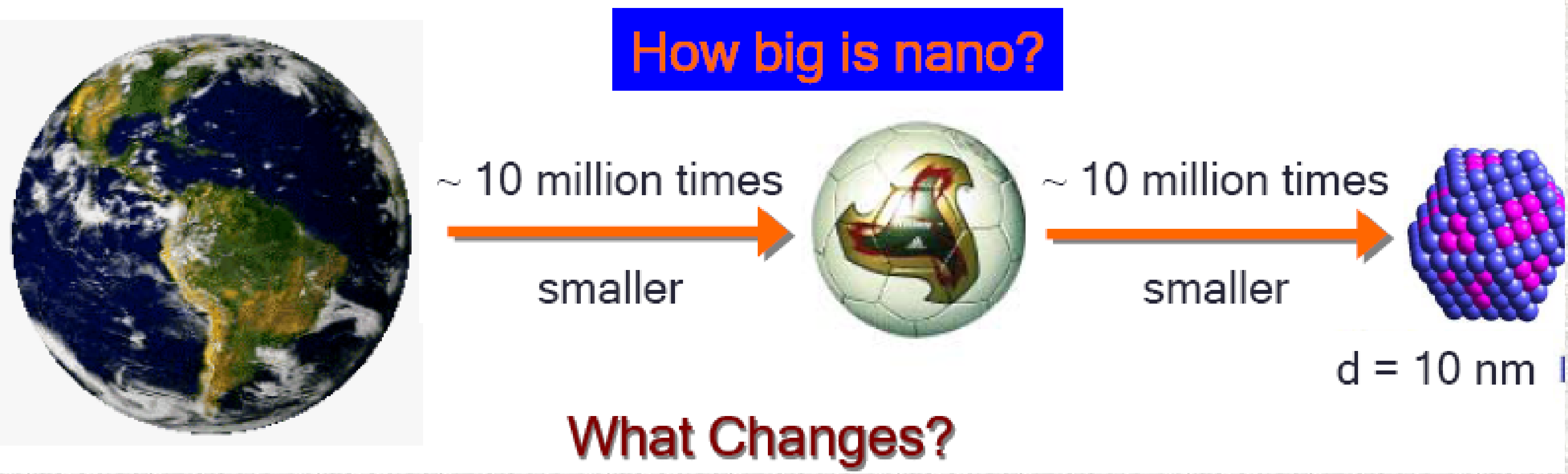
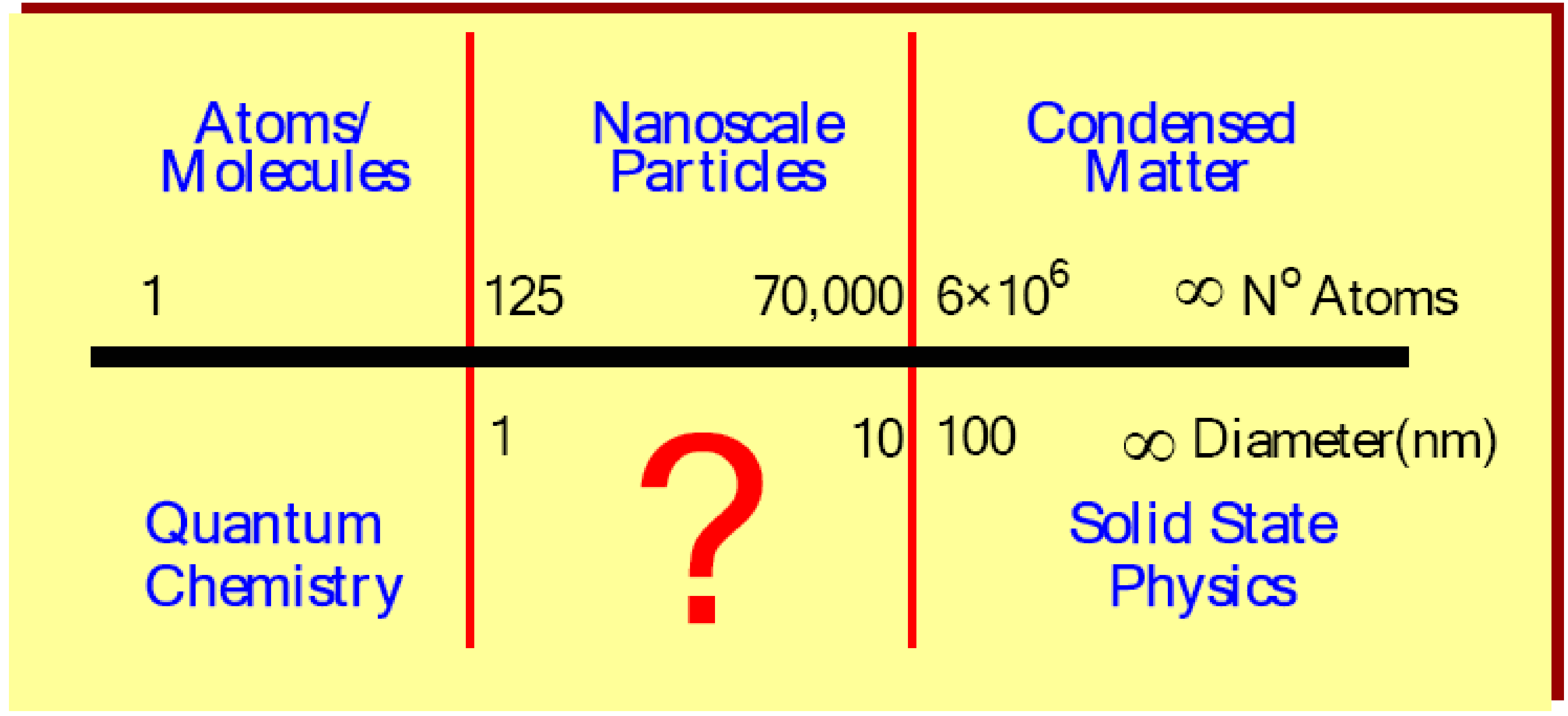
Nanoscopic Materials



- **Chemical methods to change physical and chemical properties – composition, substituents,….**
- **Size is another variable to change physical and chemical properties for constant chemical composition**
- **Each physical property or fenomenon has a characteristic length**
- **When particle size is comparable to the characteristic length, property start to depend on the size**

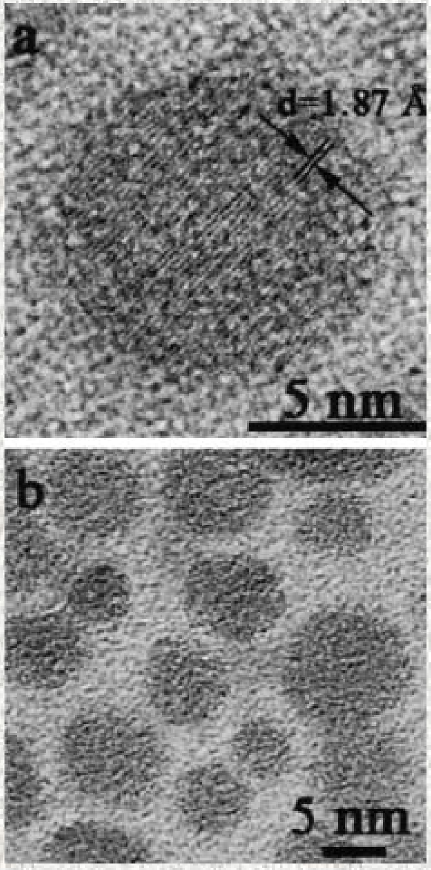
Nanoscopic Scales



Atoms/ Molecules	Nanoscale Particles		Condensed Matter	
1	125	70,000	6×10^6	∞ N° Atoms
	1	10	100	∞ Diameter(nm)
Quantum Chemistry	?		Solid State Physics	

Nanoscopic Materials

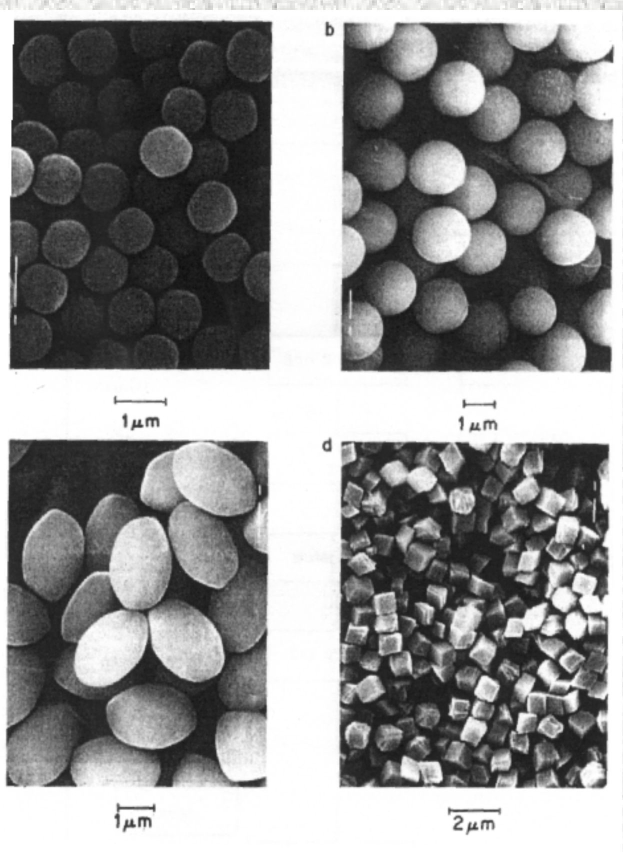
Nanoparticles 1 – 100 nm



1 nm = 10^{-9} m

1 nm = 10 Å

Traditional materials > 1 μm



Nanoscopic Materials

Size 1 – 100 nm

EU definition (2011):

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm.

http://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm

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 $Ca_5(PO_4)_3(OH)$ + collagen**
☯ **Asbestos, opals, calcedon**
☯ **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.

Nanostructural Materials

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

The horrible beasties 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.

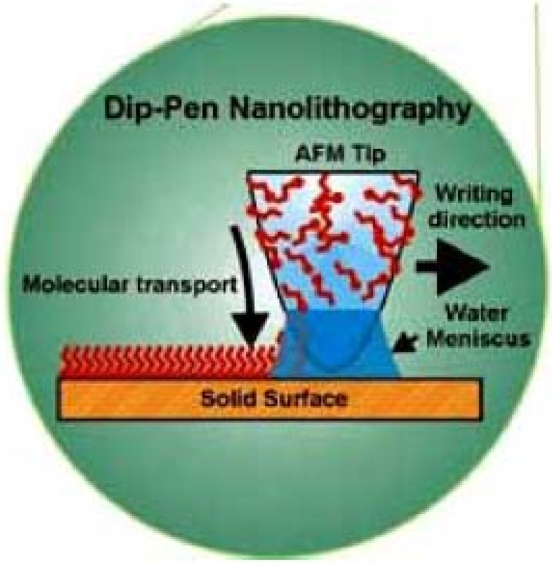
Room at the Bottom

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

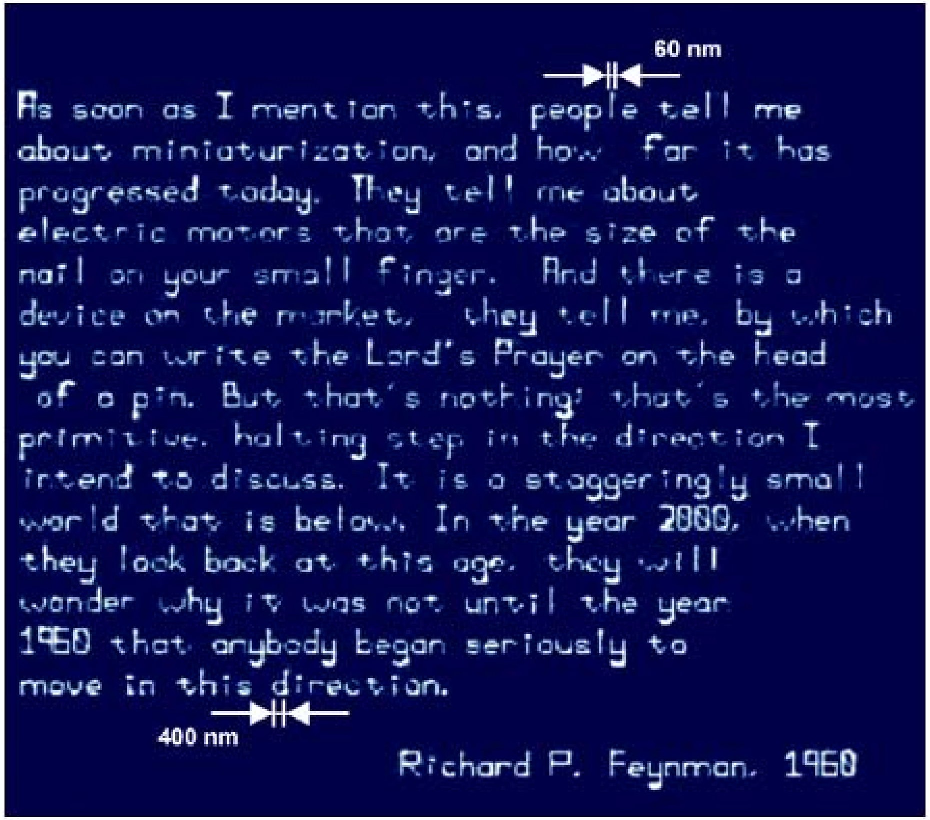
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. 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.)



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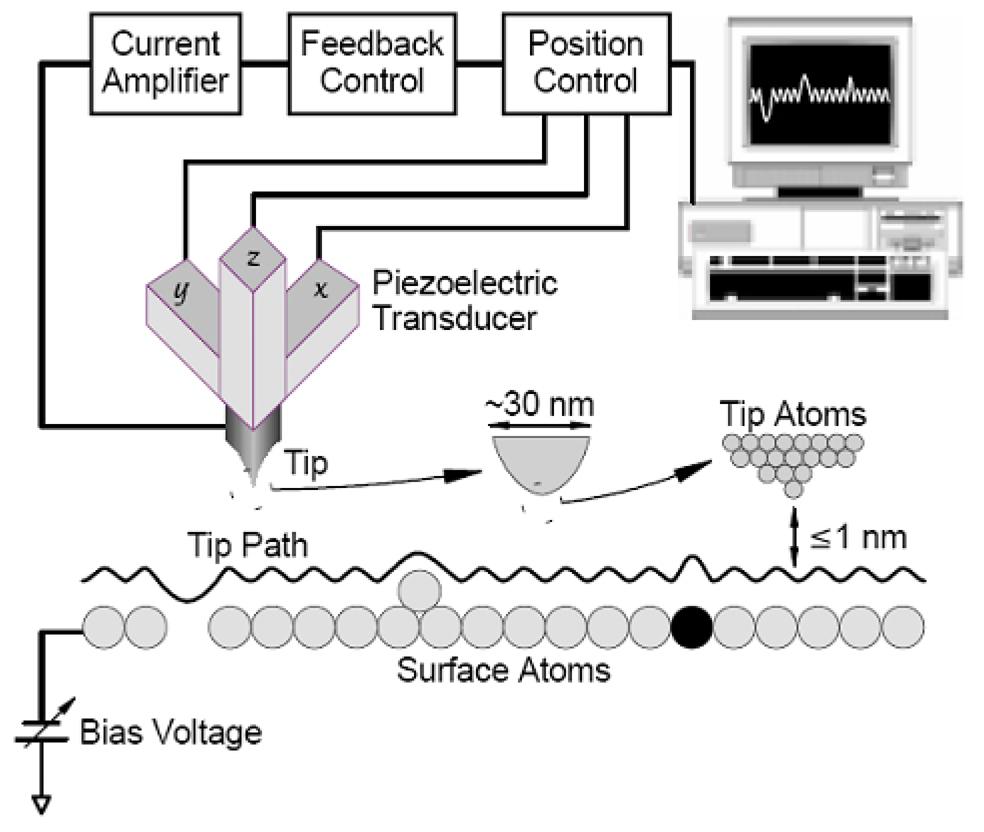
Richard P. Feynman, 1960

STM

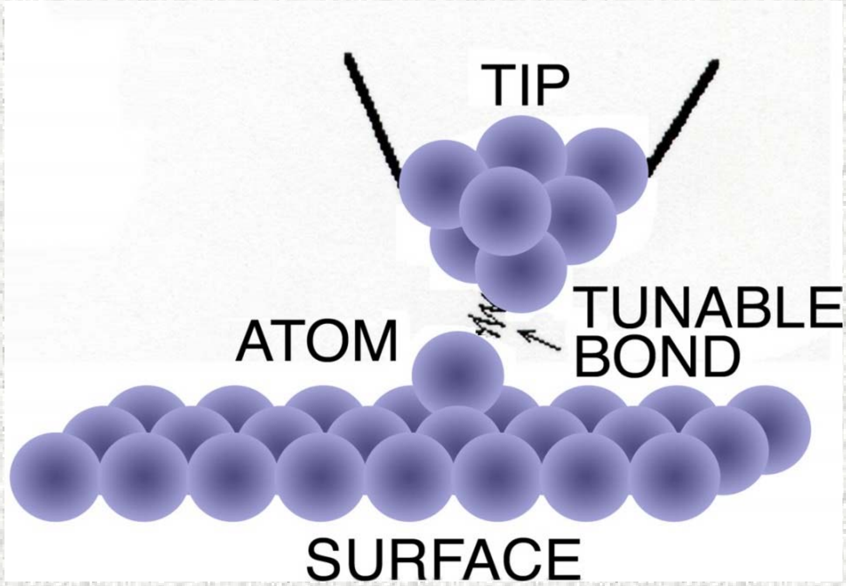
Scanning Tunelling Microscopy

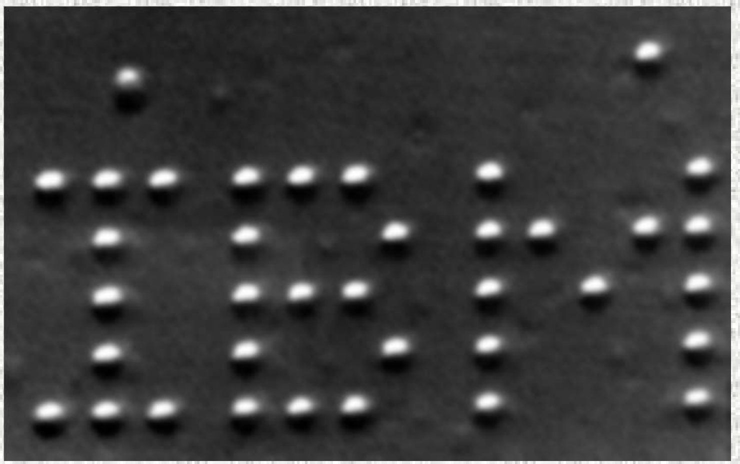


Binning and Rohrer
Nobel Prize 1986

Nanoscale Writing

STM positioned Xe atoms on Ni crystal, 5 nm letters





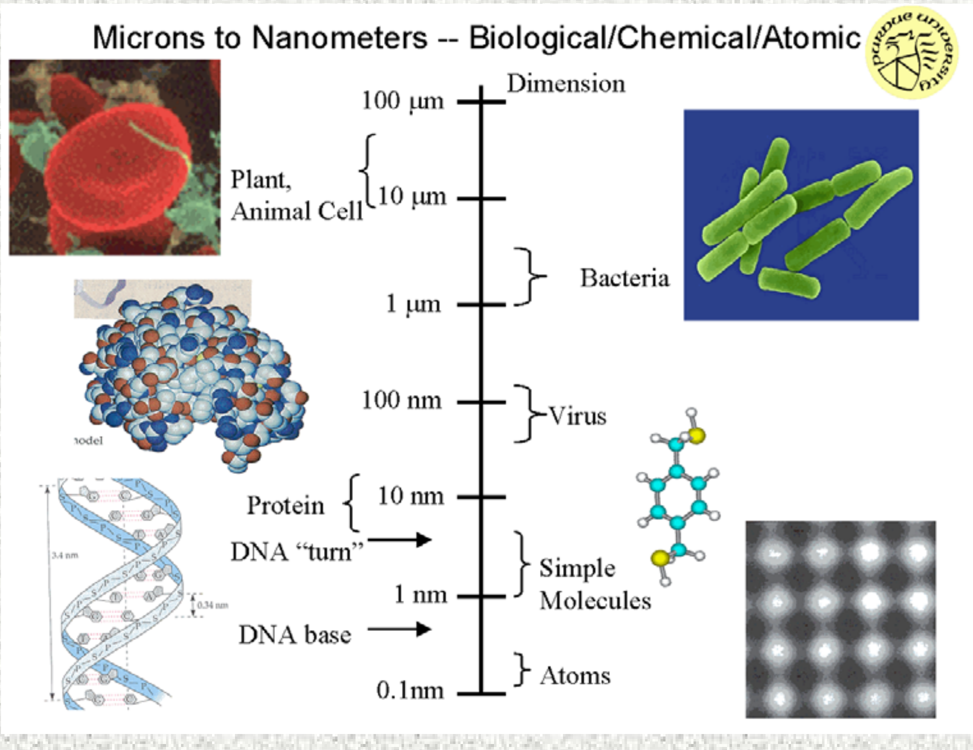
Properties of Nanoscopic Materials

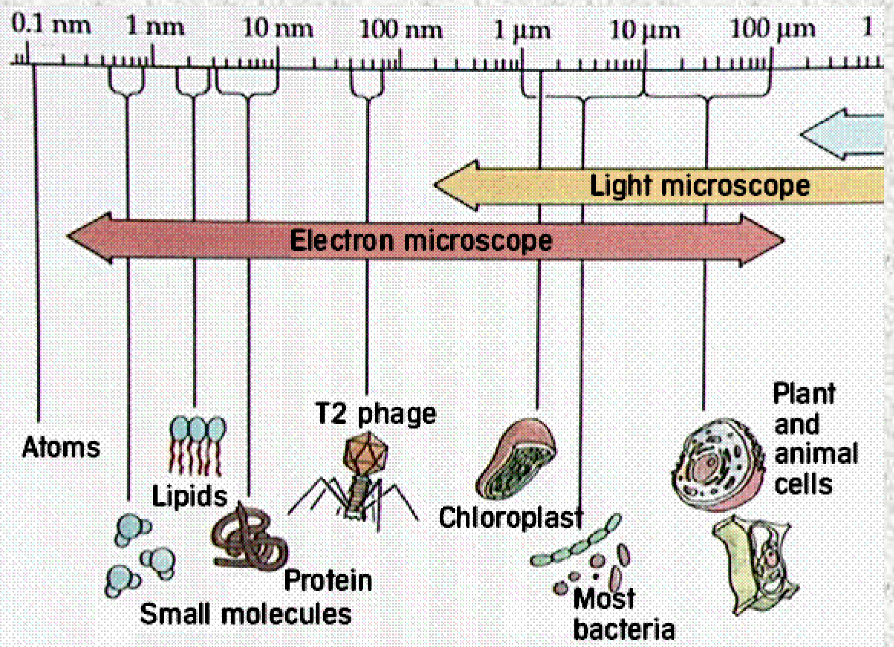
- **Metallic behavior - a single atom cannot behave as a metal, nonmetal to metal transition : 100-1000 atoms**
- **Magnetic behavior - Single domain particles, large coercive field**
- **Depression of melting points in nanocrystals**

bulk Au mp 1064 °C → 10 nm Au 550 °C

- **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, medical and biological applications**

Nanoscopic Size





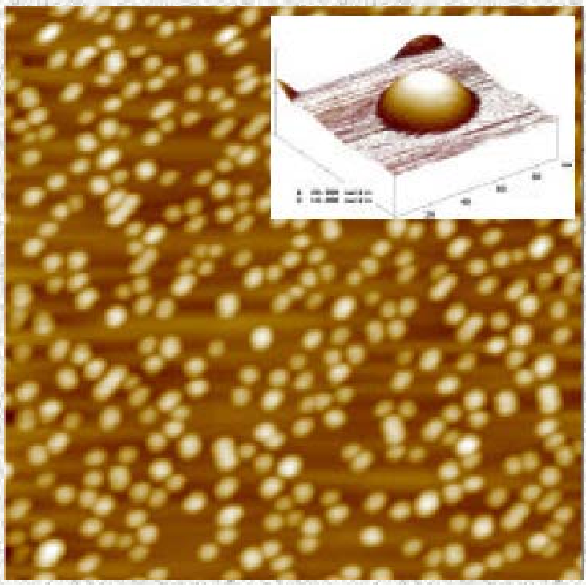
The largest known bacterium -
Thiomargarita namibiensis - 100-750 microns

The Nano-Family

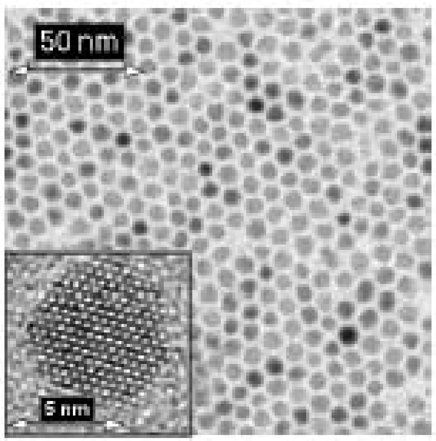
At least one dimension is between 1 - 100 nm

0-D structures (3-D confinement):

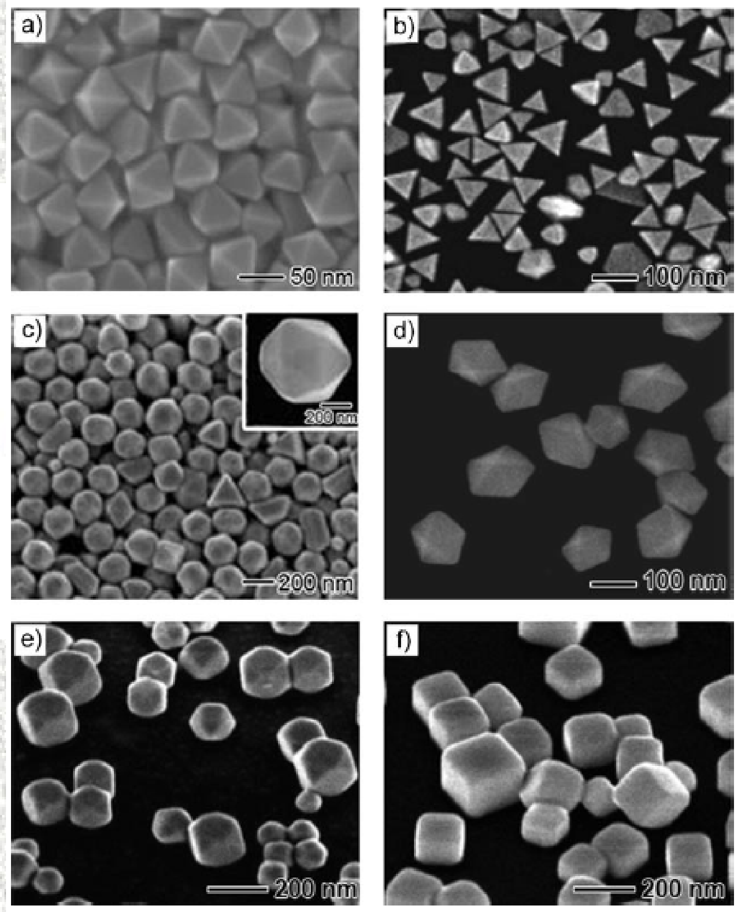
- **Quantum dots**
- **Nanoparticles**



AFM 1 µm x 1 µm
InAs on GaAs/InP



CdTe nanoparticles



Au nanoparticles

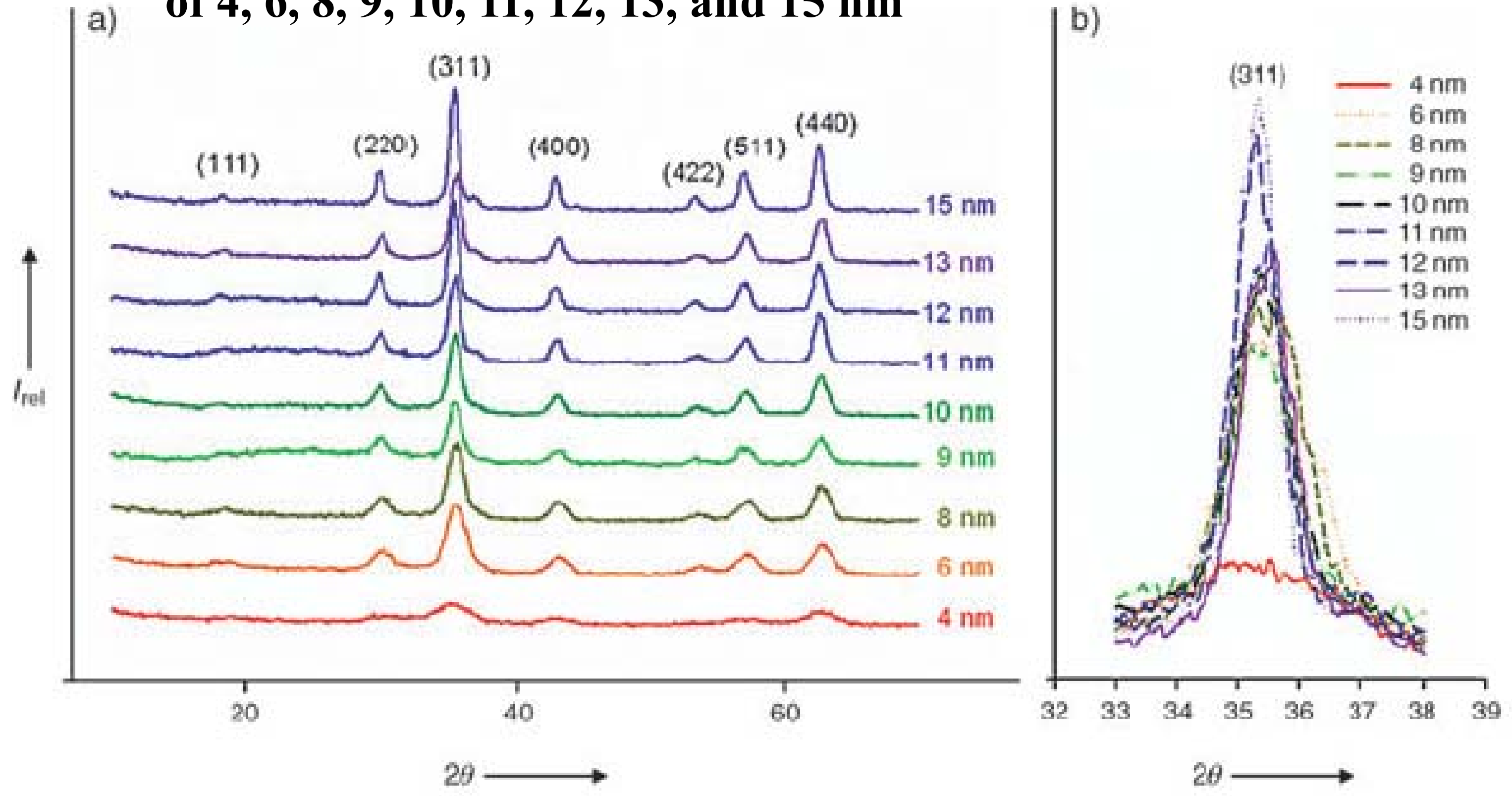
Coherence Length, *d*

Scherrer equation

$$d = \frac{k\lambda}{\beta \cos\theta}$$

k = 0.89, λ = wavelength,
β = full width at half-maximum of a standard (Si)

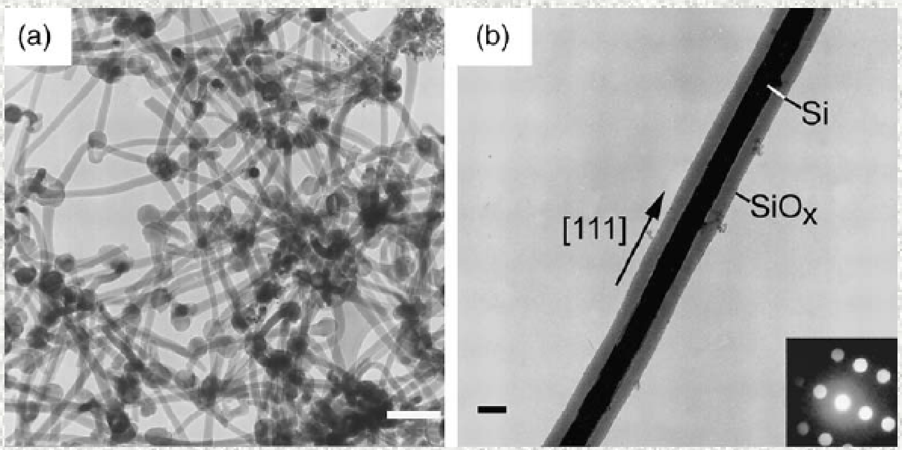
XRD patterns of iron oxide nanocrystals of 4, 6, 8, 9, 10, 11, 12, 13, and 15 nm

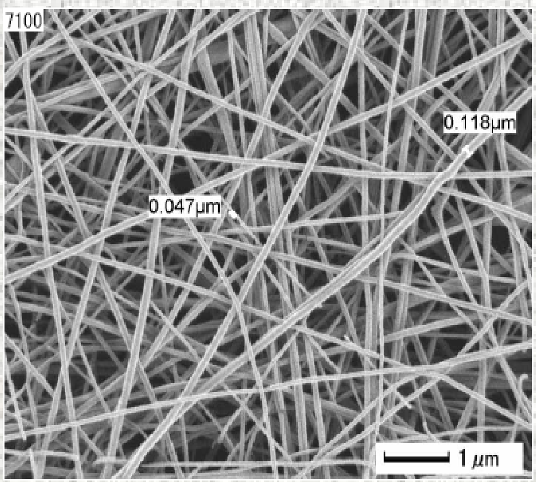


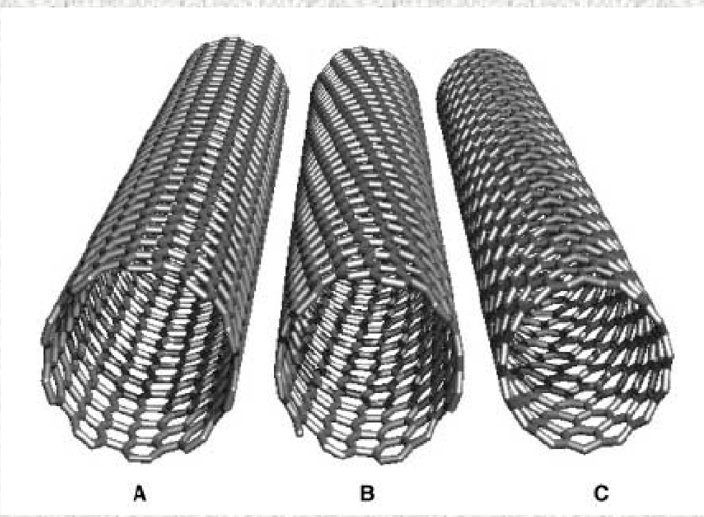
The Nano-Family

1-D structures (2-D confinement):

- **Nanowires**
- **Nanorods**
- **Nanotubes**
- **Nanofibers**



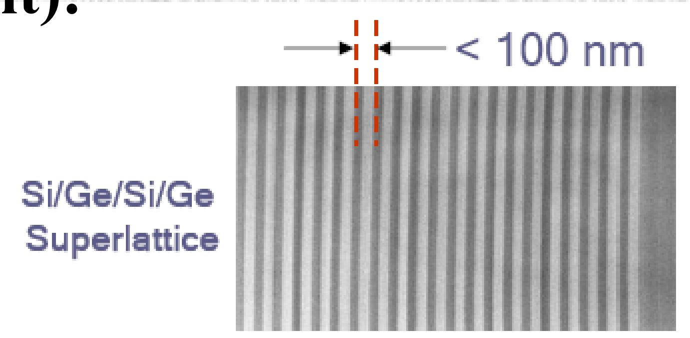


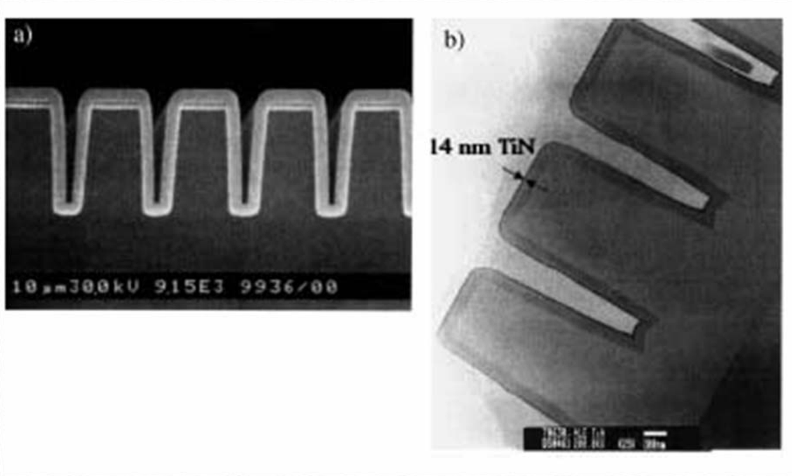


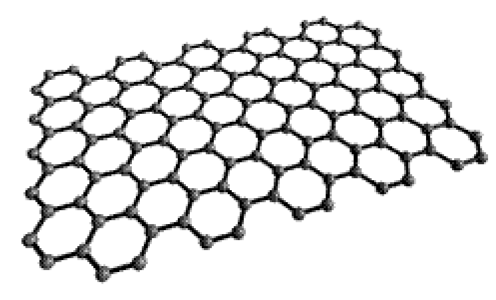
The Nano-Family

2-D structures (1-D confinement):

- **Thin films - CVD, ALD**
- **Planar quantum wells**
- **Superlattices**
- **Graphene**
- **SAM**



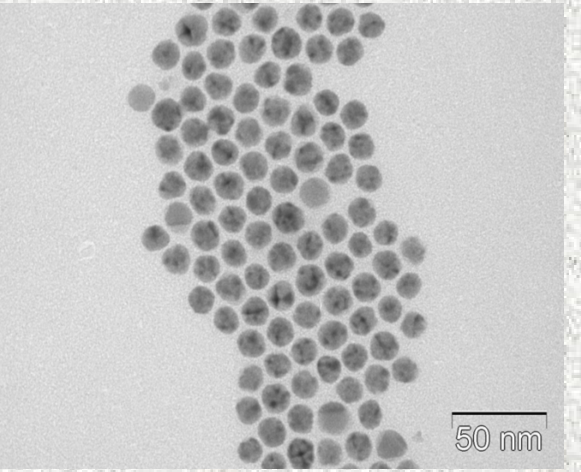




Nanoscopic Behavior of Materials

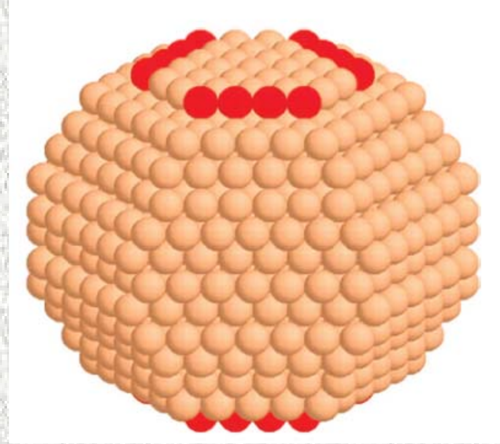
Differences between bulk and nanoscale materials

- **Surface Effects**
- **Quantum Confinement Effects**

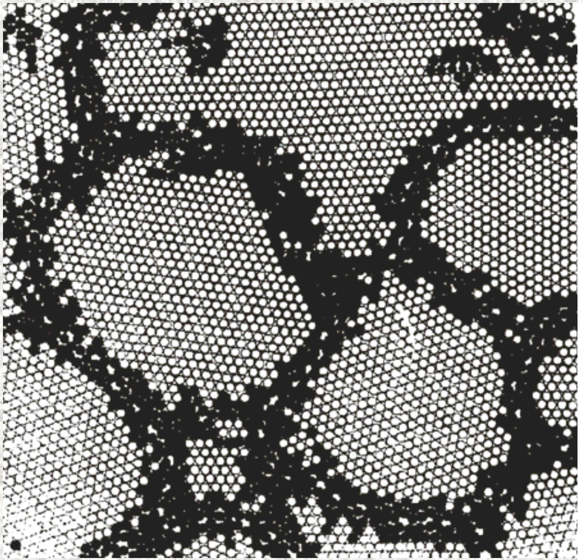


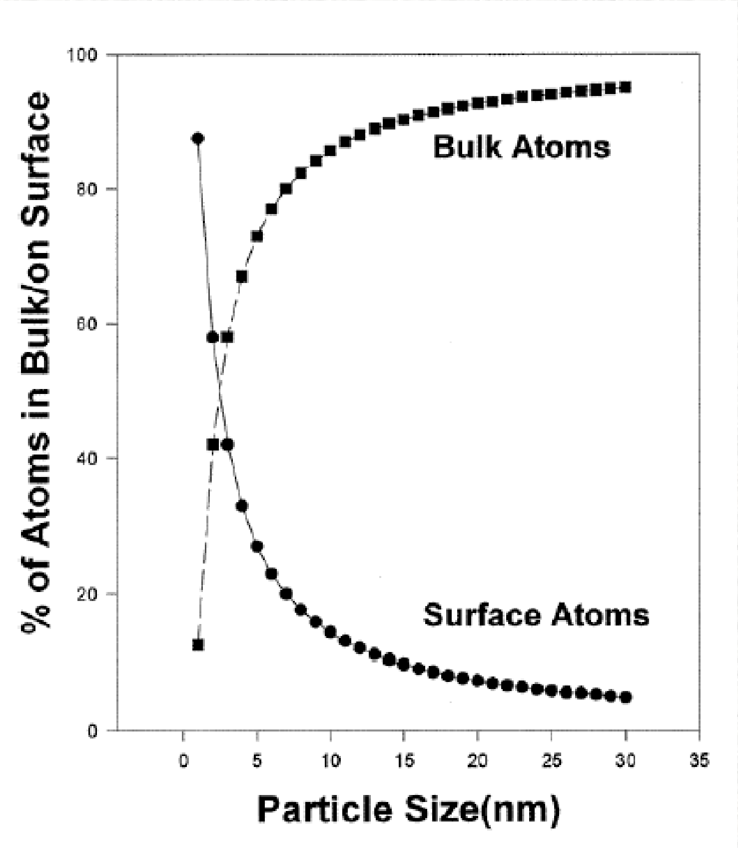
Surface Effects

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



Ru particle diameter 2.9 nm





Surface Effects

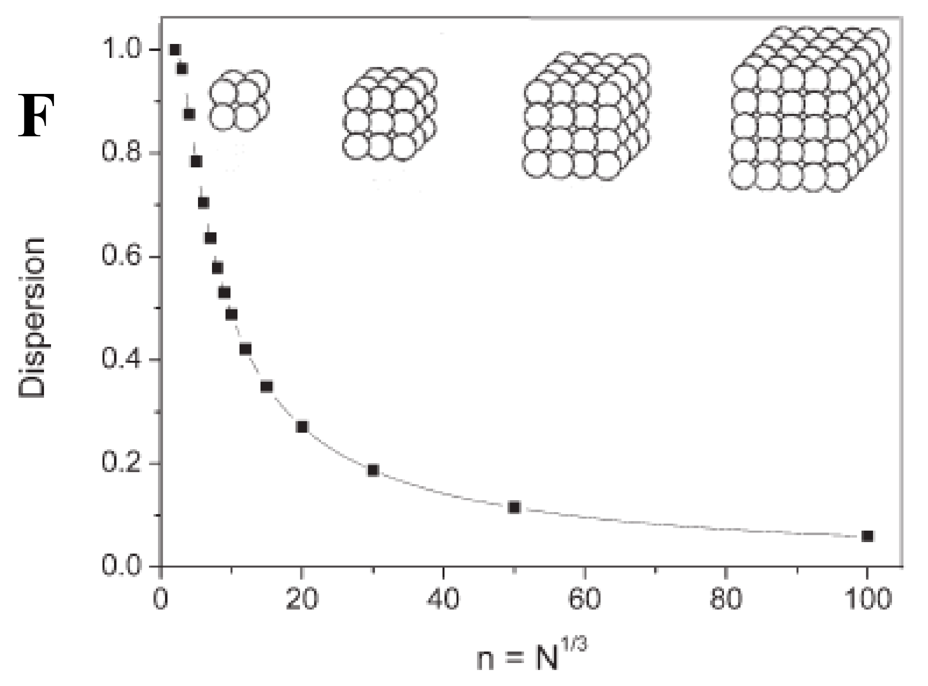
Dispersion F = the fraction of atoms at the surface

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

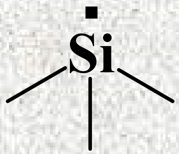
- Lower coordination number of atoms
- Reduced atomic density (by 10 – 30 %)
- Broad spectrum of interatomic distances

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

- fewer neighbors than atoms in the bulk = lower coordination number
- stronger and shorter bonds
- unsatisfied bonds
- surface atoms are less stabilized than bulk atoms

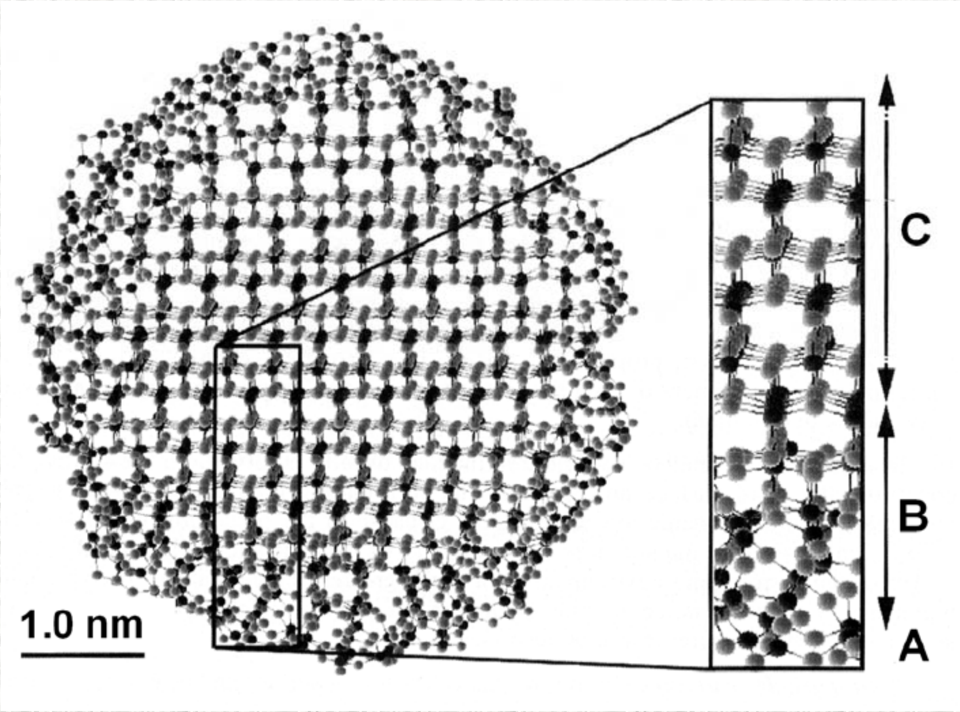
The smaller a particle the larger the fraction of atoms at the surface, and the higher the average binding energy per atom

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

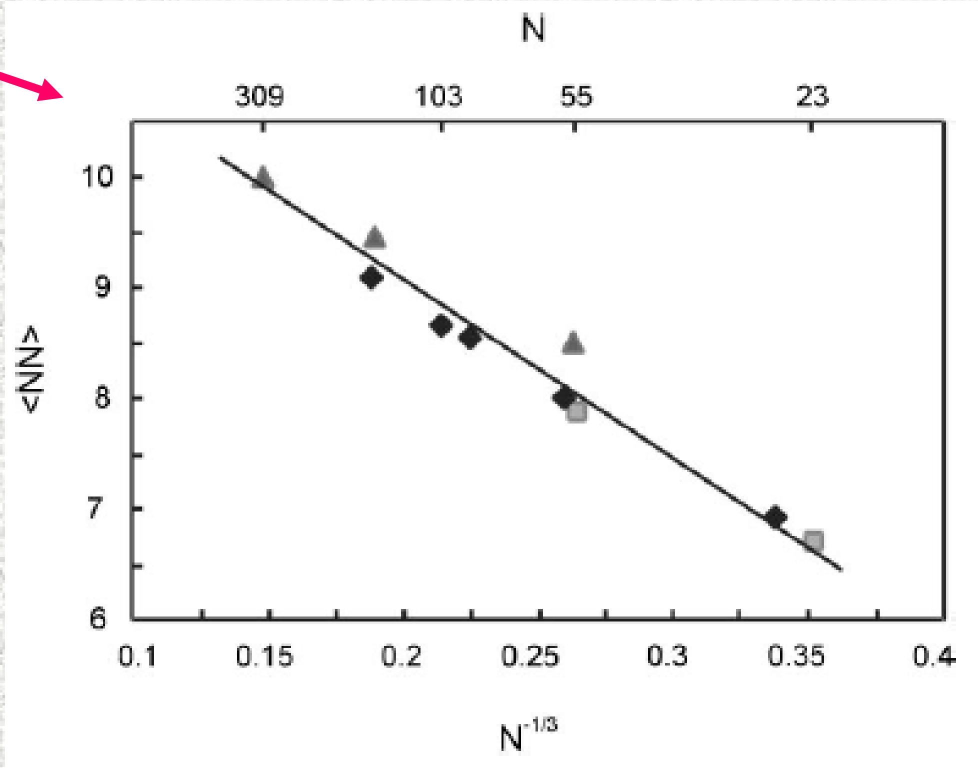


A = Atoms at surfaces (one layer) – fewer neighbors, lower coordination, unsatisfied (dangling) bonds
B = Atoms close to surface (several layers) – deformation of coordination sphere, distorted bond distances and angles
C = Bulk atoms, regular ordering – not present in particles below 2 nm

Graphite shells

What value ?

Surface Effects



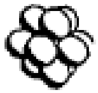
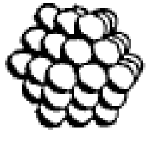
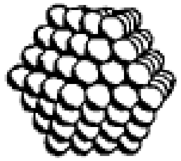
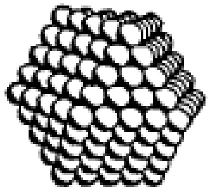
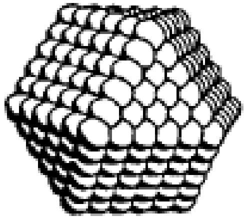
Mean coordination number

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

Surface Effects

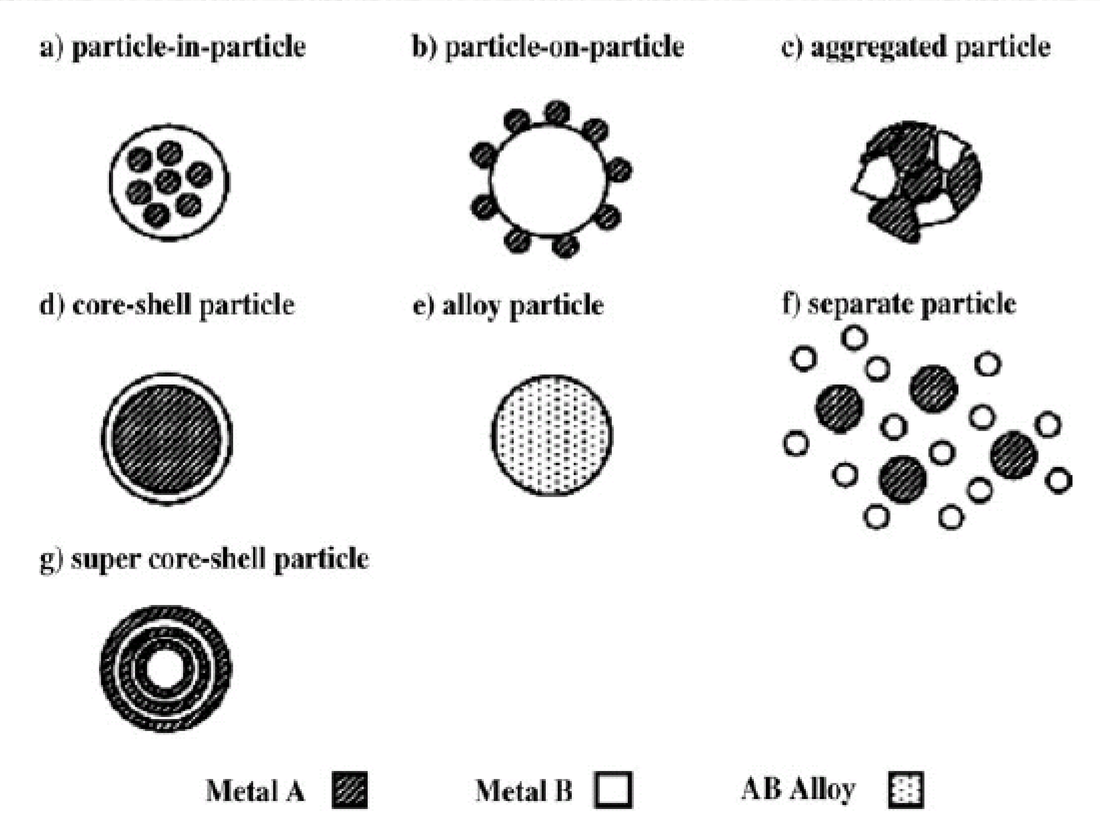
Atom binding (vaporization) energies lower in nanoparticles, fewer neighbors to keep atoms from escaping

Plasticity of nanocrystalline ceramics

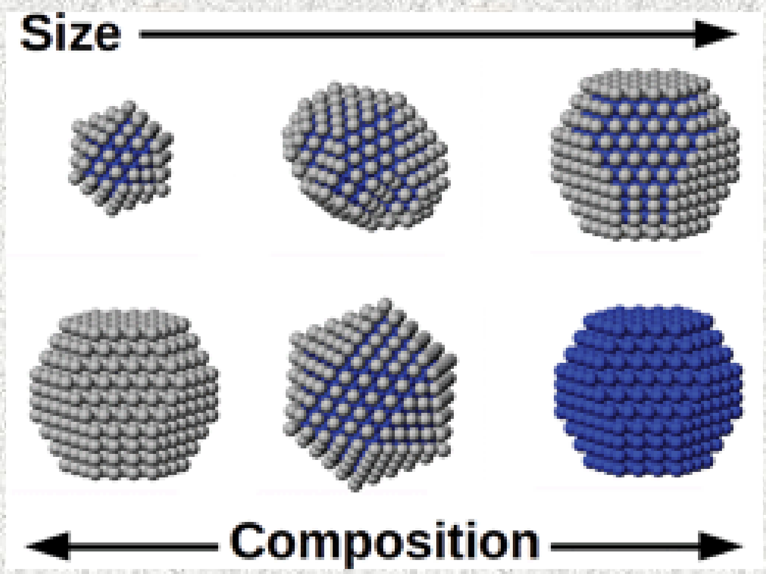
Full-shell "magic number" clusters					
Number of shells	1	2	3	4	5
Number of atoms in cluster	13	55	147	309	561
Percentage of surface atoms	92	76	63	52	45

Surface Effects

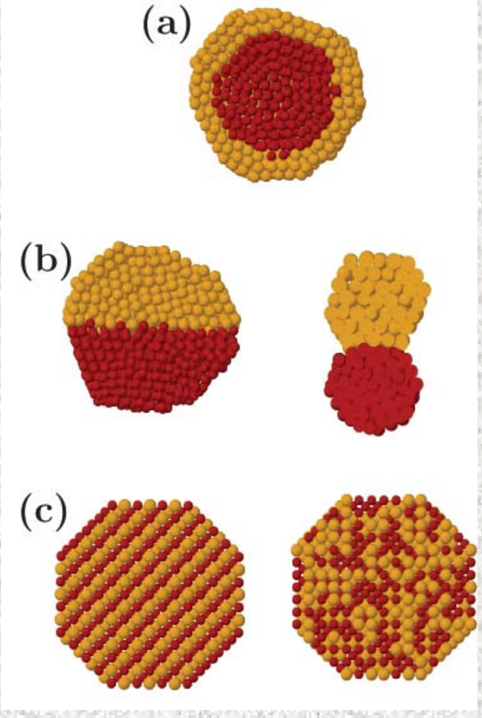
Morphologies of bimetallic nanoparticles

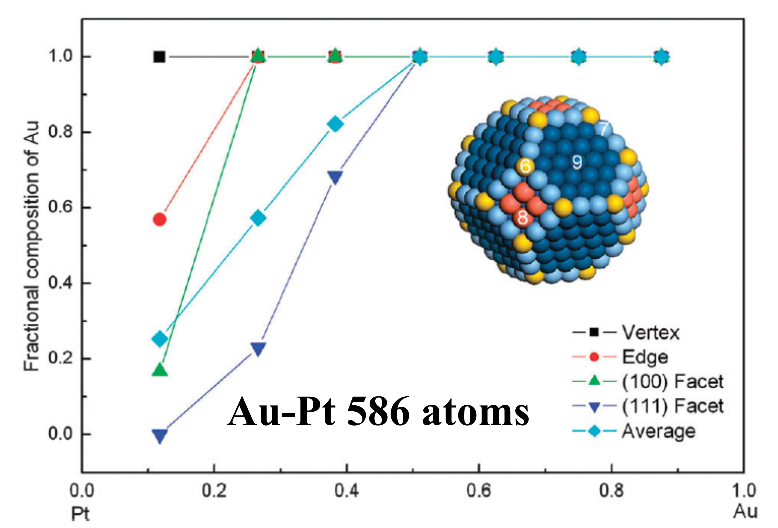


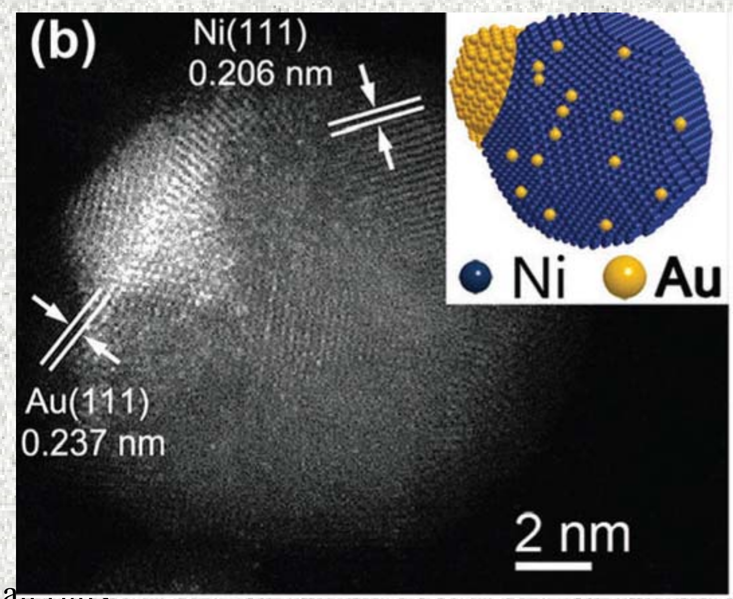
Surface Effects in Alloys



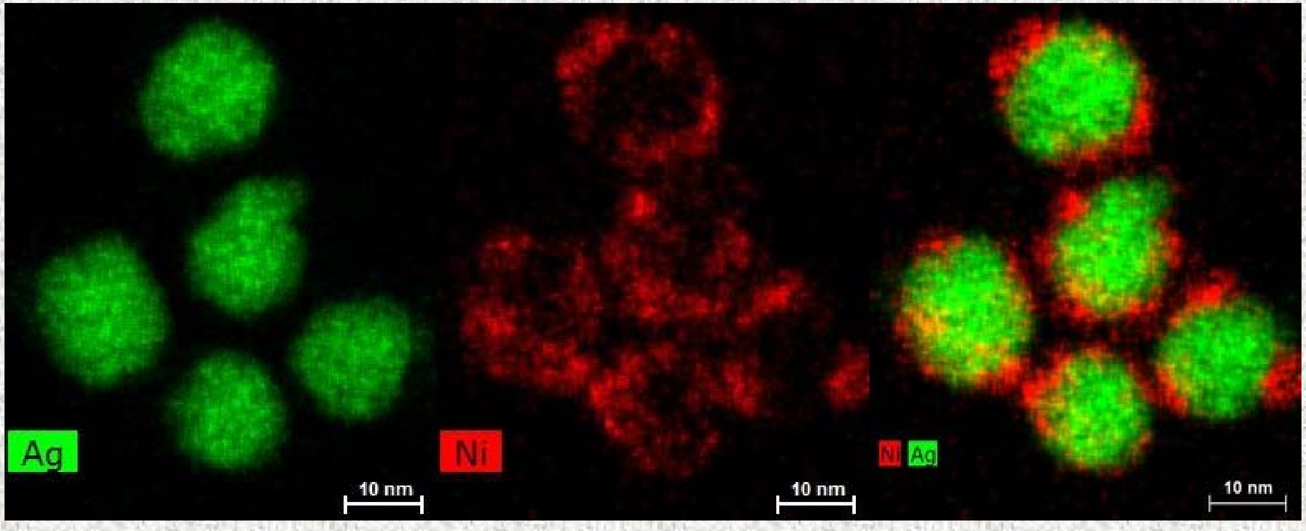
Alloys:
Core-shell
Janus
Random mixture



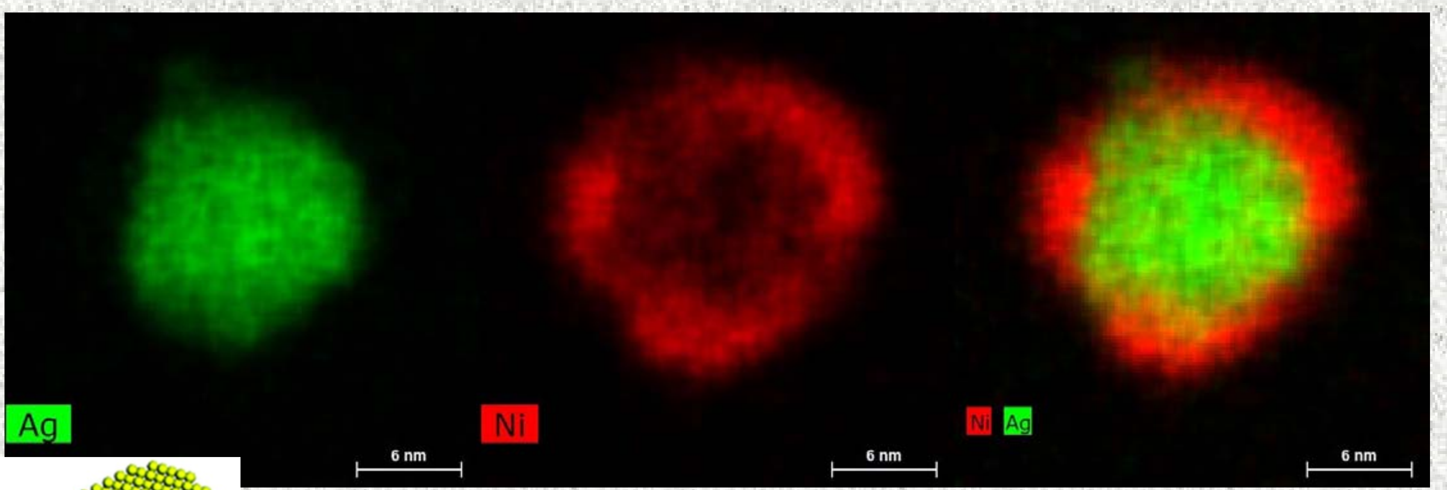




Transition Electron Microscopy Energy Dispersive X-ray Spectroscopy

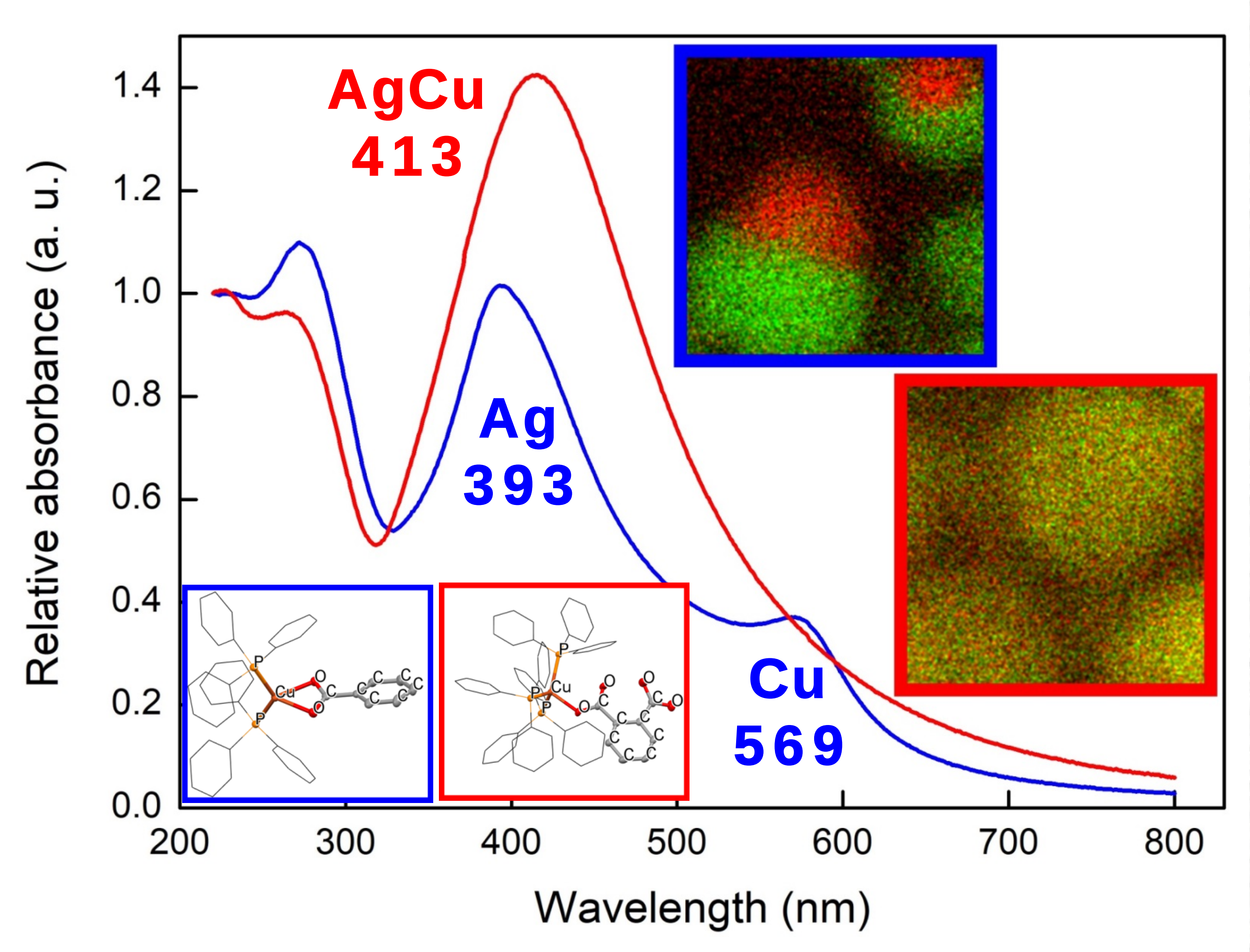


ICP-OES: Ag 68.8 mol%, EDS: Ag 84.2 mol%

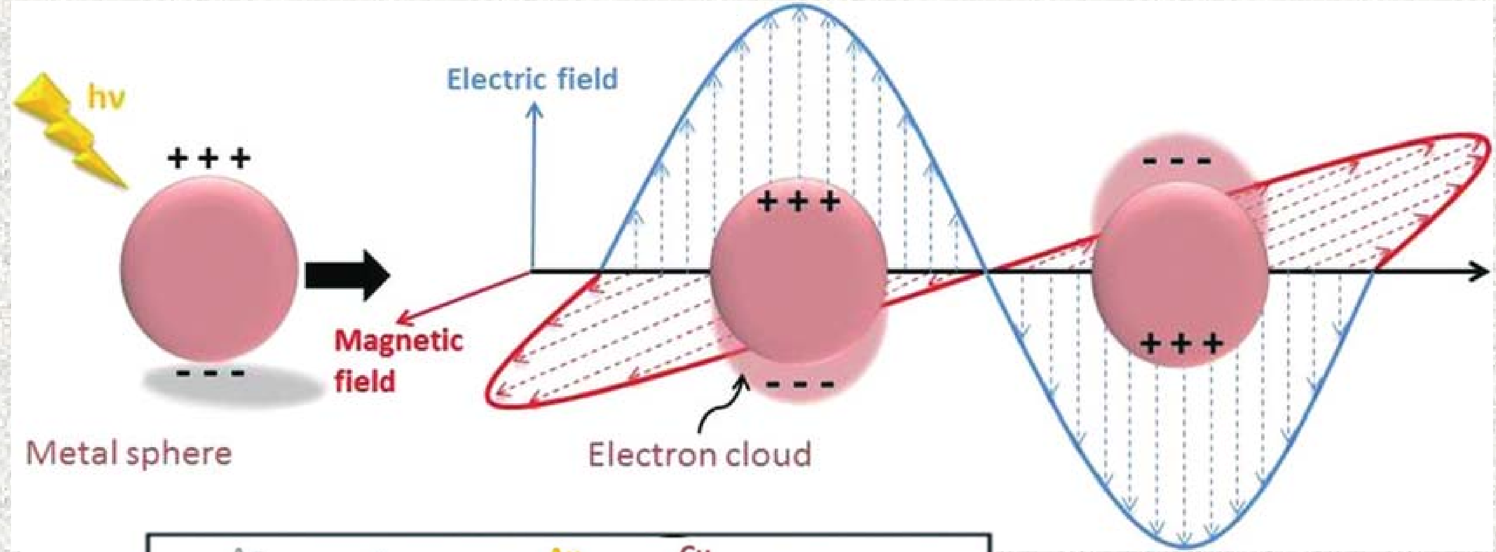


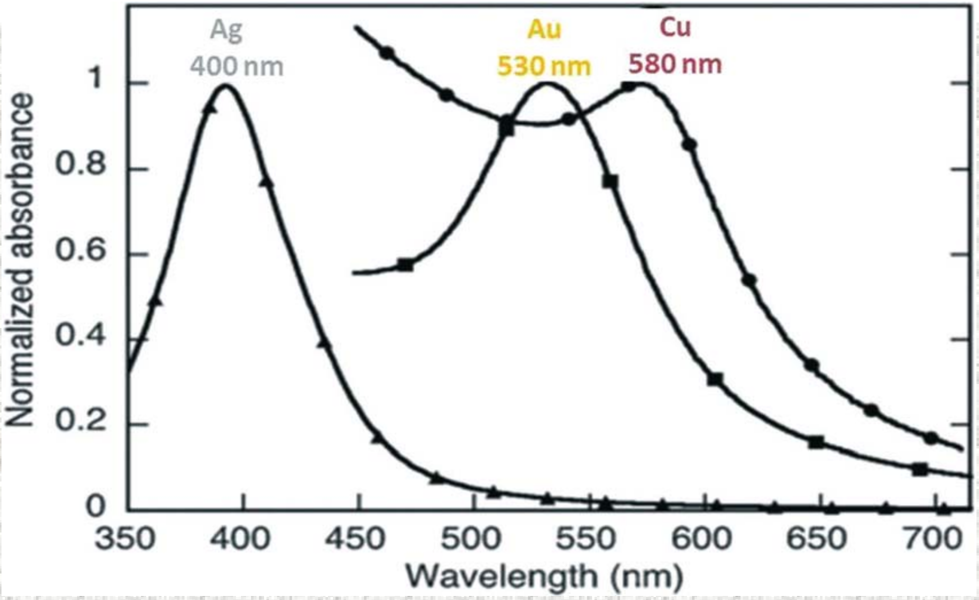
ICP-OES: Ag 50.3 mol%, EDS: Ag 62.5 mol%

Effects of Synthesis

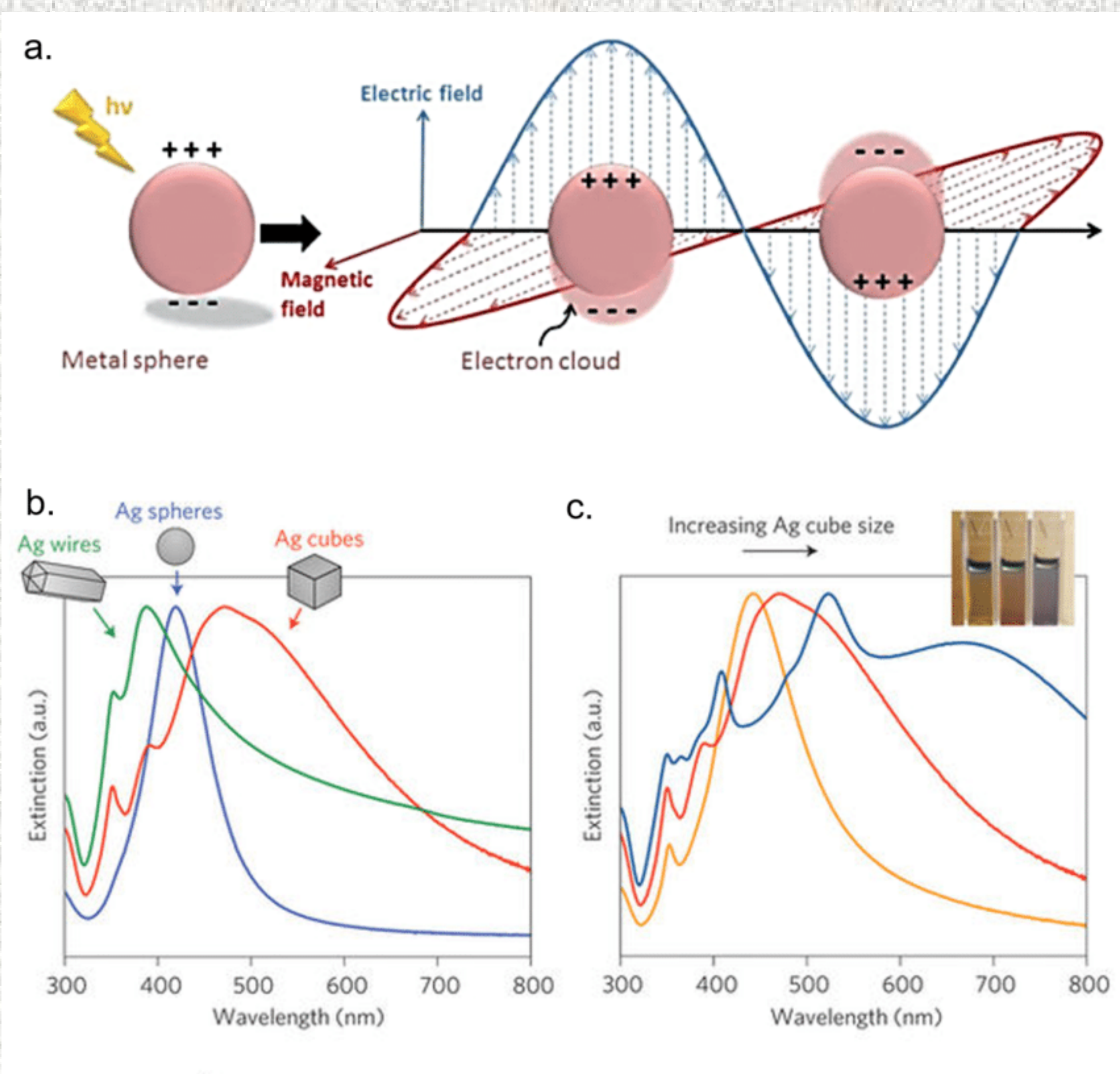


Localized Surface Plasmon Resonance (LSPR)





Localized Surface Plasmon Resonance (LSPR)

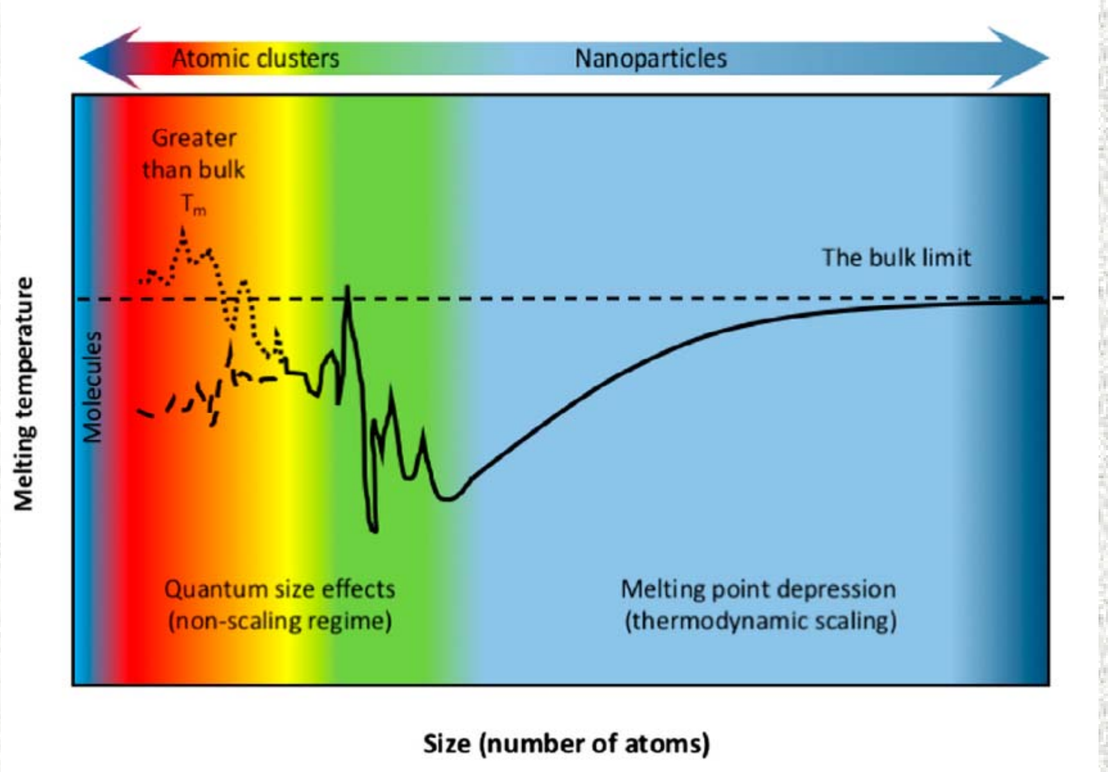


Melting Point Depression

Surface atoms in solids are bound by a lower number of shorter and stronger bonds
Nanoparticles with a large fraction of surface atoms

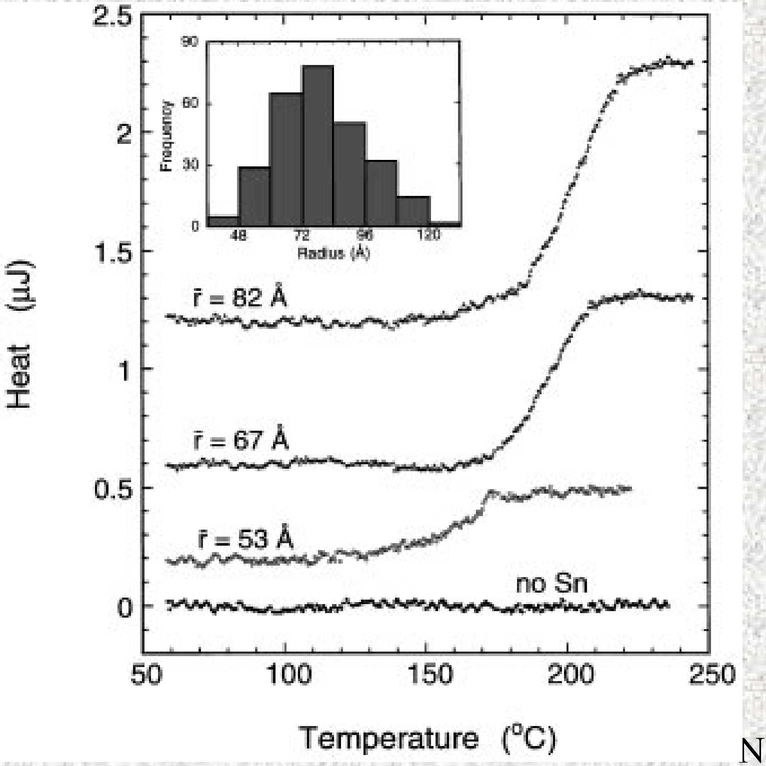
- **Lowering of average cohesion energy**
- **Increasing average amplitude of thermal**
- **Increasing internal pressure**

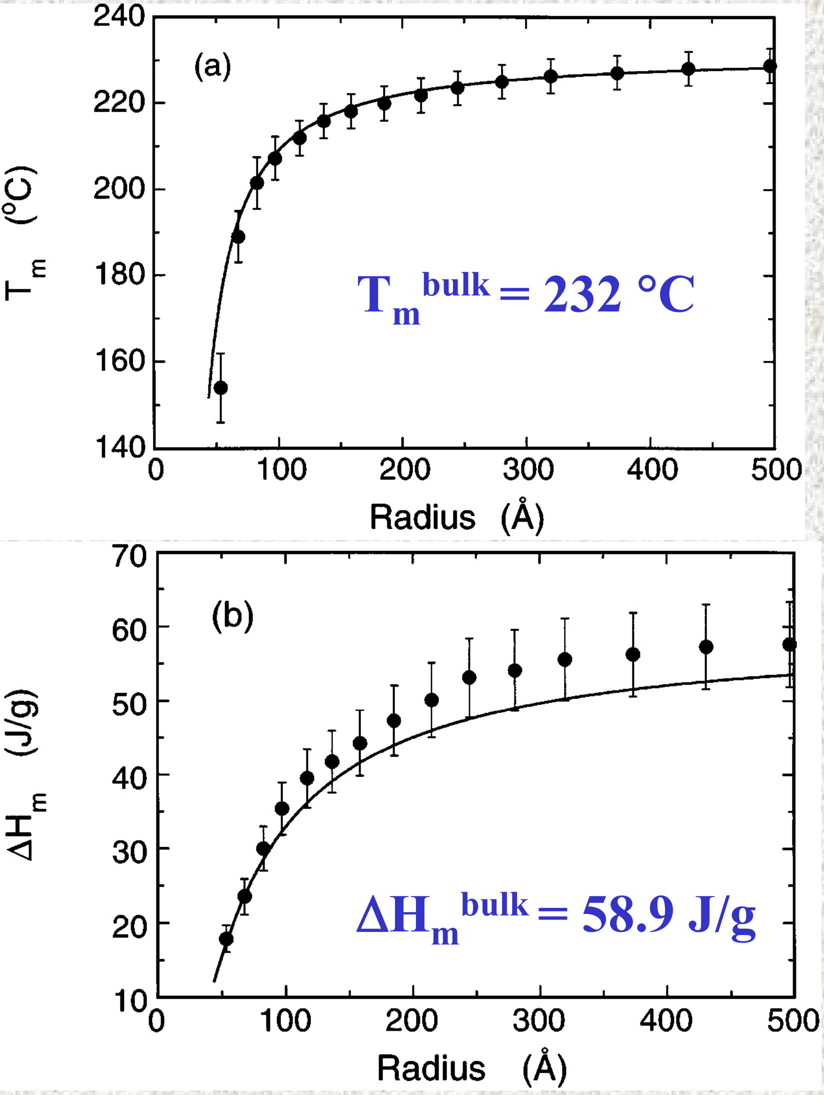
Result = deprssion of melting point of nanoparticles.



Melting Point and Enthalpy Depression

Nanocalorimetry of
Sn nanoparticles



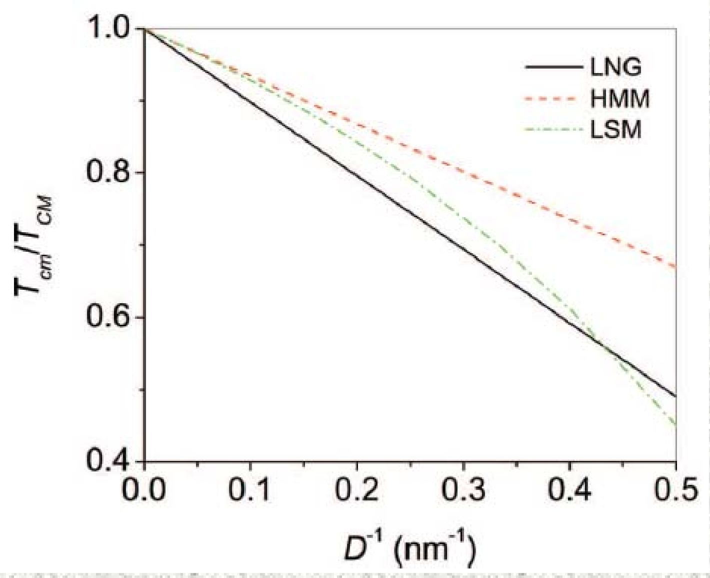


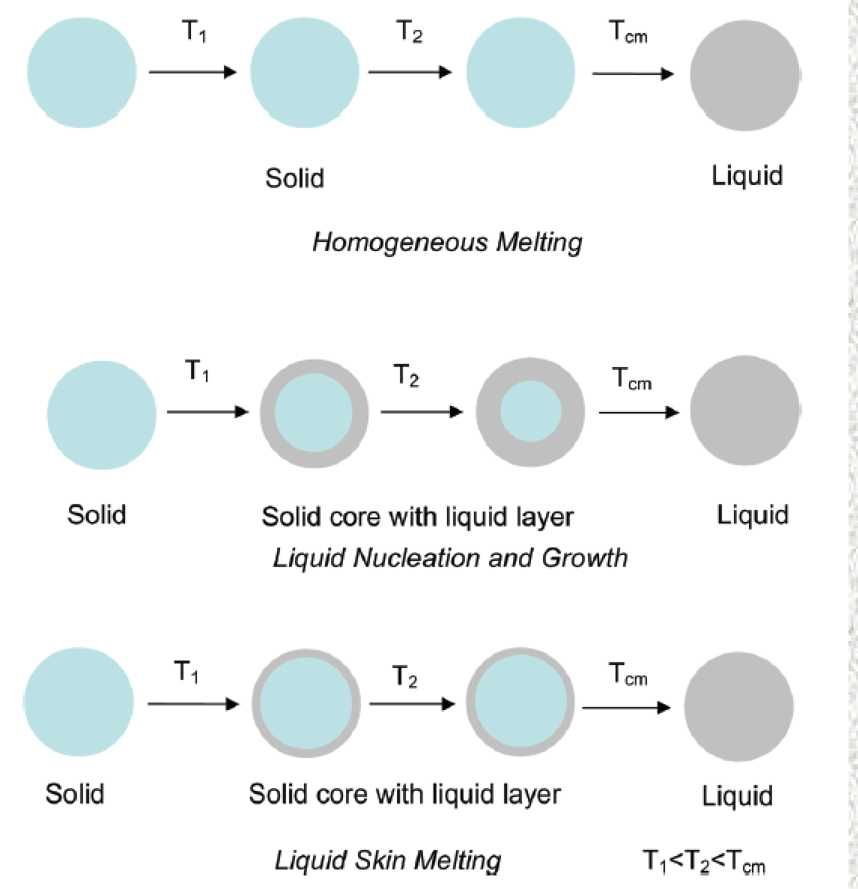
$T_m^{bulk} = 232$ °C

$\Delta H_m^{bulk} = 58.9$ J/g

Melting Point and Enthalpy Depression

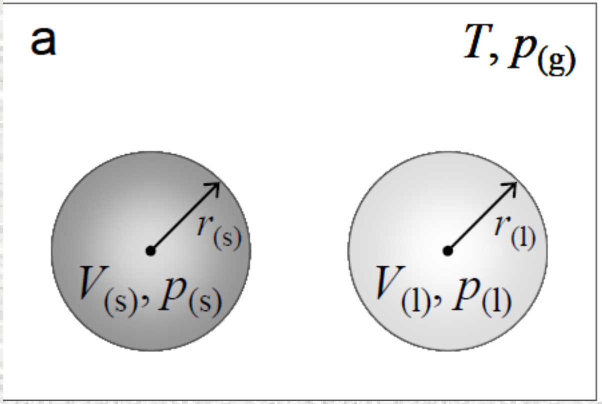
Nanocalorimetry of Sn nanoparticles





Melting Point Depression

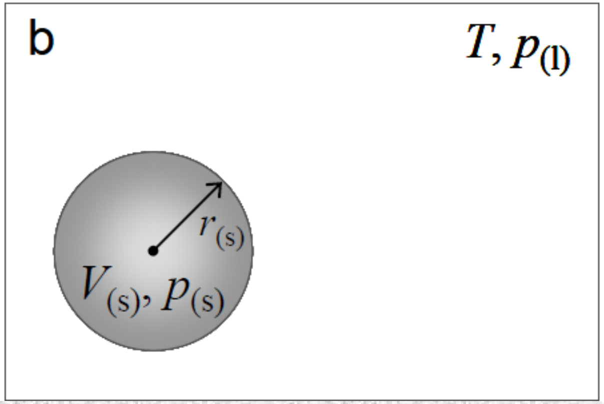
Homogeneous melting model



Triple point of coexisting solid and liquid nanoparticles of the same mass surrounded by vapor

$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(\mathrm{s})} r_{(\mathrm{s})}}\left[\gamma_{(\mathrm{sg})} - \gamma_{(\mathrm{lg})}\left(\frac{\rho_{(\mathrm{s})}}{\rho_{(\mathrm{l})}}\right)^{2/3}\right]$$

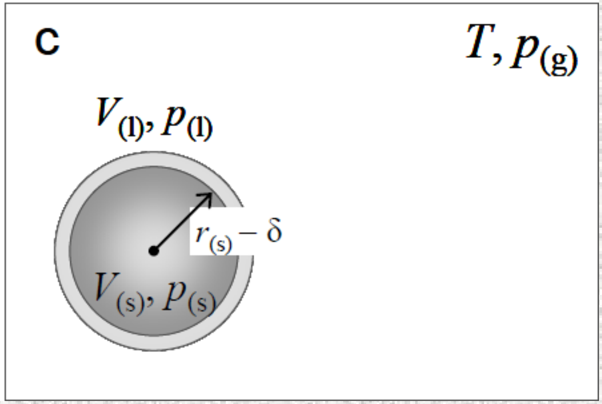
Continuous Liquid Meling



Melting particle is surrounded by liquid

$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(\mathrm{s})} r_{(\mathrm{s})}}\gamma_{(\mathrm{sl})}$$

Liquid Skin Melting



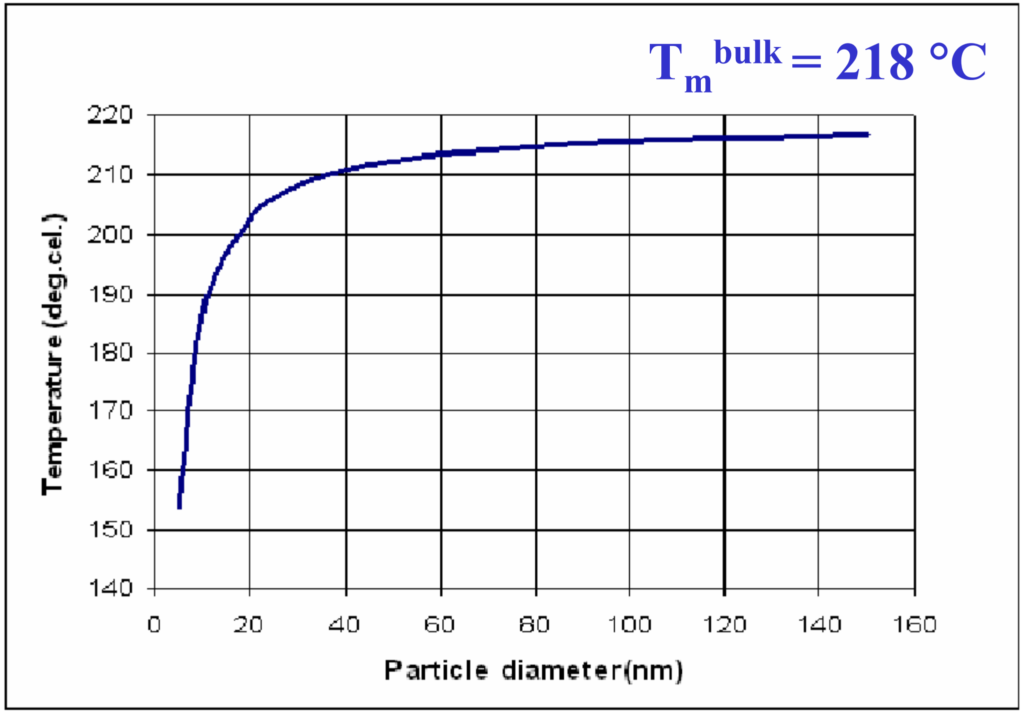
Thin melted layer of a constant thickness δ coexisting with solid core and vapor

$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(\mathrm{s})} r_{(\mathrm{s})}}\left[\frac{\gamma_{(\mathrm{sl})}}{1-\delta/r_{(\mathrm{s})}} + \gamma_{(\mathrm{lg})}\left(1-\frac{\rho_{(\mathrm{s})}}{\rho_{(\mathrm{l})}}\right)\right]$$

Melting Point Depression

$$T_m(r) = T_m(\text{bulk}) - \frac{2T_m(\text{bulk})M}{\Delta H_m^{bulk}\rho_s r}\left[\gamma_{sg} - \gamma_{lg}\left(\frac{\rho_s}{\rho_l}\right)^{\frac{2}{3}}\right]$$

Sn – 4wt%**Ag –** 0.5wt%**Cu** Nano alloy particles



Homogeneous melting model:

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

T_m^{bulk} = mp of the bulk material

γ_{sg} = the interfacial energies between the s and g phases

γ_{lg} = the interfacial energies between the l and g phases

ρ_s and ρ_l = solid and liquid phase densities

M = molar mass

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

Gibbs–Thomson Equation

for $\rho_s \sim \rho_l$

$\gamma_{sl} = \gamma_{sg} - \gamma_{lg}$ **Continuous Liquid Meling**

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

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

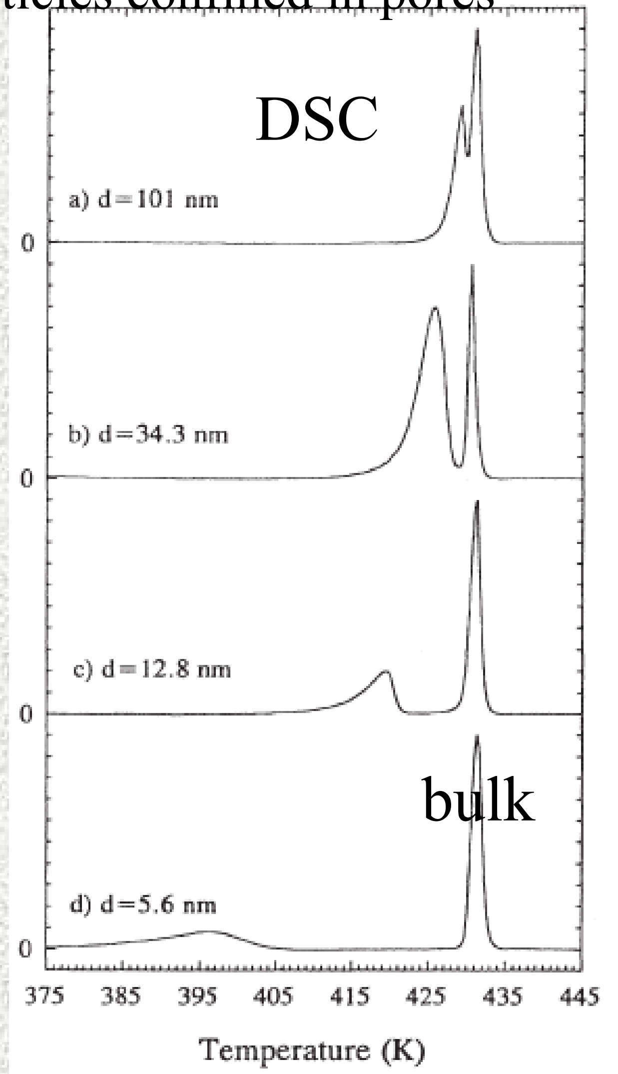
T_m^{bulk} = mp of the bulk material

V_{mol}^{l} = the molar volume of the liquid = M/ρ_s solid?

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

ΔH_m^{bulk} = the bulk molar enthalpy of melting, endothermic

In nanoparticles confined in pores

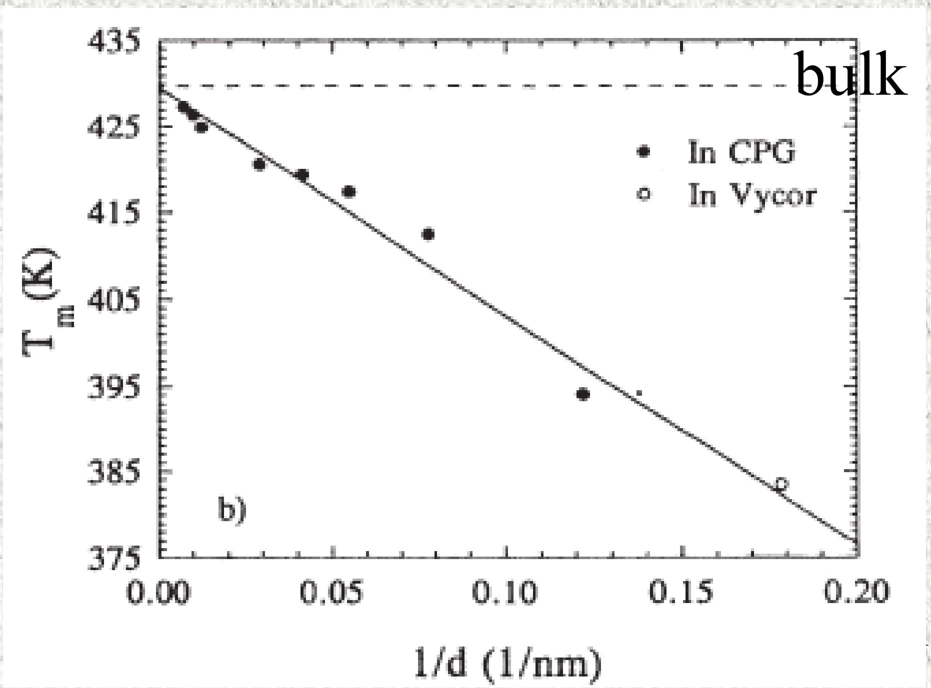


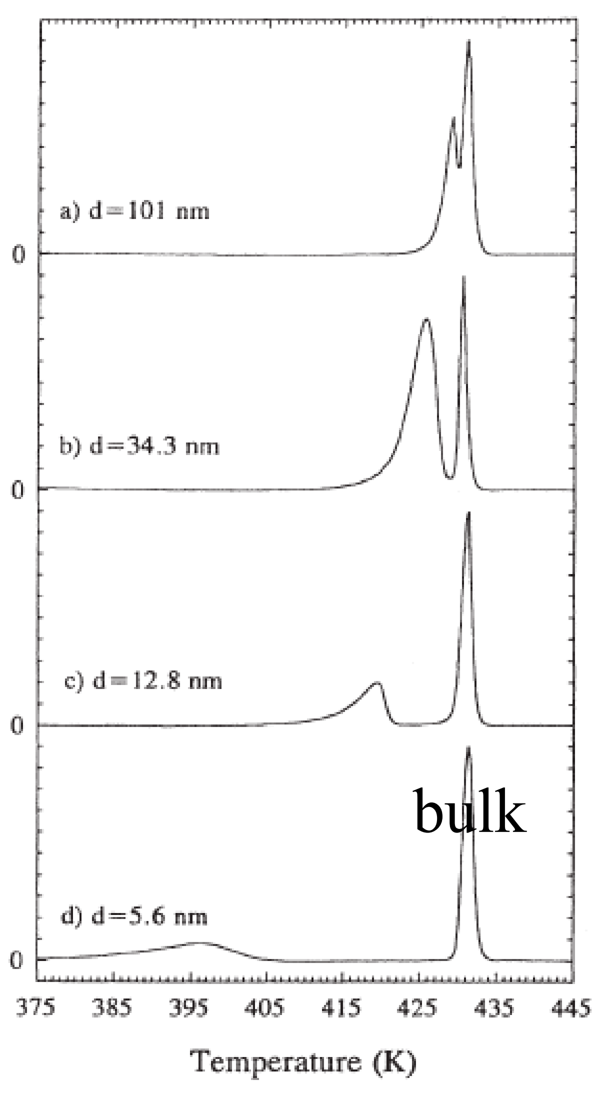
Phase Transitions

Phase transitions = collective phenomena

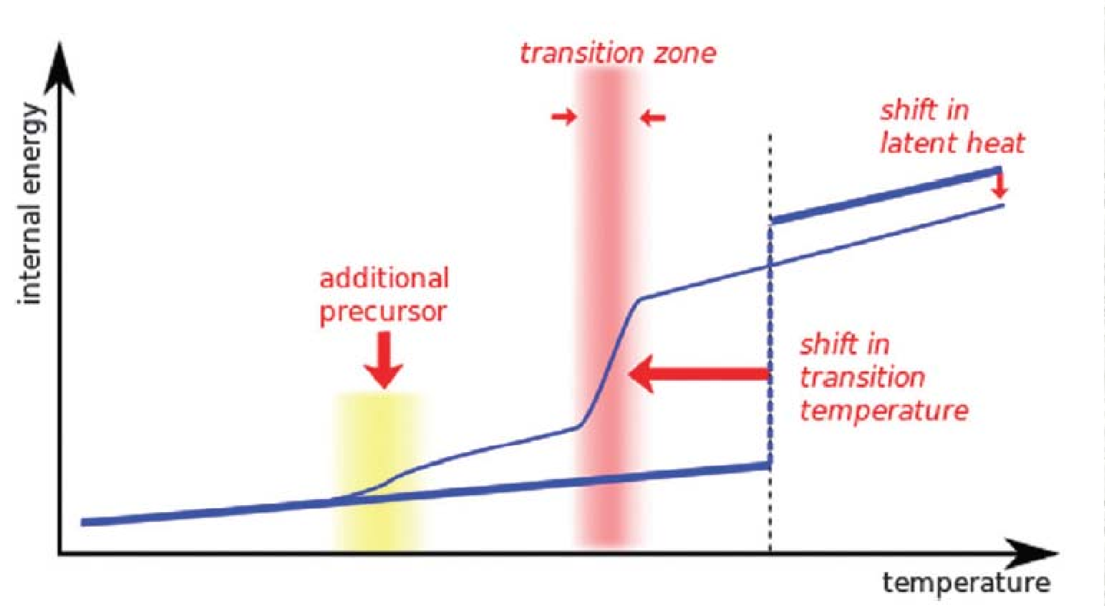
With a lower number of atoms in a cluster a phase transition is less well defined and broadened

Small clusters behave more like molecules than as bulk matter





First-Order Phase Transitions



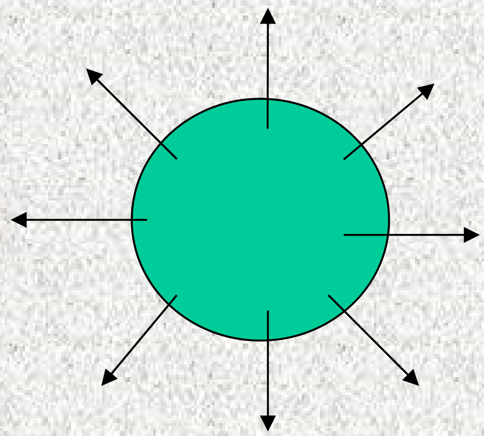
3 main consequences of a size decrease on caloric curve:

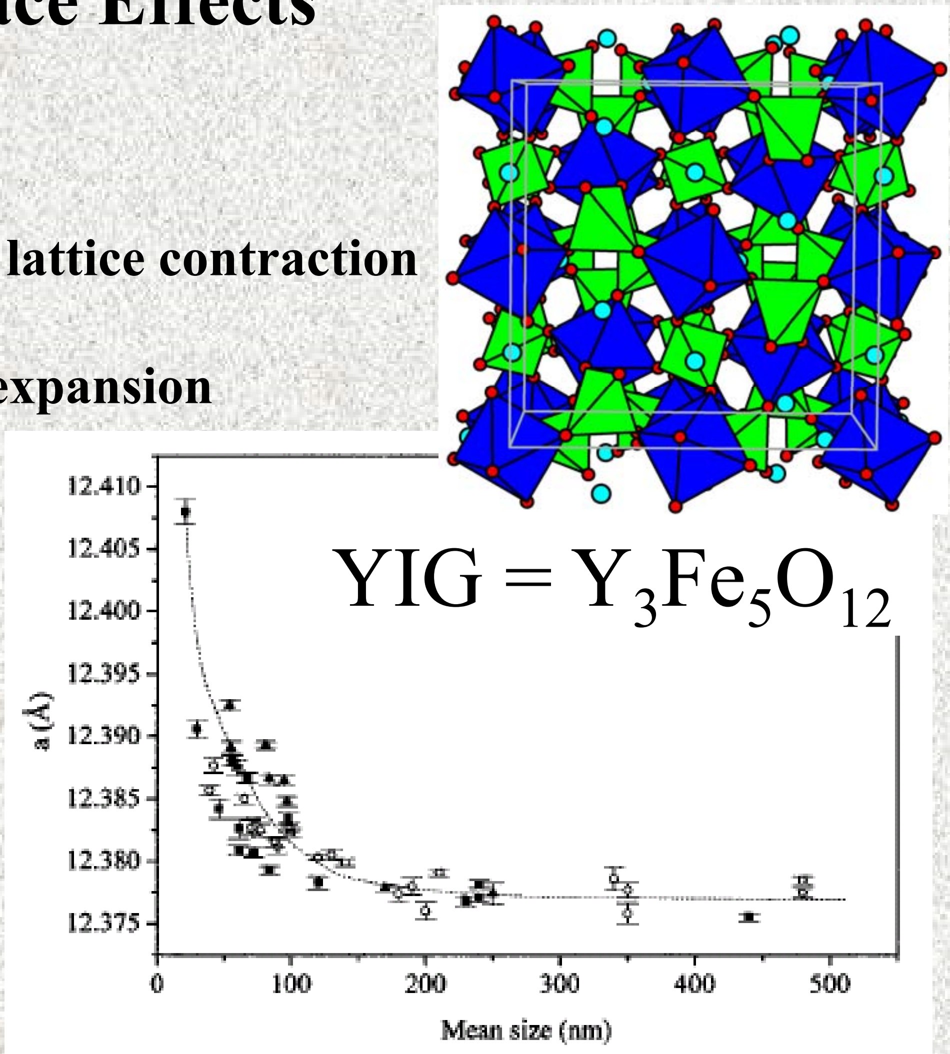
*** The transition is shifted, usually to a lower temperature (surface atoms are less coordinated and less bound than interior atoms)**
*** The transition temp. is no longer sharp but becomes smooth and takes place over a finite range (fluctuations in TD quantities)**
*** The latent heat is lower than in the bulk limit**

Surface Effects

Reduction in particle size

- Metal particles usually exhibit a lattice contraction
- Oxide particles exhibit a lattice expansion



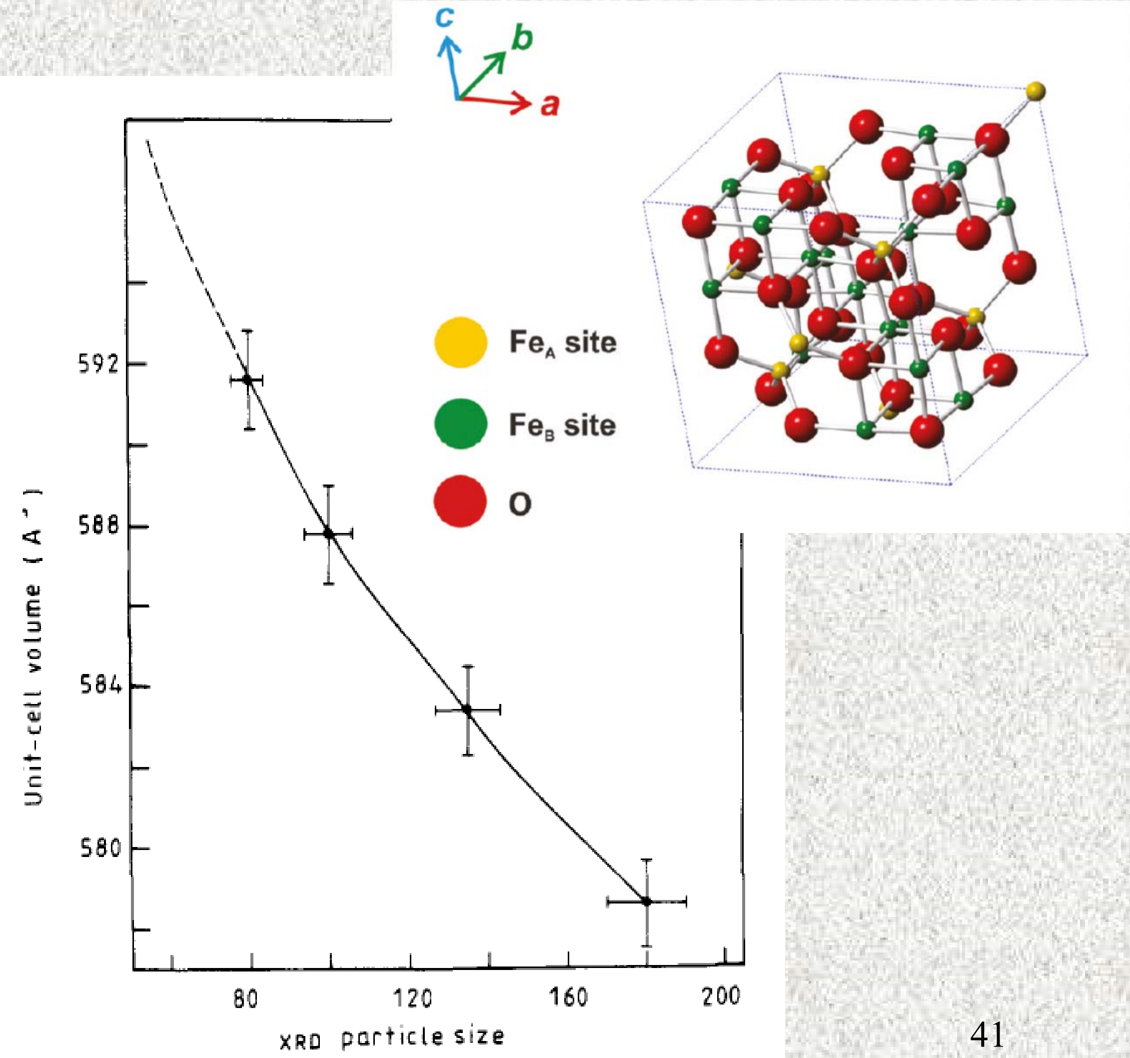


YIG = $Y_3Fe_5O_{12}$

Surface Effects

Correlation between the unit-cell volume (cubic) and the XRD particle size in γ-Fe_2O_3 nanoparticles

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



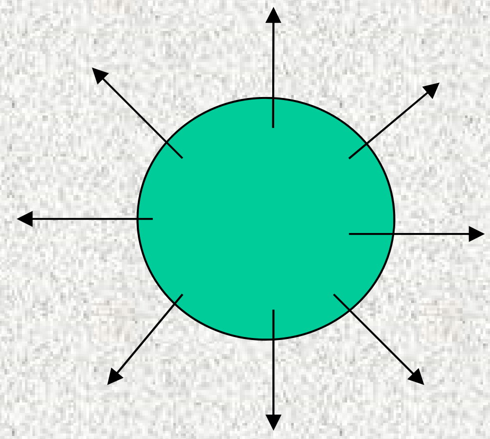
Surface Effects

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

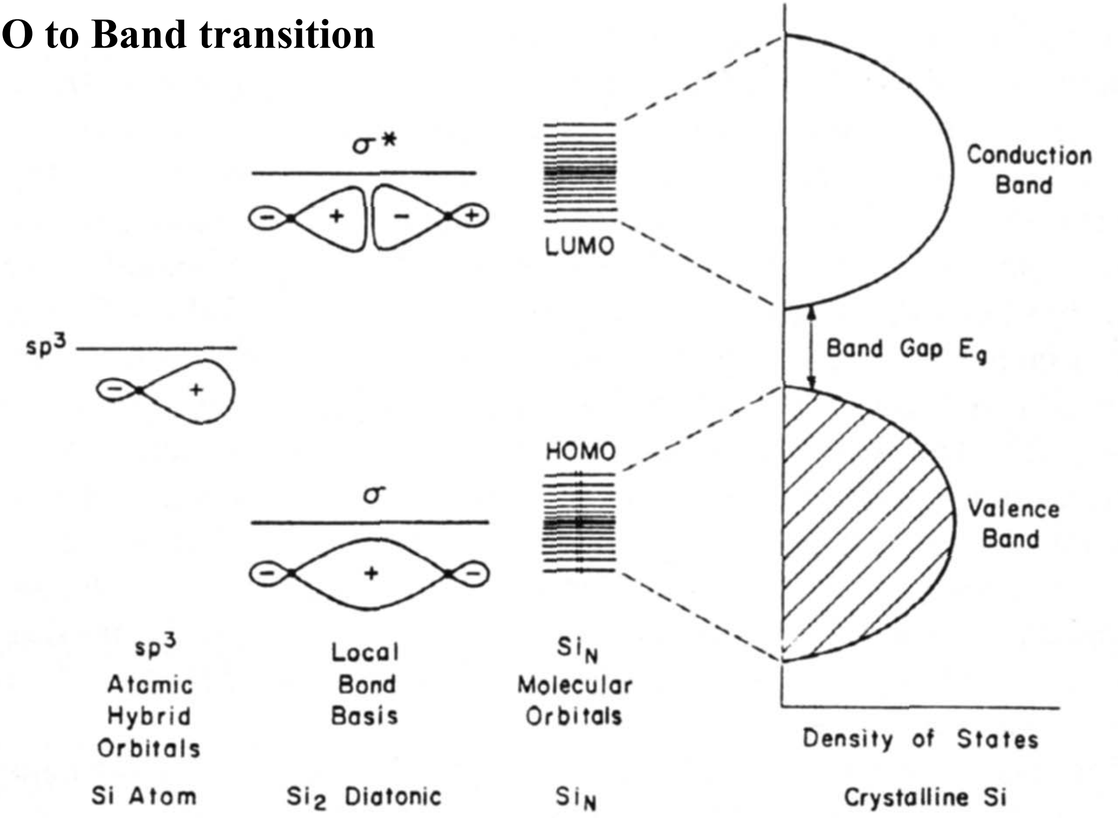
The repulsive dipolar interactions increase in smaller particles reduced by allowing unit cell volume to increase



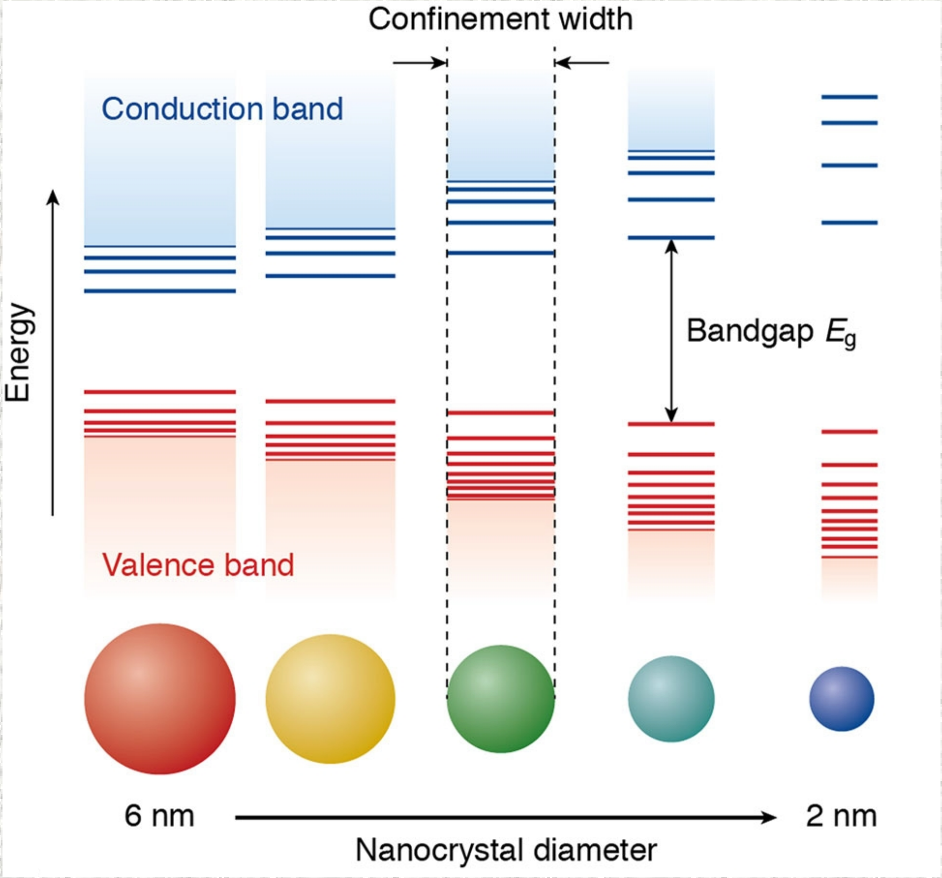
Quantum Confinement Effects

Physical and chemical properties depend on the size !!

ⓘ **Finite-size effects**
MO to Band transition



Quantum Size Effects

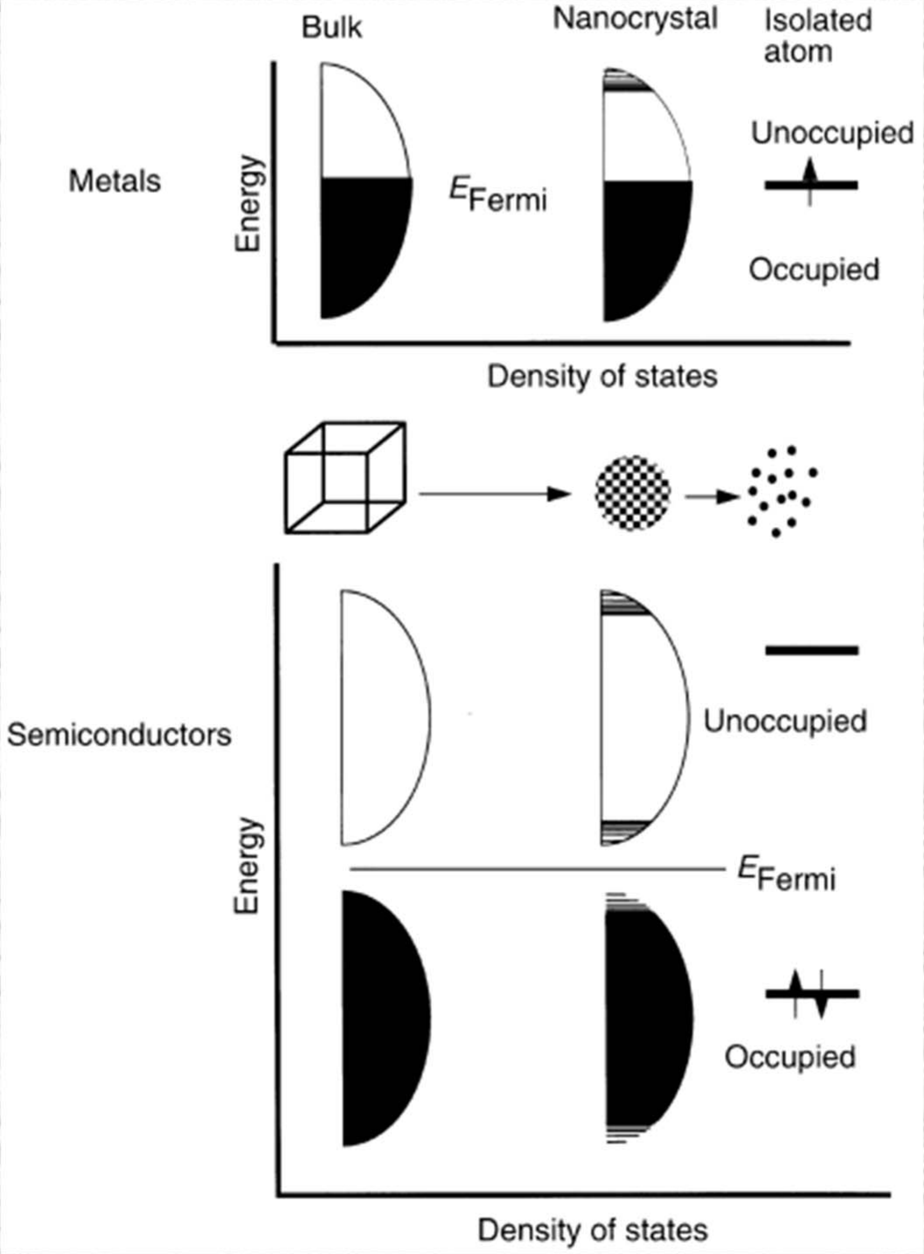


Band gap dependency on the nanoparticle size

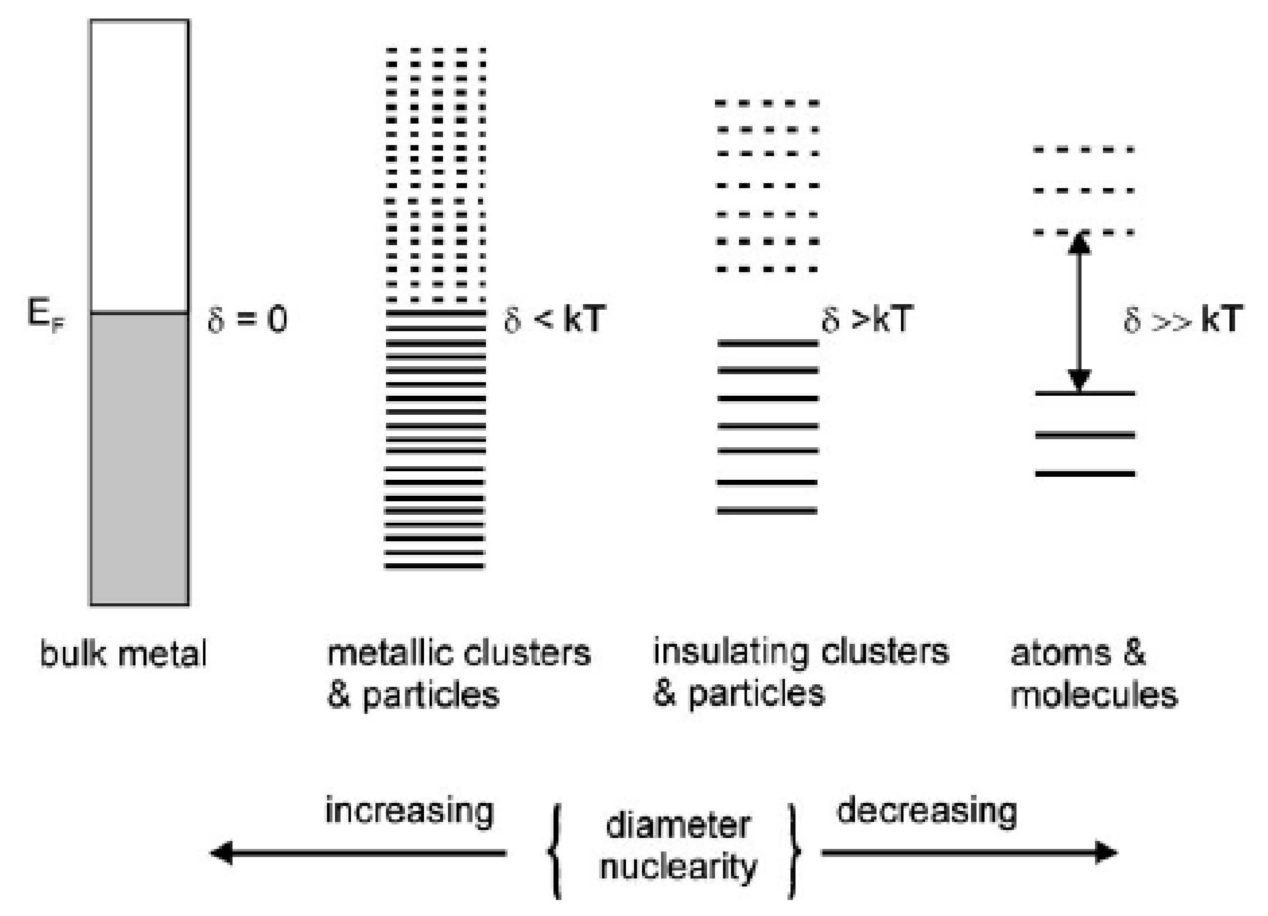
Quantum Size Effects

Metals

Semiconductors

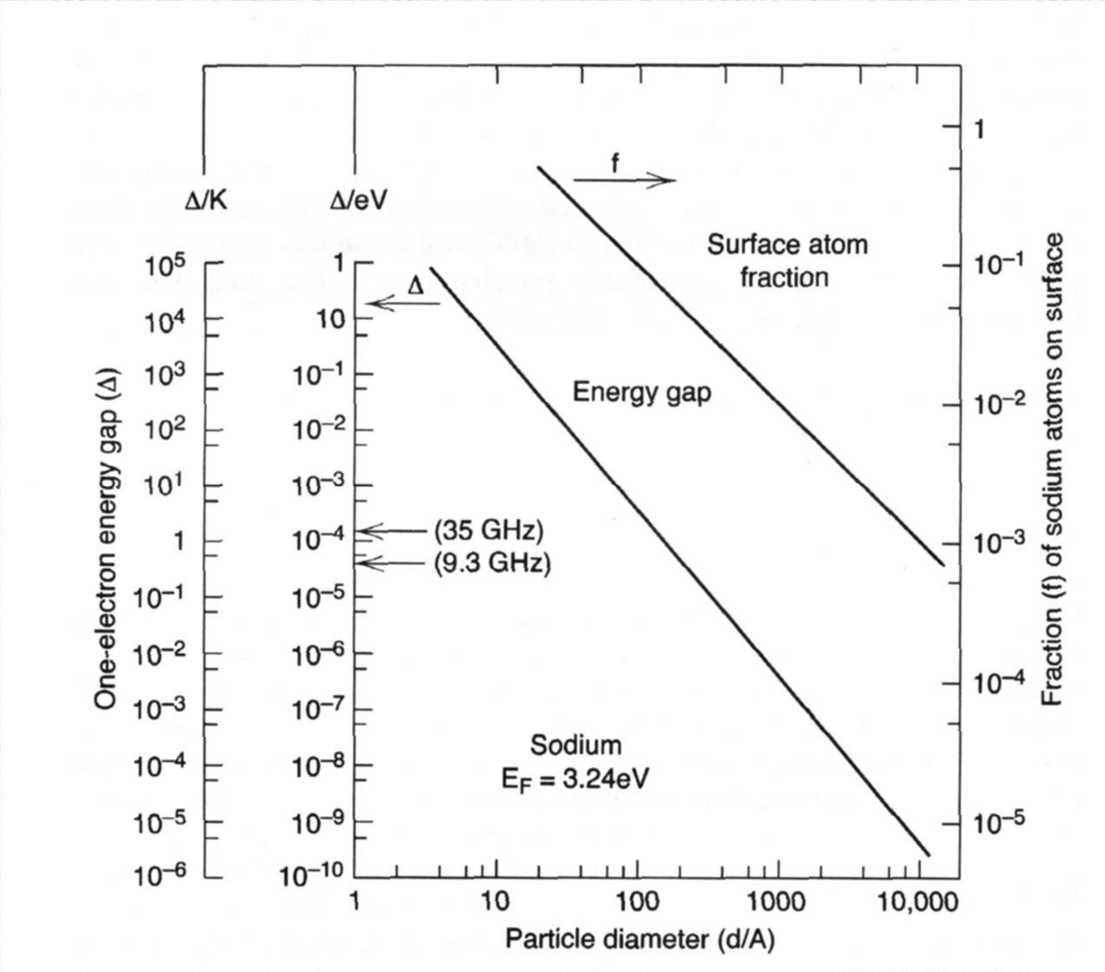


Metal-to-Insulator Transition



Metal-to-Insulator Transition

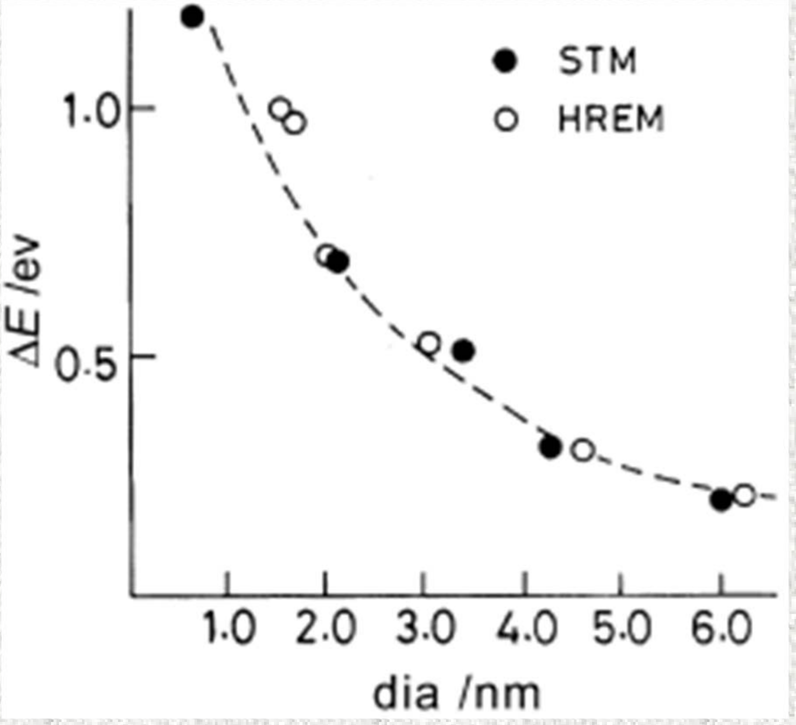
Band gap increases with decreasing size



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



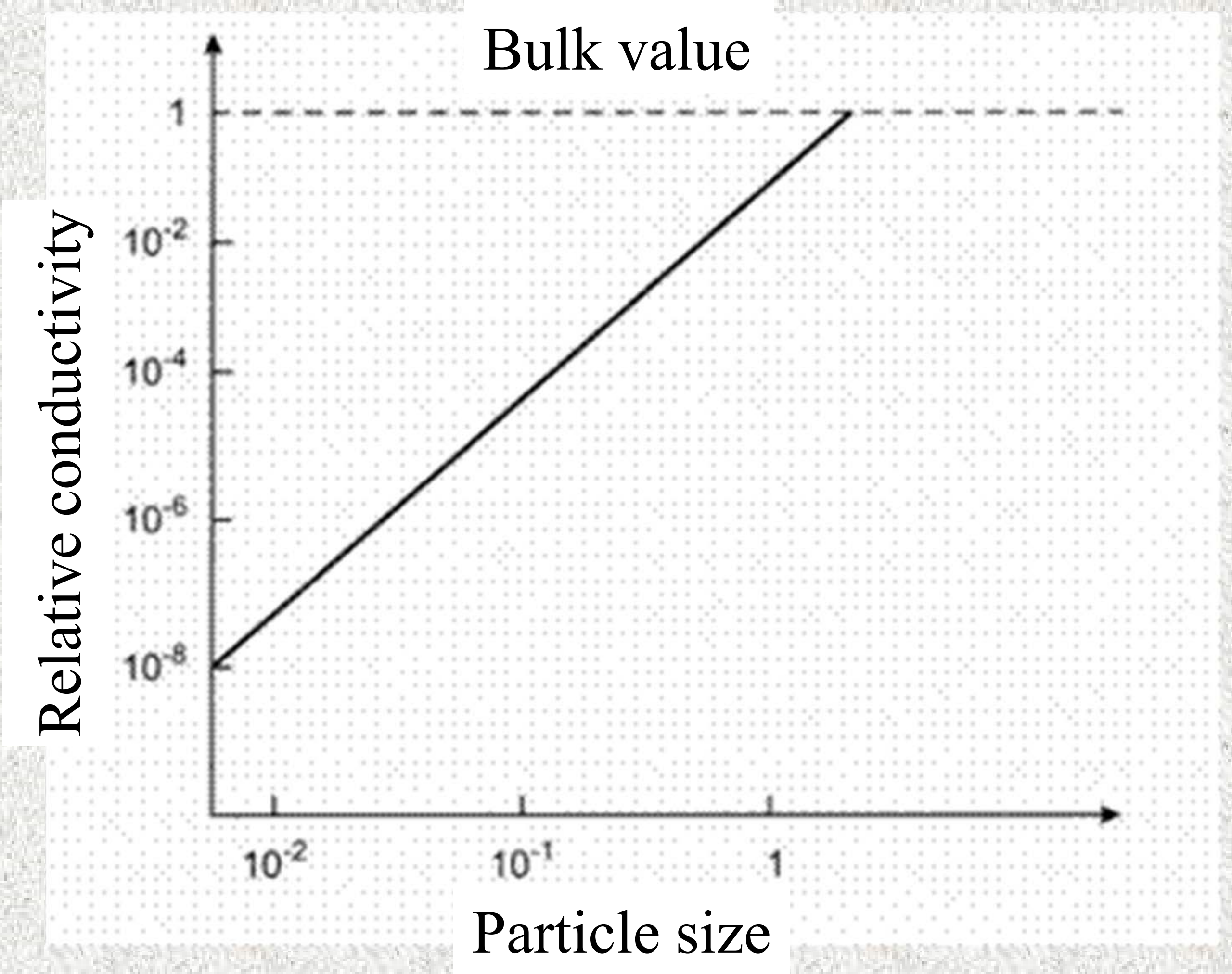
The increase in the core-level binding energy in small particles

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

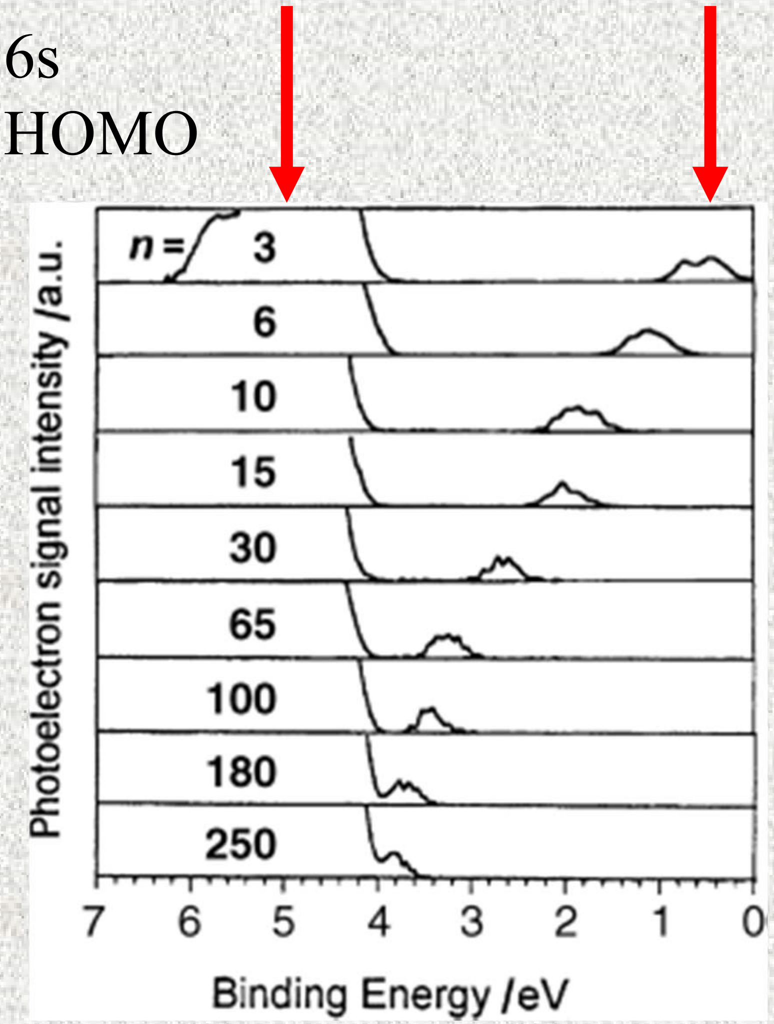


Hg

Valence electron configuration?

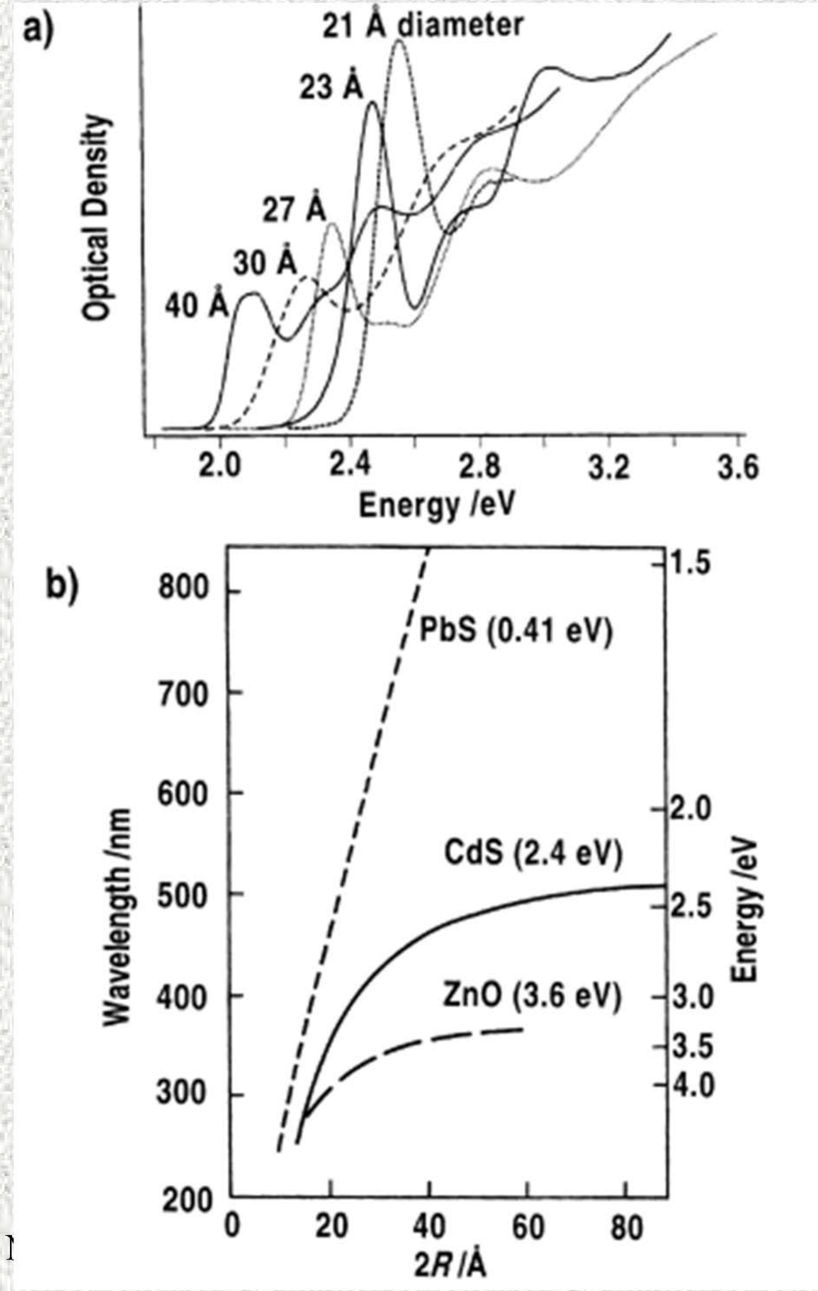
6s
HOMO

6p
LUMO



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

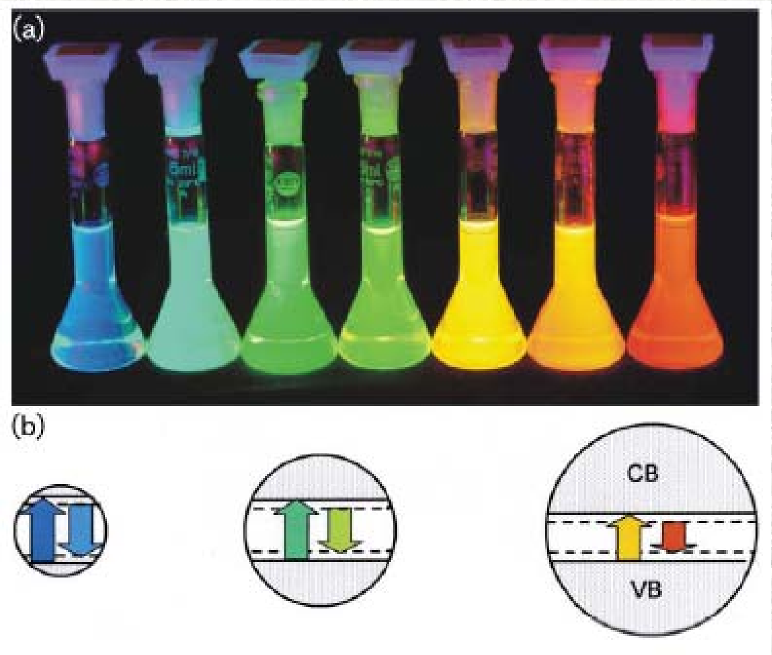
Quantum Size Effects In Semiconductors



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

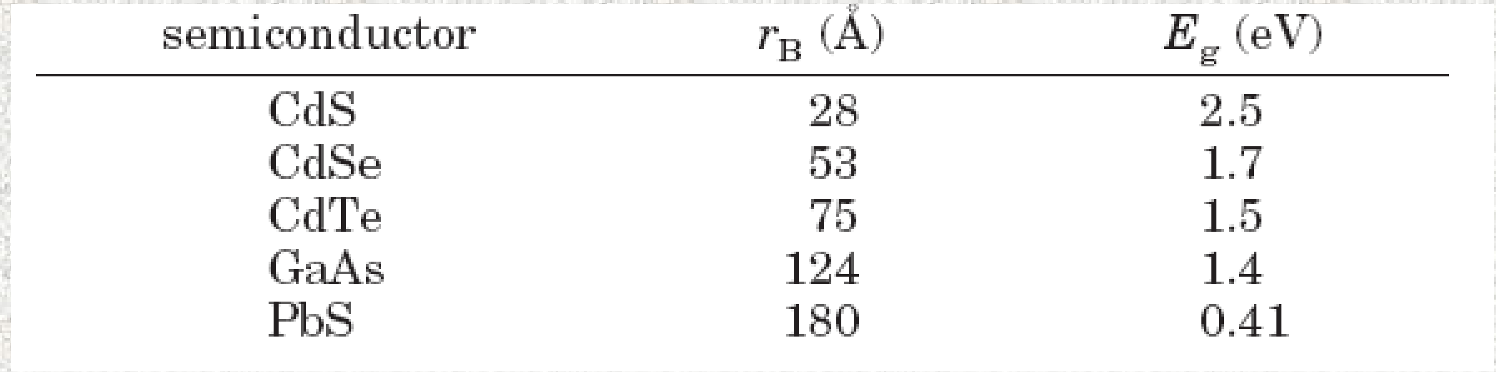


Fluorescence of CdSe–CdS core–shell nanoparticles with a diameter of 1.7 nm (blue) up to 6 nm (red)

Smaller particles have a wider band gap

Bohr Radii

Quantum confinement - particles must be smaller than the Bohr radius of the electron-hole pair



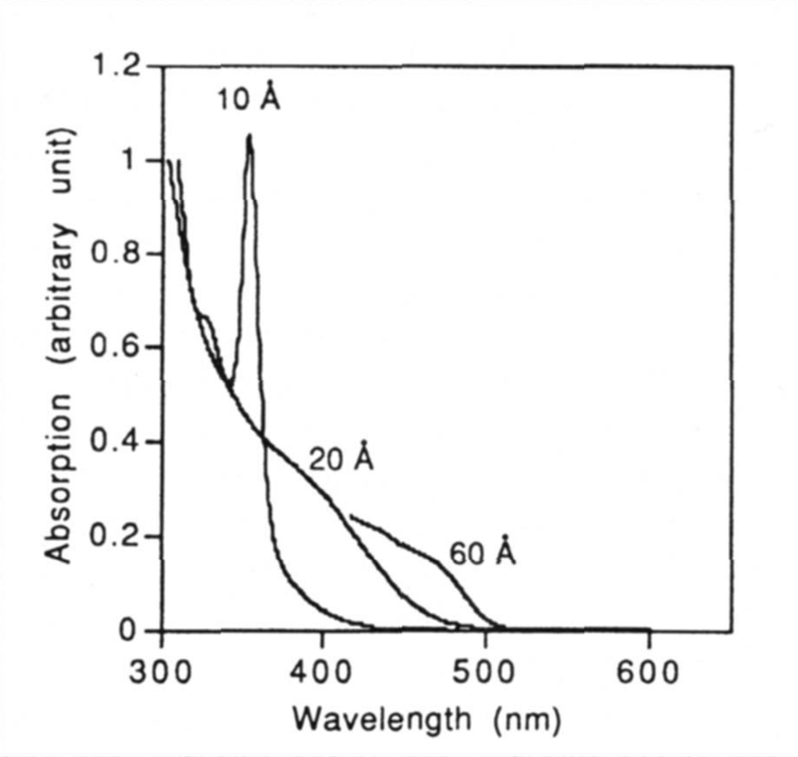
semiconductor	r_B (Å)	E_g (eV)
CdS	28	2.5
CdSe	53	1.7
CdTe	75	1.5
GaAs	124	1.4
PbS	180	0.41

Quantum Confinement Effects

Optical properties

nc-TiO_2 is transparent - applications?

Blue shift in optical spectra of TiO_2 nanoparticles



Nanoscopic Materials

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

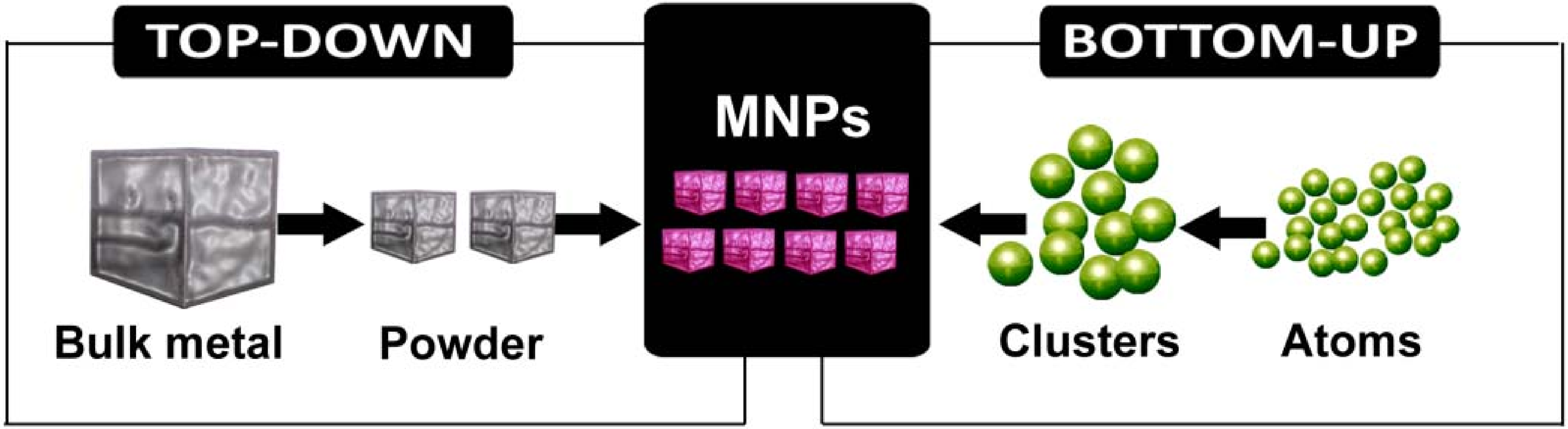
Nanostructured materials = nonequilibrium character

- **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

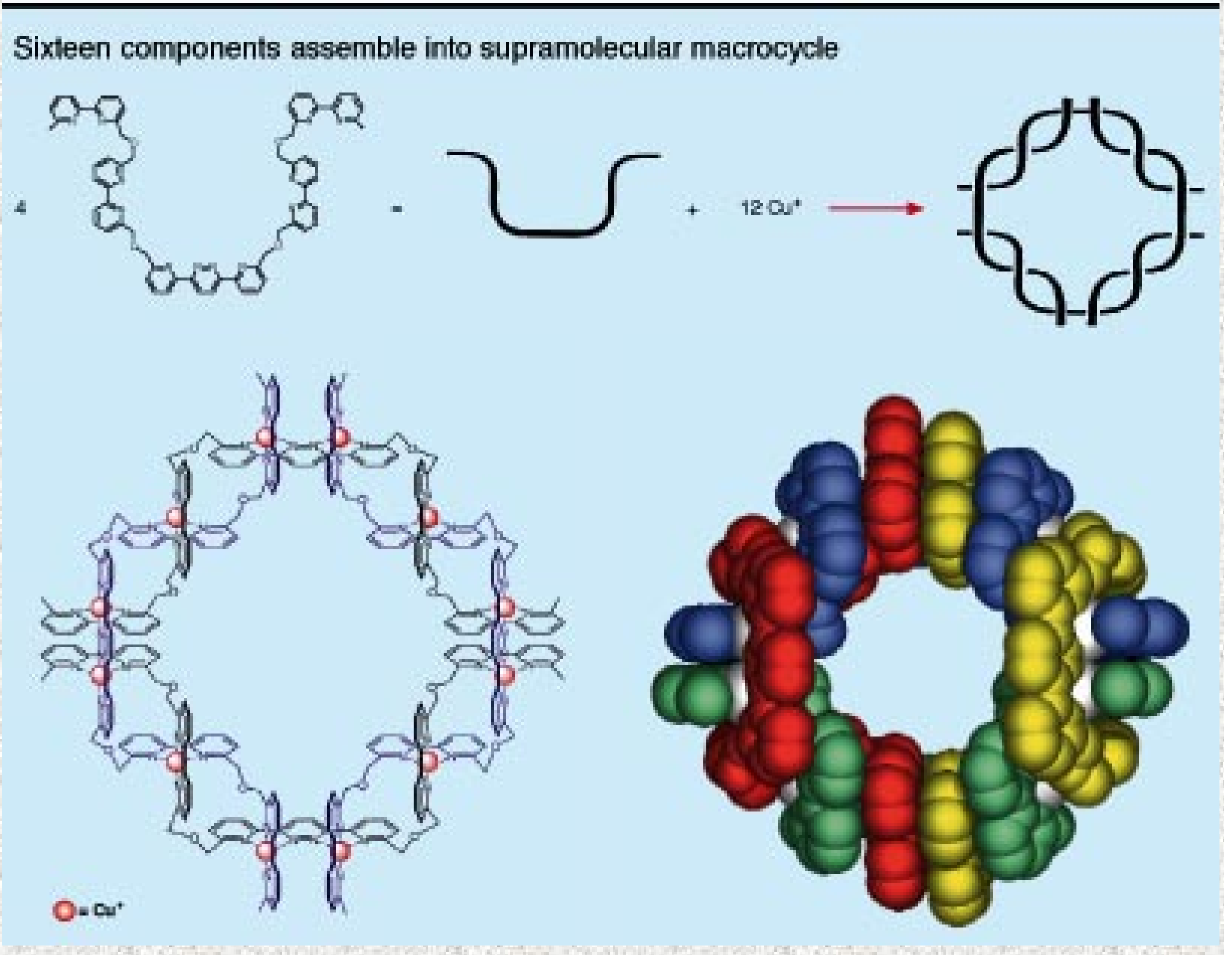
Preparation Methods



Top-down: from bulk to nanoparticles

Bottom-up: from atoms to nanoparticles

Bottom-up Synthesis: Atom Up



Sixteen components assemble into supramolecular macrocycle

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, C_{60}

in a reactive gas	**O_2**	**TiO_2, MgO, Al_2O_3, Cu_2O**
	N_2, NH_3	**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 N_2
more polar solvent (more strongly ligating) gives smaller particles
Ni powder: THF < toluene < pentane = hexane

Carbide formation

$$\text{Ni(g)} + \text{pentane} \xrightarrow{77 \text{ to } 300\text{ K}} Ni_xC_yH_z \xrightarrow{180\ ^\circ\text{C, octane}} Ni_3C$$

Bottom-up Synthesis

🛠 **Thermal or Sonocative Decomposition of Precursors**

$\mathrm{Fe(CO)_5} \longrightarrow \text{nc-Fe} + 5\,\mathrm{CO}$ sono

$\mathrm{[Co(en)_3]WO_4} \longrightarrow \text{nc-WC} - 23\%\ \mathrm{Co}$

$\mathrm{PhSi(OEt)_3} + \mathrm{Si(OEt)_4} + \mathrm{H_2O} \longrightarrow \text{gel} \xrightarrow{\text{Ar, 1500 °C}} \beta\text{-SiC}$

$\mathrm{(CH_3SiHNH)_n\ (l)} \longrightarrow \mathrm{Si_3N_4} + \mathrm{SiC}$ laser

$\mathrm{M(BH_4)_4\ (g)} \xrightarrow{300\text{-}400°\mathrm{C}} \text{borides } \mathrm{MB_{2+x}}$ (M = Ti, Zr, Hf)

$\mathrm{Si(OEt)_4} + \mathrm{Ag^+} \text{ or } \mathrm{Cu^{2+}} + \mathrm{H_2O} \longrightarrow \mathrm{SiO_2/Ag^+/Cu^{2+}}$

$\xrightarrow{\mathrm{H_2},\ 550\ °\mathrm{C}} \mathrm{SiO_2/Ag/Cu}$

Bottom-up Synthesis

🛠 **Reduction of Metal Ions**

Borohydride Reduction - Manhattan Project

Aqueous, under Ar
$2\ Co^{2+} + 4\ BH_4^- + 9\ H_2O \longrightarrow Co_2B + 12.5\ H_2 + 3\ B(OH)_3$

Under air
$4\ Co_2B + 3\ O_2 \longrightarrow 8\ Co + 2\ B_2O_3$

Nonaqueous
$Co^{2+} + BH_4^- + \text{diglyme} \longrightarrow Co + H_2 + B_2H_6$

$TiCl_4 + 2\ NaBH_4 \longrightarrow TiB_2 + 2\ NaCl + 2\ HCl + H_2$

$MX_n + n\ NR_4[BEt_3H] \longrightarrow M + NR_4X + n\ BEt_3 + n/2\ H_2$
M = group 6 to 11; n = 2,3; X = Cl, Br

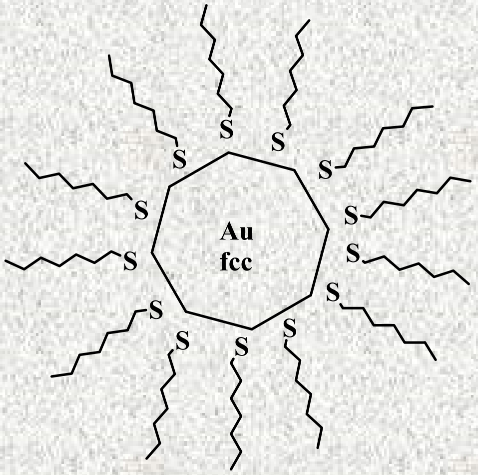
mixed-metal particles

NANOSTRUCTURAL MATERIALS

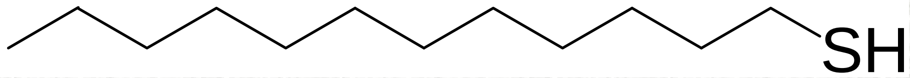
Bottom-up Synthesis

Au colloidal particles

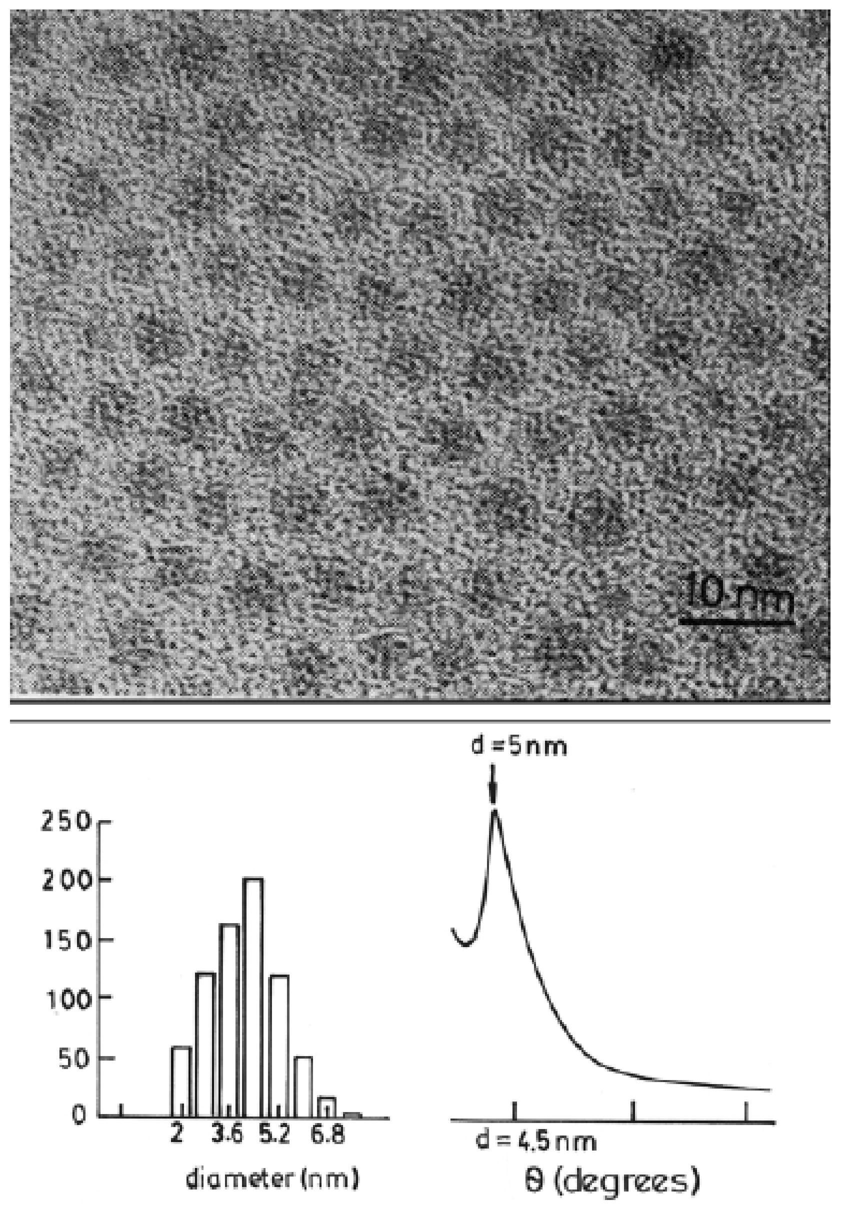
$HAuCl_4$ + $NaBH_4$ in toluene/H_2O system, TOABr as a phase transfer agent, Au particles in the toluene layer, their surface covered with Br, addition of RSH gives stable Au colloid



Bottom-up Synthesis



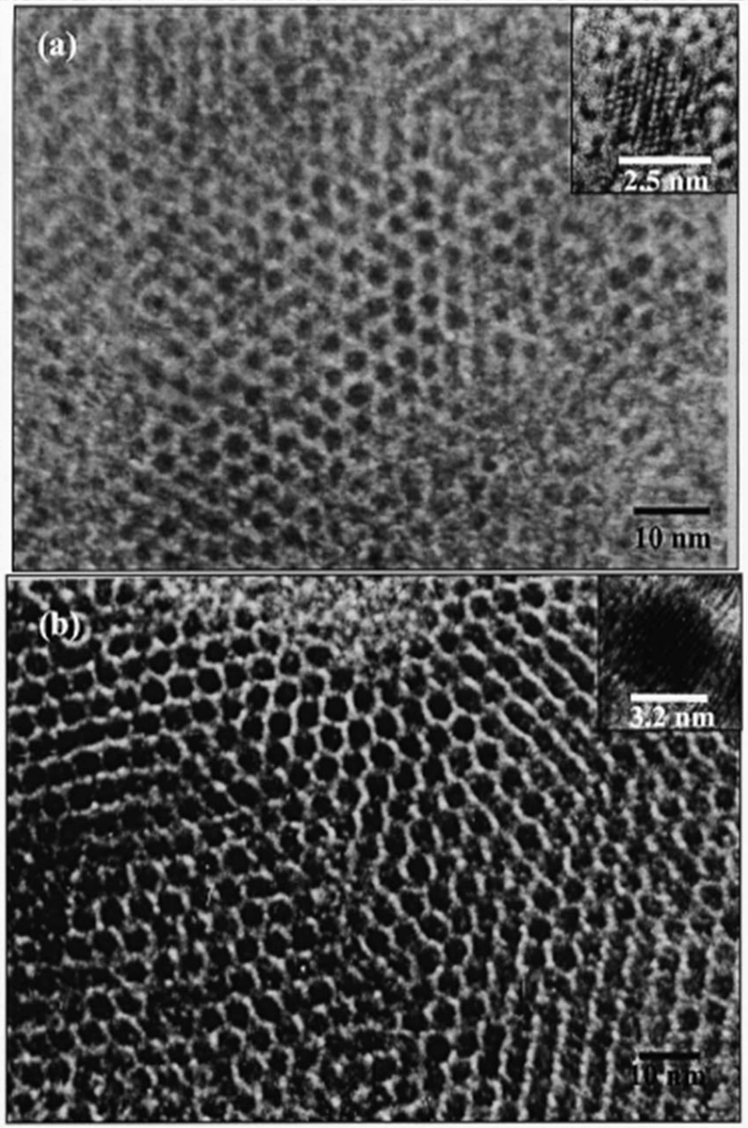
Two-dimensional array of thiol-derivatised Au particles (mean diam 4.2 nm)

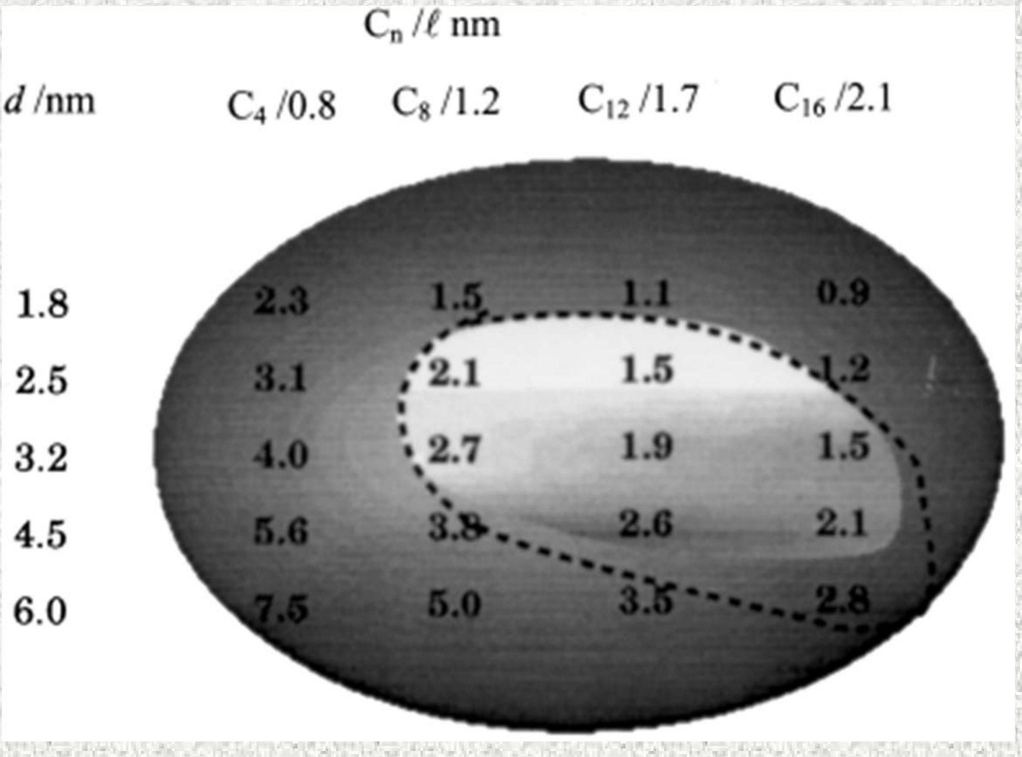


TEM micrograph of hexagonal arrays of thiolized Pd nanocrystals:

a) 2.5 nm, octane thiol

b) 3.2 nm, octane thiol





	C_n/ℓ nm			
d /nm	C_4 /0.8	C_8 /1.2	C_{12} /1.7	C_{16} /2.1
1.8	2.3	1.5	1.1	0.9
2.5	3.1	2.1	1.5	1.2
3.2	4.0	2.7	1.9	1.5
4.5	5.6	3.8	2.6	2.1
6.0	7.5	5.0	3.5	2.8

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

Alkali Metal Reduction

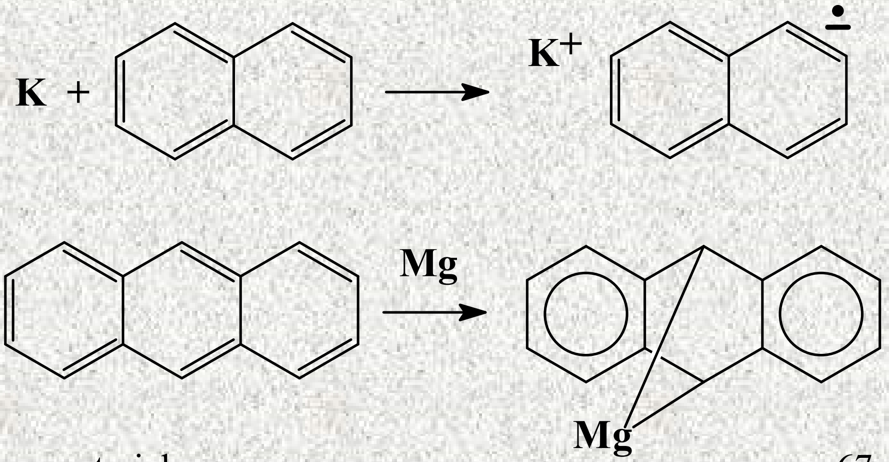
in dry anaerobic diglyme, THF, ethers, xylene

$NiCl_2 + 2 K \rightarrow Ni + 2 KCl$

$AlCl_3 + 3 K \rightarrow Al + 3 KCl$

Reduction by Glycols or Hydrazine

"Organically solvated metals"



Alkalide Reduction

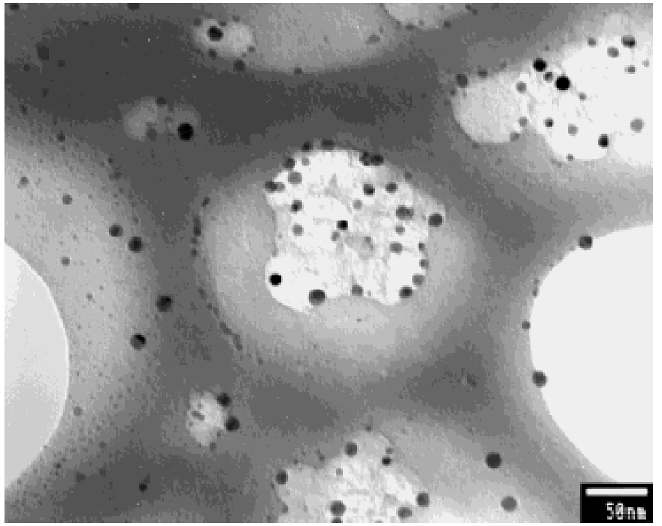
$13\ K^+(15\text{-crown-}5)_2Na^- + 6\ FeCl_3 + 2CBr_4$

$$\Big\downarrow \text{THF}, -30\ ^\circ C$$

$2\ Fe_3C\ (\text{nano}) + 13\ K(15\text{-crown-}5)_2Cl_{0.43}Br_{0.57} + 13\ NaCl$

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

$M^{2+} + H_2E \xrightarrow{\quad} ME$ M = Cd, Pb; E = S, Se

Ship-in-the-Bottle Synthesis

$Ru^{3+} + Na\text{-}Y \xrightarrow{\quad} Ru(III)\text{-}Y$

$Ru(III)\text{-}Y + 3\ bpy \xrightarrow{\quad} Ru(bpy)_3^{2+}$ reduction of Ru(III)

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

$$3Gd(NO_3)_3 + 5\ Fe(NO_3)_3 \longrightarrow Ga_3Fe_5O_{12} + 6\ O_2 + 24\ NO_2$$

$$MnCl_2 + 2\ FeCl_3 + 4\ H_2O \longrightarrow MnFe_2O_4 + 8\ HCl$$

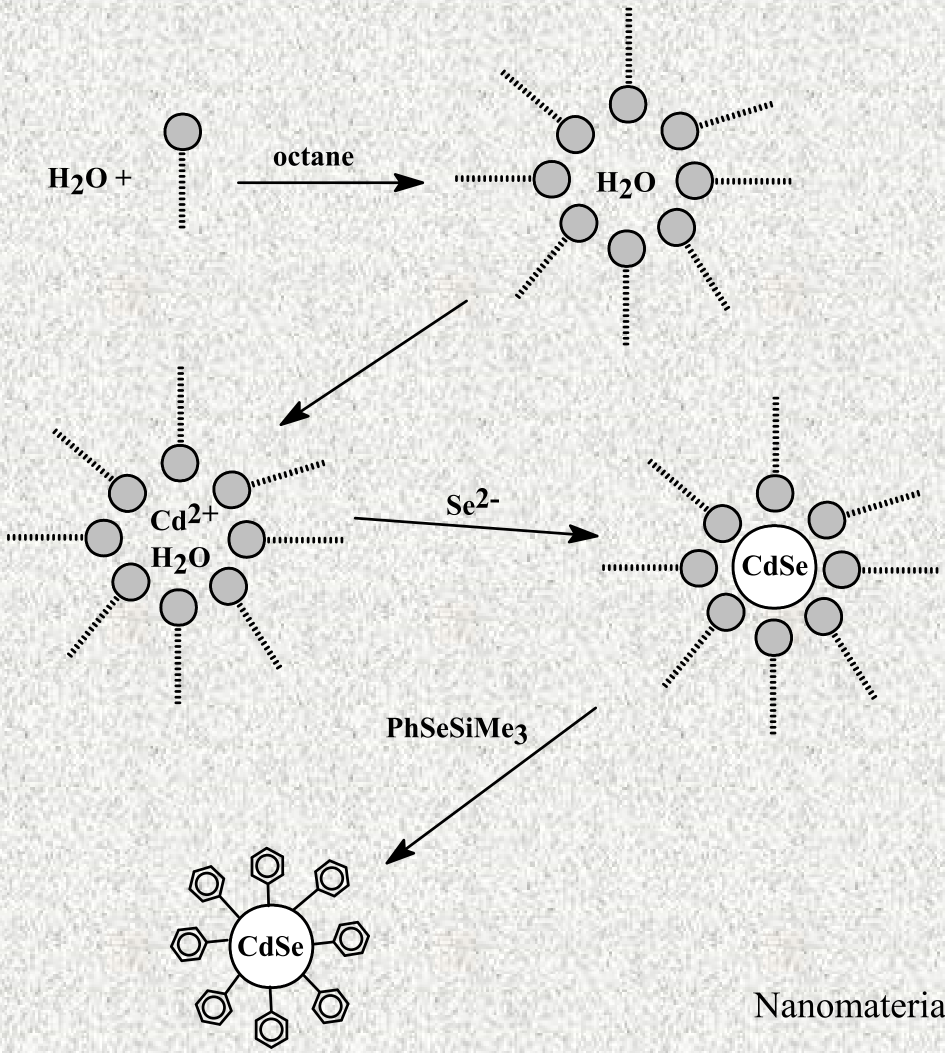
$Mn(NO_3)_2 + Fe(NO_3)_3$ no go, why?

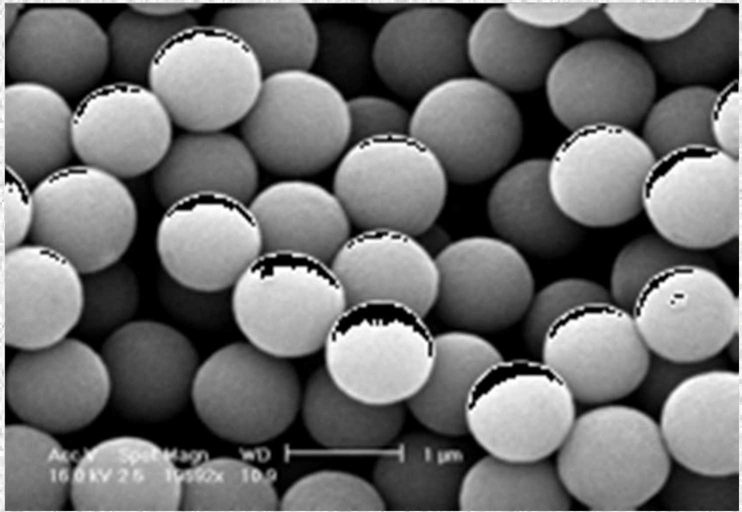
$$2\ MCl_n\ (g) + n\ H_2 \xrightarrow{850\text{-}900\ °C} \underset{3\text{-}11\ \text{nm}}{M^0} + 2n\ HCl$$

NANOSTRUCTURAL MATERIALS

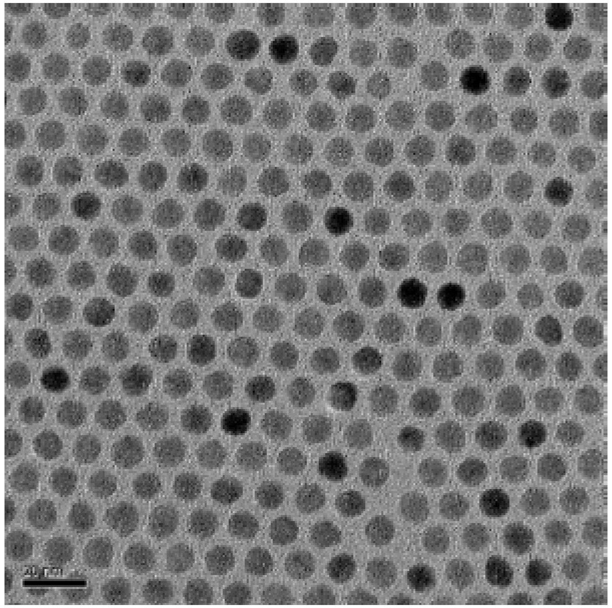
Bottom-up Synthesis

- **Inverse Micelles**

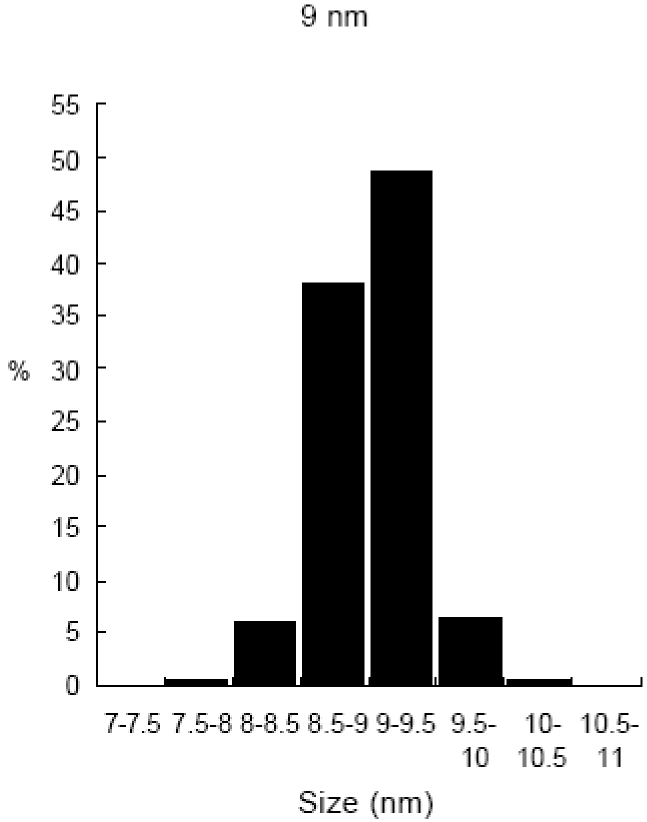




Bottom-up Synthesis



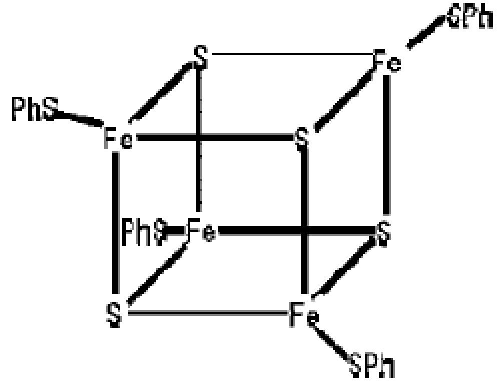
Number of counted particles: 204
Average size: 9.04 nm
Standard deviation: 0.33 nm (3.7%)



Bottom-up Synthesis

Phase Control

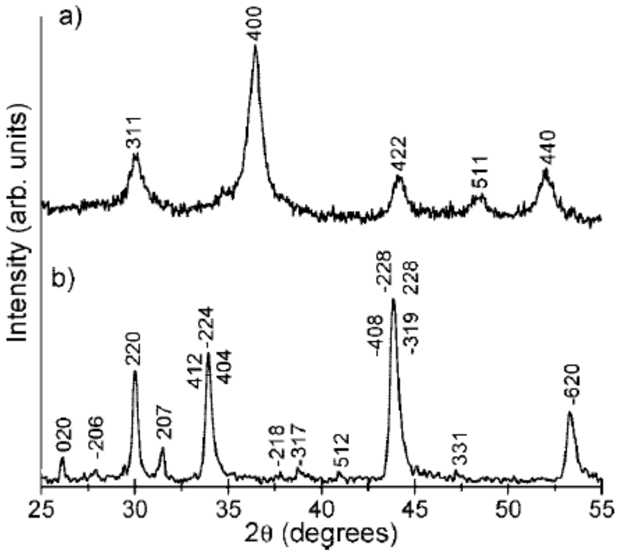
$[N^{n}Bu_4]_2[Fe_4S_4(SPh)_4]$

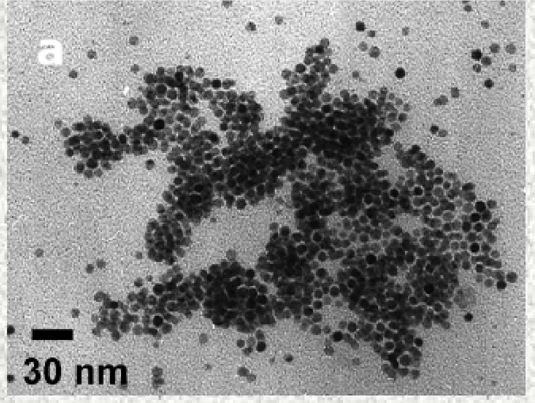


180 °C in octylamine

200 °C in dodecylamine

pyrrhotite Fe_7S_8

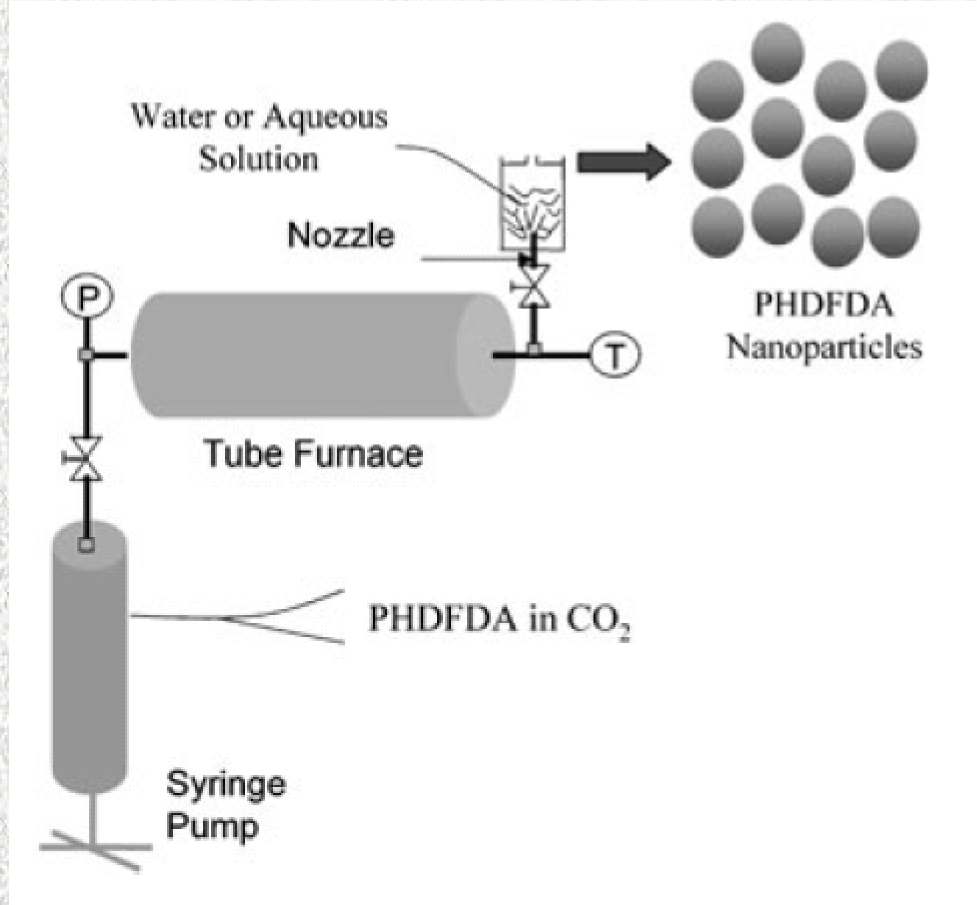


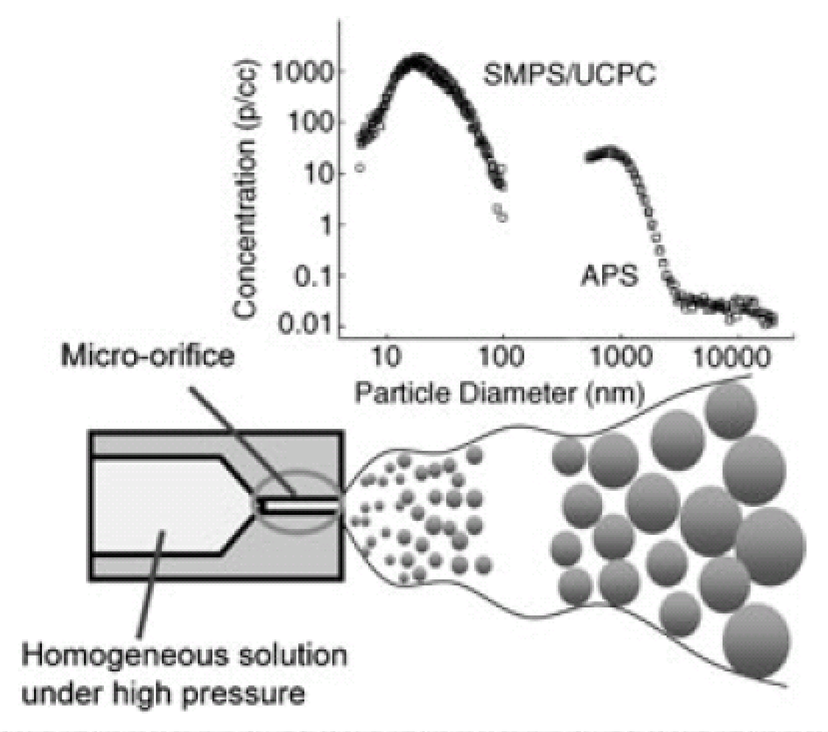


greigite Fe_3S_4

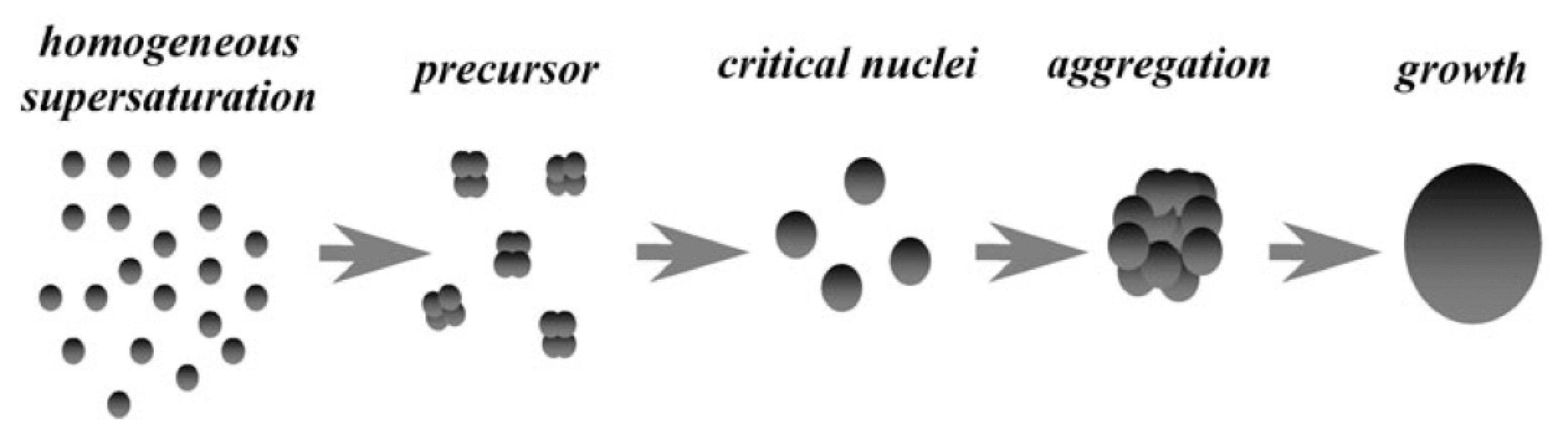
thiospinel, the sulfide analogue of magnetite

Polymeric Nanoparticles from Rapid Expansion of Supercritical Fluid Solution

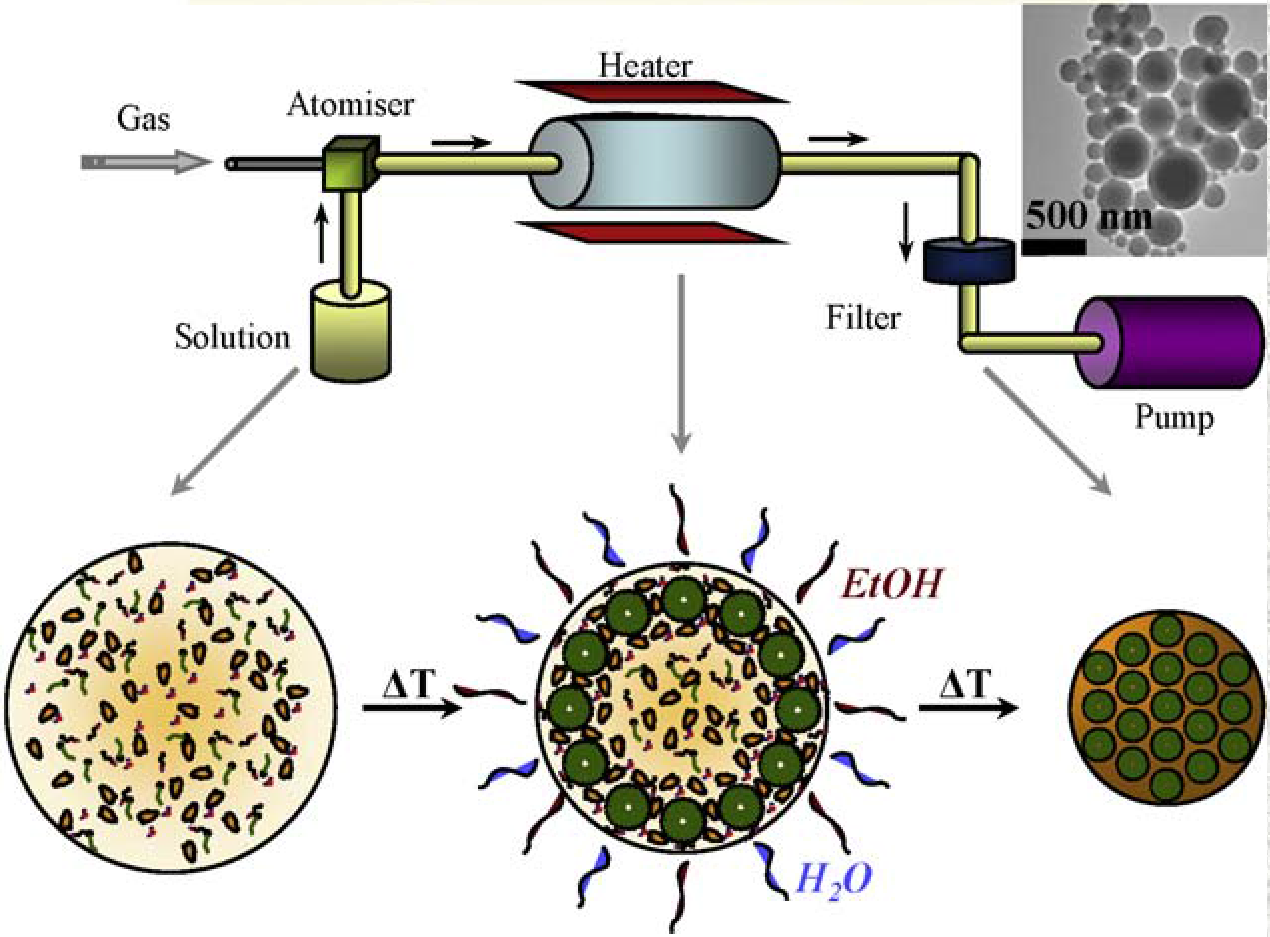


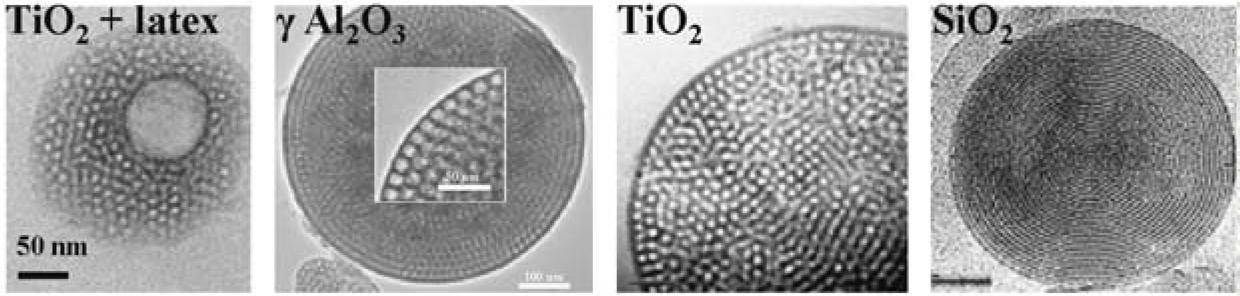


Polymeric Nanoparticles from Rapid Expansion of Supercritical Fluid
Solution



Nanoparticles *via* Spray-drying

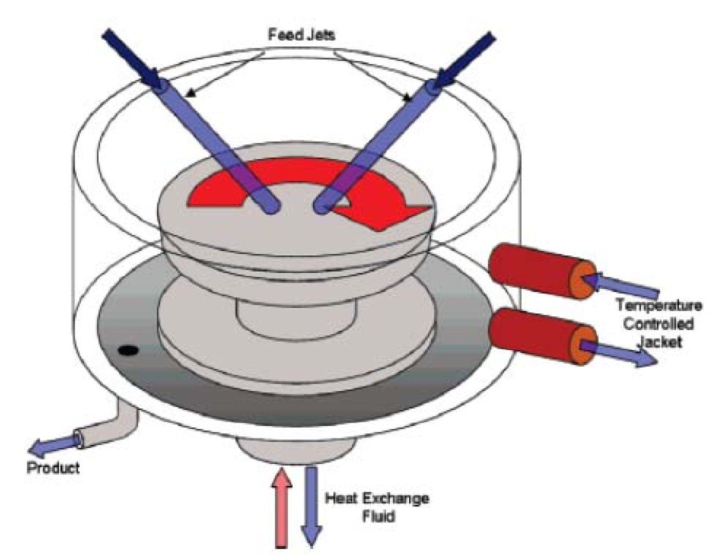




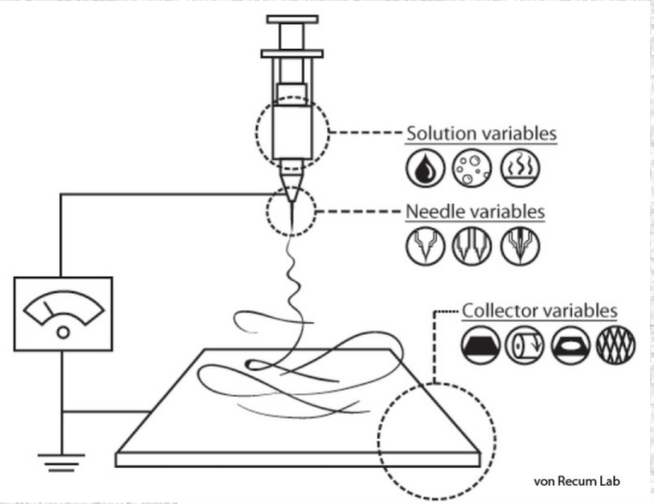
Spinning Disc Processing (SDP)

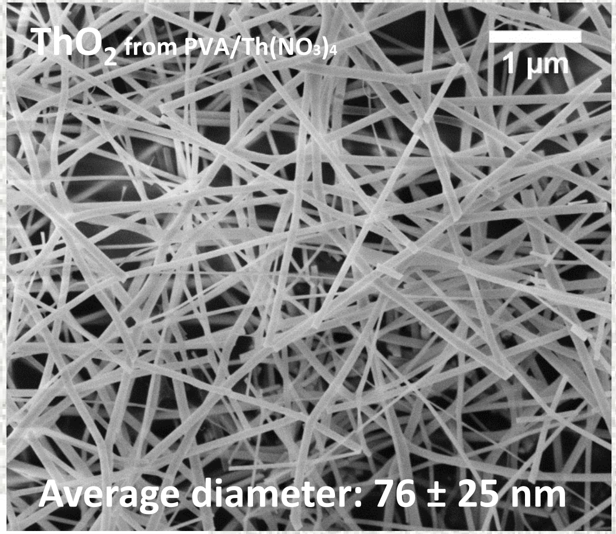
A rapidly rotating disc (300-3000 rpm)
Ethanolic solutions of $Zn(NO_3)_2$ and NaOH, polyvinylpyrrolidone (PVP) as a capping agent
Very thin films of fluid (1 to 200 μm) on a surface
Synthetic parameters = temperature, flow rate, disc speed, surface texture influence on the reaction kinetics and particle size

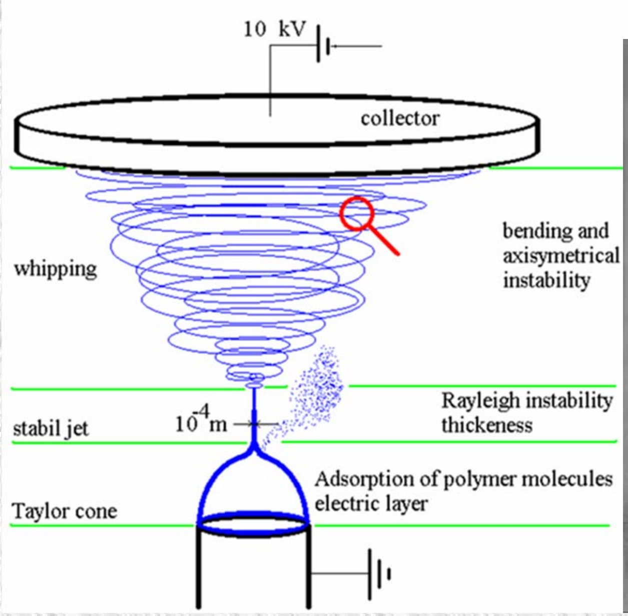
Intense mixing, accelerates nucleation and growth,
affords monodispersed ZnO nanoparticles with controlled particle size down to a size of 1.3 nm and polydispersities of 10%

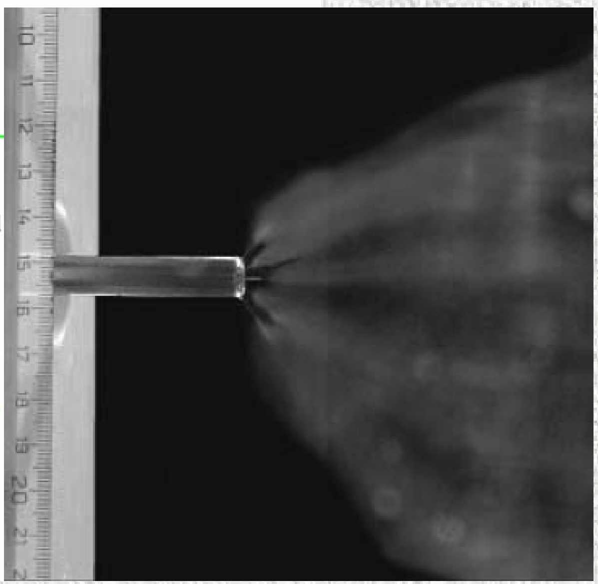


Electrospinning









Vapor-Liquid-Solid (VLS) Growth

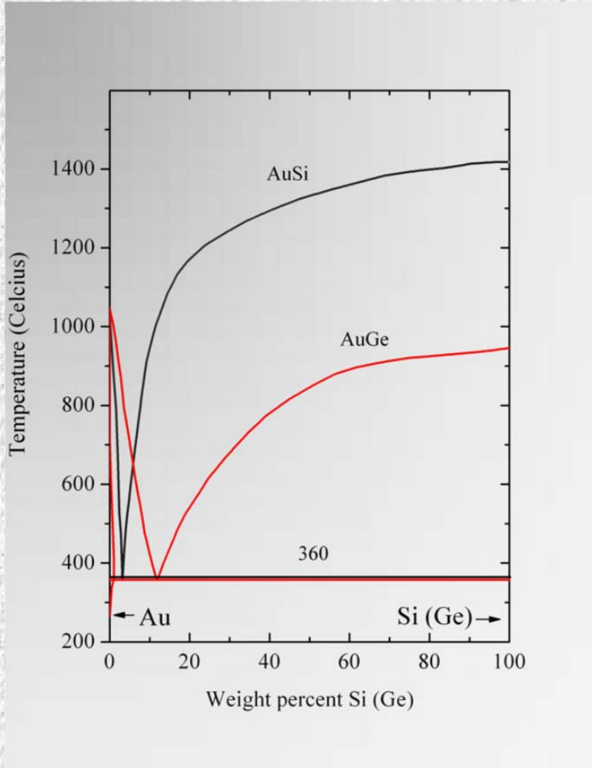
(1) Metal catalyst nanoparticles - Au(s)

Feed another element (Ge vapor, GeH_4 or SiH_4) at an elevated temperature (440-800 °C/ultra-high-vacuum)

Gaseous precursor feedstock is absorbed/dissolved in Au(s) till the solid solubility limit is reached (2)

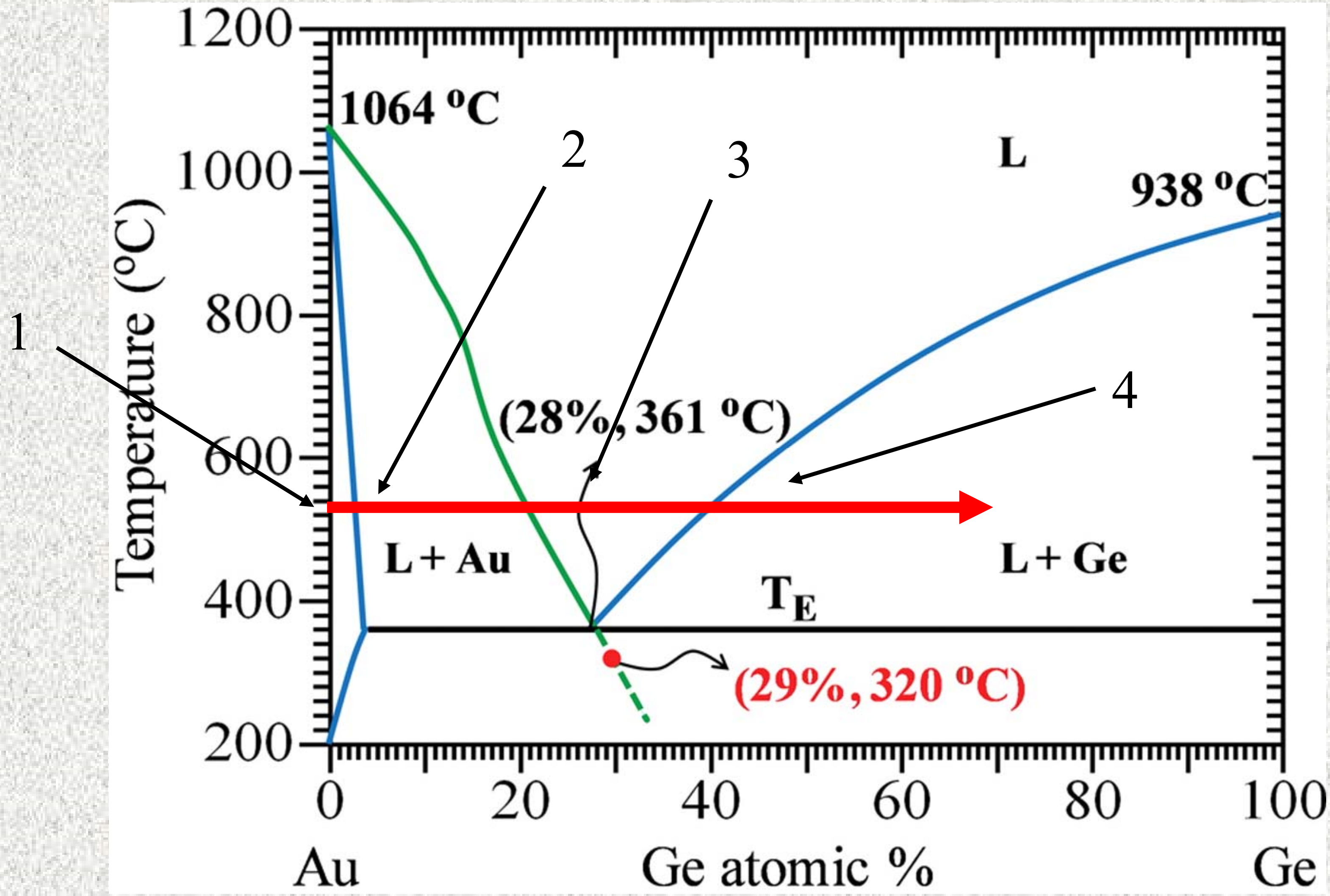
A liquid phase appears, melts to a droplet (3)
The droplet becomes supersaturated with Ge

When the solubility limit is reached (4), an excess material is precipitated out to form solid NWs beneath the droplet

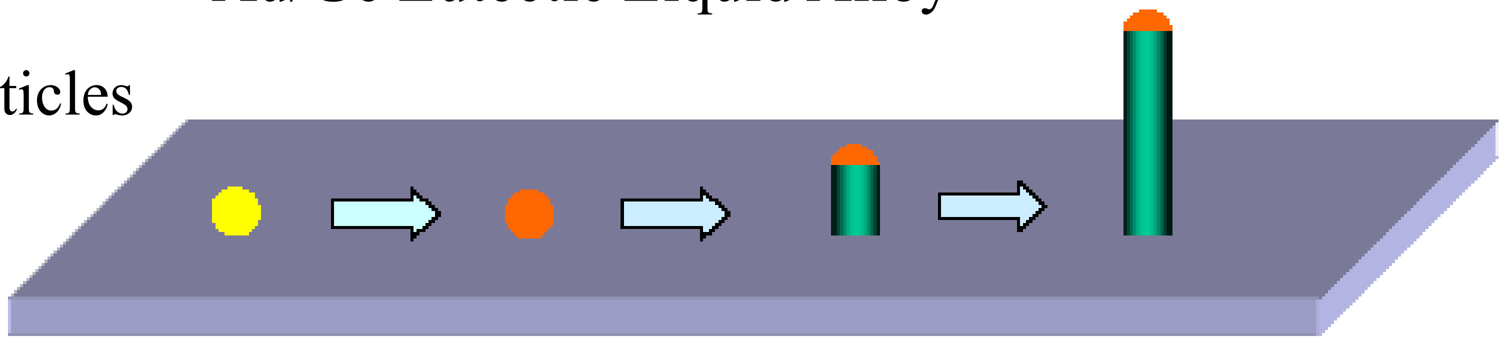


Eutectic 360 °C
Au (mp 1064 °C)
Si (mp 1410 °C)
Ge (mp 938 °C)

Vapor-Liquid-Solid (VLS) Growth



Vapor-Liquid-Solid (VLS) Growth

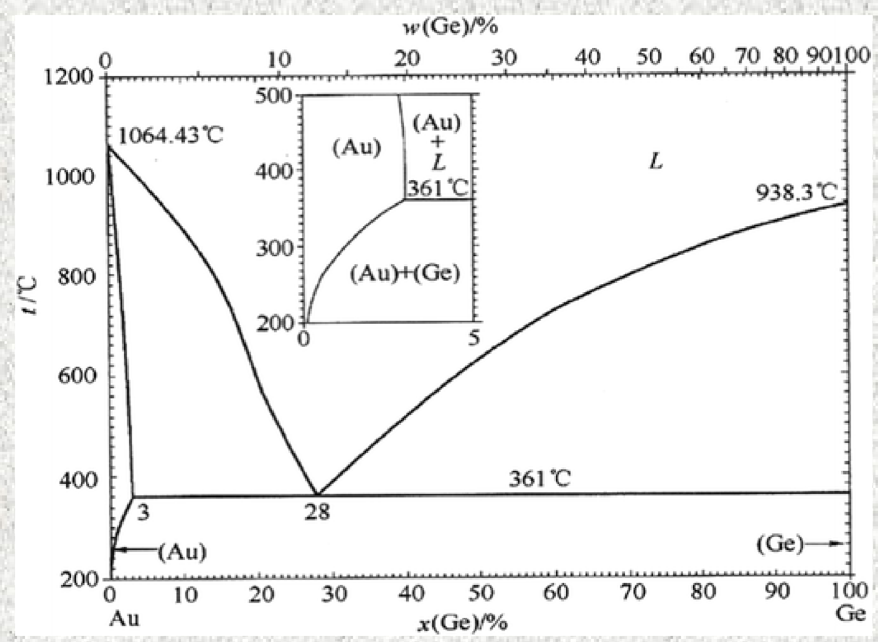


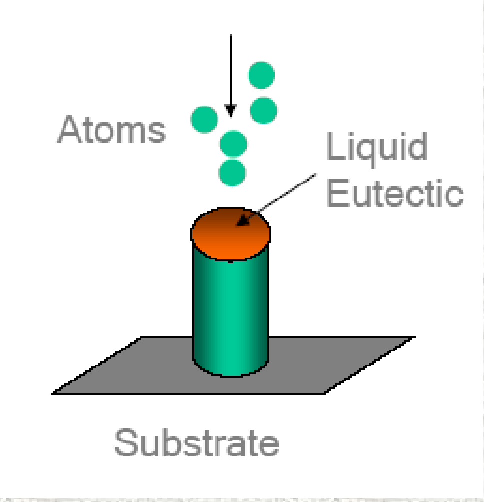
Au/Ge Eutectic Liquid Alloy

Au Particles

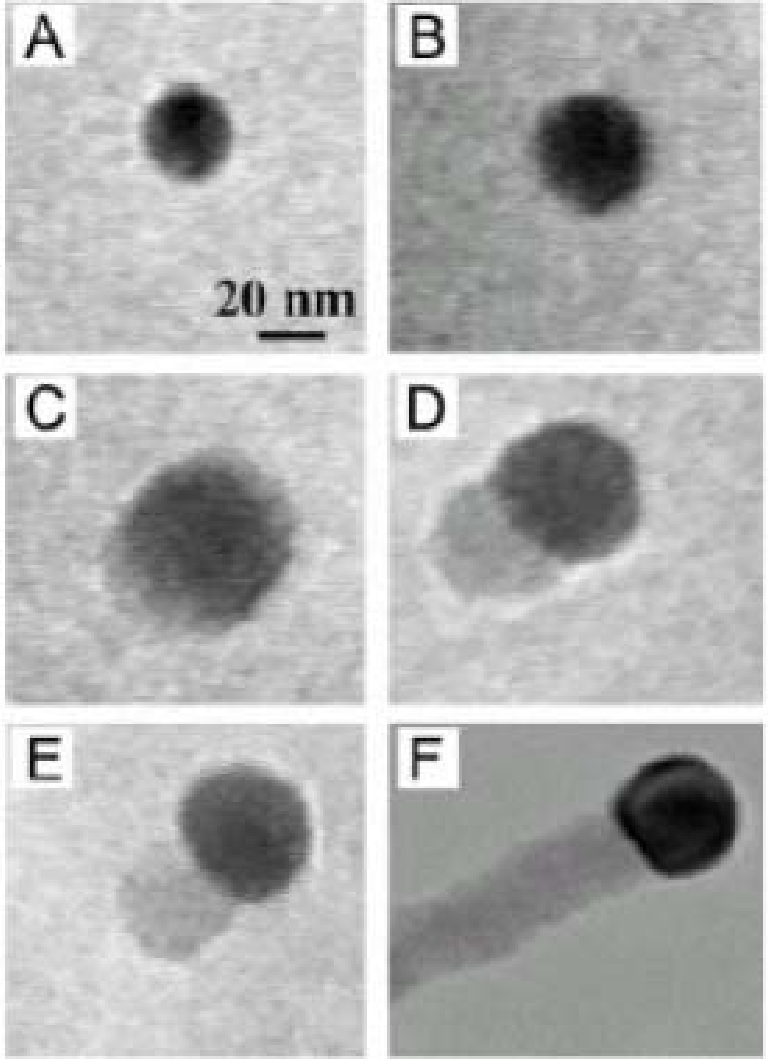
Nucleation of NWs

NW Growth





In-situ TEM images of the VLS process



In-situ TEM images recorded during the process of nanowire growth:

(a) Au nanoclusters in solid state at 500 °C

(b) alloying initiated at 800 °C, at this stage Au exists mostly in solid state

(c) liquid Au/Ge alloy

(d) the nucleation of Ge nanocrystal on the alloy surface

(e) Ge nanocrystal elongates with further Ge condensation

(f) Ge forms a wire

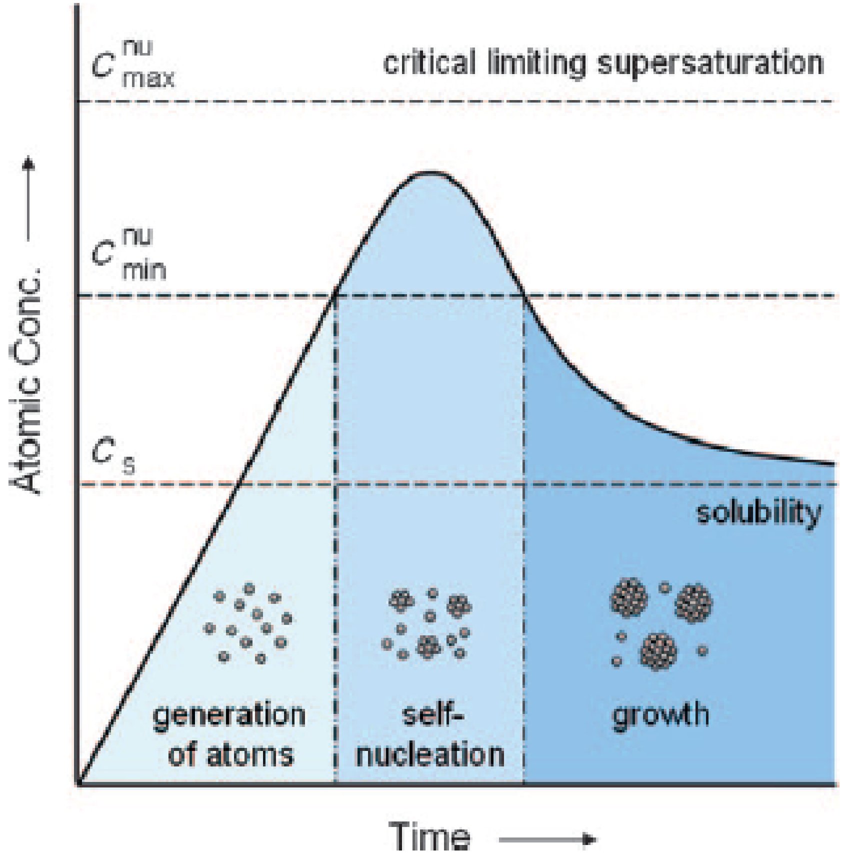
LaMer Mechanism

Supersaturated solution

Burst of nucleation

Slow growth of particles without additional nucleation

Separation of nucleation and growth



Other Mechanisms

Watzky-Finke mechanism

Slow continuous nucleation - Fast autocatalytic surface growth

Seed-mediated mechanism

Au nanoclusters as seeds - Bi, Sn, In, Au, Fe, Fe_3O_4

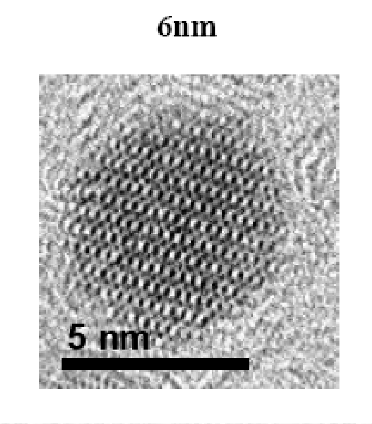
Digestive rippening

Surfactant exchange

Thermal Decomposition of Precursors

$$Fe(CO)_5 \xrightarrow[\text{oleic acid, trioctylamine}]{350\ ^oC,\ 1\ h} Fe \xrightarrow[Me_3NO]{350\ ^oC,\ 1\ h} Fe_2O_3$$

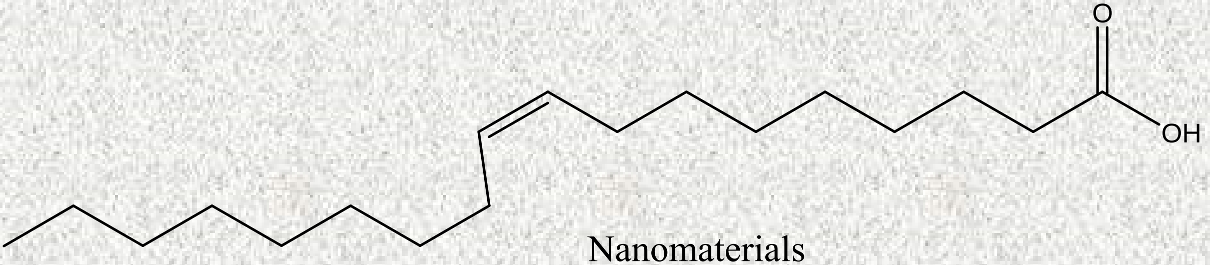
6 nm



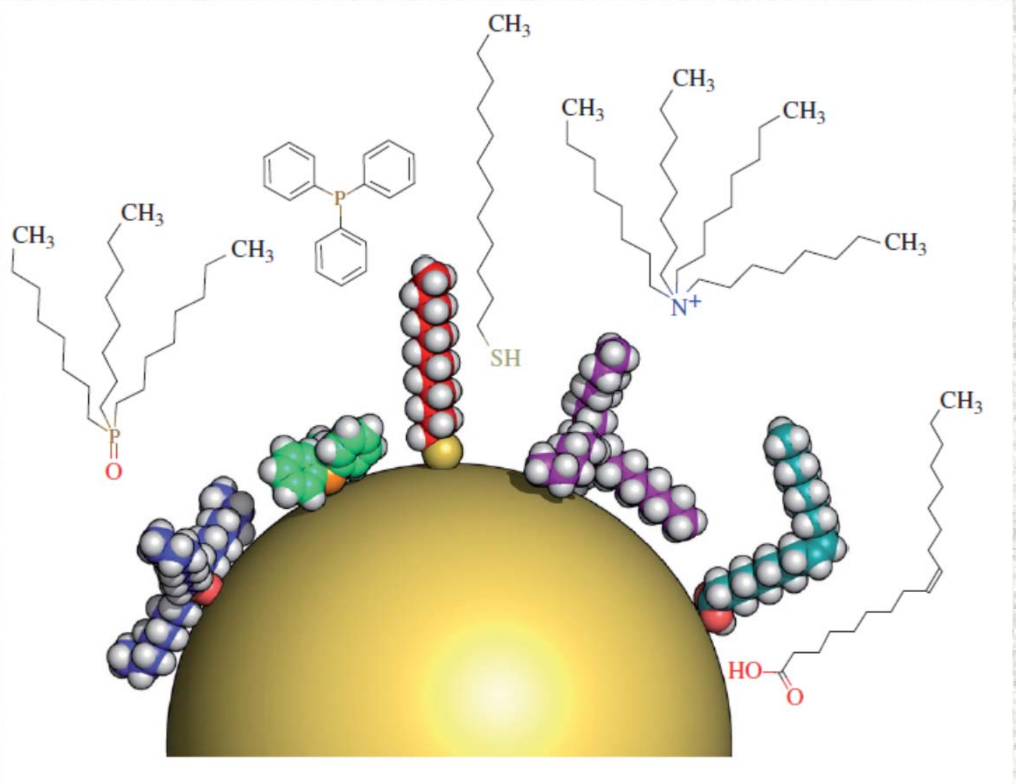
Separation of nucleation and growth

$Fe(CO)_5$ thermal decomposition at 100 ^{o}C contributes to nucleation

Fe(oleate) thermal decomposition at 350 ^{o}C contributes to growth



Surface Modification



A nanoparticle of 5nm core diameter with different hydrophobic ligand molecules both drawn to scale.

The particle is idealized as a smooth sphere.

trioctylphosphine oxide (TOPO)
triphenylphosphine (TPP)
dodecanethiol (DDT)
tetraoctylammonium bromide (TOAB)
oleic acid (OA)

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**

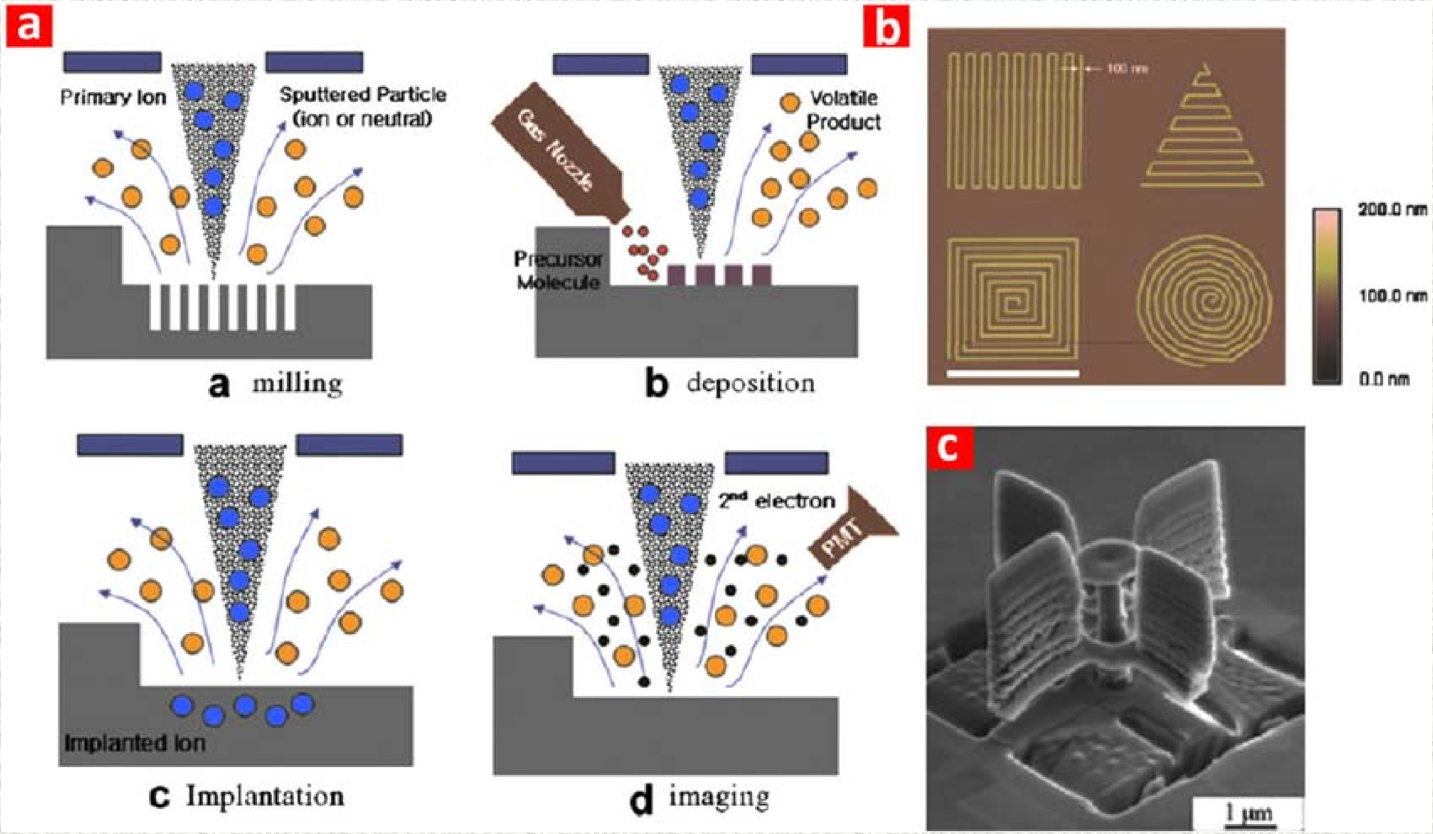
🛠 **Crystallization from Unstable States of Condensed Matter**

- **Crystallization from Glasses**
- **Precipitation from Supersaturated Solid or Liquid Solutions**

Top-down Synthesis: Bulk Down

🛠**Lithographic Techniques**

✧electron beam and focused ion beam (FIB) lithography



Top-down Synthesis: Bulk Down

🛠Lithographic Techniques

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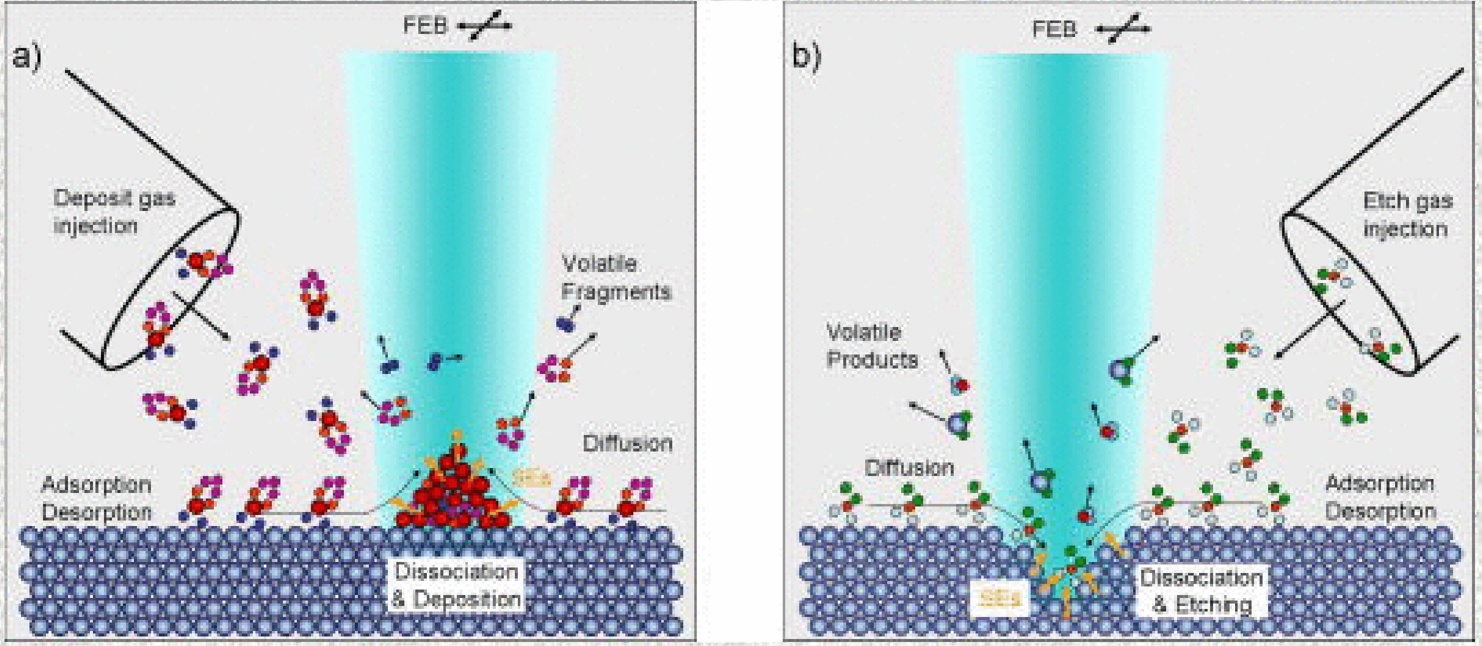
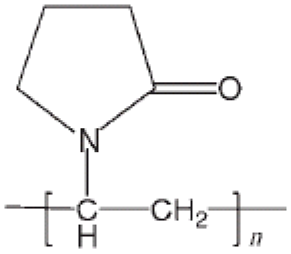


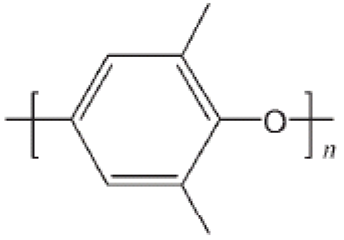
Nanocatalysis

Polymers used as metal NP supports for catalysis



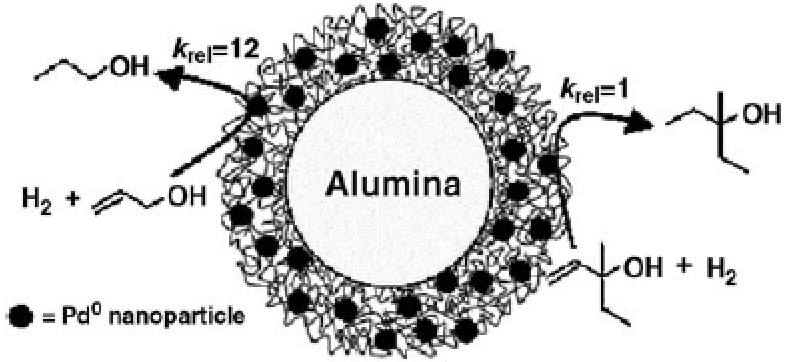
PVP

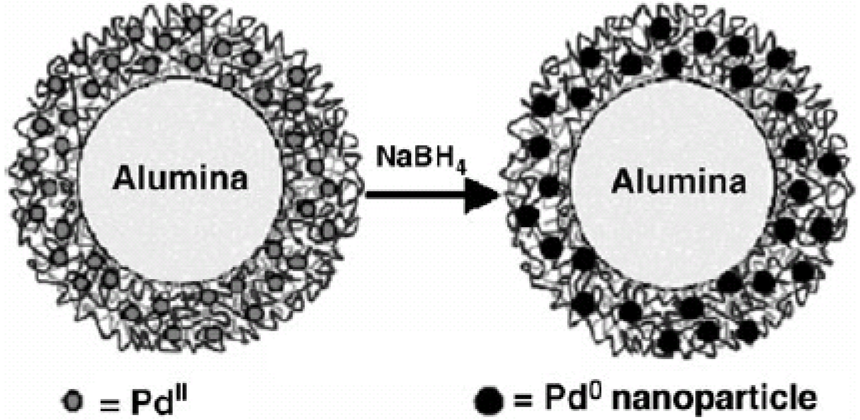
poly(vinylpyrrolidone)



PPO

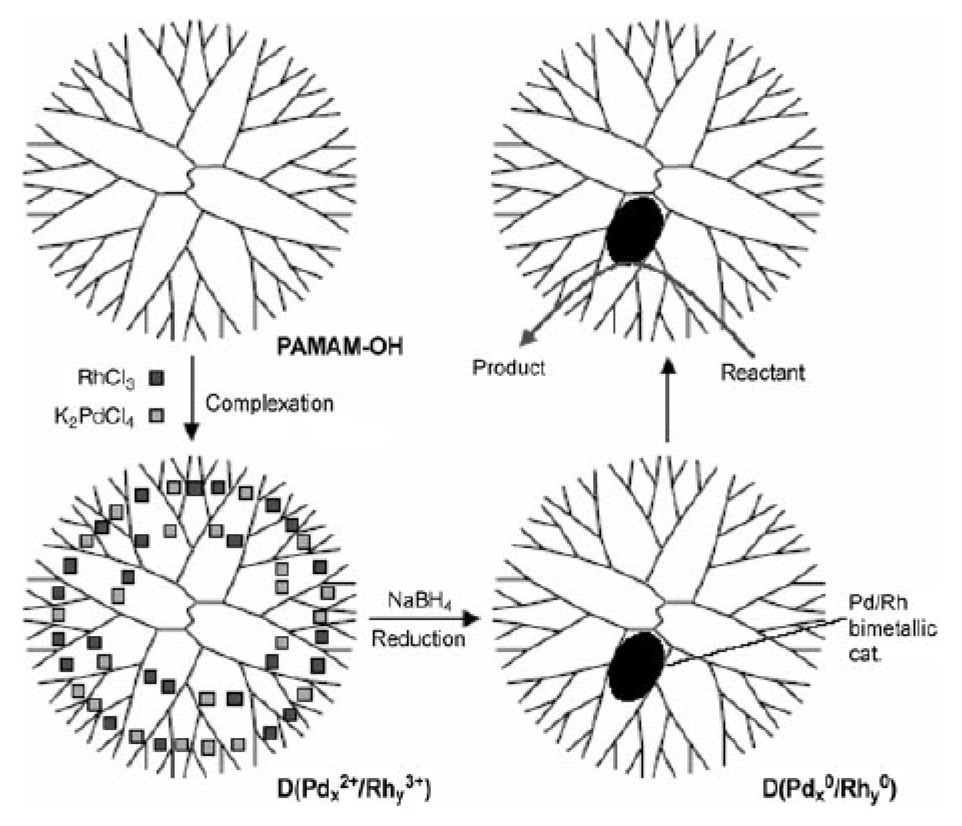
poly(2,5-dimethylphenylene oxid





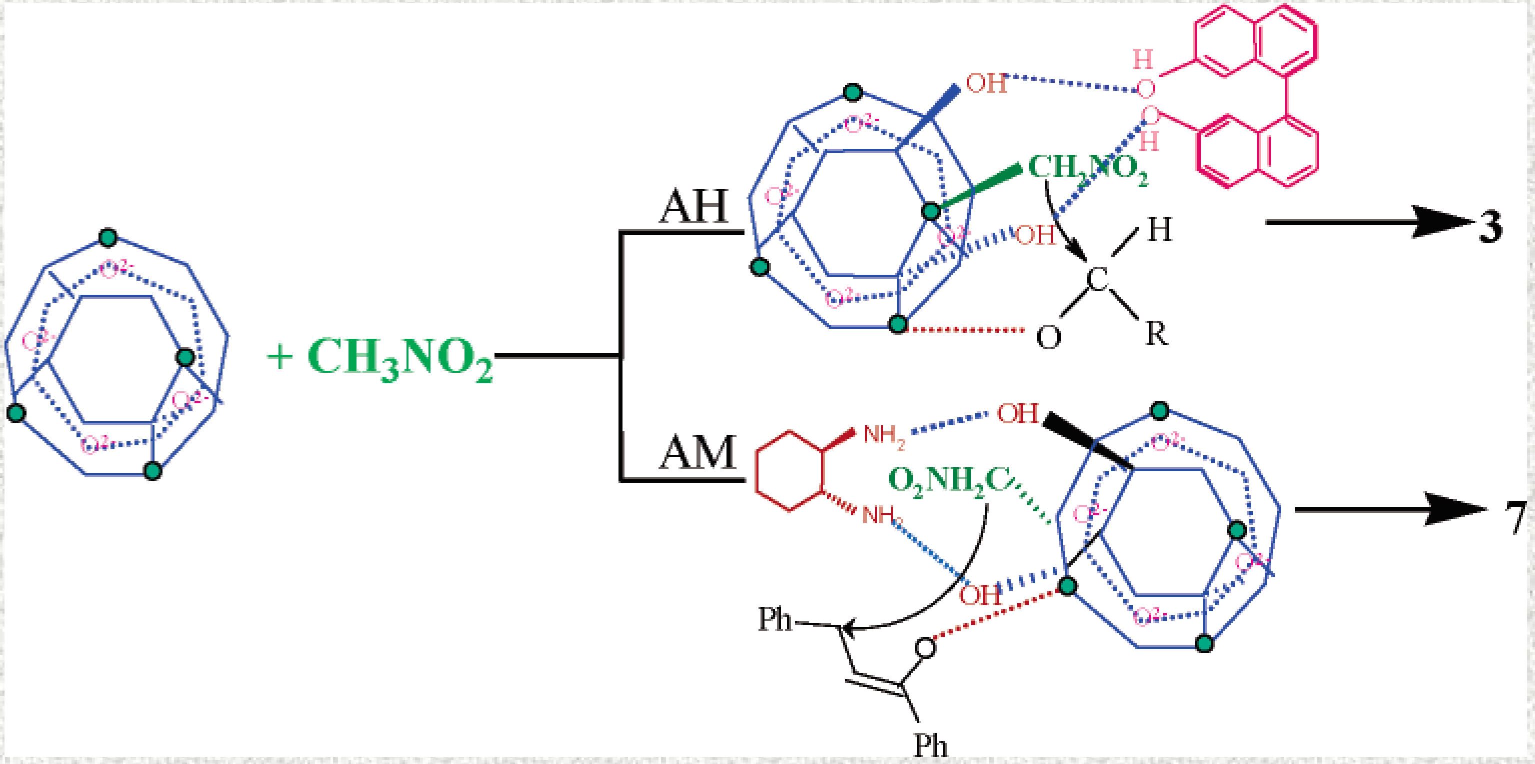
Nanocatalysis

Catalysis by nanoparticles encapsulated in PAMAM or PPI dendrimers



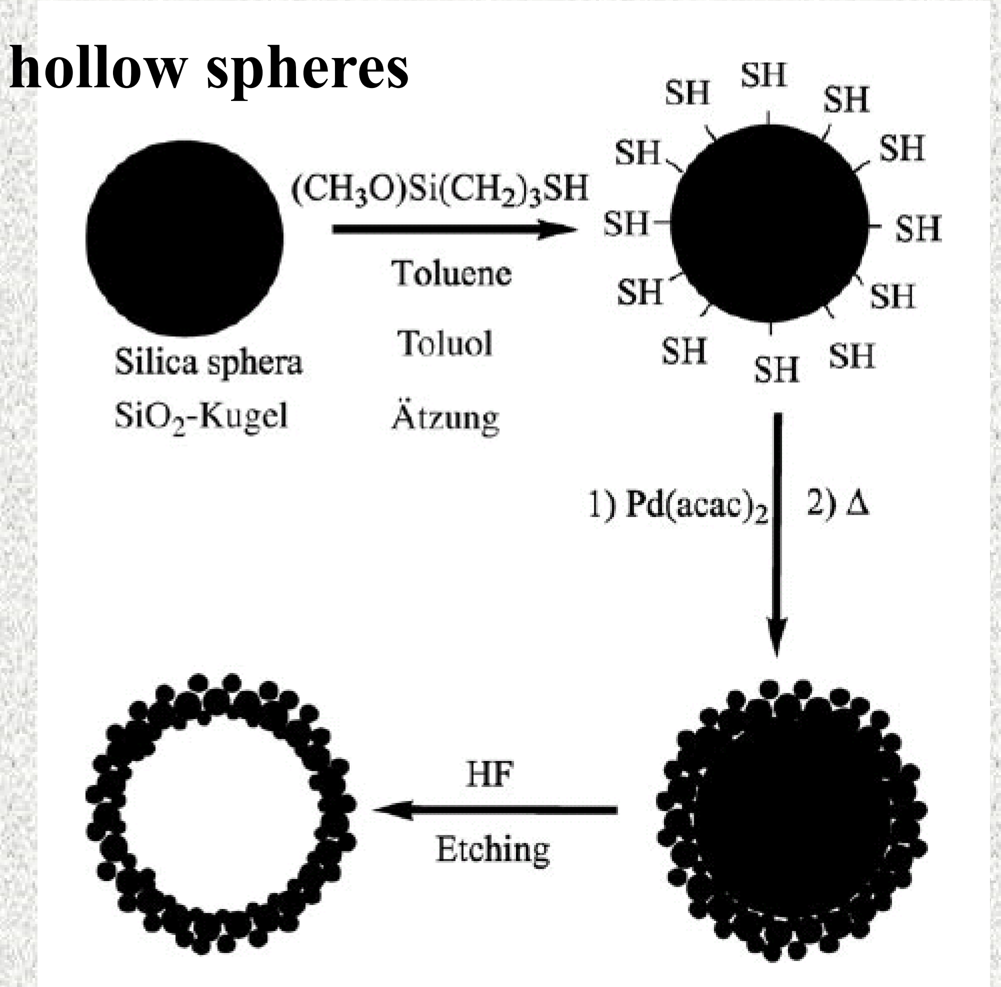
Nanocatalysis

Asymmetric heterogeneous catalysis on nanoparticles



Hollow Nanoparticles

formation of hollow spheres



Applications

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

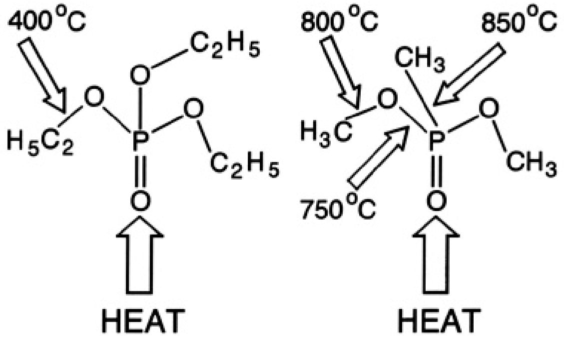


Figure 3. Cleavages of bonds in $(C_2H_5O)_3P(O)$ and DMMP under thermal decomposition condition.

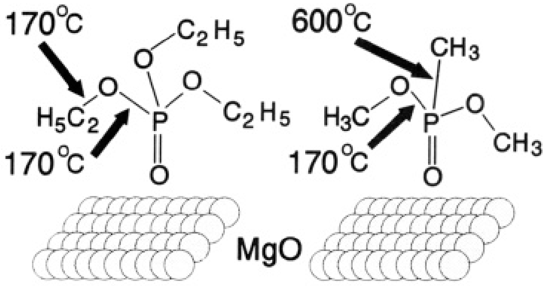


Figure 4. Cleavages of bonds of $(C_2H_5O)_3P(O)$ and DMMP on MgO.