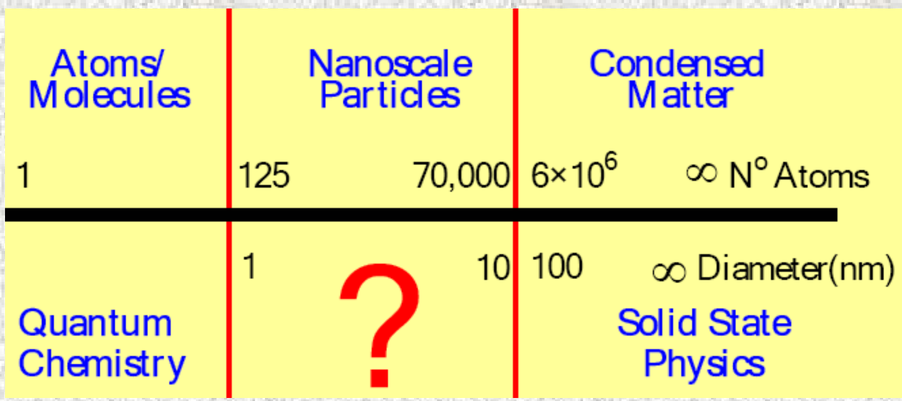
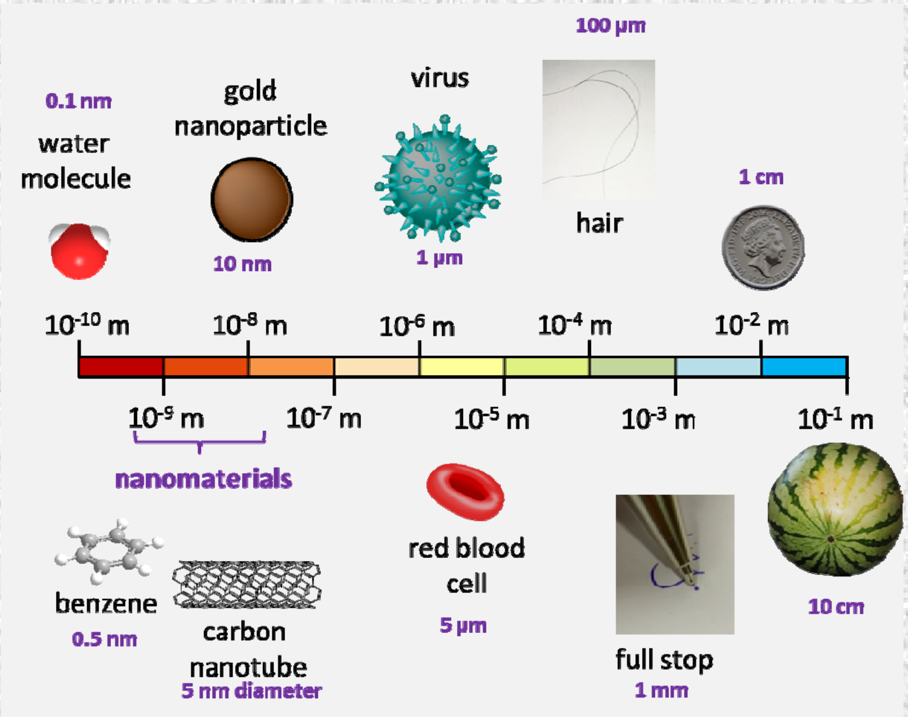
Nanoscopic Materials

- **Chemical methods used to change physical and chemical properties – chemical composition, substituents, concentration, crystal structure….**
- **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 starts to depend on the size**

Nanoscopic Scales



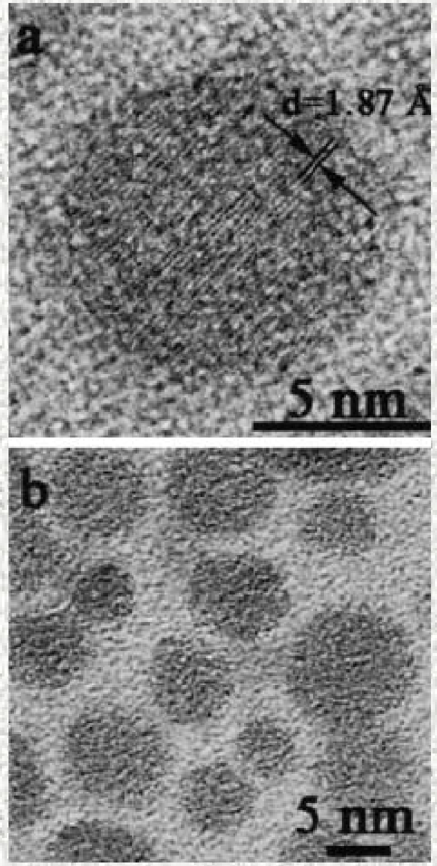


Nanomaterials

1 – 100 nm

Nanoscopic Materials

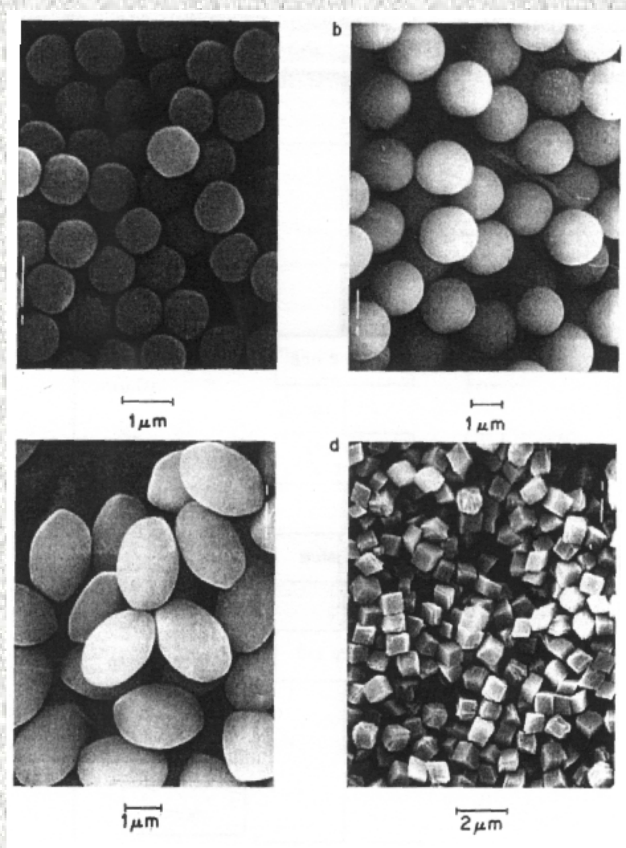
Nanoparticles 1 – 100 nm



1 nm = 10^{-9} m

1 nm = 10 Å

Traditional materials > 1 μm



Nanoscopic Materials

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 - Physical and chemical properties depend on the size !!

Natural examples:

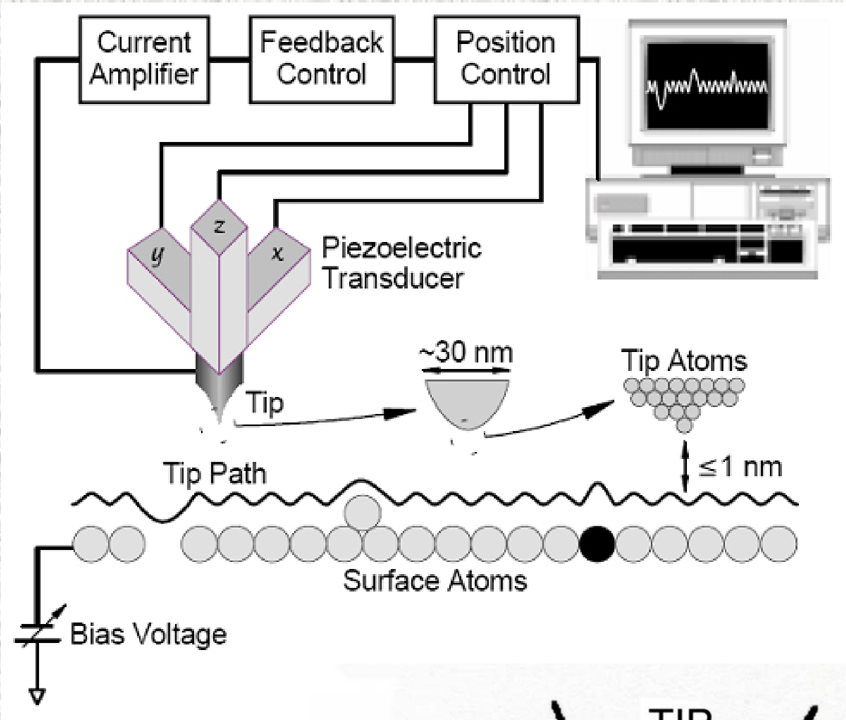
- ☯ **Human teeth, 1-2 nm fibrils of hydroxyapatite $Ca_5(PO_4)_3(OH)$ + collagen**

- ☯ **Asbestos, opals, chalcedony**

- ☯ **Primitive meteorites, 5 nm C or SiC, early age of the Solar system**

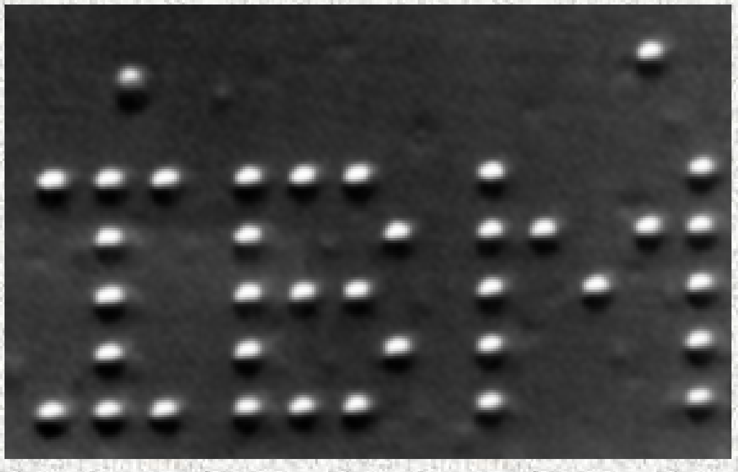
Nanoscale objects have been around us, but only now we can observe them, manipulate, and synthesize them

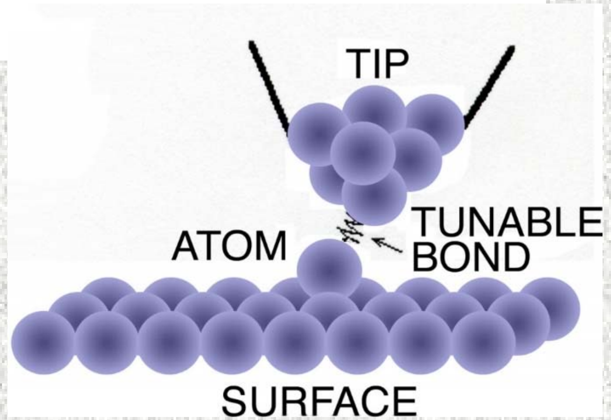
Scanning Tunelling Microscopy STM



Binning and Rohrer
Nobel Prize 1986

Nanoscale Writing
STM positioned Xe atoms
on a Ni crystal, 5 nm letters



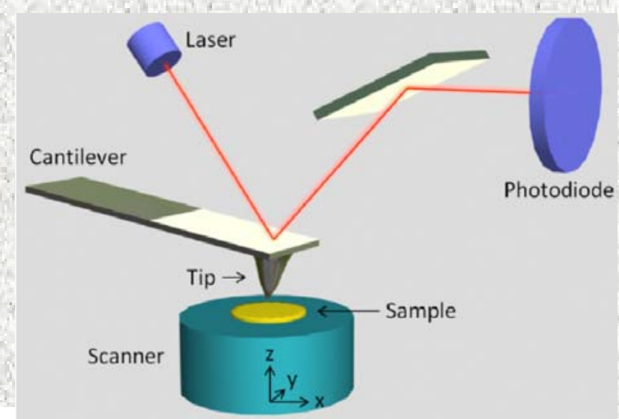


There's Plenty of Room at the Bottom

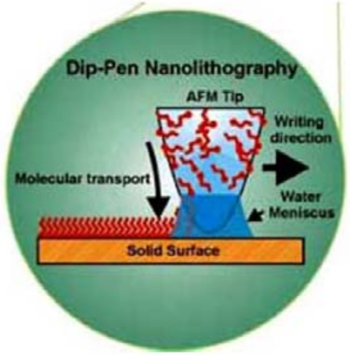
What I want to talk about is the problem of manipulating and controlling things on a small scale …

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……

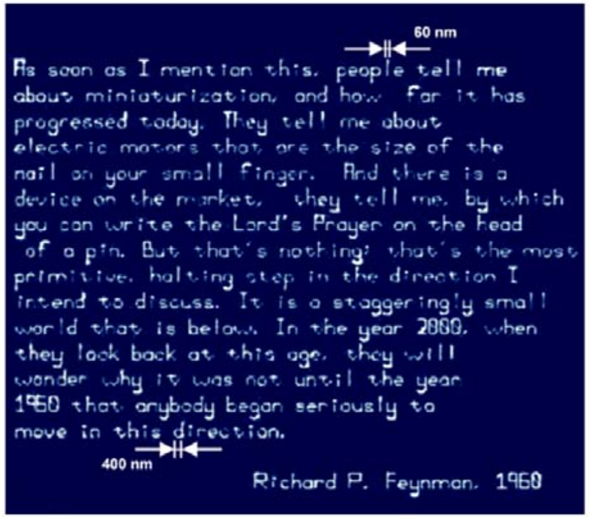
Prof. Richard Feynman in "There's plenty of room at the bottom", lecture delivered at the annual meeting of the APS, Caltech, 29 December, 1959.



Richard Feynman
(1918–1988)
NP in Physics 1965



Nanoscale writing with an AFM (Mirkin et al.)



Properties of Nanoscopic Materials

• Metallic behavior - a single atom cannot behave as a metal, metal to nonmetal transition on decreasing the size: 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

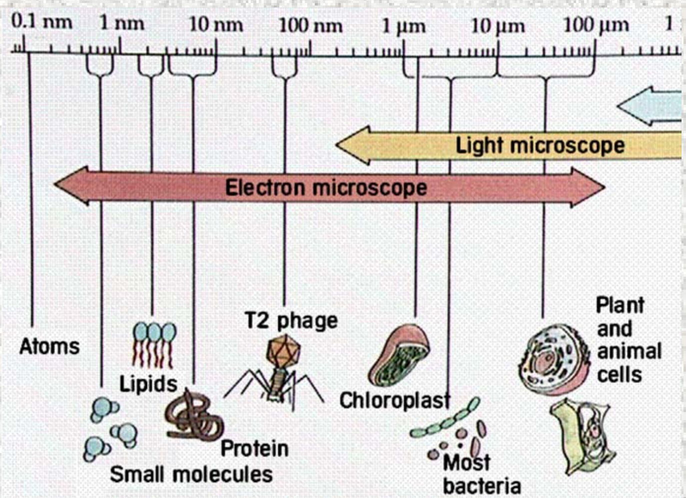
• Negligible light scattering - new optics

• 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



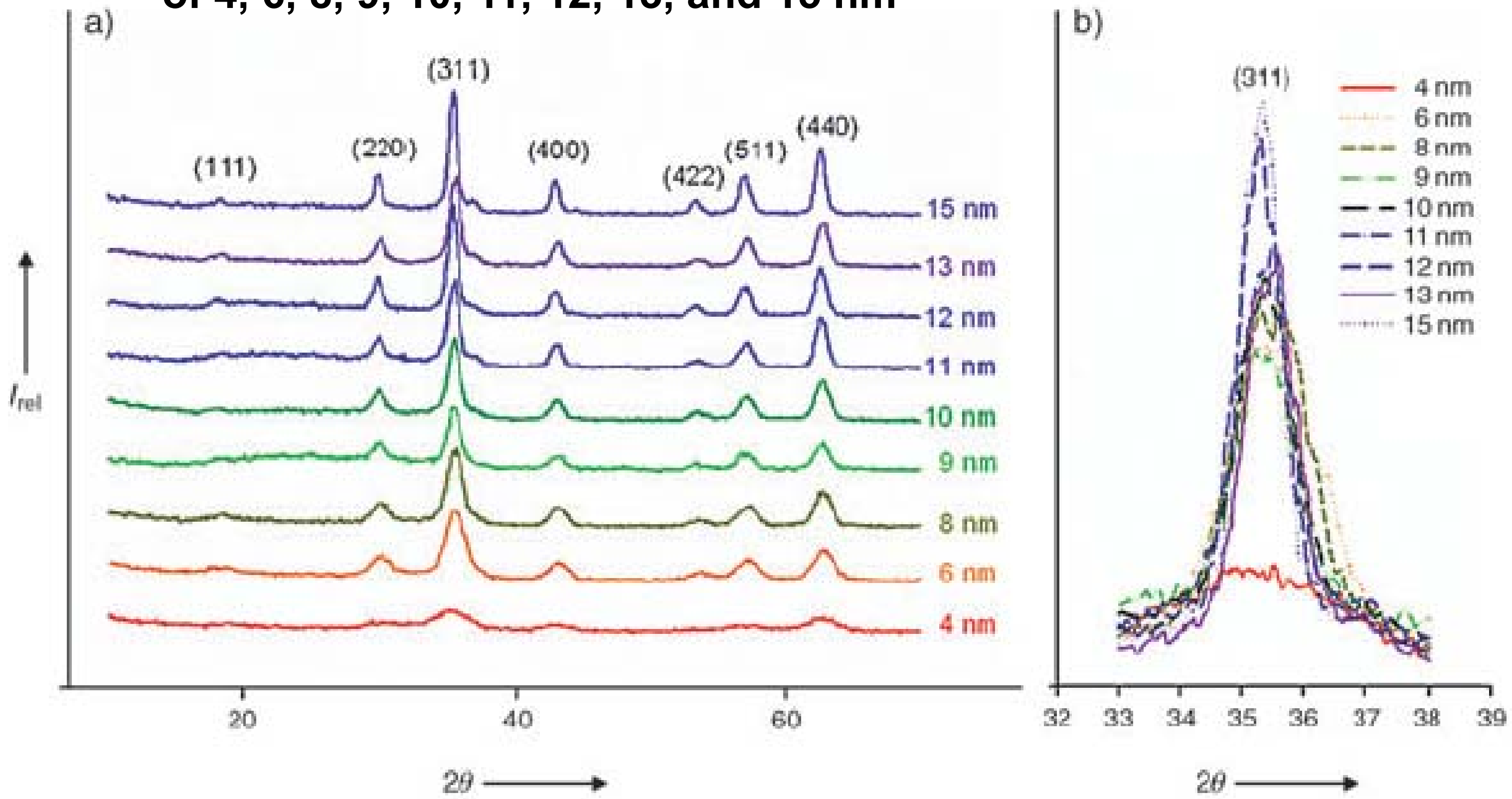
Coherence Length, *d*

Scherrer Equation

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

k = 0.89, λ = wavelength,
β = full width at half-maximum (corrected for a natural linewidth standard, such as Si, LaB_6)

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

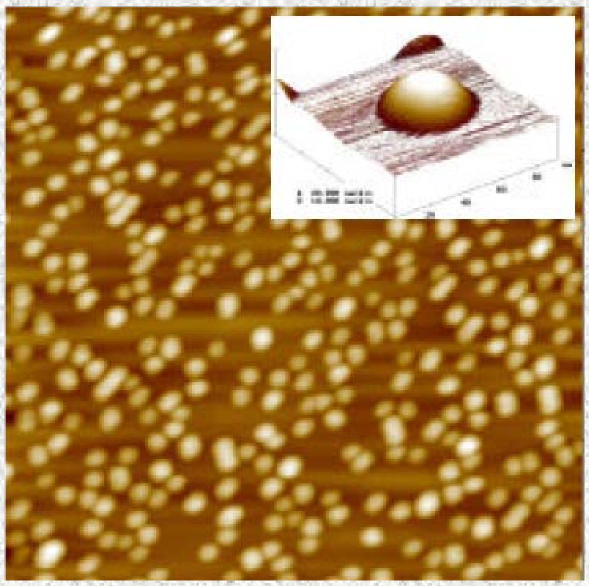


The Nano-Family

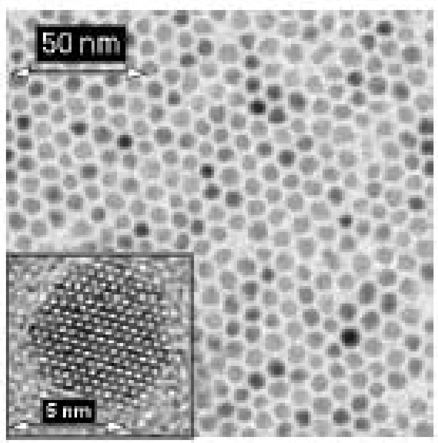
3 dimensions are between 1 - 100 nm

0-D structures (3-D confinement):

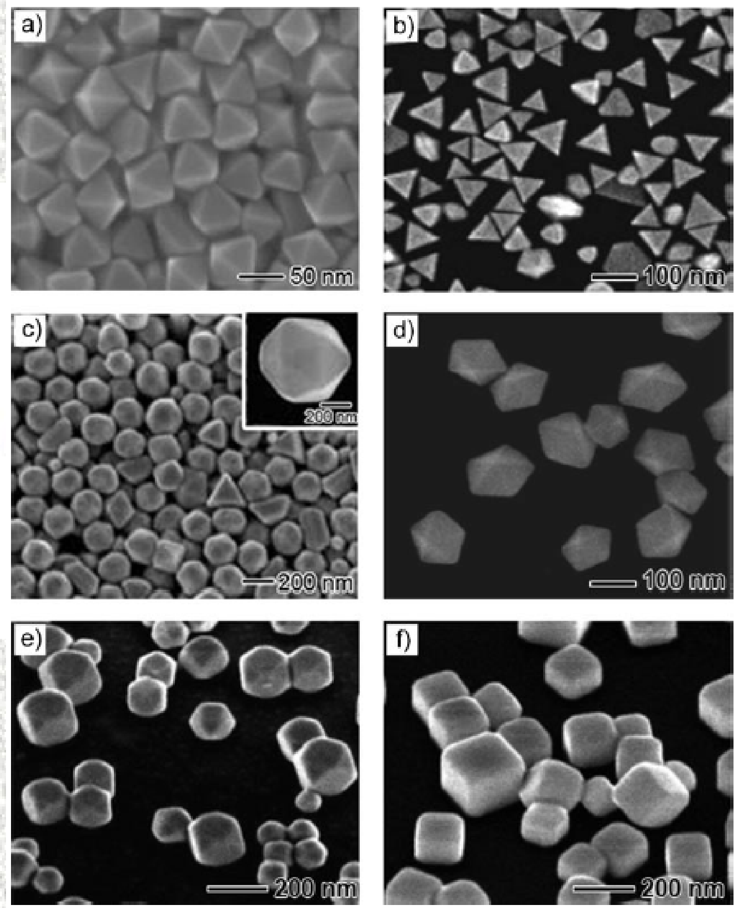
- **Quantum dots**
- **Nanoparticles**



AFM 1 µm x 1 µm
InAs on GaAs/InP



CdTe nanoparticles



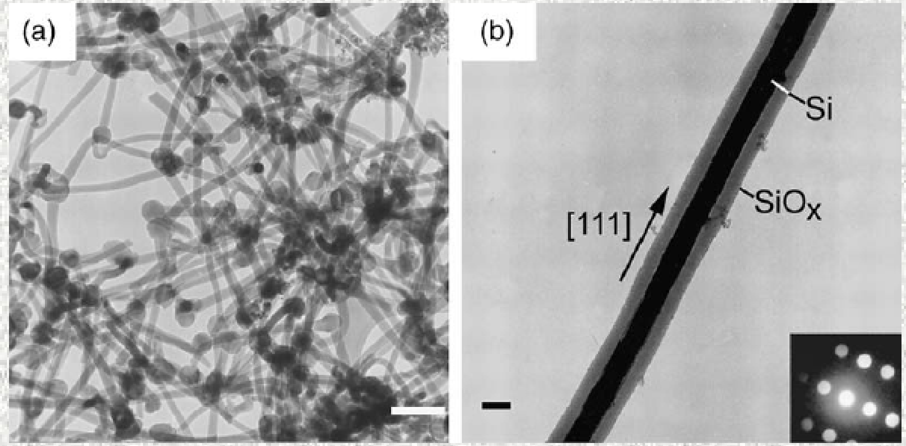
Au nanoparticles

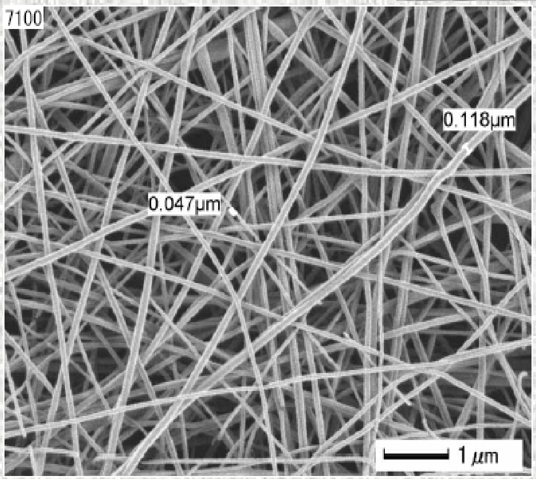
The Nano-Family

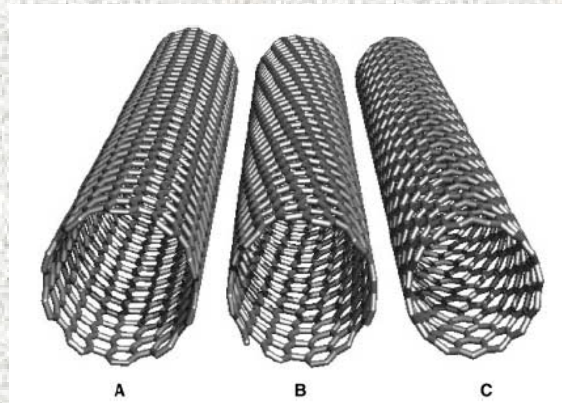
At least 2 dimensions are between 1 - 100 nm

1-D structures (2-D confinement):

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



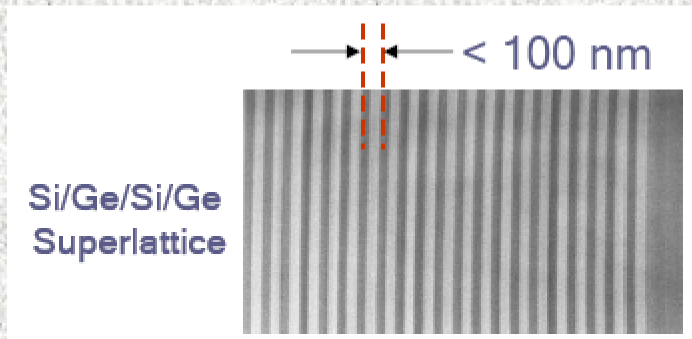


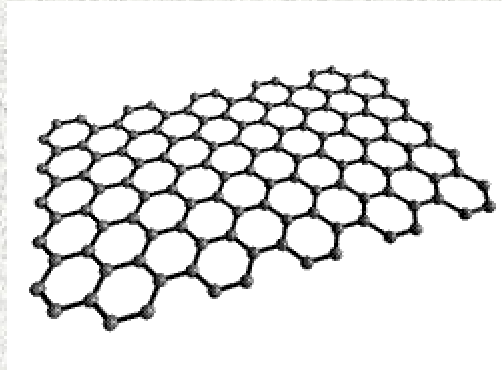


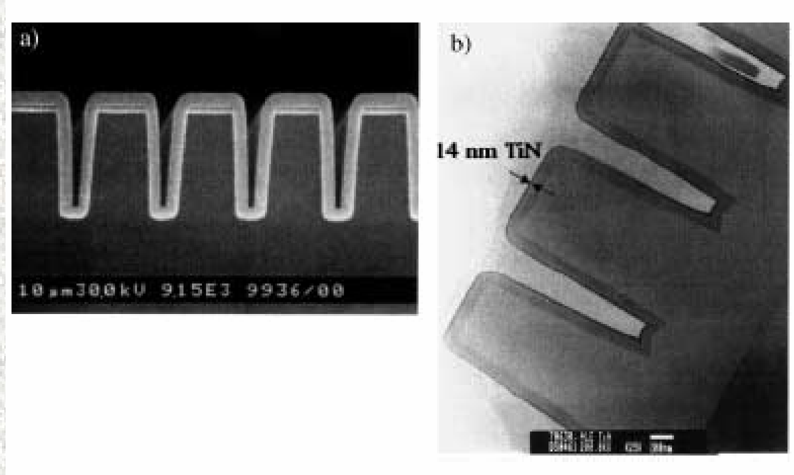
The Nano-Family

At least one dimension is between 1 - 100 nm

2-D structures (1-D confinement):
- **Thin films - CVD, ALD**
- **Planar quantum wells**
- **Superlattices**
- **Graphene**
- **SAM**



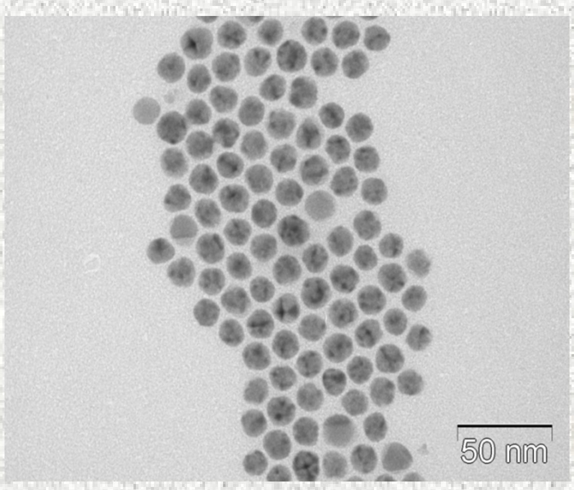




Nanoscopic Behavior of Materials

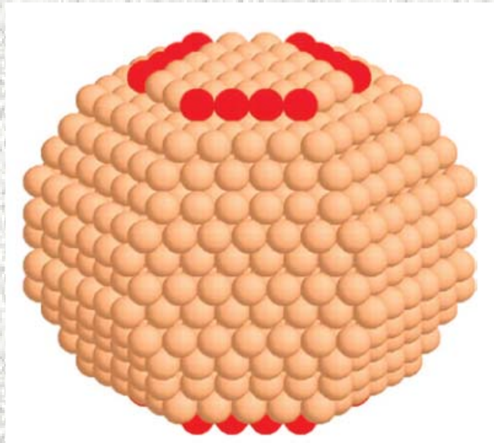
Differences between bulk and nanoscale materials

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

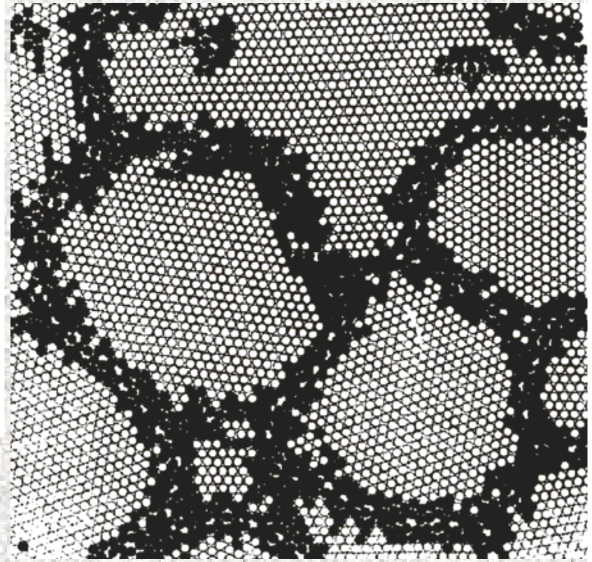


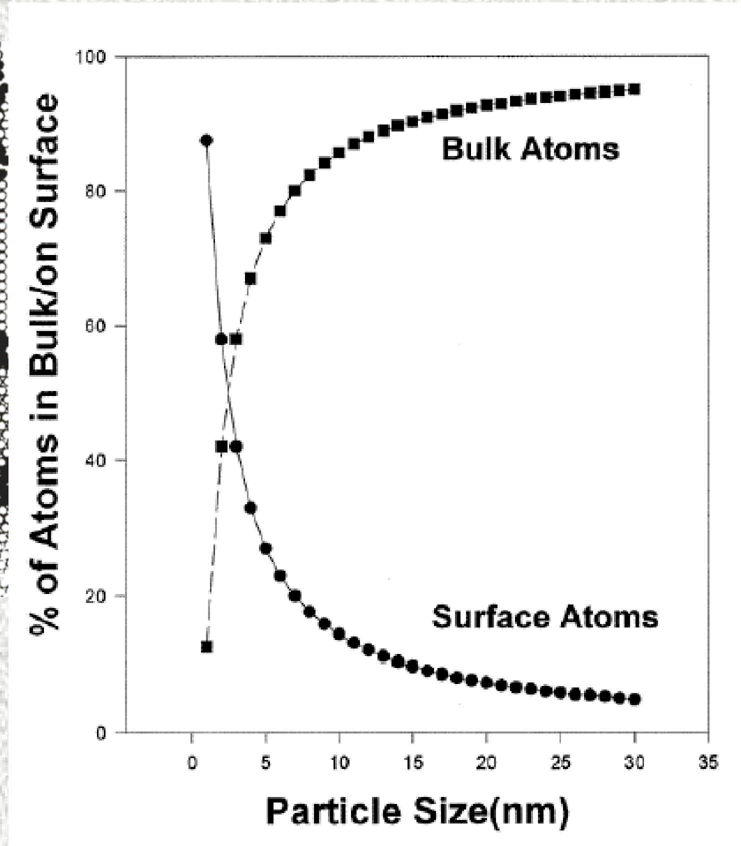
Surface Effects

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



Ru particle
diameter 2.9 nm





Surface Effects

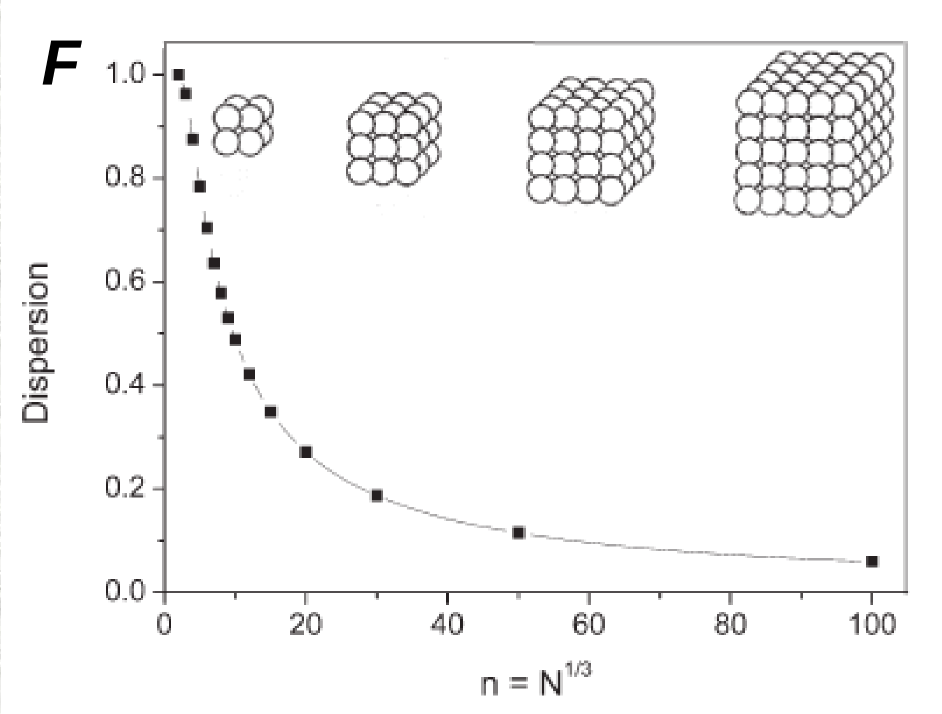
Dispersion *F* = the fraction of atoms at the surface

F is proportional to surface area divided by volume

N = total number of atoms
r = radius
V = volume

V ~ r^3 ~ 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

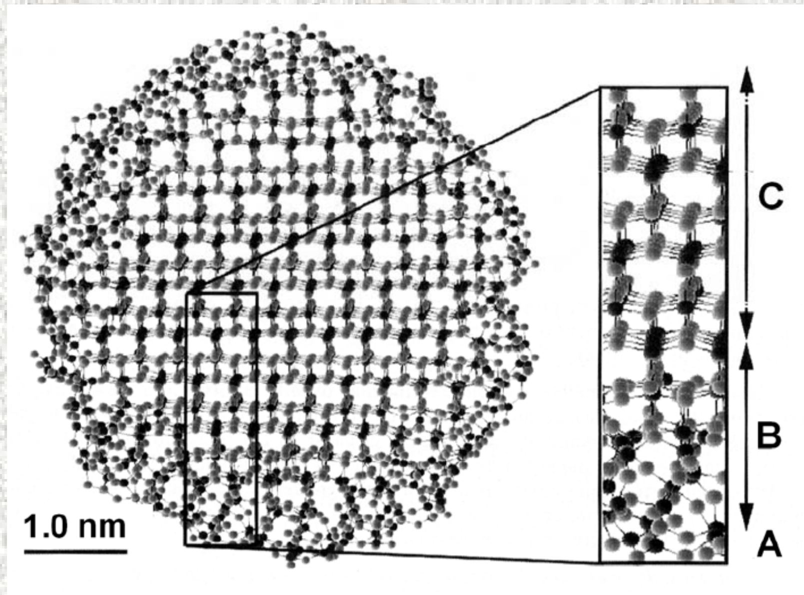
Atoms at surfaces

- Fewer neighbors than atoms in the bulk = lower coordination number
- Stronger and shorter bonds
- Unsatisfied bonds
- Broad spectrum of interatomic distances and angles
- Surface atoms are less stabilized than bulk atoms
- Reduced atomic density (by 10 – 30 %)

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

The melting and other phase transition temperatures scale with surface-to-volume ratio and with the inverse size 1/r

Surface Effects

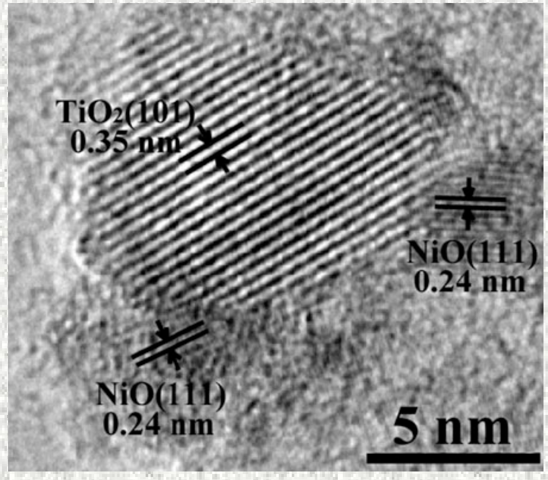


A = Atoms at surfaces (one layer) – fewer neighbors, lower coordination, unsatisfied (dangling) bonds

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

Surface Effects

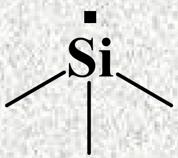


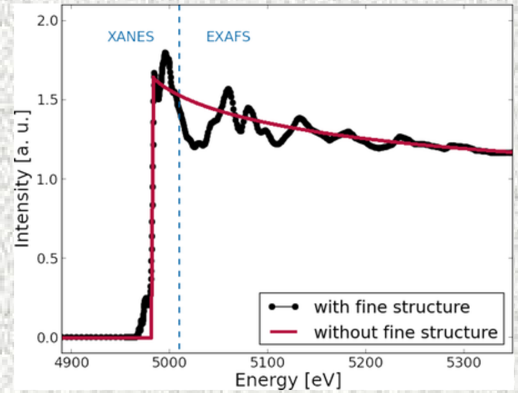
Experimental evidence

- HR-TEM
- 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

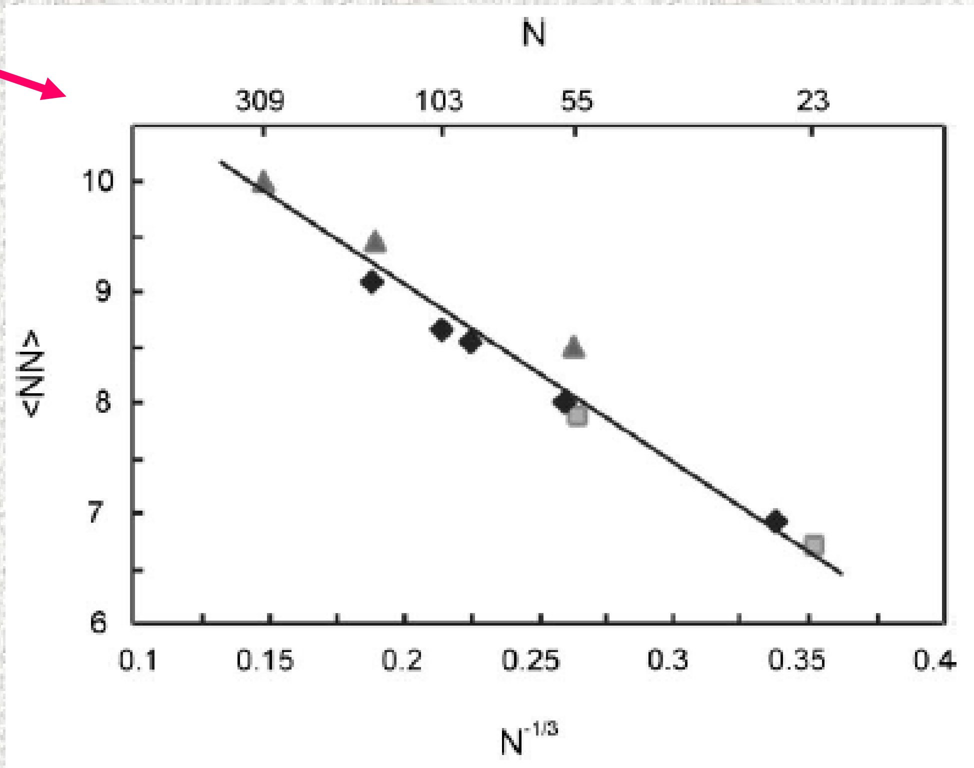




What value ?

Surface Effects

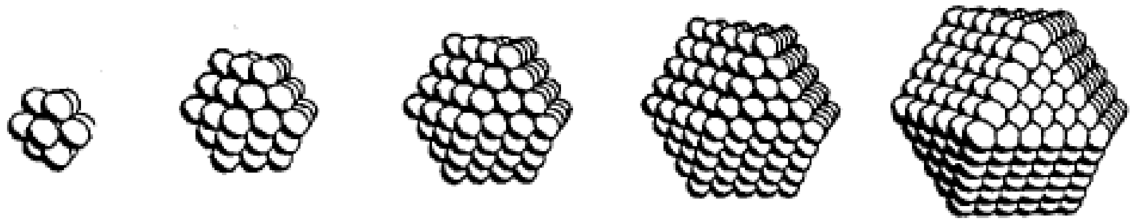
Mean coordination number



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

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



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

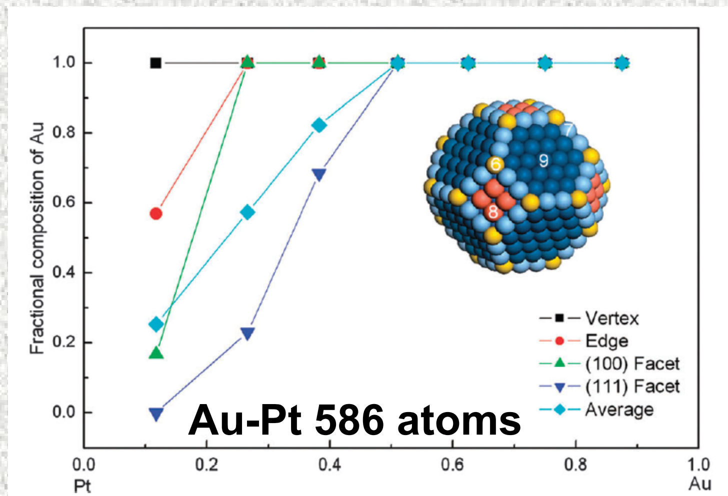
Atom binding (vaporization) energies lower in nanoparticles, fewer neighbors to keep atoms from escaping

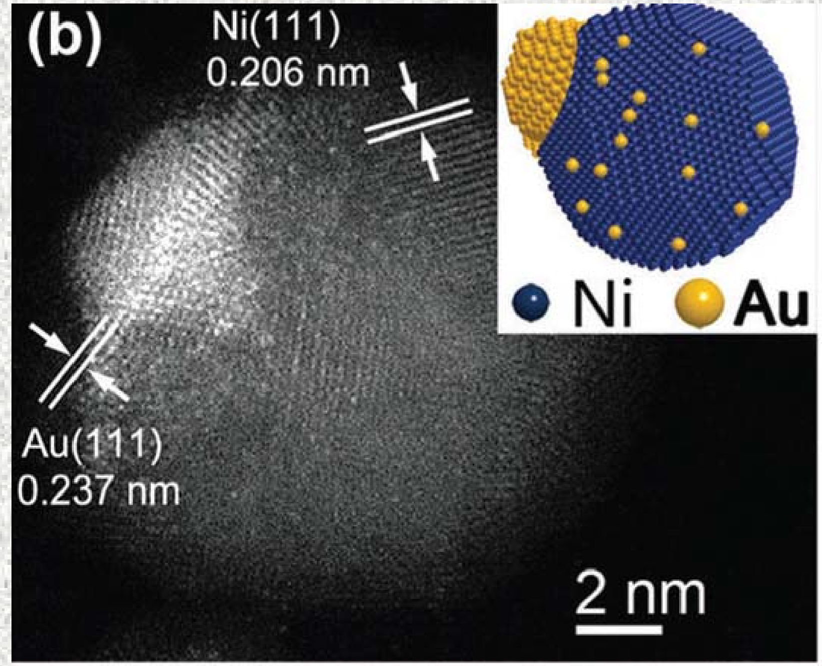
Plasticity of nanocrystalline ceramics

Surface Effects in Nanoalloys

Parameters influencing miscibility
- **Atomic size**
- **Electronegativity**
- **Surface energy**

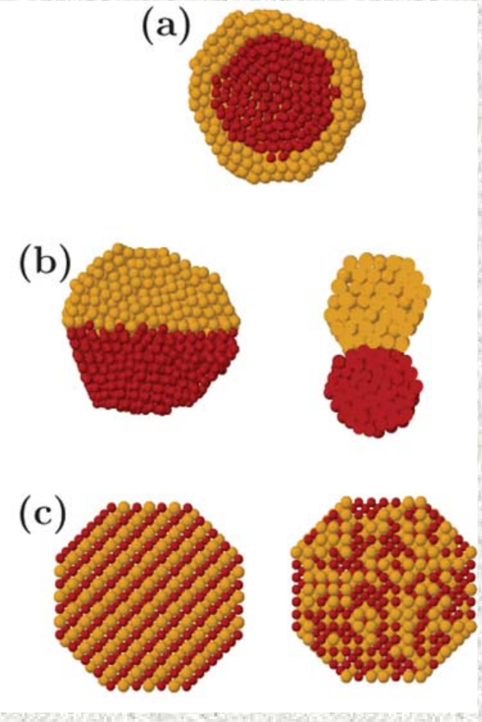
Alloys:
- **Random mixture**
- **Core-shell**
- **Janus**

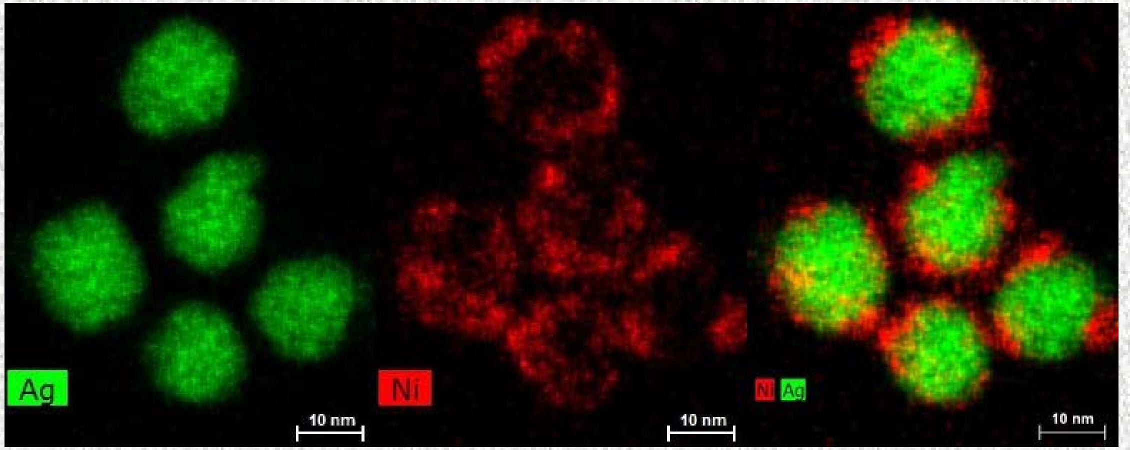




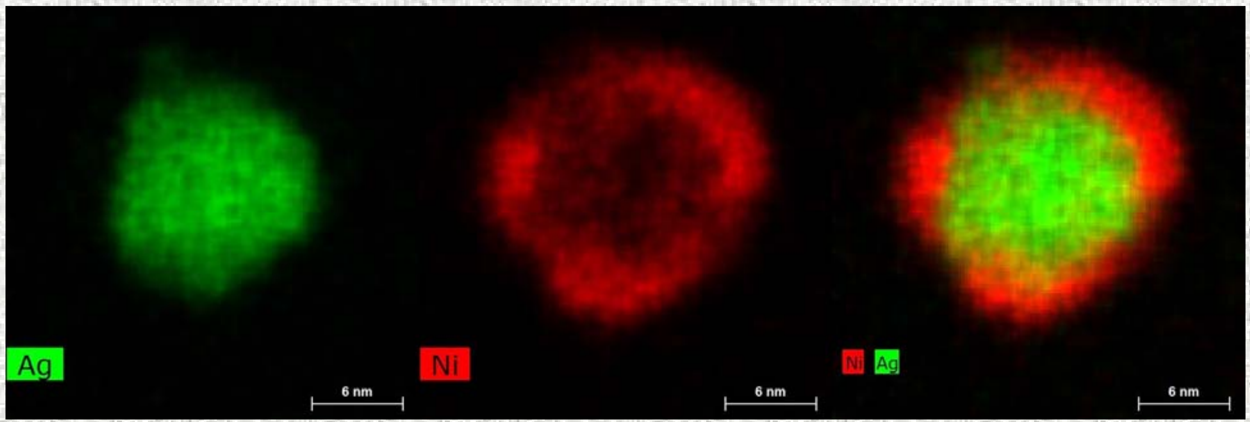
Transmission Electron Microscopy – Energy Dispersive X-ray Spectroscopy

Ag@Ni Core-shell NPs



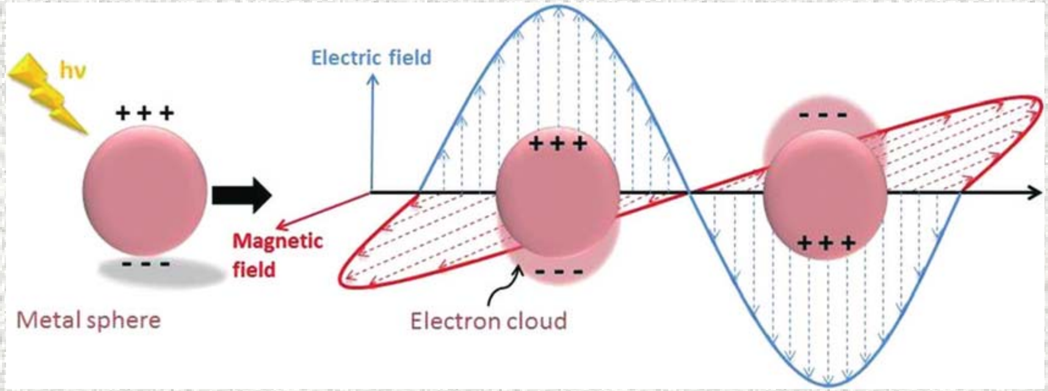


ICP-OES: Ag 68.8 mol%, EDS: Ag 84.2 mol%

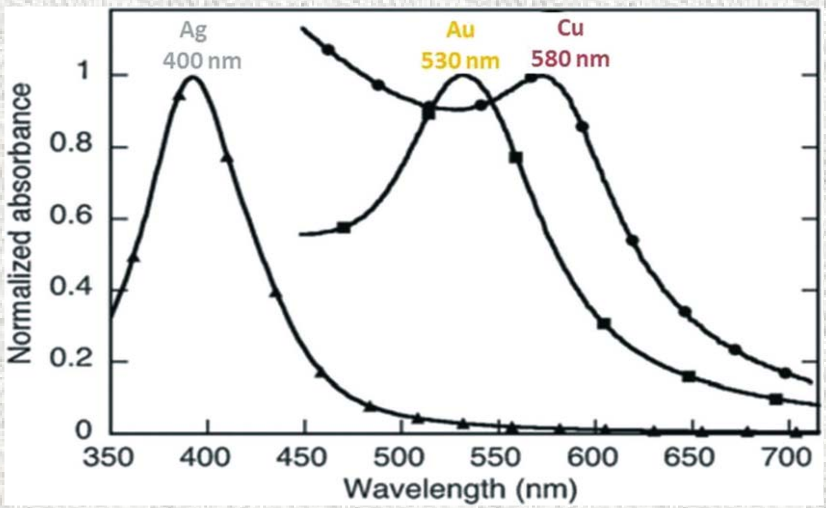


ICP-OES: Ag 50.3 mol%, EDS: Ag 62.5 mol%

Localized Surface Plasmon Resonance (LSPR)



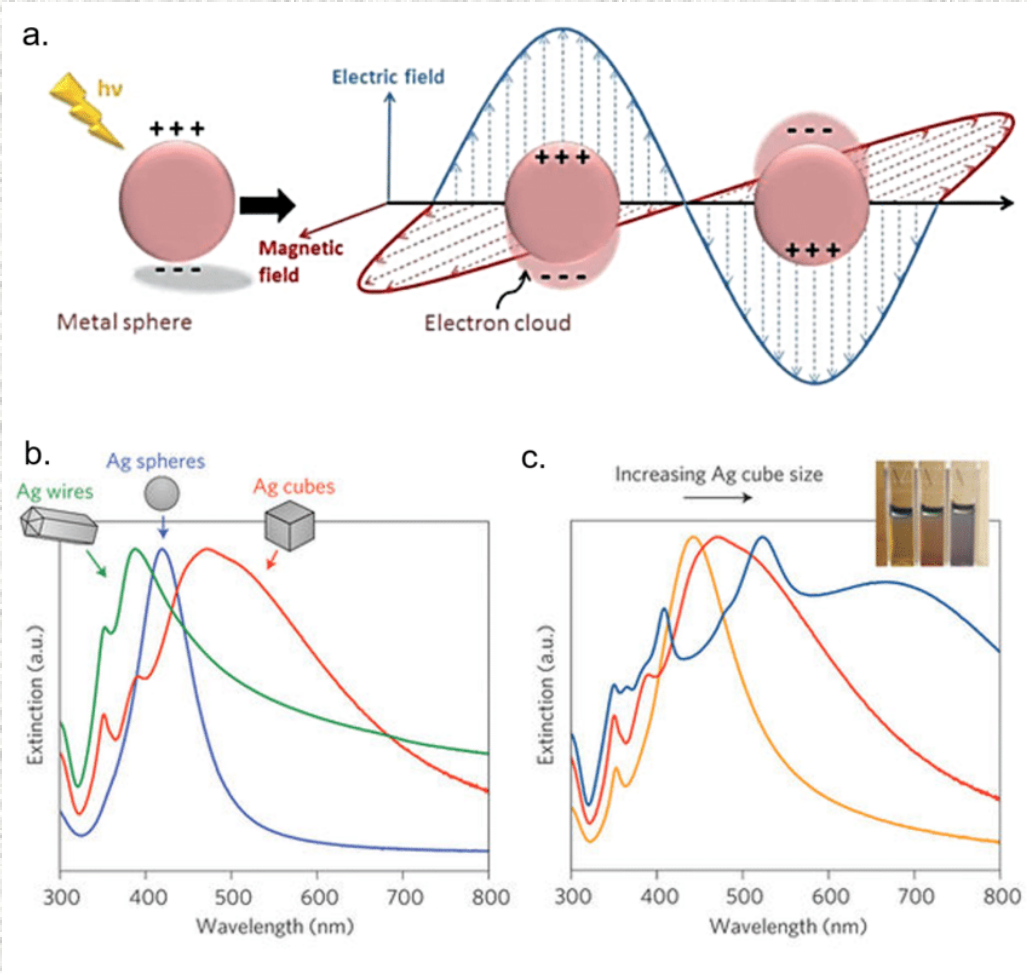
LSPR = the collective oscillation of the conduction electrons on the metallic NPs excited by the incident photons at the resonant frequency coupled to the electromagnetic field



Metallic NPs with sizes smaller than the wavelength of light

The resonance frequency of the oscillation = the surface plasmon (SP) energy

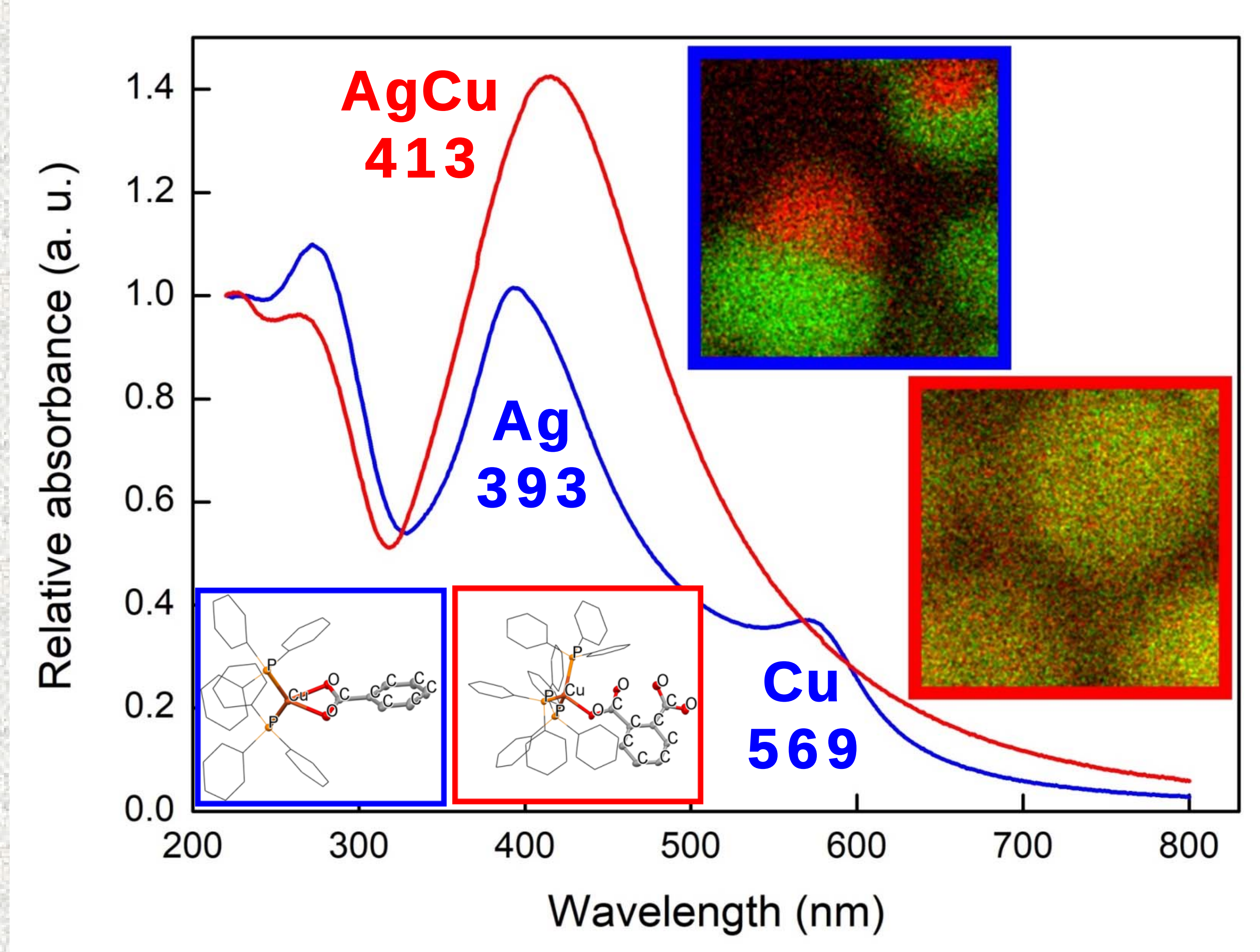
Localized Surface Plasmon Resonance (LSPR)



The resonance frequency of the oscillation (LSPR)

- **dielectric properties of the metal**
- **the surrounding medium**
- **the particle size**
- **the particle shape**

Effects of Synthesis on Ag-Cu NPs



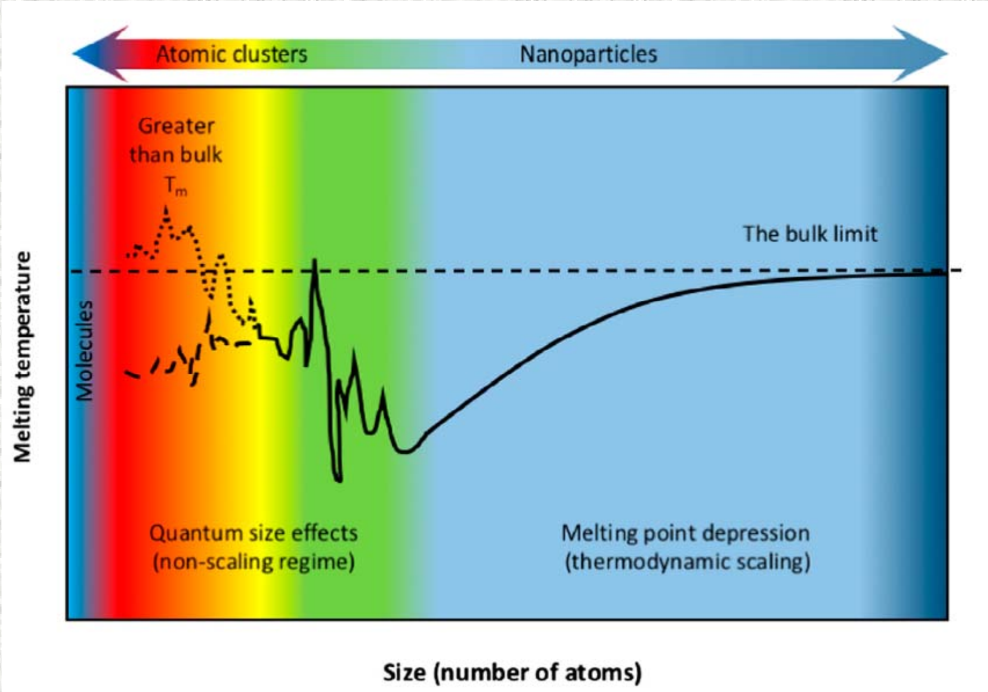
Melting Point Depression

Surface atoms in solids are bound by a lower number of shorter and stronger bonds

Nanoparticles with a large fraction of surface atoms

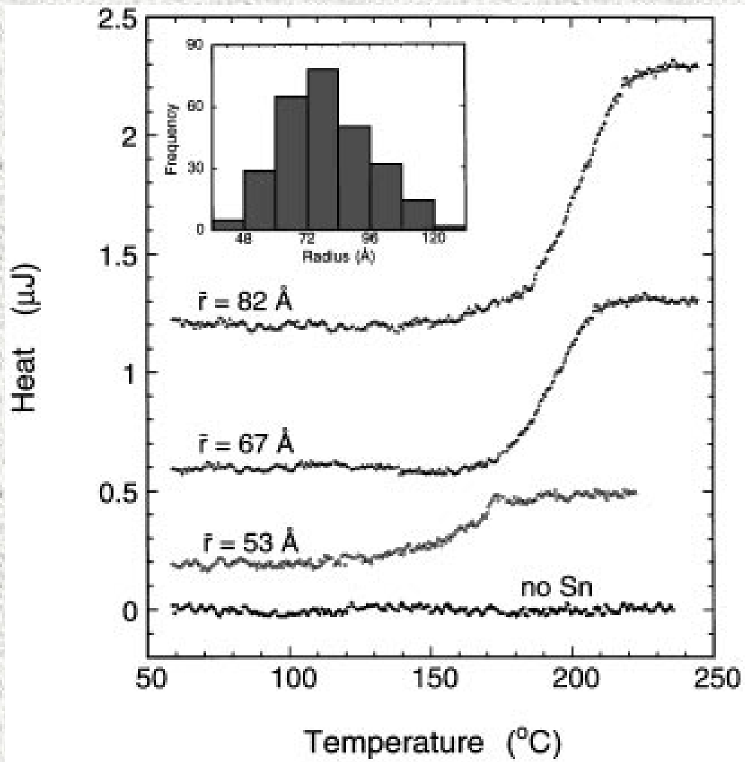
- **Lowering of average cohesion energy**
- **Increasing average amplitude of thermal vibrations**
- **Increasing internal pressure**

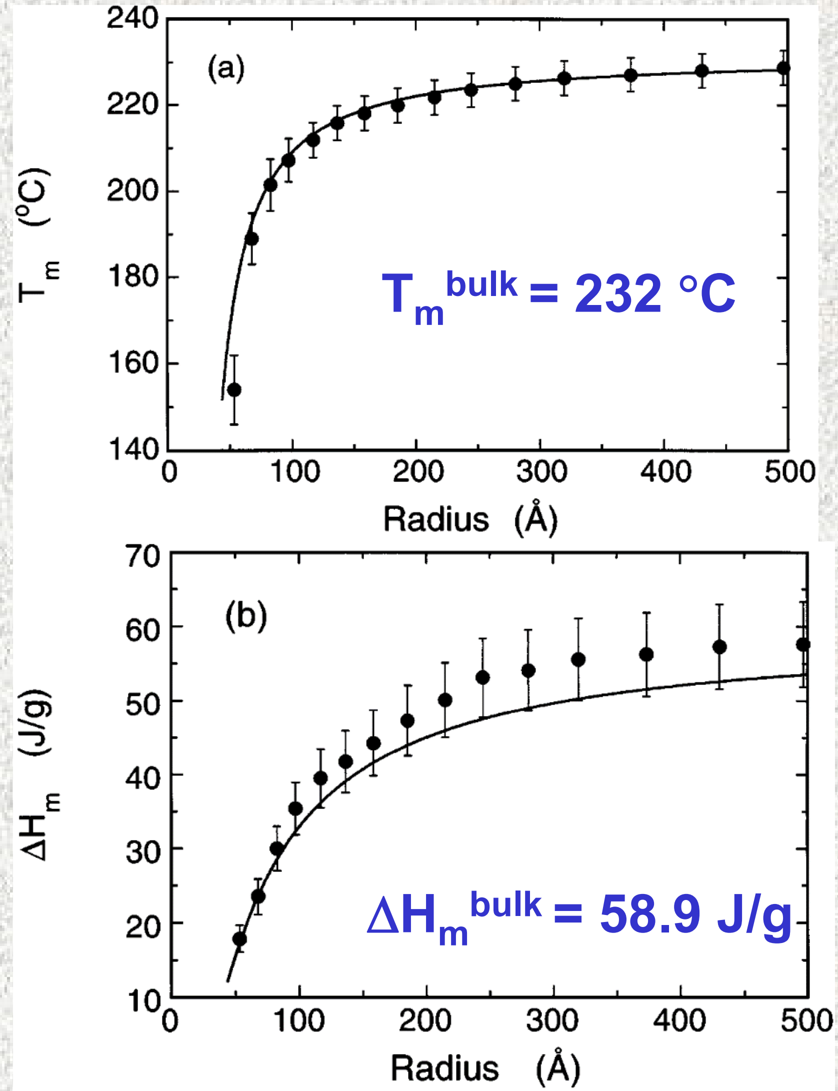
Result = depression of melting point of nanoparticles



Melting Point and Enthalpy Depression

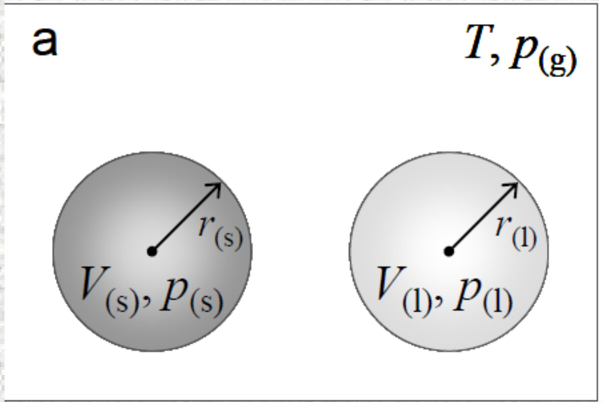
Nanocalorimetry of Sn nanoparticles





Melting Models

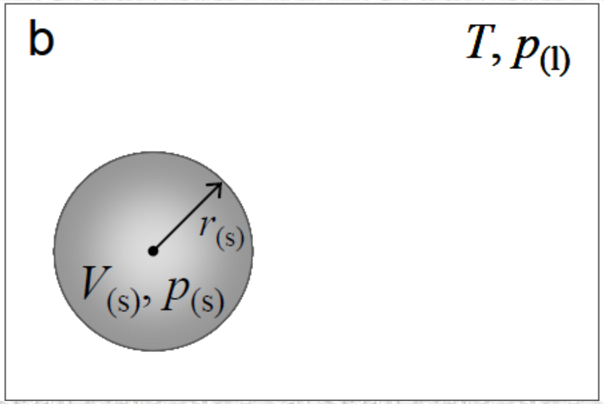
Homogeneous Melting



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

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

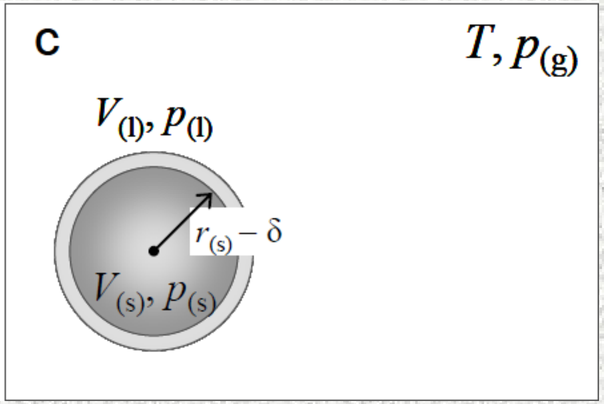
Continuous Liquid Melting



Melting particle is surrounded by liquid

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

Liquid Skin Melting



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

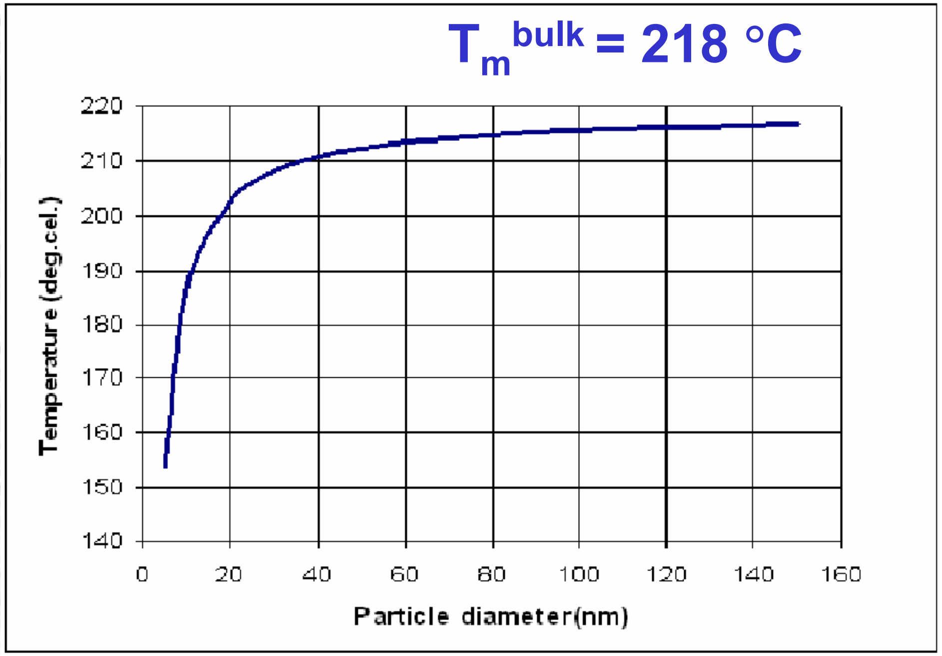
$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(s)} r_{(s)}} \left[\frac{\gamma_{(sl)}}{1 - \delta / r_{(s)}} + \gamma_{(lg)} \left(1 - \frac{\rho_{(s)}}{\rho_{(l)}} \right) \right]$$

Homogeneous Melting Model

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

Sn – 4wt%**Ag** – 0.5wt%**Cu**

Nano alloy particles



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

T_m^{bulk} = mp of the bulk material

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

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

ρ_s and ρ_l = solid and liquid phase densities

M = molar mass

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

Continuous Liquid Melting Model

Gibbs–Thomson Equation

for $\rho_s \sim \rho_l$

$$\gamma_{sl} = \gamma_{sg} - \gamma_{lg}$$

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

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

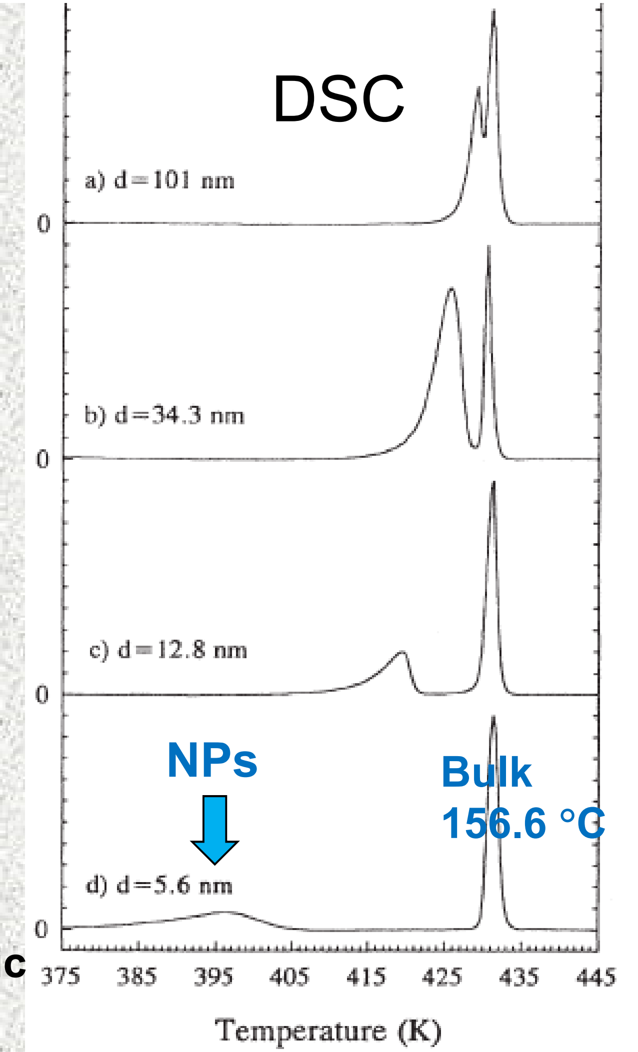
T_m^{bulk} = mp of the bulk material

V^l_{mol} = the molar volume of the liquid = M/ρ_s

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

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

Indium NPs confined in pores

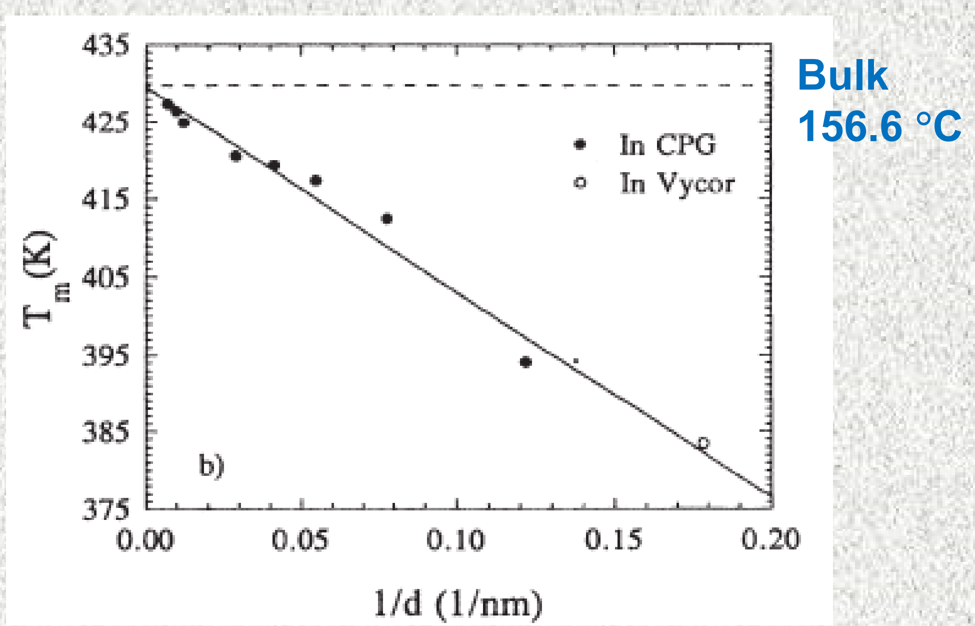


Phase Transitions

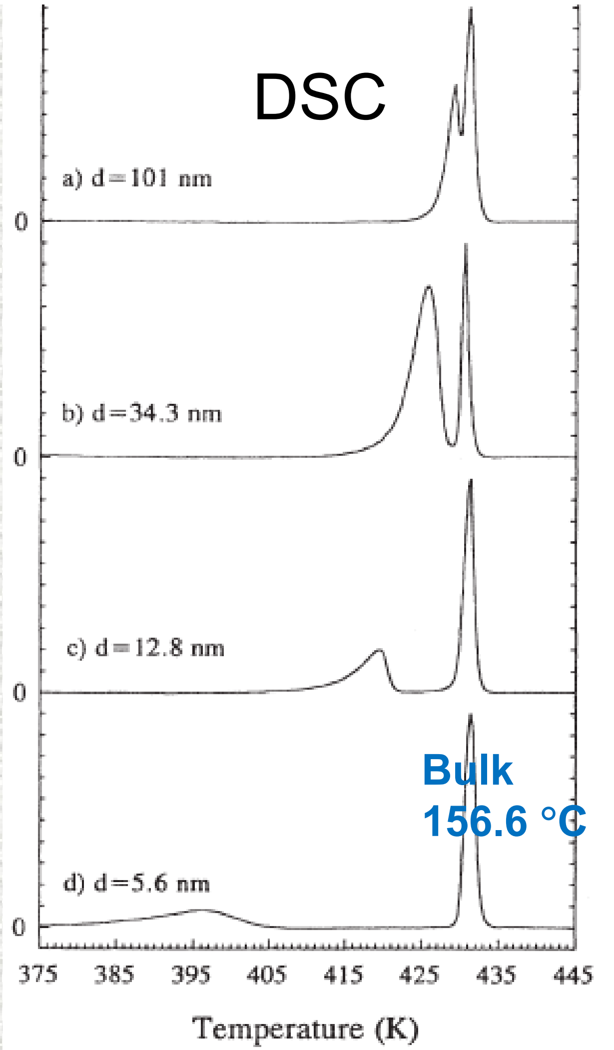
Phase transitions = collective phenomena

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

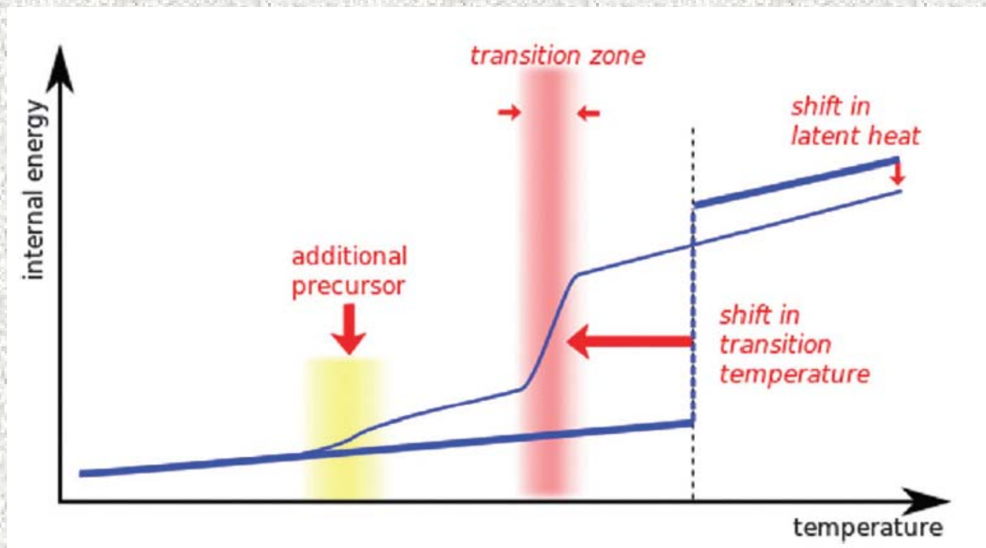
Small clusters behave more like molecules than as bulk matter



Indium NPs confined in pores



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)**

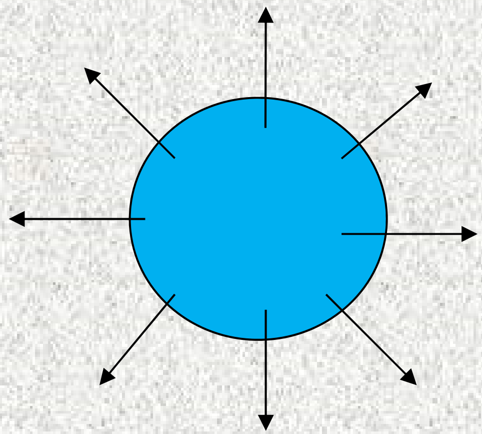
- **The transition temperature is no longer sharp but becomes broad and takes place over a finite range (fluctuations in TD quantities)**

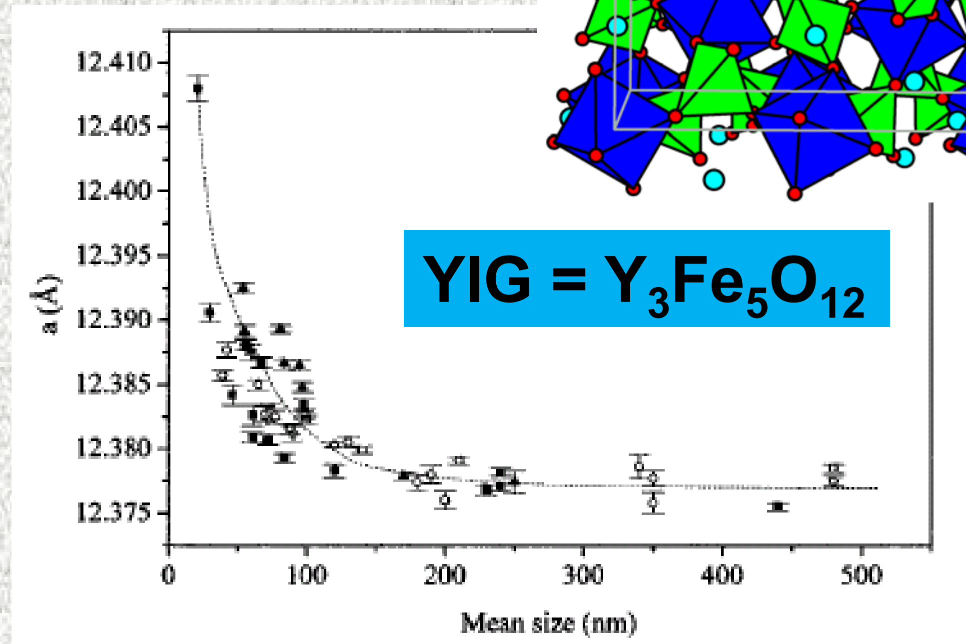
- **The latent heat of melting is lower than in the bulk limit**

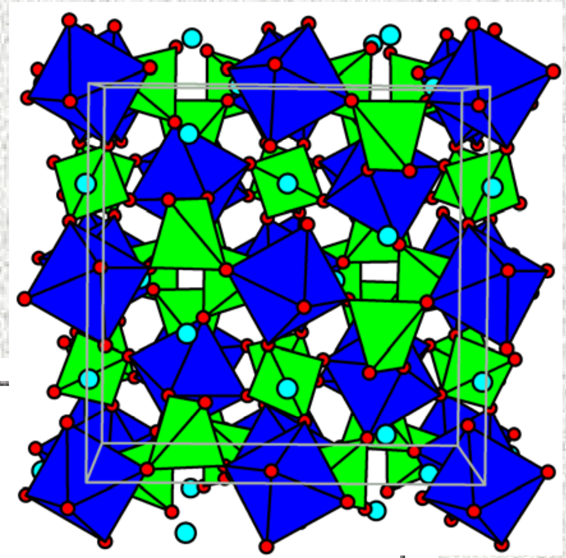
Surface Effects on Lattice Constants

Reduction in particle size

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





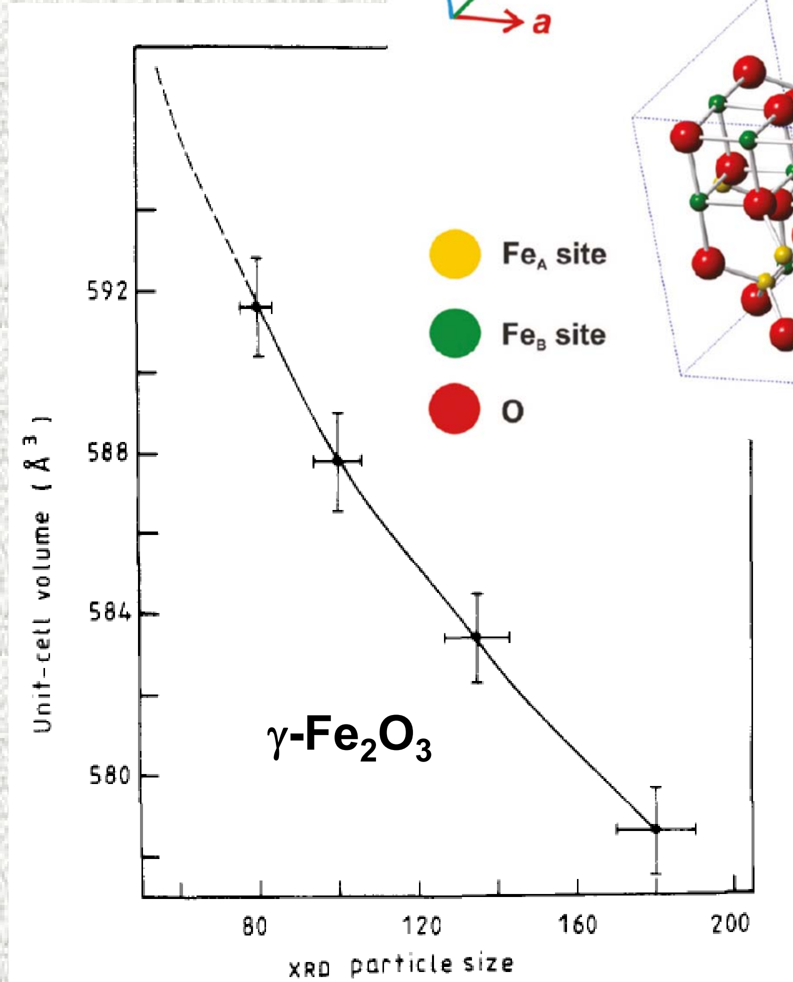


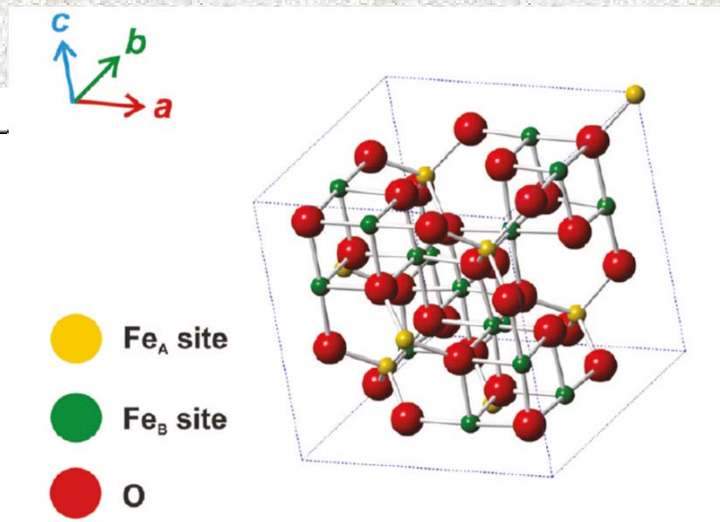
YIG = $Y_3Fe_5O_{12}$

Surface Effects on Lattice Constants

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 on Lattice Constants

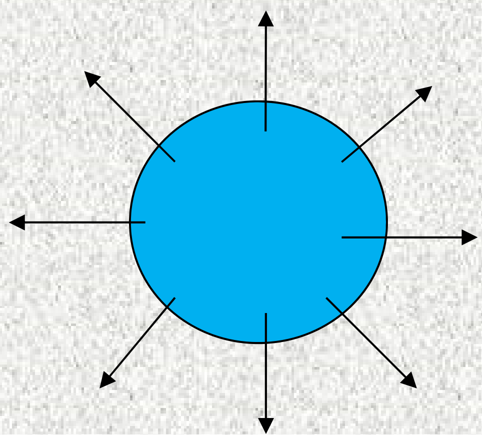
The inter-ionic bonding in nanoparticles has a directional character

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

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



Surface Effects on Lattice Constants

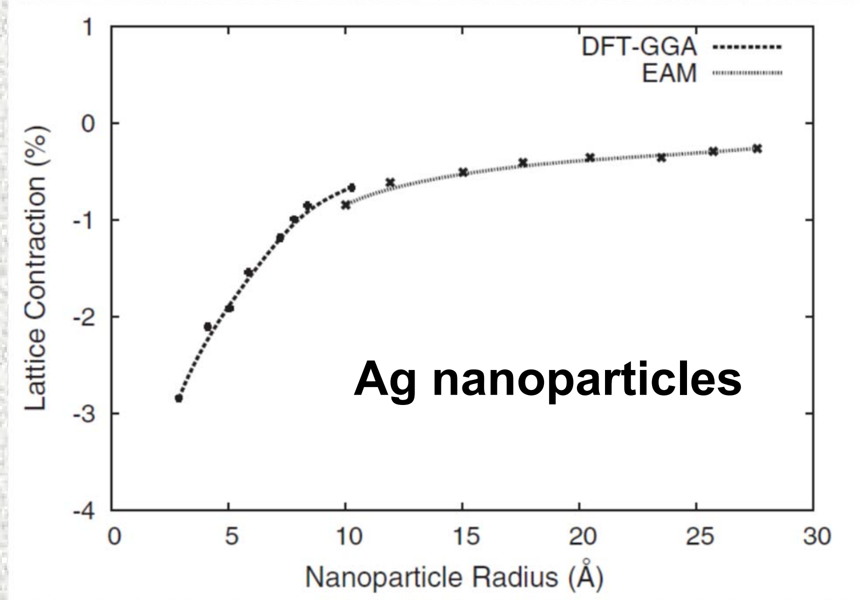
Metal nanocrystals

A continuum elastic model

The lattice contraction observed in Ag nanoclusters

Interpreted as the result of hydrostatic pressure exerted by the surface stress

The surface stress 6.3 N/m for free Ag NPs 1–7 nm in diameter

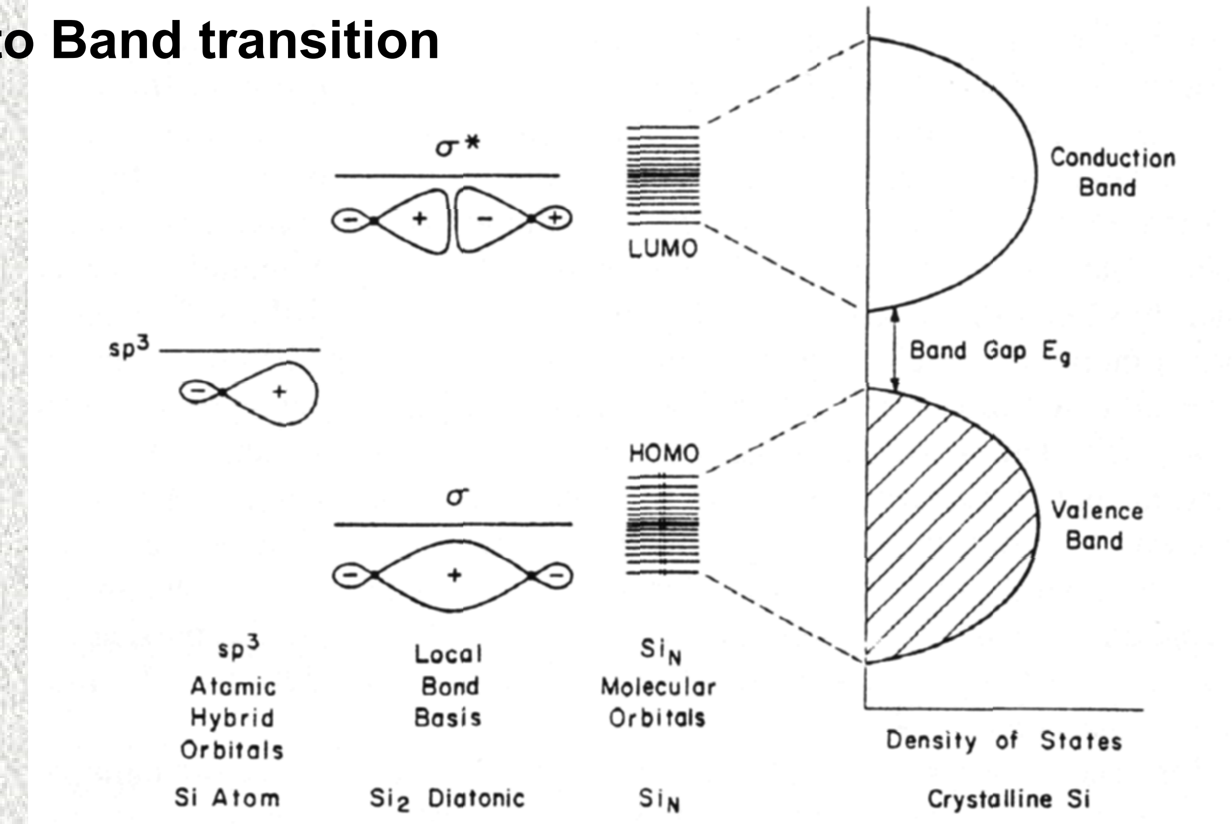


The smaller the particle size, the smaller the unit cell volume

Quantum Confinement Effects

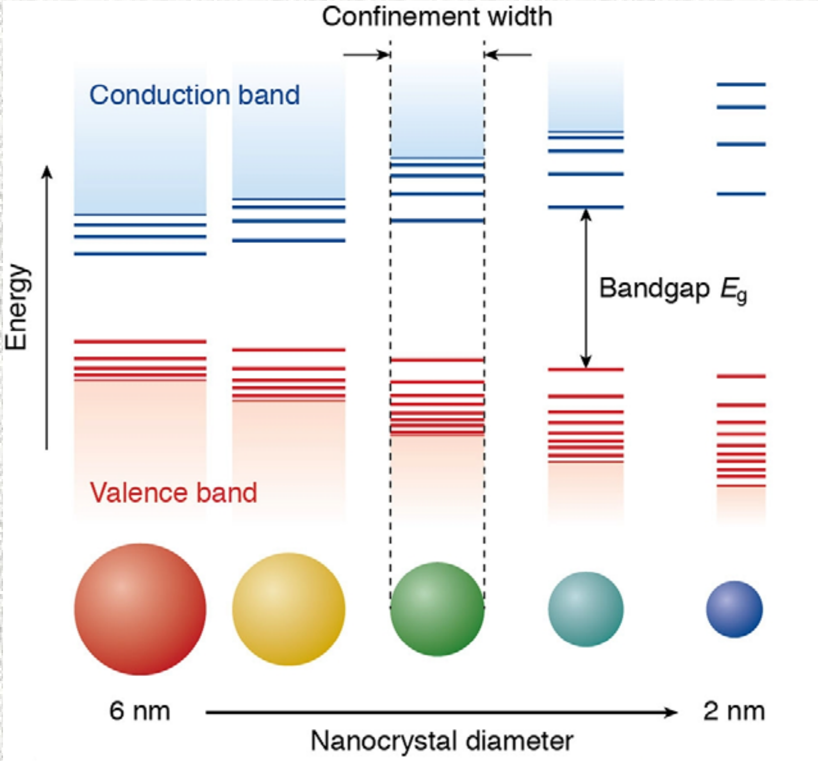
Physical and chemical properties depend on the size !!

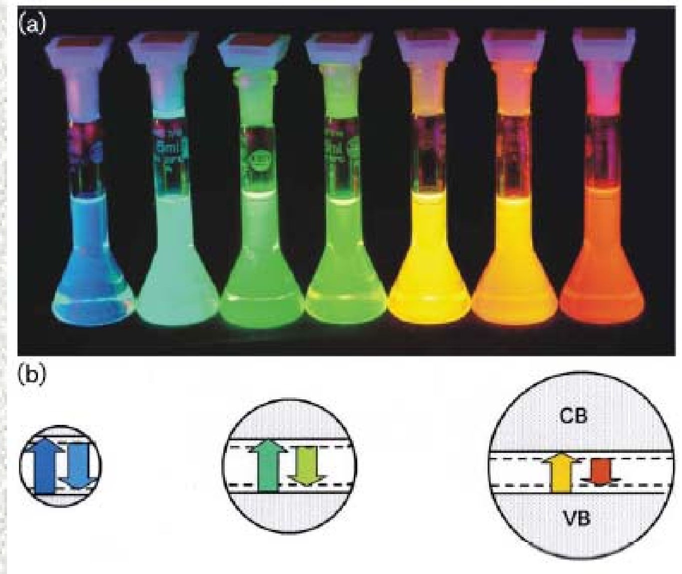
Finite-size effects
MO to Band transition



Quantum Size Effects

Band gap dependency on the nanoparticle size

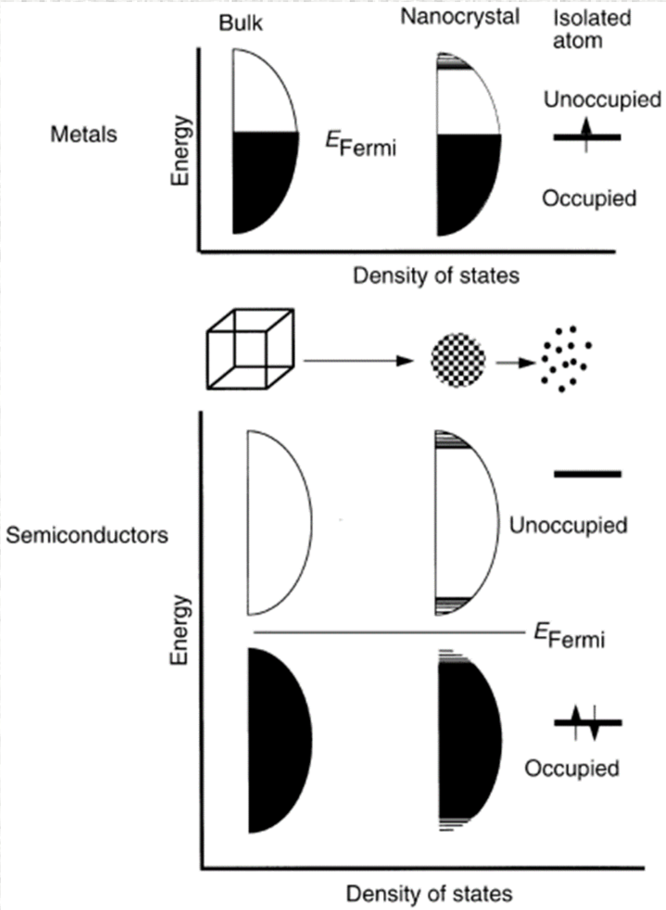




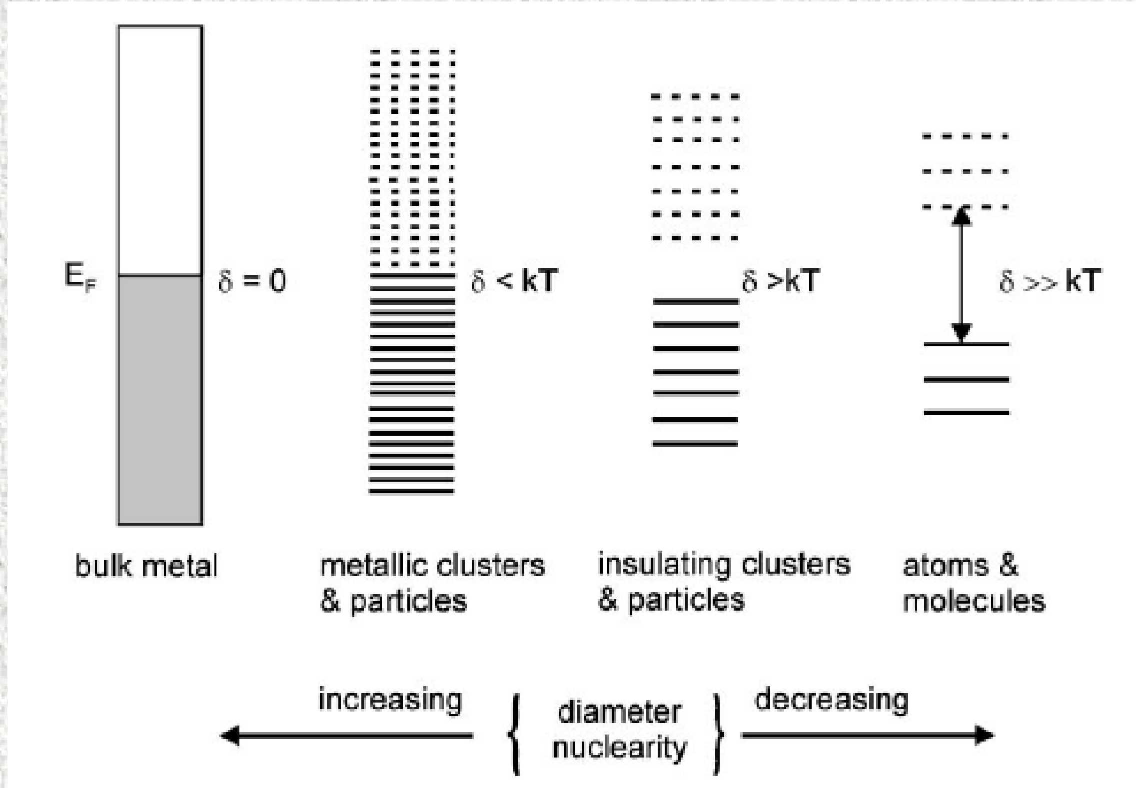
Fluorescence of CdSe–CdS core–shell nanoparticles with a diameter of 1.7 nm (blue) up to 6 nm (red)

Smaller particles have a wider band gap = blue shift

Quantum Size Effects

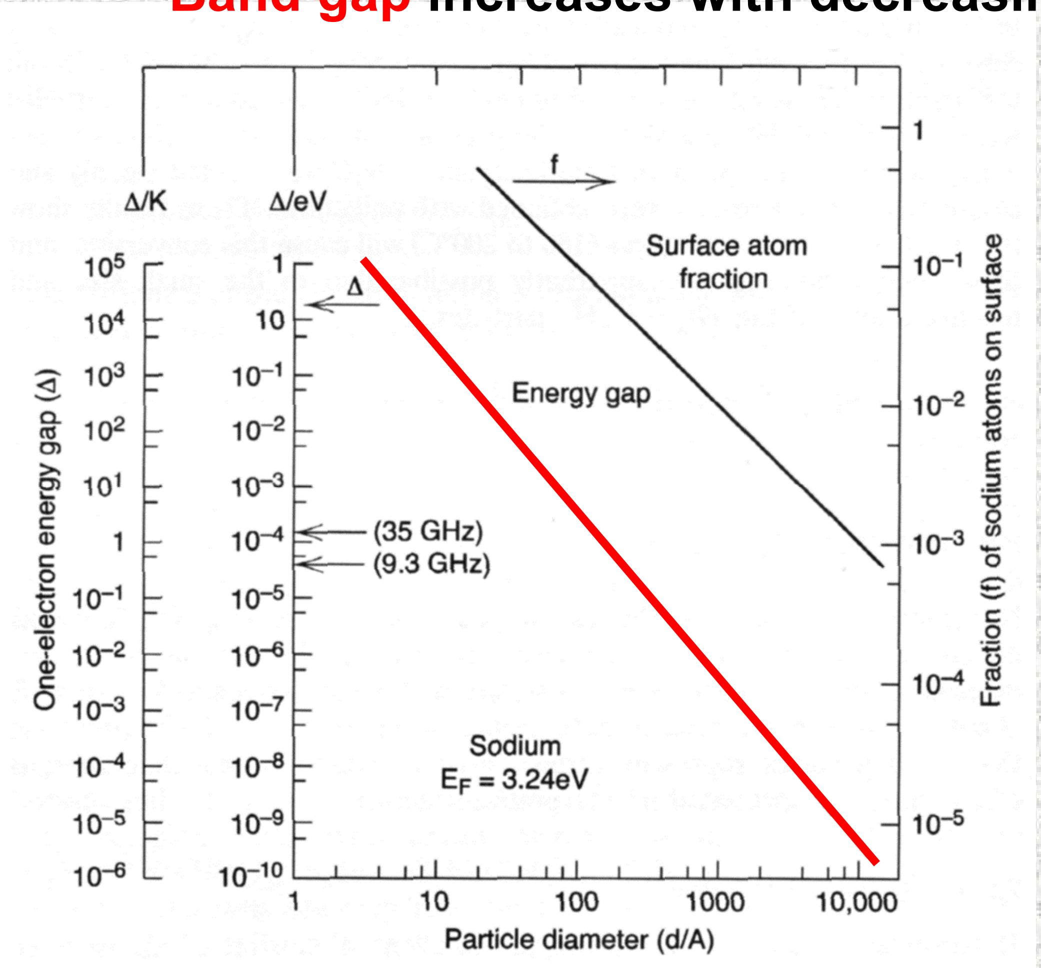


Metal-to-Insulator Transition



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

Quantum Size Effects

Hg

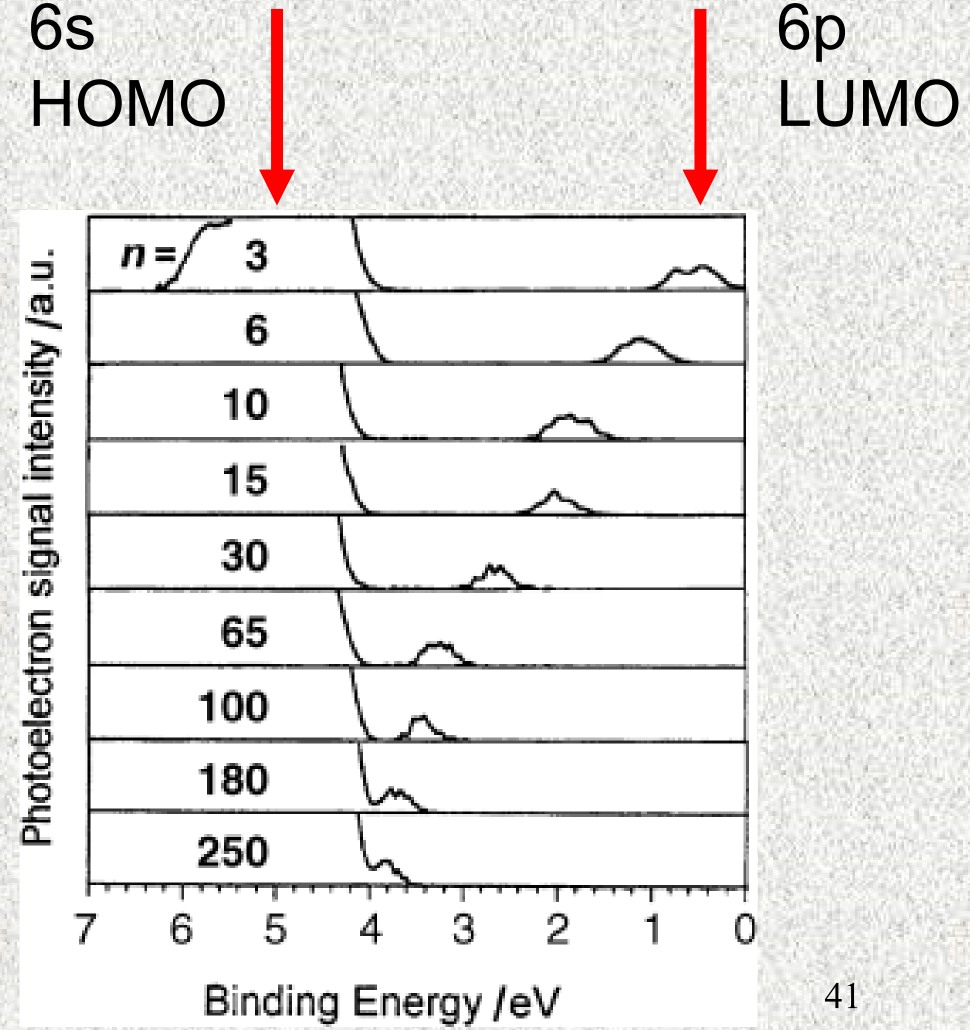
Valence electron configuration

[Xe] $4f^{14}$ $5d^{10}$ $6s^2$

Photoelectron spectra of Hg clusters of nuclearity *n*

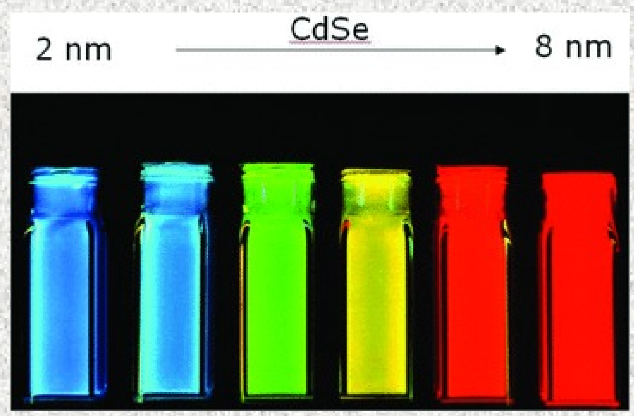
The 6p peak moves gradually towards the Fermi level

The band gap shrinks with increase in cluster size
Hg clusters become metalic

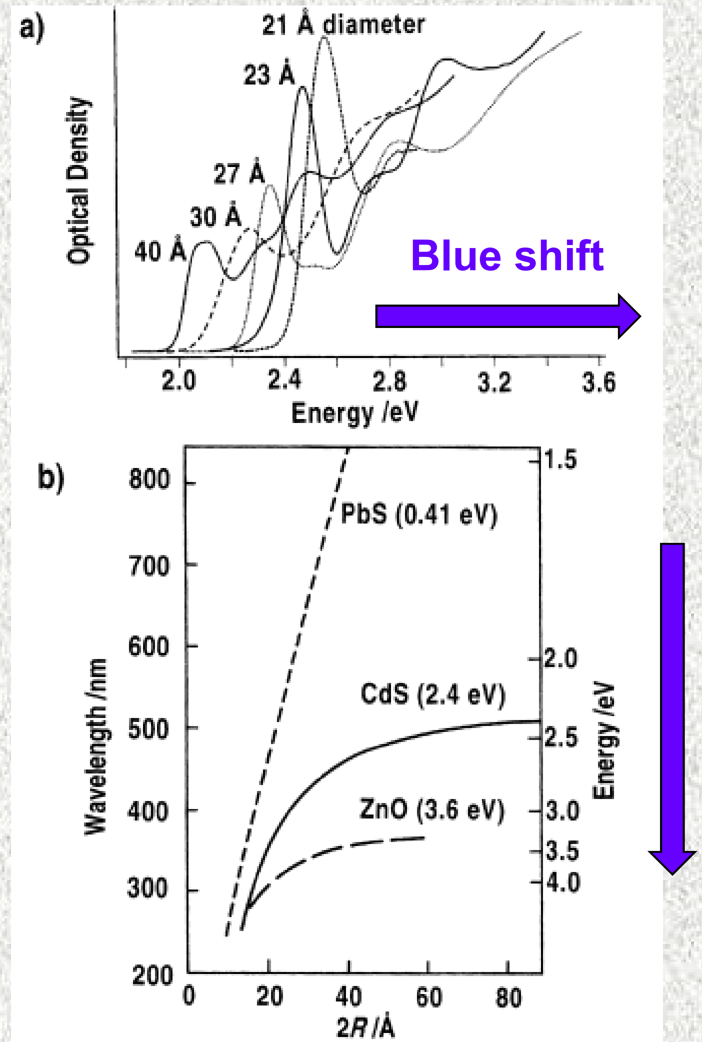


Quantum Size Effects in Semiconductors

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



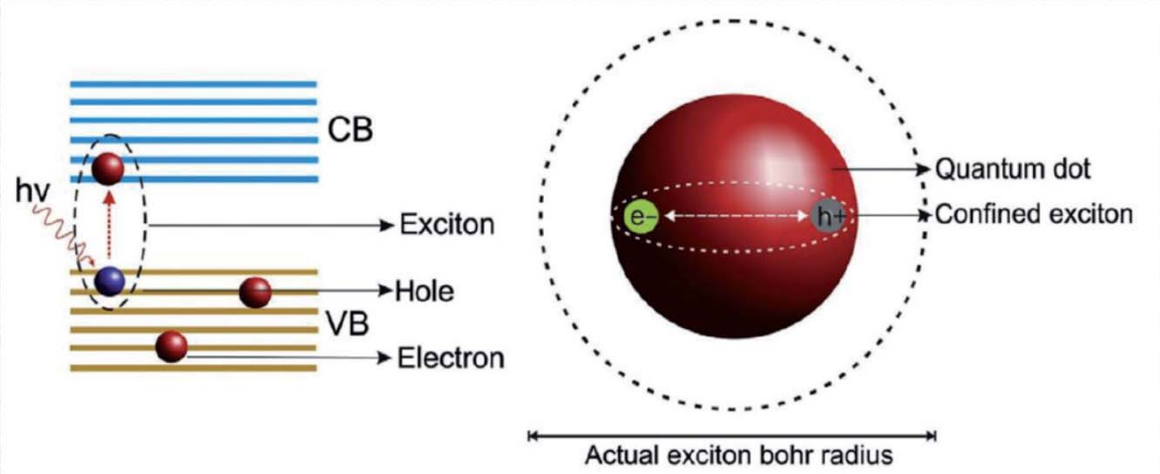
b) Wavelength of the absorption threshold and band gap as a function of the particle diameter for various semiconductors
The energy gap in the bulk state in parenthesis



Bohr Radii

Quantum confinement - particles must be smaller than the Bohr radius r_B of the electron-hole pair (exciton)

r_B = the spatial separation of the electron-hole pair



$$r_B = \frac{\hbar^2 \varepsilon}{e^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)$$

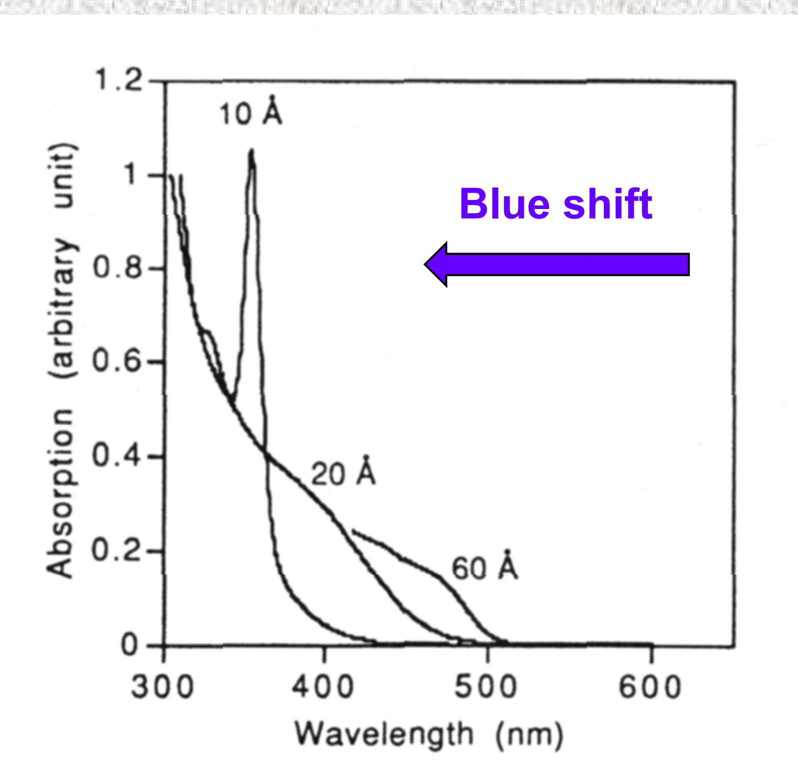
semiconductor	r_B (Å)	E_g (eV)
CdS	28	2.5
CdSe	53	1.7
CdTe	75	1.5
GaAs	124	1.4
PbS	180	0.41

Quantum Confinement Effects

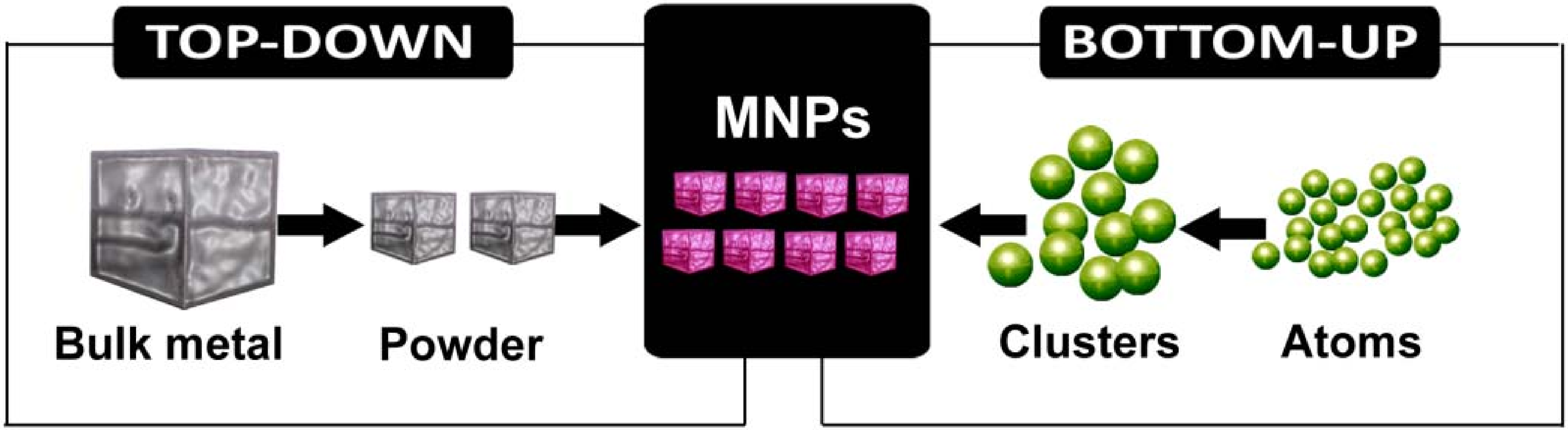
Optical properties

nc-TiO_2 is transparent - applications in suncreens

Blue shift in optical spectra of TiO_2 nanoparticles



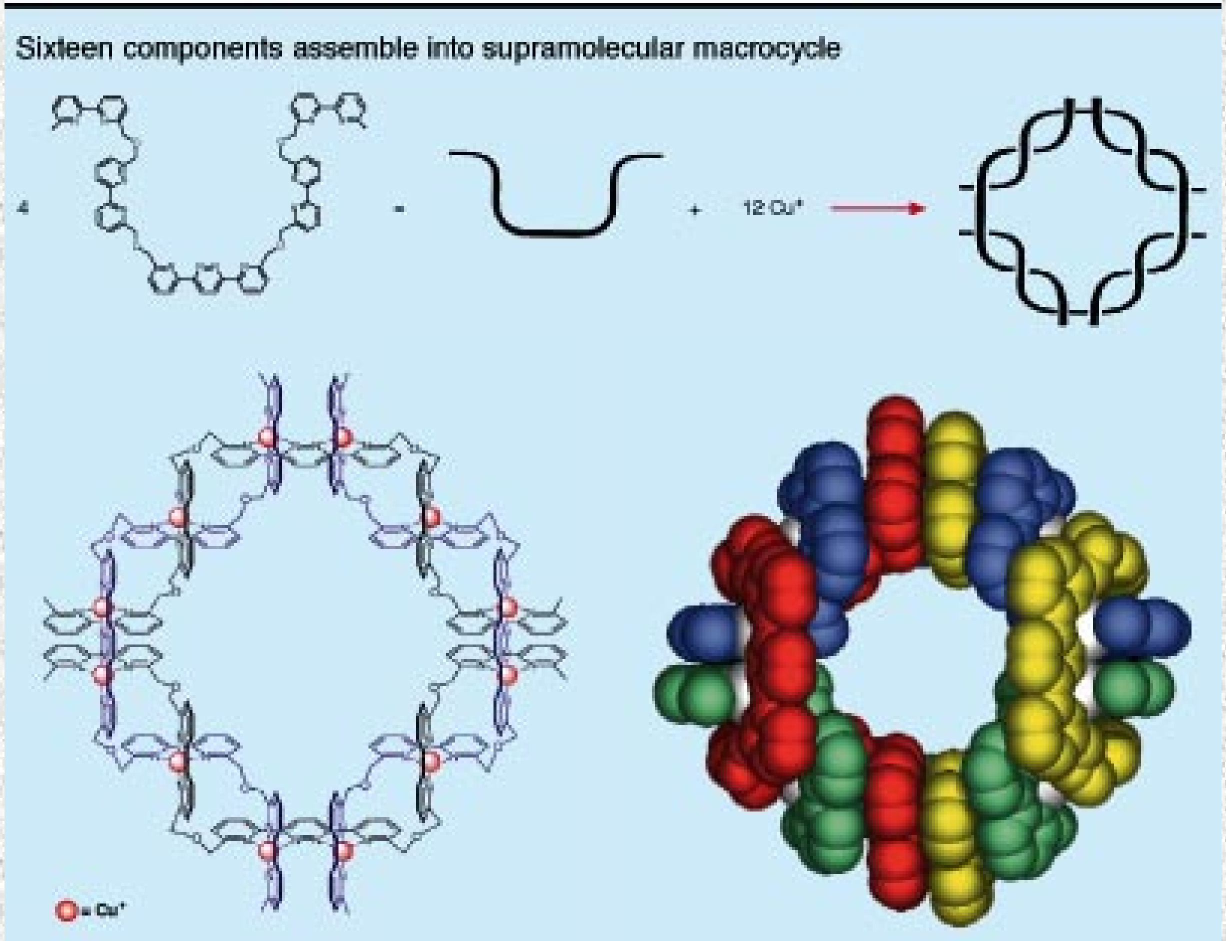
Preparation Methods



Top-down: from bulk to nanoparticles

Bottom-up: from atoms to nanoparticles

Bottom-up Synthesis: Atom Up



Atom Aggregation Methods

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, 1 kPa) on a cold finger and walls
metals, intermetallics, alloys, SiC, C_{60}

- in a reactive gas O_2 - oxides TiO_2, MgO, Al_2O_3, Cu_2O
N_2, NH_3 - nitrides

- in an organic solvent matrix - metals, carbides

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 = hexan
Carbide formation

$$\text{Ni (g)} + \text{pentane} \xrightarrow{77\text{–}300\ \text{K}} Ni_xC_yH_z \xrightarrow{450\ \text{K}} Ni_3C$$

Bottom-up Synthesis

Thermal or Sonocative Decomposition of Precursors

$Fe(CO)_5$ $\rightarrow$ nc-Fe + 5 CO sonolytic decomposition

$[Co(en)_3]WO_4$ $\rightarrow$ nc-WC – 23% Co thermolysis

$PhSi(OEt)_3$ + $Si(OEt)_4$ + $H_2O \rightarrow$ gel $\rightarrow$ β-SiC (in Ar, 1500 °C)

$(CH_3SiHNH)_n$ (l) $\rightarrow$ Si_3N_4 + SiC laser pyrolysis

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

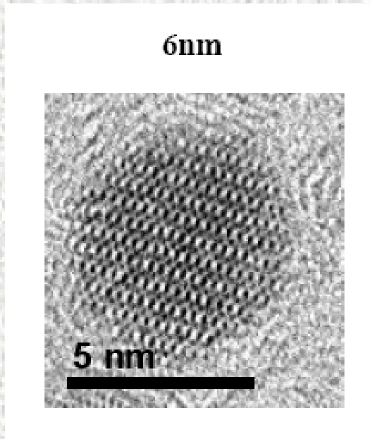
$Si(OEt)_4$ + Ag^+ or Cu^{2+} + H_2O $\rightarrow$ $SiO_2/Ag^+/Cu^{2+}$ metal-impregnated gel

$SiO_2/Ag^+/Cu^{2+}$ + H_2 $\rightarrow$ $SiO_2/Ag/Cu$ (550 °C)
metal NPs embedded in xerogel

Thermal Decomposition of Precursors

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

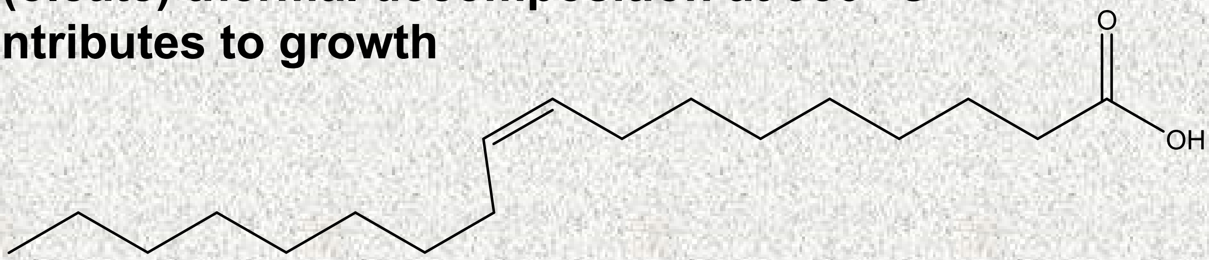
6 nm



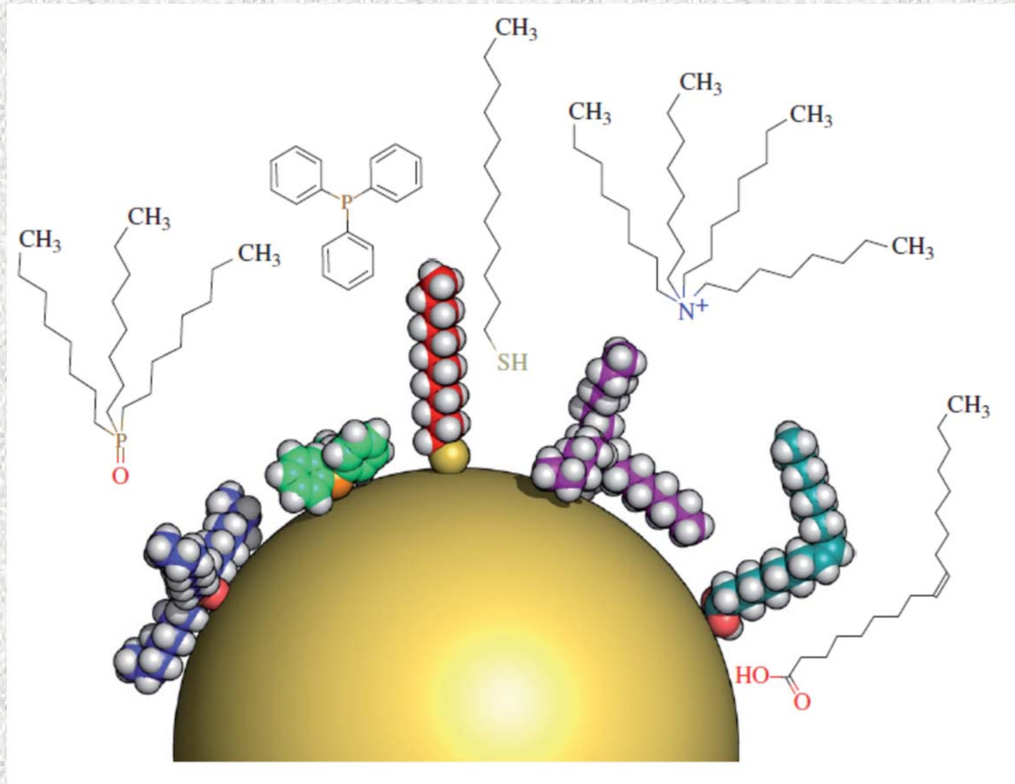
Separation of nucleation and growth

$Fe(CO)_5$ 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 5 nm core diameter with different hydrophobic ligand molecules both drawn to scale

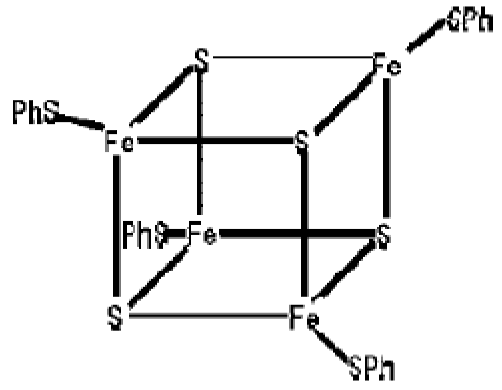
The particle is idealized as a smooth sphere

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

Thermal Decomposition of Precursors

Phase Control

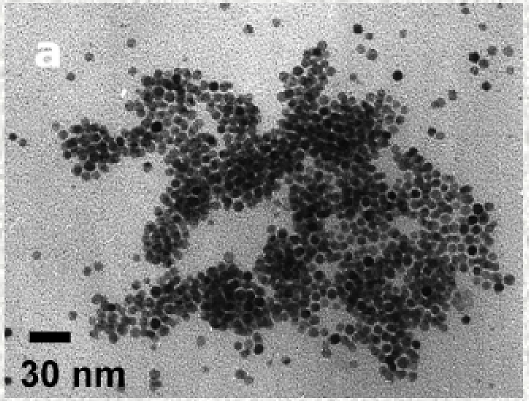
$[N^{n}Bu_4]_2[Fe_4S_4(SPh)_4]$



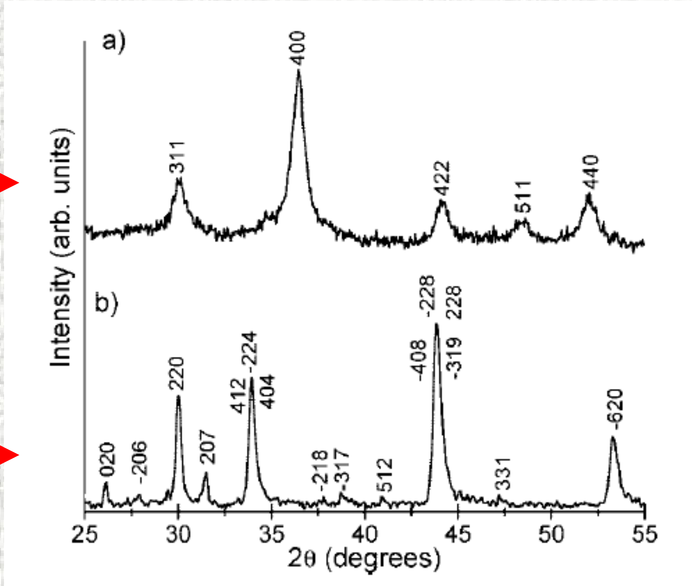
Thermolysis

180 °C in octylamine

200 °C in dodecylamine



pyrrhotite Fe_7S_8



greigite Fe_3S_4

thiospinel, the sulfide analogue of magnetite

LaMer Mechanism

Hot-injection synthesis

1) Monomer formation

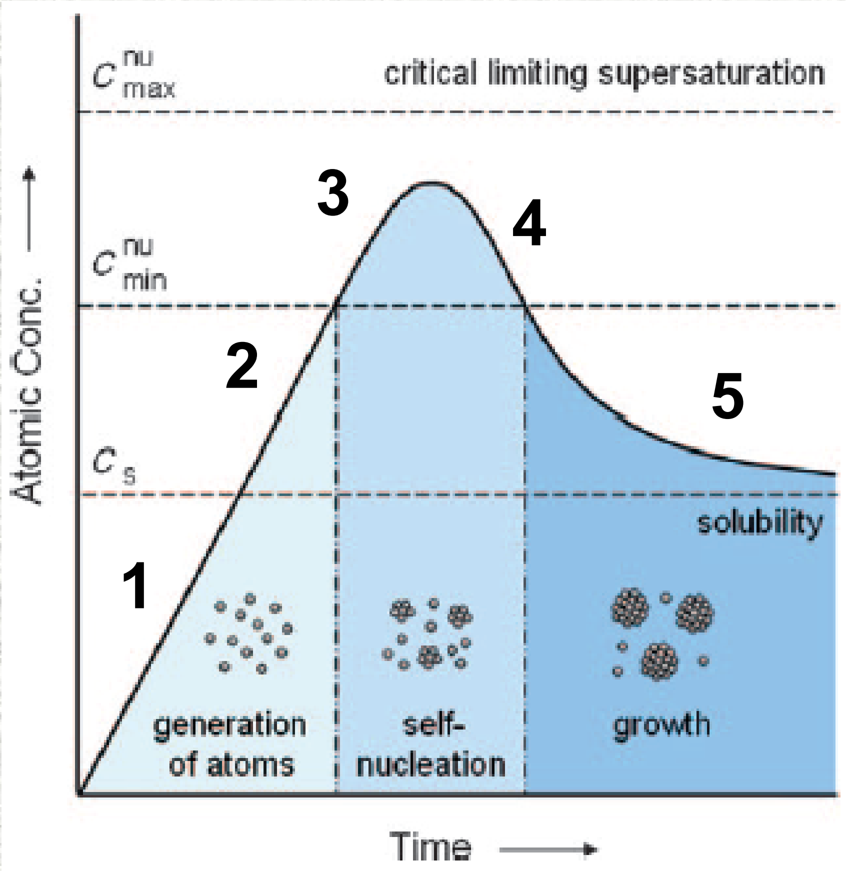
2) Supersaturated solution

3) Burst of nucleation

4) Depletion of monomer

5) Slow growth of particles without additional nucleation

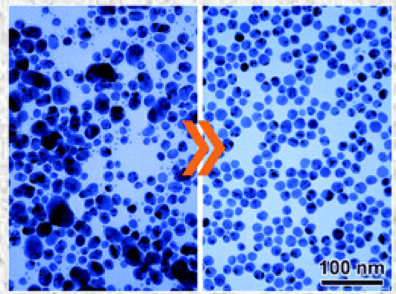
Separation of nucleation and growth - monodisperse



Other Mechanisms

Digestive Rippening

The conversion of polydisperse NPs into monodisperse ones
The etching of large NPs by dissolution of clusters/atoms by digestive ripening agents - strongly coordinating ligands
Clusters/atoms redeposited on small NPs = the growth of smaller NPs
Narrowing of the particle size distribution = monodisperse system
A thermodynamic equilibrium size of the NPs is usually obtained
Depends on the specific ligand and the reaction temperature



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

Borohydride Reduction

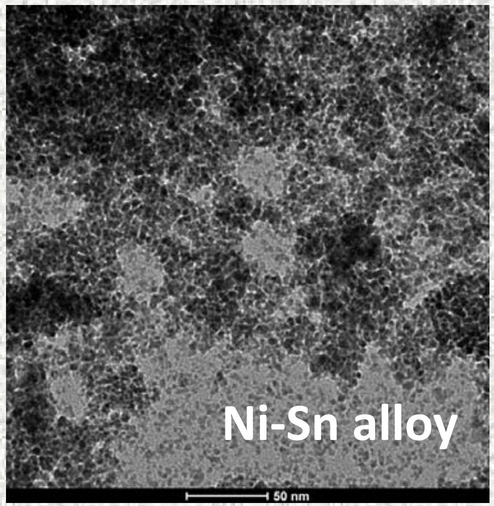
$NaBH_4$
BH_3NH_2tBu
$NR_4[BEt_3H]$

Reduction of Metal Ions
Manhattan Project

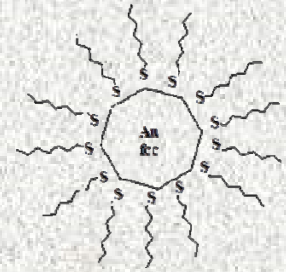
Aqueous, under Ar
$2\ Co^{2+} + 4\ BH_4^- + 9\ H_2O \rightarrow Co_2B + 12.5\ H_2 + 3\ B(OH)_3$
Under air
$4\ Co_2B + 3\ O_2 \rightarrow 8\ Co + 2\ B_2O_3$
Nonaqueous
$Co^{2+} + BH_4^- + \text{diglyme} \rightarrow Co + H_2 + B_2H_6$

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

$MX_n + n\ NR_4[BEt_3H] \rightarrow \textbf{M} + NR_4X + n\ BEt_3 + n/2\ H_2$



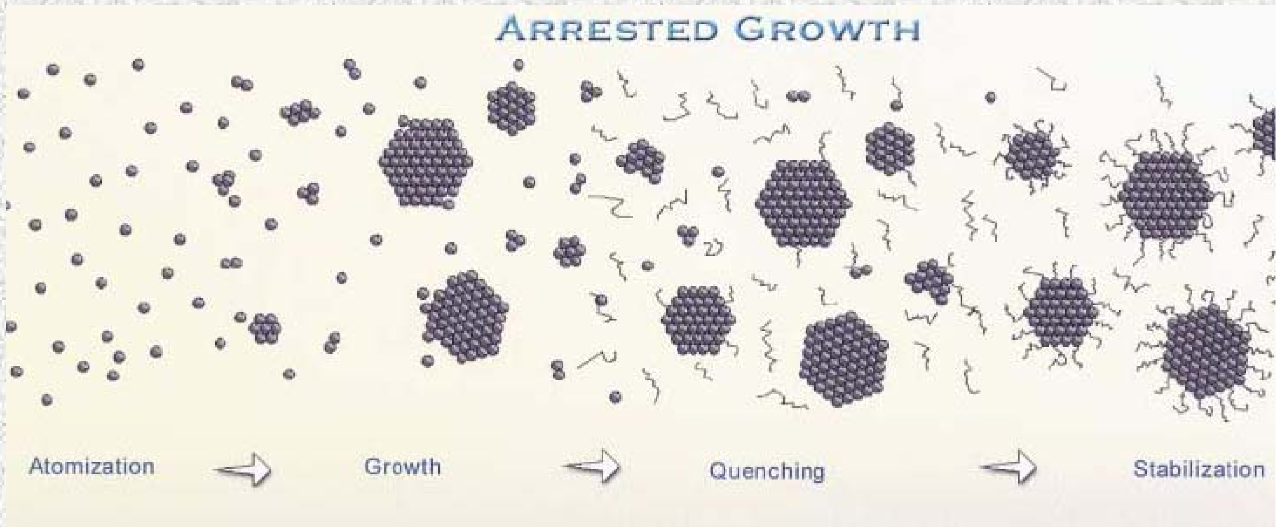
M = group 6 to 11, Bi, Sn, ; n = 2,3; X = Cl, Br, NO_3, OAc, OOC-R, acac, O-R
Solvents: Diethylenglycol, Oleylamine, ….
Surfactant
Mixed-metal particles AgNi, AgCu, BiNi, ….

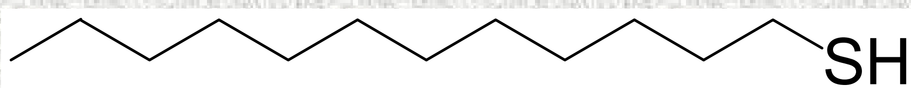


Borohydride Reduction

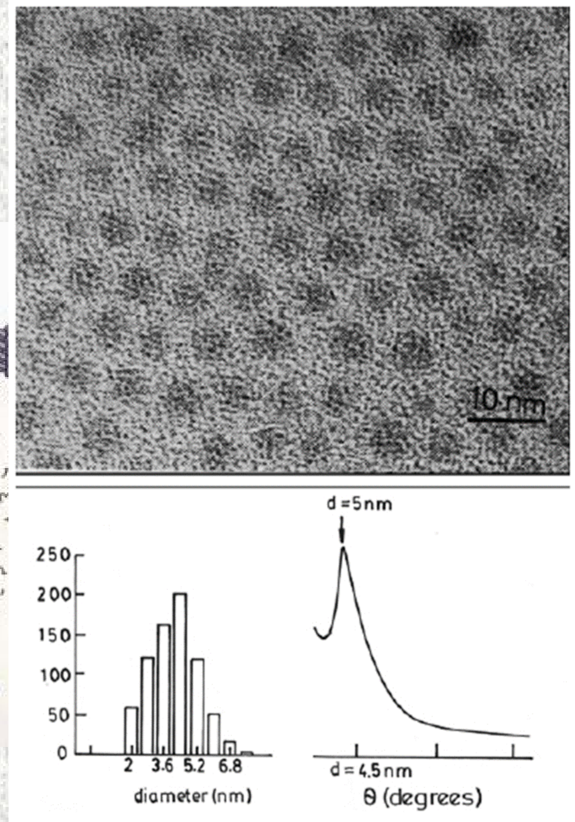
Au colloidal particles

$HAuCl_4$ + $NaBH_4$ 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





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



Alkali Metal Reduction

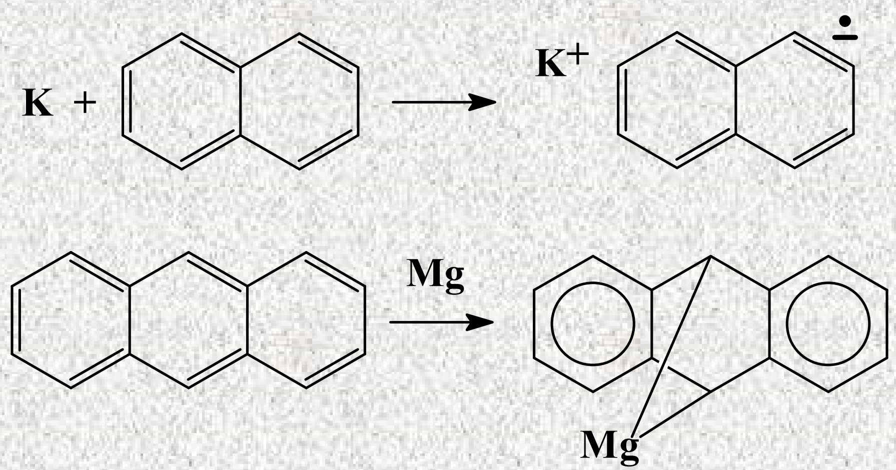
Solvents: dry anaerobic diglyme, THF, ethers, xylene

$NiCl_2$ + 2 K → Ni + 2 KCl

$AlCl_3$ + 3 K → Al + 3 KCl

Reduction by Glycols or Hydrazine

"Organically solvated metals"



Alkalide Reduction

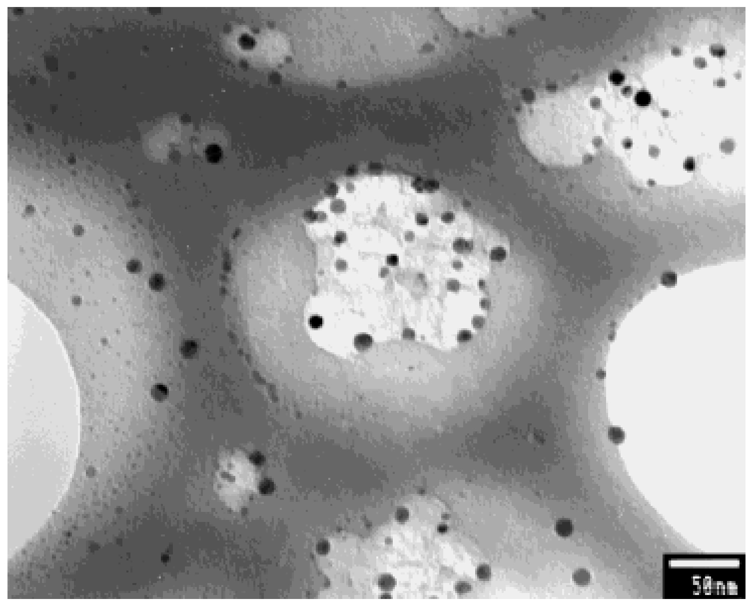
$13\ K^{+}(15\text{-crown-}5)_2Na^{-} + 6\ FeCl_3 + 2\ CBr_4$

THF ↓ –30 °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



Reactions in Porous Solids

Zeolites, Mesoporous materials

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

$M^{2+} + Na\text{-}Y \rightarrow M\text{-}Y + 2\ Na^{+}$

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

Ship-in-the-Bottle Synthesis

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

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

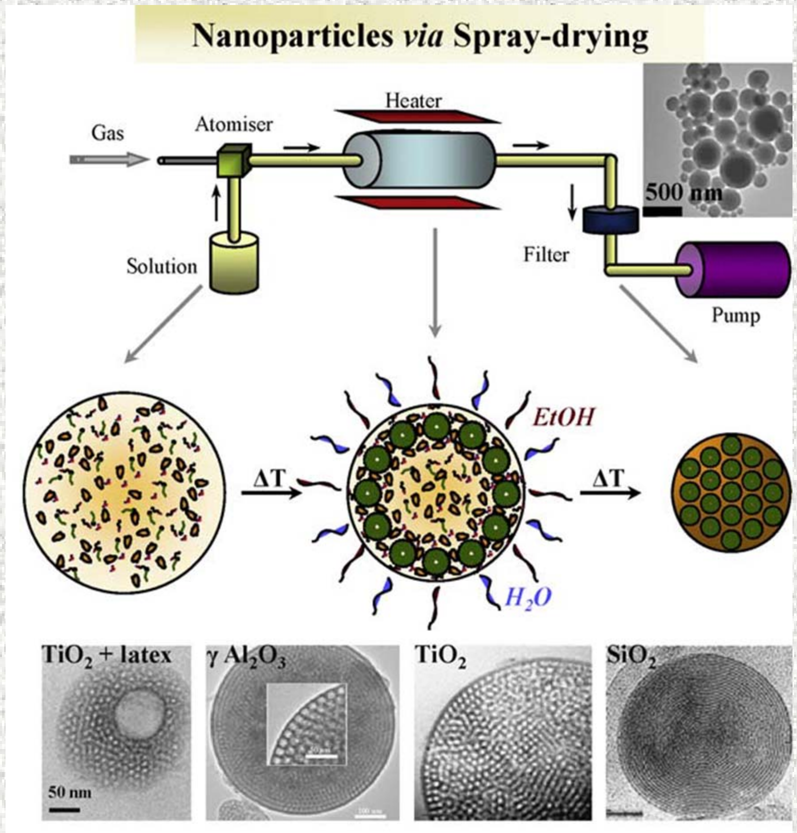
Conducting carbon nanowires

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

Radical polymerization

Pyrolysis gives carbon filaments

Bottom-up Synthesis



Sol-Gel Methods

Sol drying
Aerogels, supercritical drying

Aerosol Spray Pyrolysis

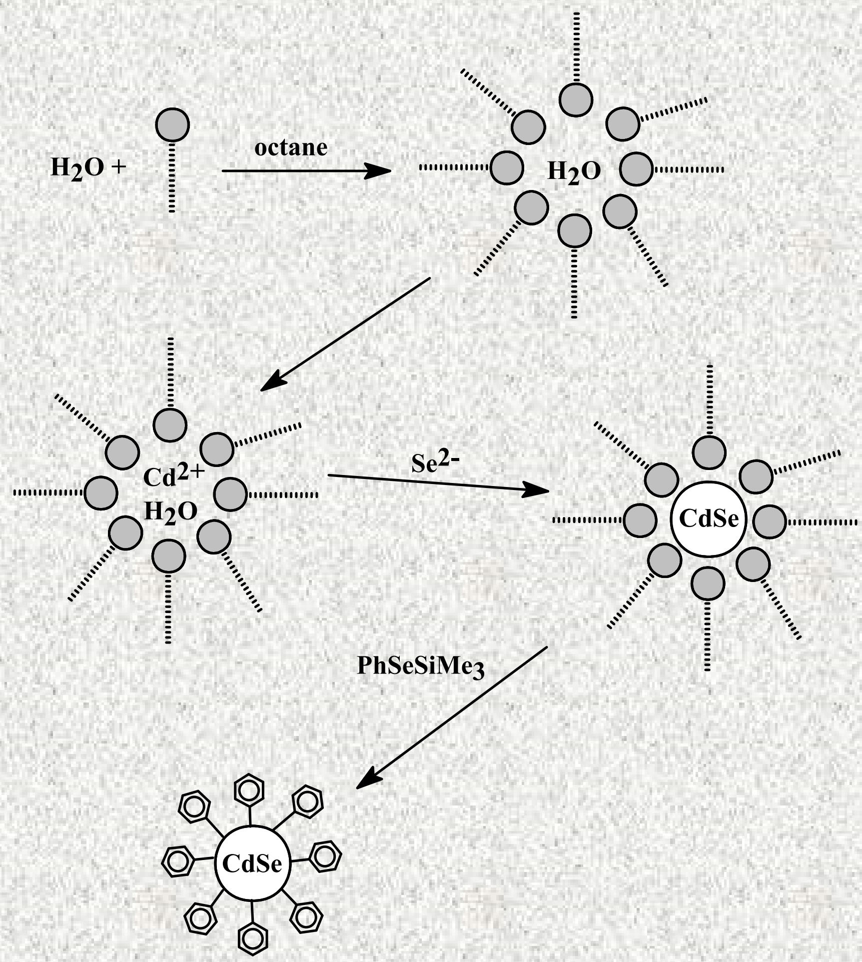
Aqueous solution, nebulization, droplet flow, solvent evaporation, chemical reaction, particle consolidation, up to 800 °C

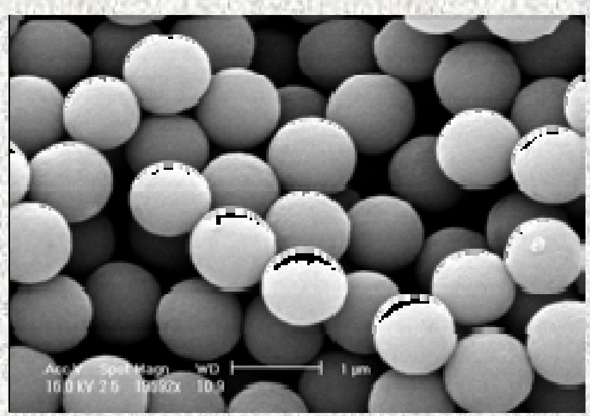
$$3\ Gd(NO_3)_3 + 5\ Fe(NO_3)_3 \rightarrow Gd_3Fe_5O_{12} + 6\ O_2 + 24\ NO_2$$

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

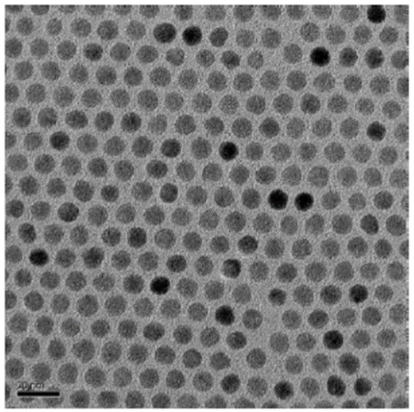
Bottom-up Synthesis

Inverse micelles

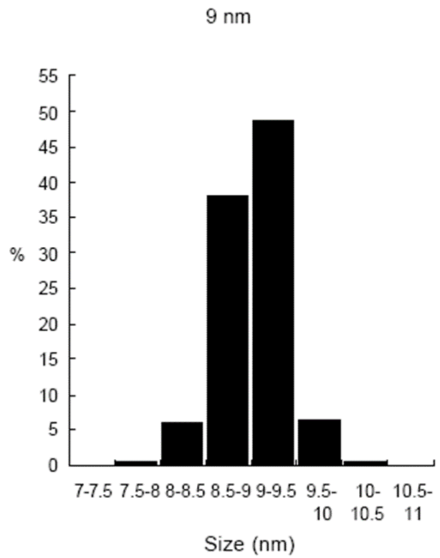




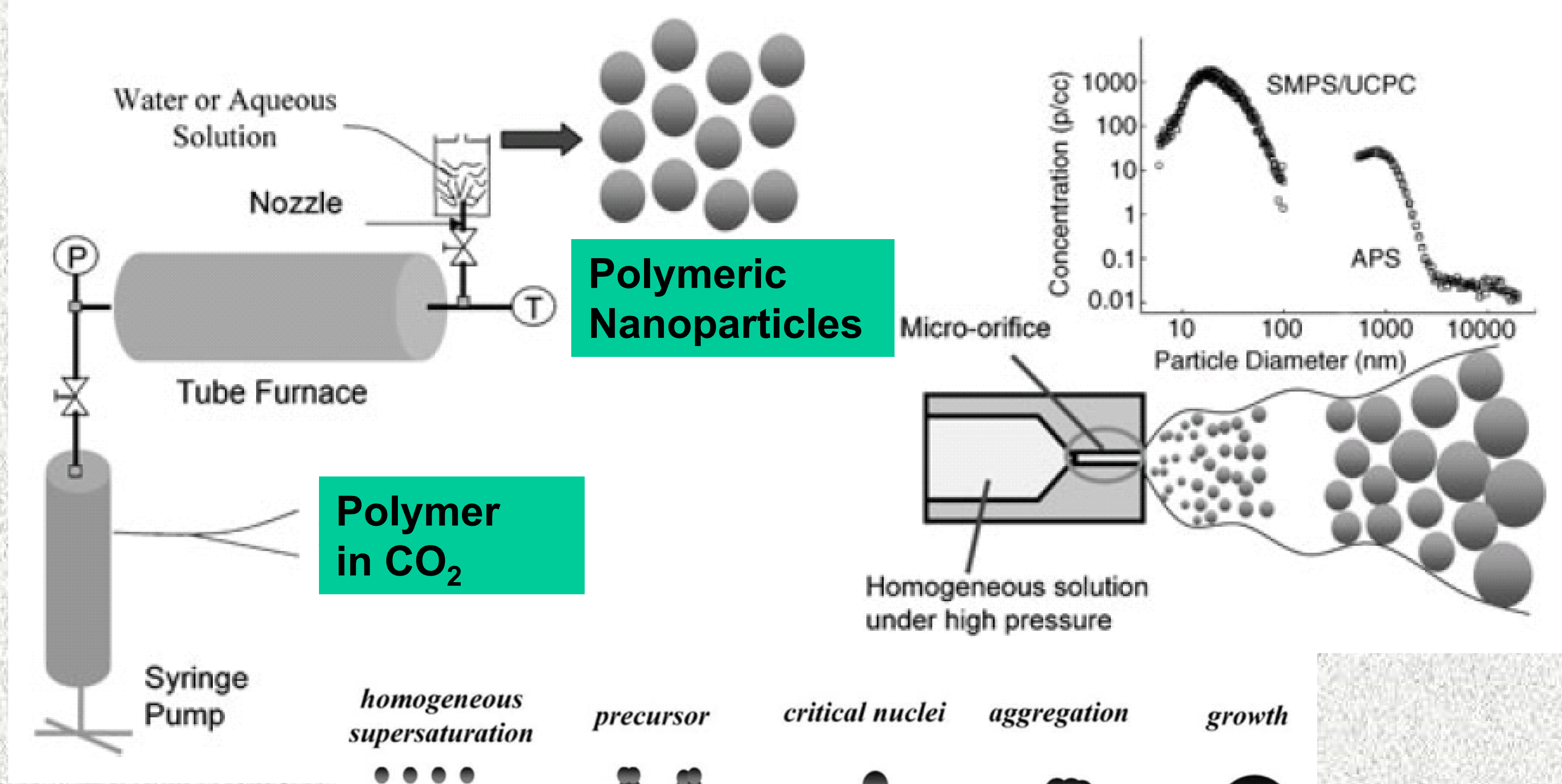
Size distribution histogram

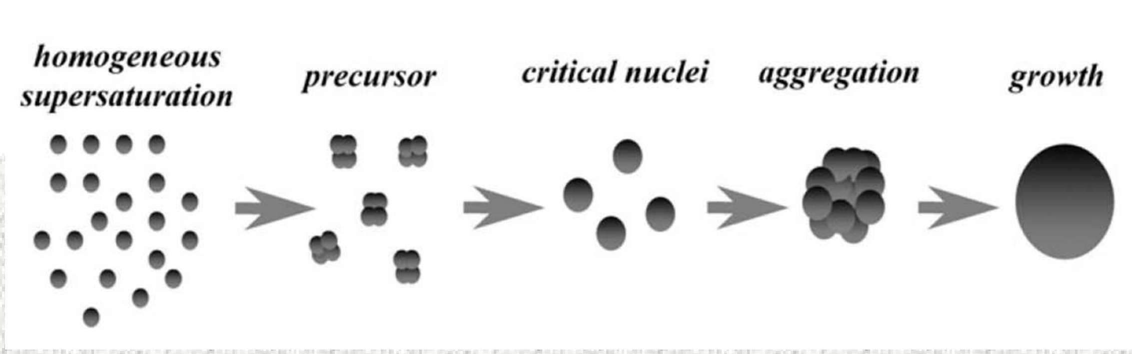


Number of counted particles: 204
Average size: 9.04 nm
Standard deviation: 0.33 nm (3.7%)



Rapid Expansion of Supercritical Fluid Solution

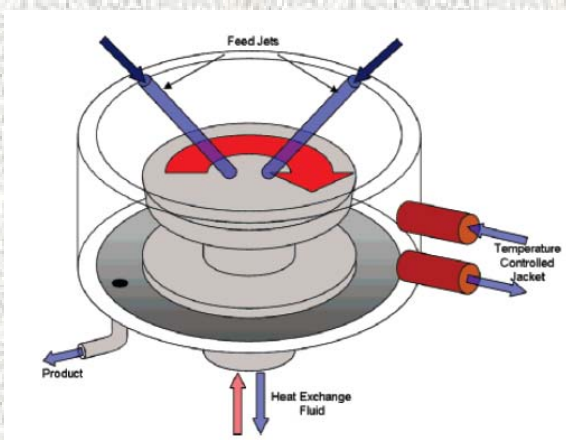




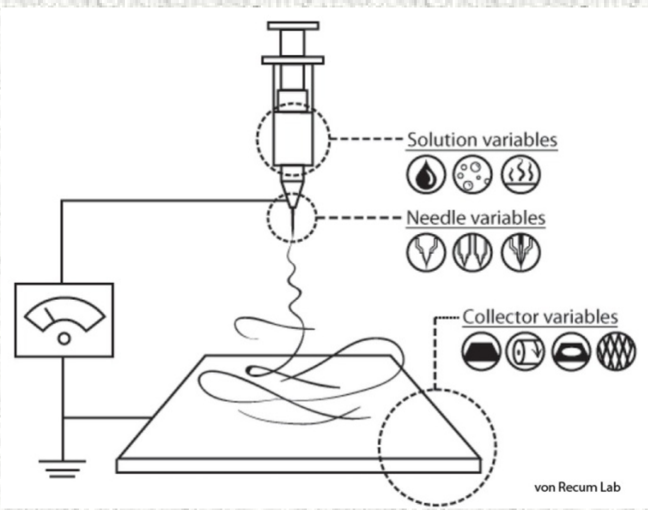
Spinning Disc Processing SDP

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%

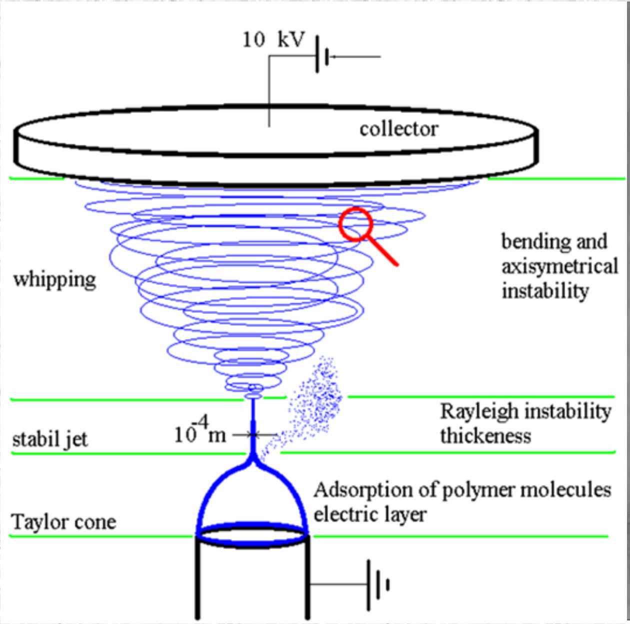


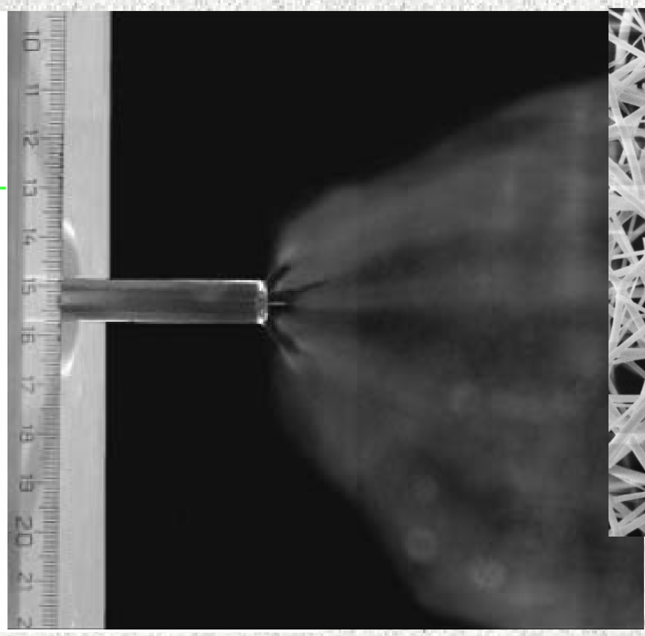
Electrospinning

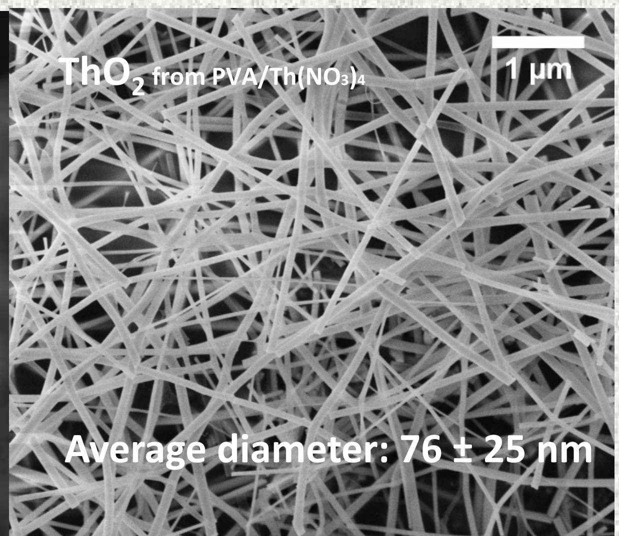


Parameters

- **Solution – precursor + polymer + solvent (viscosity, conductivity, surface tension)**
- **Instruments (voltage, distance b/w electrodes, collector shape)**
- **Ambient (temperature, humidity, atmosphere)**







Vapor-Liquid-Solid (VLS) Growth

Synthesis of nanowires NW

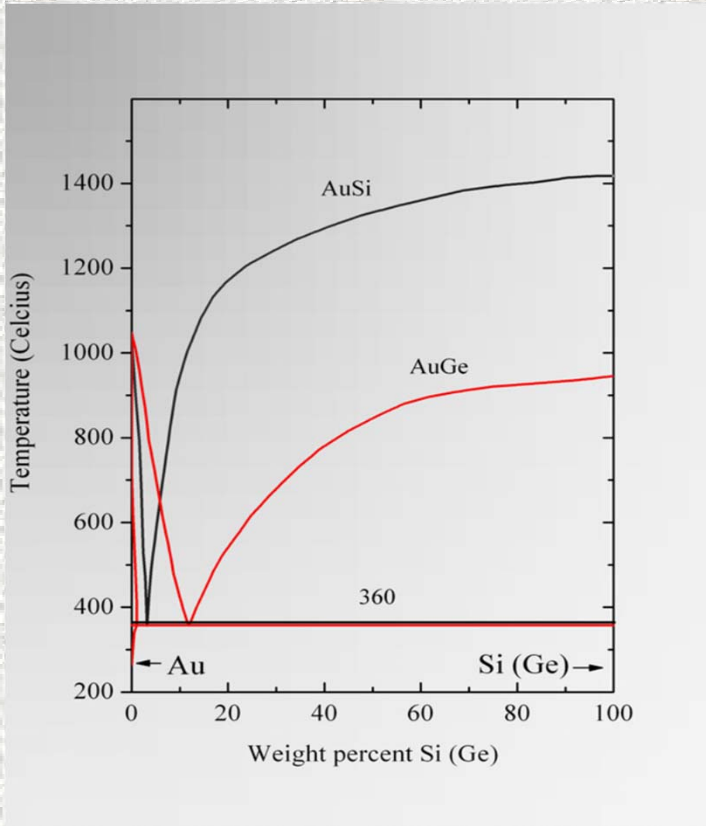
Metal catalyst nanoparticles - Au(s) – (1)

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)

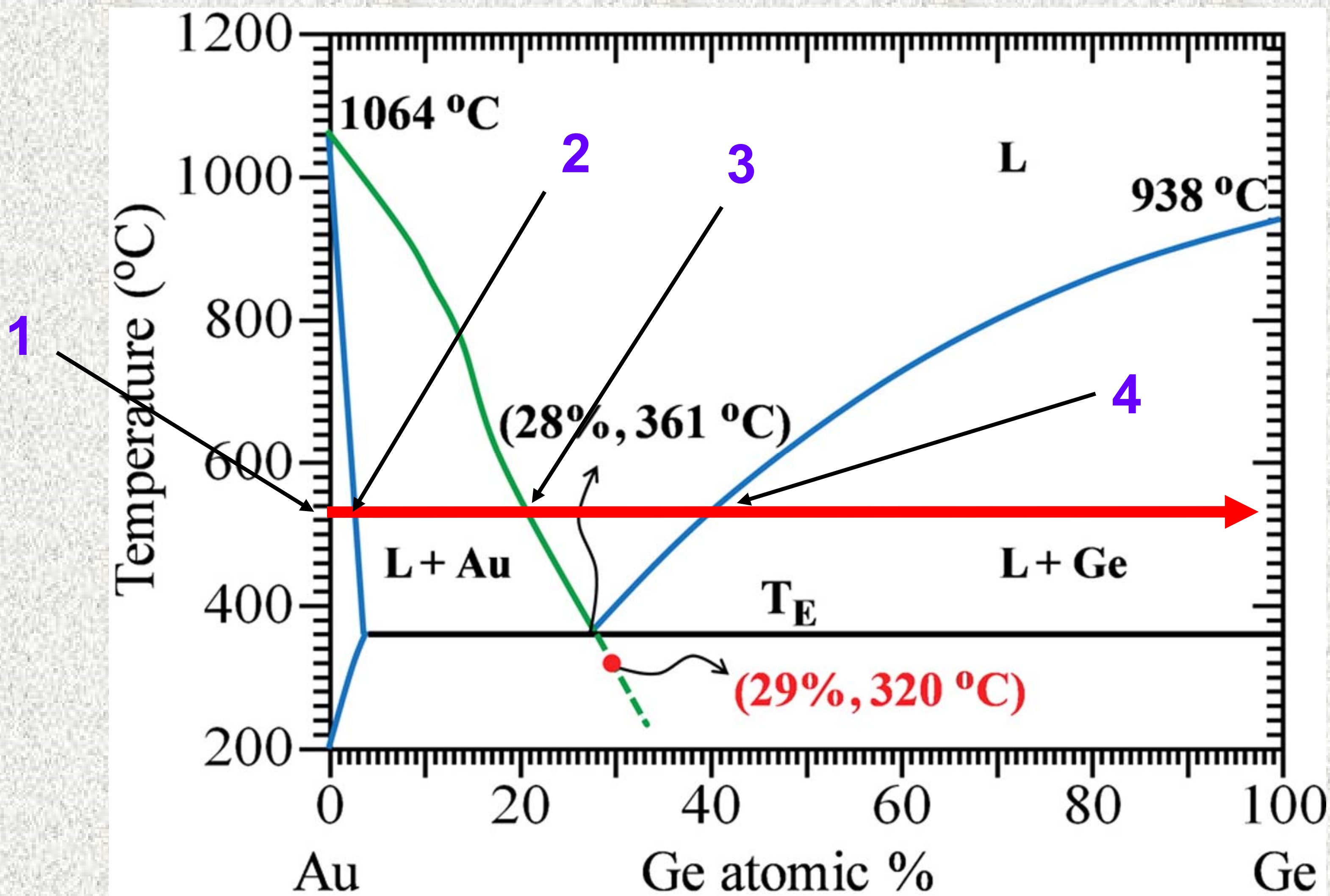
A liquid phase appears (3), melts to a droplet
The droplet becomes supersaturated with Ge

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

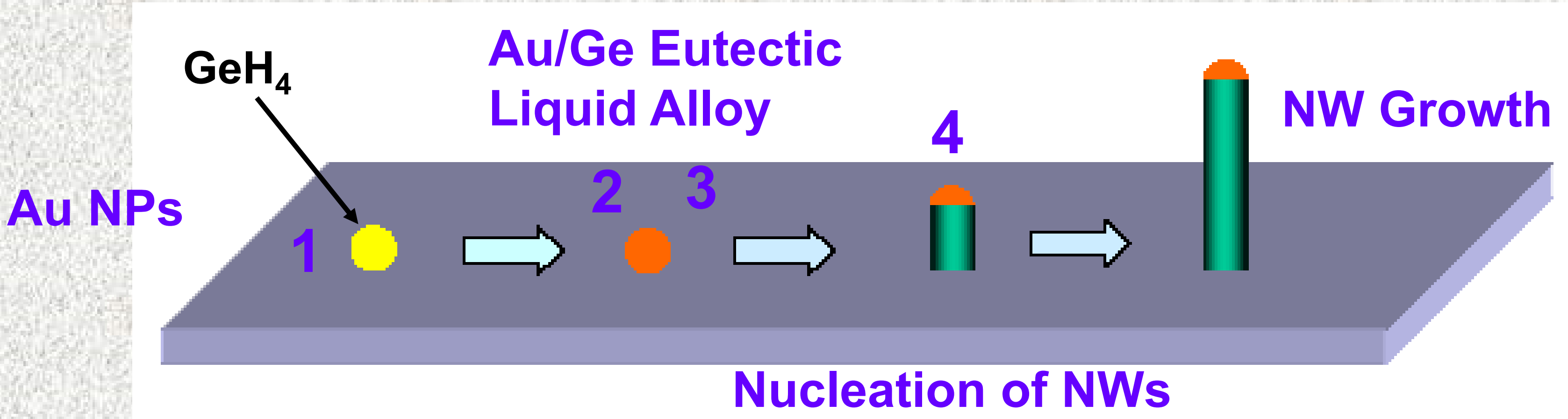


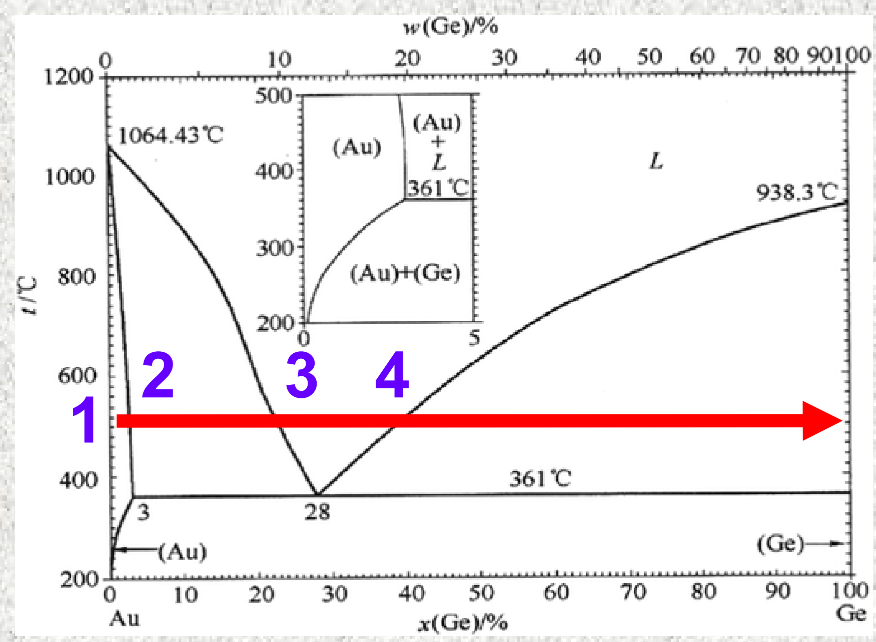
Eutectic 360 °C
Au (mp 1064 °C)
Si (mp 1410 °C)
Ge (mp 938 °C)

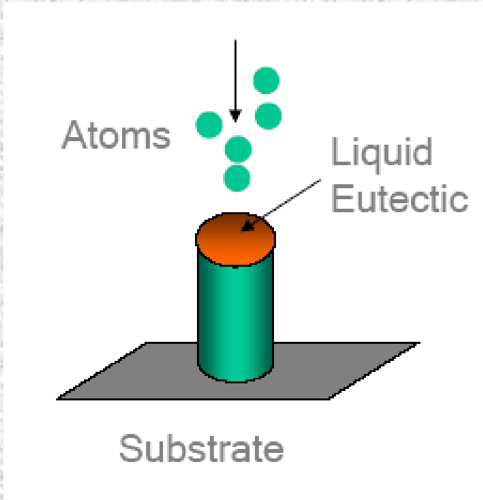
Vapor-Liquid-Solid (VLS) Growth



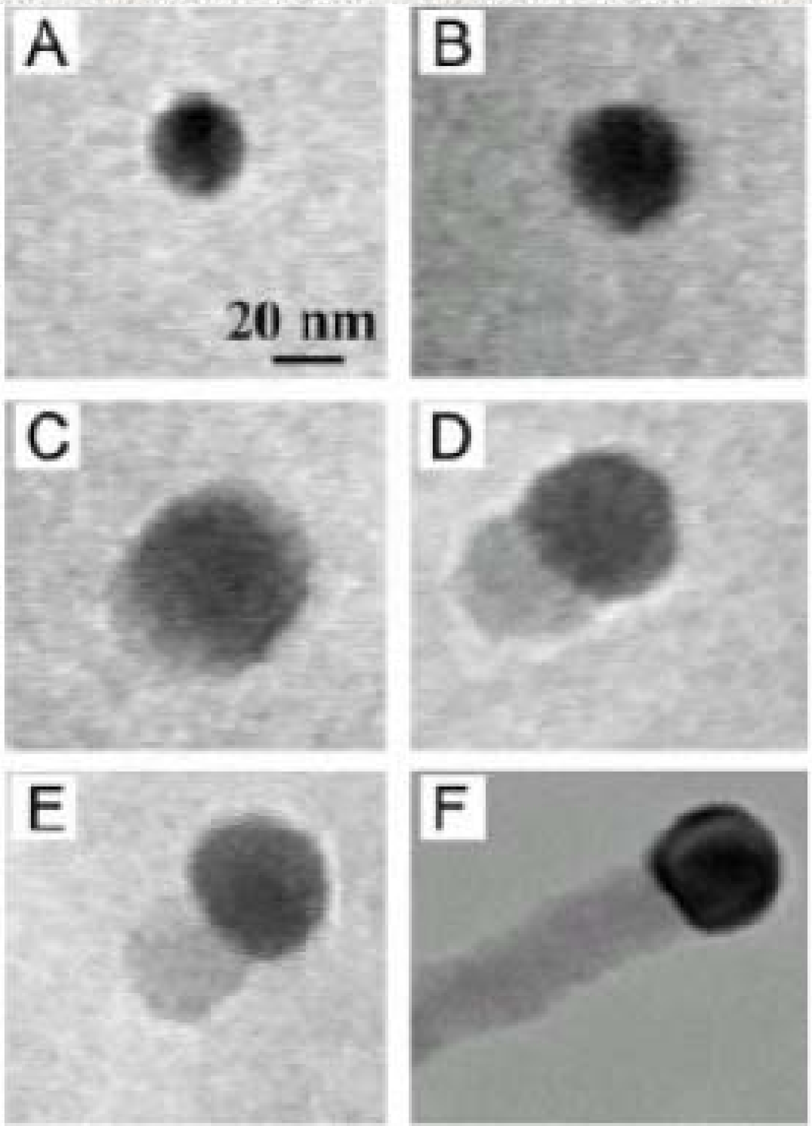
Vapor-Liquid-Solid (VLS) Growth







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

Top-down Synthesis: Bulk Down

🛠 **Introduction of Crystal Defects (Dislocations, Grain Boundaries)**

- **High-Energy Ball Milling - final size only down to 100 nm (contamination issues)**
- **Extrusion, Shear, Wear**
- **High-Energy Irradiation**
- **Detonative Treatment**

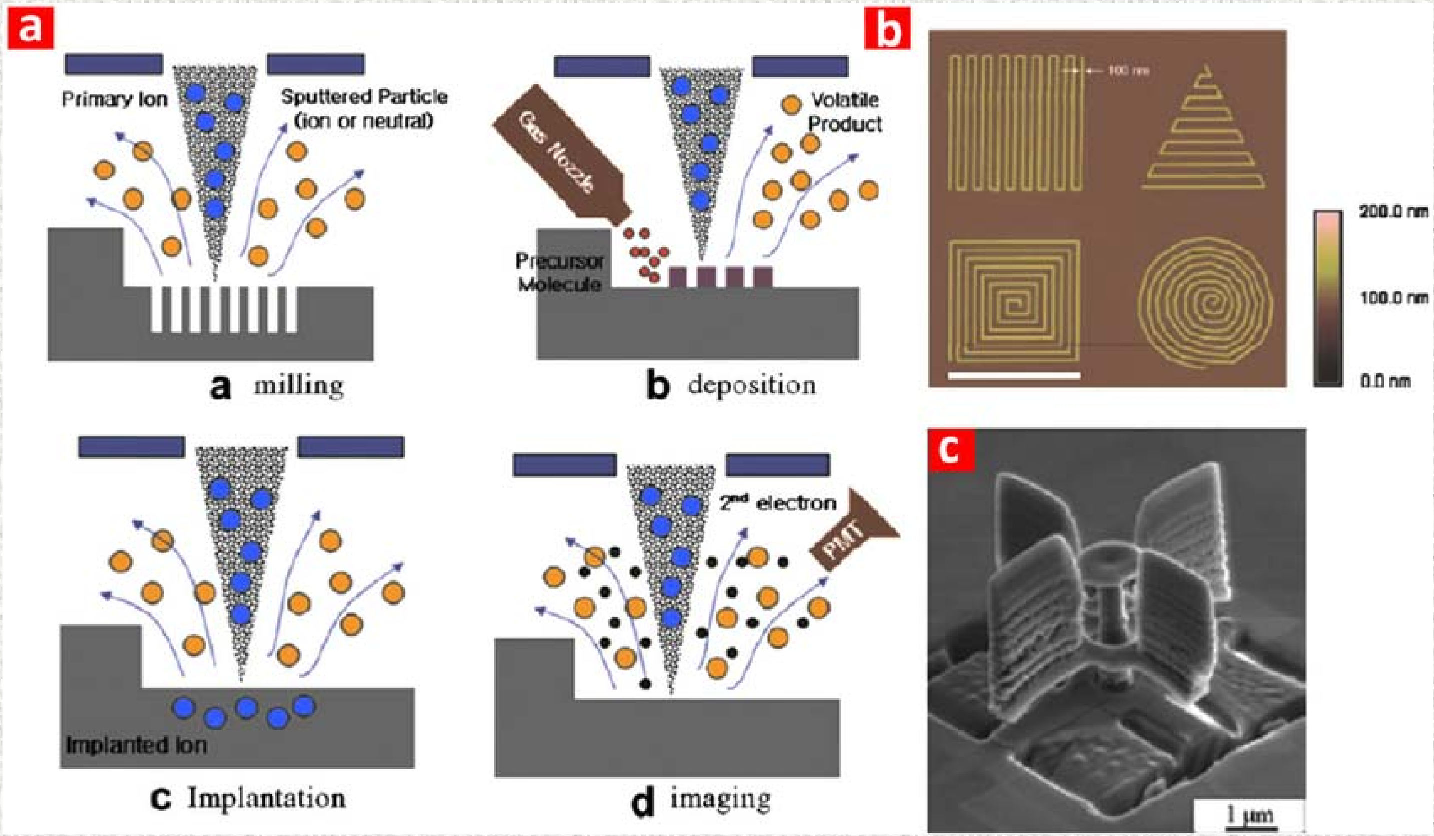
🛠 **Crystallization from Unstable States of Condensed Matter**

- **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

✧electron beam and focused ion beam (FIB) lithography