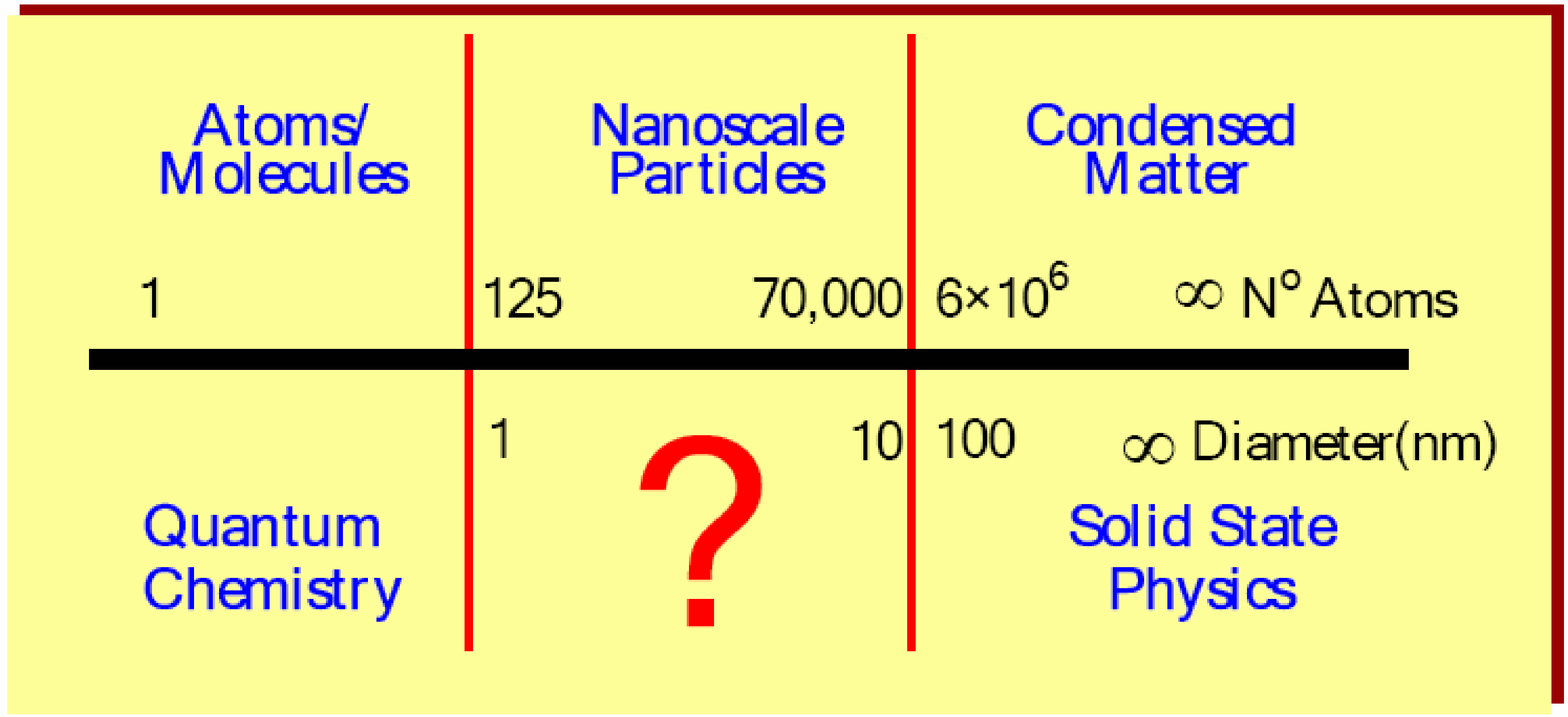
Nanoscopic Materials



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.

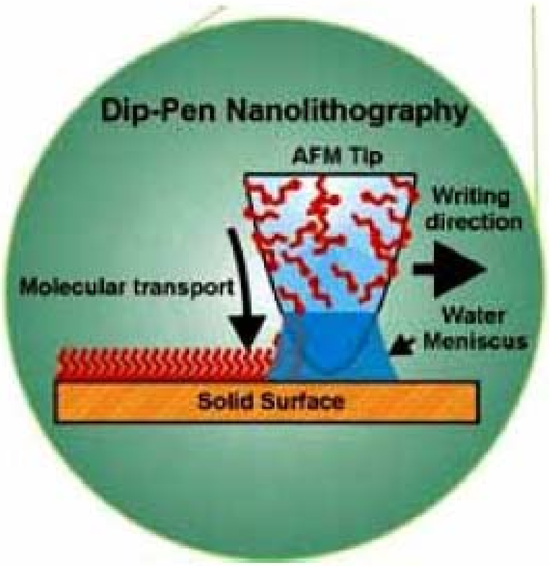
Room at the Bottom

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

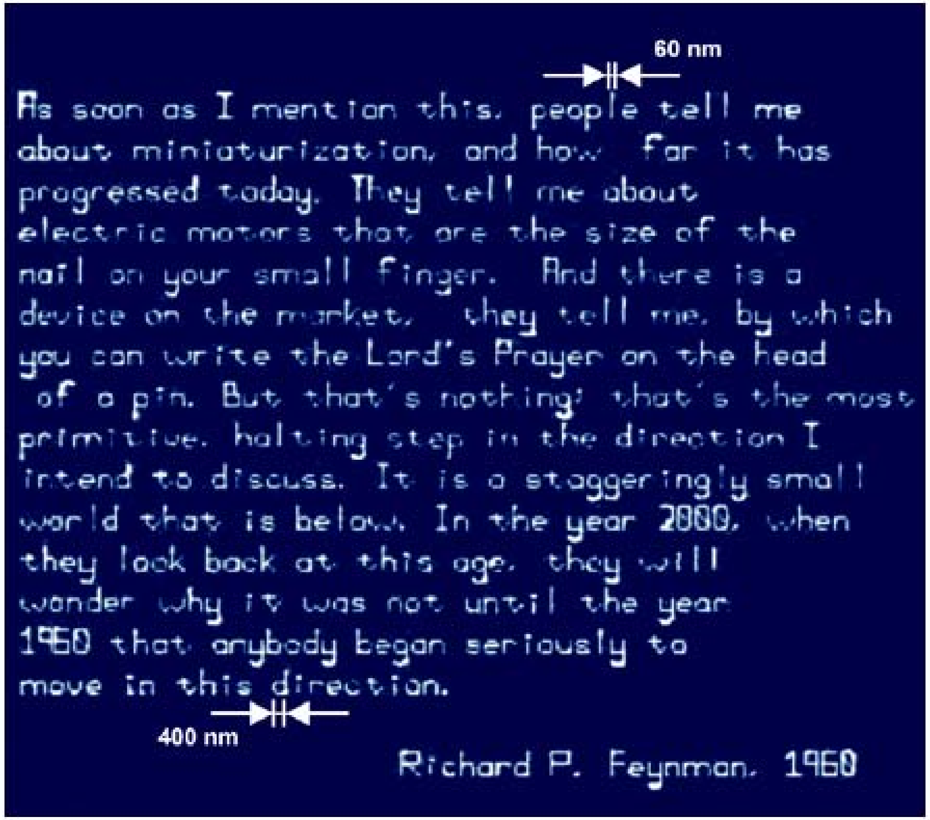
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin.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

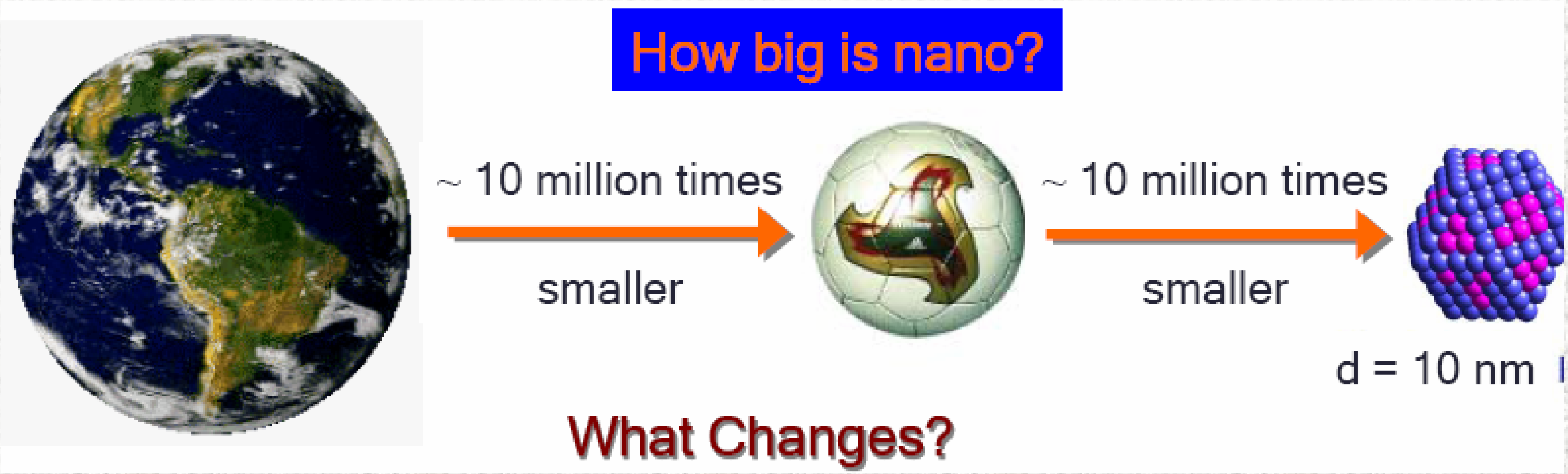
Nanoscale Writing



Nanoscale writing with an AFM (Mirkin et al.)



Nanoscopic Materials



Size is another variable to change physical and chemical properties

Nanoscopic Materials

Small Negligible light scattering New optics

Quantum size effects Information technology, Storage media

High surface area Catalysts, Adsorbents

Large Interfacial area New composites

Surface modifications Targeted Drug Delivery

Nanoscopic Materials

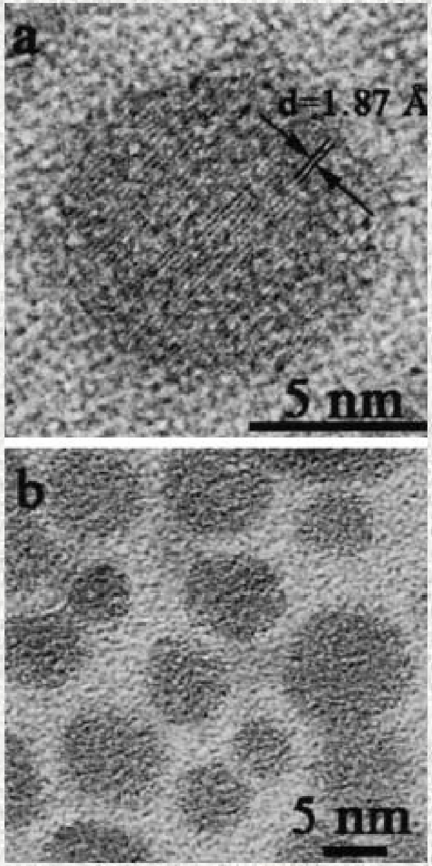
Nanoscale regime
Size 1 – 100 nm (traditional materials > 1 μm)

Physical and chemical properties depend on the size !!

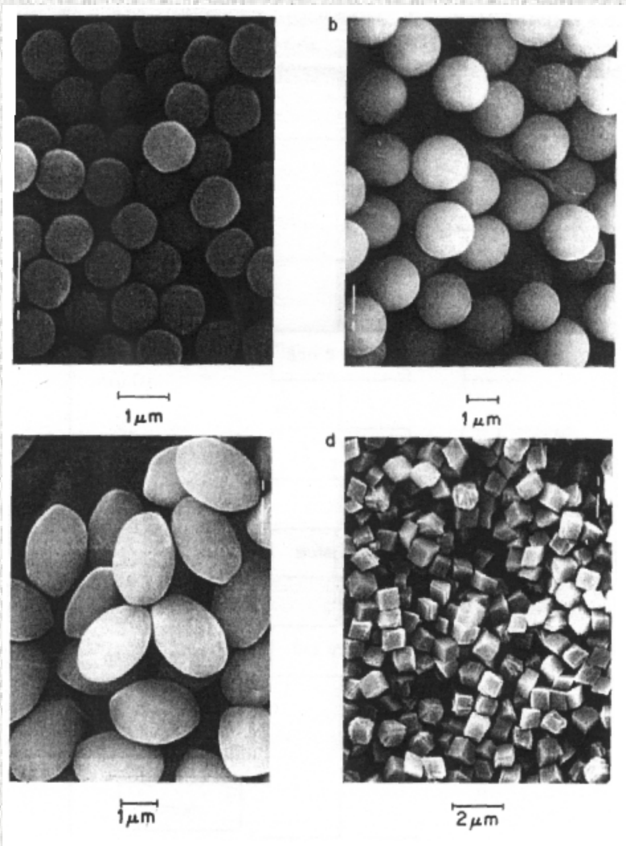
Natural examples:
- ☯ **Human teeth, 1-2 nm fibrils of hydroxyapatite $Ca_5(PO_4)_3(OH)$ + collagen**
- ☯ **Asbestos, opals, calcedon**
- ☯ **Primitive meteorites, 5 nm C or SiC, early age of the Solar system**

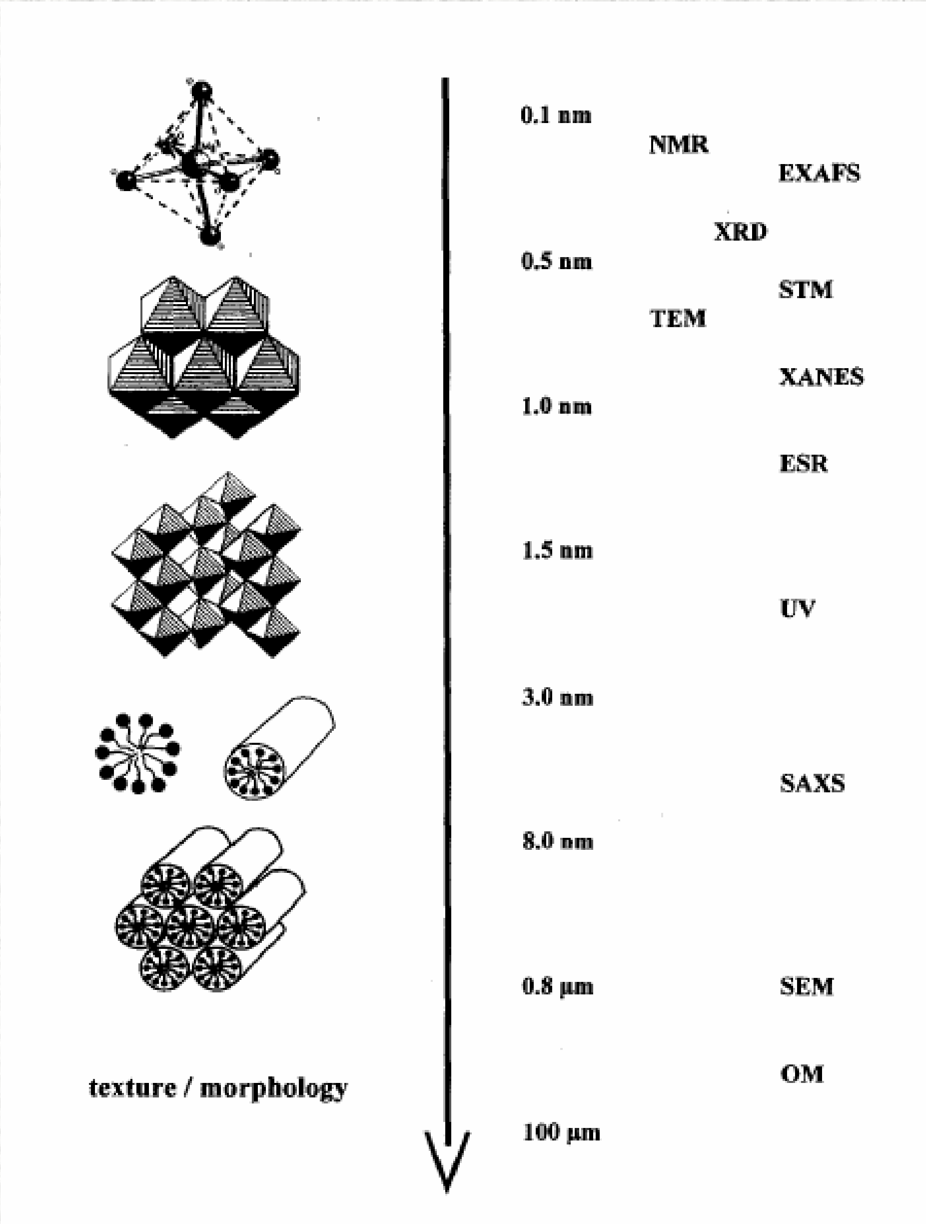
Nanoscopic Materials

Nanoparticles 1 – 100 nm



Traditional materials > 1 μm

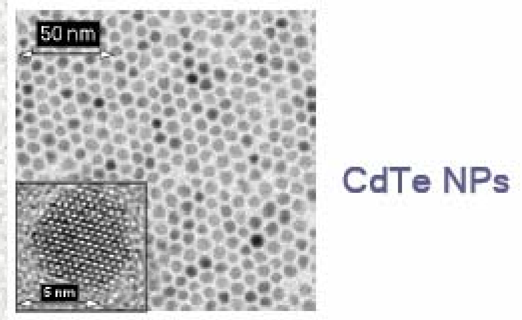



0.1 nm
NMR
EXAFS
XRD
0.5 nm
STM
TEM
XANES
1.0 nm
ESR
1.5 nm
UV
3.0 nm
SAXS
8.0 nm
0.8 µm
SEM
OM
texture / morphology
100 µm

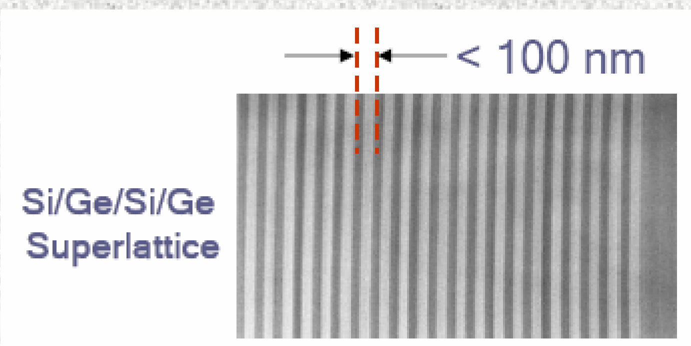
The nano-Family

At least one dimension is between 1 - 100 nm

0-D structures (3-D confinement):
- Quantum dots
- Nanoparticles

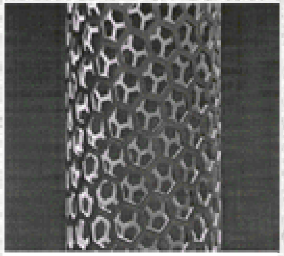


1-D structures (2-D confinement):
- Nanowires
- Nanorods
- Nanotubes

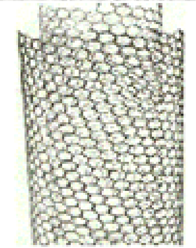


2-D structures (1-D confinement):
- Thin films
- Planar quantum wells
- Superlattices

CARBON NANOTUBES



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

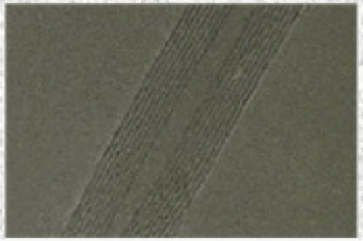


A multi-shell nanotube image
(Ebbesen, T. W., 1994.
Annu. Rev. Mater. Sci. 24:235-64.
courtesy of NEC/Handa)

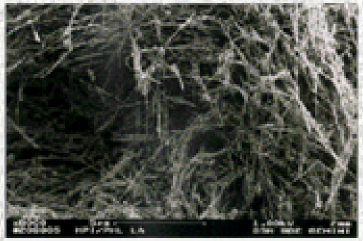
1. A unique species somewhere between traditional carbon fibers and novel forms of carbon such as fullerenes.

2. A seamless cylindrical sheet of graphite whose diameter is so small and its aspect ratio (diameter vs. length) is so great that it can be considered from the electronic point of view as a one-dimensional structure.

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



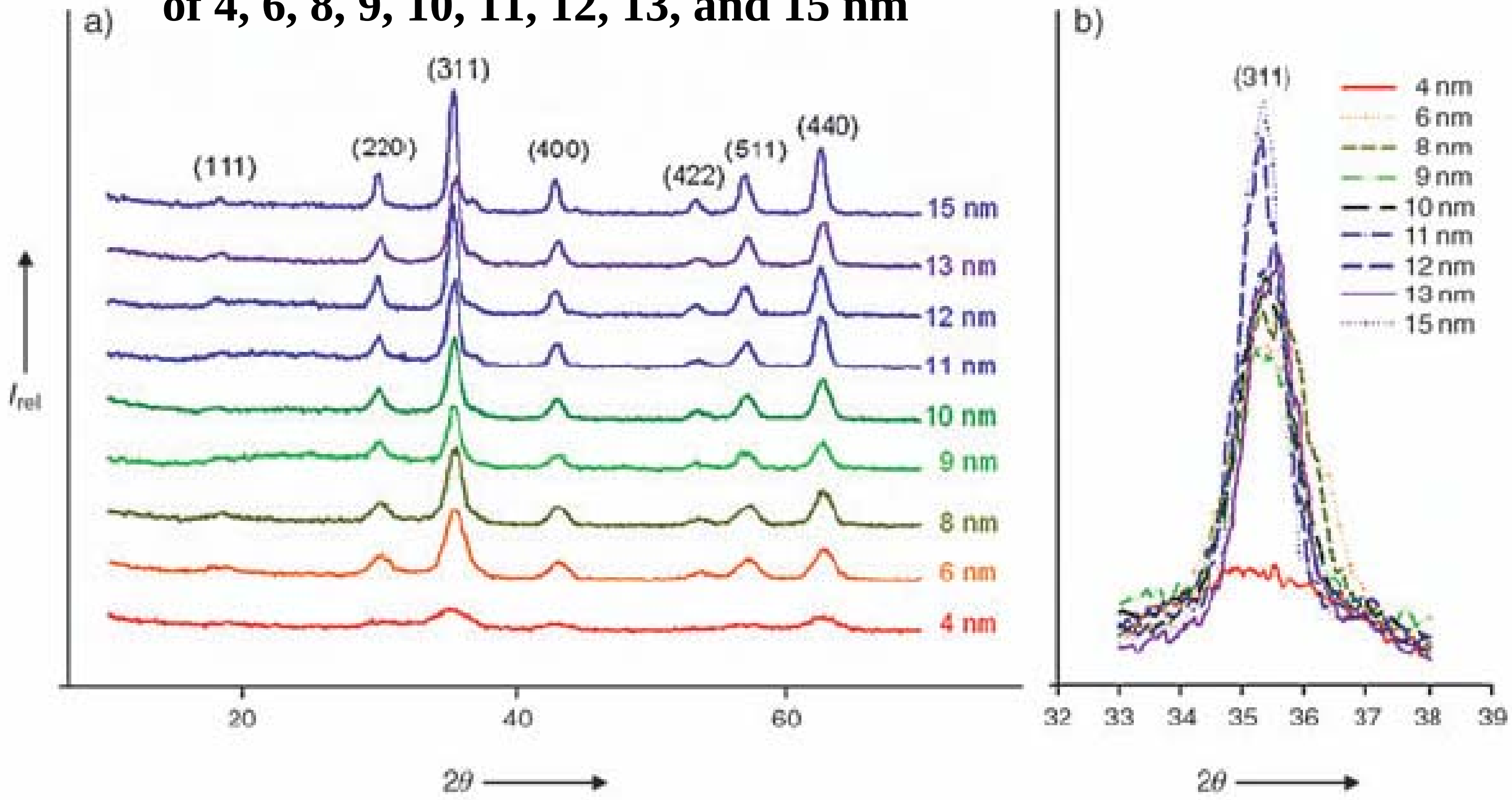
A picture of a typical multi-shell
nanotube taken using TEM
(Source from Dr. P. M. Ajayan)



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

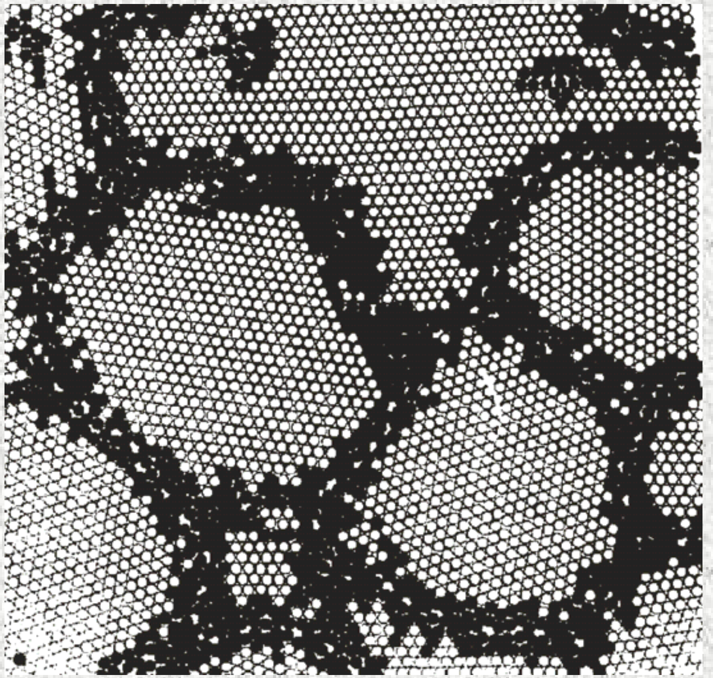
Coherence Length

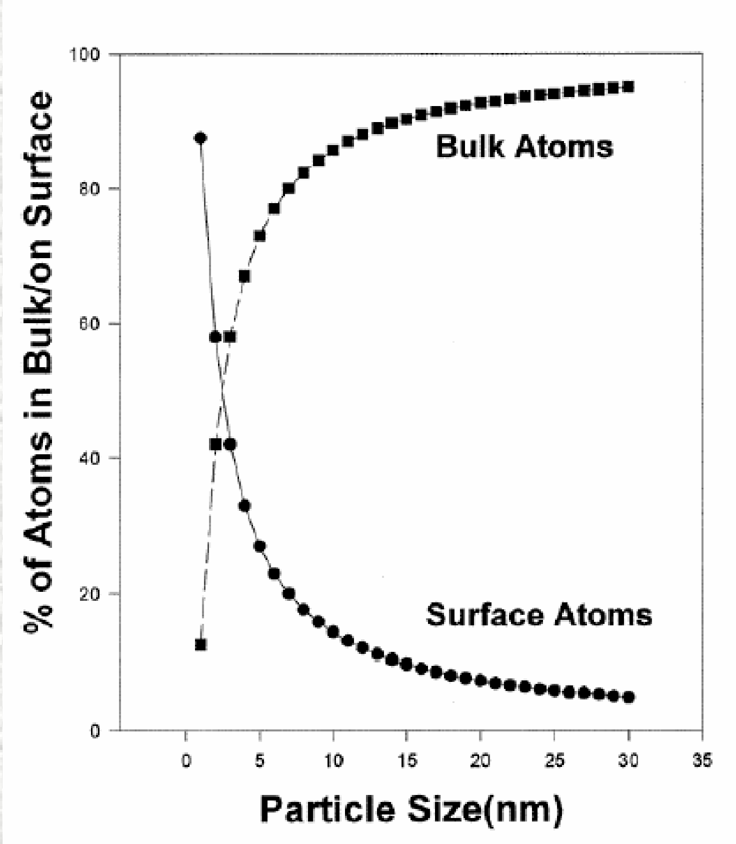
XRD patterns of iron oxide nanocrystals of 4, 6, 8, 9, 10, 11, 12, 13, and 15 nm



Surface Effects

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





Surface Effects

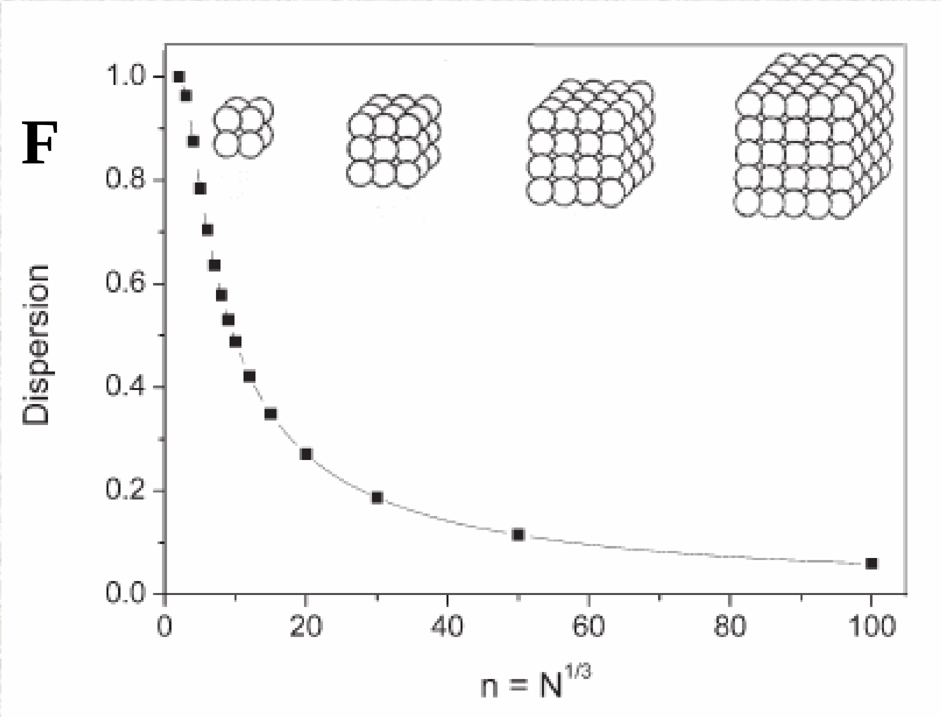
Dispersion F = the fraction of atoms at the surface

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

Atoms at surfaces have fewer neighbours than atoms in the bulk

lower coordination and unsatisfied bonds
surface atoms are less stabilized than bulk atoms

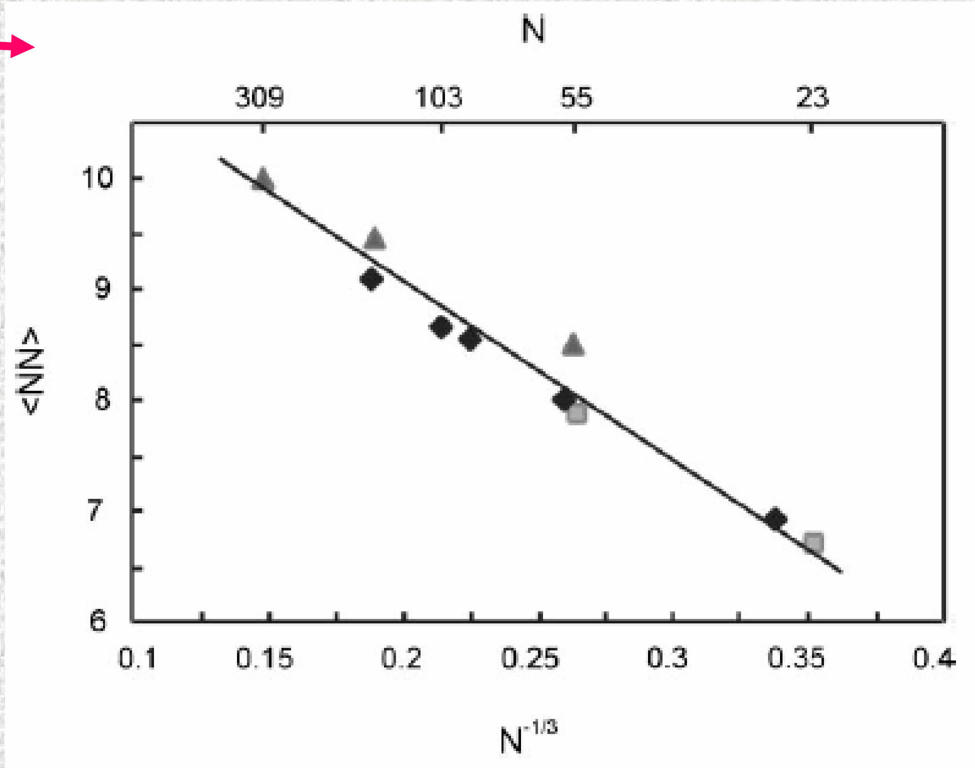
The smaller a particle the larger the fraction of atoms at the surface, and the higher the average binding energy per atom.

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

Example: the melting point depression in nanocrystals
2.5 nm Au particles 930 K
bulk Au 1336 K

coordination number

Surface Effects



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

Surface Effects

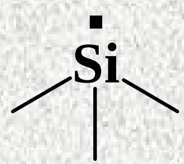
Properties of grain boundaries

- **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**



Gibbs–Thomson Equation

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

T_m = mp of the cluster with radius r

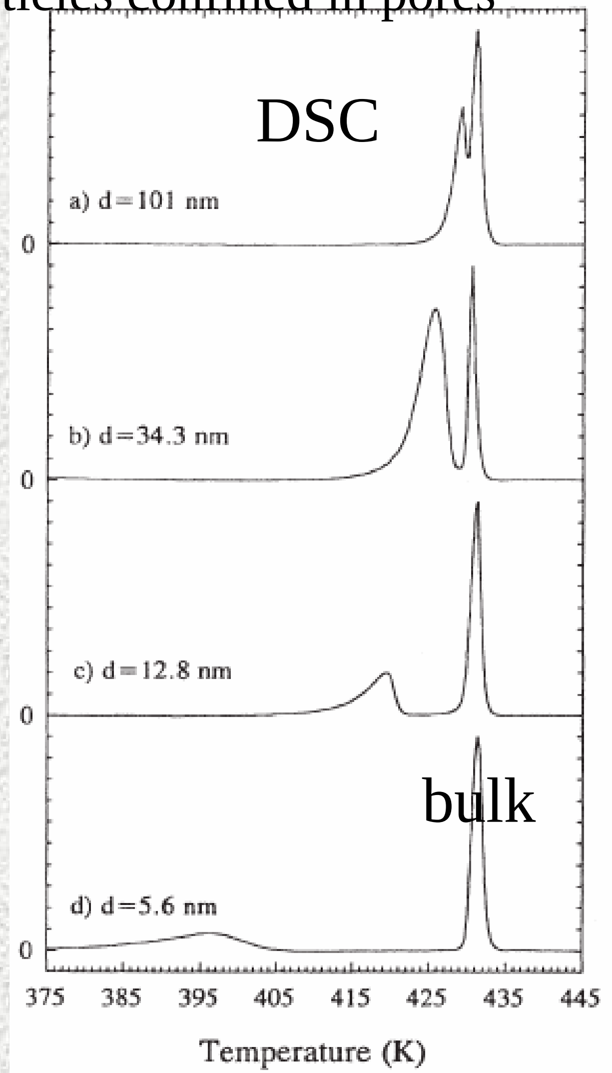
T_m^b = mp of the bulk

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

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

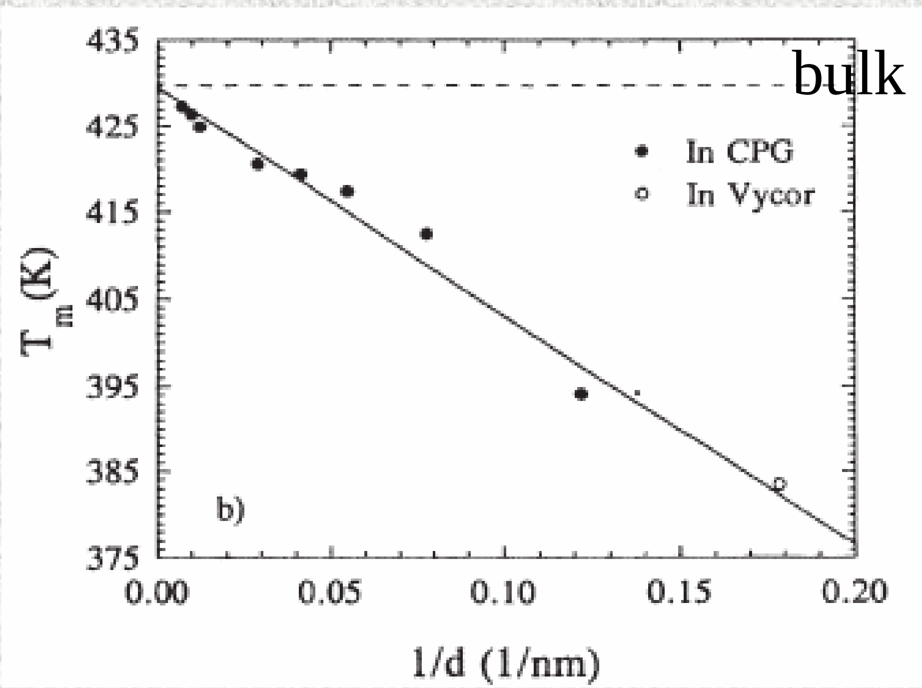
ΔH_m = the bulk latent heat of melting

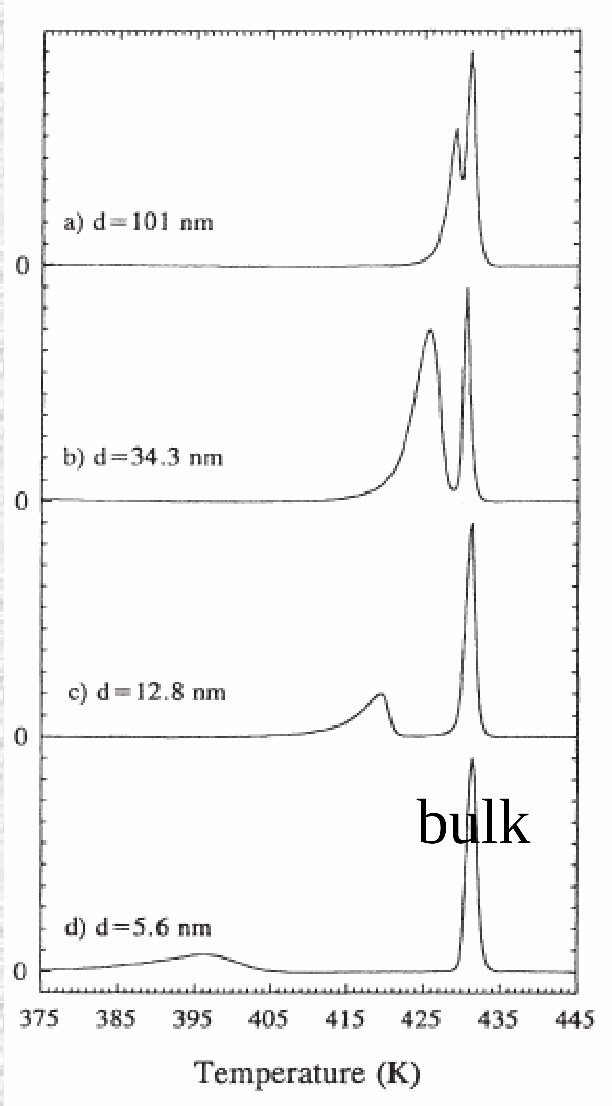
In nanoparticles confined in pores



Phase Transitions

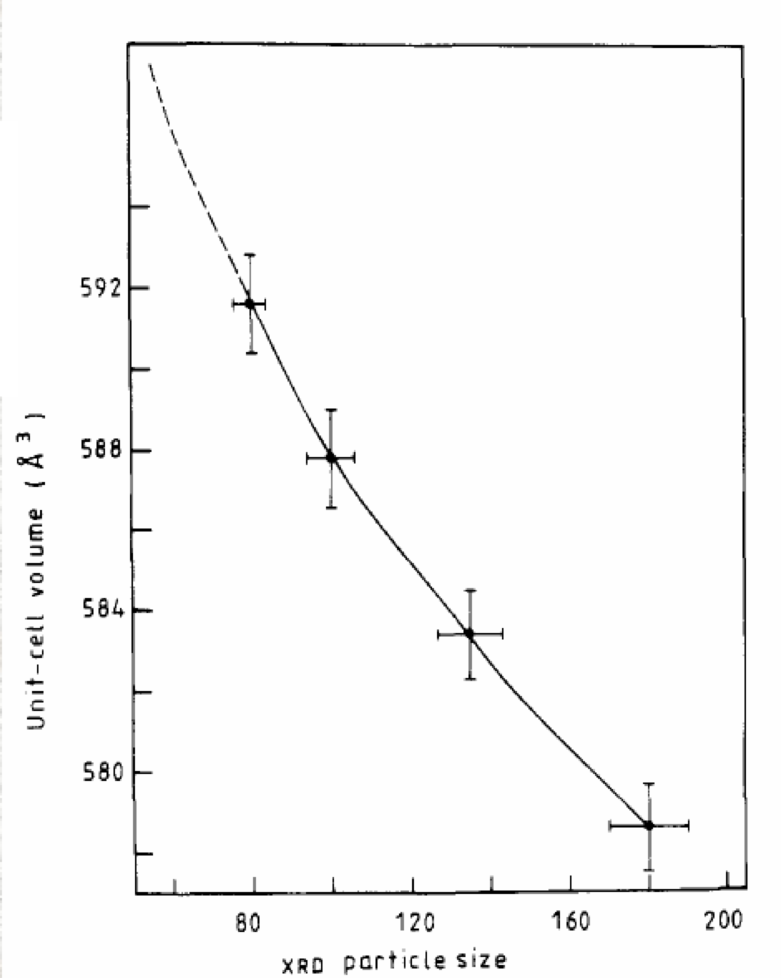
Phase transitions are collective phenomena
With a lower number of atoms in a cluster a phase transition is less well
defined, it is therefore broadened
Small clusters behave more like molecules than as bulk matter





Surface Effects

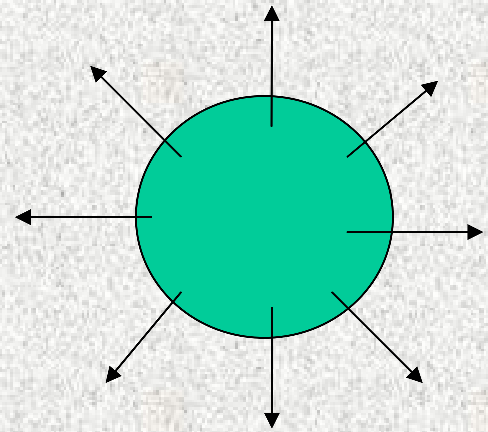
Correlation between the unit-cell volume (cubic) and the XRD particle size in γ-Fe_2O_3 nanoparticles



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

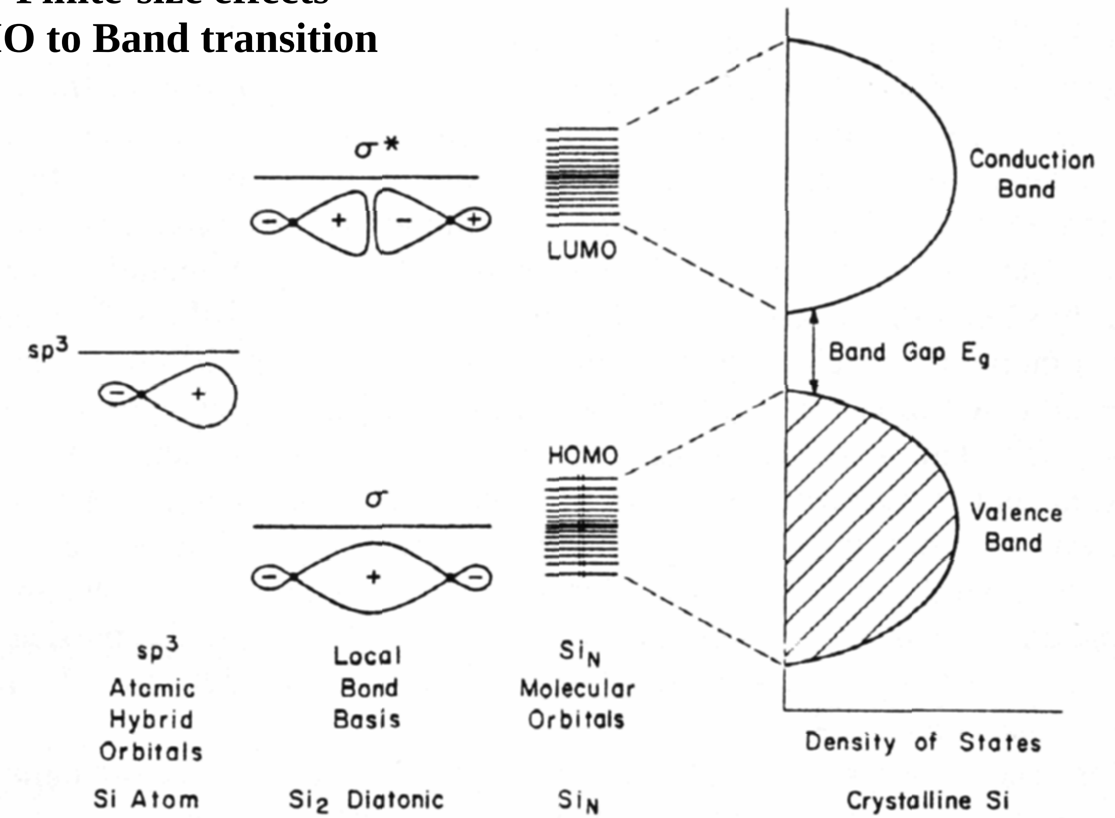
the repulsive dipolar interactions increase in smaller particles
reduced by allowing unit cell volume to increase



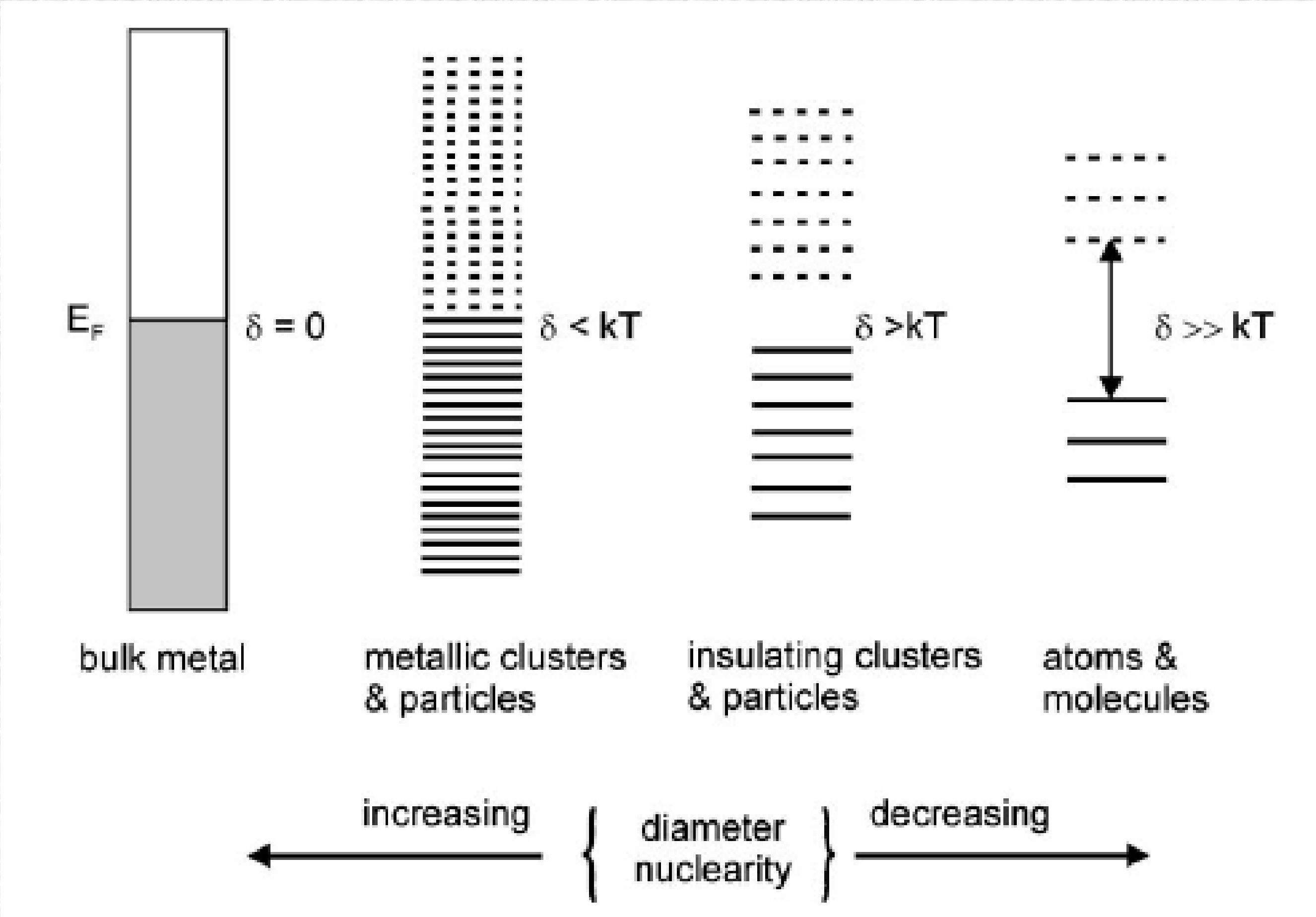
Quantum Confinement Effects

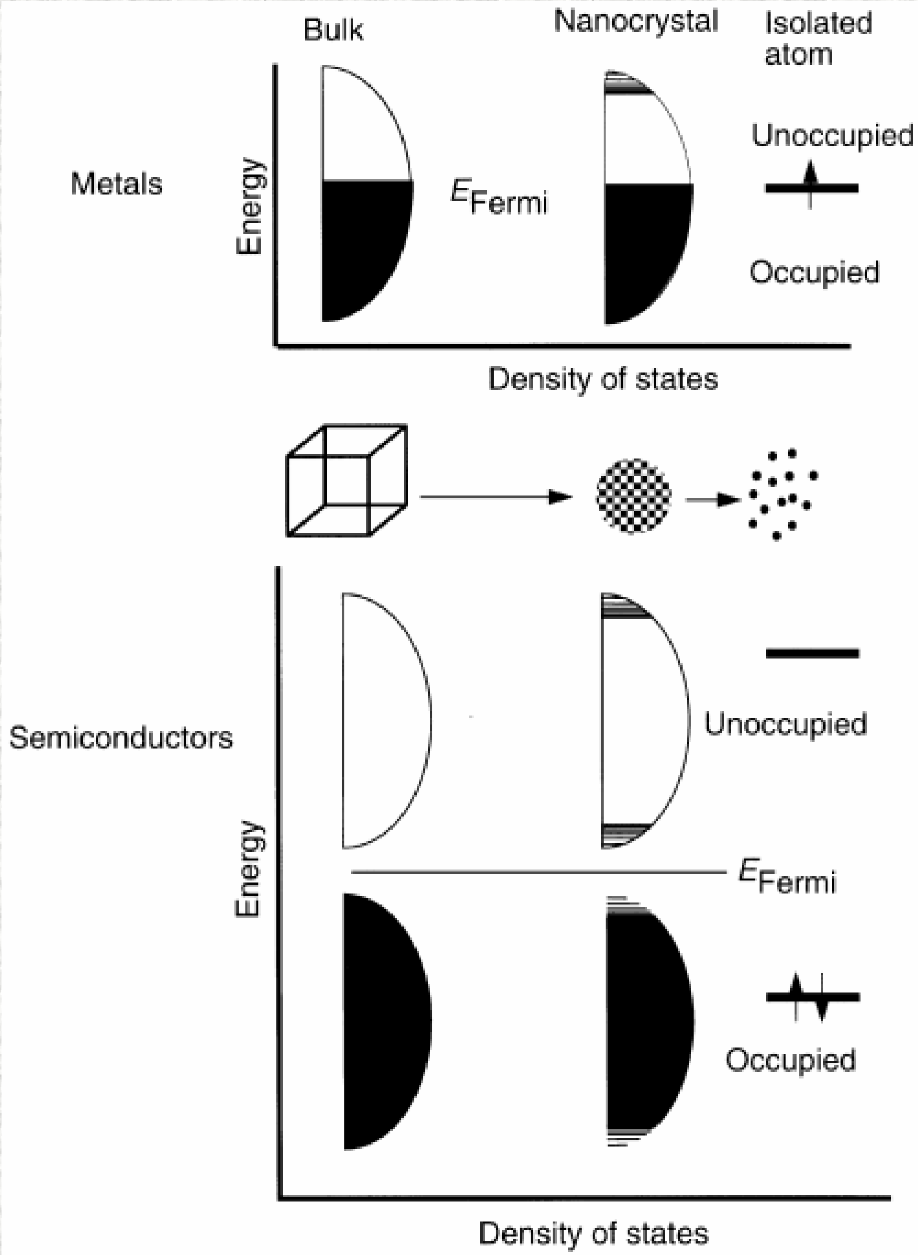
Physical and chemical properties depend on the size !!

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



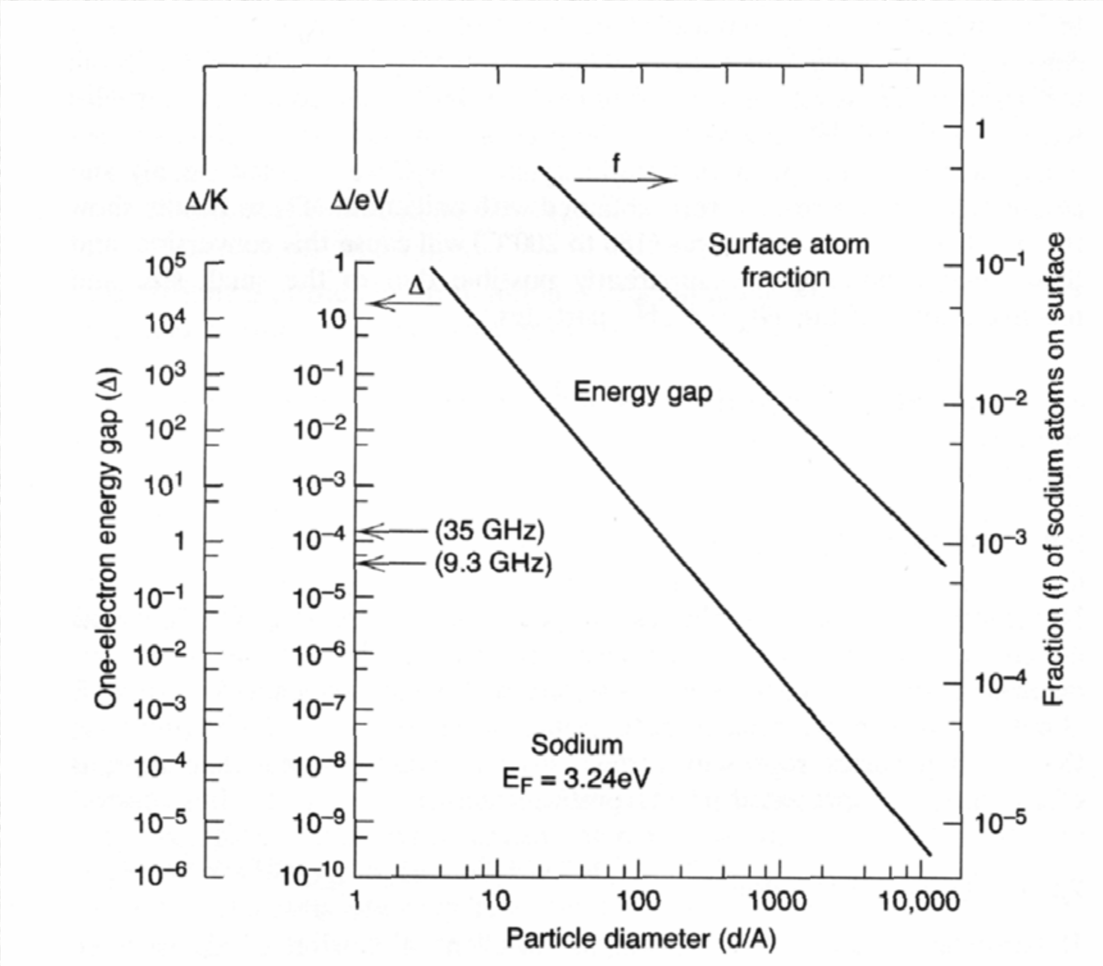
Metal-to-Insulator Transition




Bulk
Nanocrystal
Isolated atom
Metals
Energy
E_{Fermi}
Unoccupied
Occupied
Density of states
Semiconductors
Energy
Unoccupied
E_{Fermi}
Occupied
Density of states

Metal-to-Insulator Transition

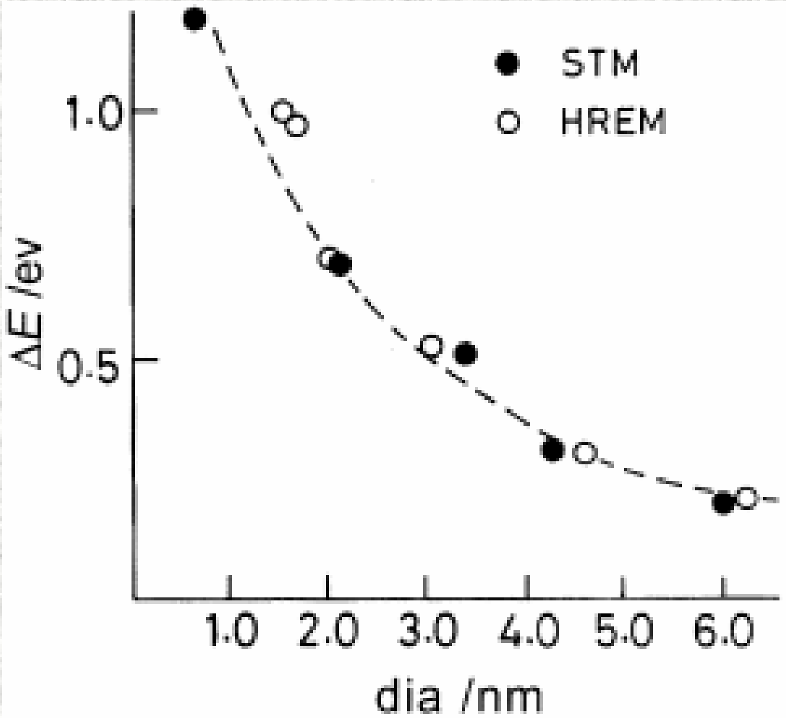
Band gap increases with decreasing size



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

Magnetic behavior
Single domain particles
large coercive field

Metal-to-Insulator Transition

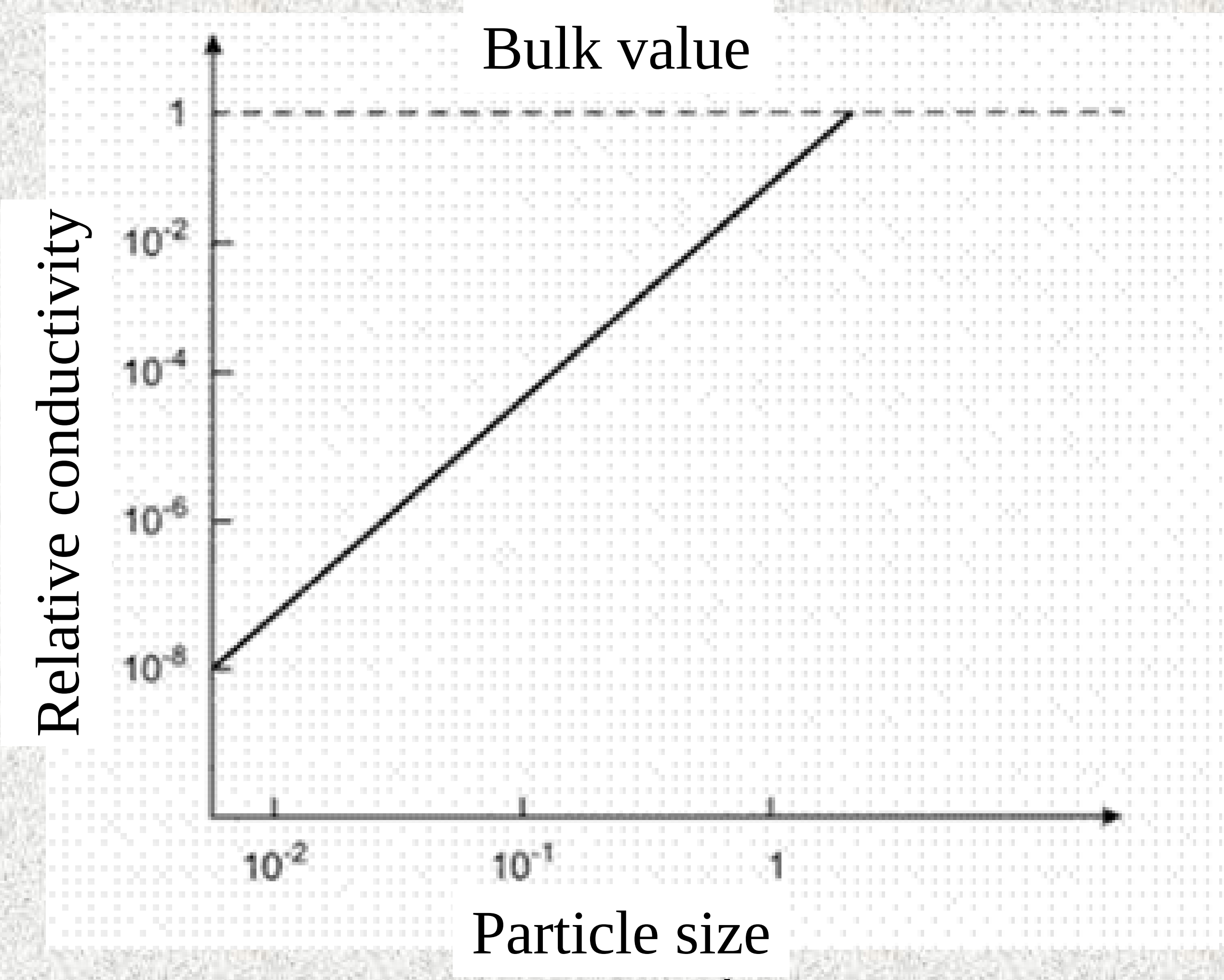


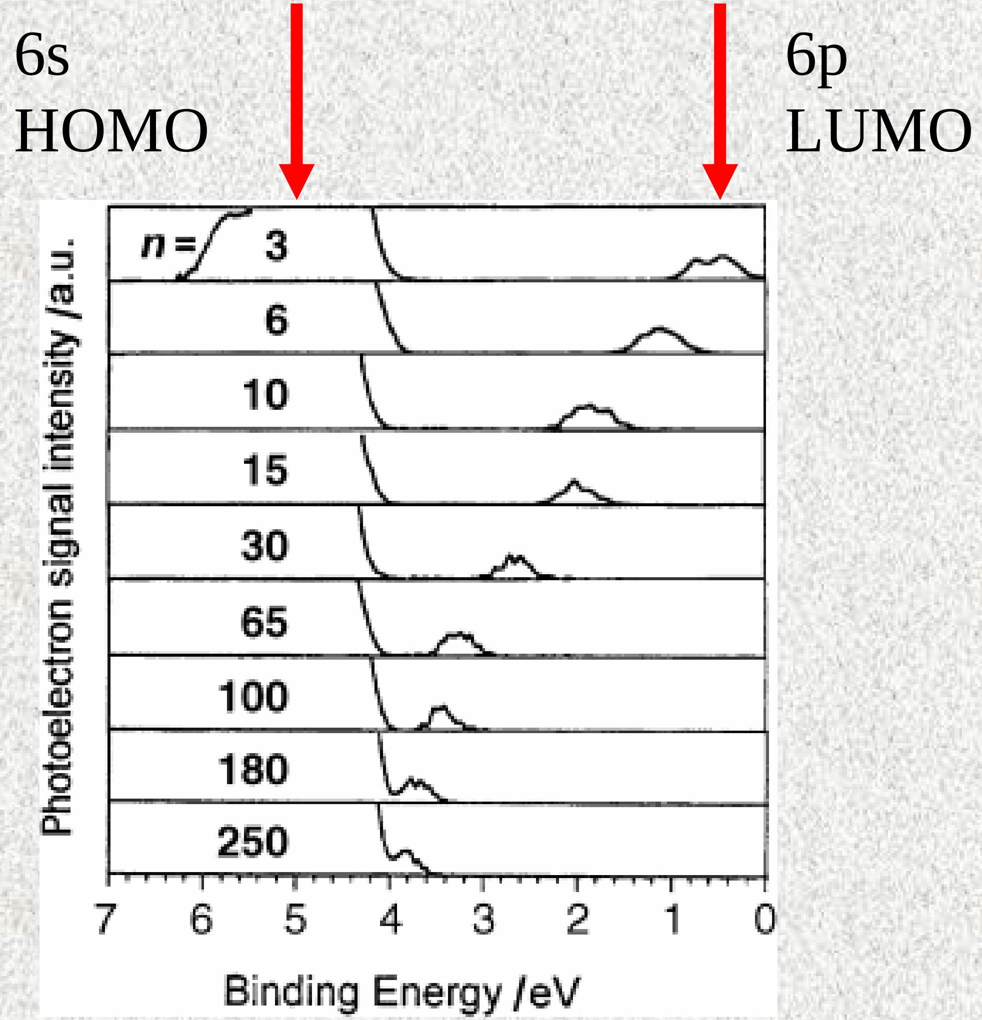
The increase in the core-level binding energy in small particles
poor screening of the core charge

the size-induced metal-nonmetal transition in nanocrystals

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

Electrical Conductivity

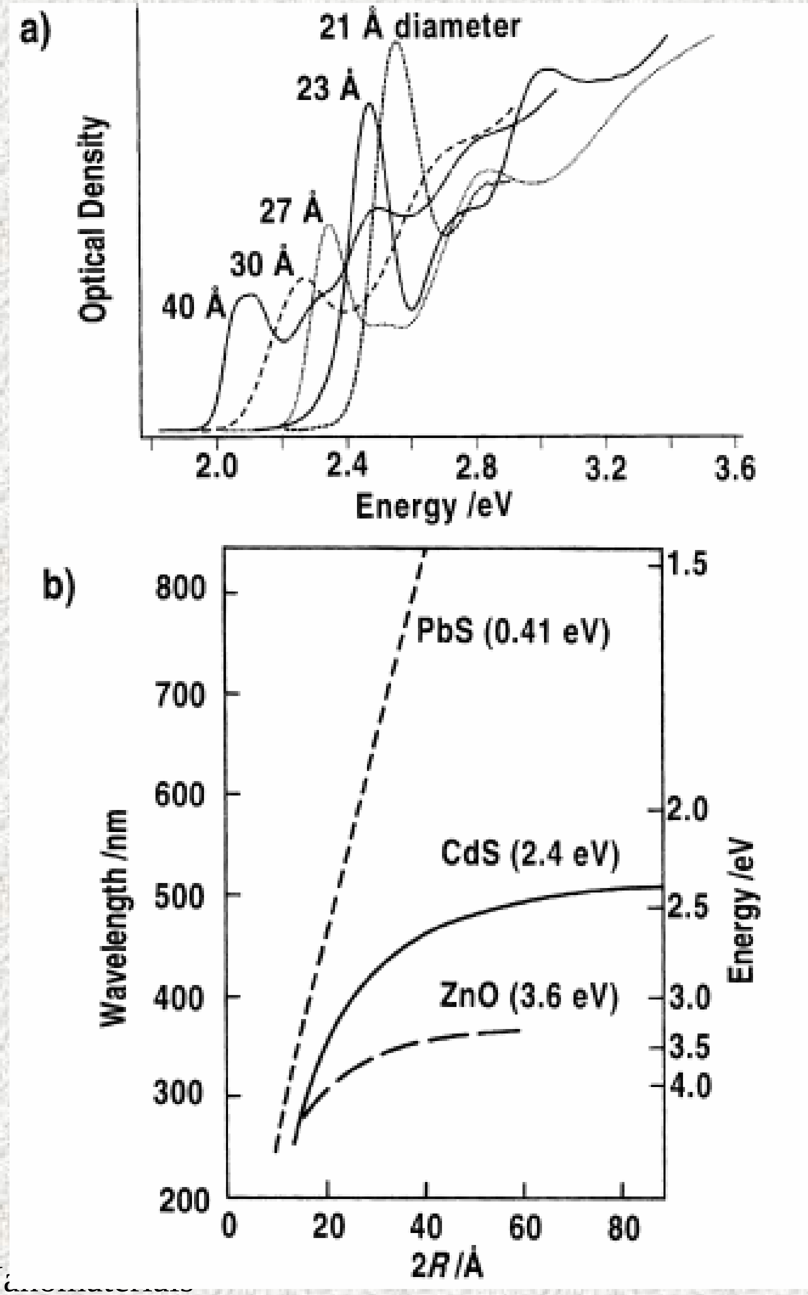




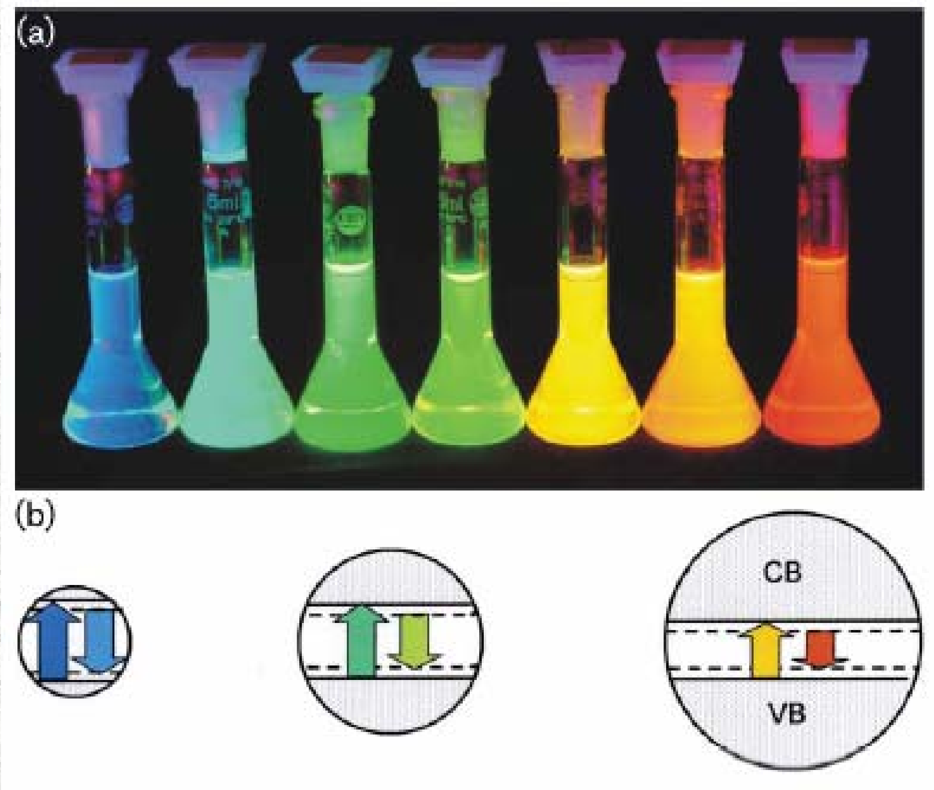
Photoelectron spectra of Hg clusters of nuclearity n
The 6p peak moves gradually towards the Fermi level
the band gap shrinks with increase in cluster size

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

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



Quantum Confinement Effects

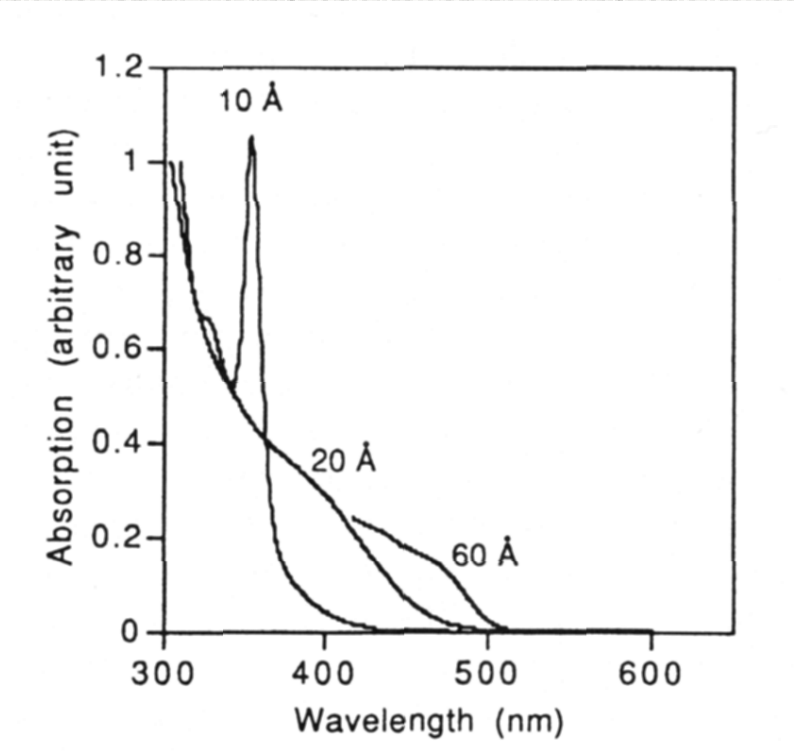


Fluorescence of CdSe–CdS core–shell nanoparticles with a diameter of 1.7 nm (blue) up to 6 nm (red), smaller particles have a wider band gap

Quantum Confinement Effects

℗ Optical properties
nc-TiO_2 is transparent

Blue shift in optical spectra of nanoparticles



Nanoscopic Materials

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

Nanostructured materials = nonequilibrium character

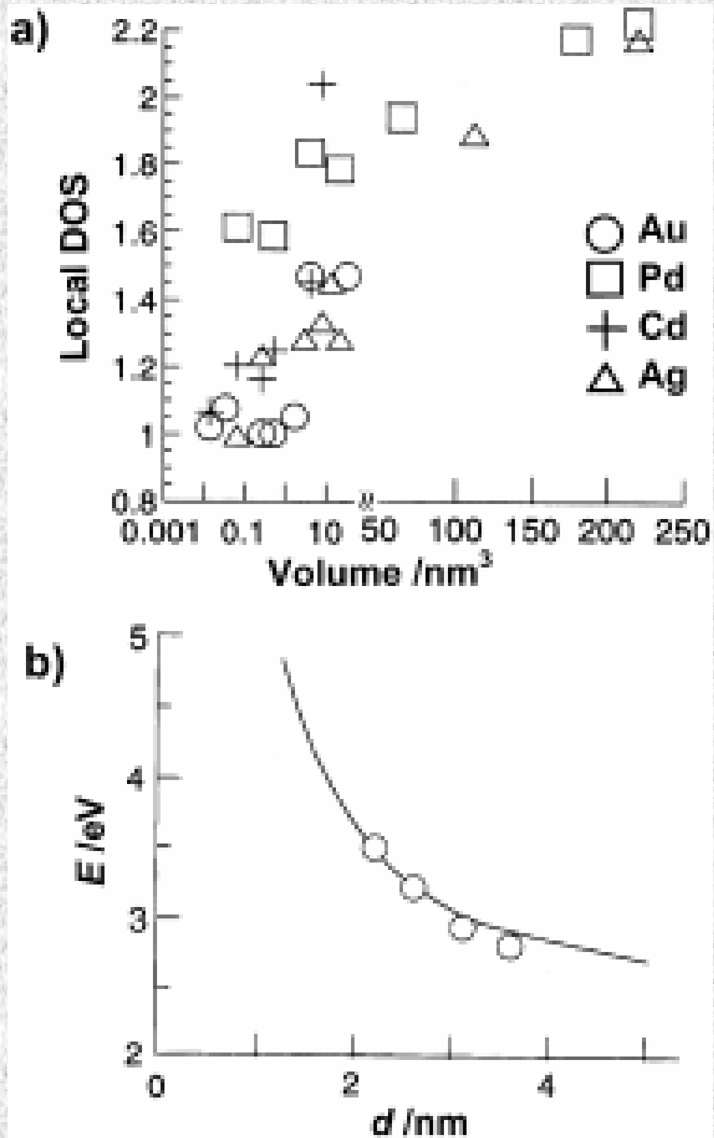
- **good sinterability**
- **high catalytic activity**
- **difficult handling**
- **adsorption of gases and impurities**
- **poor compressibility**

PREPARATION METHODS

Top-down: from bulk to nanoparticles
Bottom-up: from atoms to nanoparticles

a) Variation of the nonmetallic band gap with nanocrystal size

b) in CdS nanocrystals



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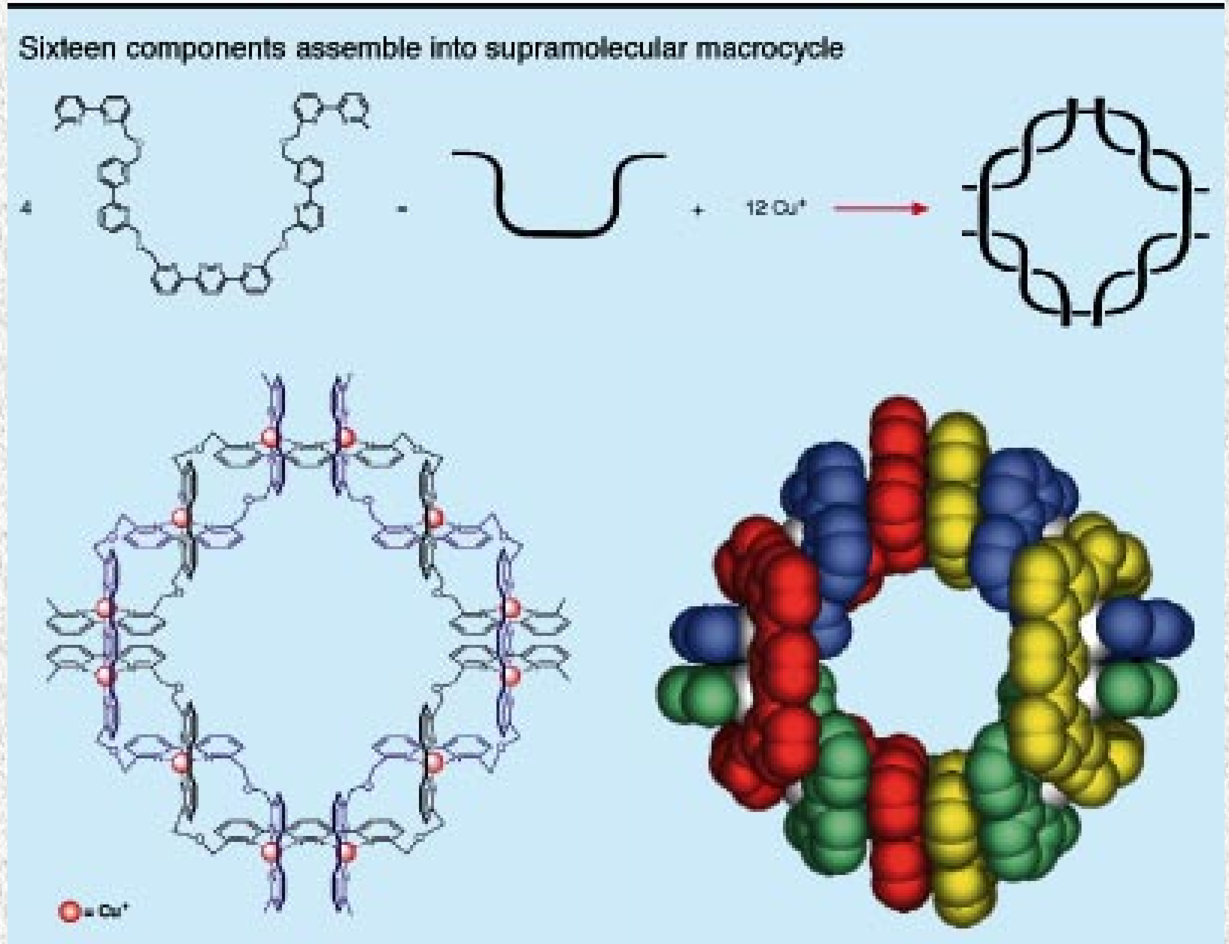
PREPARATION METHODS

Top-down: from bulk to nanoparticles
Bottom-up: from atoms to nanoparticles

Bottom-up Synthesis: Atom Up



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

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

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

NANOSTRUCTURAL MATERIALS

Bottom-up Synthesis

Thermal or Sonocative Decomposition of Precursors

$Fe(CO)_5 \longrightarrow$ nc-Fe + 5 CO   sono

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

Ar, 1500 °C

$PhSi(OEt)_3 + Si(OEt)_4 + H_2O \longrightarrow$ gel $\longrightarrow$ β-SiC

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

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

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

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

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

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

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

$MX_n + n\ NR_4[BEt_3H] \longrightarrow M + NR_4X + n\ BEt_3 + n/2\ H_2$

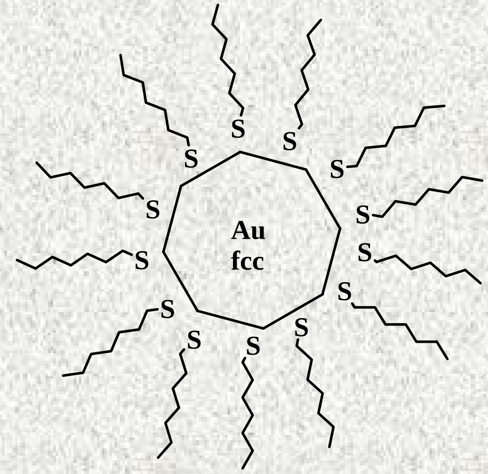
M = group 6 to 11; n = 2,3; X = Cl, Br

mixed-metal particles

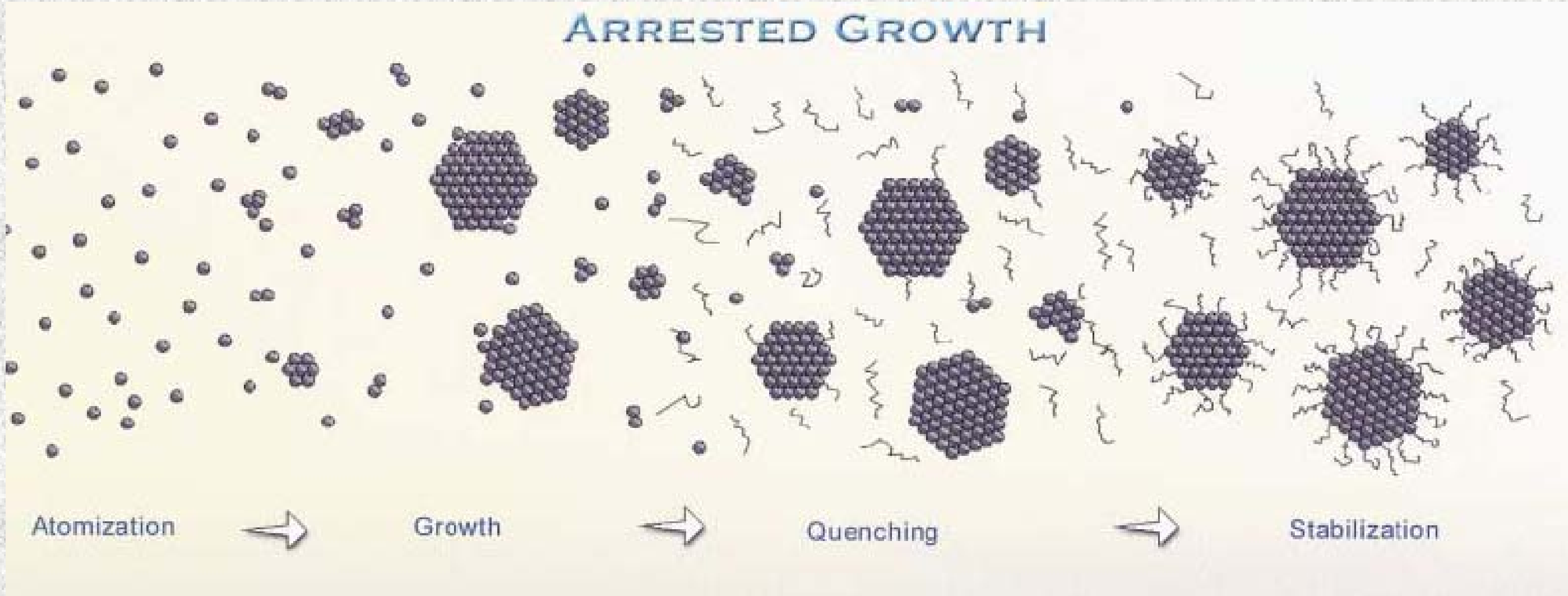
Bottom-up Synthesis

Au colloidal particles

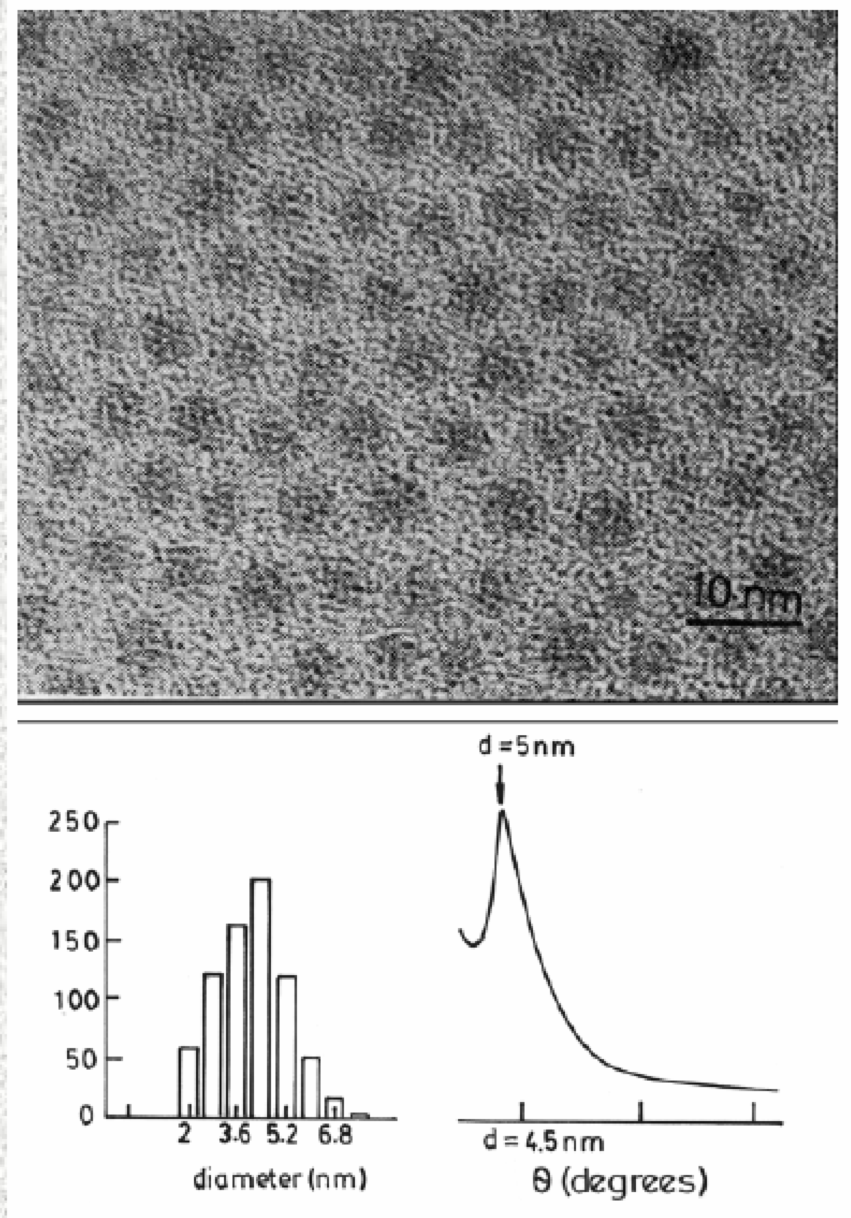
$HAuCl_4$ + $NaBH_4$ in toluene/H_2O system, TOABr as a phase transfer agent, Au particles in the toluene layer, their surface covered with Br, addition of RSH gives stable Au colloid



Bottom-up Synthesis



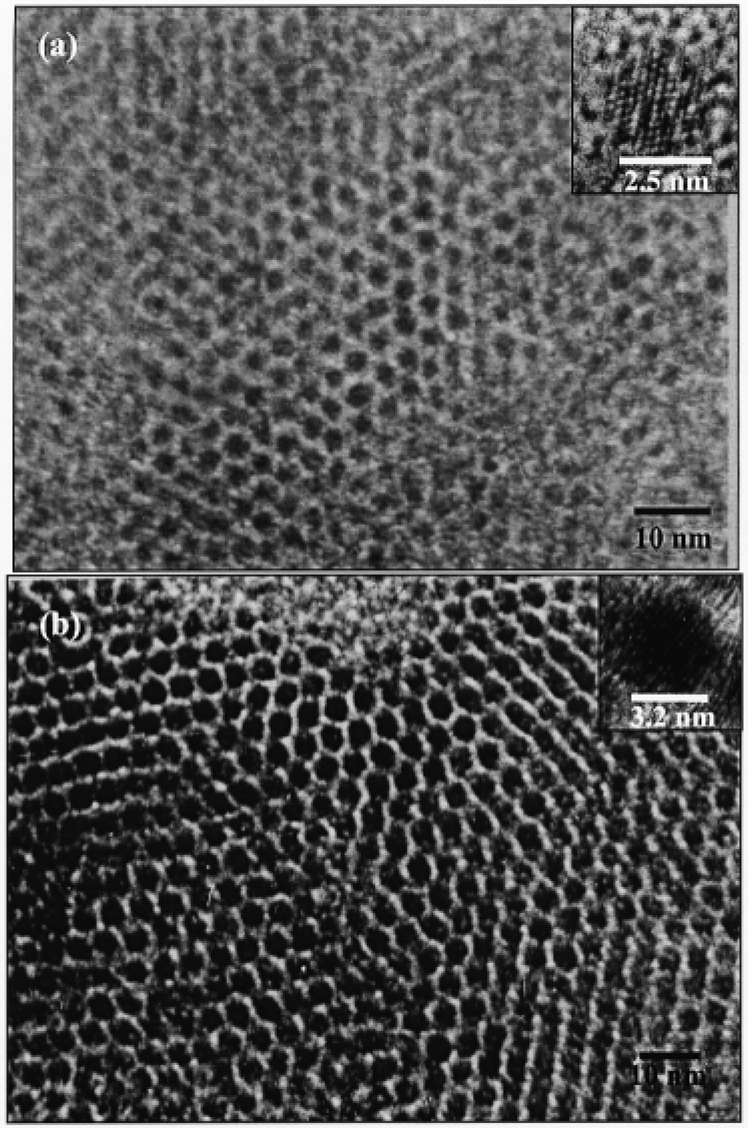
Two-dimensional array of thiol-derivatised Au particles (mean diam 4.2 nm)

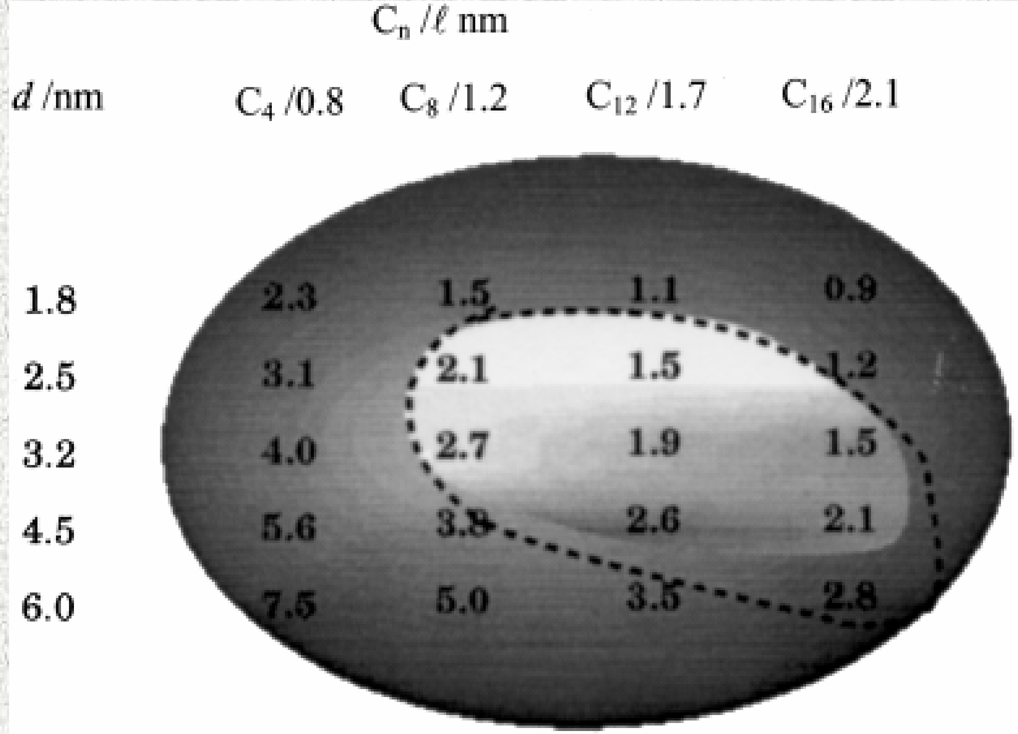


TEM micrograph of hexagonal arrays of thiolized Pd nanocrystals:

a) 2.5 nm, octane thiol

b) 3.2 nm, octane thiol





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

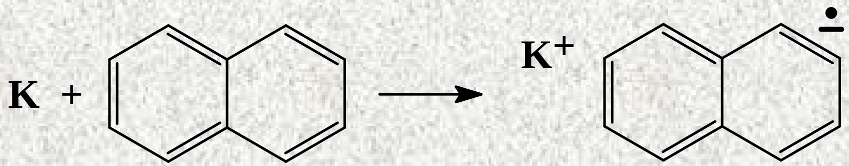
in dry anaerobic diglyme, THF, ethers, xylene

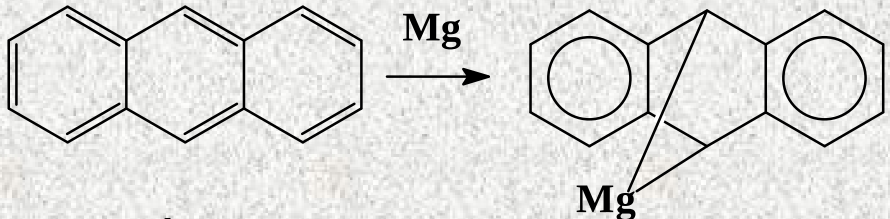
$NiCl_2$ + 2 K $\rightarrow$ Ni + 2 KCl

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

Reduction by Glycols or Hydrazine

"Organically solvated metals"





Alkalide Reduction

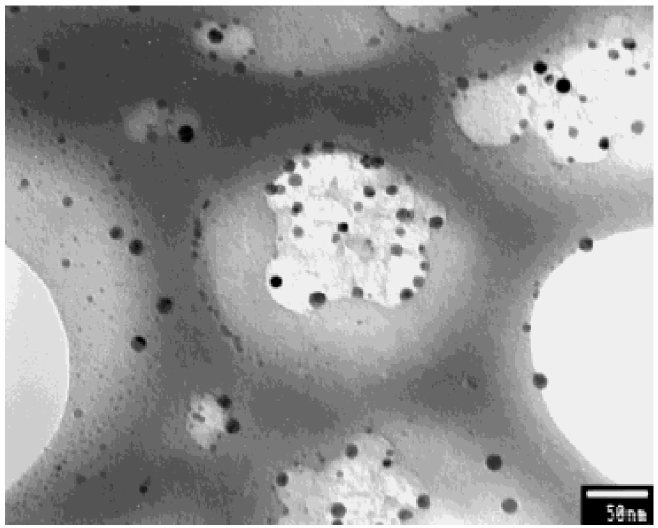
$13\ K^+(15\text{-crown-}5)_2Na^- + 6\ FeCl_3 + 2CBr_4$

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



Bottom-up Synthesis

🛠 **Reactions in Porous Solids – Zeolites, Mesoporous materials**

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

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

Ship-in-the-Bottle Synthesis

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

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

Conducting carbon wires

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

Radical polymerization

Pyrolysis gives carbon filaments

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

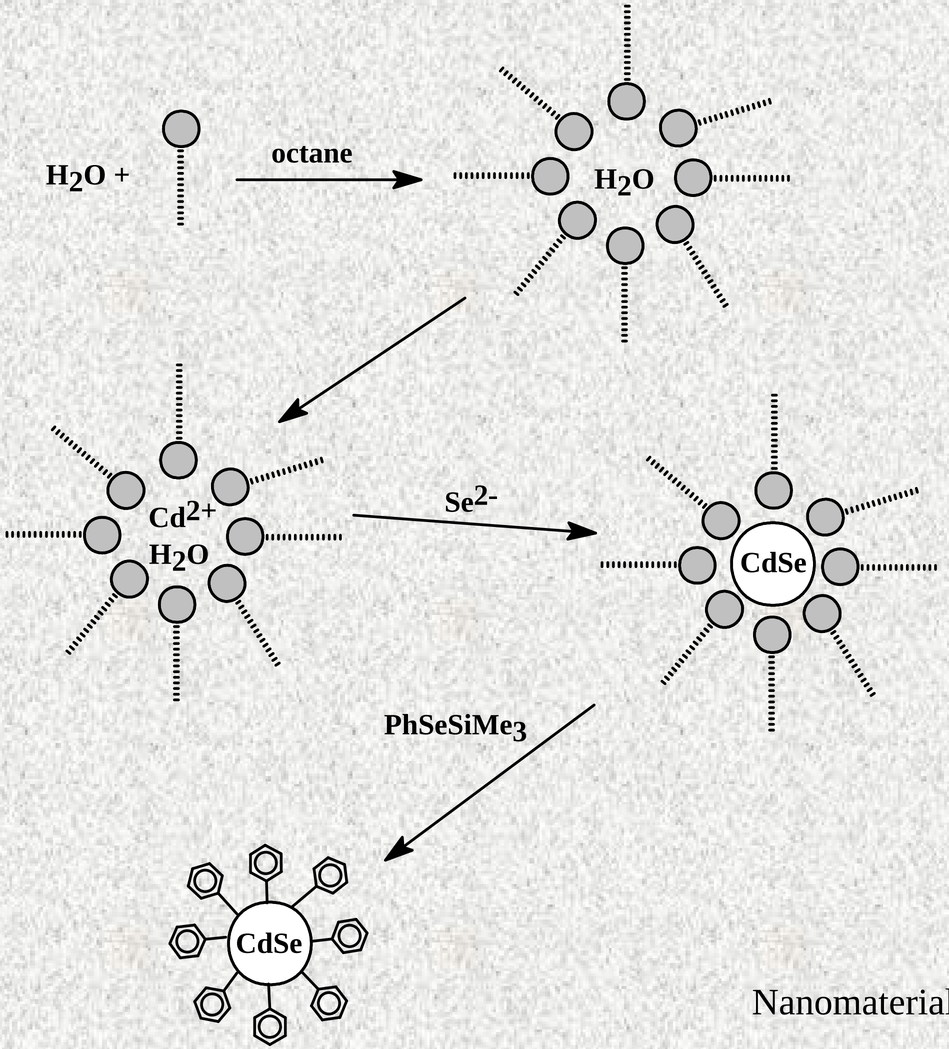
$$3Gd(NO_3)_3 + 5\ Fe(NO_3)_3 \longrightarrow Ga_3Fe_5O_{12} + 6\ O_2 + 24\ NO_2$$

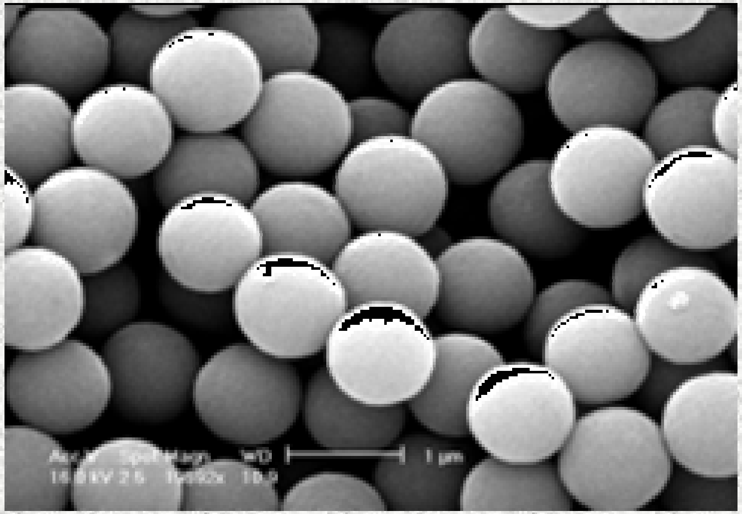
$$MnCl_2 + 2\ FeCl_3 + 4\ H_2O \longrightarrow MnFe_2O_4 + 8\ HCl$$

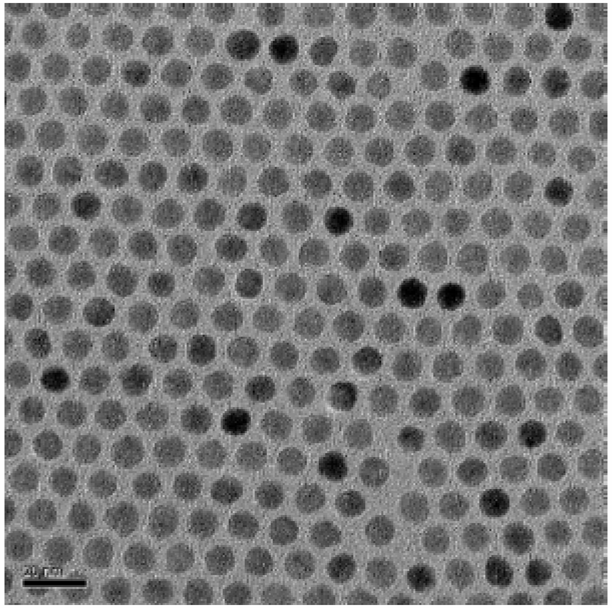
$Mn(NO_3)_2 + Fe(NO_3)_3$ **no go, why?**

Bottom-up Synthesis

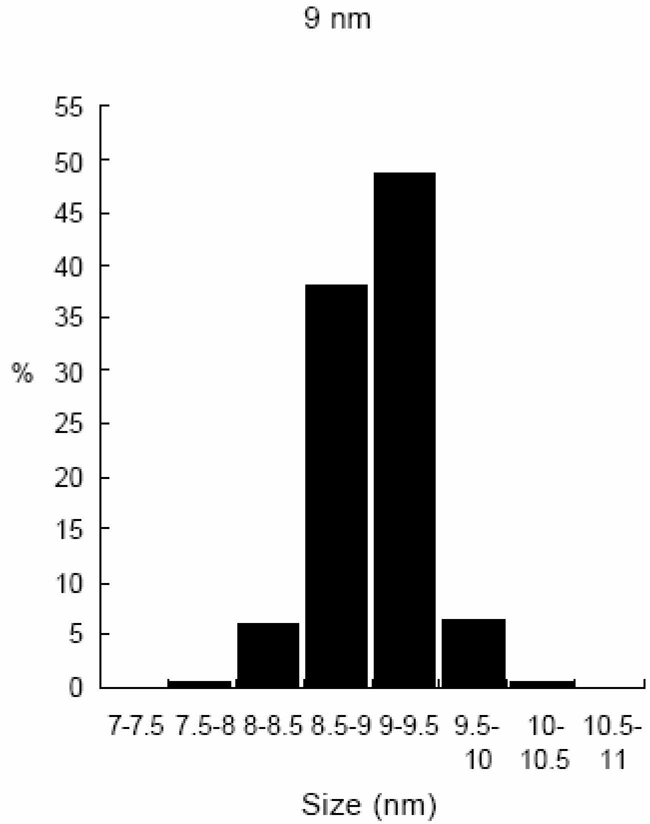
- **Inverse Micelles**







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



NANOSTRUCTURAL MATERIALS

Properties on Nanostructured Materials

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

Ⓟ Magnetic behavior
Single domain particles, large coercive field

Ⓟ Depression of melting points in nanocrystals
bulk Au mp 1064 °C 10 nm Au 550 °C

LaMer mechanism

Supersaturated solution

Burst of nucleation

Slow growth of particles without additional nucleation

Separation of nucleation and growth

Watzky-Finke mechanism

Slow continuous nucleation

Fast autocatalytic surface growth

Seed-mediated mechanism

Au nanoclusters as seeds

Bi, Sn, In, Au, Fe, Fe_3O_4

Other mechanisms

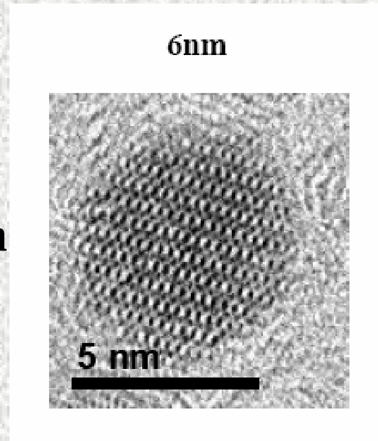
Digestive rippening

Surfactant exchange

Thermal Decomposition of Precursors

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

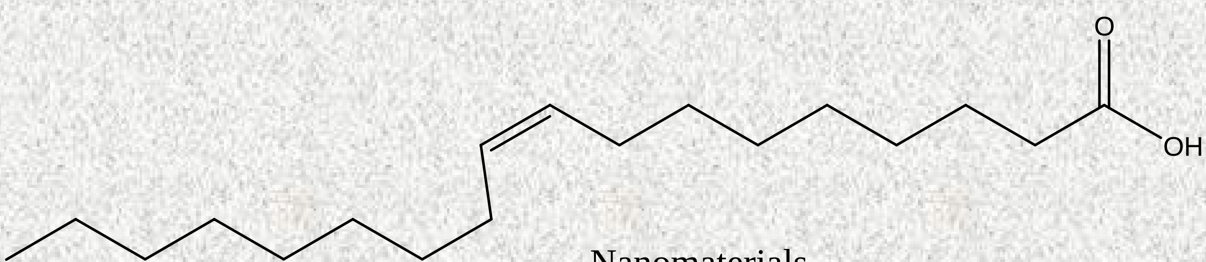
6 nm



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



Top-down Synthesis: Bulk Down

NANOSTRUCTURAL MATERIALS

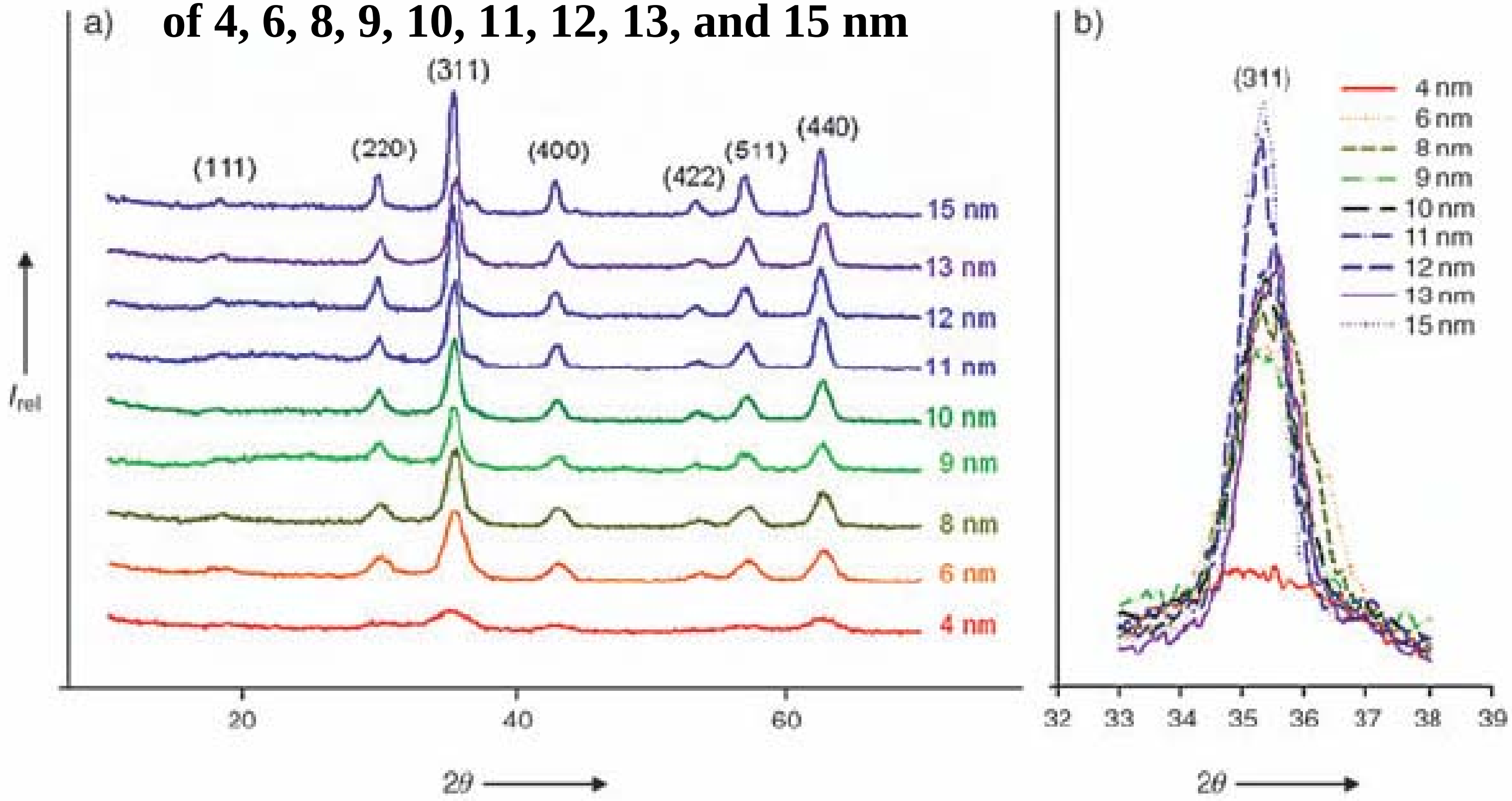
Top-down Synthesis: Bulk Down

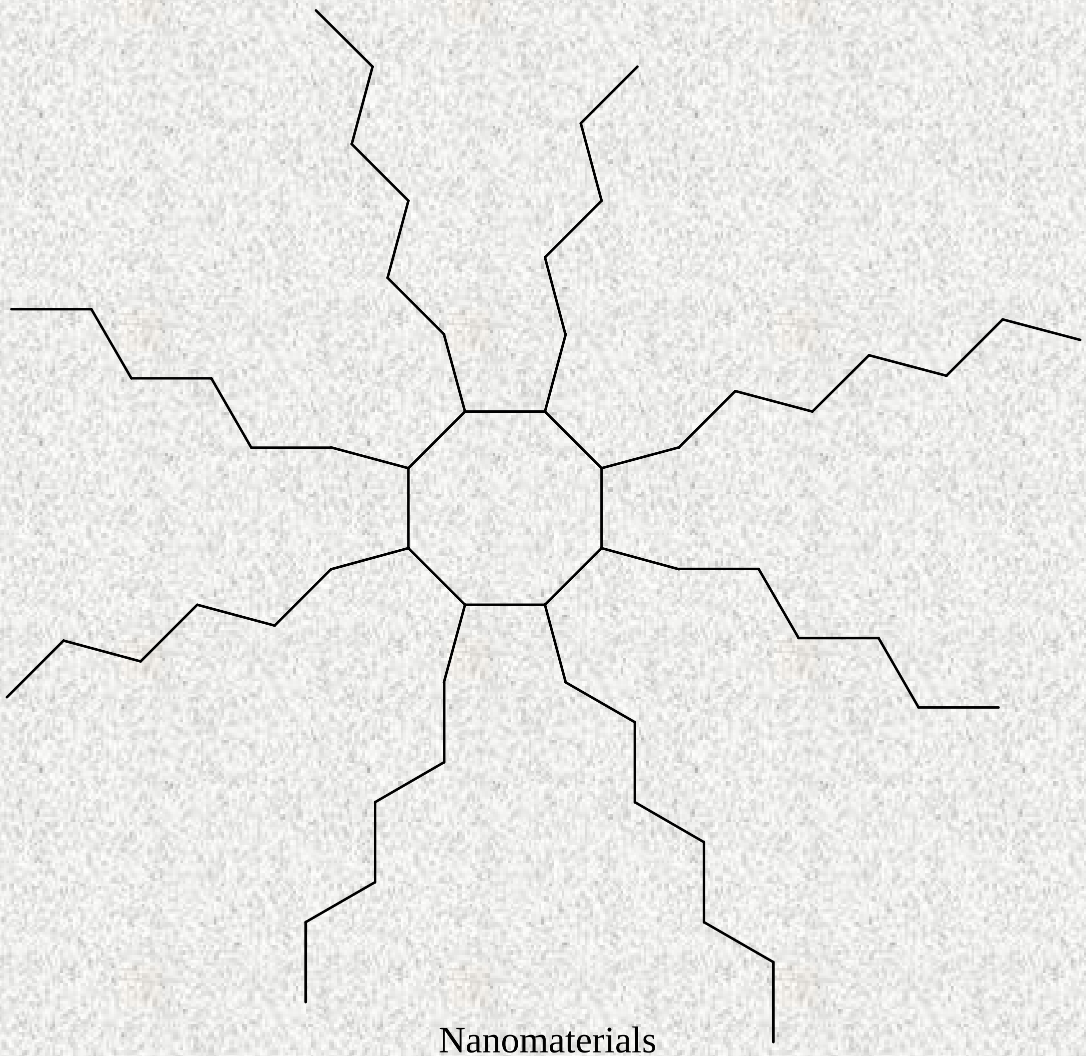
🛠 **Introduction of Crystal Defects (Dislocations, Grain Boundaries)**

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

🛠 **Crystallization from Unstable States of Condensed Matter**
✧ **Crystallization from Glasses**
✧**Precipitation from Supersaturated Solid or Liquid Solutions**

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

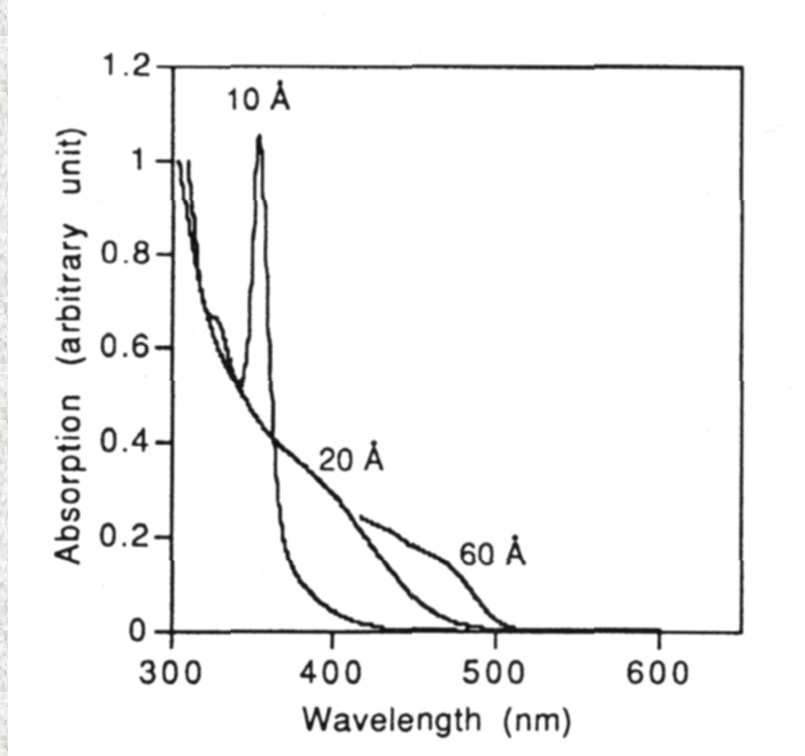




NANOSTRUCTURAL MATERIALS

Ⓟ Optical properties
nc-TiO_2 is transparent

Blue shift in optical spectra of nanoparticles

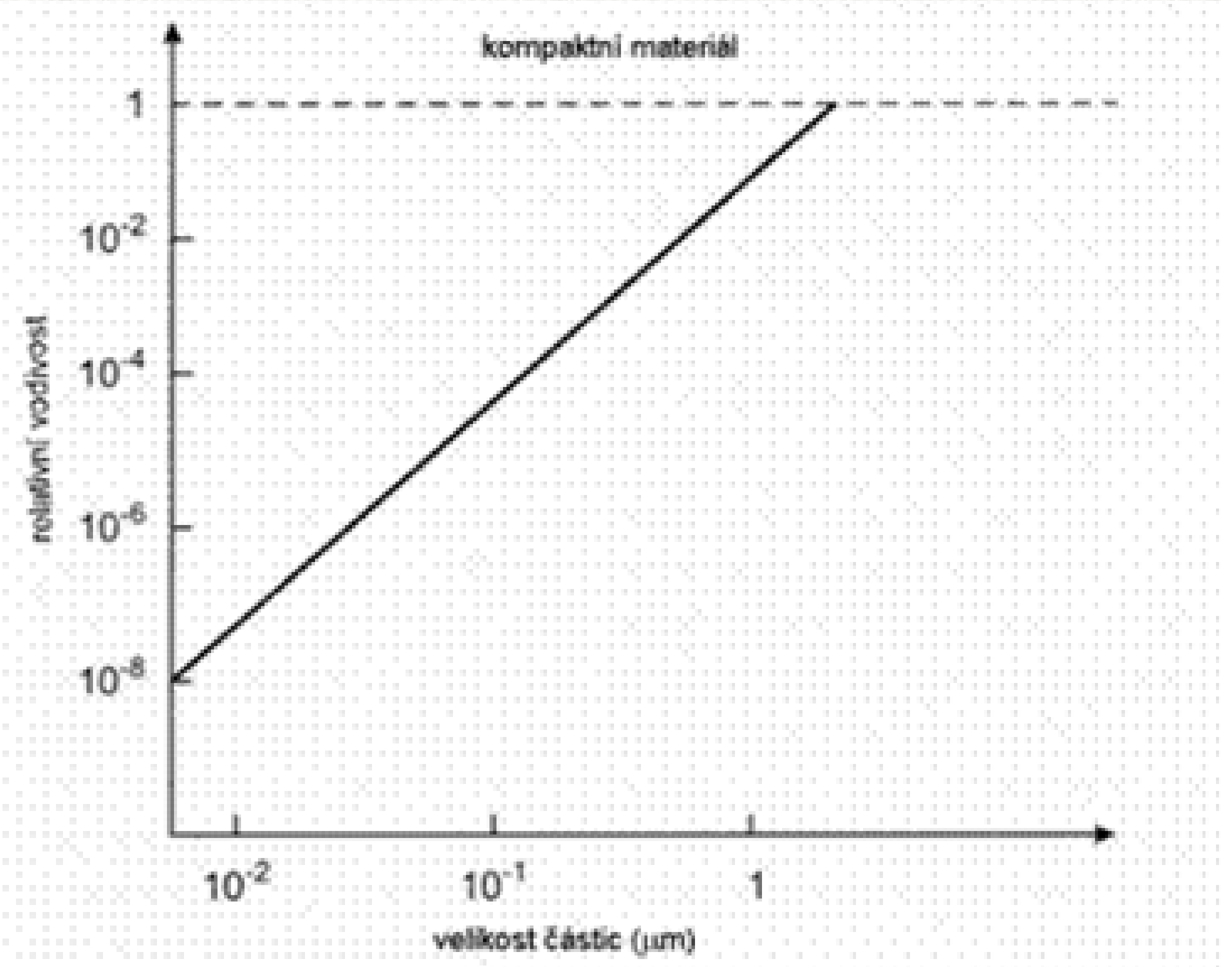


NANOSTRUCTURAL MATERIALS

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

ⓟ Plasticity of nanocrystalline ceramics

Electrical conductivity



Applications

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

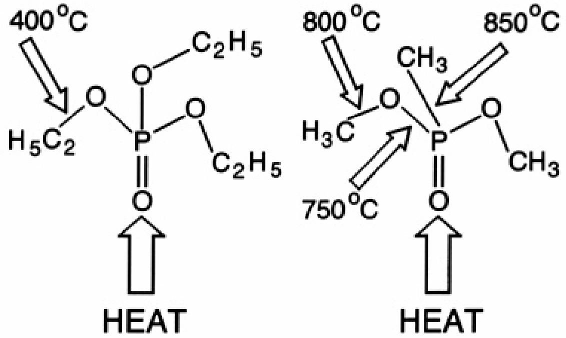


Figure 3. Cleavages of bonds in $(C_2H_5O)_3P(O)$ and DMMP under thermal decomposition condition.

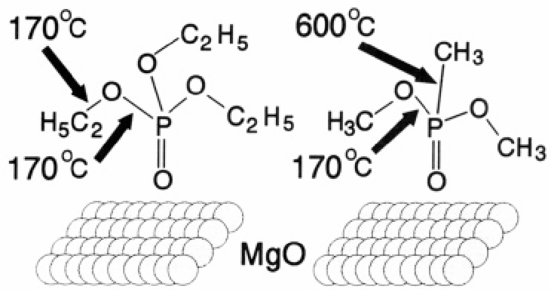
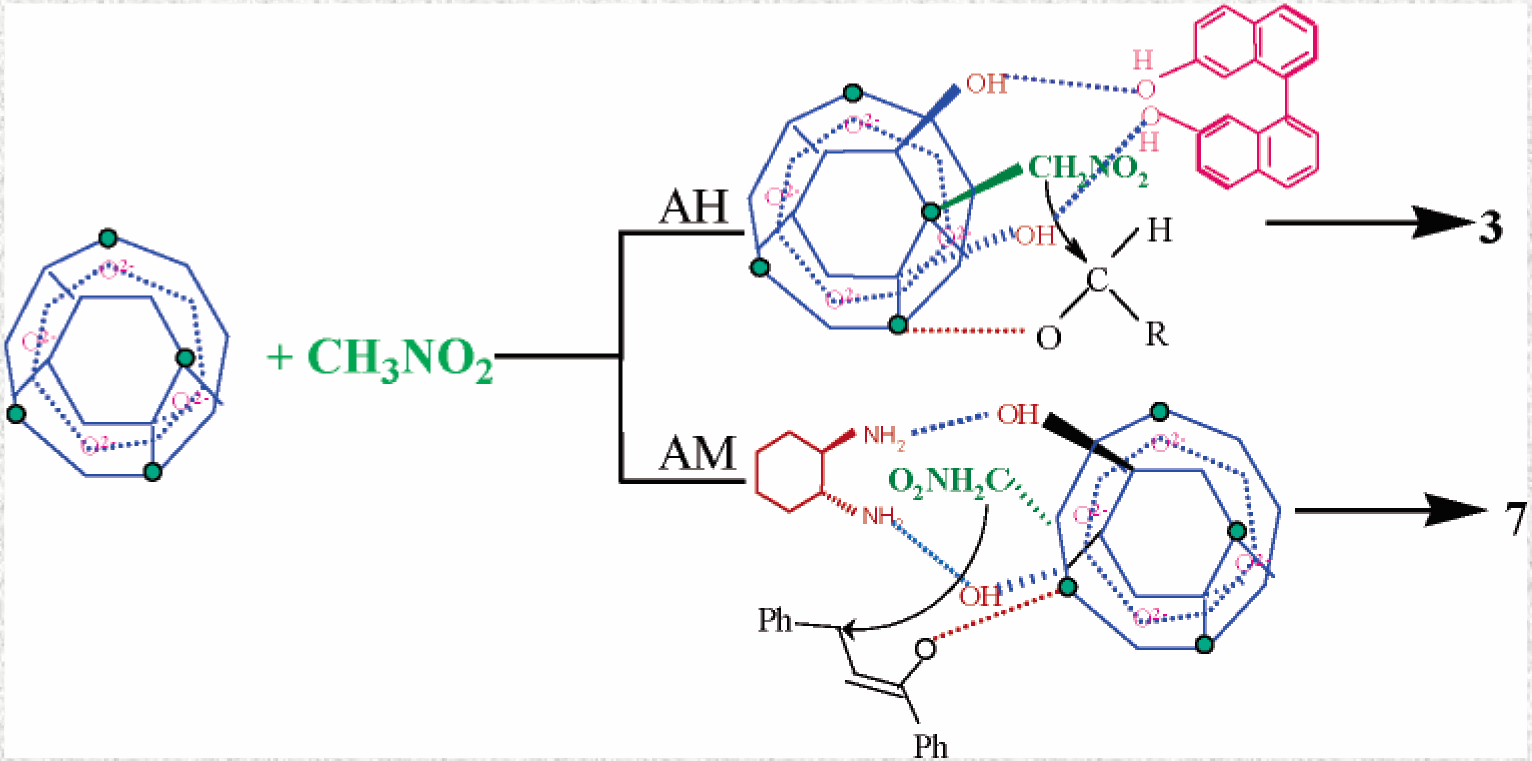


Figure 4. Cleavages of bonds of $(C_2H_5O)_3P(O)$ and DMMP on MgO.

Asymmetric heterogeneous catalysis on nanoparticles



CNT growth