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**

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

Unique Features of the Nano-scale

Smallness: physical size

Size compatibility with the basic biological structures (cells, liposomes, enzymes…)
delivery vehicles for medical applications
surface chemistry - functionalization

Smallness: surface versus bulk forces

A large to surface to volume ratio
Bulk forces - gravity - unimportant for nanoparticles
Surface forces - Brownian motion - colloidal particles never settle

Unique Features of the Nano-scale

Smallness: surface versus bulk atom properties

Increasing surface to bulk atom number ratio with decreasing size enhances the role of surface (boundary)

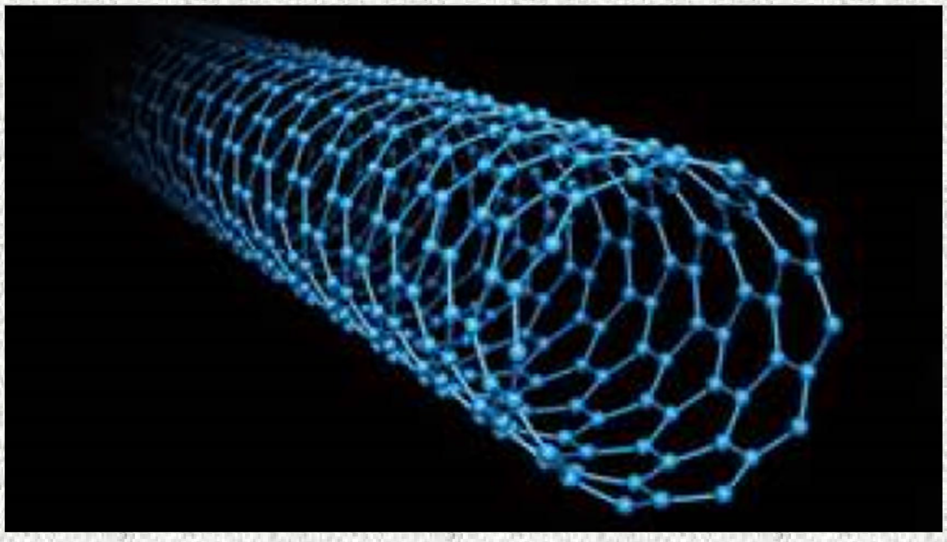
- surface phonon scattering
- surface electron scattering
- surface atom electric charge distribution
- surface atom spins in ferromagnetic, ferrimagnetic, and antiferromagnetic materials - transition to superparamagnetic state

Unique Features of the Nano-scale

Chemical bonding in nanostructures

Single wall carbon nanotubes (SWCNT)
hexagonal bonding of C in graphite and graphene - sp^2

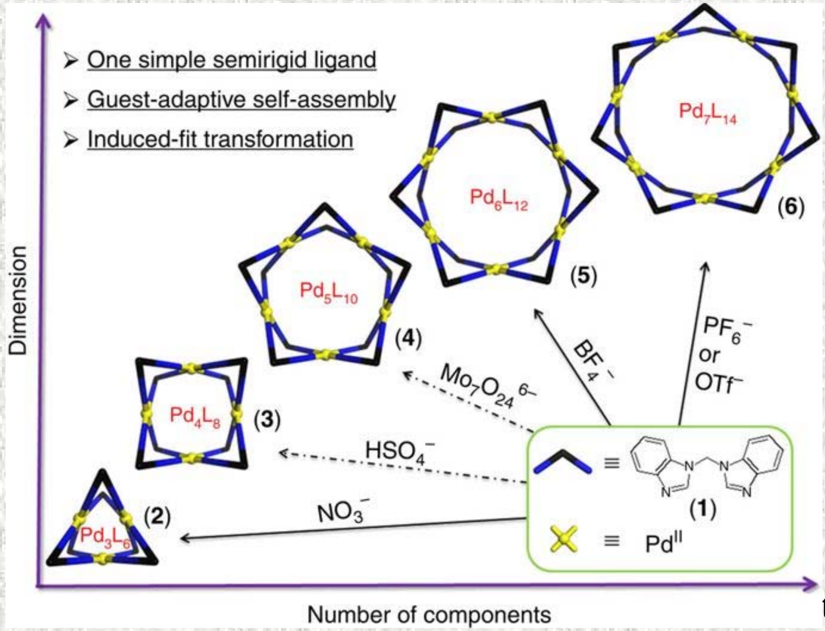
C bonding in SWCNT is contorted $sp^2 \rightarrow sp^3$
Chirality - variable amounts of twisting



Unique Features of the Nano-scale

Self-assembly

combination of particles, atoms, or molecules, selfassemble into predetermined new materials and structures (micelles, SAM, MOF, DNA, proteins, ...)



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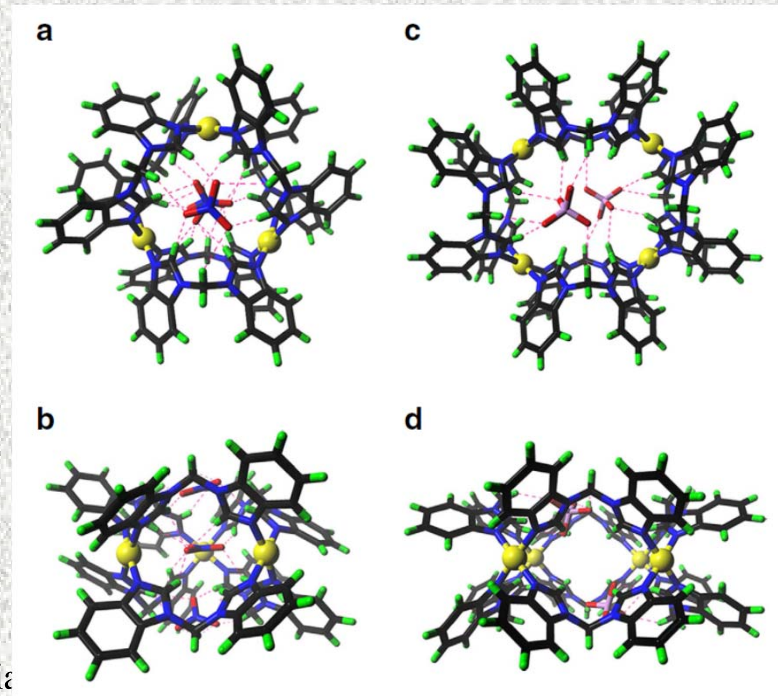
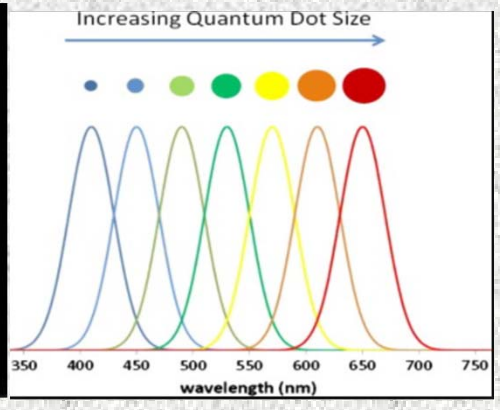


Unique Features of the Nano-scale

Quantum confinement and tunneling

Electron quantum confinement - the spatial restrictions of nanoscale structures confine electrons resulting in the presence of energy levels whose values and spacing depend on the degree of confinement = size

Quantum tunneling (the opposite of confinement) - an electron wave function leaks across classically forbidden energy barriers of nano-scale size



Unique Features of the Nano-scale

Quantum confinement and tunneling

Electron in a box - an infinitely deep 3D box
the difference between two energetically adjacent electron energy levels:

$$E_{n+1} - E_n = \frac{h^2}{8m_e L^2}[2n + 1]$$

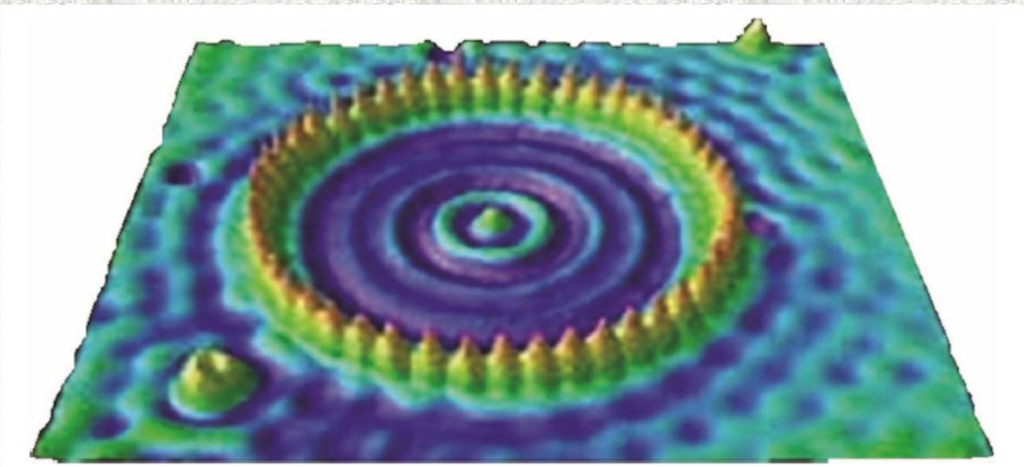
h is Planck's constant, m_e is the electron mass, Lx L x L is the confining volume

Decreasing L increases the inter-level spacing
Nanoscale - quantization of energy due to confinement
Micro- and larger scales - energy appears as a continuum

Unique Features of the Nano-scale

Wave-particle duality

Quantum interference between particle waves that are scattered off the boundaries of a nanostructure thereby forming a standing wave



Atoms arranged on a surface form a corral confining their valence electrons. The probability density image determined by the wave function distribution captured by STM - wave function leakage into a positively biased scanning probe

Unique Features of the Nano-scale

Relativistic phenomena at the nano-scale

In 2D materials, graphene - mass-less Dirac electrons

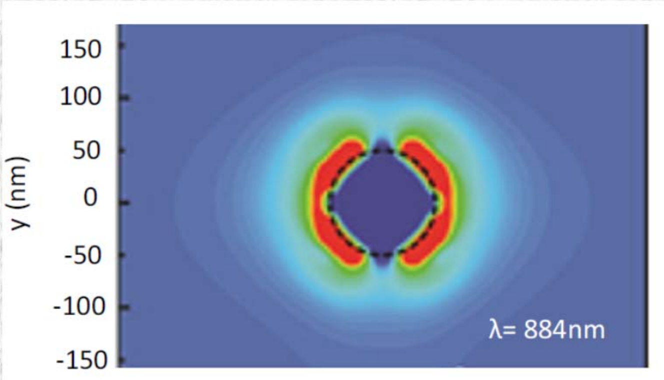
Mass-less behavior can produce

- ballistic (collision-free) charge transport
- unusual Hall effects
- enormously high carrier mobilities
- topologically dependent phases

Unique Features of the Nano-scale

Electromagnetic interactions with nanostructures

Plasmonic mode of a metal nanoparticle excited by the electric field of an incoming light wave - a cooperative excitation of free valence electrons



Relaxation

- reradiation of photons from the nanoparticle
- collisions of oscillating valence electrons within the particle

The electric field distribution of the metal nanoparticle

- radiating far-field component = the emitted photons
- near-field component around the nanoparticle

Unique Features of the Nano-scale

Fluctuations

Thermodynamic fluctuations - a system gets smaller, fluctuations away from the thermodynamic equilibrium distribution become important, the statistics of huge numbers of particles

Quantum fluctuations - the small separation distances between objects at the nano-scale, the temporary change ΔE in the amount of energy (or mass of particles) that can occur in a region for a time Δt, the fluctuation time - conservation of energy is violated during the fluctuation time

$$\Delta E \, \Delta t \geq \hbar$$

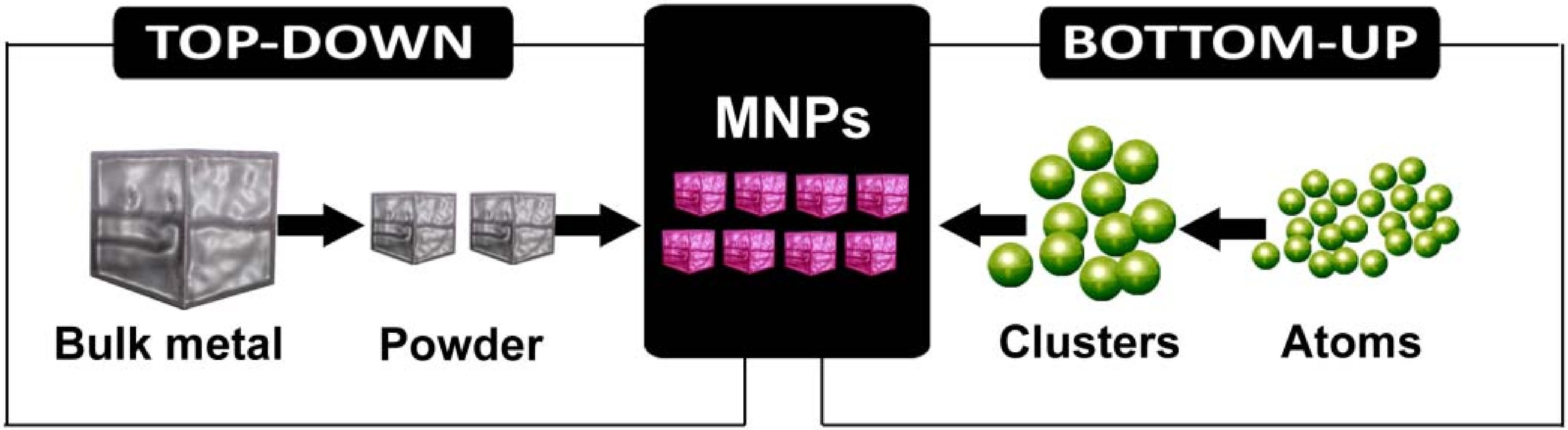
Unique Features of the Nano-scale

Fluctuations

Casimir force (theor. 1948, exp. 1996) - quantum phenomenon, a pressure that pushes objects having a nano-scale separation together, vacuum energy, fluctuating electromagnetic waves, restricted wavelengths of standing waves between nanoobjects = lower energy of vacuum between nanoobjects, pressure form outside

The Casimir force affects friction and results in striction (the permanent adhesion of surfaces)
- a critical problem for moving systems at the nano-scale
- the force increases with decreasing distance

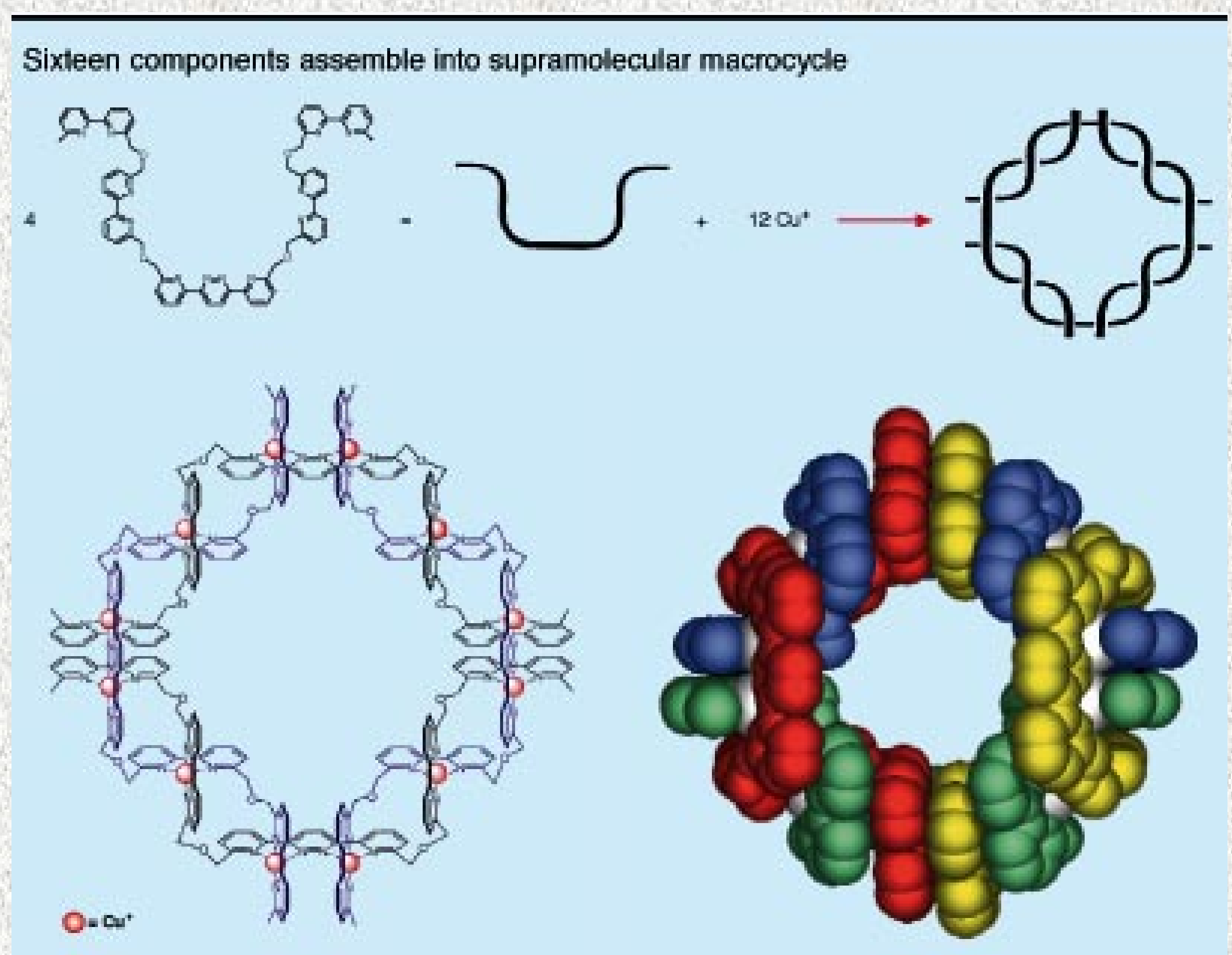
Synthesis Methods



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

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

Bottom-up Synthesis

🛠 **Thermal or Sonocative Decomposition of Precursors**

$Fe(CO)_5$ ⟶ nc-Fe + 5 CO sono

$[Co(en)_3]WO_4$ ⟶ nc-WC – 23% Co

Ar, 1500 °C

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

$(CH_3SiHNH)_n$ (l) ⟶ Si_3N_4 + SiC laser

300-400°C

$M(BH_4)_4$ (g) ⟶ borides MB_{2+x} (M = Ti, Zr, Hf)

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

H_2, 550 °C

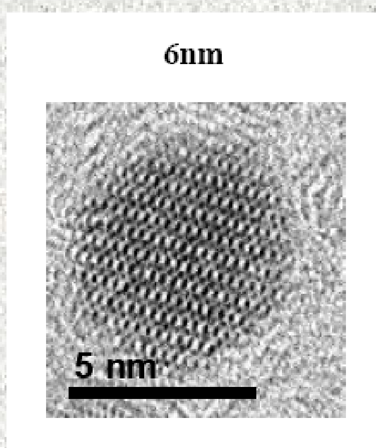
⟶ $SiO_2/Ag/Cu$

Bottom-up Synthesis

Thermal decomposition of precursors

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

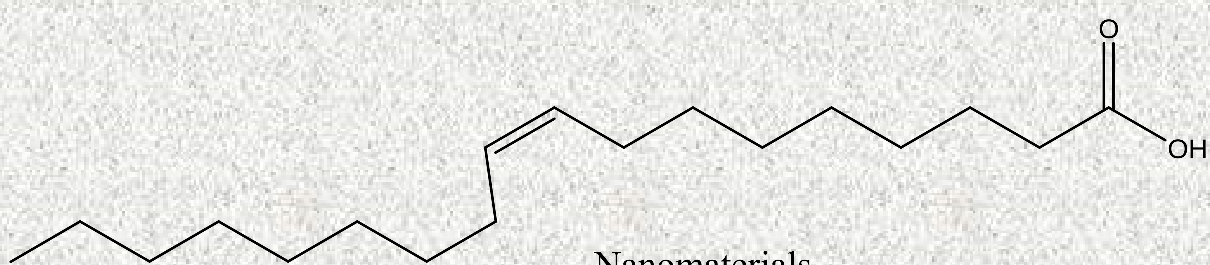
6 nm



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



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

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

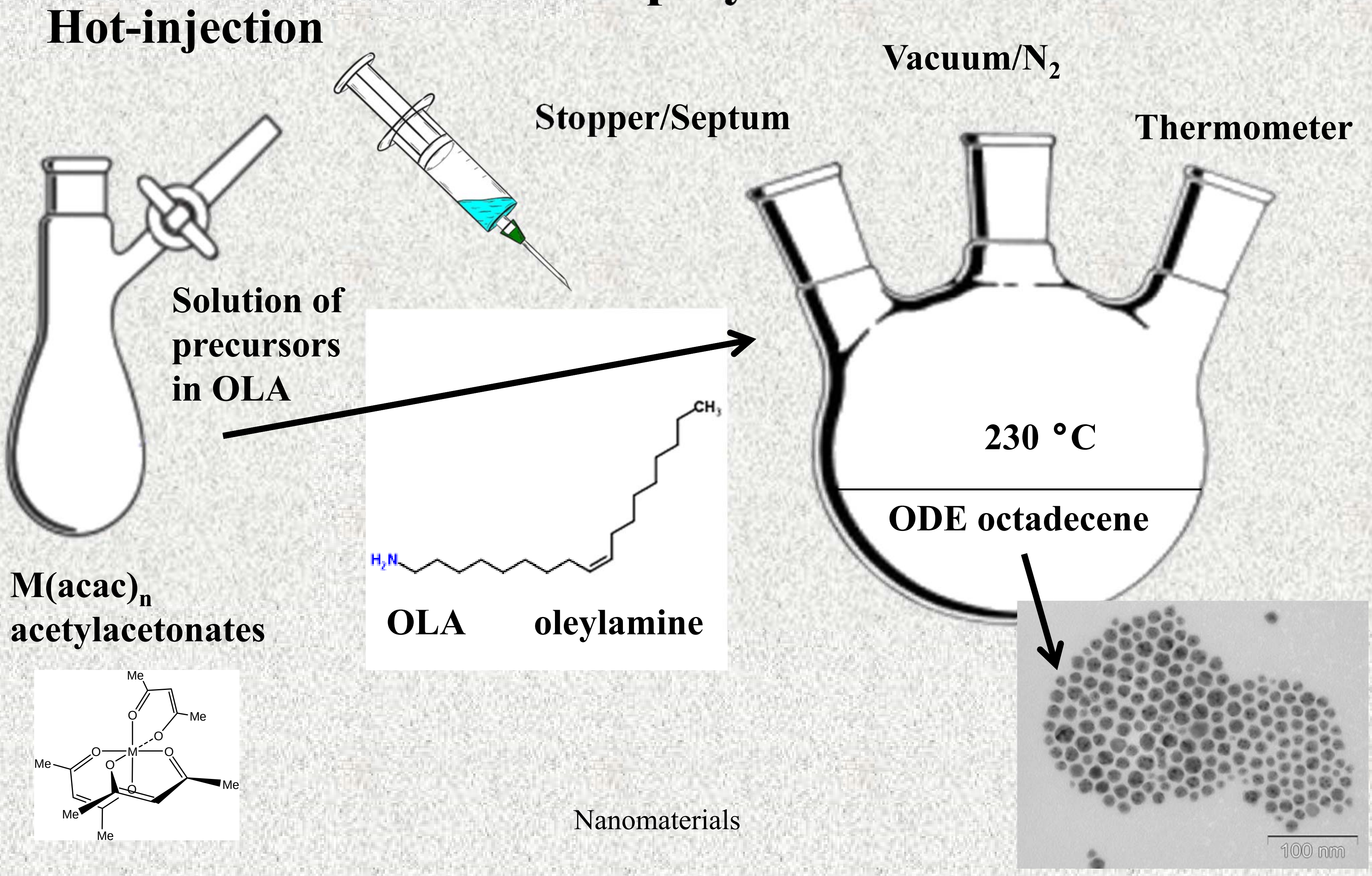
$$TiCl_4 + 2\ NaBH_4 \longrightarrow TiB_2 + 2\ NaCl + 2\ HCl + H_2$$

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

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

mixed-metal particles

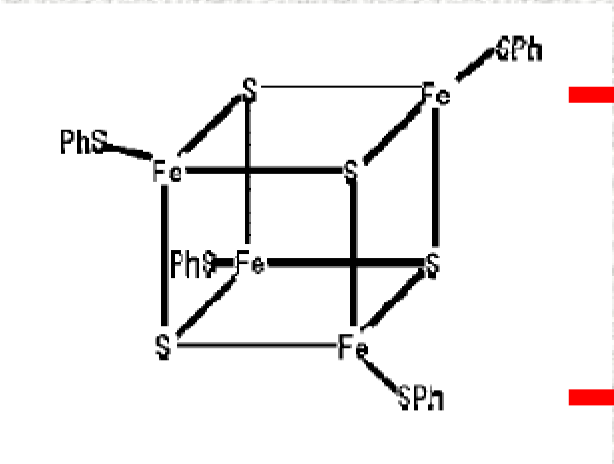
Bottom-up Synthesis



Bottom-up Synthesis

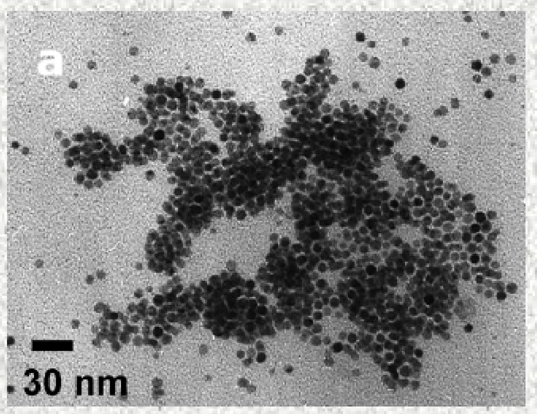
Phase Control

$[N^nBu_4]_2[Fe_4S_4(SPh)_4]$

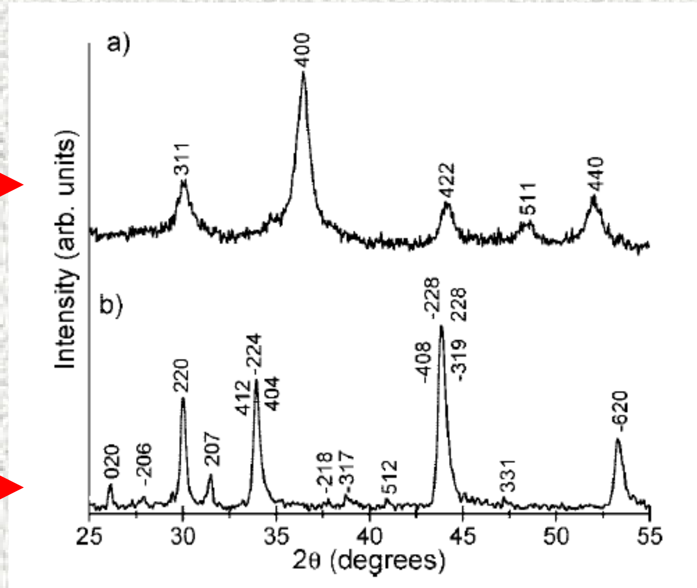


180 °C in octylamine

200 °C in dodecylamine



pyrrhotite Fe_7S_8

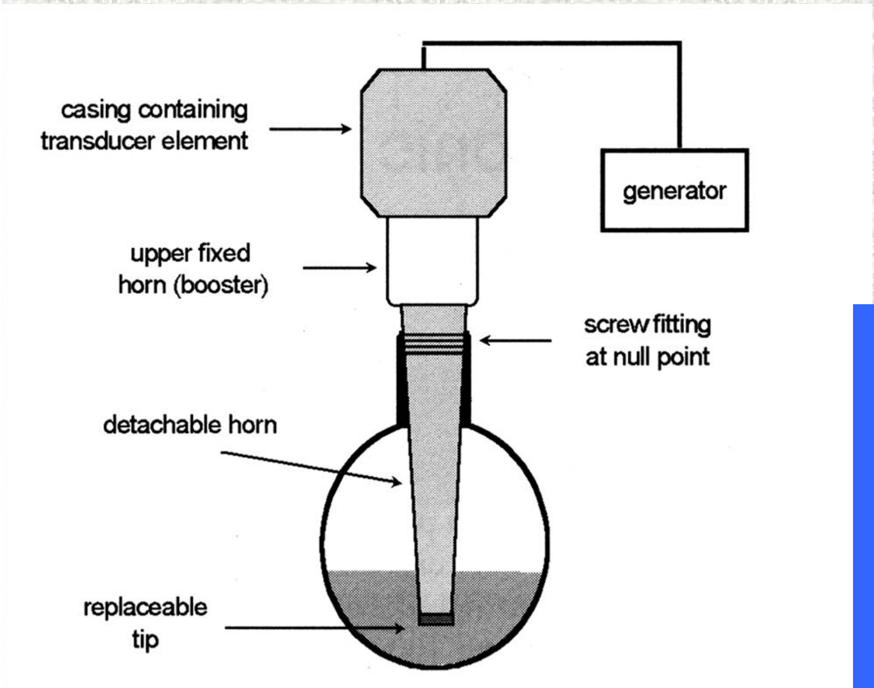


greigite Fe_3S_4

thiospinel, the sulfide analogue of magnetite

Bottom-up Synthesis

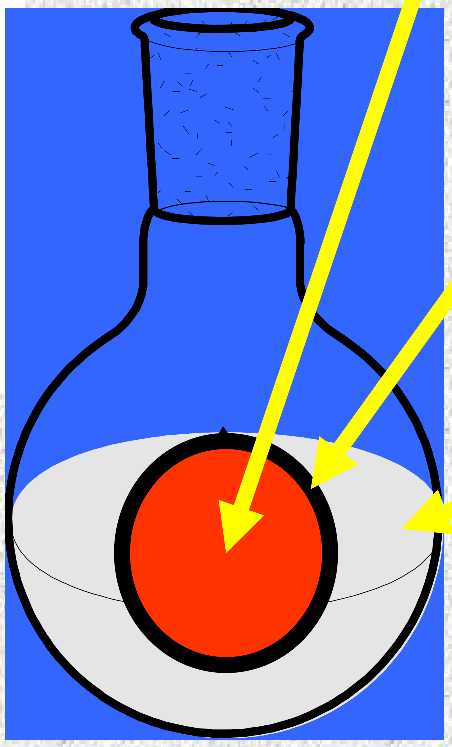
Sonocative decomposition of precursors



Cavity interior
Filled with gases and vapors
5 000 – 20 000 °C / 500 – 1500 bar

Surrounding liquid layer
2000 °C

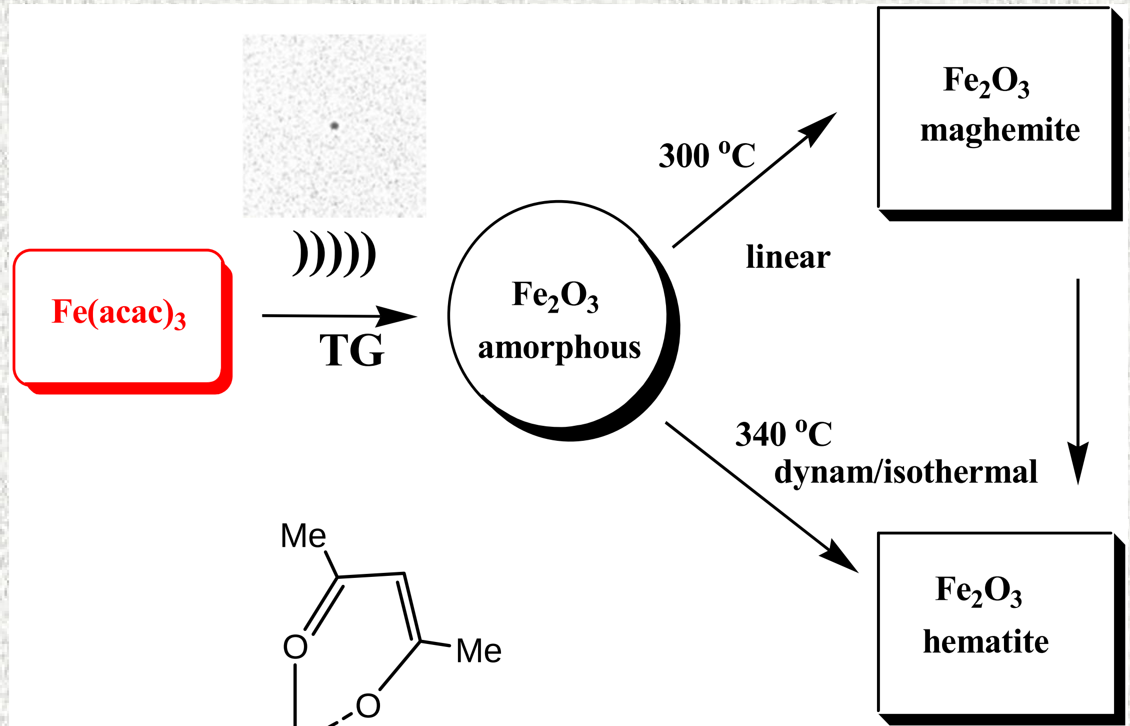
Bulk liquid
shock waves
shear forces

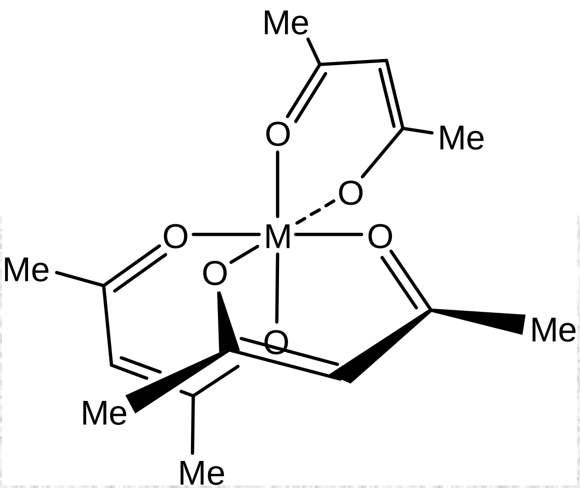


Cavitation
creation, growth, and implosive collapse of bubbles in a liquid

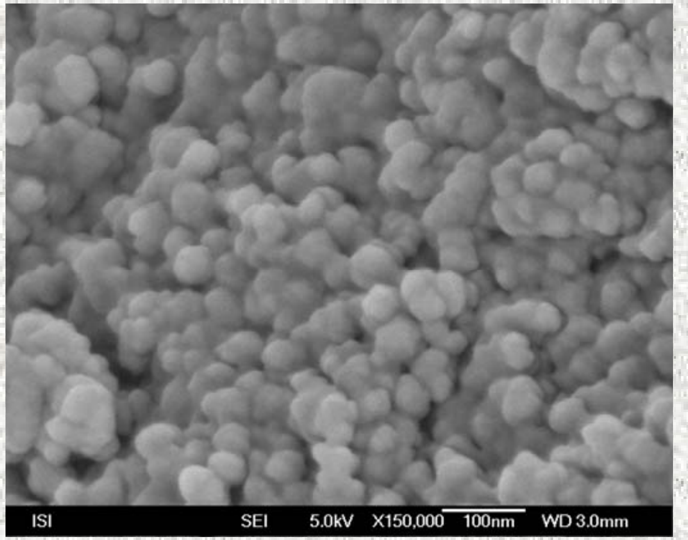
Bottom-up Synthesis

Sonocative decomposition of precursors





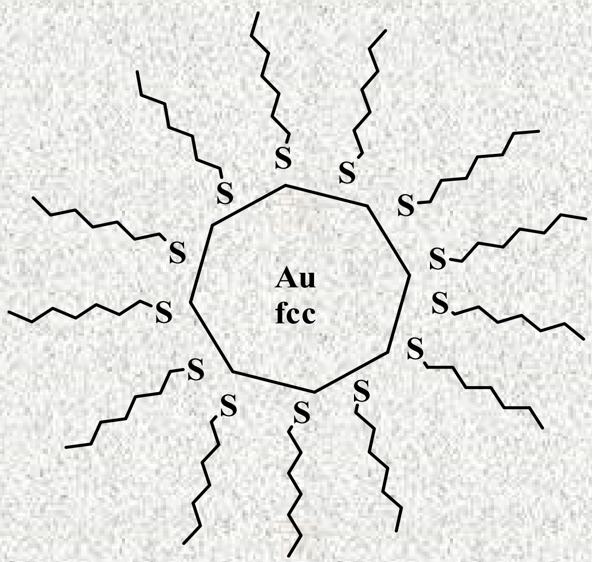
Particle size 20 - 30 nm
Spherical shape
Uniform size distribution



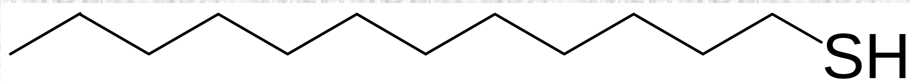
Bottom-up Synthesis

Au colloidal particles

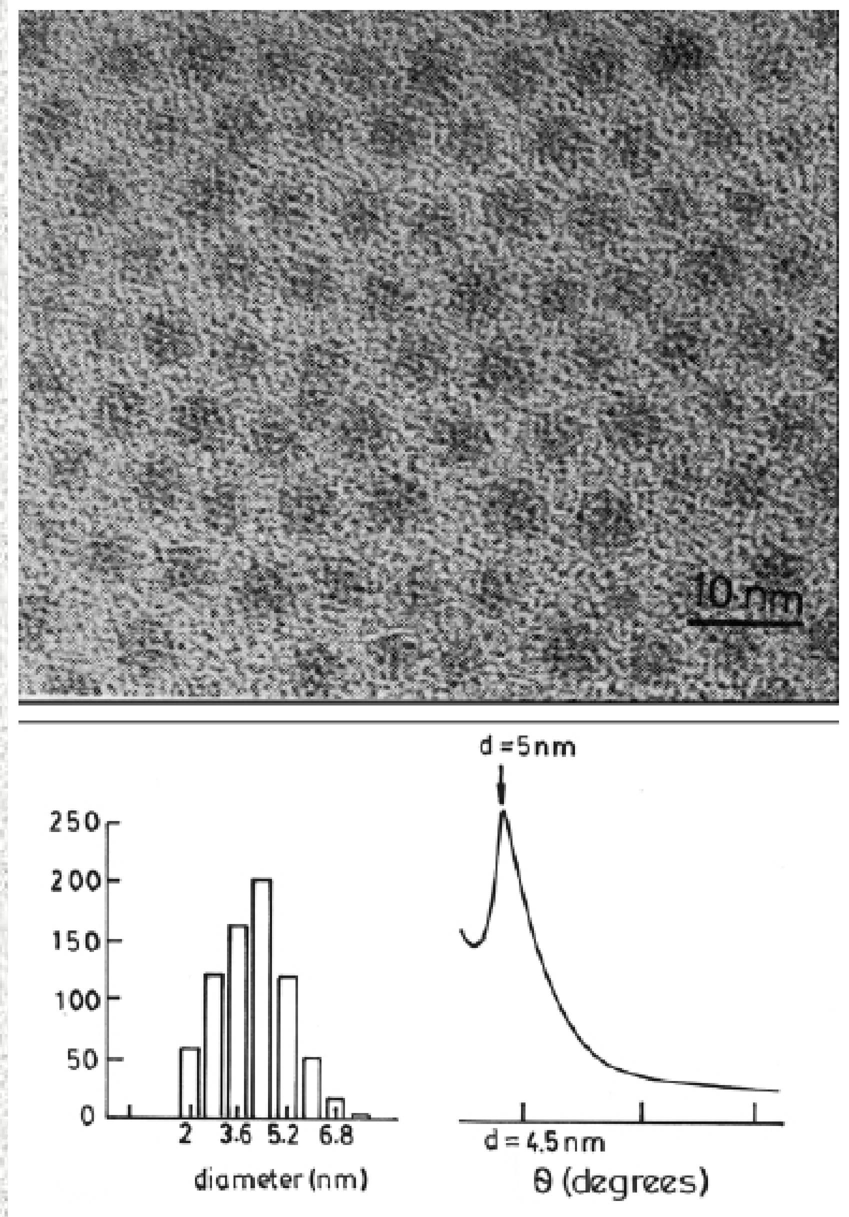
$HAuCl_4$ + $NaBH_4$ in toluene/H_2O system, TOABr as a phase transfer agent, Au particles in the toluene layer, their surface covered with Br, addition of RSH gives stable Au colloid



Bottom-up Synthesis



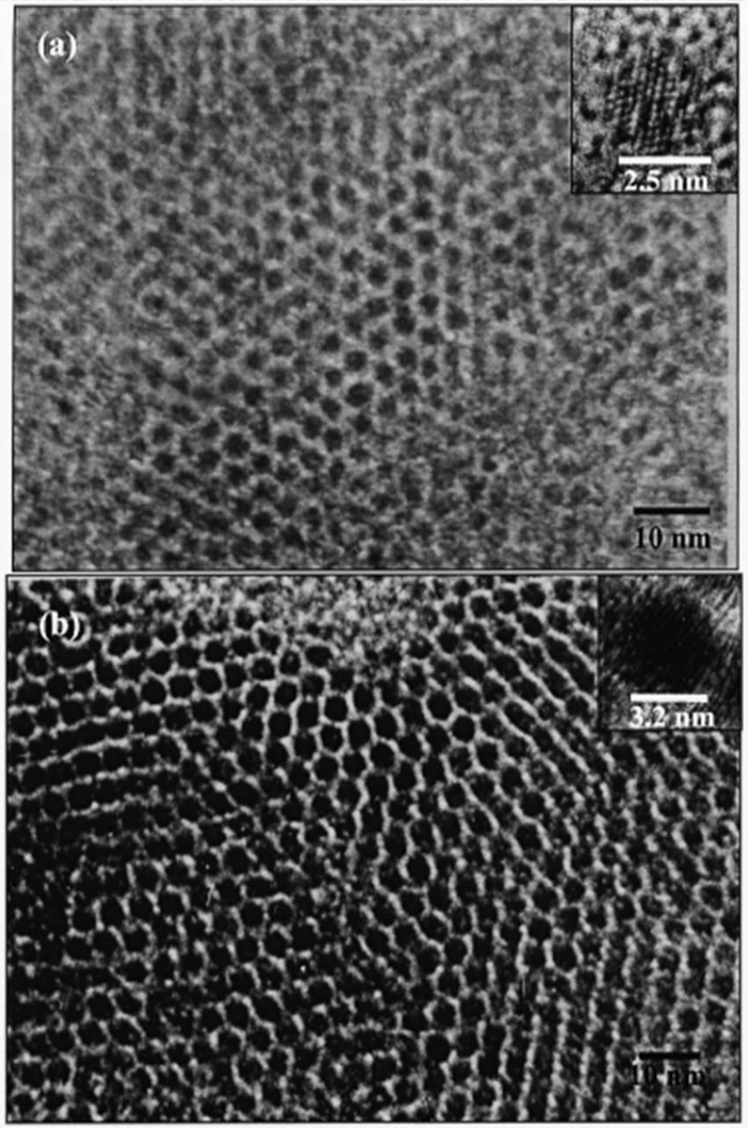
Two-dimensional array of thiol-derivatised Au particles (mean diam 4.2 nm)

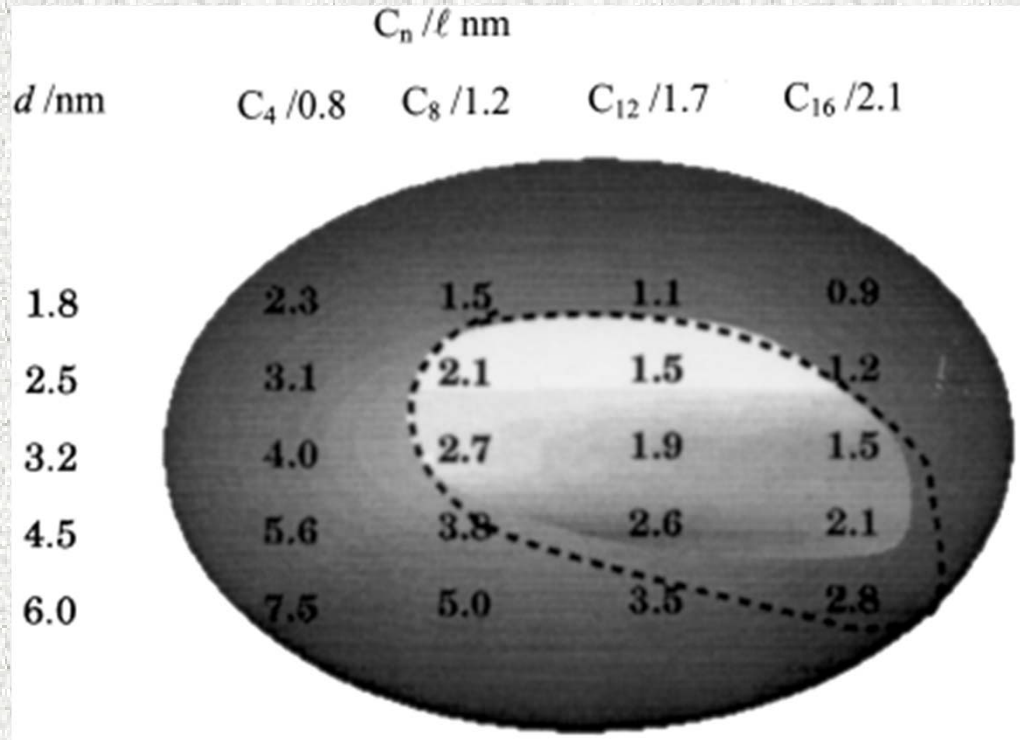


TEM micrograph of hexagonal arrays of thiolized Pd nanocrystals:

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 - 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

Bottom-up Synthesis

Alkali Metal Reduction

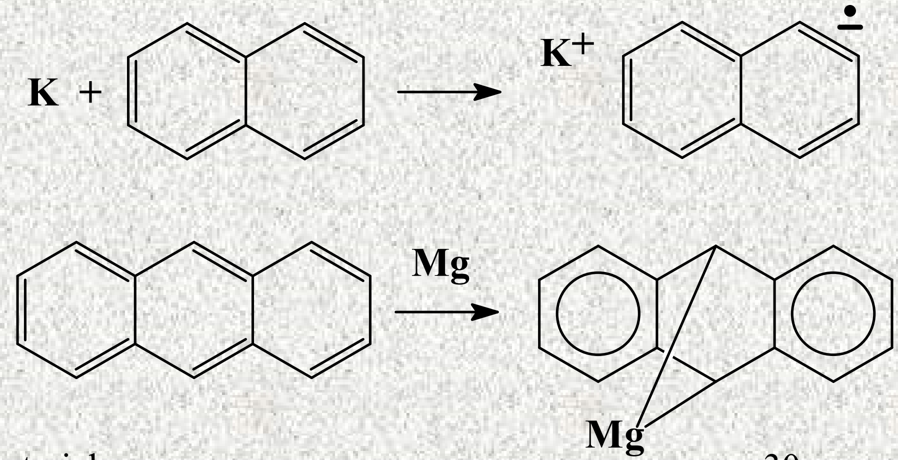
in dry anaerobic diglyme, THF, ethers, xylene

$NiCl_2$ + 2 K → Ni + 2 KCl

$AlCl_3$ + 3 K → Al + 3 KCl

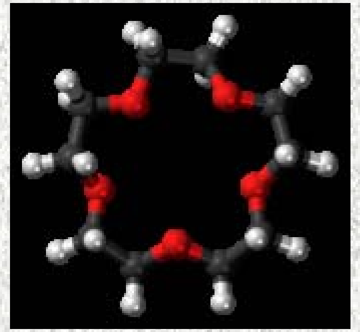
Reduction by Glycols or Hydrazine

"Organically solvated metals"



Bottom-up Synthesis

Alkalide Reduction



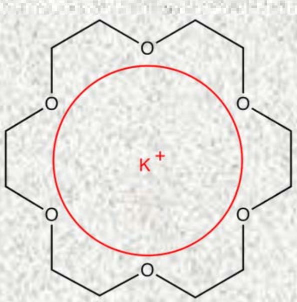
13 $K^{+}(15\text{-crown-}5)_2Na^{-}$ + 6 $FeCl_3$ + 2CBr_4

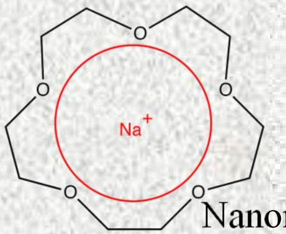
THF ↓ **–30 °C**

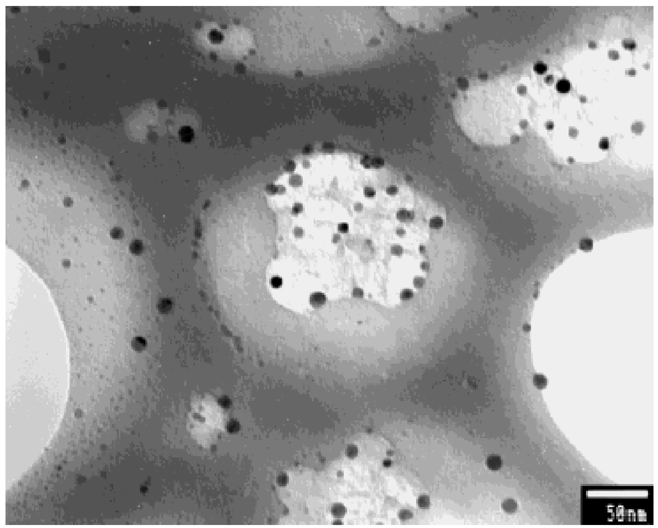
2 Fe_3C (nano) + 13 $K(15\text{-crown-}5)_2Cl_{0.43}Br_{0.57}$ + 13 NaCl

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

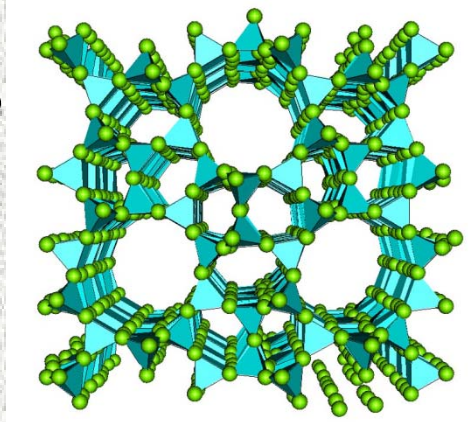
Ru(III)-Y + 3 bpy $\longrightarrow$ $Ru(bpy)_3^{2+}$ reduction of Ru(III)

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

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

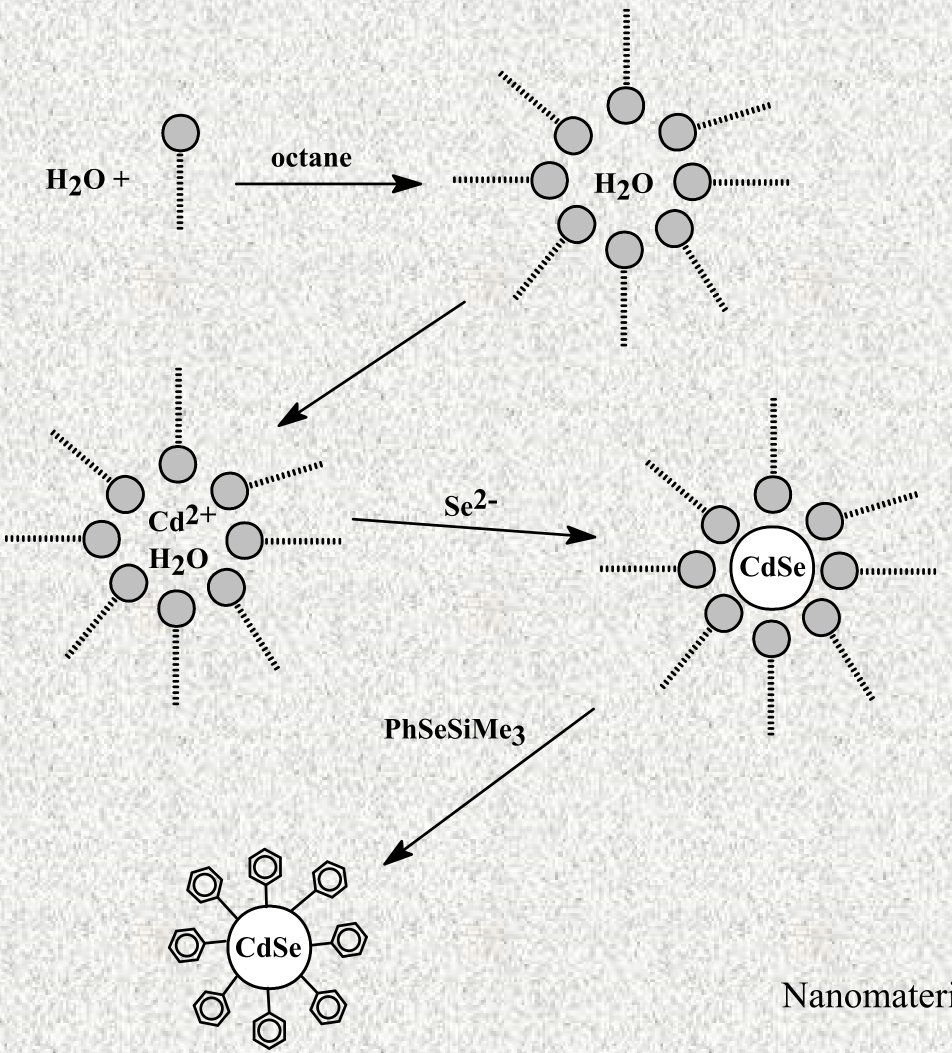
$MnCl_2 + 2\ FeCl_3 + 4\ H_2O \longrightarrow MnFe_2O_4 + 8\ HCl$

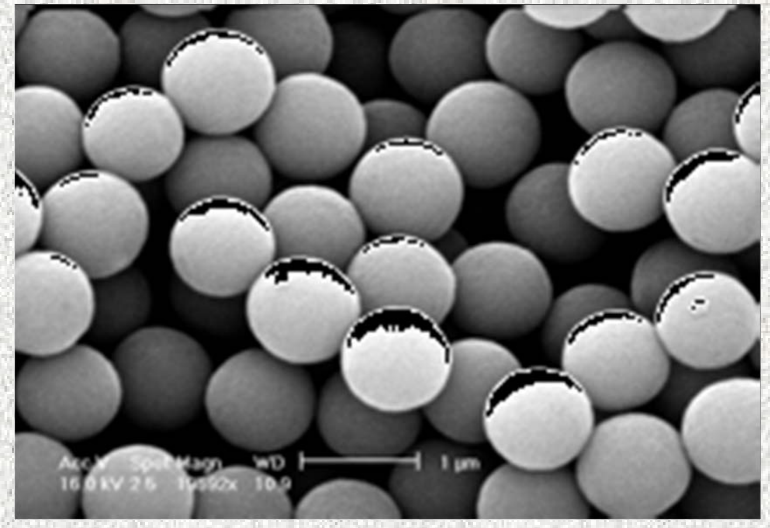
$Mn(NO_3)_2 + Fe(NO_3)_3$ **no go, why?**

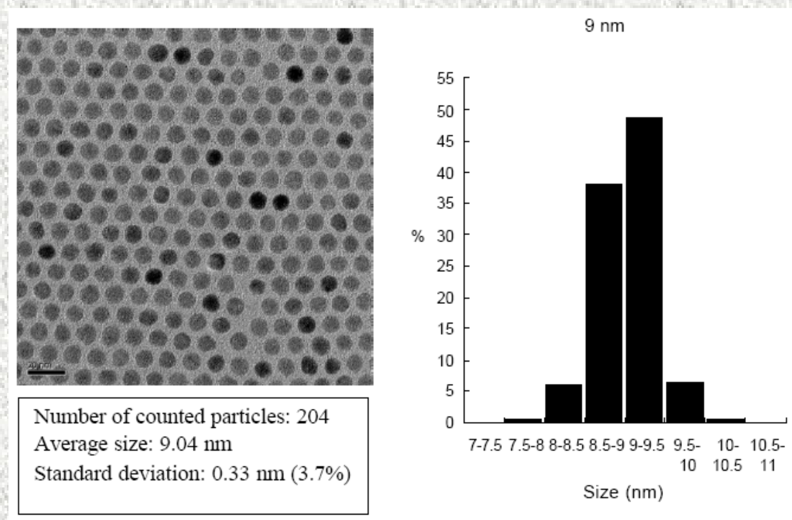
$$2\ MCl_n\ (g) + n\ H_2 \xrightarrow{850\text{-}900\ °C} \underset{3\text{-}11\ nm}{M^0} + 2n\ HCl$$

Bottom-up Synthesis

🛠 Inverse Micelles

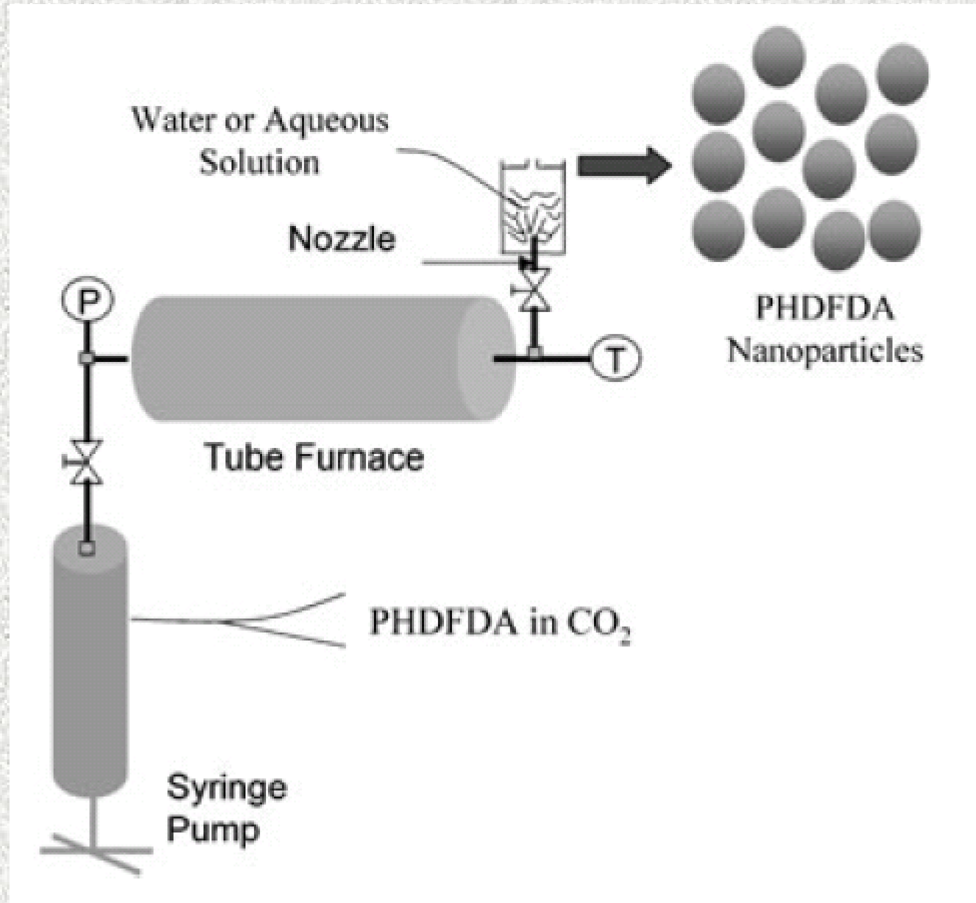


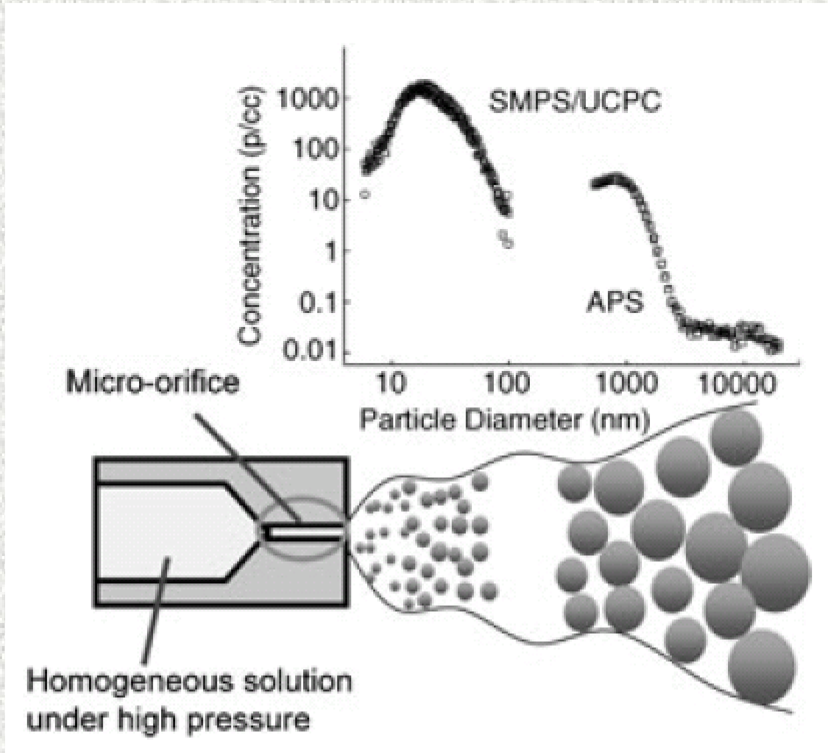




Bottom-up Synthesis

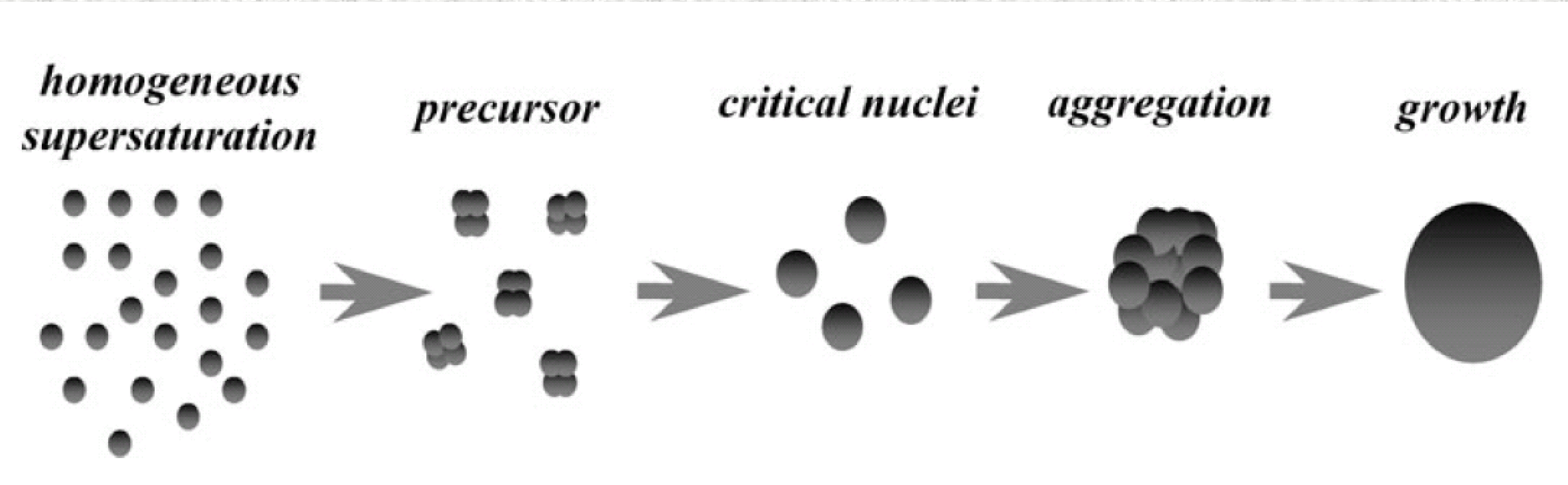
Polymeric Nanoparticles from Rapid Expansion of Supercritical Fluid Solution



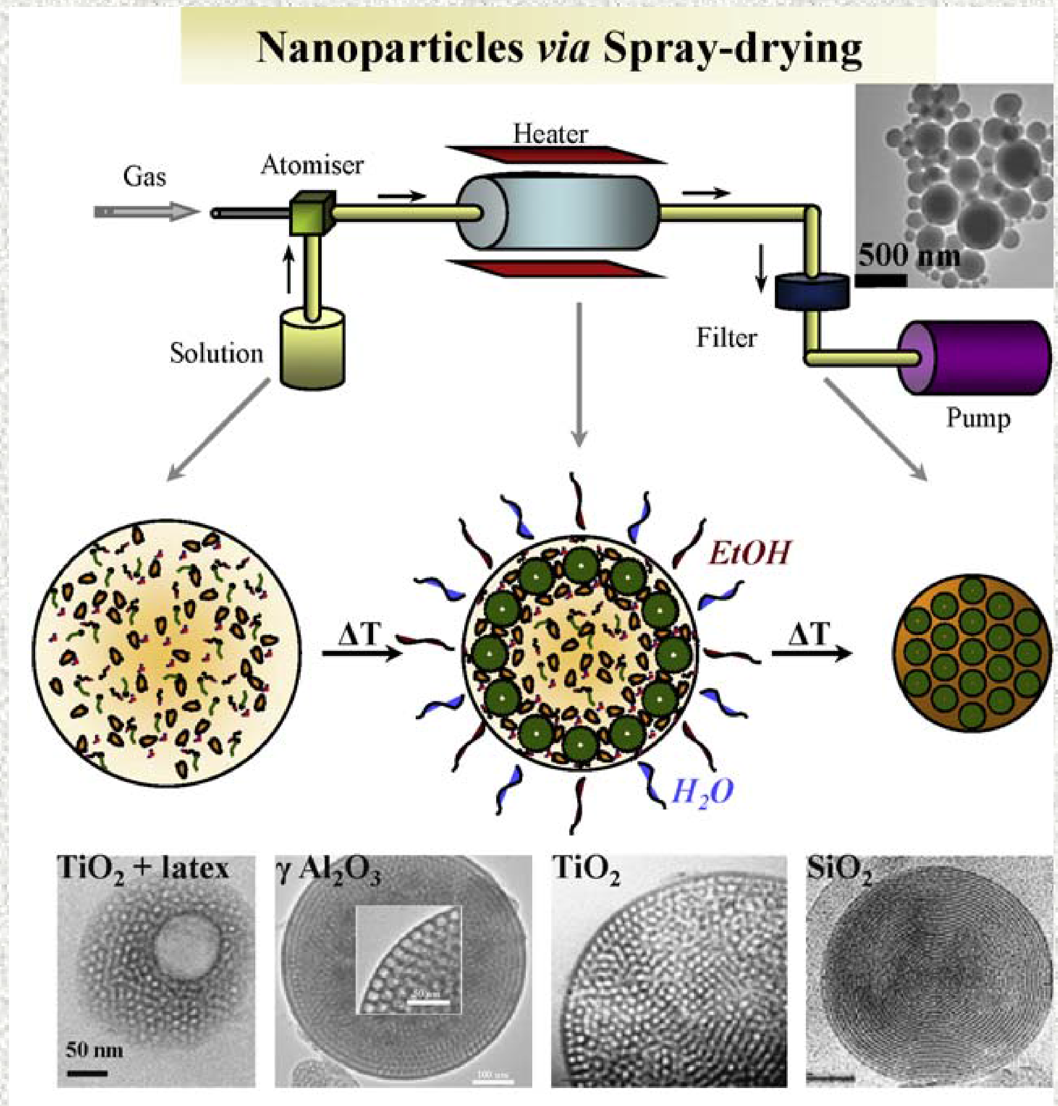


Bottom-up Synthesis

Polymeric Nanoparticles from Rapid Expansion of Supercritical Fluid Solution



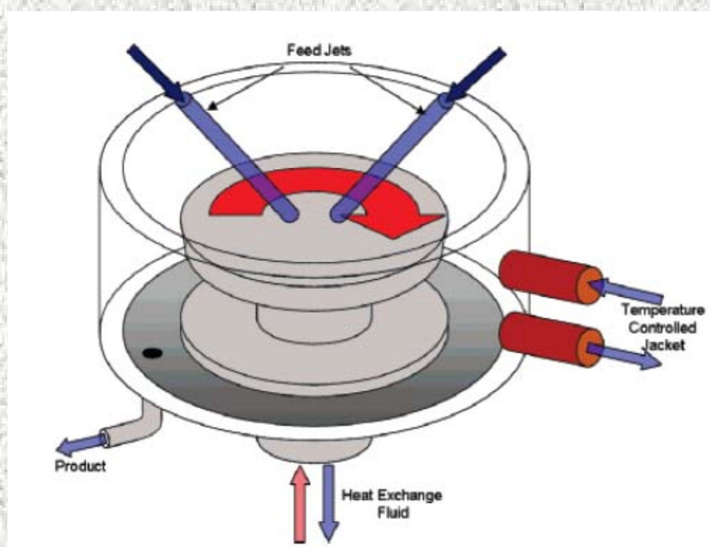
Bottom-up Synthesis



Bottom-up Synthesis

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

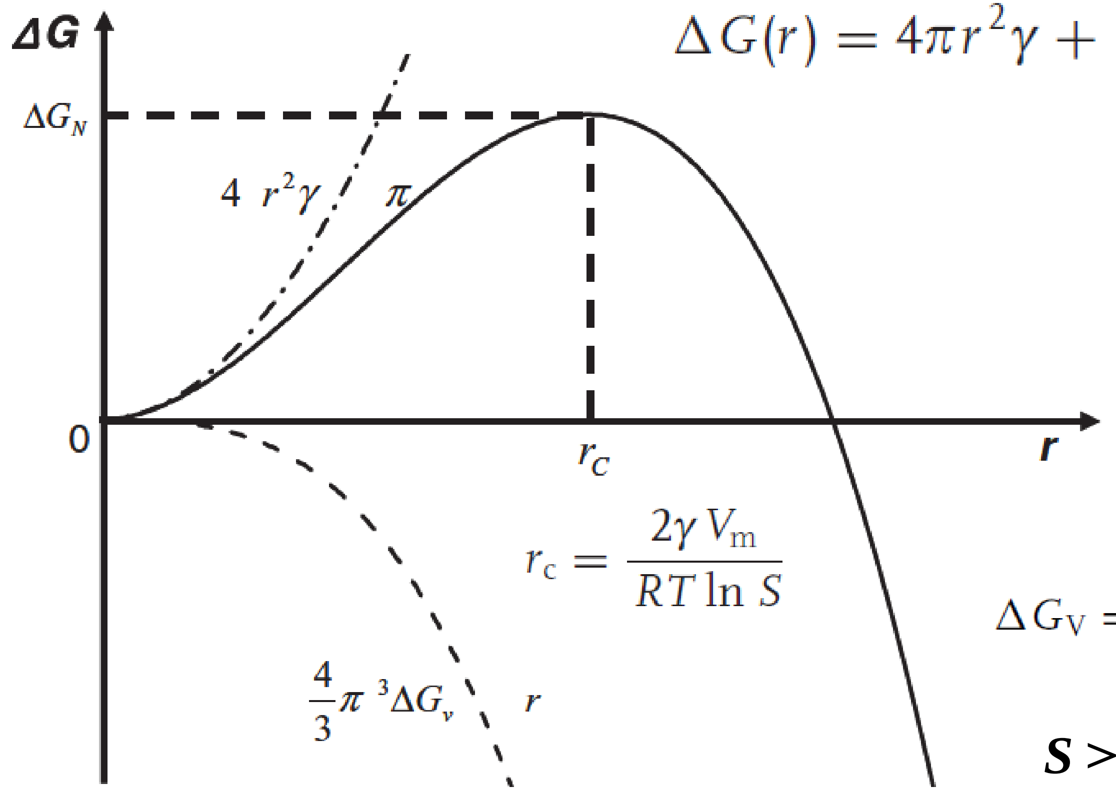
Intense mixing, accelerates nucleation and growth, affords monodispersed ZnO nanoparticles with controlled particle size down to a size of 1.3 nm and polydispersities of 10%



Bottom-up Synthesis

Crystallization free energy

$$\Delta G(r) = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_V$$



$$r_c = \frac{2\gamma V_m}{RT \ln S}$$

$$\Delta G_V = -\frac{RT \ln S}{V_m}$$

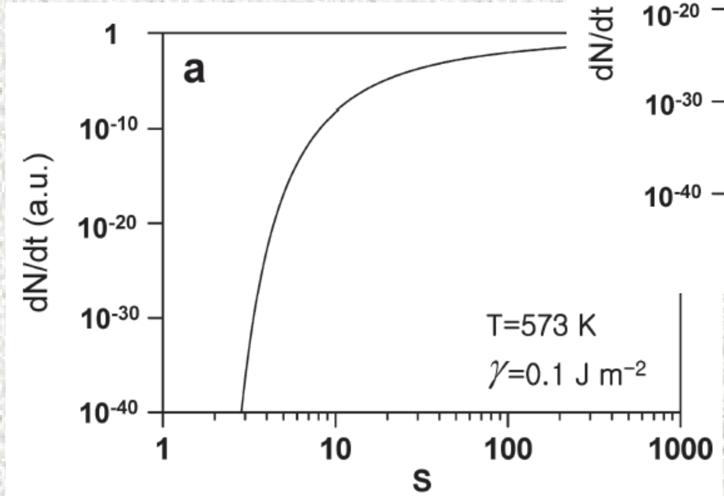
***S* > 1 supersaturation**

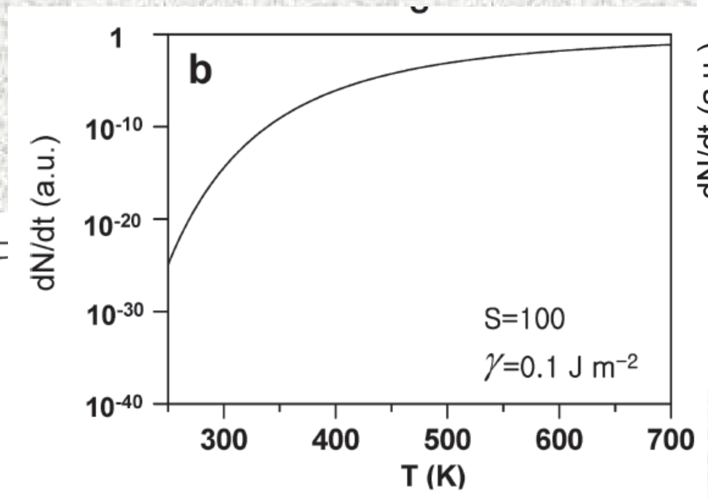
Bottom-up Synthesis

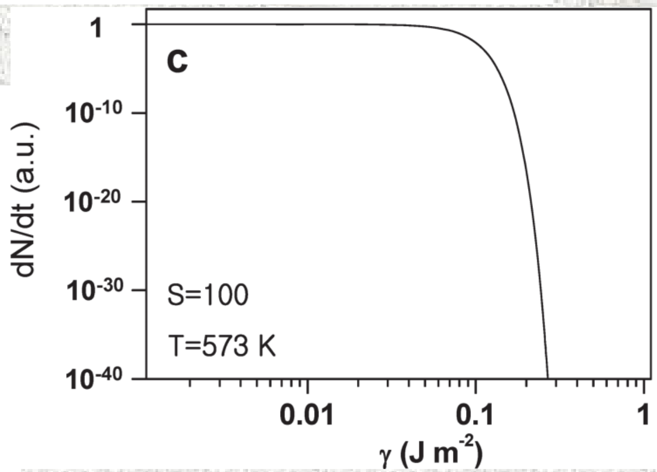
Nucleation rate

$$\frac{dN}{dt} = A\exp\left[\frac{-\Delta G_N}{k_B T}\right] = A\exp\left[-\frac{16\pi\gamma^3 V_m^2}{3k_B^3 T^3 N_A^2 (\ln S)^2}\right]$$

experimentally controllable parameters:
a) level of supersaturation
b) temperature
c) surface free energy







$V_m = 3.29 \times 10^{-5}\ m^3\ mol^{-1}$ (CdSe)

Bottom-up Synthesis

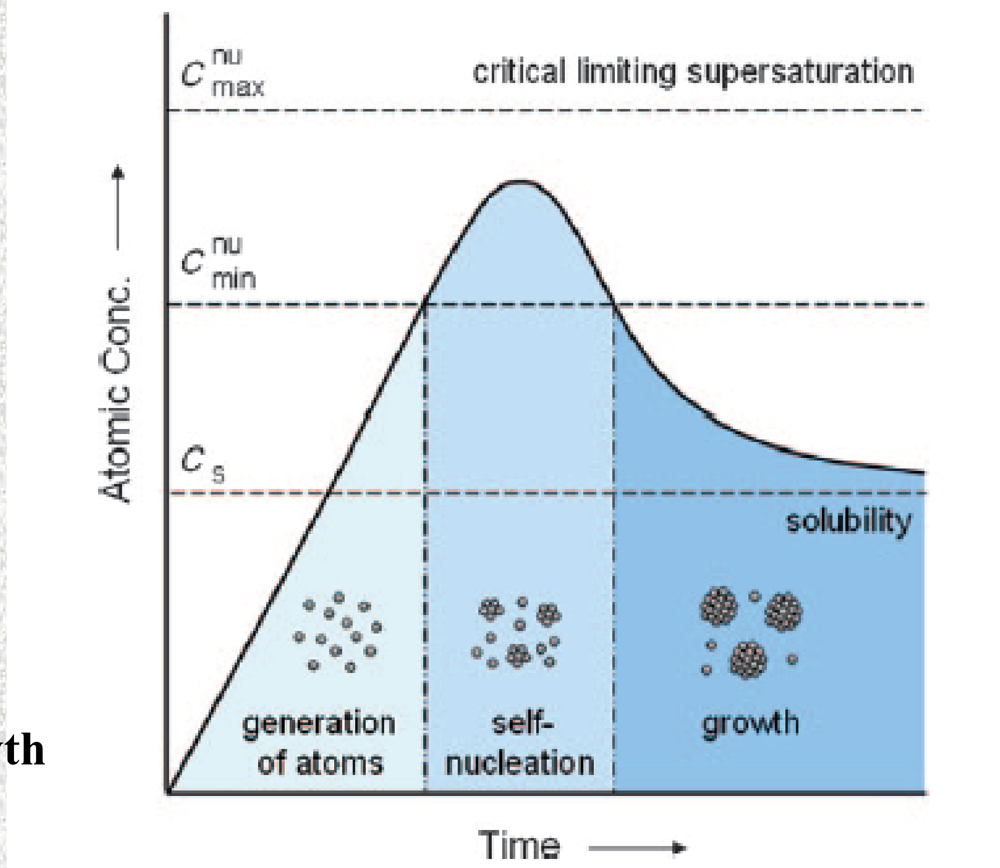
LaMer mechanism

Accumulation of the monomers
Supersaturated solution

Burst of nucleation

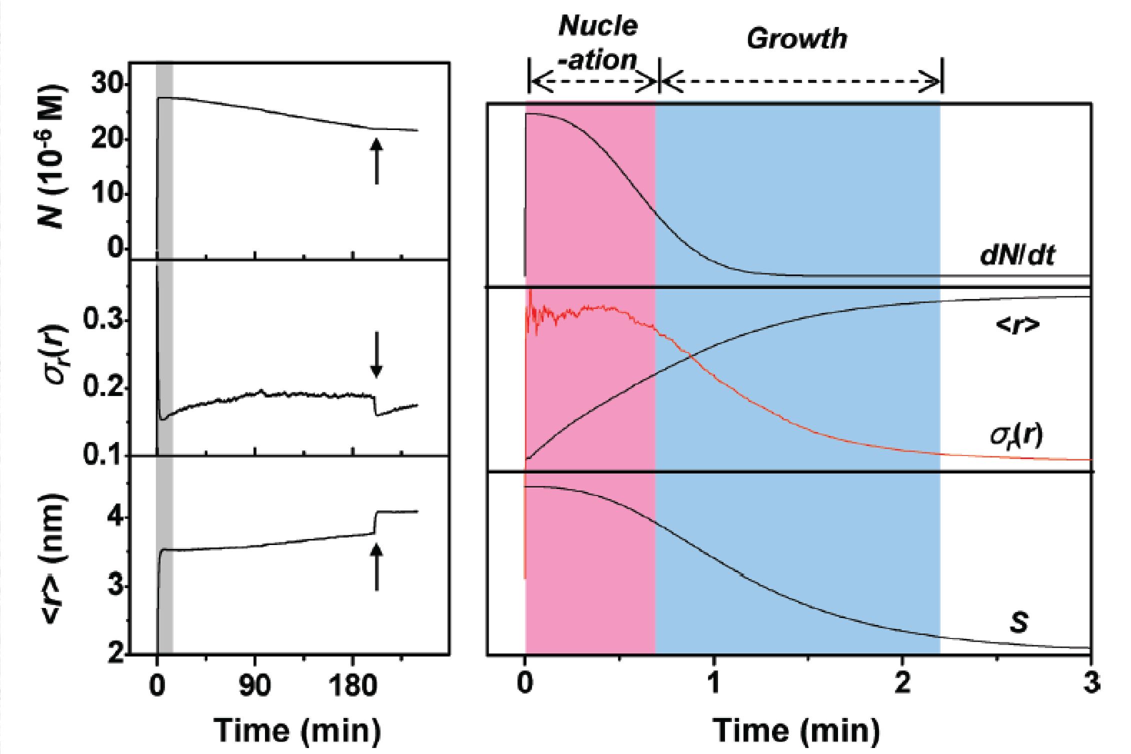
Slow growth of particles without additional nucleation
the size focusing

Separation of nucleation and growth



Bottom-up Synthesis

Hot-injection



N = the number concentration of the nanocrystals

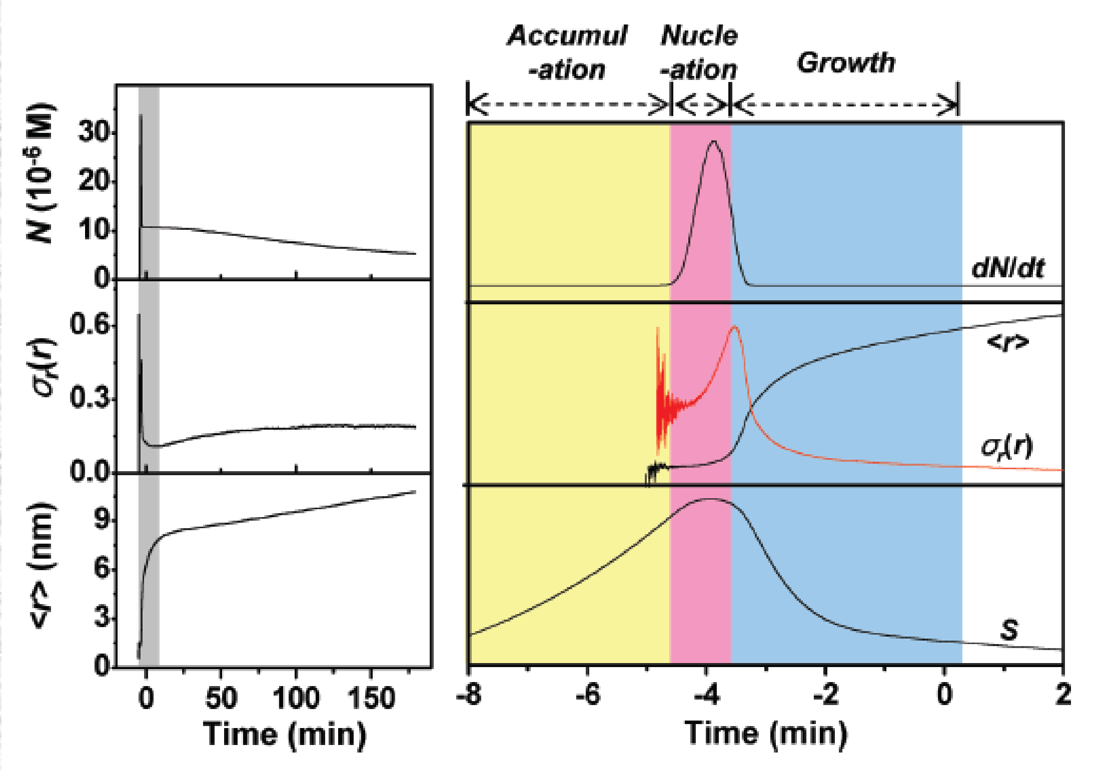
$\sigma(r)$ = relative standard deviation of their radii r

$< r >$ = mean radius

dN / dt = nucleation rate

Bottom-up Synthesis

Heat-up



N **= the number concentration of the nanocrystals**
σ(***r*** **) = relative standard deviation of their radii r**
< ***r*** **> = mean radius**
dN **/** ***dt*** **= nucleation rate**

Watzky-Finke mechanism

Slow continuous nucleation

Fast autocatalytic surface growth

Seed-mediated mechanism

Au nanoclusters as seeds

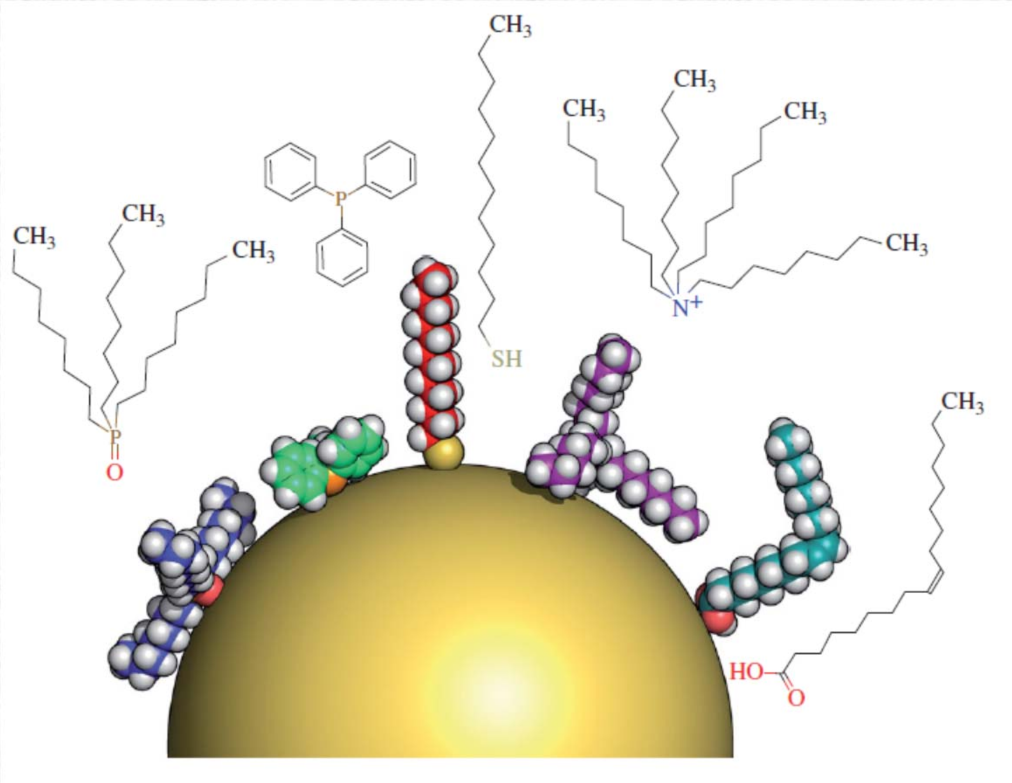
Bi, Sn, In, Au, Fe, Fe_3O_4

Other mechanisms

Digestive rippening

Surfactant exchange

Surface Modification



A nanoparticle of 5 nm core diameter with different hydrophobic ligands

NP and molecules drawn to scale

The particle is idealized as a smooth sphere

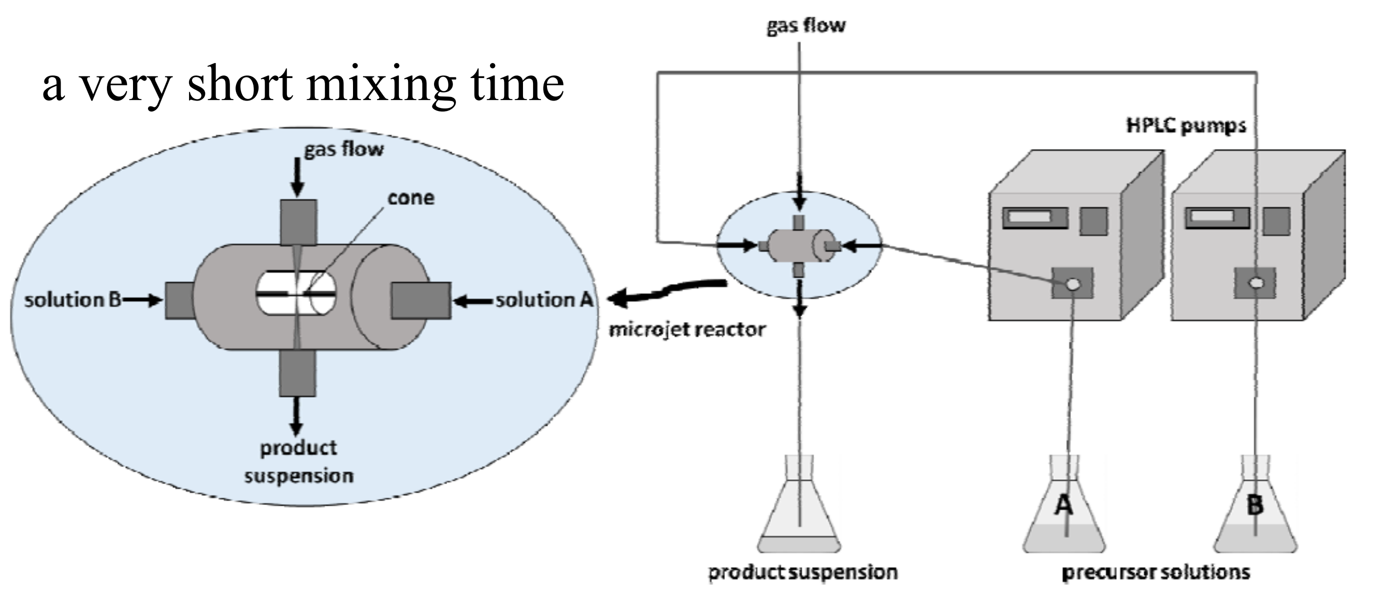
trioctylphosphine oxide (TOPO)
triphenylphosphine (TPP)
dodecanethiol (DDT)
tetraoctylammonium bromide (TOAB)
oleic acid (OA)

Bottom-up Synthesis

Continuous Synthesis of Inorganic Nanoparticles

rapid mixing of two precursor solutions and the fast removal of the nuclei from the reaction environment

a very short mixing time



transport from the reactor to a tubing for the particle growth, the length of tubing up to the collection vessel influences the particle growth

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**

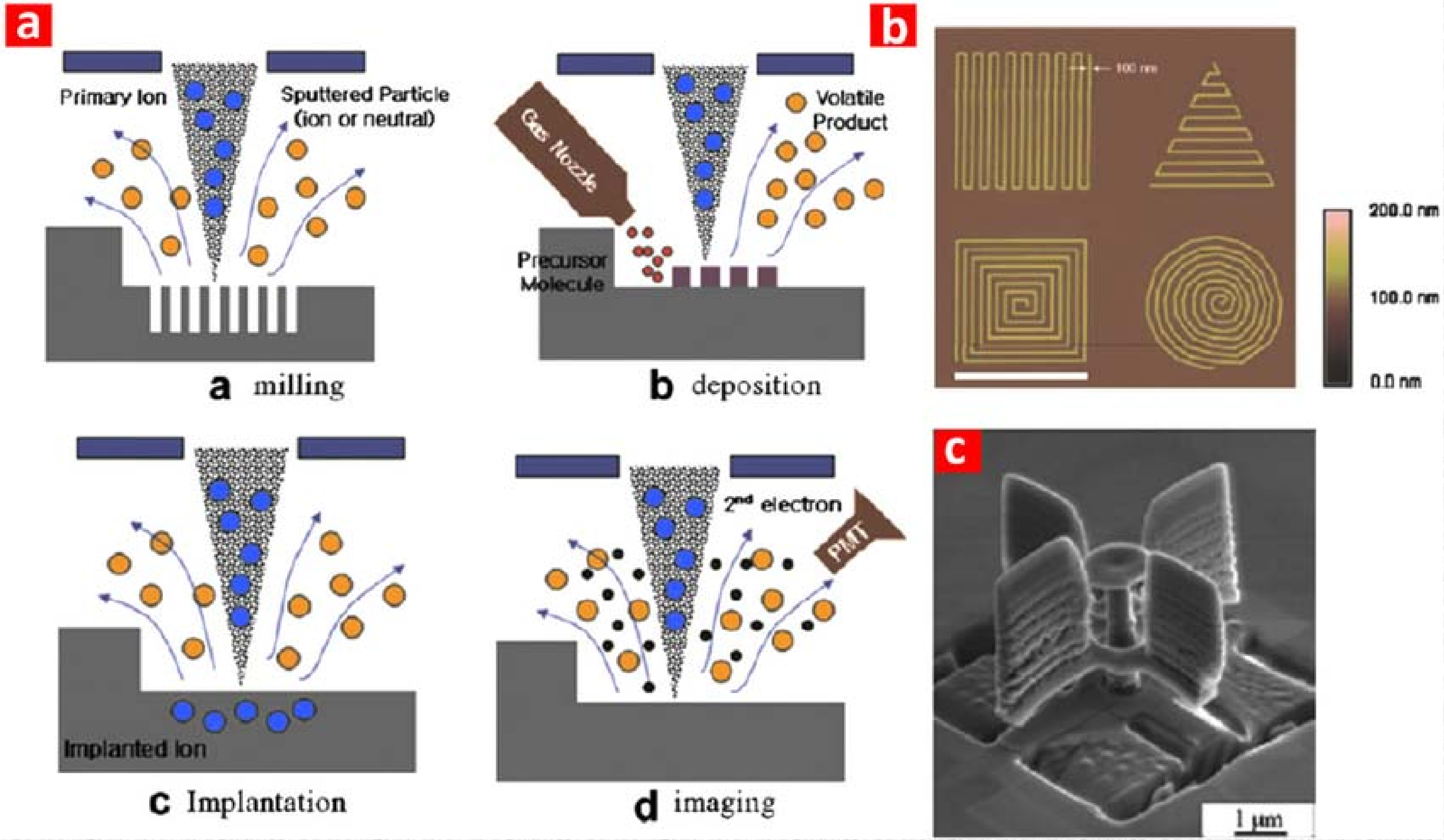
✧ **Crystallization from Glasses**

✧**Precipitation from Supersaturated Solid or Liquid Solutions**

Top-down Synthesis

🛠Lithographic Techniques

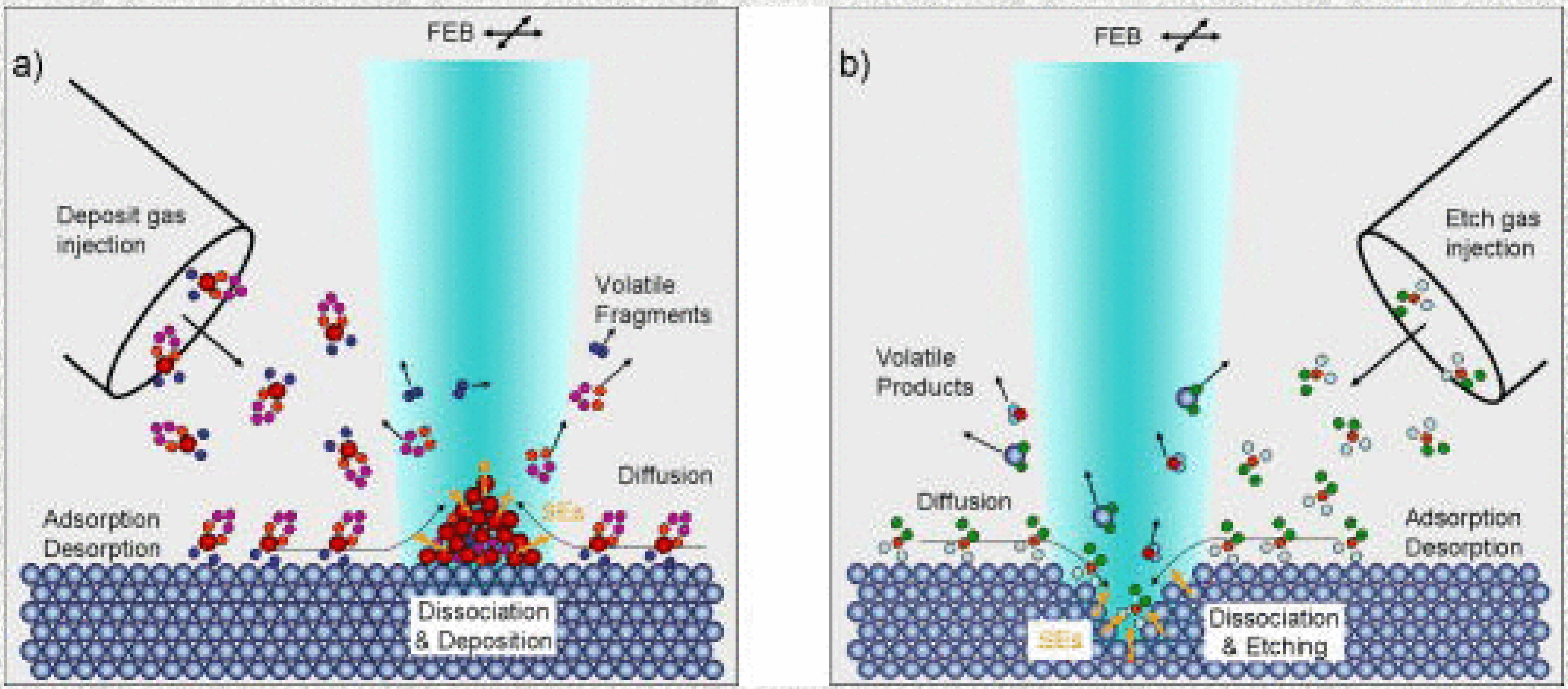
✧electron beam and focused ion beam (FIB) lithography



Top-down Synthesis

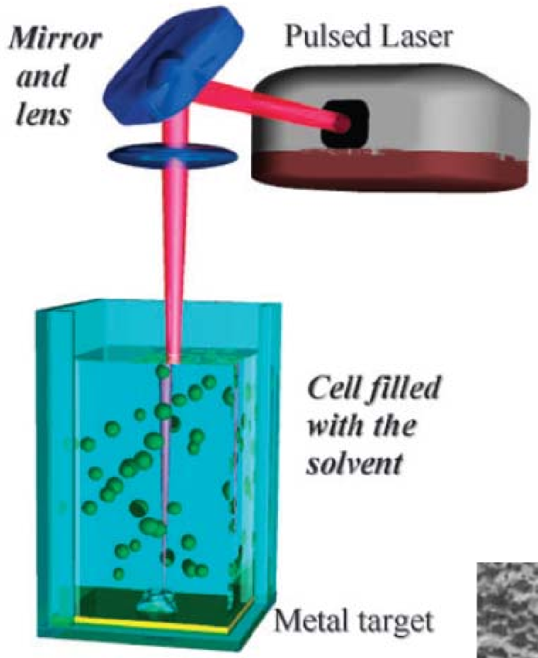
🛠Lithographic Techniques

✧electron beam and focused ion beam (FIB) lithography



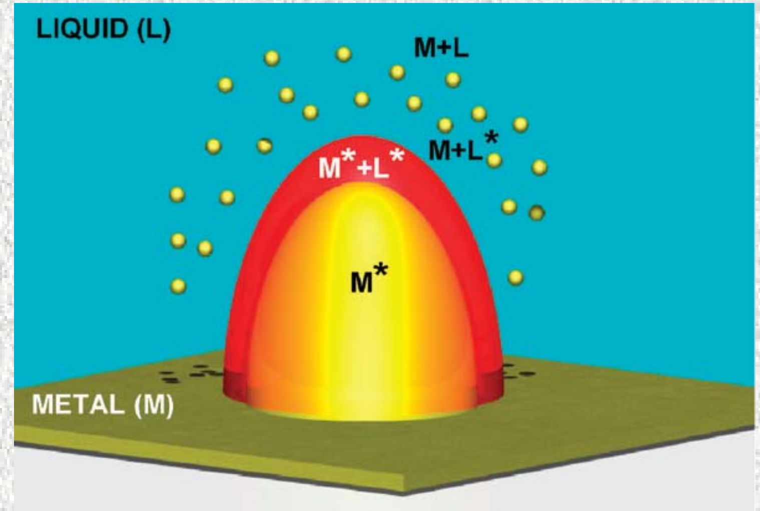
Top-down Synthesis

Laser ablation synthesis in solution

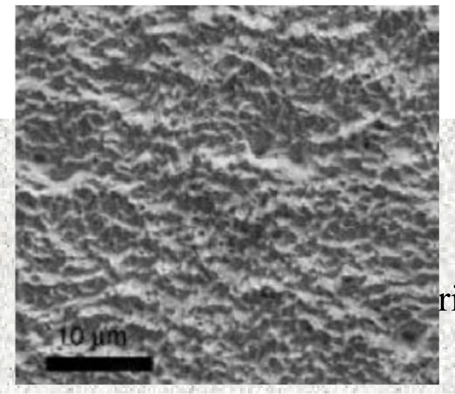


Parameters of LASiS:

- **Metal target**
- **Solvent**
- **Solutes**
- **Laser pulses**
  - **Fluence**
  - **Wavelength**
  - **Duration**
  - **Number**

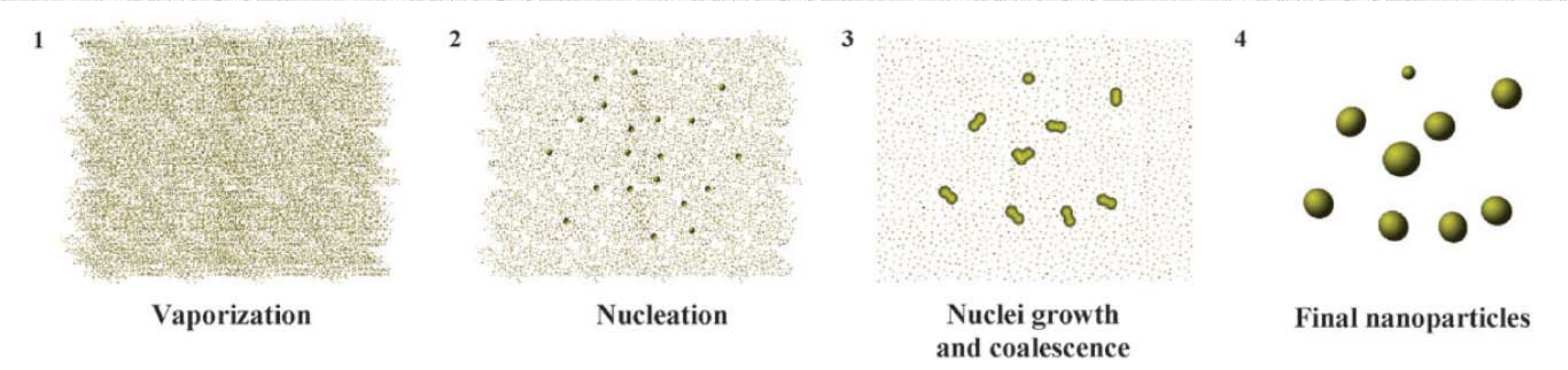


SEM image of Pt target
after ablation at 355 nm
for 15 min at 14 J/cm^2



Top-down Synthesis

Laser ablation synthesis in solution



HRTEM images of AgNP (left) and AuNP (right) obtained by LASiS in DMF and water, respectively