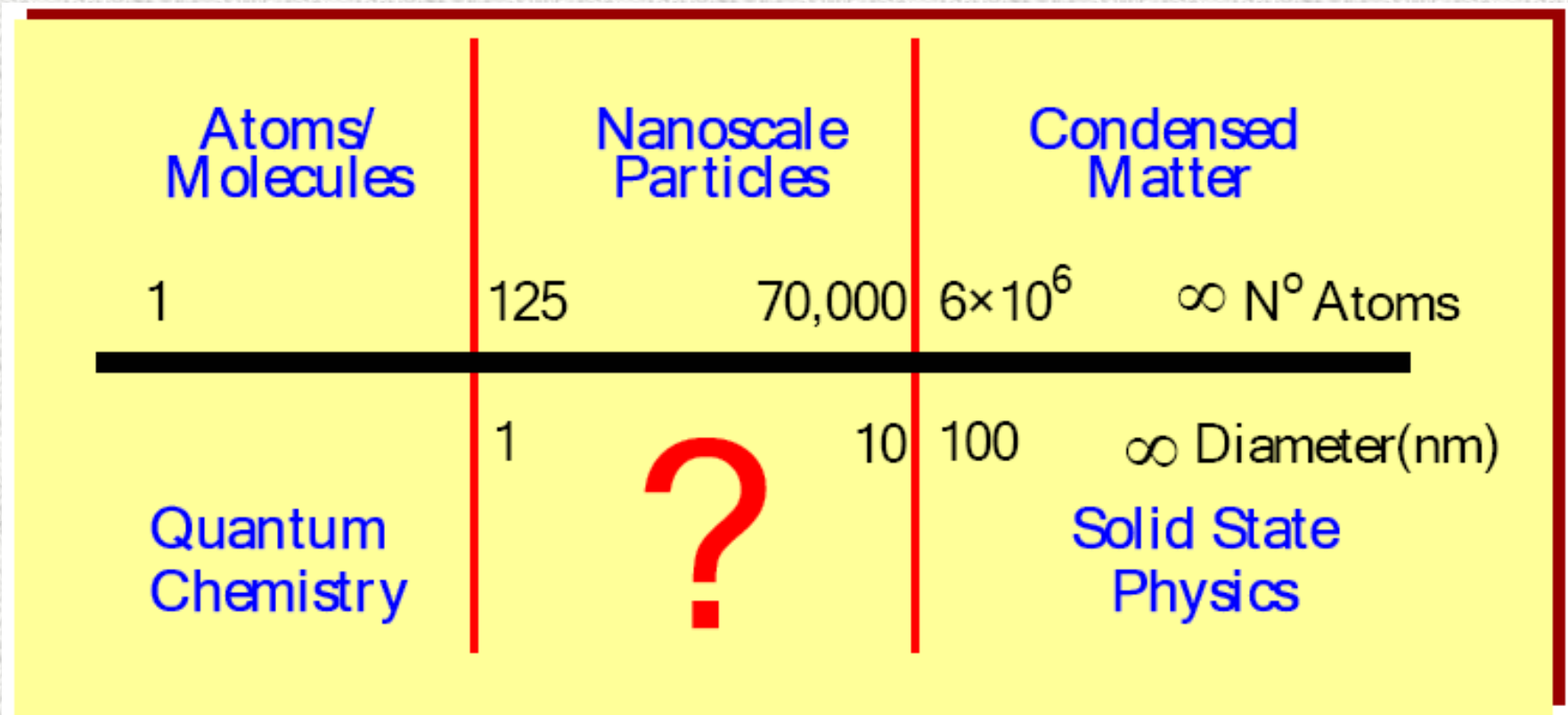


Nanoscopic Materials



Nanostructural Materials

“Prey”, the latest novel by Michael Crichton, author of “Jurassic Park”.

The horrible beasts threatening humanity in this new thriller are not giant dinosaurs, but swarms of minute “nanobots” that can invade and take control of human bodies.

Last summer, a report issued by a Canadian environmental body called the action group on erosion, technology and concentration took a swipe at nanotechnology. It urged a ban on the manufacture of new nanomaterials until their environmental impact had been assessed. The group is better known for successfully campaigning against biotechnology, and especially against genetically modified crops.

The research, led by a group at the National Aeronautics and Space Administration's Johnson Space Centre in Houston, has found in preliminary studies that inhaling vast amounts of nanotubes is dangerous. Since they are, in essence, a form of soot, this is not surprising. But as most applications embed nanotubes in other materials, they pose little risk in reality.

Room at the Bottom

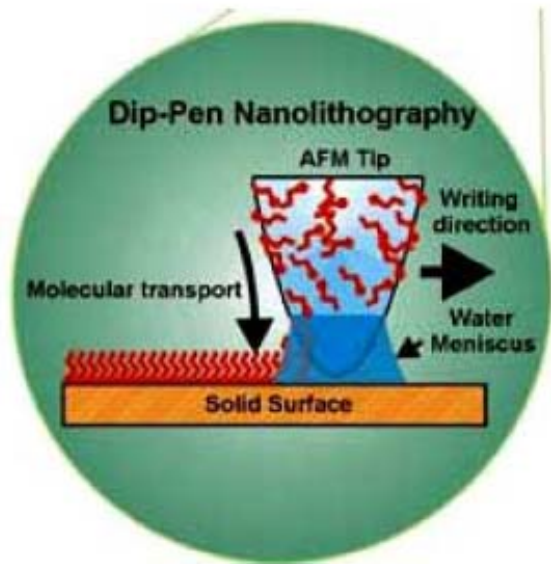
What I want to talk about is the problem of **manipulating and controlling things on a small scale ...**

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It's a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.....

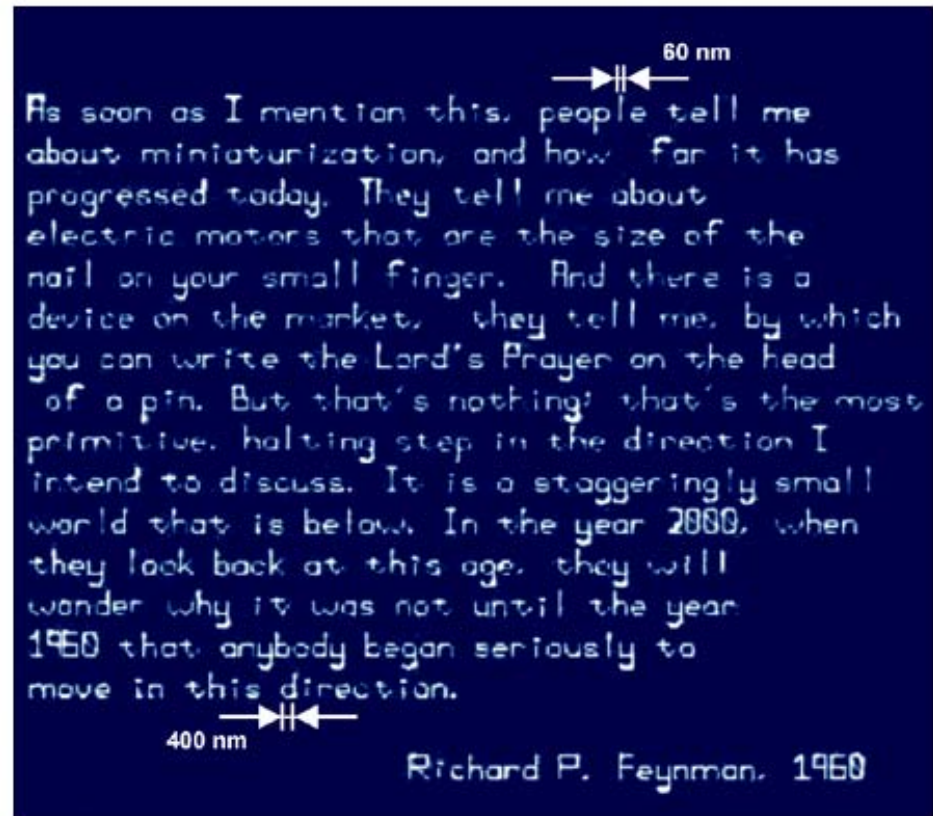


Prof. Richard Feynman in "There's plenty of room at the bottom", lecture delivered at the annual meeting of the APS, Caltech, 29 December, 1959.

Nanoscale Writing



Nanoscale writing with an AFM (Mirkin et al.)



Nanoscopic Materials

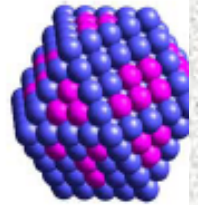
How big is nano?



~ 10 million times
smaller



~ 10 million times
smaller



d = 10 nm

What Changes?

Size is another variable to change physical and chemical properties

Nanoscopic Materials

Negligible light scattering - New optics

Quantum size effects - Information technology, Storage media

High surface area - Catalysts, Adsorbents

Large interfacial area - New composites

Surface modifications - Targeted drug delivery

Nanoscopic Materials

Nanoscale regime

Size 1 – 100 nm (traditional materials > 1 μm)

Physical and chemical properties depend on the size !!

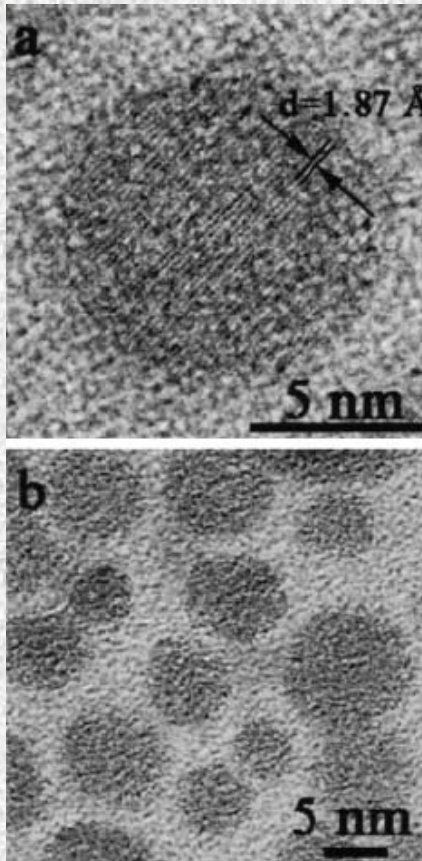
Natural examples:

- ☉ **Human teeth, 1-2 nm fibrils of hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ + collagen**
- ☉ **Asbestos, opals, calcidon**
- ☉ **Primitive meteorites, 5 nm C or SiC, early age of the Solar system**

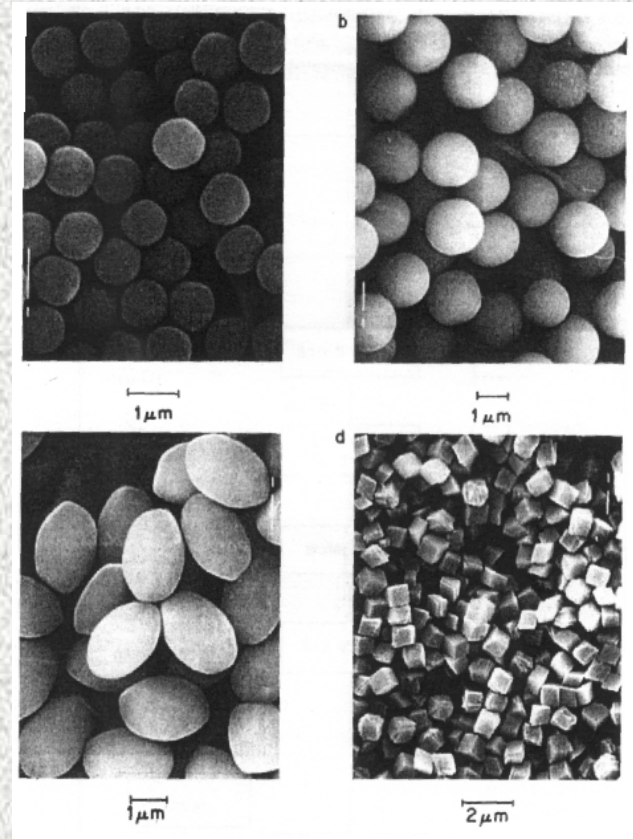
Nanoscale objects have been around us, but only now we can observe them, manipulate and synthesize them.

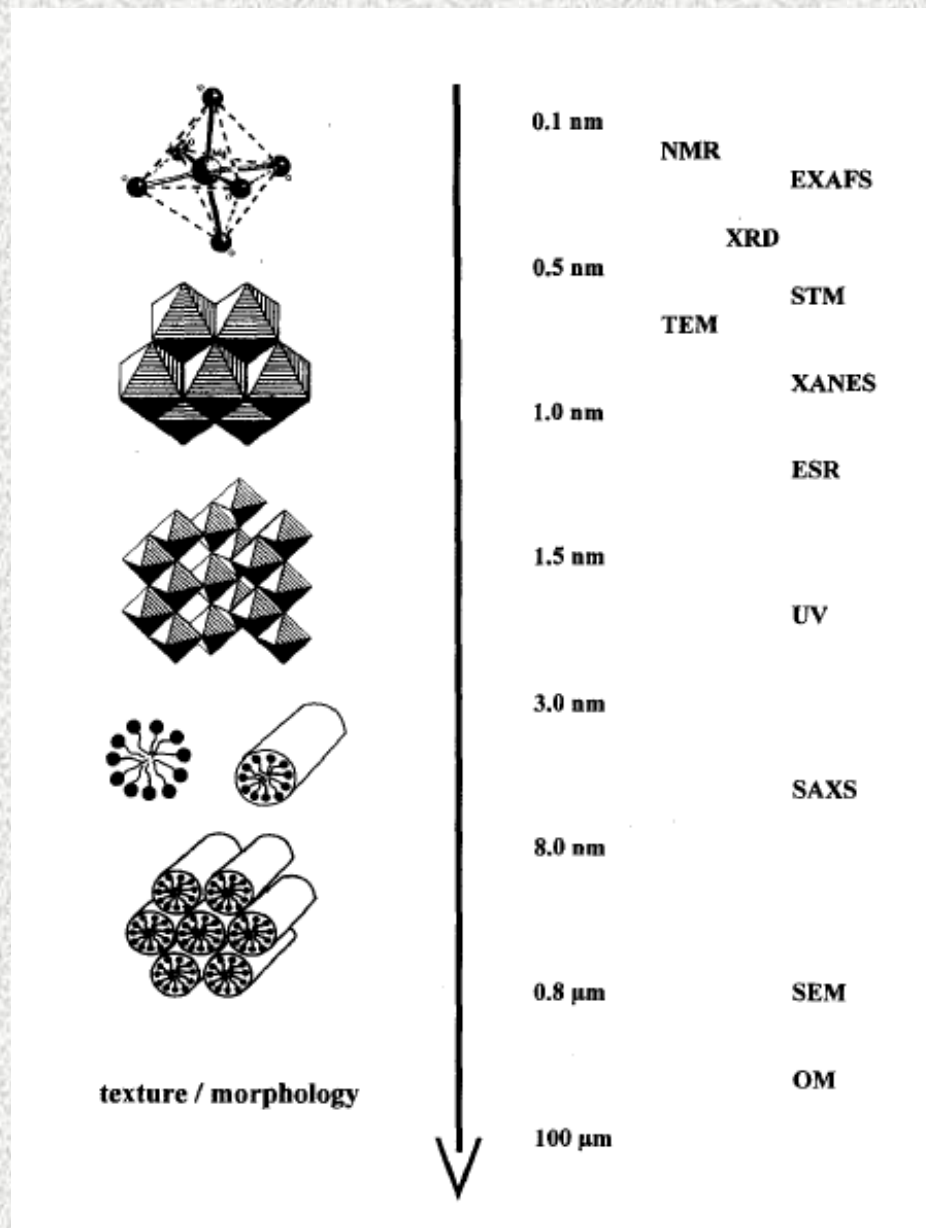
Nanoscopic Materials

Nanoparticles 1 – 100 nm



Traditional materials $> 1 \mu\text{m}$



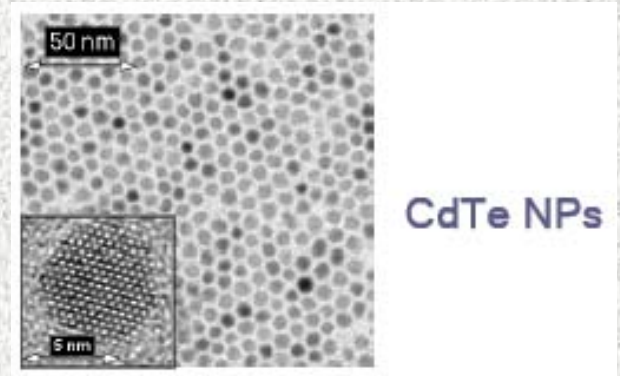


The nano-Family

At least one dimension is between 1 - 100 nm

0-D structures (3-D confinement):

- Quantum dots
- Nanoparticles

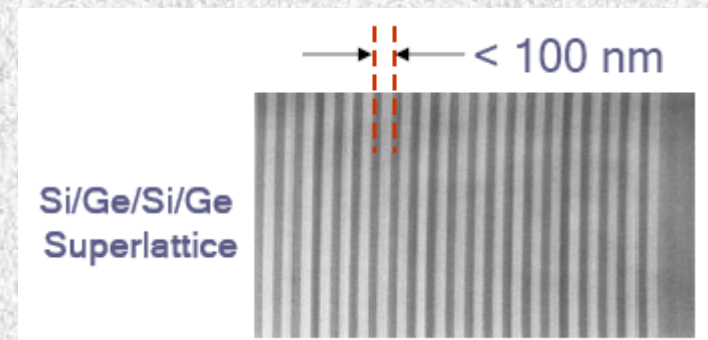


1-D structures (2-D confinement):

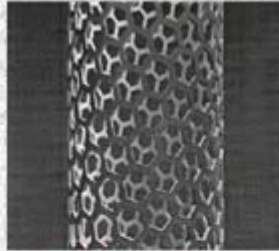
- Nanowires
- Nanorods
- Nanotubes

2-D structures (1-D confinement):

- Thin films
- Planar quantum wells
- Superlattices



CARBON NANOTUBES



A single-shell nanotube image
(Source from Dr. P. M. Ajayan)



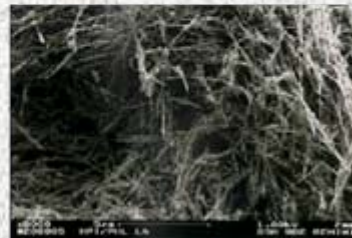
A multi-shell nanotube image
(Ebbesen, T. W., 1994.
Annu. Rev. Mater. Sci. 24:235-64.
courtesy of NEC/Handa)

1. A unique species somewhere between traditional carbon fibers and novel forms of carbon such as fullerenes.
2. A seamless cylindrical sheet of graphite whose diameter is so small and its aspect ratio (diameter vs. length) is so great that it can be considered from the electronic point of view as a one-dimensional structure.

There are two sorts of carbon nanotubes. One is multi-shell nanotubes and the other is single-shell nanotubes. The former have two or more layers such as the left-side figure below and about 2 to 20 nm diameter while the latter have only one layer and about 1 to 2 nm diameter. Both are a few tens of microns long. In multi-shell nanotubes, the inter layer spacing is ~ 0.34 nm. In both cases, each carbon atom is completely bonded to neighboring carbon atoms through sp^2 hybridization to form a seamless shell. In the absence of external strain, carbon nanotubes are always straight unless carbon rings having a number of carbons defiant from six (pentagons, heptagons, octagons, etc.) are present in the hexagonal network.



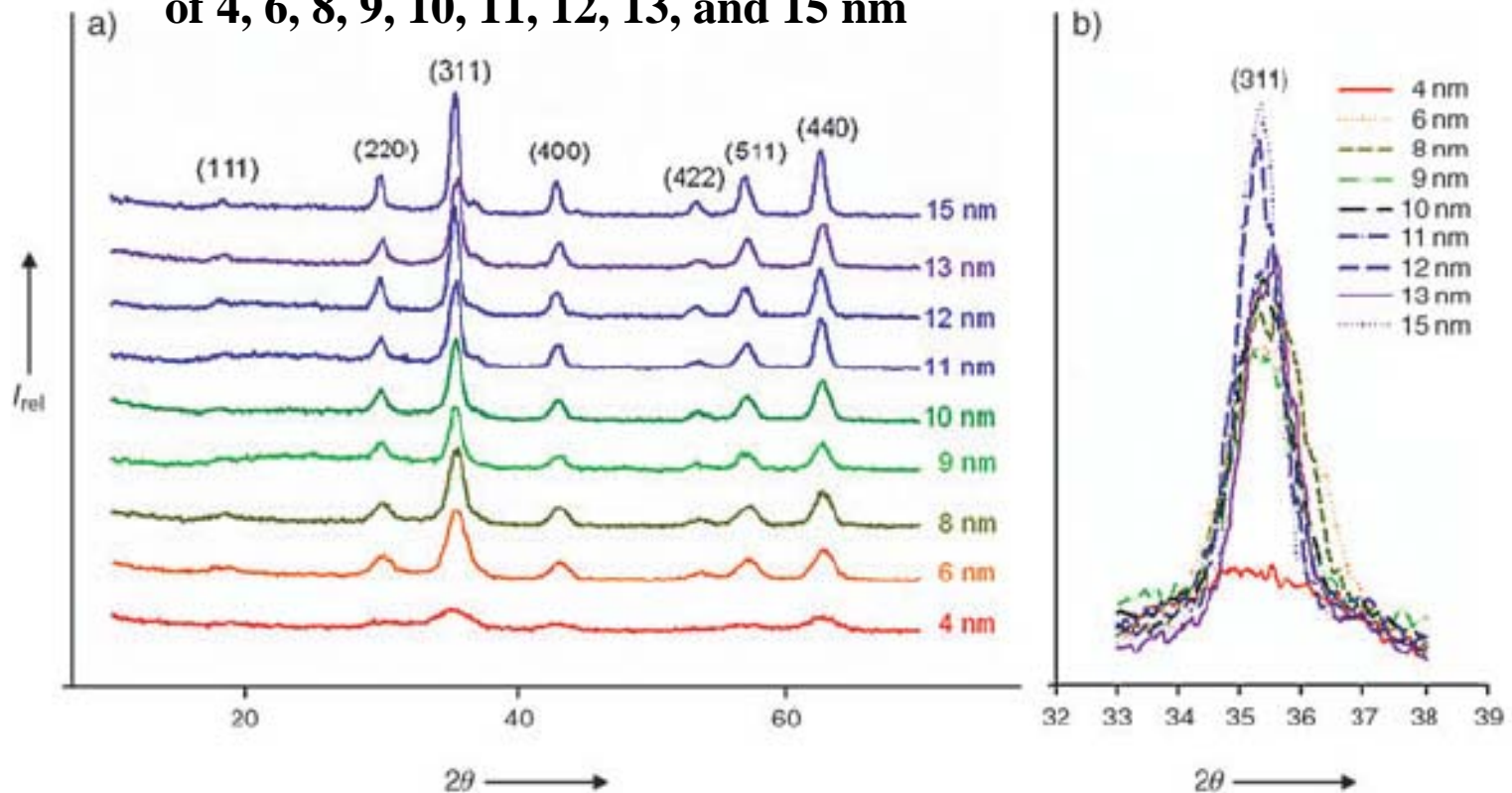
A picture of a typical multi-shell
nanotube taken using TEM
(Source from Dr. P. M. Ajayan)



A SEM image of multi-shell
carbon nanotubes and particles
(Source from Dr. P. M. Ajayan)

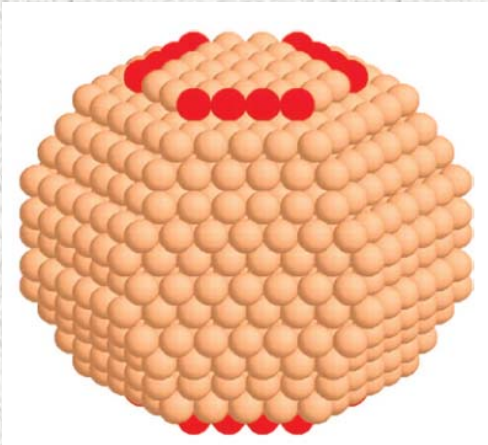
Coherence Length

XRD patterns of iron oxide nanocrystals of 4, 6, 8, 9, 10, 11, 12, 13, and 15 nm

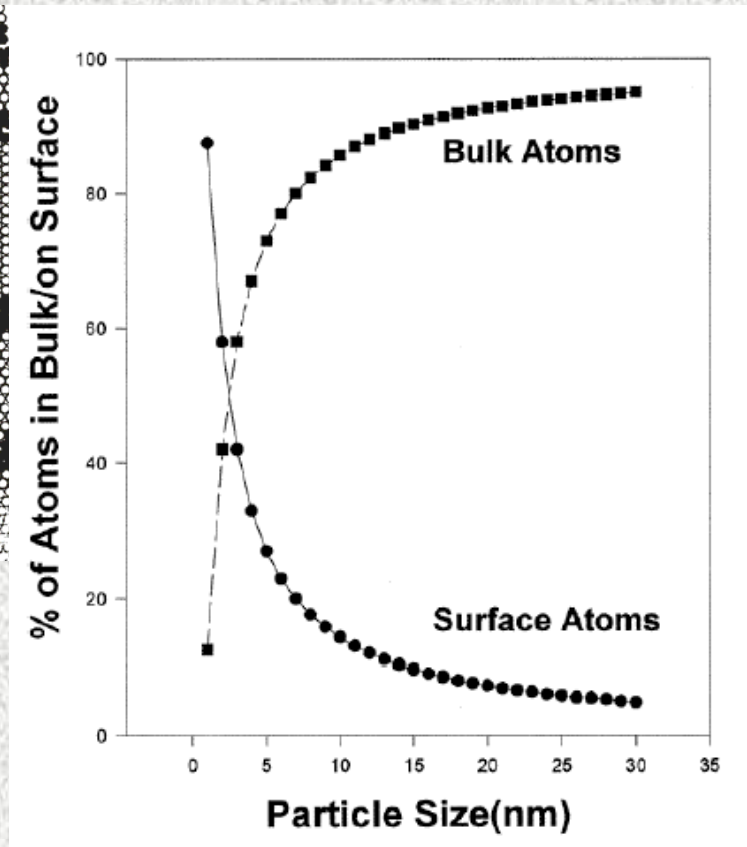
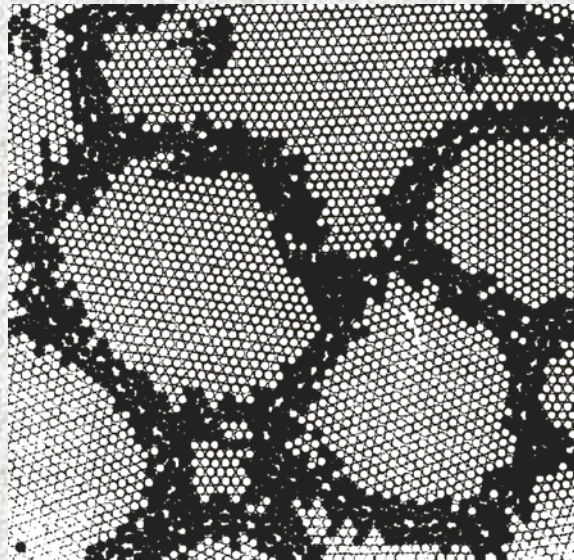


Surface Effects

Decreasing grain size = Increasing volume fraction of grain boundaries (50% for 3 nm particles)



Ru particle
diameter 2.9 nm



Surface Effects

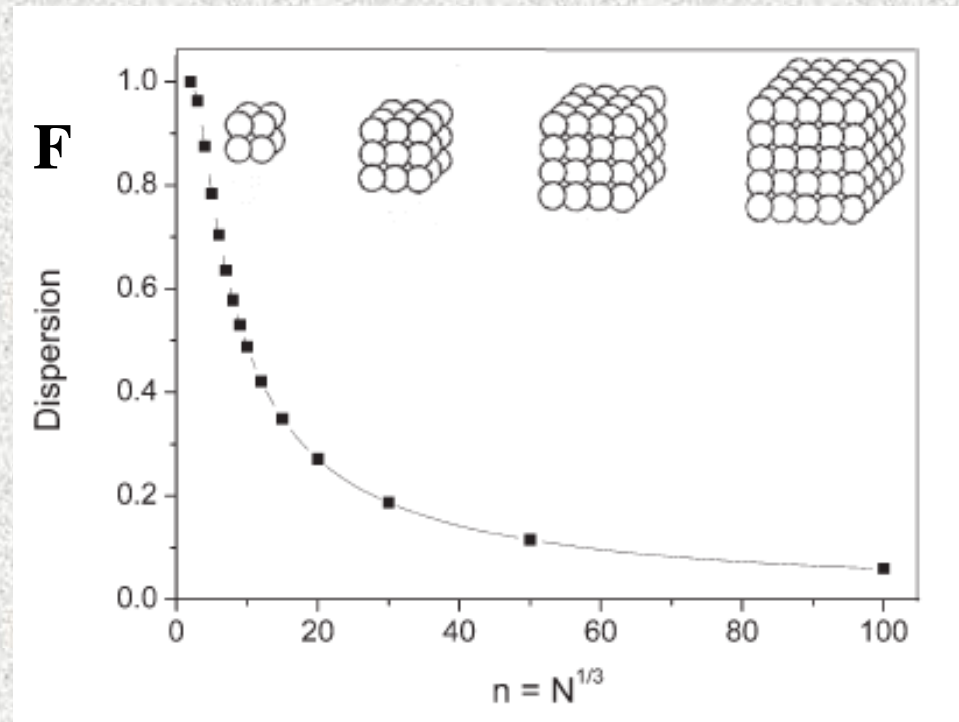
Dispersion F = the fraction of atoms at the surface

F is proportional to surface area divided by volume

N = total number of atoms

$V \sim r^3 \sim N$

$$F \approx \frac{r^2}{r^3} \approx \frac{1}{r} \approx \frac{1}{\sqrt[3]{N}}$$



n = number of atoms at the cube edge

Surface Effects

Properties of grain boundaries

- **Lower coordination number of atoms**
- **Reduced atomic density (by 10 – 30 %)**
- **Broad spectrum of interatomic distances**

Experimental evidence

- **HREM**
- **EXAFS, reduced number of nearest and next-nearest neighbors**
- **Raman spectroscopy**
- **Mössbauer spectroscopy, quadrupole splitting distribution broadened**
- **Diffusivity enhanced by up to 20 orders of magnitude !!**
- **Solute solubility in the boundary region**
 - Ag (fcc) and Fe (bcc) immiscible in (s) or (l), but do form solid solution as nanocrystalline alloy**
- **EPR, nano-Si gives a sharp signal**



Surface Effects

Atoms at surfaces have fewer neighbours than atoms in the bulk

**Lower coordination and unsatisfied bonds
surface atoms are less stabilized than bulk atoms**

The smaller a particle the larger the fraction of atoms at the surface, and the higher the average binding energy per atom

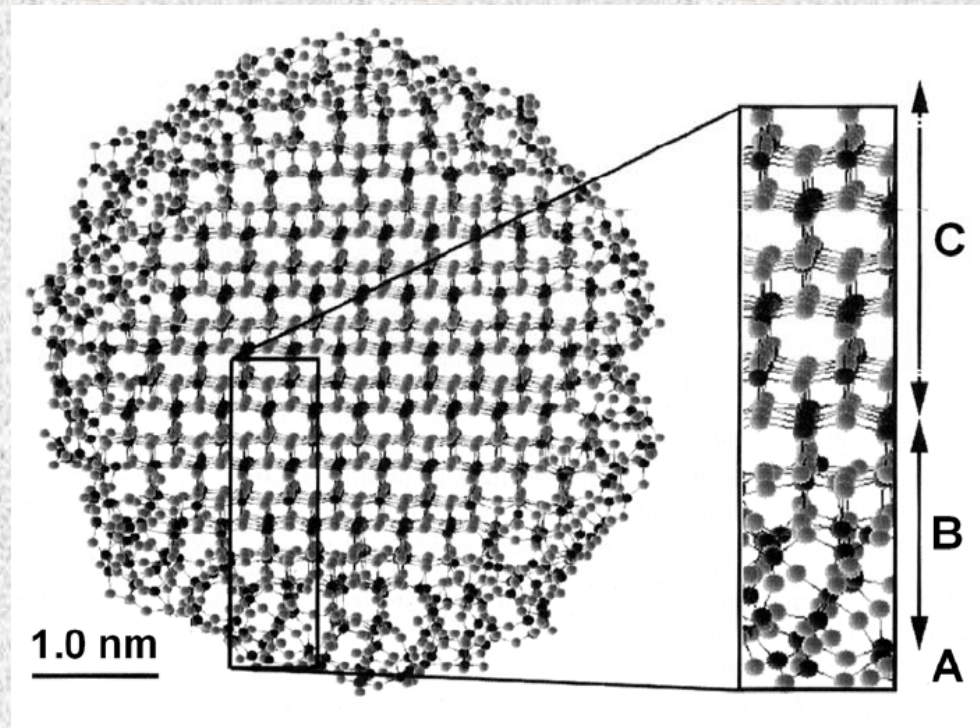
The melting and other phase transition temperatures scale with surface-to-volume ratio and with the inverse size

Example: the melting point depression in nanocrystals

2.5 nm Au particles 930 K

bulk Au 1336 K

Surface Effects



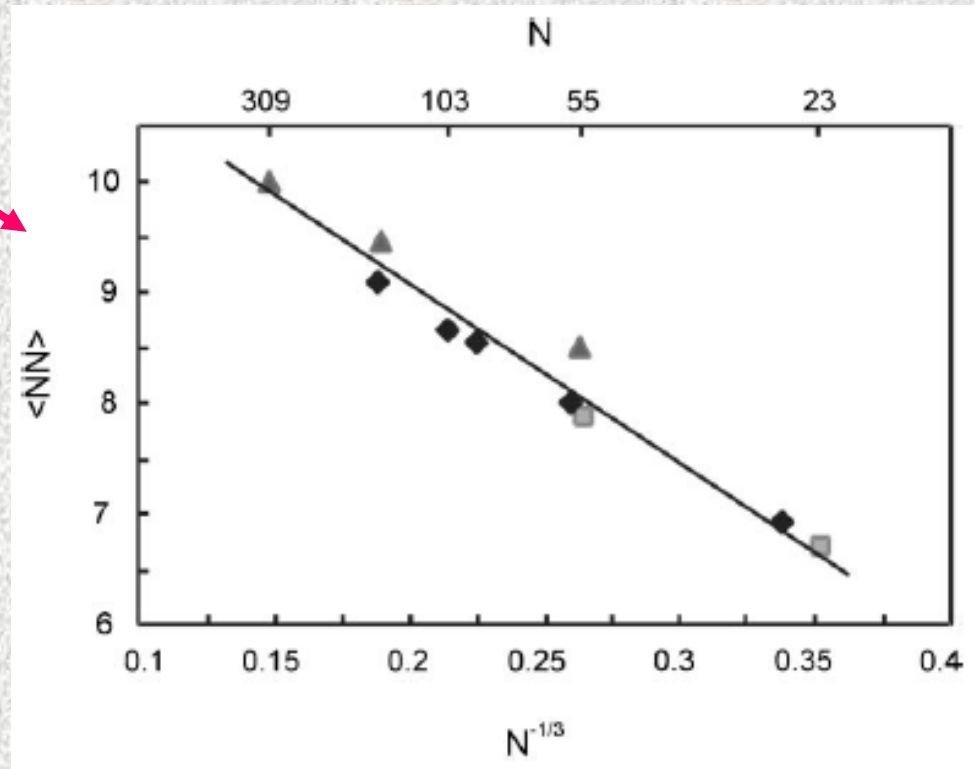
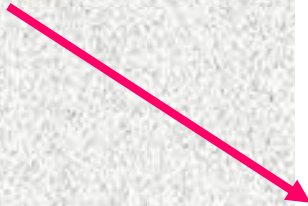
A = Atoms at surfaces (one layer) – fewer neighbours, lower coordination, unsatisfied (dangling) bonds

B = Atoms close to surface (several layers) – deformation of coordination sphere, distorted bond distances and angles

C = Bulk atoms – not present in particles below 2 nm

Surface Effects

coordination number



Calculated mean coordination number $\langle NN \rangle$ as a function of inverse radius, represented by $N^{-1/3}$ for Mg clusters (triangles = icosahedra, squares = decahedra, diamonds = hcp)

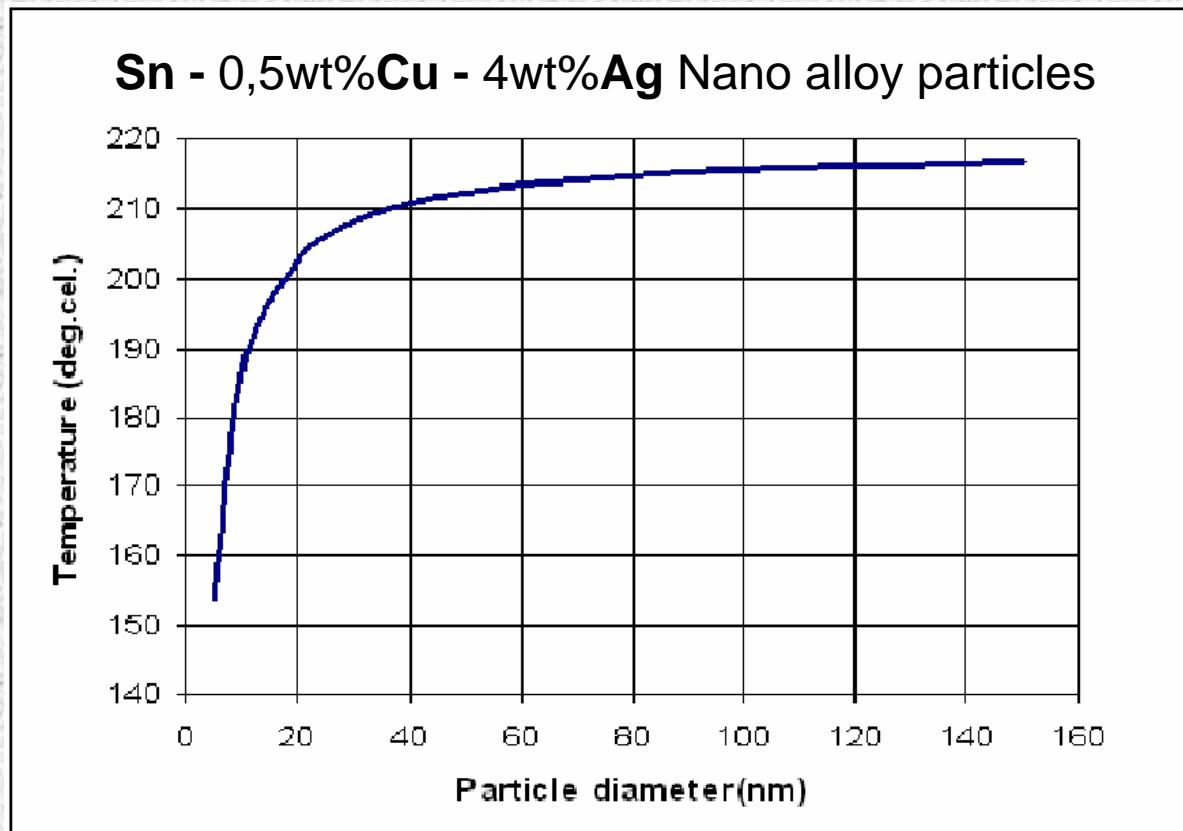
Surface Effects

Atom binding (vaporization) energies lower in nanoparticles, fewer neighbors to keep atoms from escaping

Plasticity of nanocrystalline ceramics

Melting Point Depression

$$\Delta T = T_m^{bulk} - T_m(r) = \frac{2T_m^{bulk}}{H_m^{bulk} \rho_s r} \left[\sigma_s - \sigma_L \left(\frac{\rho_s}{\rho_L} \right)^{\frac{2}{3}} \right]$$



Gibbs–Thomson Equation

$$\frac{T_m(r) - T_m^{bulk}}{T_m^{bulk}} = - \frac{2V_{mol}^l \gamma_{sl}}{\Delta H_m r}$$

In nanoparticles confined in pores

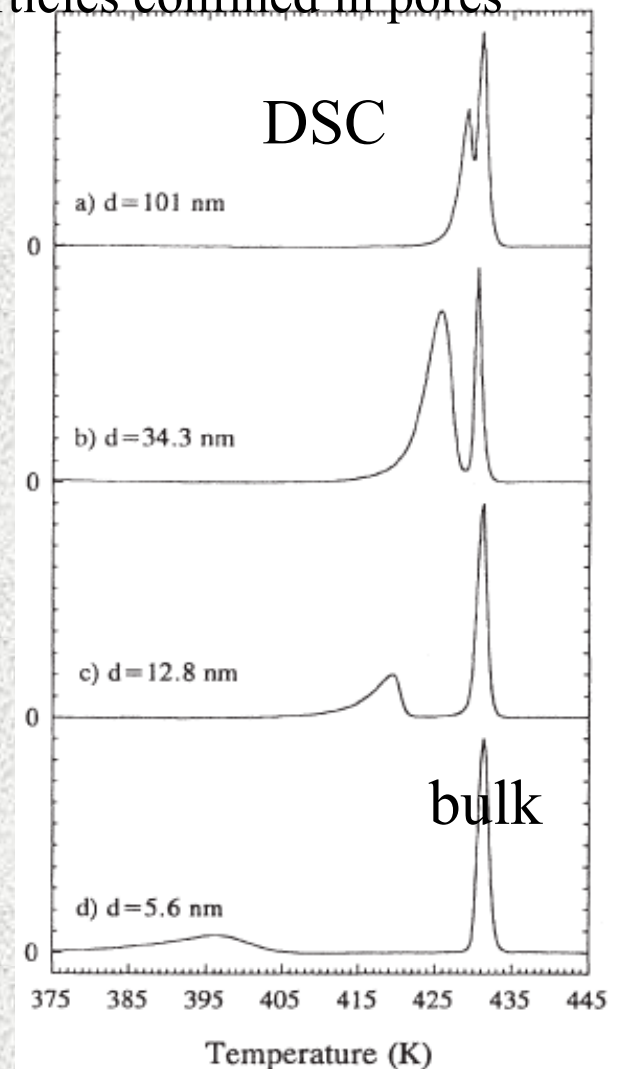
$T_m(r)$ = mp of the cluster with radius r

T_m^{bulk} = mp of the bulk

V_{mol}^l = the molar volume of the liquid

γ_{sl} = the interfacial tension between the s and l surface

ΔH_m^{bulk} = the bulk latent heat of melting

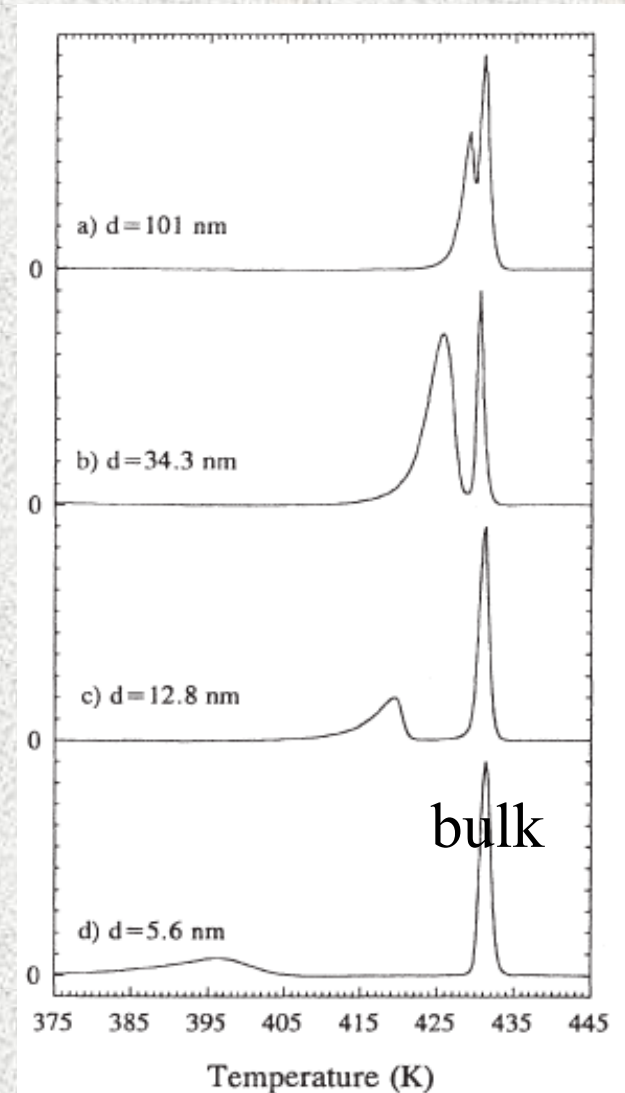
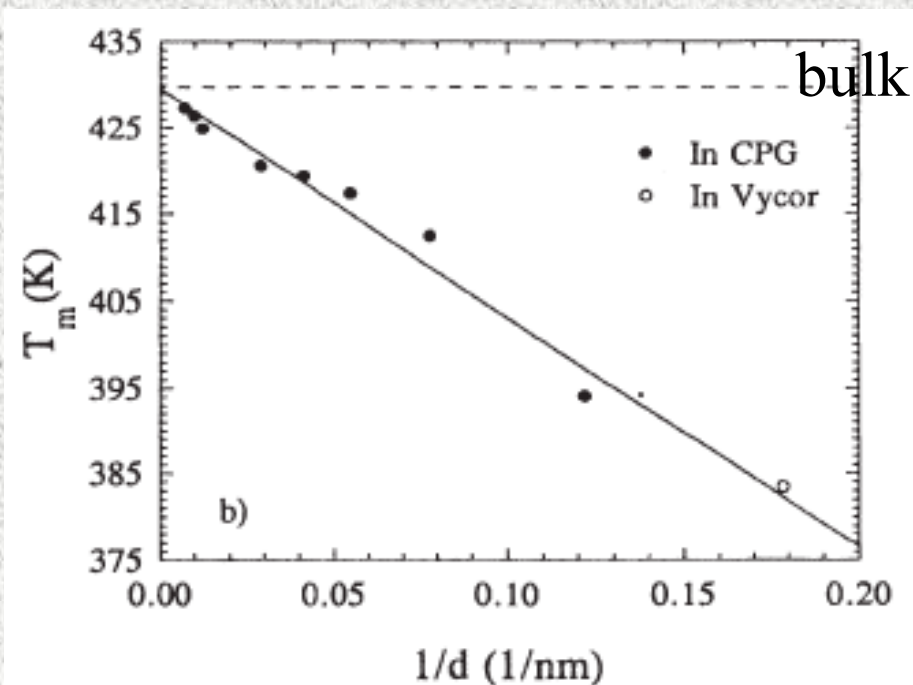


Phase Transitions

Phase transitions = collective phenomena

With a lower number of atoms in a cluster a phase transition is less well defined and broadened

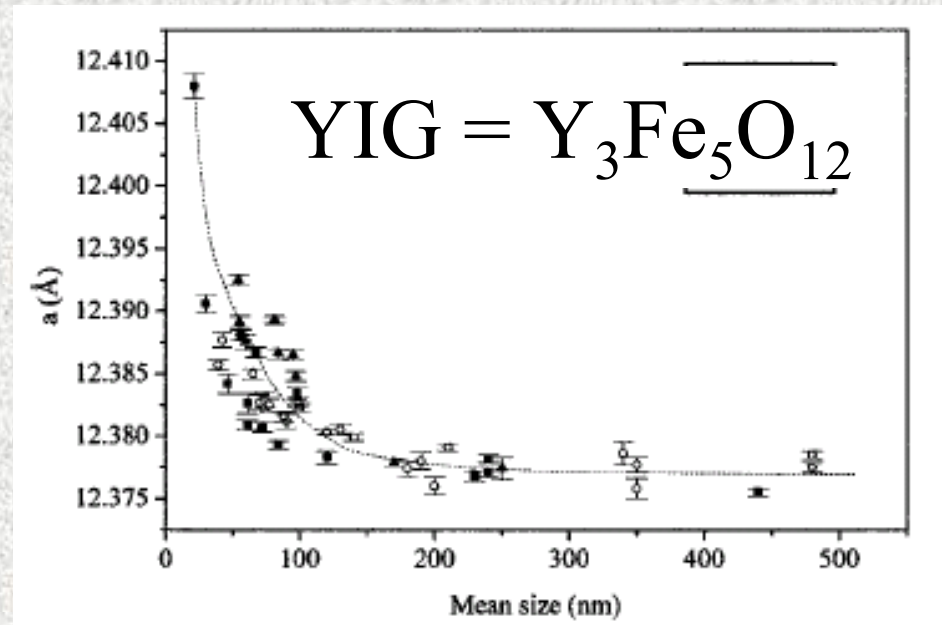
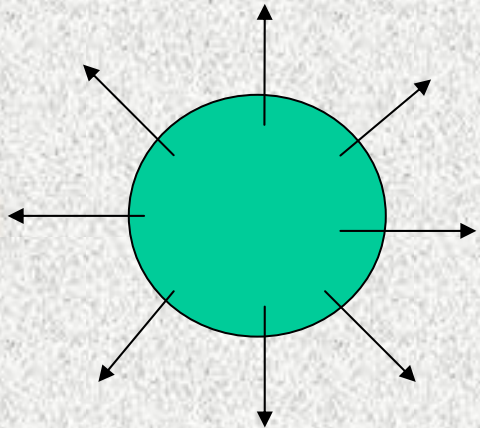
Small clusters behave more like molecules than as bulk matter



Surface Effects

Reduction in particle size

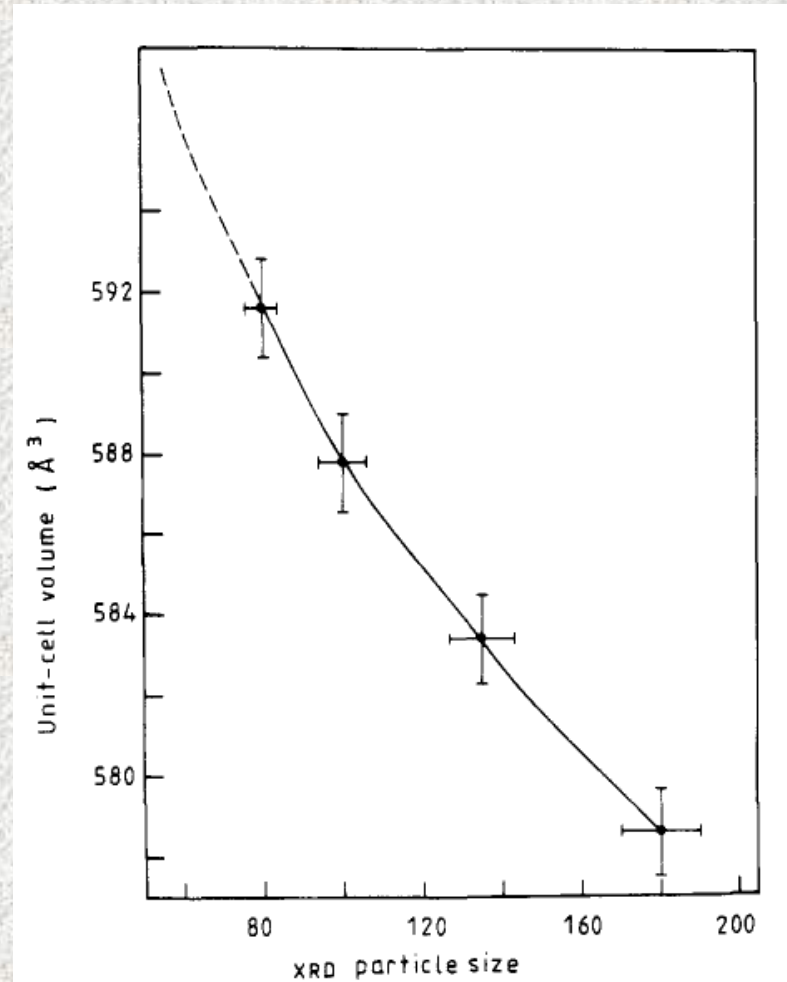
- metal particles usually exhibit a lattice contraction
- oxide particles exhibit a lattice expansion



Surface Effects

Correlation between the unit-cell volume (cubic) and the XRD particle size in $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles

The smaller the particle size the larger the unit cell volume.

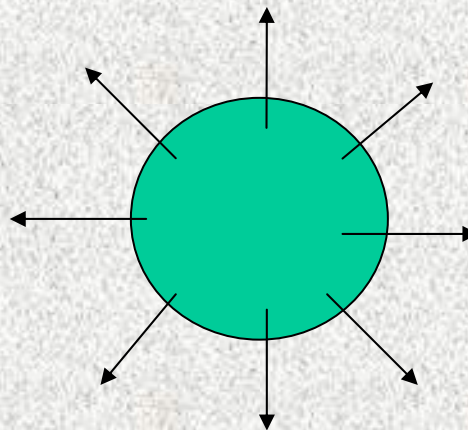


Surface Effects

**The inter-ionic bonding in nanoparticles has a directional character
ions in the outermost layer of unit cells possess unpaired electronic orbitals**

Associated electric dipole moments, aligned roughly parallel to each other point outwards from the surface

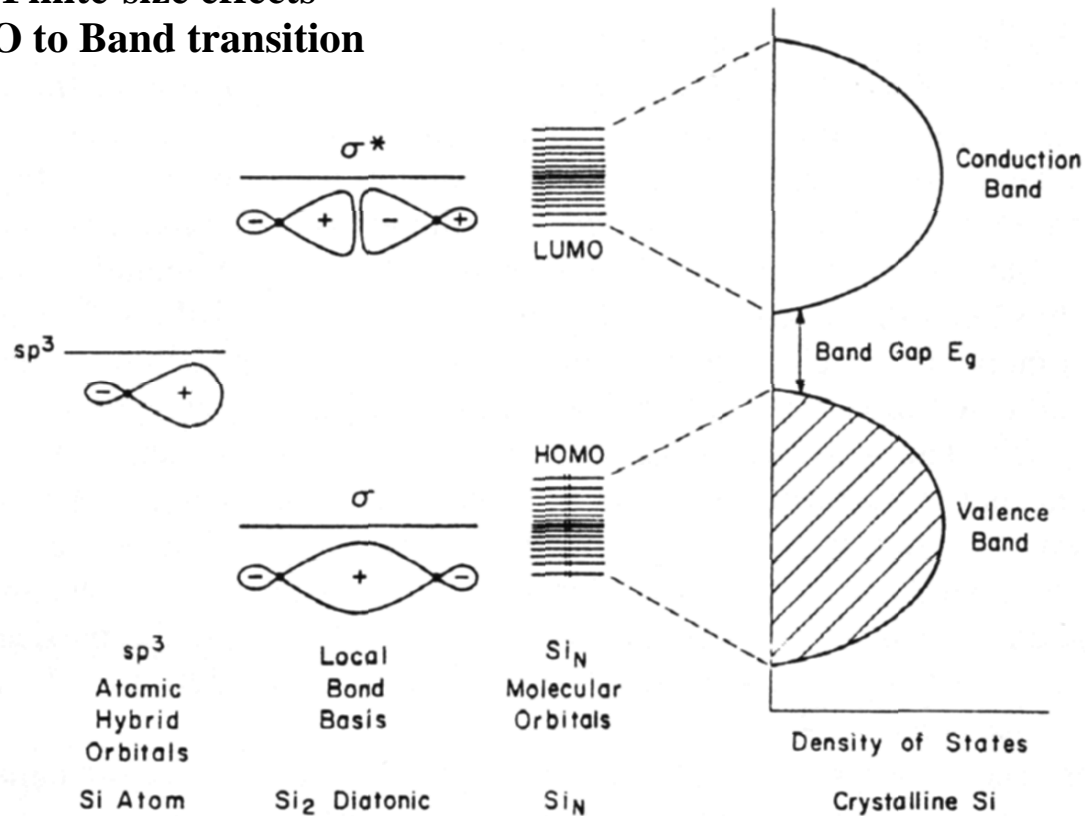
**The repulsive dipolar interactions increase in smaller particles
reduced by allowing unit cell volume to increase**



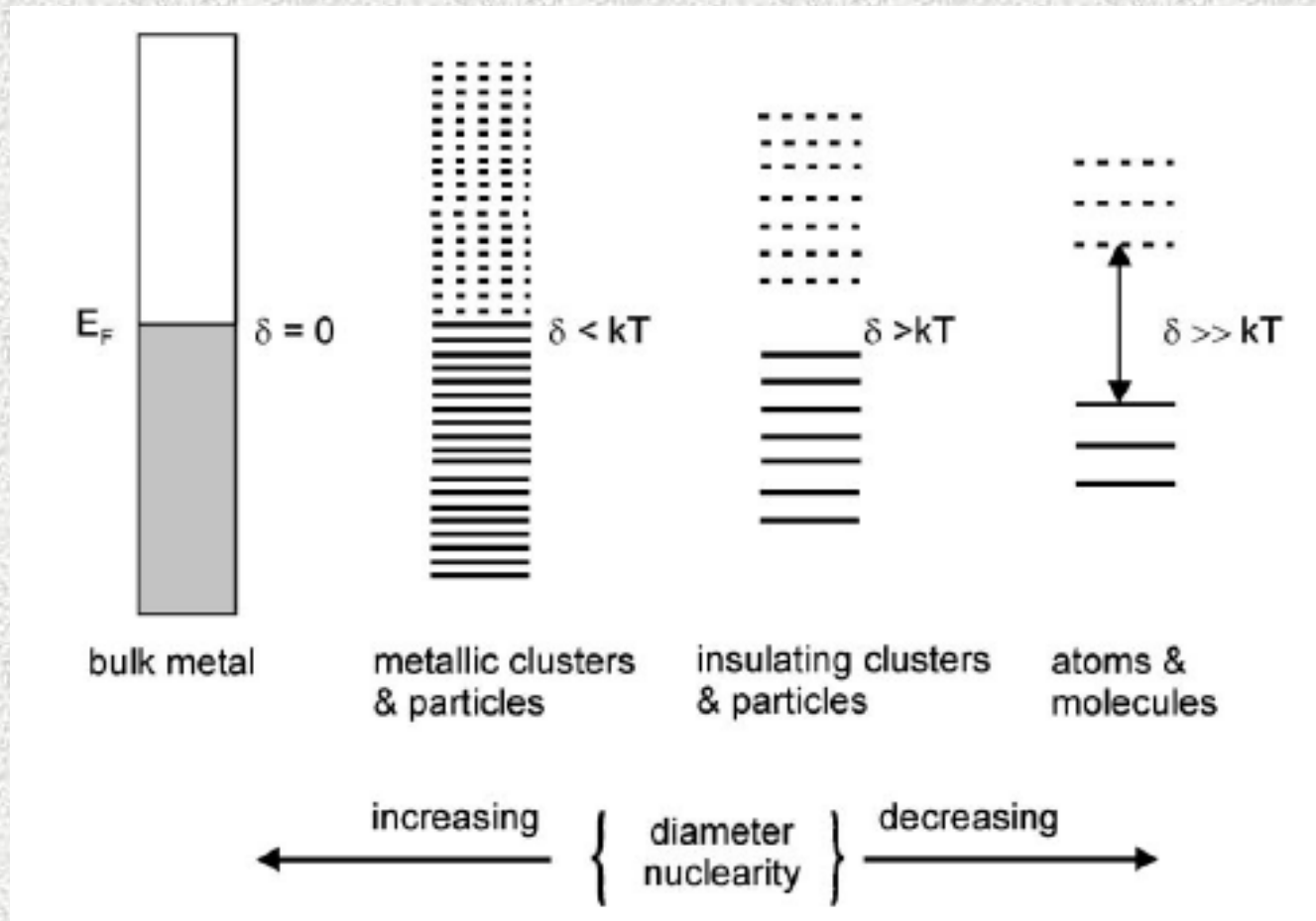
Quantum Confinement Effects

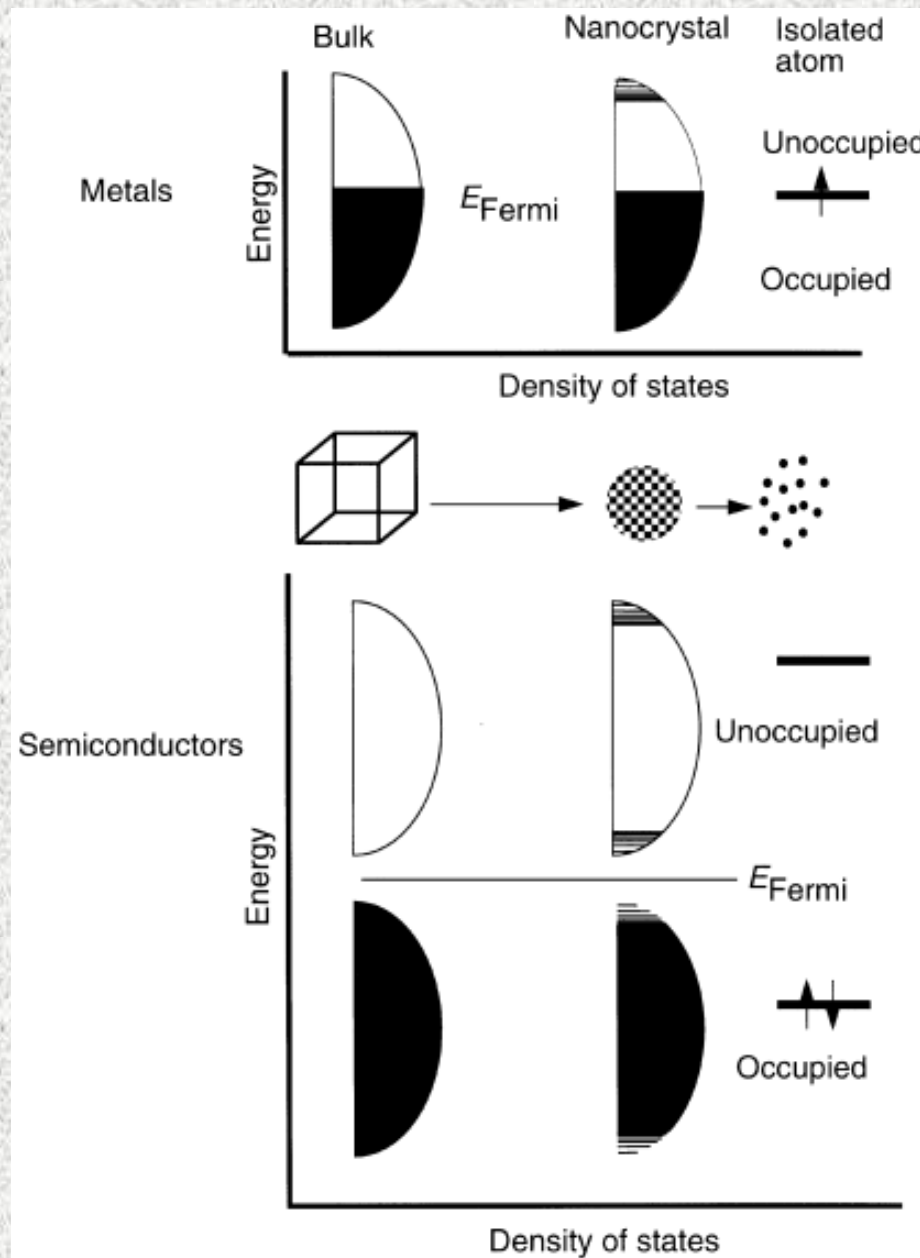
Physical and chemical properties depend on the size !!

① Finite-size effects
MO to Band transition



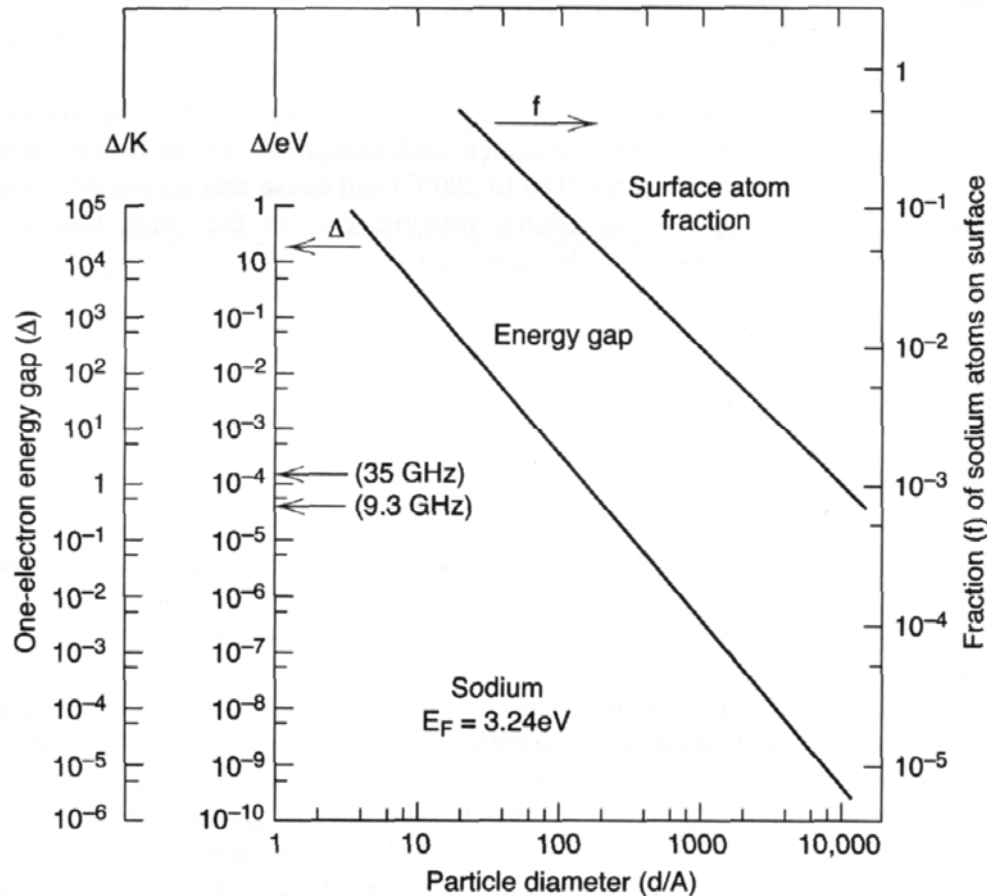
Metal-to-Insulator Transition





Metal-to-Insulator Transition

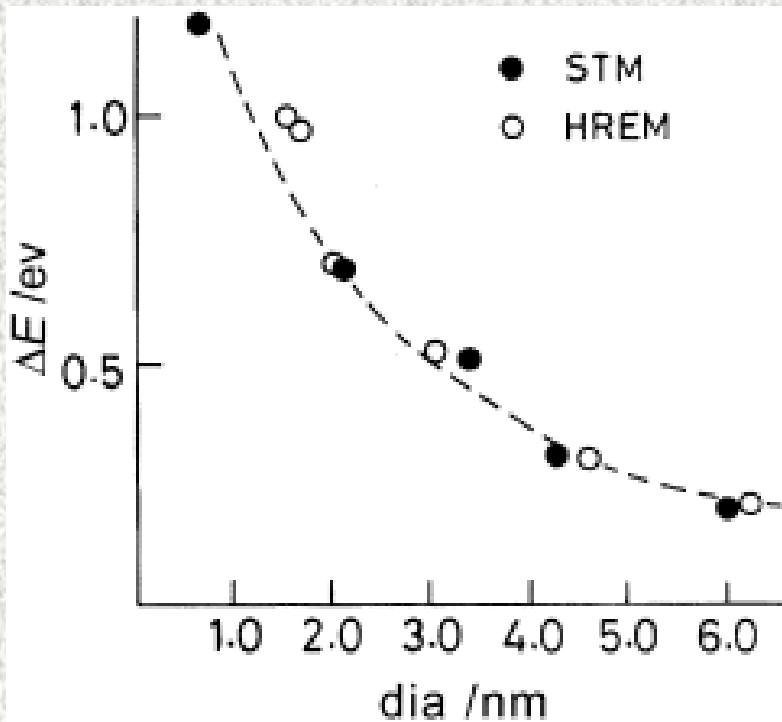
Band gap increases with decreasing size



Metallic behavior
Single atom cannot behave
as a metal
nonmetal to metal transition
100-1000 atoms

Magnetic behavior
Single domain particles
large coercive field

Metal-to-Insulator Transition

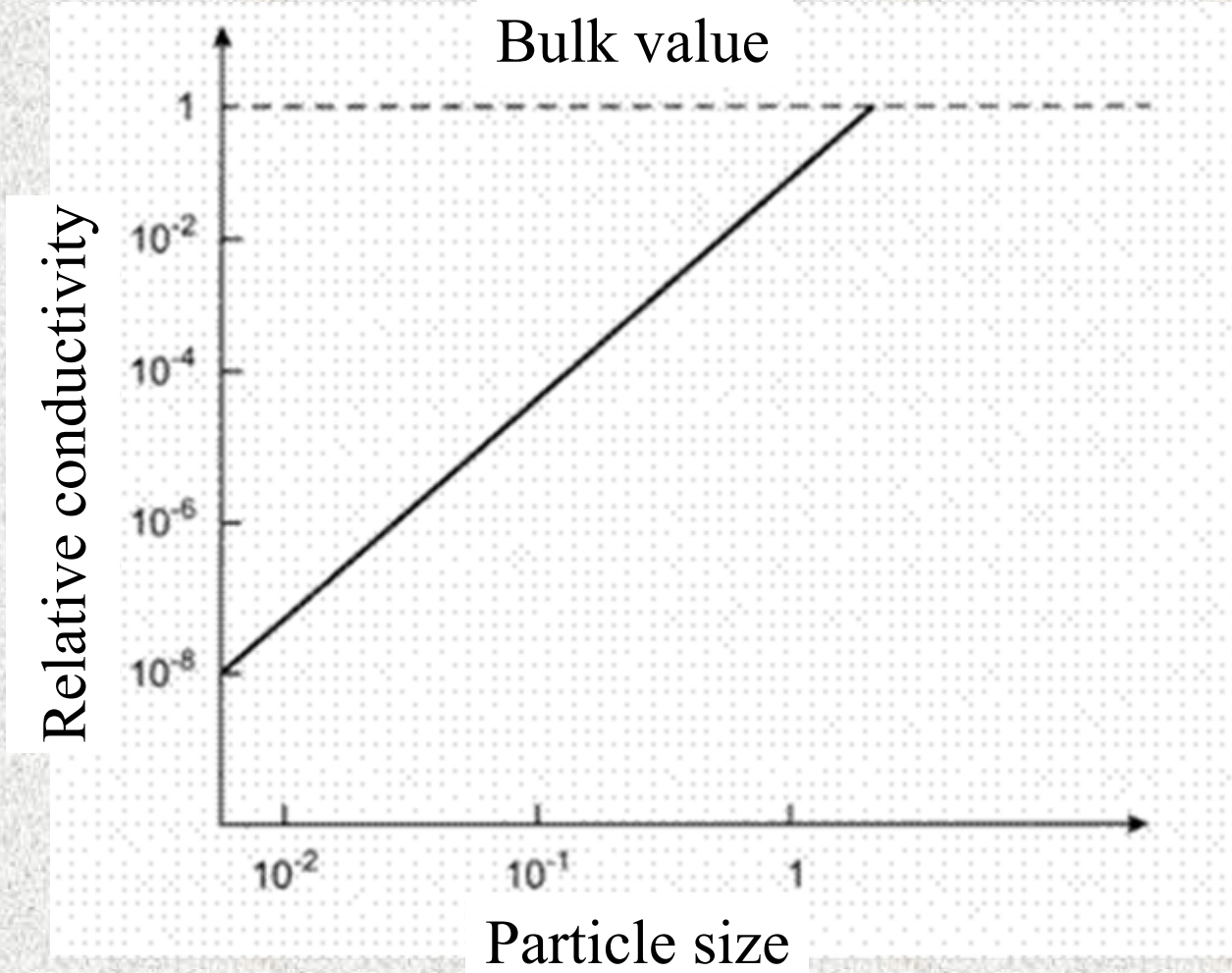


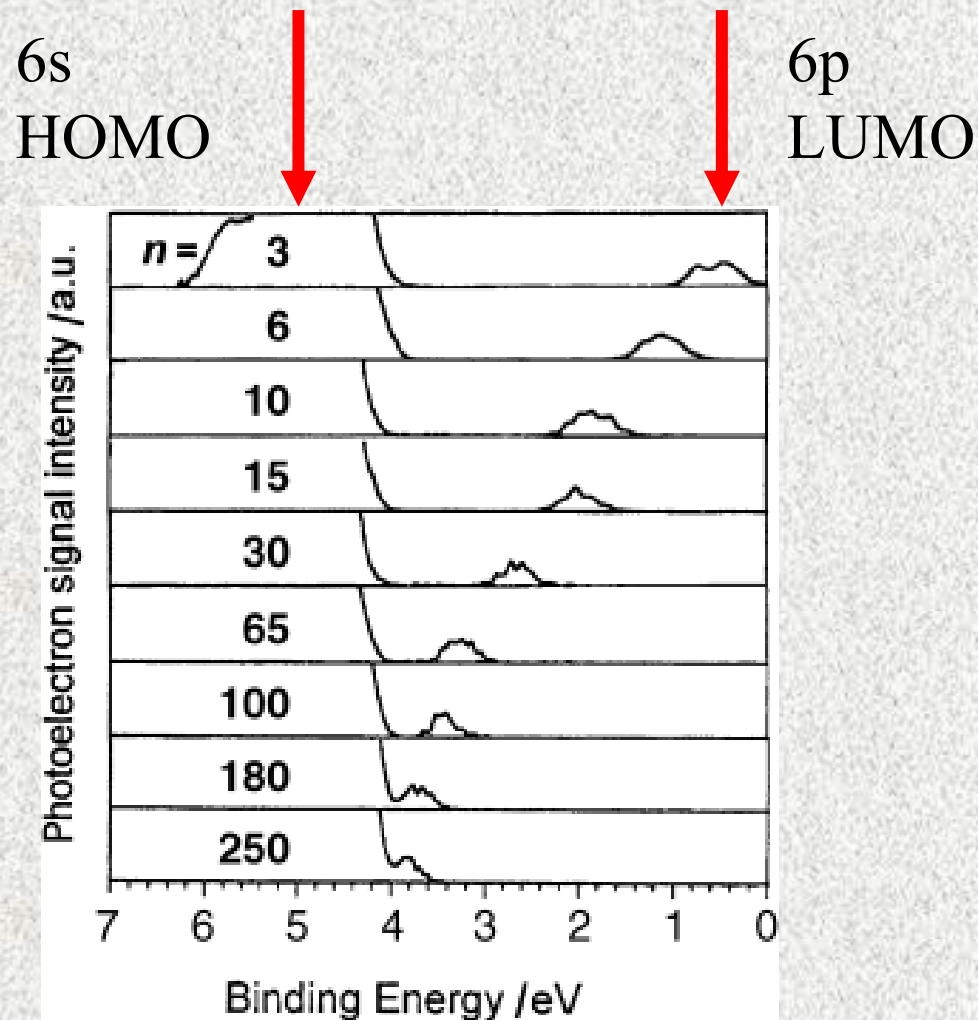
**The increase in the core-level binding energy in small particles
poor screening of the core charge**

**the size-induced metal-nonmetal
transition in nanocrystals**

**Variation of the shift, ΔE , in the core-level binding energy
(relative to the bulk metal value) of Pd with the nanoparticle diameter**

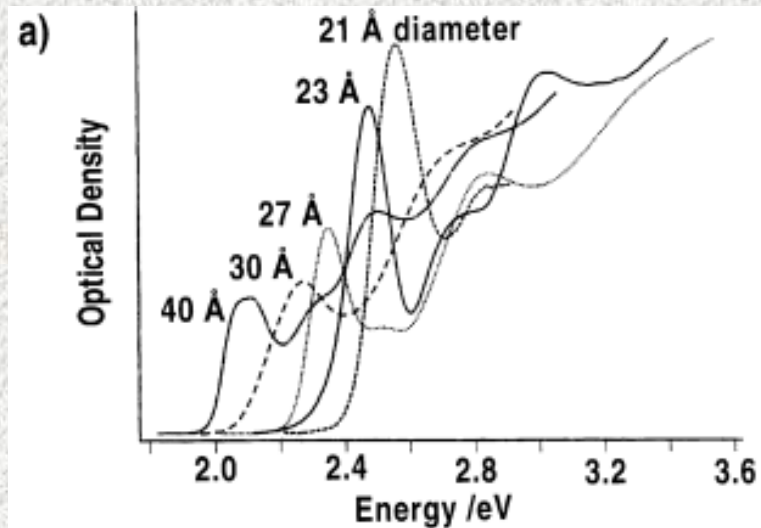
Electrical Conductivity



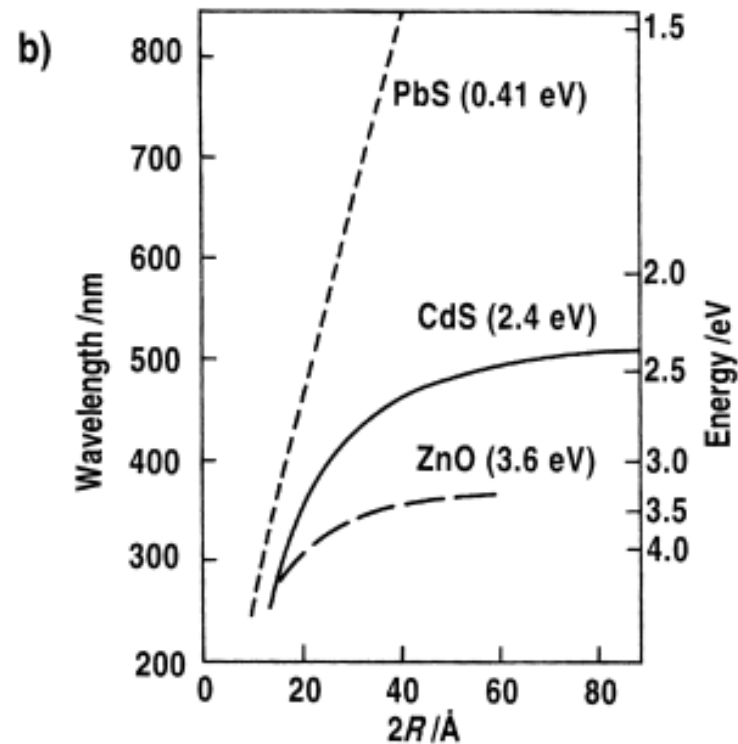


Photoelectron spectra of Hg clusters of nuclearity n
The 6p peak moves gradually towards the Fermi level
the band gap shrinks with increase in cluster size

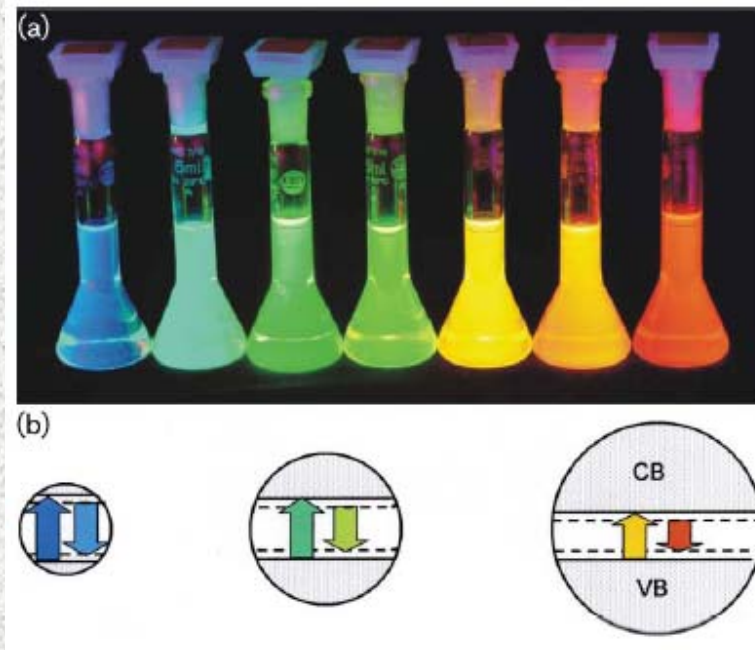
a) Absorption spectra of CdSe nanocrystals (at 10 K) of various diameters



b) Wavelength of the absorption threshold and band gap as a function of the particle diameter for various semiconductors. The energy gap in the bulk state in parenthesis



Quantum Confinement Effects



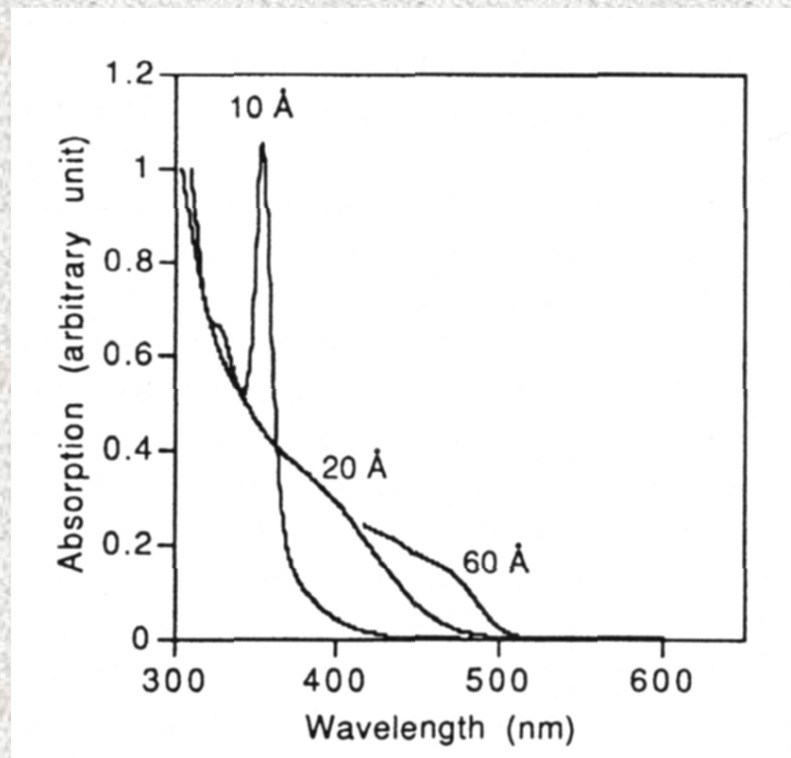
Fluorescence of CdSe–CdS core–shell nanoparticles with a diameter of 1.7 nm (blue) up to 6 nm (red)

Smaller particles have a wider band gap

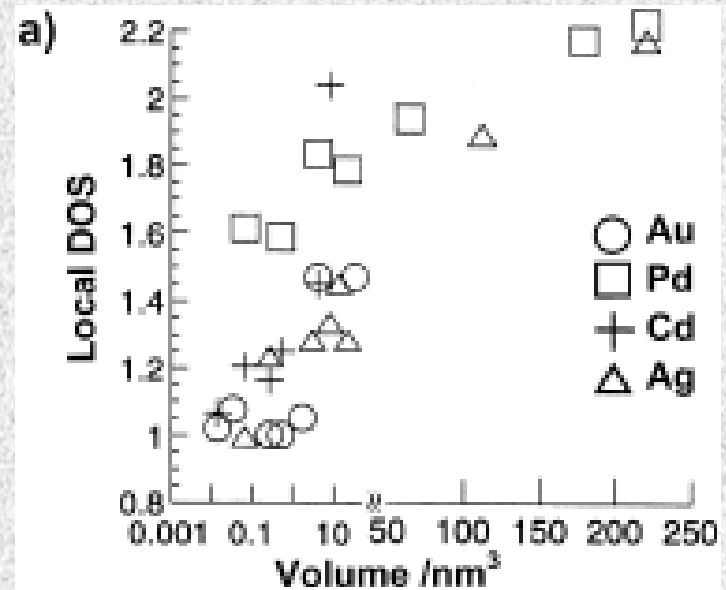
Quantum Confinement Effects

Ⓢ Optical properties
nc-TiO₂ is transparent

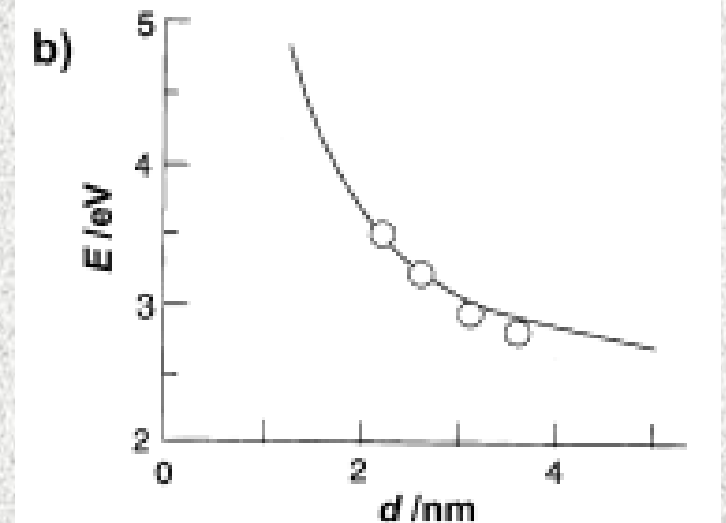
Blue shift in optical spectra of nanoparticles



a) Variation of the nonmetallic band gap with nanocrystal size



b) in CdS nanocrystals



Nanoscopic Materials

NANO -particles, crystals, powders
 -films, patterned films
 -wires, rods, tubes
 -dots

Nanostructured materials = nonequilibrium character

- **good sinterability**
- **high catalytic activity**
- **difficult handling**
- **adsorption of gases and impurities**
- **poor compressibility**

PREPARATION METHODS

Top-down: from bulk to nanoparticles

Bottom-up: from atoms to nanoparticles

Nanoscopic Materials

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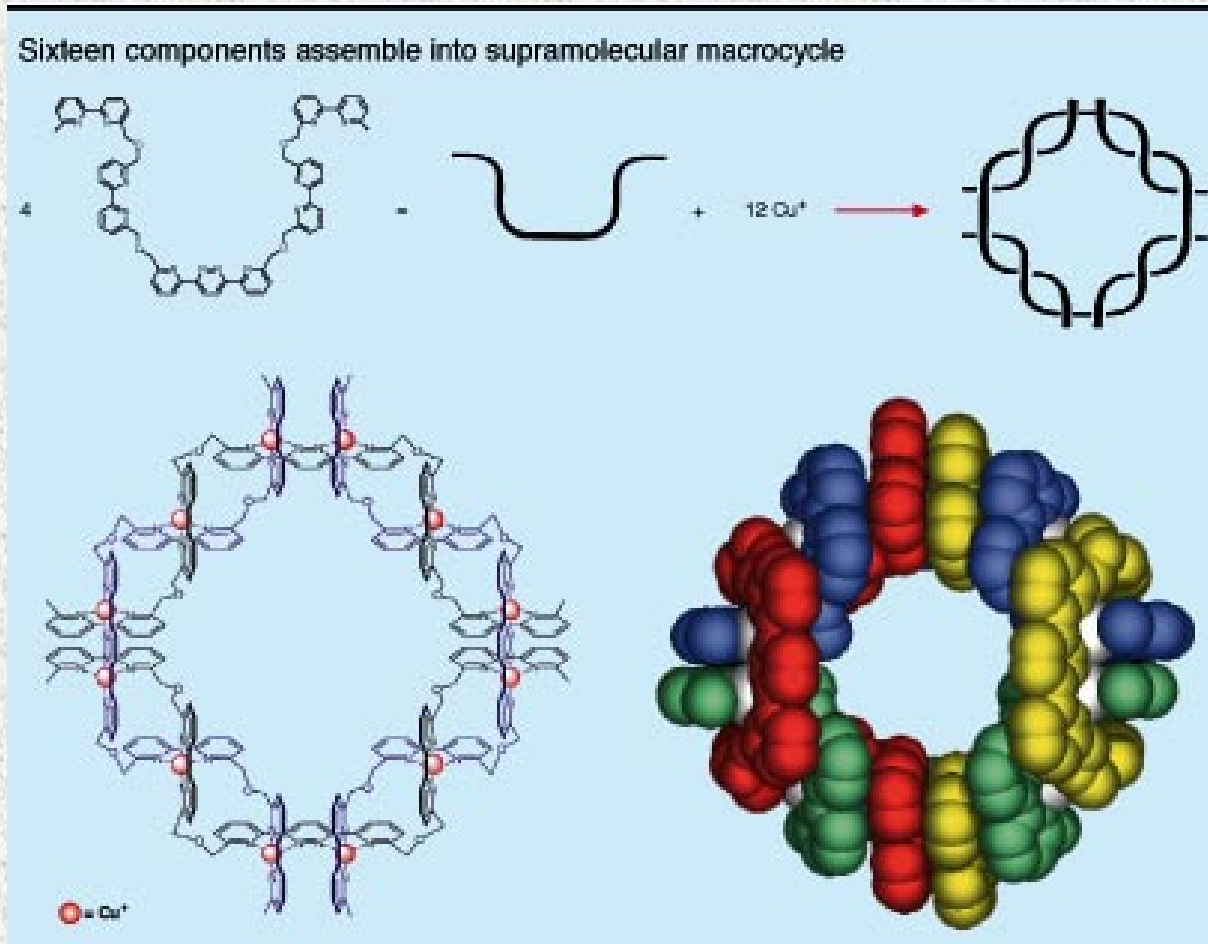
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PREPARATION METHODS

Top-down: from bulk to nanoparticles

Bottom-up: from atoms to nanoparticles

Bottom-up Synthesis: Atom Up



NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

✂ Atom Aggregation Method

GEM – gas evaporation method

✧ evaporation by heating – resistive, laser, plasma, electron beam, arc discharge

✧ the vapor nucleates homogeneously owing to collisions with the cold gas atoms

✧ condensation

in an inert gas (He, Ar, 1kPa) on a cold finger, walls - metals, intermetallics, alloys, SiC, C₆₀

in a reactive gas O₂ TiO₂, MgO, Al₂O₃, Cu₂O
 N₂, NH₃ nitrides

in an organic solvent matrix

NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

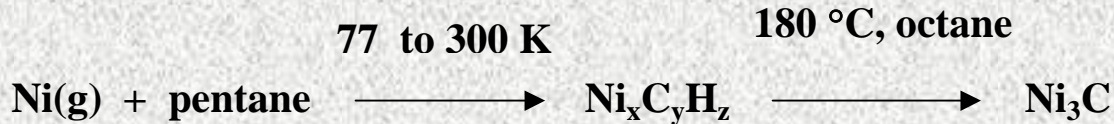
SMAD – the solvated metal atom dispersion

1 – 2 g of a metal, 100 g of solvent, cooled with liquid N₂

more polar solvent (more strongly ligating) gives smaller particles

Ni powder: THF < toluene < pentane = hexane

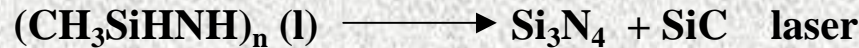
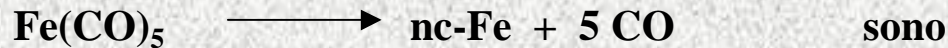
Carbide formation



NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

✂ Thermal or Sonocative Decomposition of Precursors



H₂, 550 °C



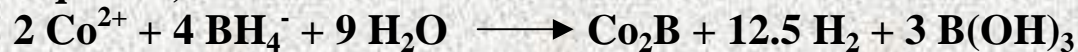
NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

✂ Reduction of Metal Ions

Borohydride Reduction - Manhattan Project

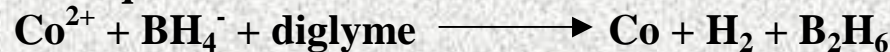
Aqueous, under Ar



Under air



Nonaqueous



M = group 6 to 11; n = 2,3; X = Cl, Br

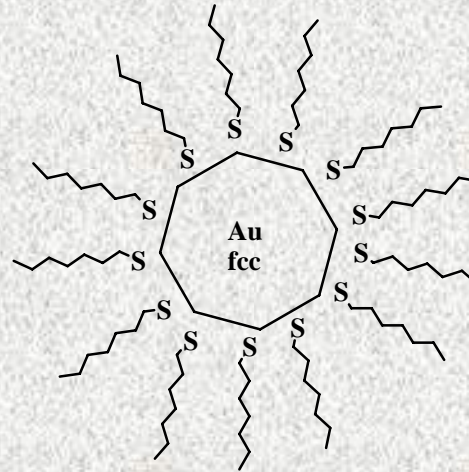
mixed-metal particles

NANOSTRUCTURAL MATERIALS

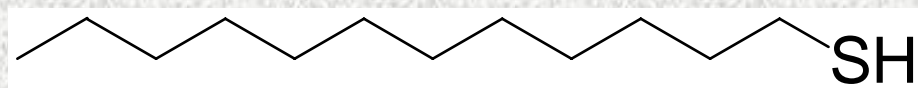
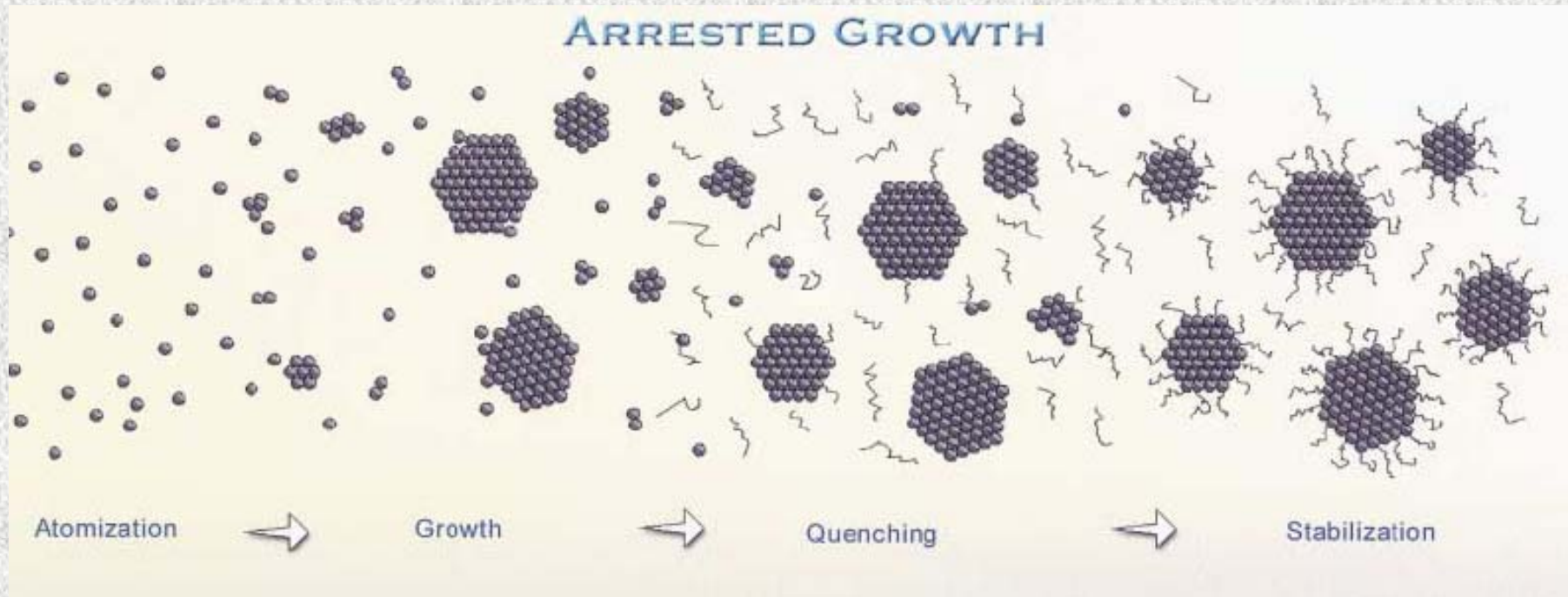
Bottom-up Synthesis

Au colloidal particles

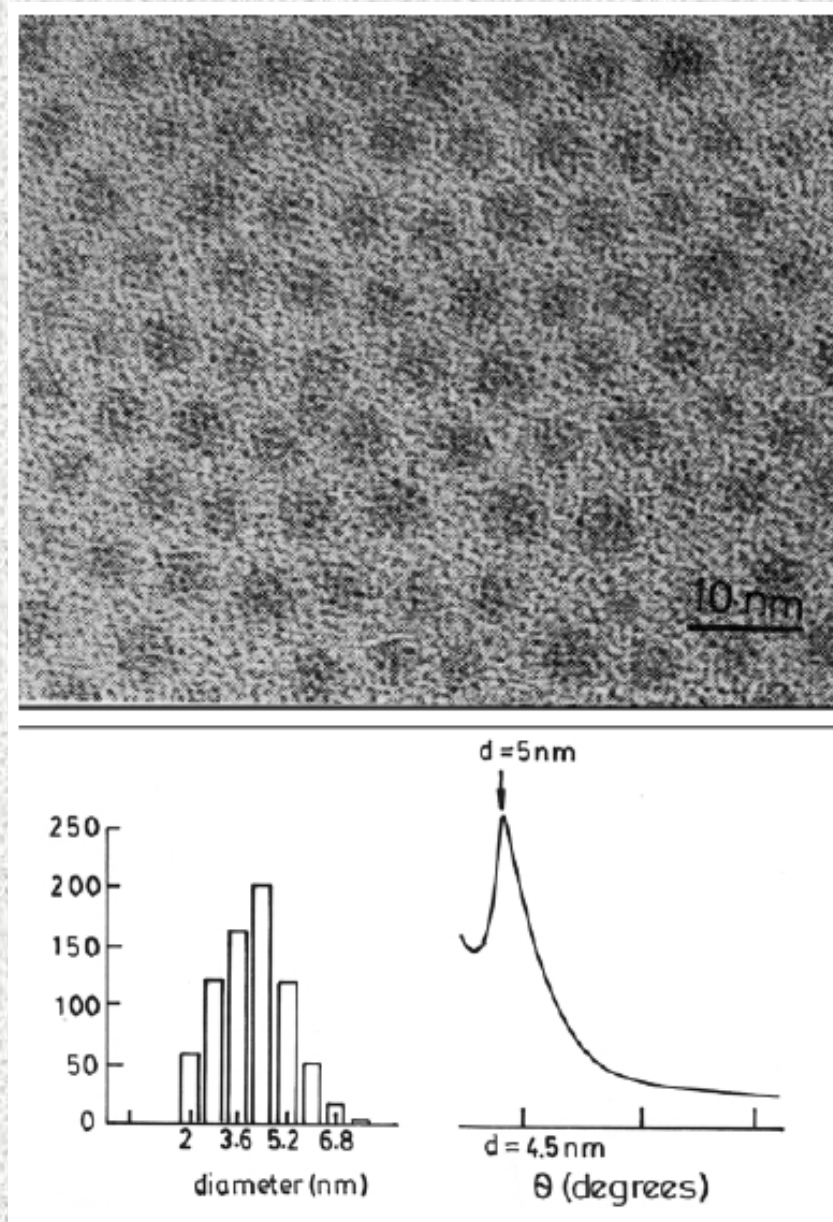
**HAuCl₄ + NaBH₄ in toluene/H₂O system,
TOABr as a phase transfer agent, Au
particles in the toluene layer, their surface
covered with Br, addition of RSH gives
stable Au colloid**



Bottom-up Synthesis



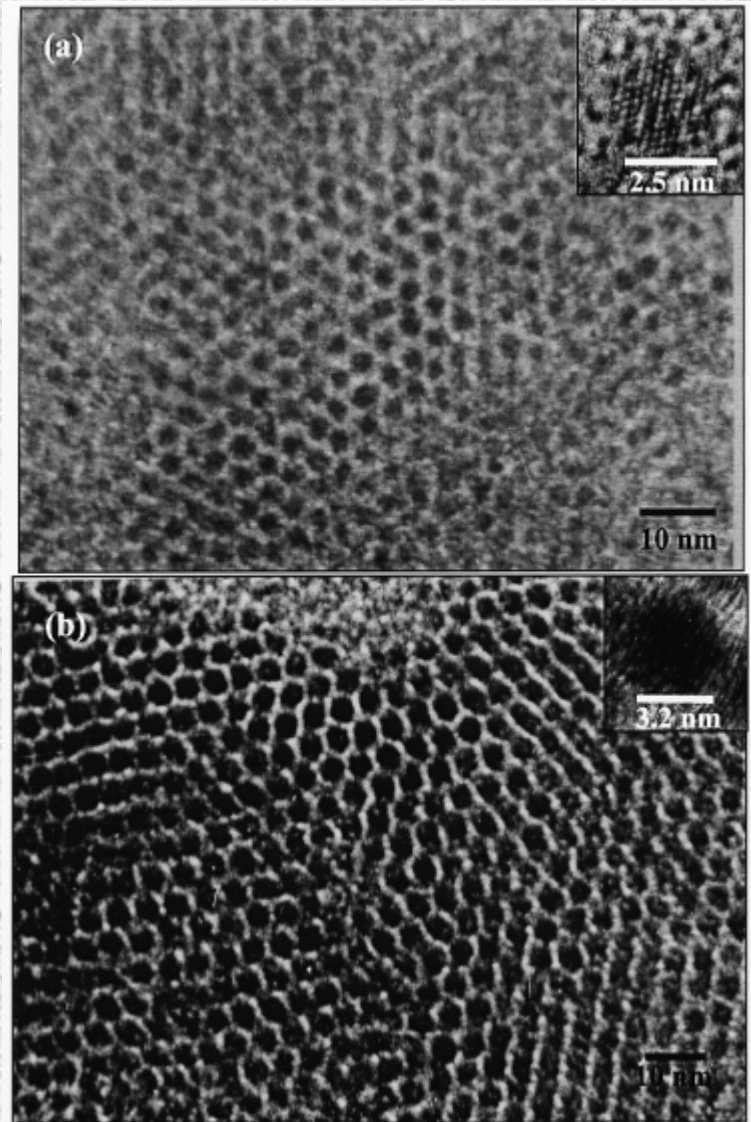
**Two-dimensional array of
thiol-derivatised Au particles
(mean diam 4.2 nm)**

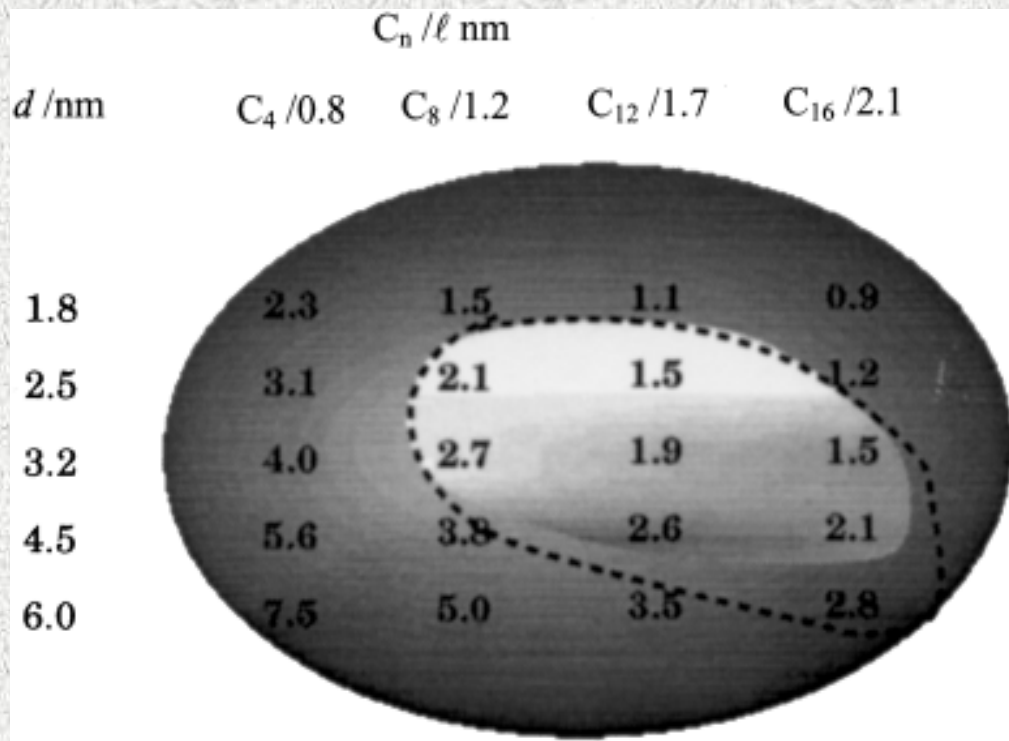


**TEM micrograph of hexagonal arrays
of thiolized Pd nanocrystals:**

a) 2.5 nm, octane thiol

b) 3.2 nm, octane thiol





The d - l phase diagram for Pd nanocrystals thiolized with different alkane thiols.

The mean diameter, d , obtained by TEM.

The length of the thiol, l , estimated by assuming an all-*trans* conformation of the alkane chain.

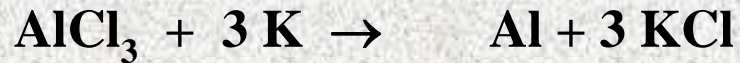
The thiol is indicated by the number of carbon atoms, C_n .

The bright area in the middle encompasses systems which form close-paced organizations of nanocrystals. The surrounding darker area includes disordered or low-order arrangements of nanocrystals. The area enclosed by the dashed line is derived from calculations from the soft sphere model

NANOSTRUCTURAL MATERIALS

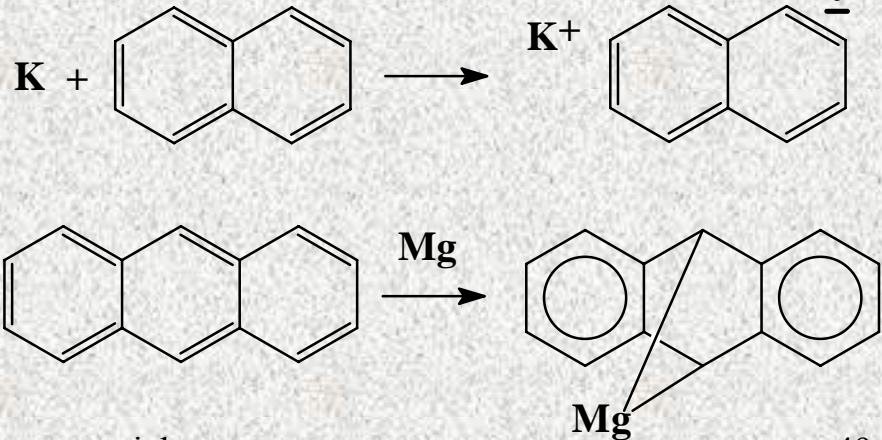
Alkali Metal Reduction

in dry anaerobic diglyme, THF, ethers, xylene

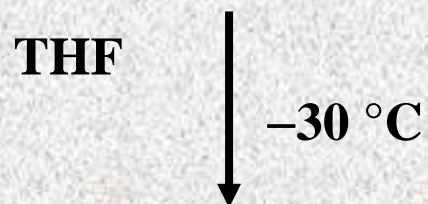


Reduction by Glycols or Hydrazine

“Organically solvated metals”

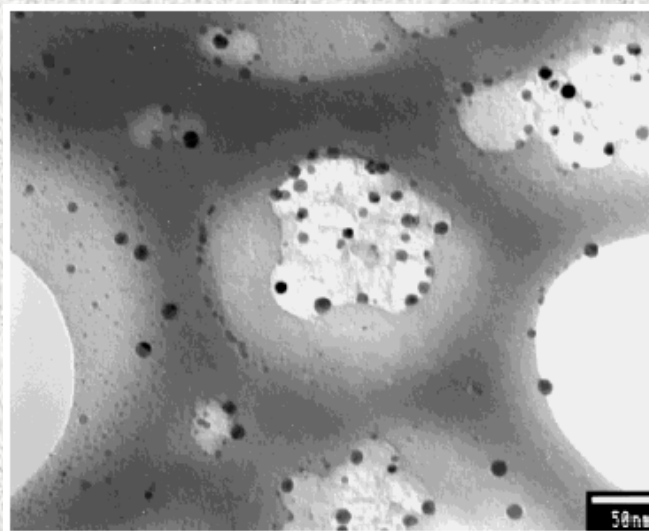


Alkalide Reduction



Anealed at 950 °C / 4 h

Fe_3C : 2 – 15 nm



NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

✂ Reactions in Porous Solids – Zeolites, Mesoporous materials

Ion exchange in solution, reaction with a gaseous reagent inside the cavities



Ship-in-the-Bottle Synthesis



Conducting carbon wires

Acrylonitrile introduced into MCM-41 (3 nm diam. channels)

Radical polymerization

Pyrolysis gives carbon filaments

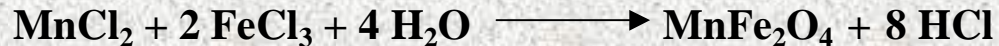
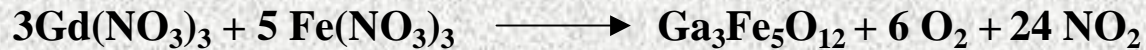
NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

✘ Gel or Polymer Matrices

✘ Sol-Gel Method
Aerogels, supercritical drying

✘ Aerosol Spray Pyrolysis
Aqueous solution, nebulization, droplet flow, solvent evaporation,
chemical reaction, particle consolidation, up to 800 °C

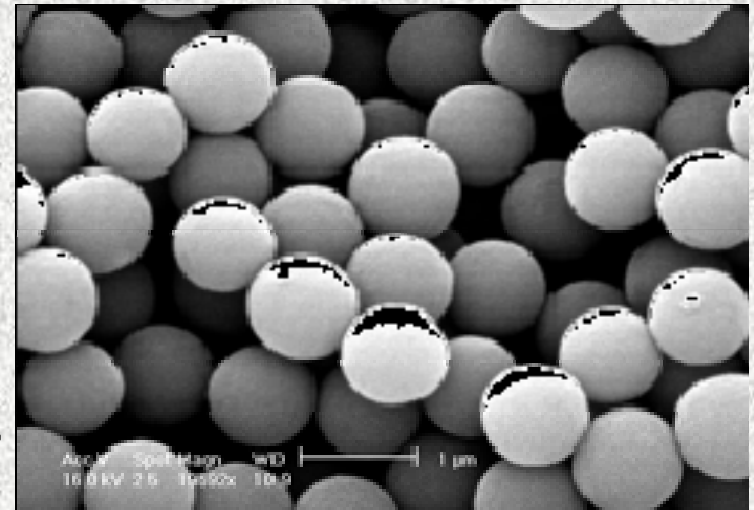
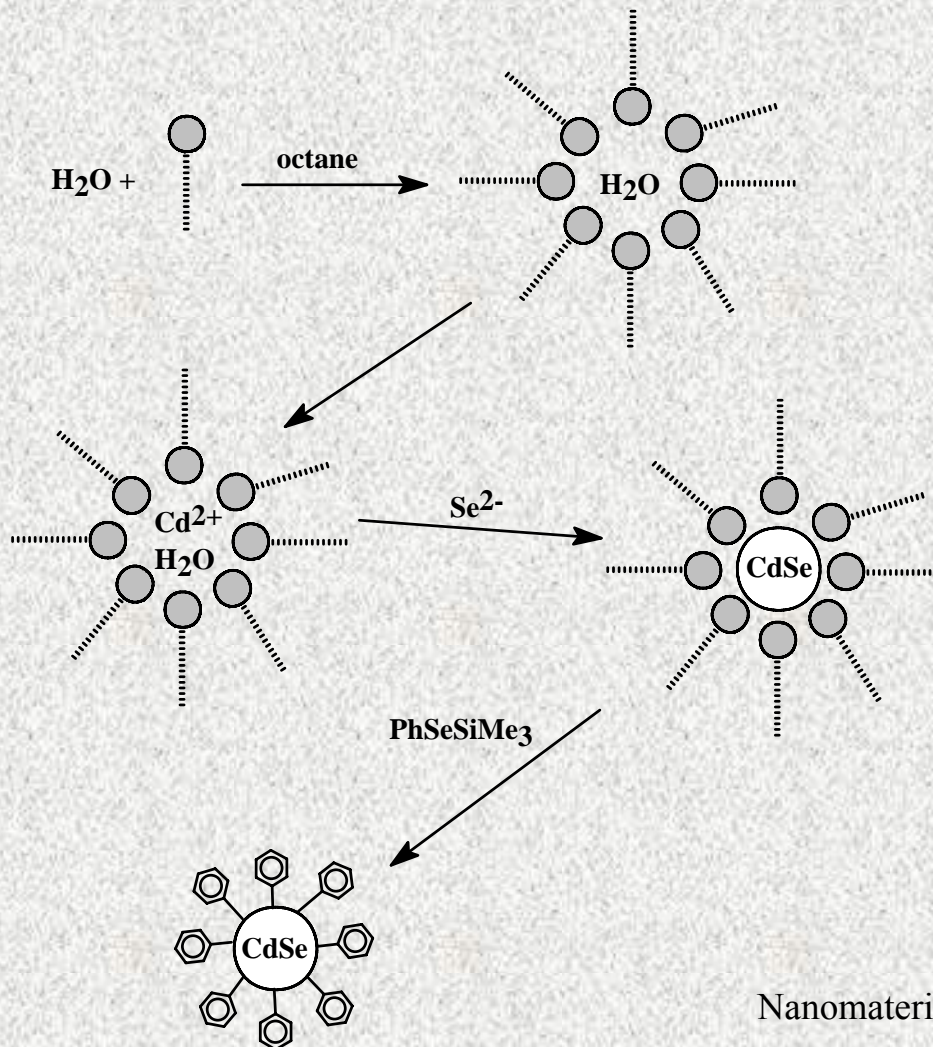


$\text{Mn}(\text{NO}_3)_2 + \text{Fe}(\text{NO}_3)_3$ no go, why?

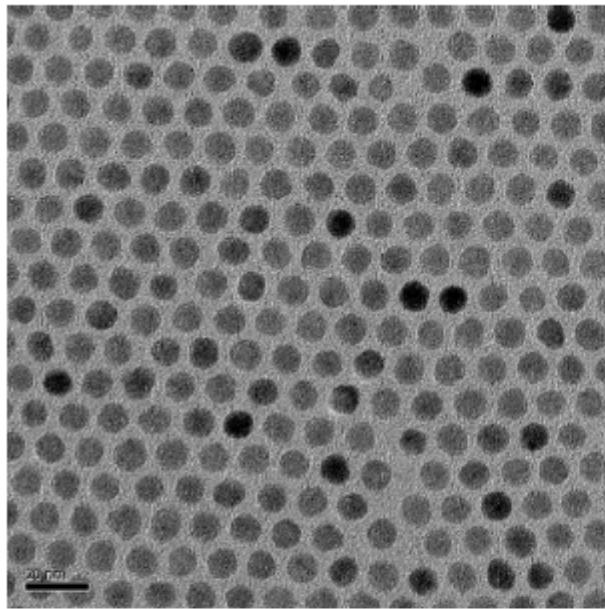
NANOSTRUCTURAL MATERIALS

✂ Inverse Micelles

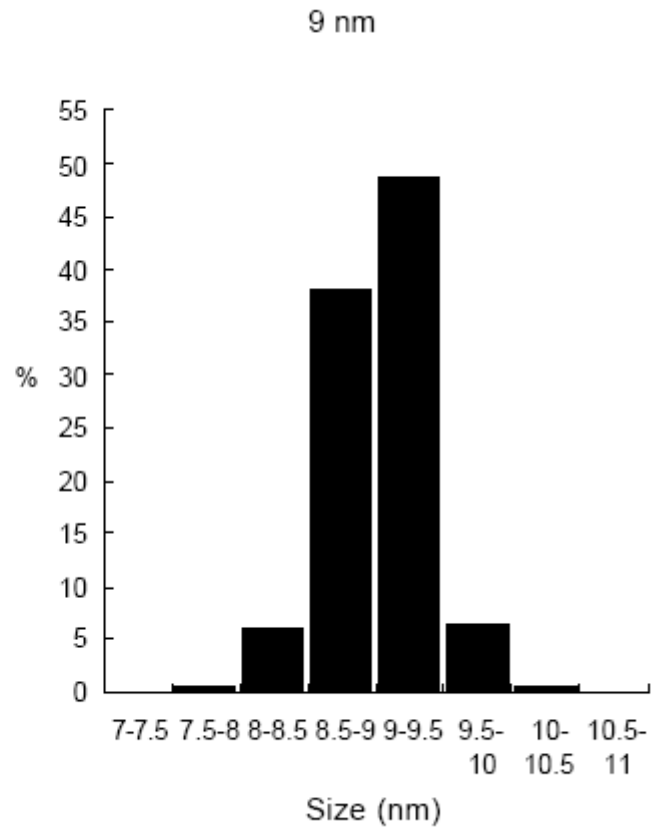
Bottom-up Synthesis



Bottom-up Synthesis

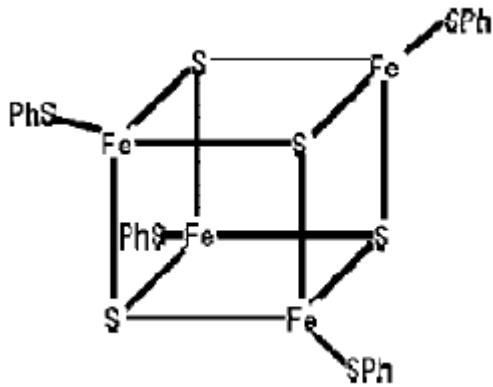


Number of counted particles: 204
Average size: 9.04 nm
Standard deviation: 0.33 nm (3.7%)



Bottom-up Synthesis

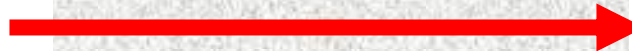
Phase Control



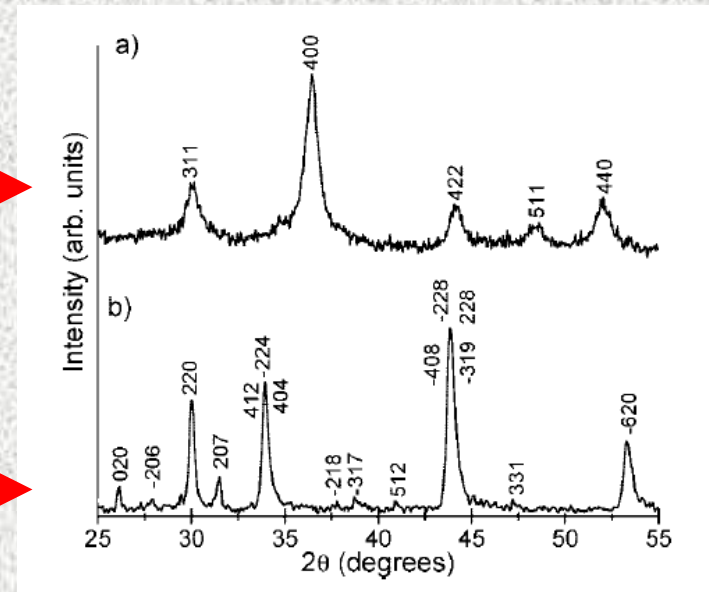
180 °C in octylamine



200 °C in dodecylamine

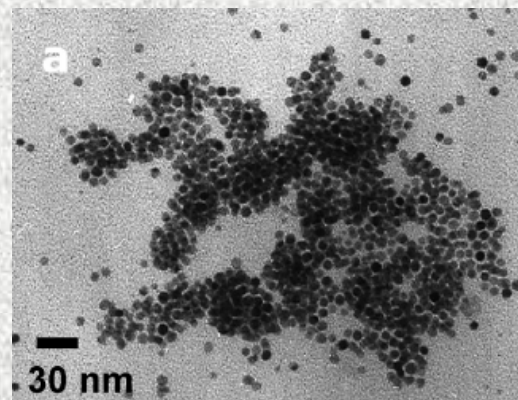


pyrrhotite Fe_7S_8

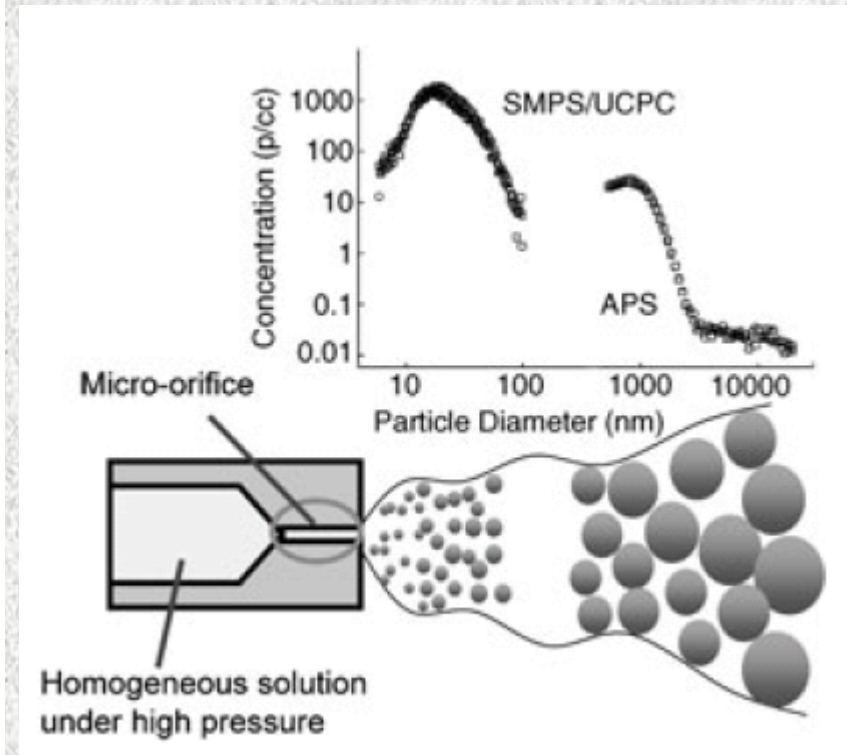
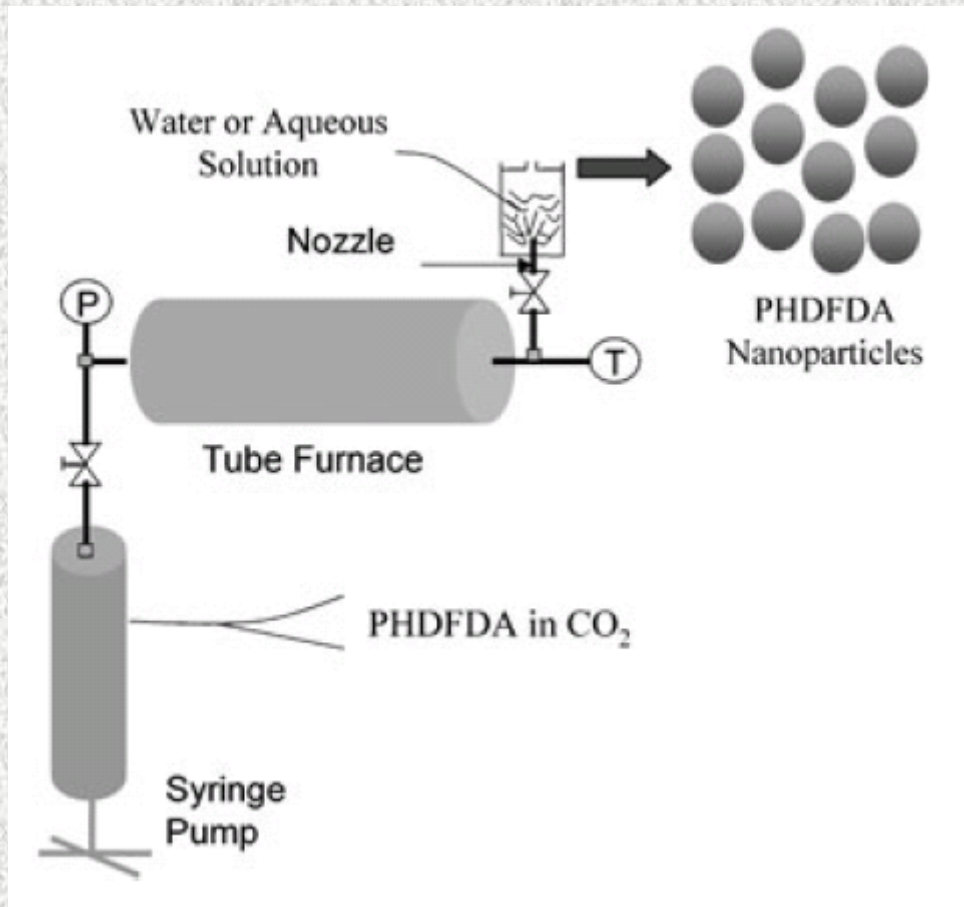


greigite Fe_3S_4

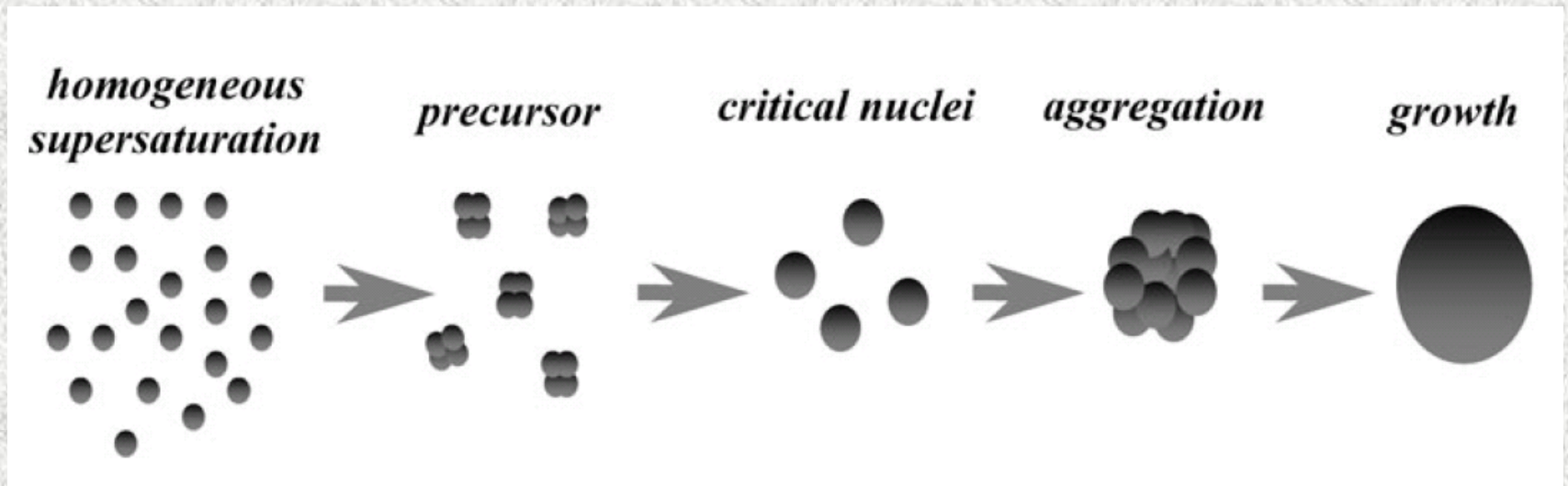
thiospinel, the sulfide analogue of magnetite



Polymeric Nanoparticles from Rapid Expansion of Supercritical Fluid Solution



Polymeric Nanoparticles from Rapid Expansion of Supercritical Fluid Solution



Spinning Disc Processing (SDP)

A rapidly rotating disc (300-3000 rpm)

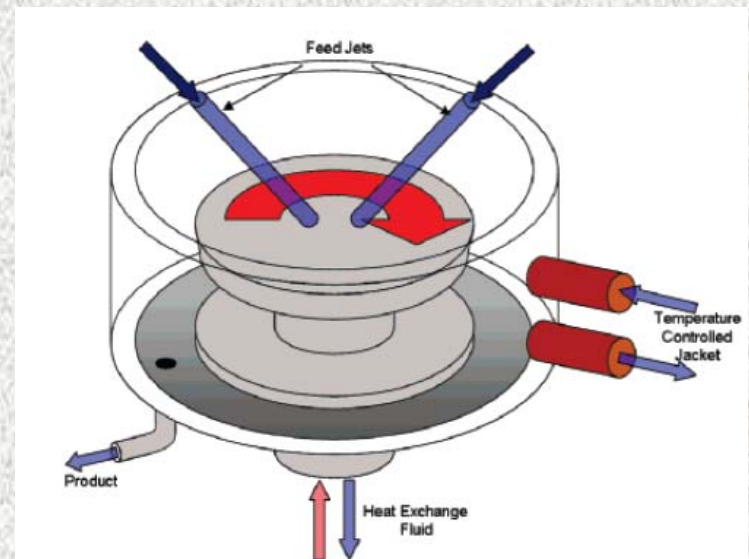
Ethanol solutions of $\text{Zn}(\text{NO}_3)_2$ and NaOH, polyvinylpyrrolidone (PVP) as a capping agent

Very thin films of fluid (1 to 200 μm) on a surface

Synthetic parameters = temperature, flow rate, disc speed, surface texture influence on the reaction kinetics and particle size

Intense mixing, accelerates nucleation and growth, affords monodispersed ZnO nanoparticles with controlled particle size down to a size of 1.3 nm and polydispersities of 10%

Nanomaterials



NANOSTRUCTURAL MATERIALS

Properties on Nanostructured Materials

Ⓢ Metallic behavior

Single atom cannot behave as a metal

nonmetal to metal transition : 100-1000 atoms

Ⓢ Magnetic behavior

Single domain particles, large coercive field

Ⓢ Depression of melting points in nanocrystals

bulk Au mp 1064 °C

10 nm Au 550 °C

LaMer mechanism

Supersaturated solution

Burst of nucleation

Slow growth of particles without additional nucleation

Separation of nucleation and growth

Watzky-Finke mechanism

Slow continuous nucleation

Fast autocatalytic surface growth

Seed-mediated mechanism

Au nanoclusters as seeds

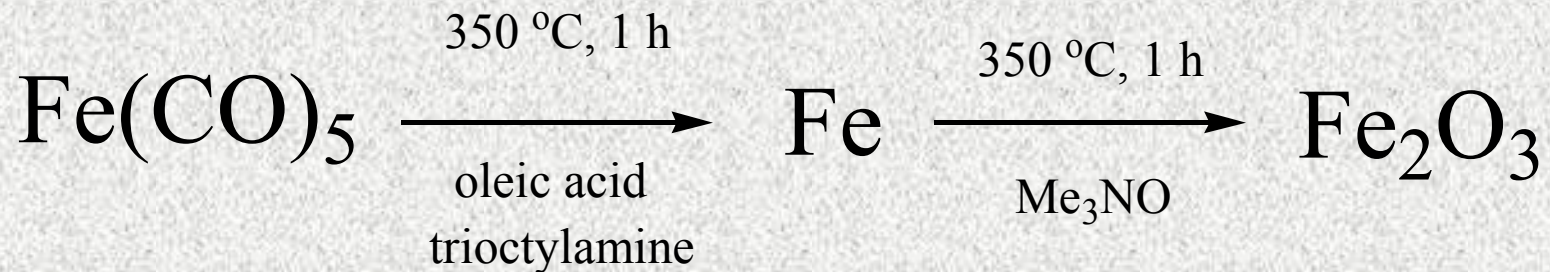
Bi, Sn, In, Au, Fe, Fe₃O₄

Other mechanisms

Digestive rippening

Surfactant exchange

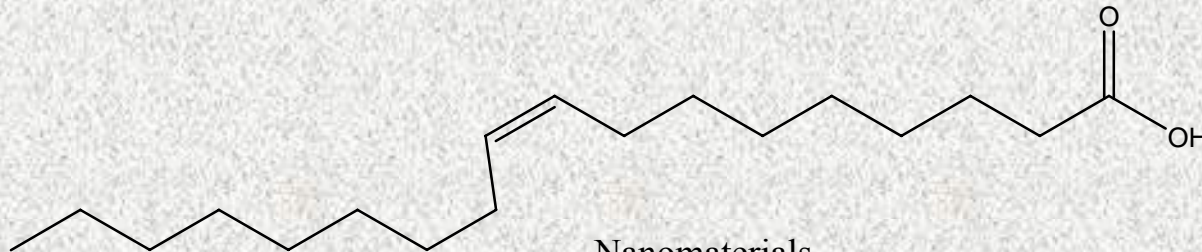
Thermal Decomposition of Precursors



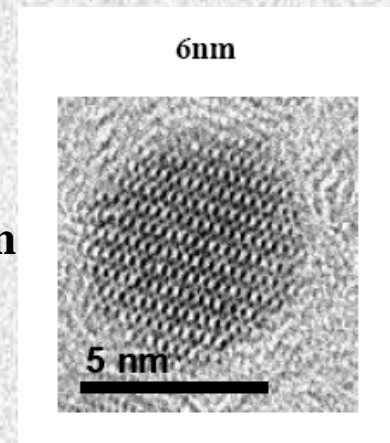
Separation of nucleation and growth

Fe(CO)₅ thermal decomposition at 100 °C contributes to nucleation

Fe(oleate) thermal decomposition at 350 °C contributes to growth



6 nm



Top-down Synthesis: Bulk Down

✘ Introduction of Crystal Defects (Dislocations, Grain Boundaries)

◇ High-Energy Ball Milling

final size only down to 100 nm, contamination

◇ Extrusion, Shear, Wear

◇ High-Energy Irradiation

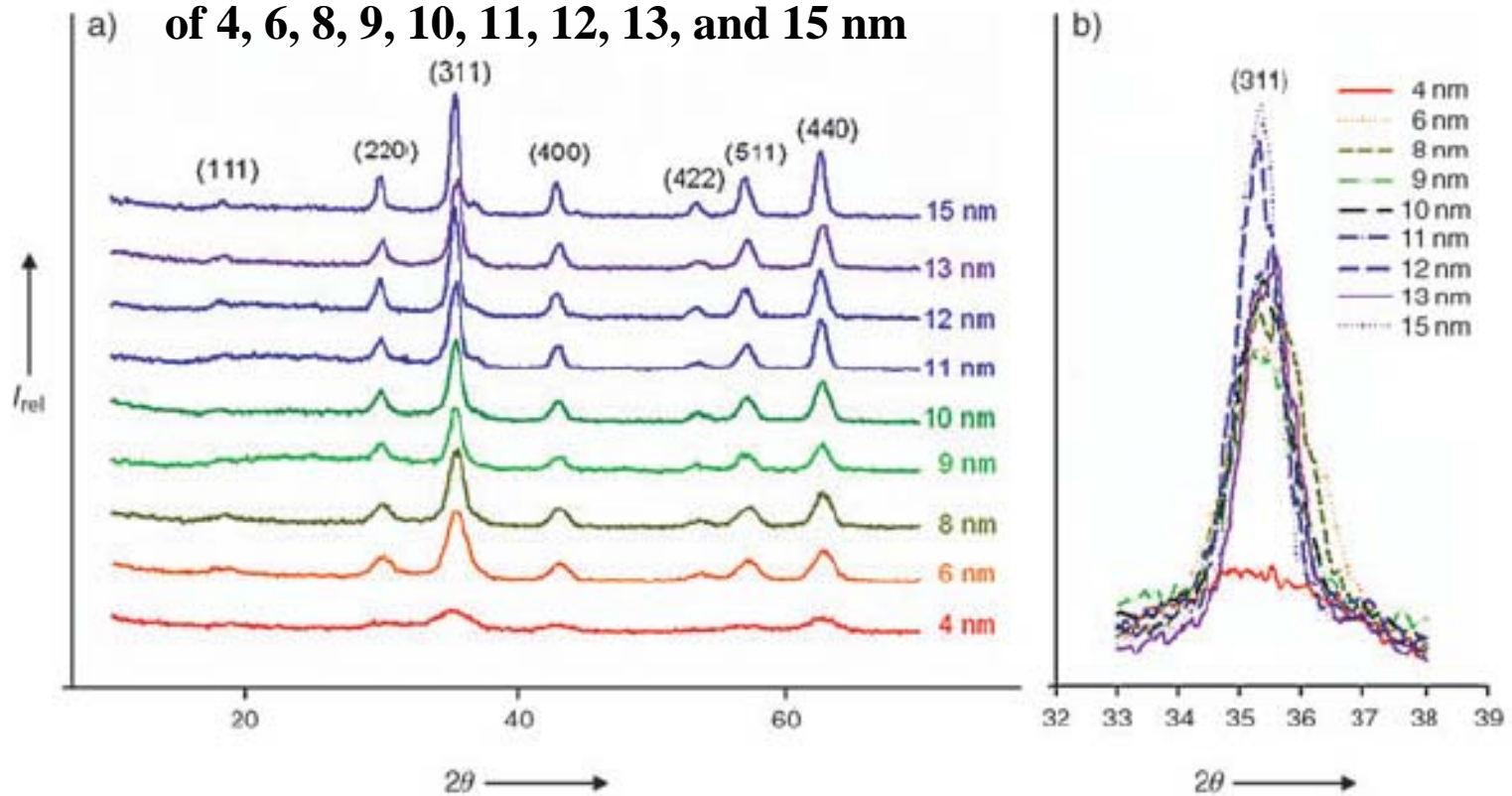
◇ Detonative Treatment

✘ Crystallization from Unstable States of Condensed Matter

◇ Crystallization from Glasses

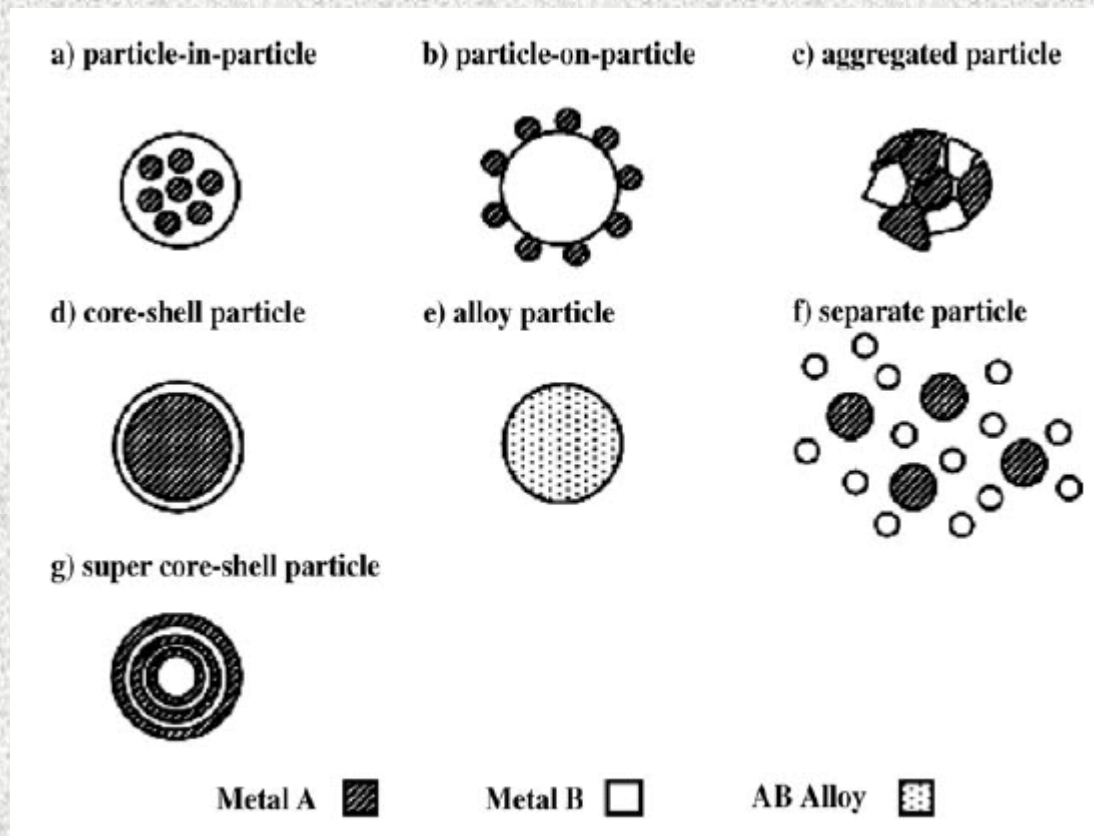
◇ Precipitation from Supersaturated Solid or Liquid Solutions

XRD patterns of iron oxide nanocrystals of 4, 6, 8, 9, 10, 11, 12, 13, and 15 nm



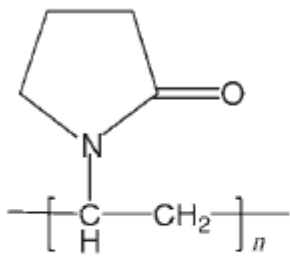
Nanocatalysis

Morphologies of bimetallic nanoparticles



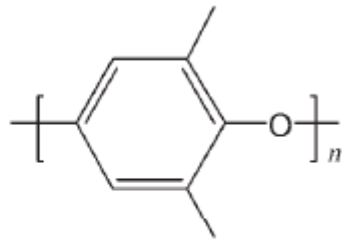
Nanocatalysis

Polymers used as metal NP supports for catalysis



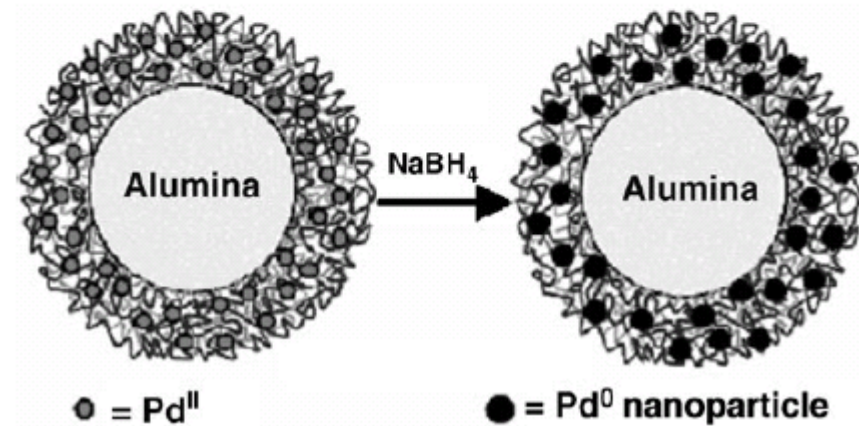
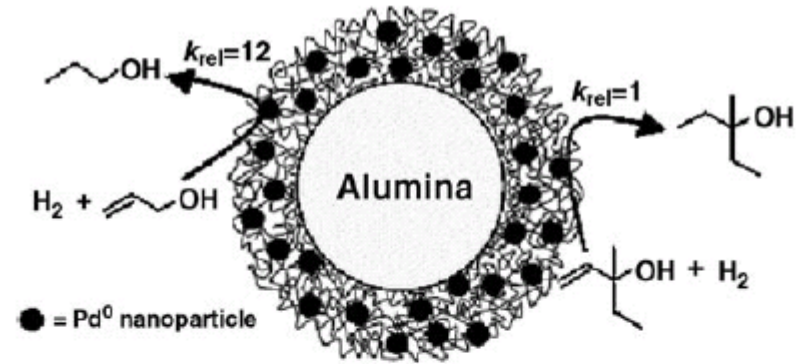
PVP

poly(vinylpyrrolidone)



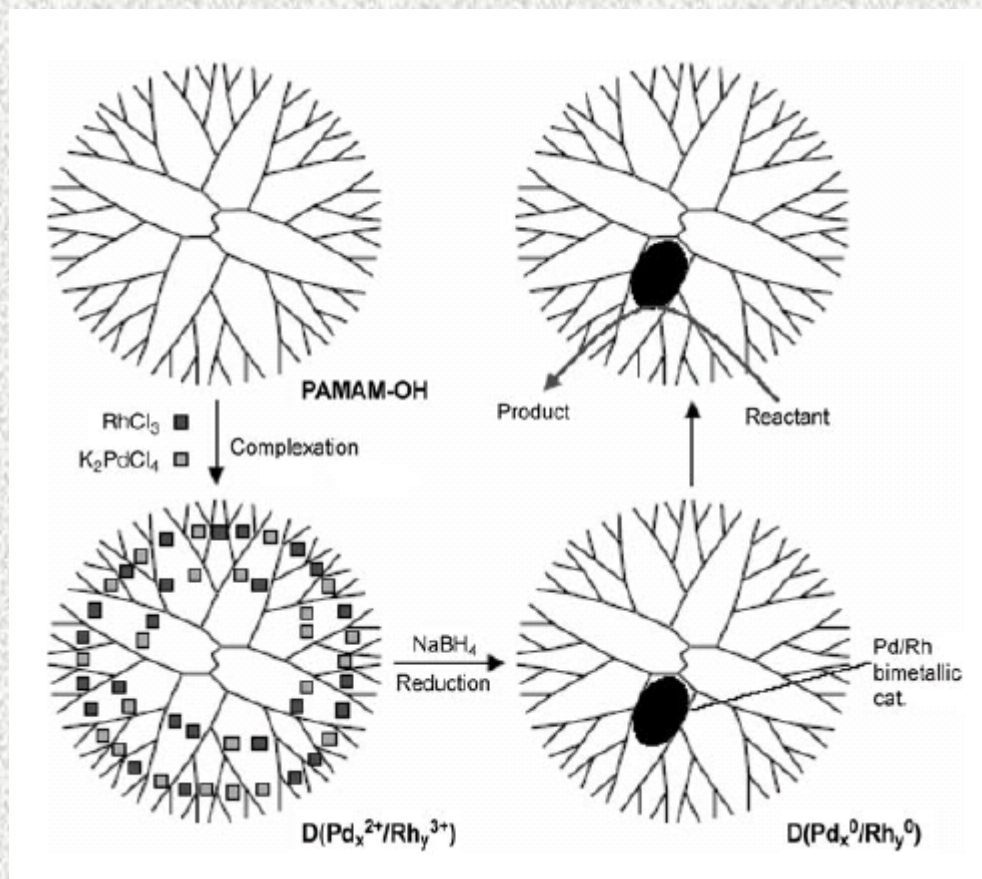
PPO

poly(2,5-dimethylphenylene oxid



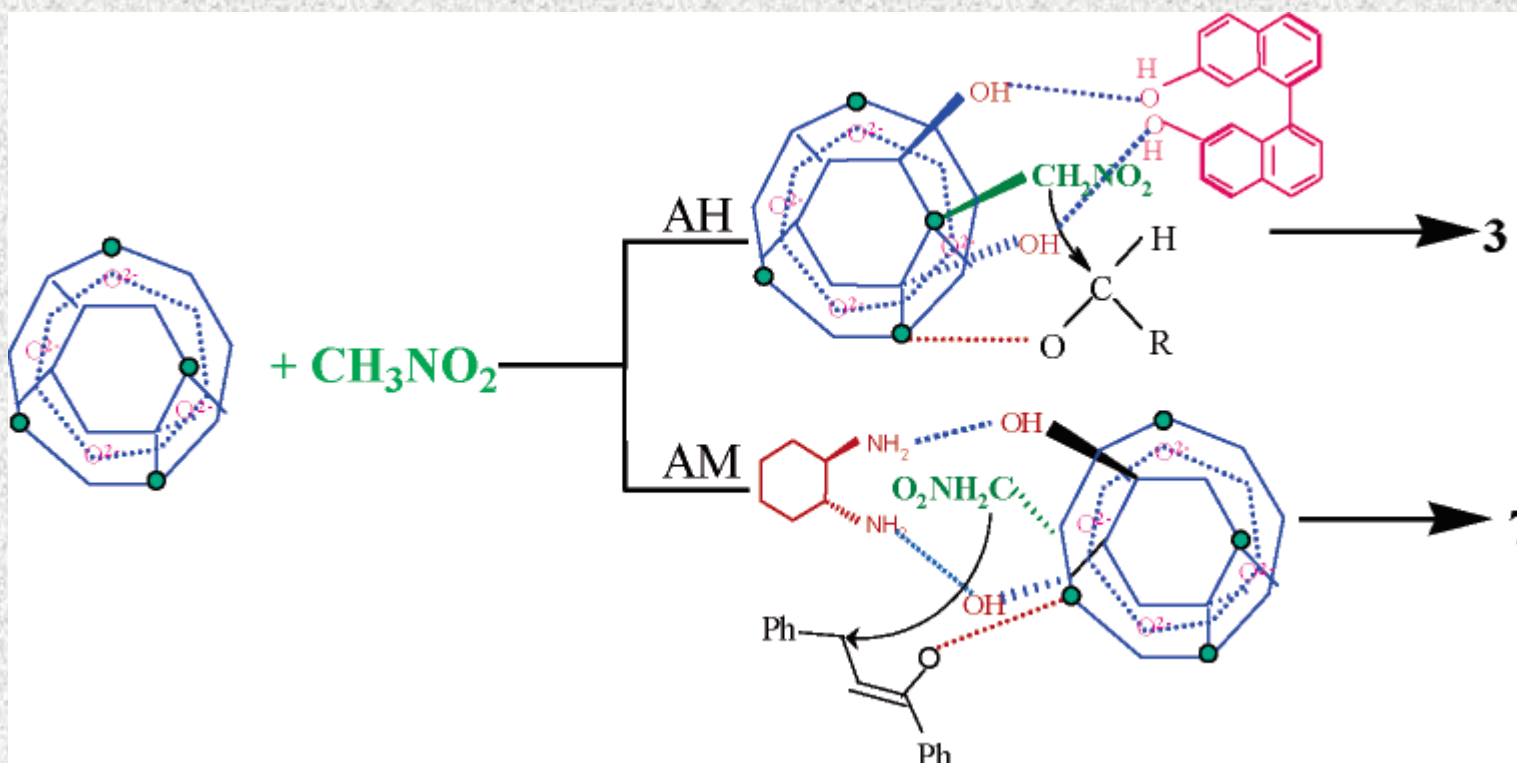
Nanocatalysis

Catalysis by nanoparticles encapsulated in PAMAM or PPI dendrimers



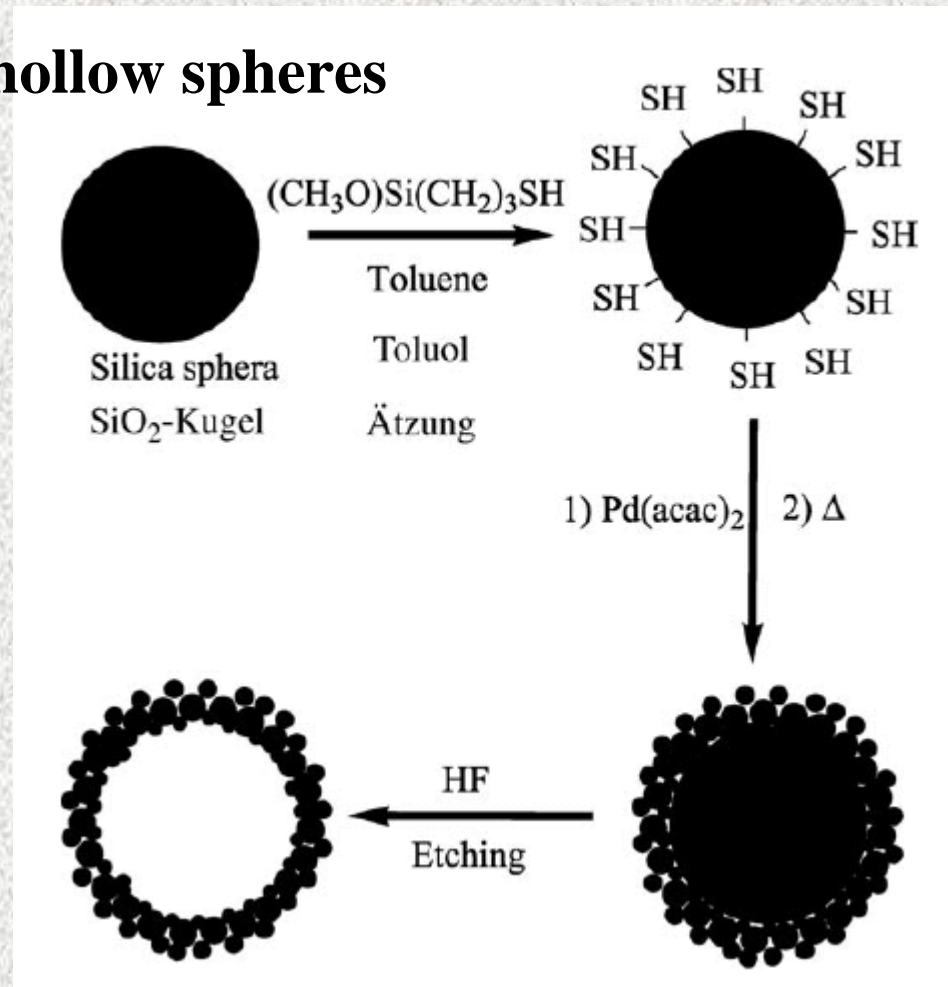
Nanocatalysis

Asymmetric heterogeneous catalysis on nanoparticles



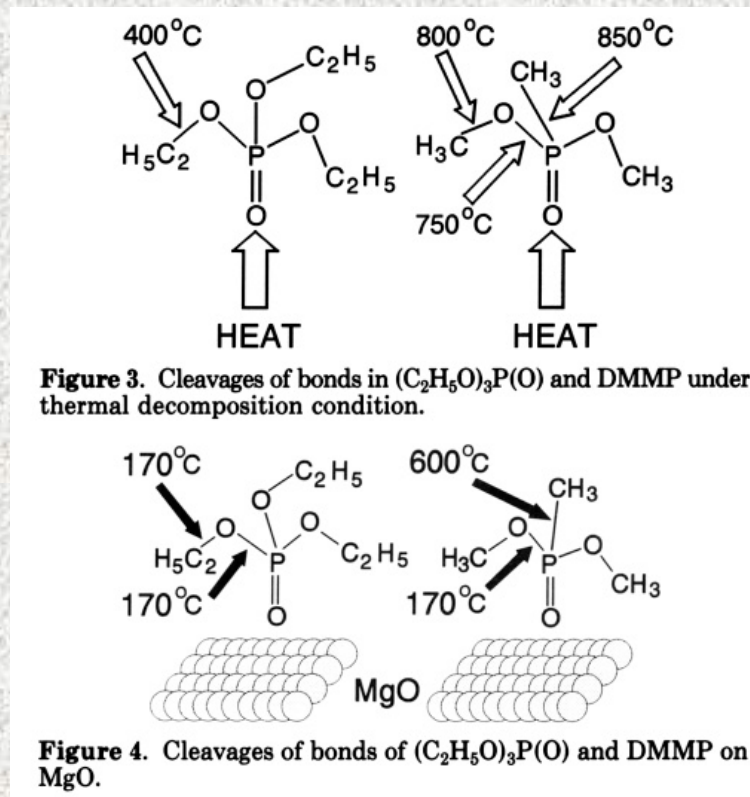
Hollow Nanoparticles

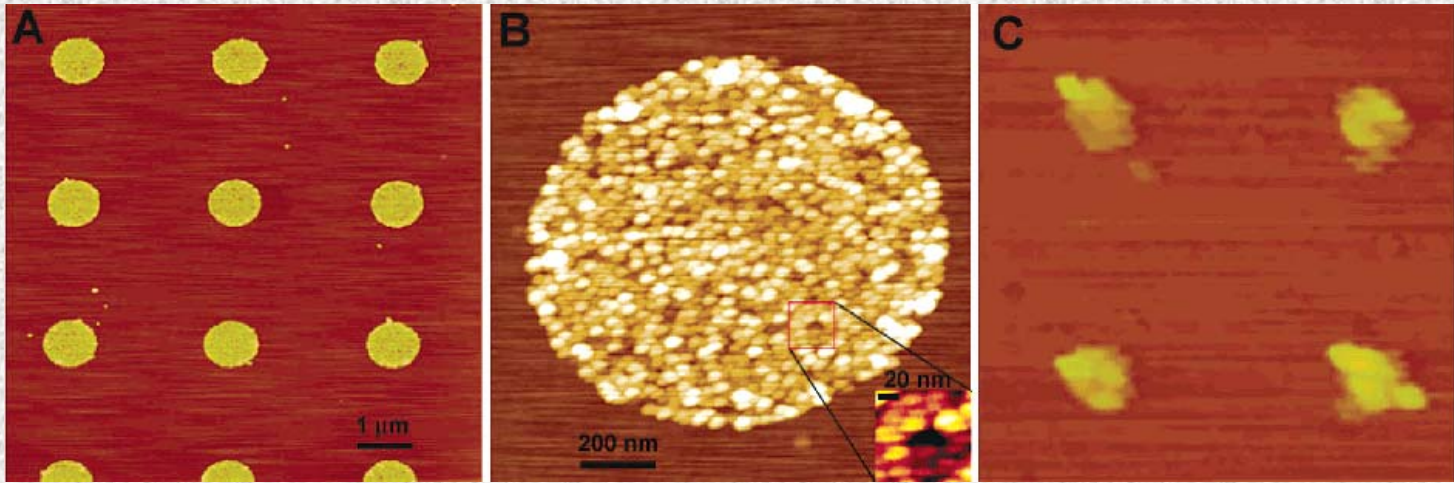
formation of hollow spheres



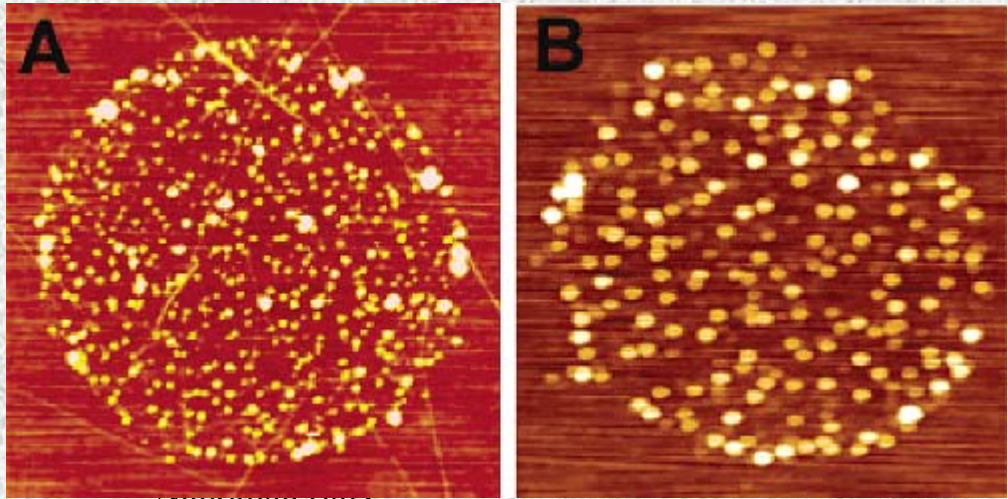
Applications

Destruction of dangerous organic compounds (organophosphates - VX, chlorinated - PCB)

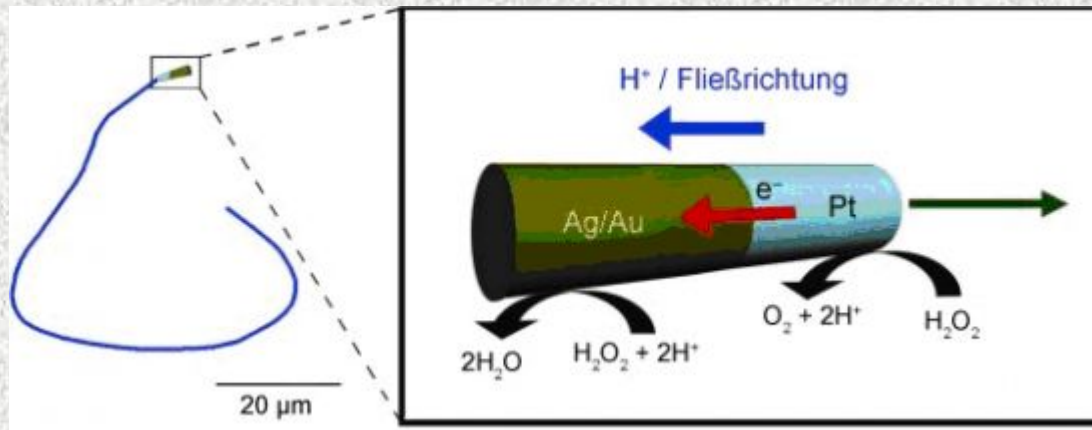




CNT growth



Nanoengine



Nanomotor funguje díky katalýze (viz obr.) U platinové části tyčinky se štěpí peroxid vodíku (H_2O_2) na kyslík (O_2) a protony (H^+). Přebytečné elektrony se přesunují k stříbrozlaté části tyčinky, čímž nastartují redukční reakci H_2O_2 a protonů a vzniká voda. Uvolnění kyslíku a vody vytváří slabé proudění, které žene nanotyčinku kapalinou, a to platinovou částí napřed. Slovo Fließrichtung na obrázku znamená směr proudění.

Slitina zlata a stříbra se postará o to, že se k ní elektrony přesunují rychleji. Tím se urychlí i rozpad pohonné látky a tyčinky jsou o to rychlejší.

150 mikrometrů za sekundu

Josepha Wanga z Kalifornské univerzity v San Diegu a Arizonské státní univerzity

Nanomaterials