# Nanoscopic Materials

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

Nanostructured materials = nonequilibrium character

- Good sinterability
- High catalytic activity
- Difficult handling
- Adsorption of gases and impurities
- Poor compressibility

# 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
Quantum size – new physical phenomena

## Smallness: surface versus bulk forces

A large 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)

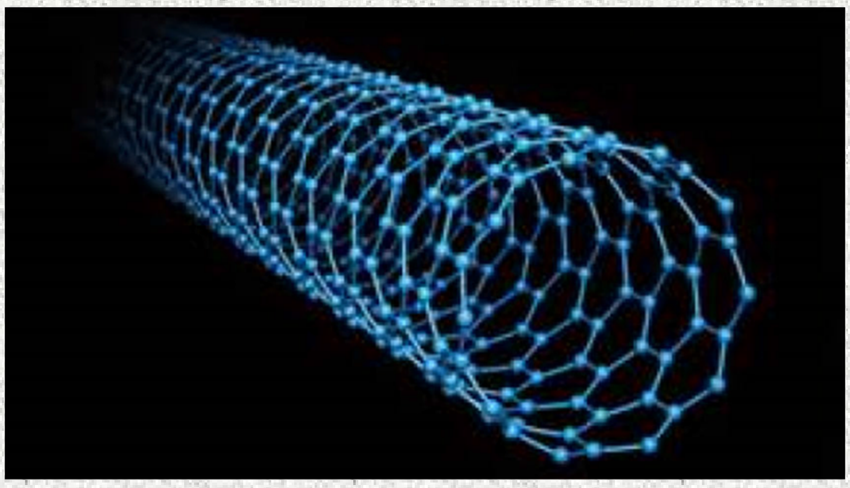
- **surface phonon scattering**
- **surface electron scattering**
- **surface atom electric charge distribution**
- **surface atom spins in ferromagnetic, ferrimagnetic, and antiferromagnetic materials - transition to superparamagnetic state**

# Unique Features of the Nano-scale

## Chemical bonding in nanostructures

Trigonal bonding of C in graphite and graphene – $sp^2$
Tetrahedral bonding of C in diamond – $sp^3$

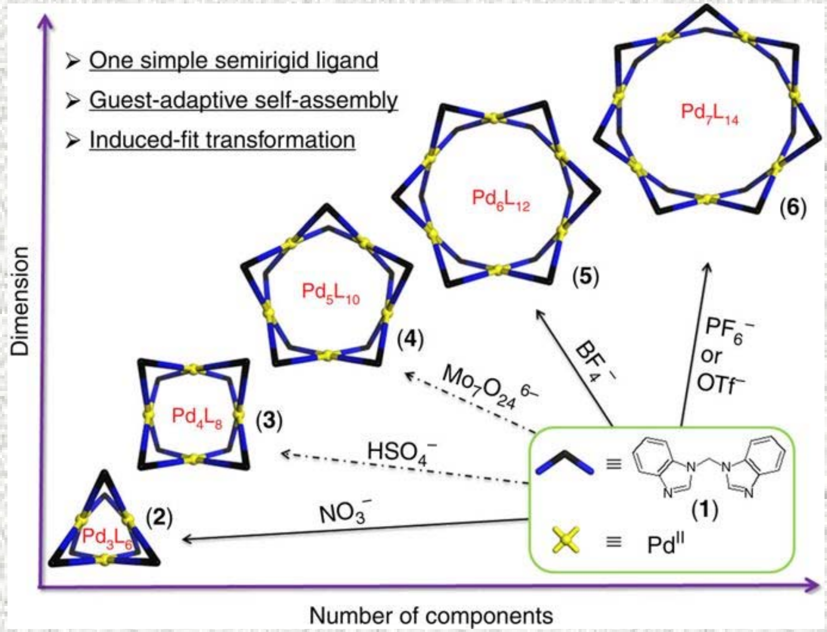
Single wall carbon nanotubes (SWCNT)
C bonding in SWCNT is contorted $sp^2 \rightarrow sp^3$
Chirality - variable amounts of twisting

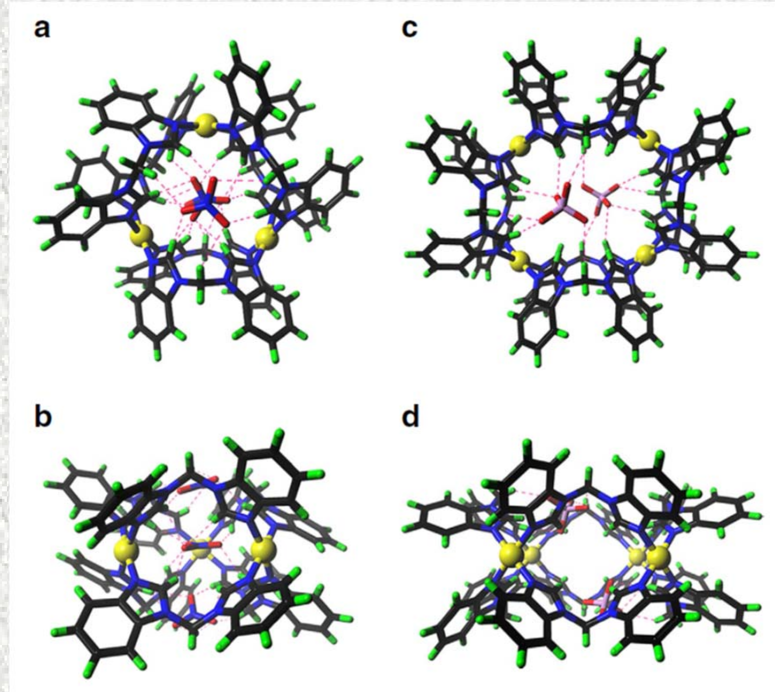


# Unique Features of the Nano-scale

## Self-assembly

Combination of particles, atoms, or molecules, self-assemble into predetermined new materials and structures (micelles, SAM, MOF, DNA, proteins, superlattices....)

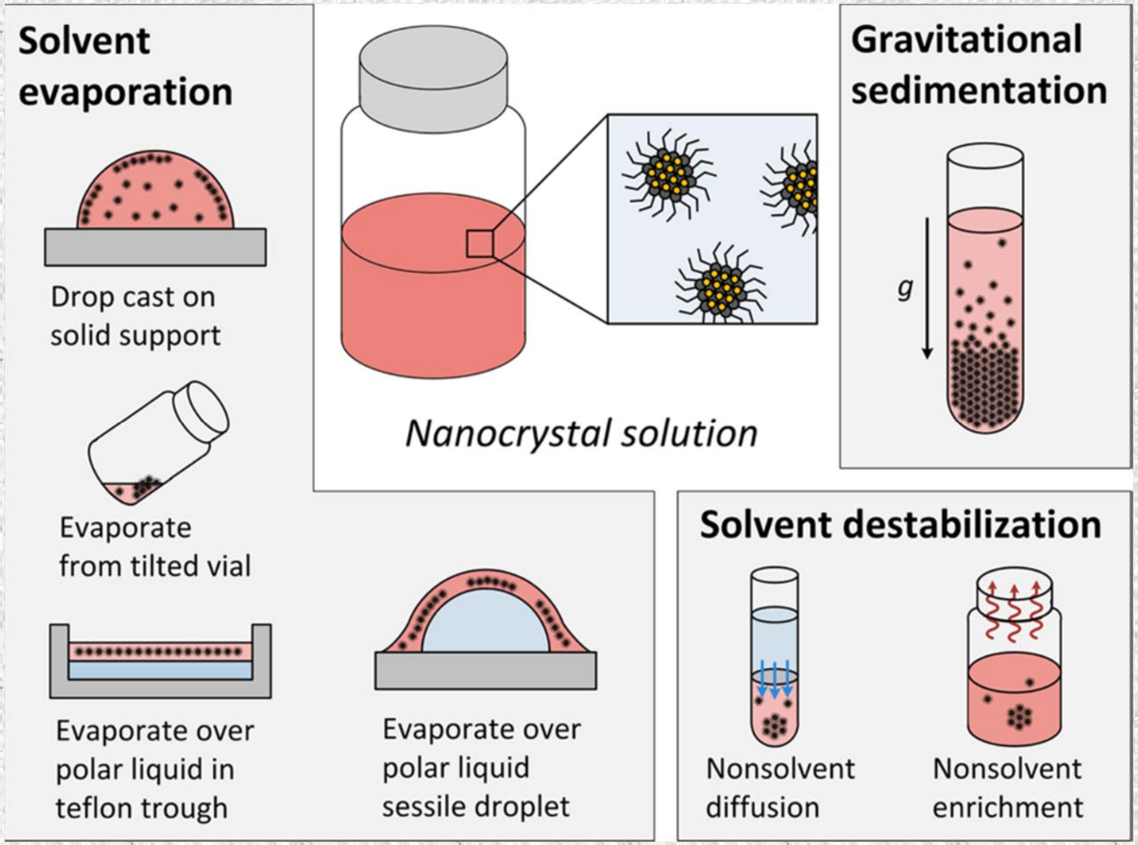


# Unique Features of the Nano-scale

## Self-assembly of NP superlattices

Synthetic routes to superlattices

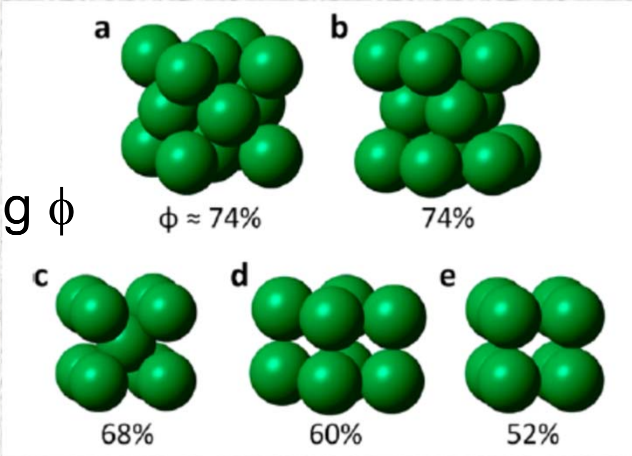


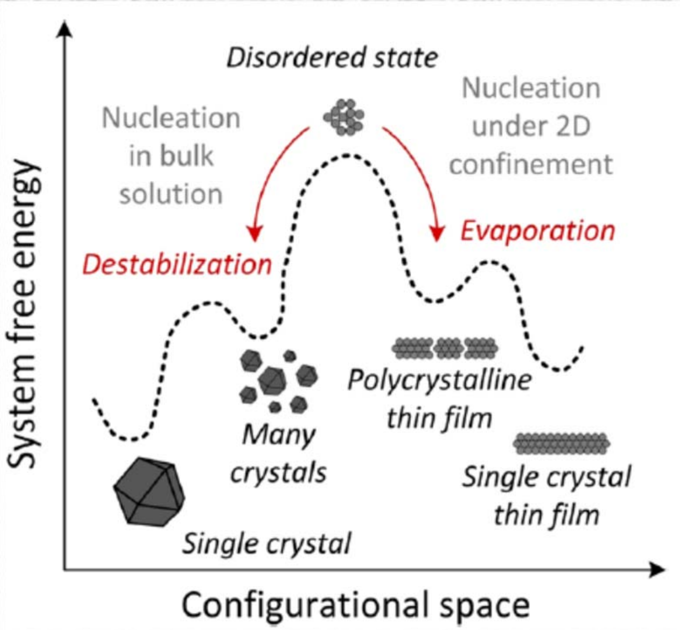
# Unique Features of the Nano-scale

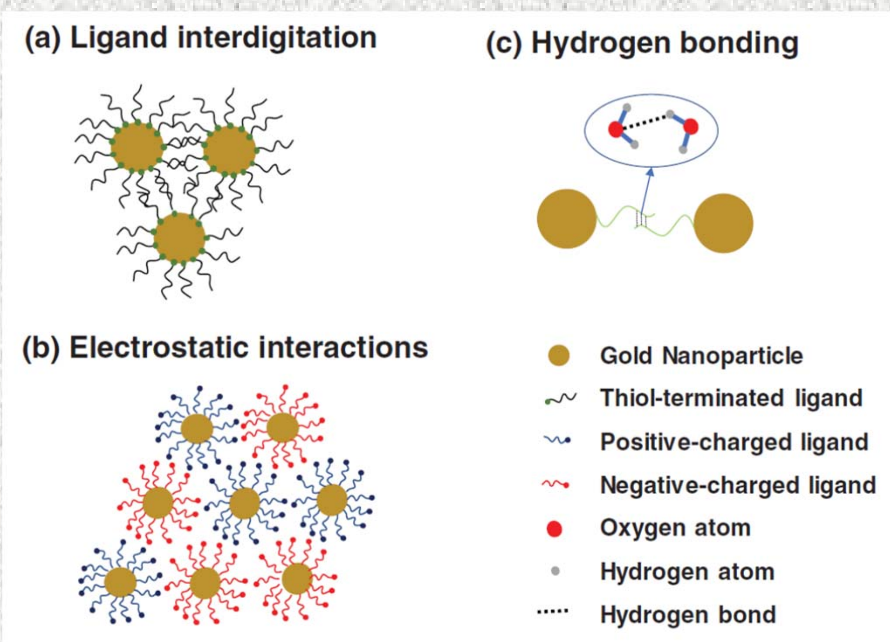
## Self-assembly of NP superlattices

- Polyhedral (3D) superlattices
- Film (2D) superlattices

Space filling $\phi$



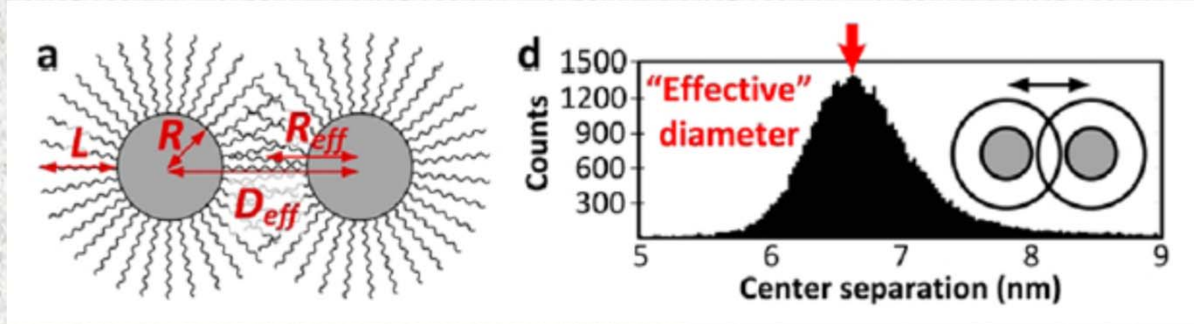



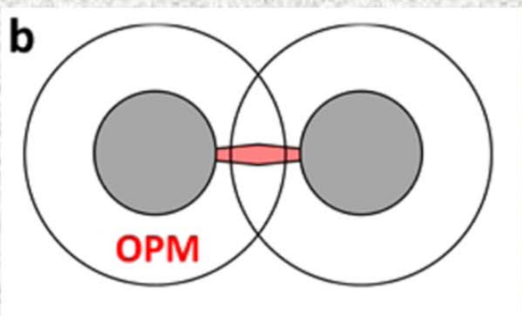
# Unique Features of the Nano-scale

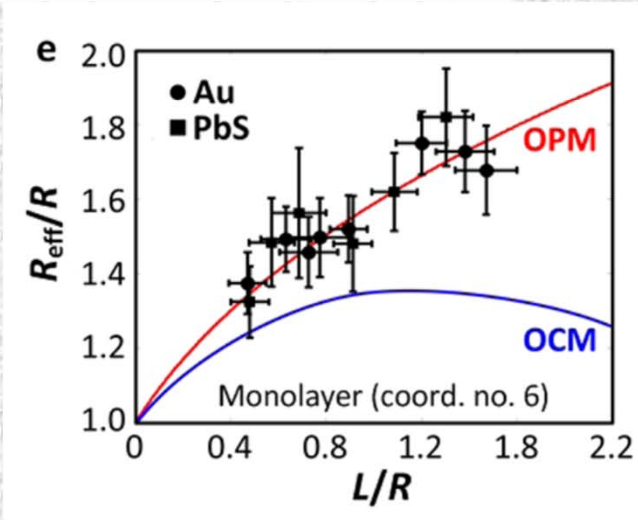
## Self-assembly of NP superlattices

**Interdigitating hydrocarbon coronas between a nanocrystal pair core radius R, ligand length L, effective radius $R_{eff}$**

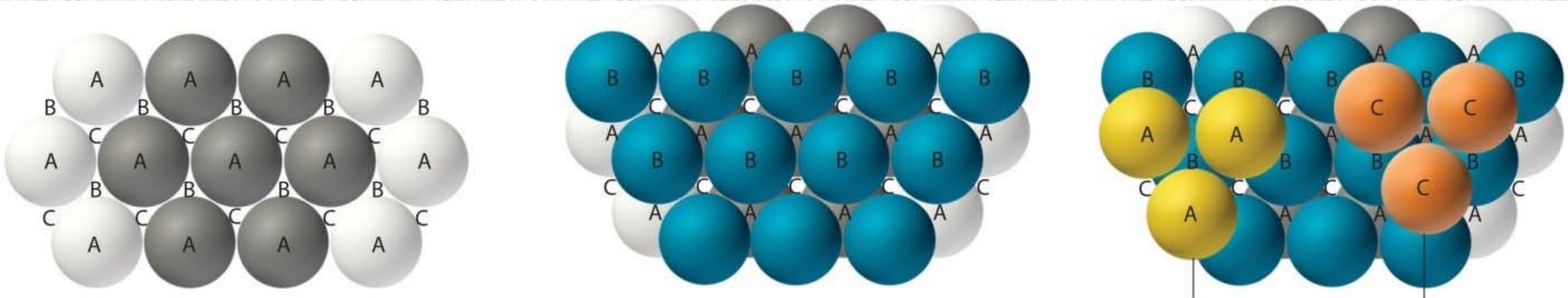



Optimal packing model (OPM)



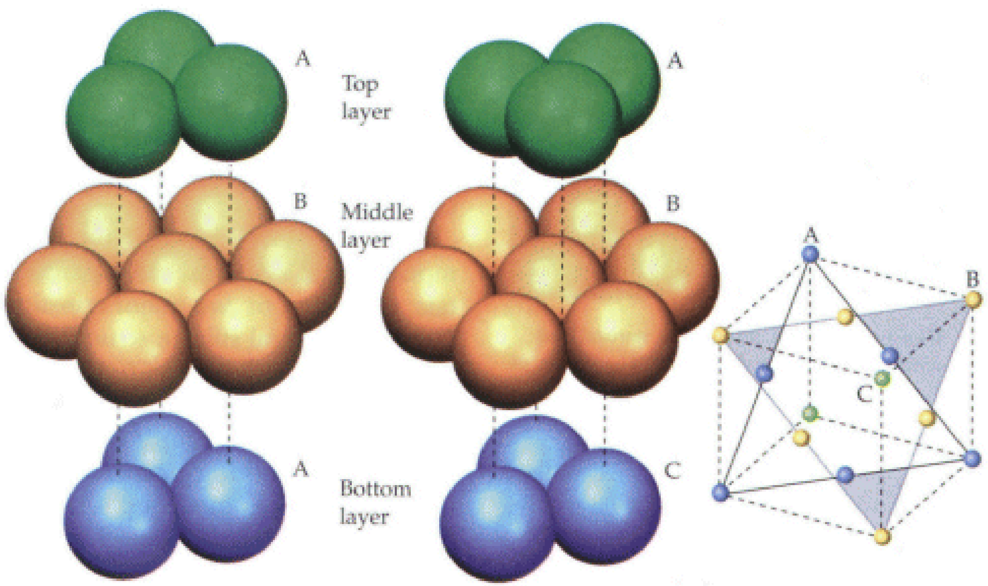



# Close Packed Atoms/Nanocrystals

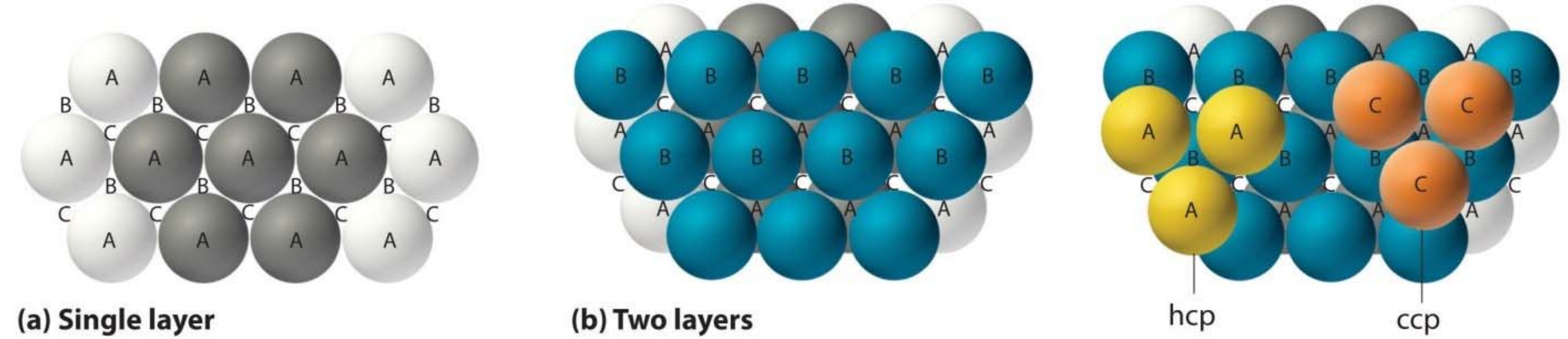



(a) Single layer (b) Two layers (c) Three layers

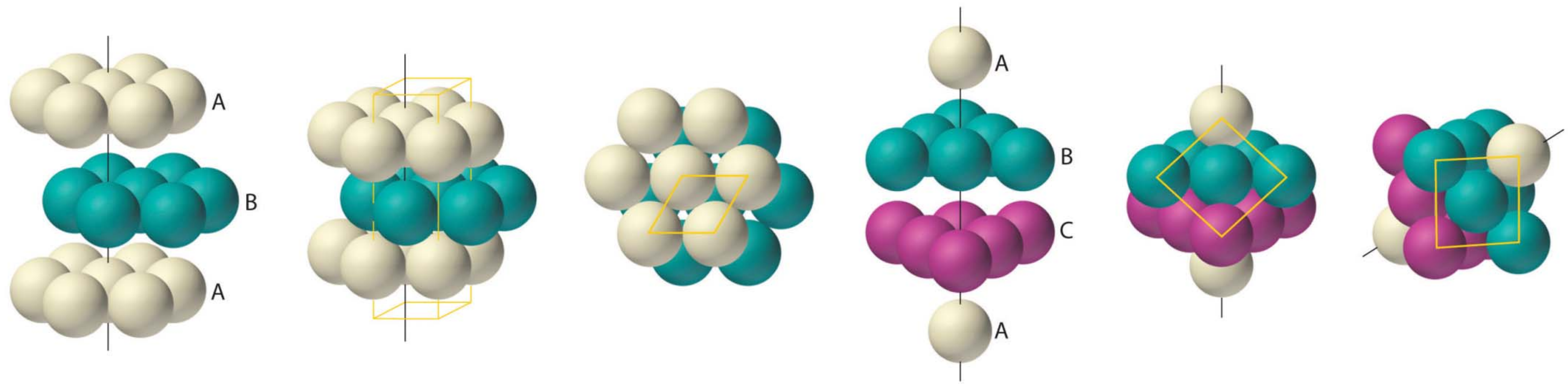
(a) Hexagonal close-packing (b) Cubic close-packing = face-centered cubic



# Close Packed Atoms/Nanocrystals



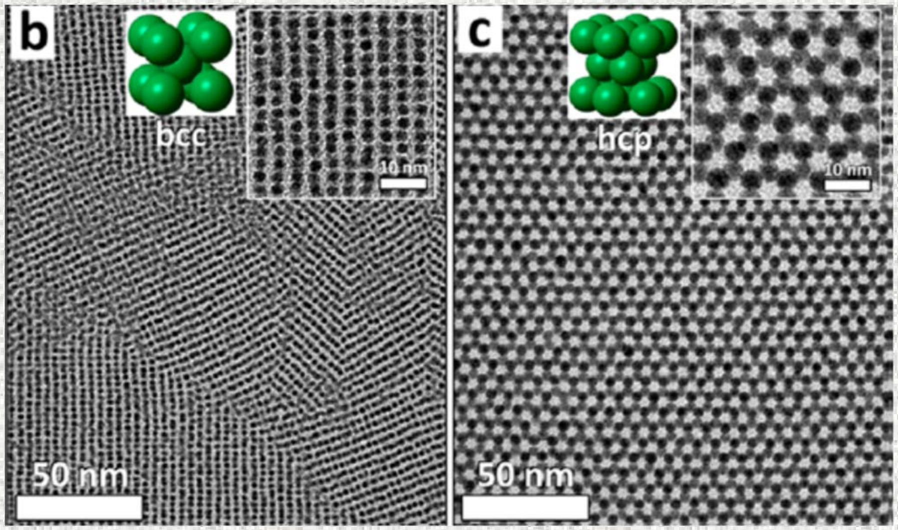

(a) Single layer (b) Two layers (c) Three layers




(a) Hexagonal close-packed (hcp) (b) Cubic close-packed (ccp)

# Quasi-Spherical Nanocrystals

The assembly of Au nanocrystal superlattices depends on the softness parameter L/R




- Small softness values L/R
**Hard spheres = FCC or HCP**

- **Borderline at L/R = 0.7**

- Large L/R values
**Soft spheres = BCC**

The fcc/hcp deforms surface hydrocarbon chains more significantly than that of bcc

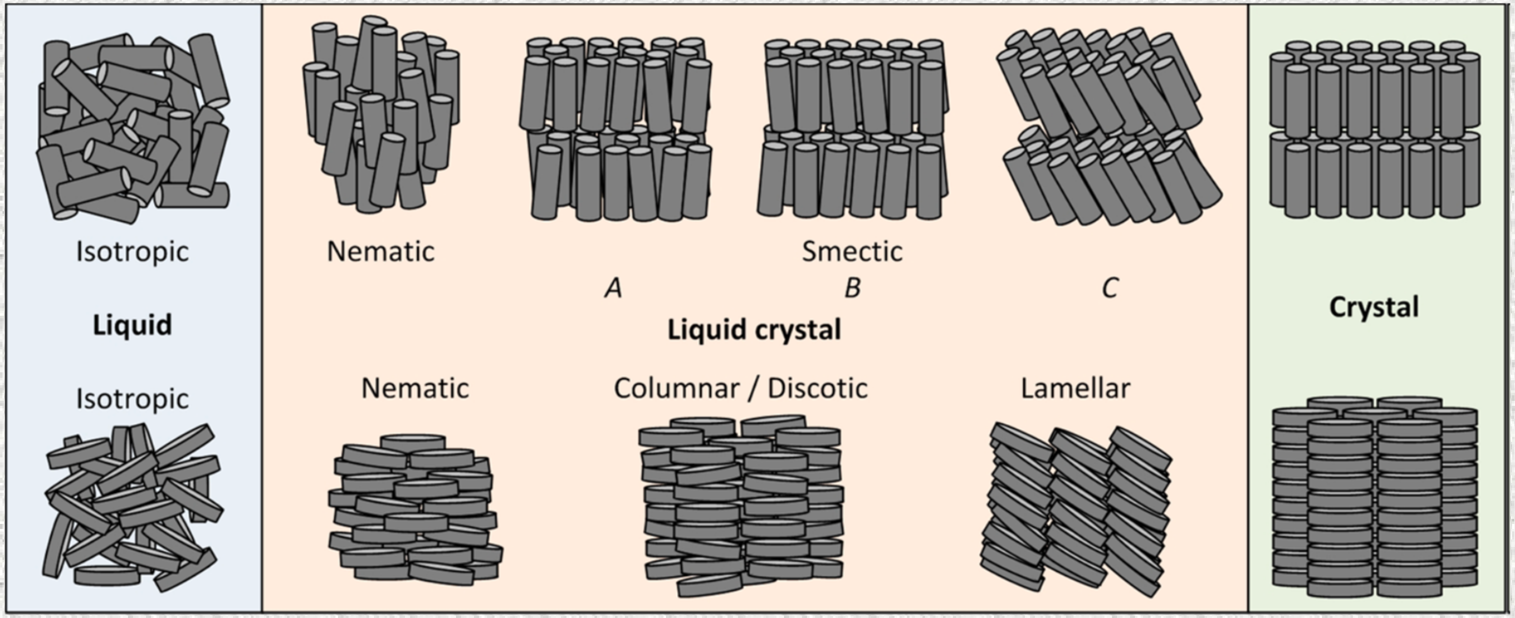
[110]-oriented bcc packing of 2.2 nm Au NPs capped with C18-thiol (L/R ≈ 1)
[100]-oriented hcp of 4.5 nm Au nanocrystals with the same ligands (L/R ≈ 0.5)

# Rod-/Platelet-Shaped Nanocrystals

Liquid crystalline phases of rods and disks

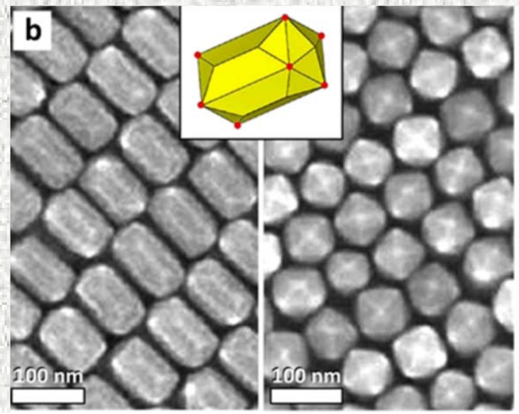
Rods

Disks




Au nanorods passivated with CTAB bilayers

Smectic




**Nematic** (random position, fixed orientation)

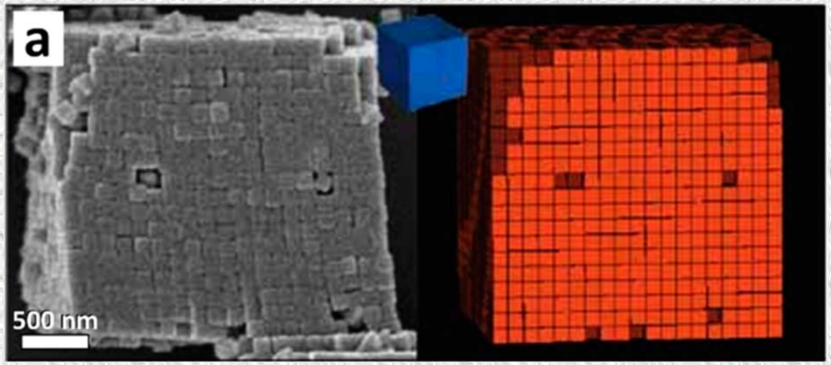
**Smectic** (fixed position in a plane, fixed orientation)

**Discotic columnar** (fixed position along one axis, fixed orientation)

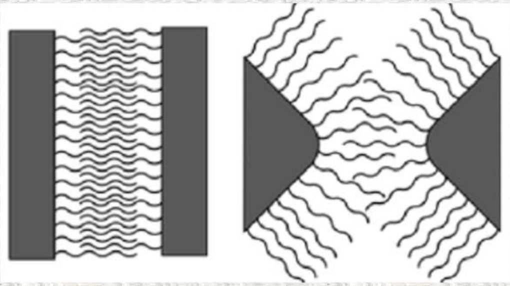
# Polyhedral Nanocrystals

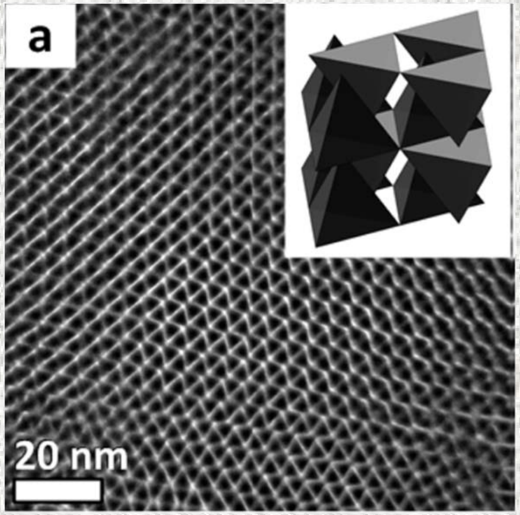
**Large NPs** - preference for **face-to-face** contacts – max. interparticle cohesion

500 nm Ag NPs densest polyhedron packings




**Small NPs** - preference for **tip-to-tip** contacts – min. interligand repulsion






Superlattice of 10 nm tetrahedral CdSe NPs capped with oleic acid ligands

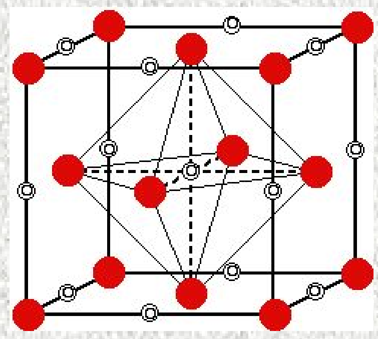
Modeled structure with contacts between tetrahedron tips

# Large + Small Sphere Nanocrystal Mixtures

The structures derived from simple rules for construction of binary lattices of cubic and hexagonal close packed spheres

N close packed large nanocrystals in a lattice cell
N Octahedral + 2N Tetrahedral holes can be filled by small nanocrystals

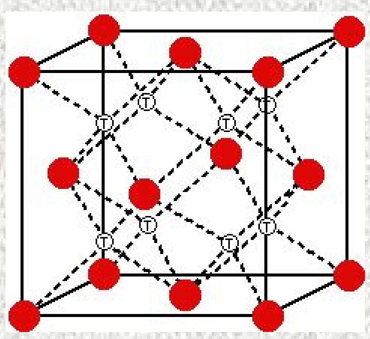
**Octahedral Holes (O)**



Z = 4
number of atoms in the CCP cell (N)

O = 4 number of octahedral holes (N)

**Tetrahedral Holes (T)**




Z = 4
number of atoms in the CCP cell (N)

T = 8 number of tetrahedral holes (2N)

# Large + Small Sphere Nanocrystal Mixtures

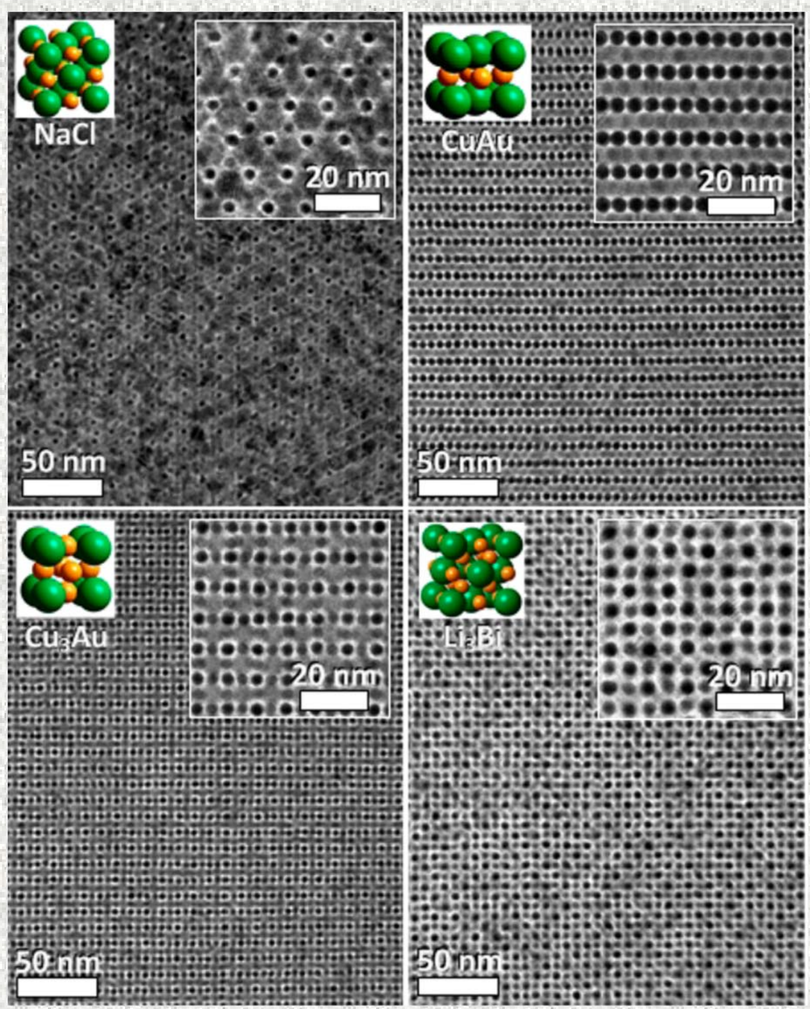
More than 20 unique binary nanocrystal superlattices

A mixture of spherical nanocrystals with two sizes produces a wide range of binary superlattices

Effective size ratio

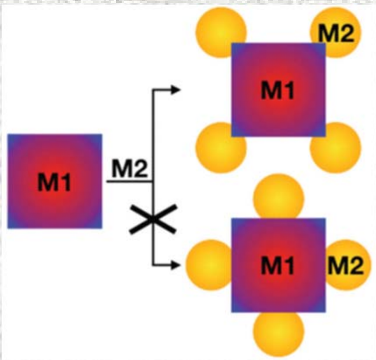
$$\gamma_{\text{eff}} = \frac{D_B + 2L_B}{D_A + 2L_A}$$

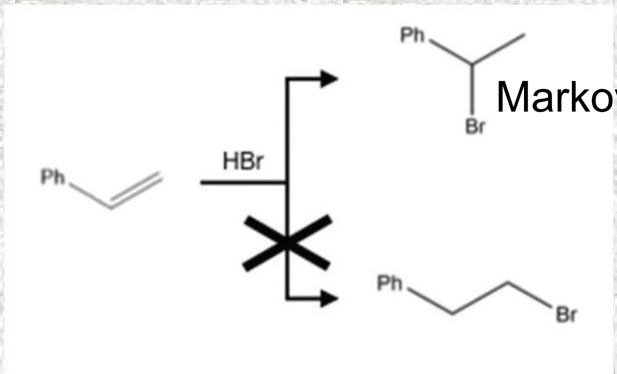
$D_A$ ($L_A$) and $D_B$ ($L_B$) are the core diameters (effective ligand thicknesses) of large and small nanocrystals



# Unique Features of the Nano-scale

## Regioselectivity



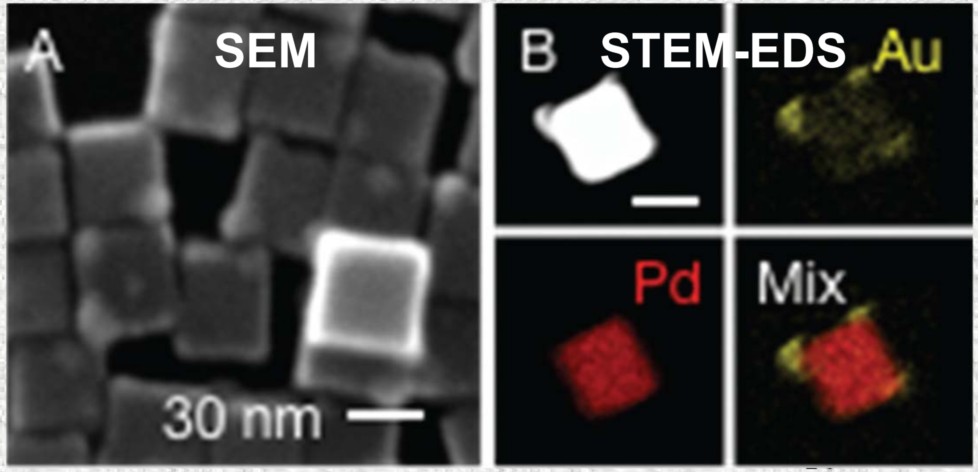




Markovnikov

Regioselectivity - difference between a nanocrystal's vertex and face
Face atoms have more bonds to neighboring atoms and are less reactive than vertex atoms

Pd cubes or octahedra as seeds
Heterogeneous nucleation of Au
Breaking the original $O_h$ symmetry
Anisotropic crystals

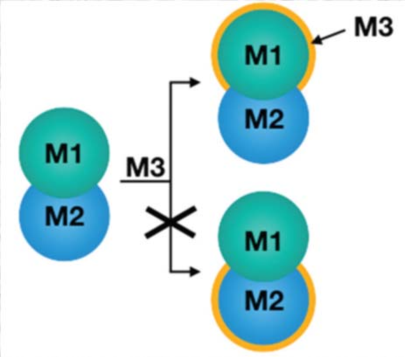
Crystallographically non-equivalent sites – mismatch different lattice constants

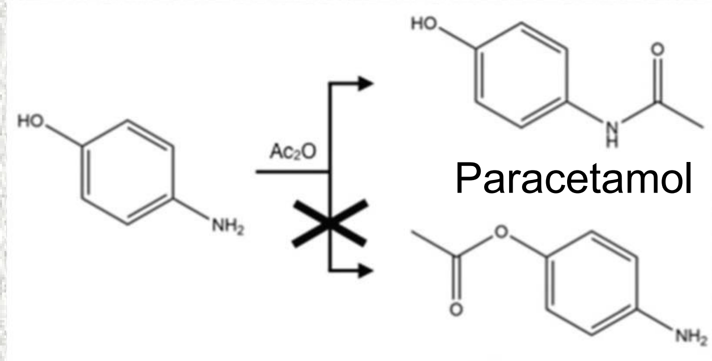


# Unique Features of the Nano-scale

## Chemoselectivity

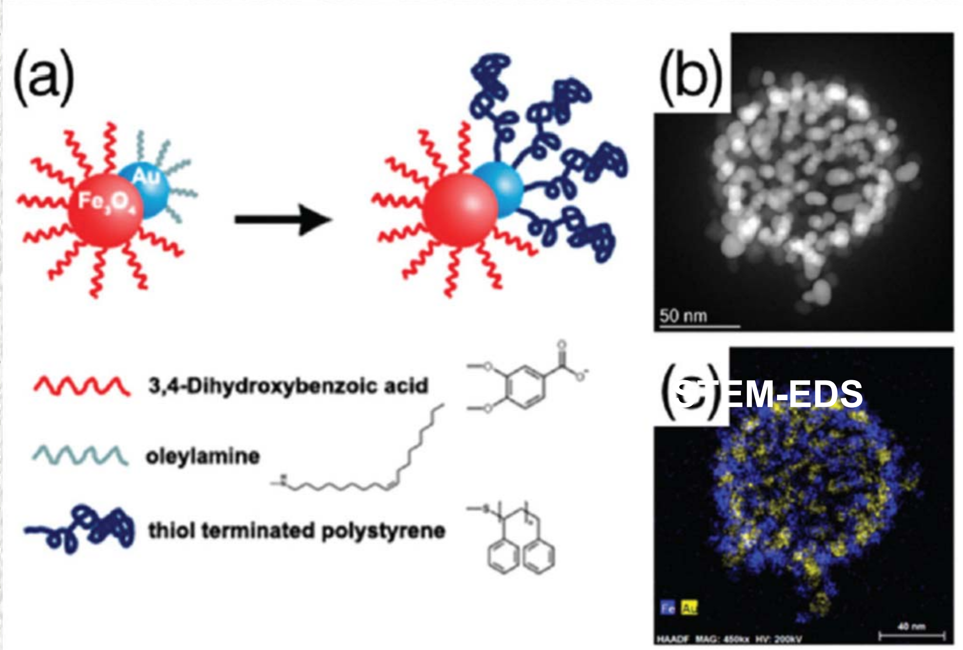
Janus nanoparticles




Chemically different phases
A chemoselective reaction occurs much more quickly at one of the phases

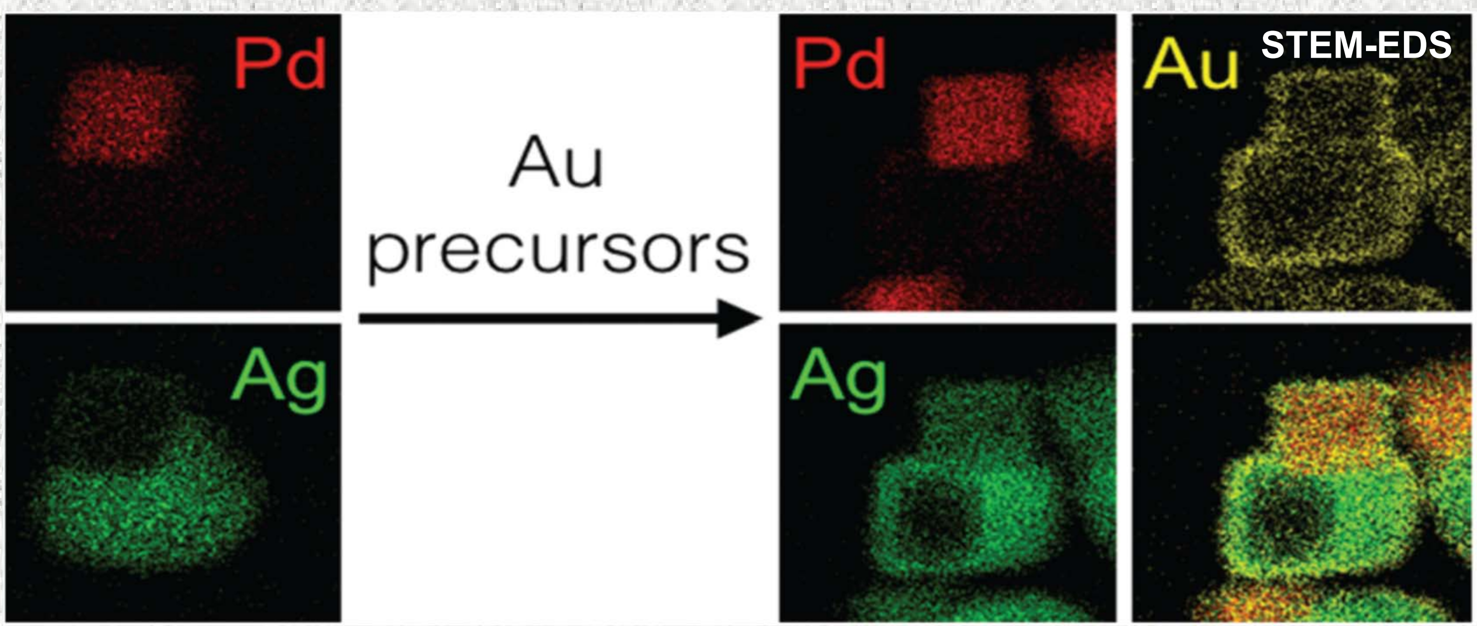
Au – thiol
$Fe_3O_4$ – 3,4-dihydroxybenzoic acid



# Unique Features of the Nano-scale

## Chemoselectivity

Janus Pd-Ag nanoparticles
Galvanic replacement with $[AuCl_4]^-$
The formation of a large void in Ag and a AgAu alloyed shell
Ag diffused elsewhere
Pd does not change

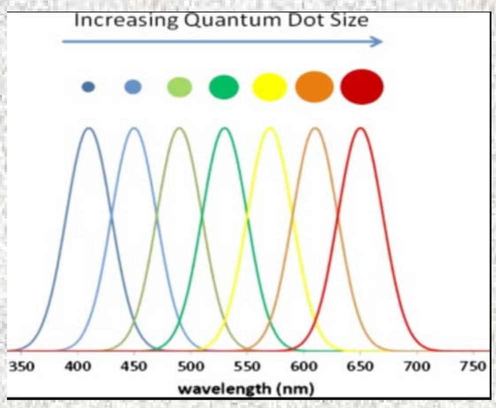


# Unique Features of the Nano-scale

## 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
= **particle 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, n:

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

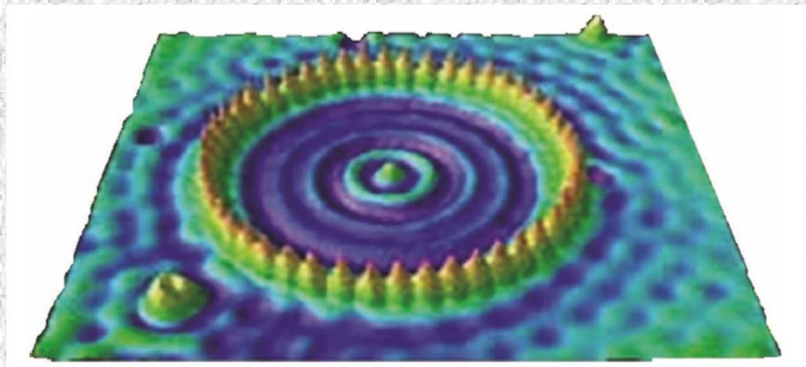
h is Planck's constant, $m_e$ is the electron mass, L x L x L is the confining volume

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

# Unique Features of the Nano-scale

## Wave-particle duality

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



48 Fe adatoms arranged on a Cu(111) surface at 4 K form a corral (radius 71.3 Å) confining the valence electrons - an electron trapped in a round two-dimensional box

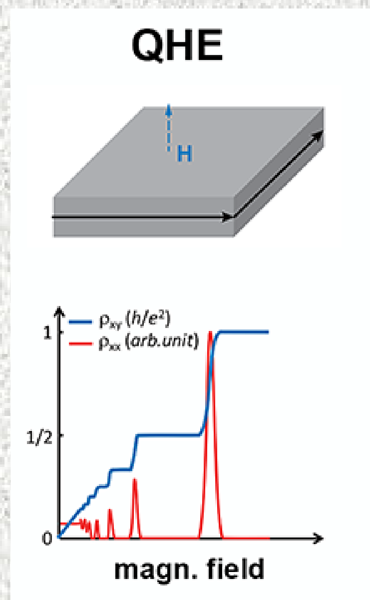
The probability density image determined by the wave function distribution captured by STM - wave function leakage into a positively biased scanning probe - discrete resonances = size quantization

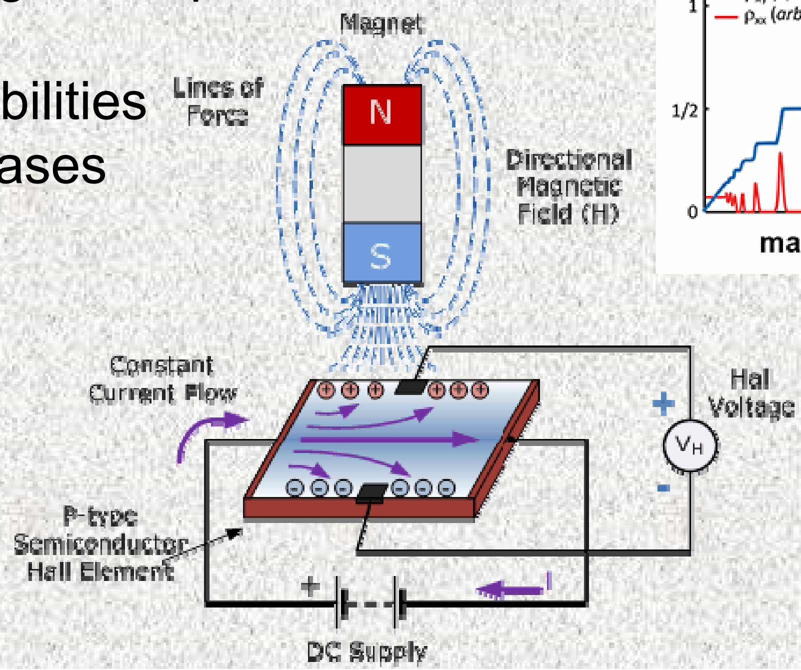
# Unique Features of the Nano-scale

## 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

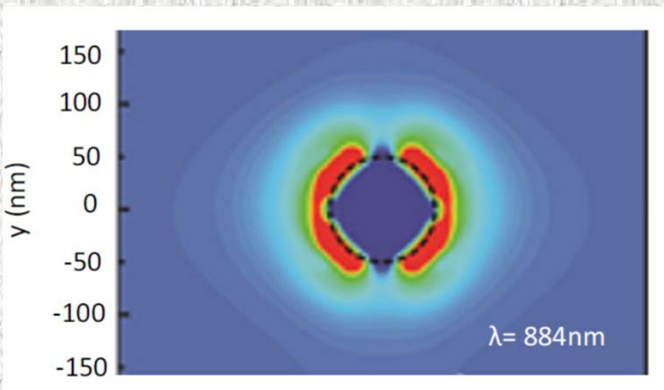


# Unique Features of the Nano-scale

## 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
- a 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 breaking down

**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

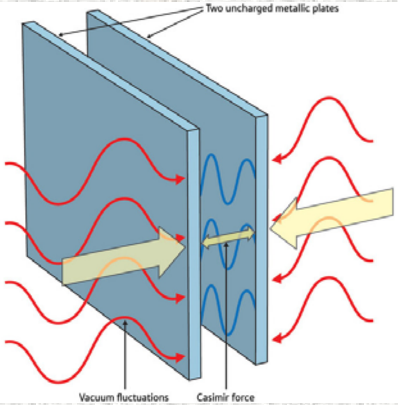
$$\Delta E \, \Delta t \geq \hbar$$

# Unique Features of the Nano-scale

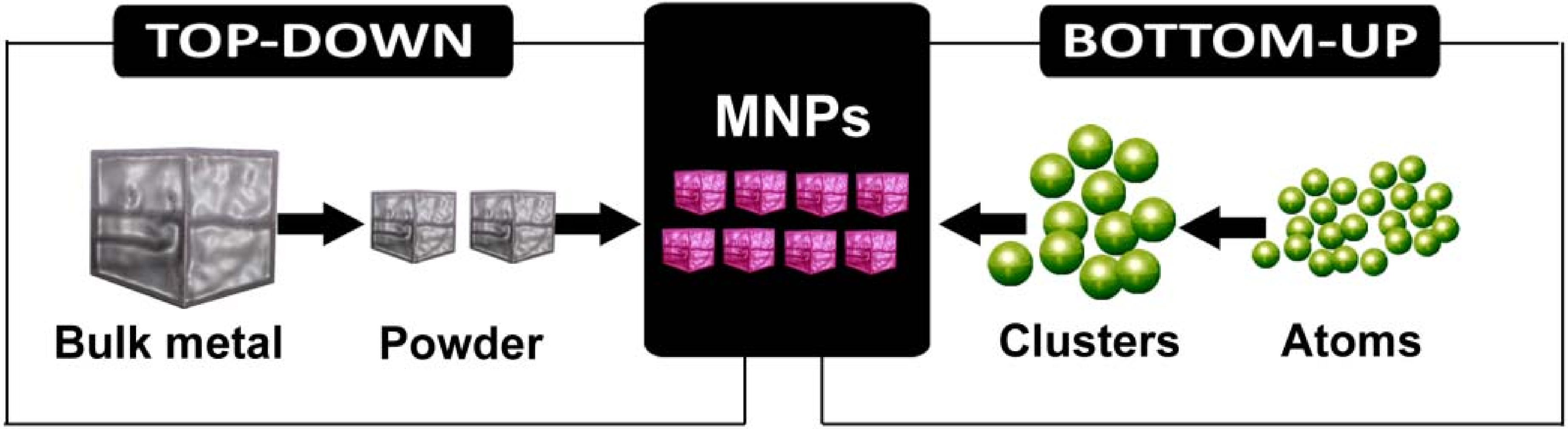
## Fluctuations

**Casimir force** (theor. 1948, exp. 1996) – a quantum phenomenon
A pressure that pushes objects of 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 quantum vacuum fluctuations - space is not empty but is filled with spontaneously appearing and disappearing particles

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



# Synthesis Methods

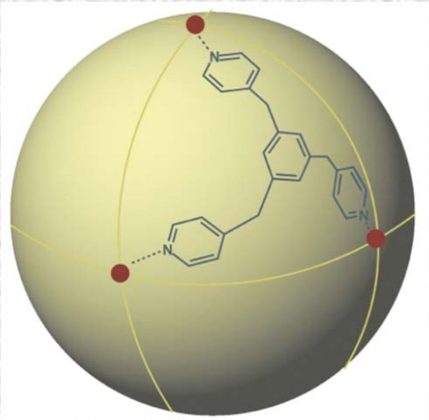


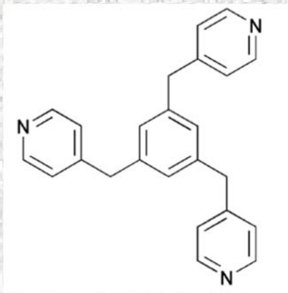

**Top-down:** from bulk to nanoparticles

**Bottom-up:** from atoms to nanoparticles

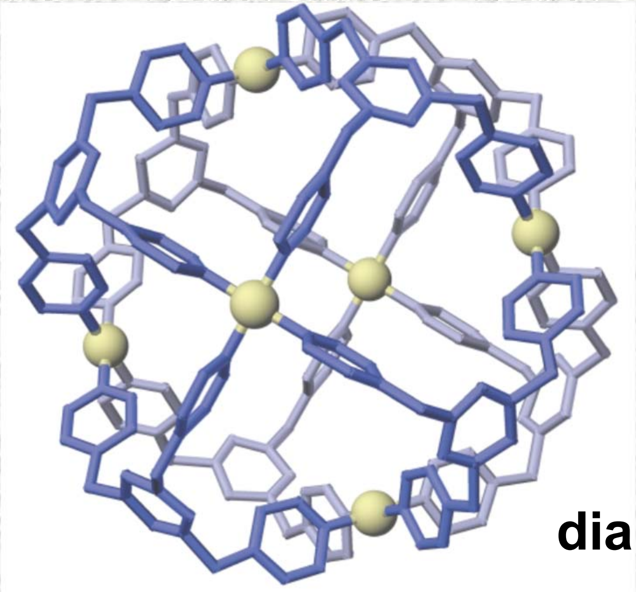
# Bottom-up Synthesis: Atom Up

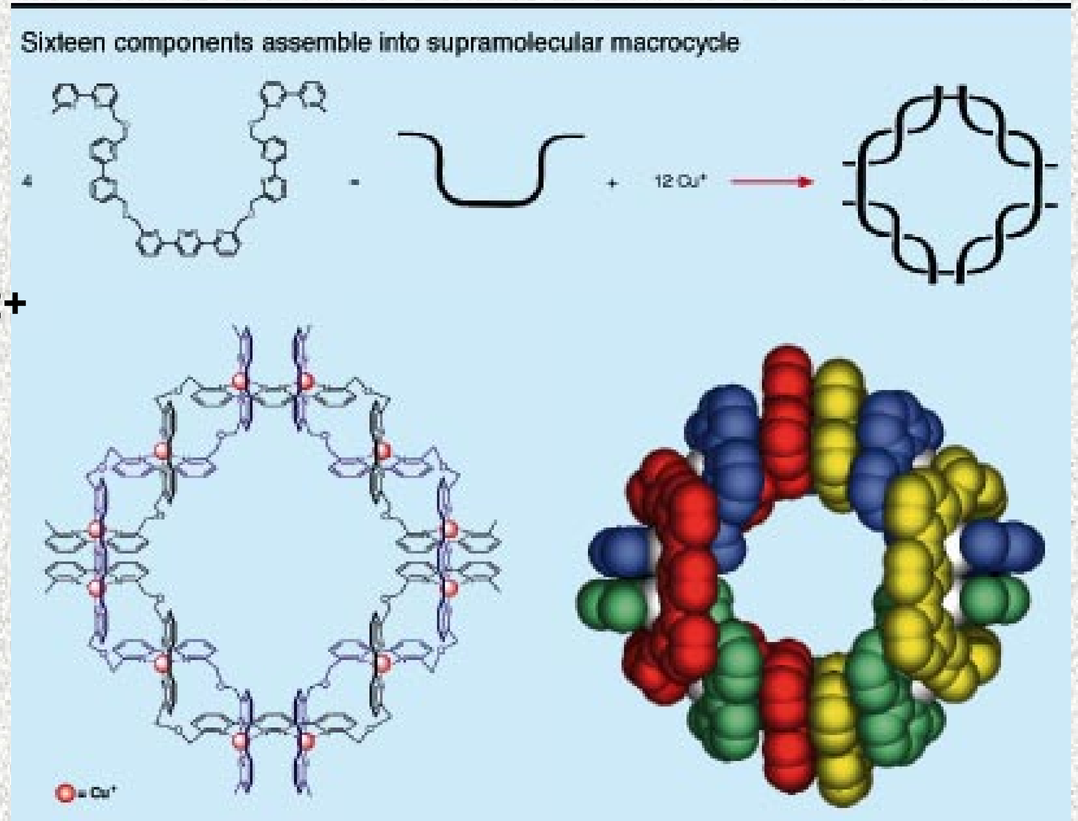
## Coordination chemistry – molecular cages





$[(Pd)_6(L)_8]^{12+}$

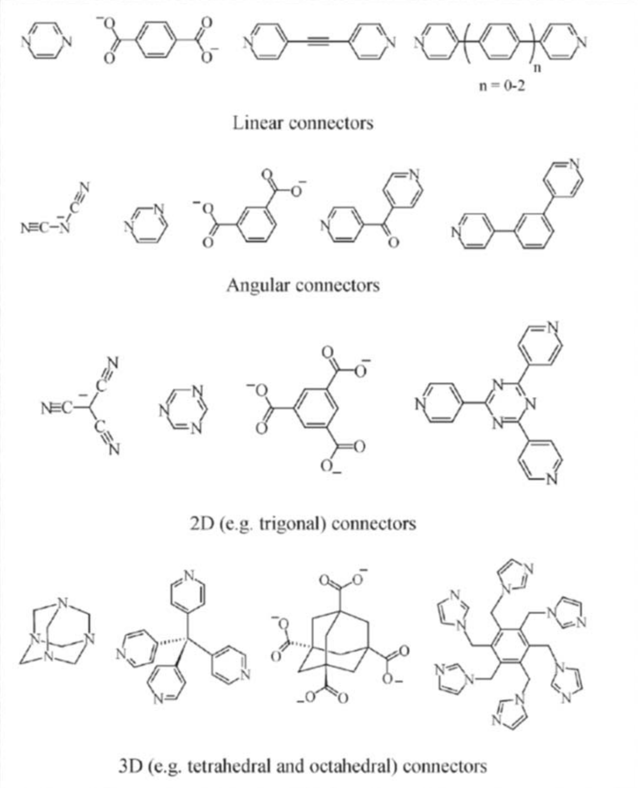





diam = 19 Å

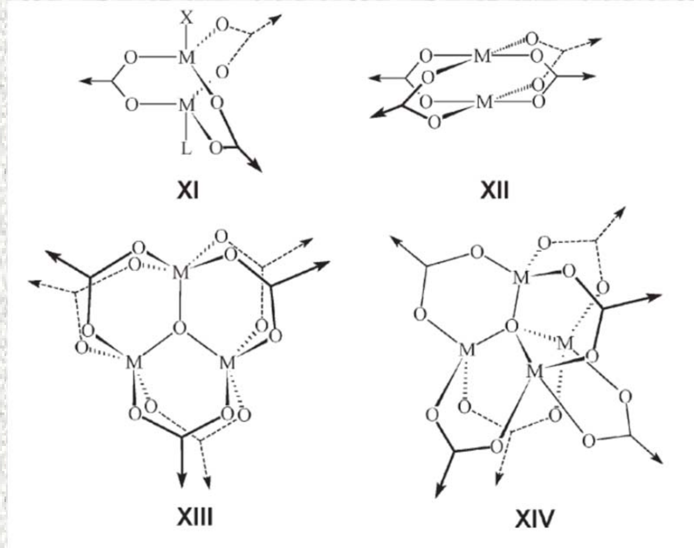
# Bottom-up Synthesis: Atom Up

## Coordination chemistry – Metal-organic frameworks (MOFs)




**Polytopic Ligands**
Organic spacers
Flexible or rigid
Variable length
Directionality

**Metal centers**
Coordinative bonds
Coordination numbers 3-6
Bond angles
Secondary Building Units



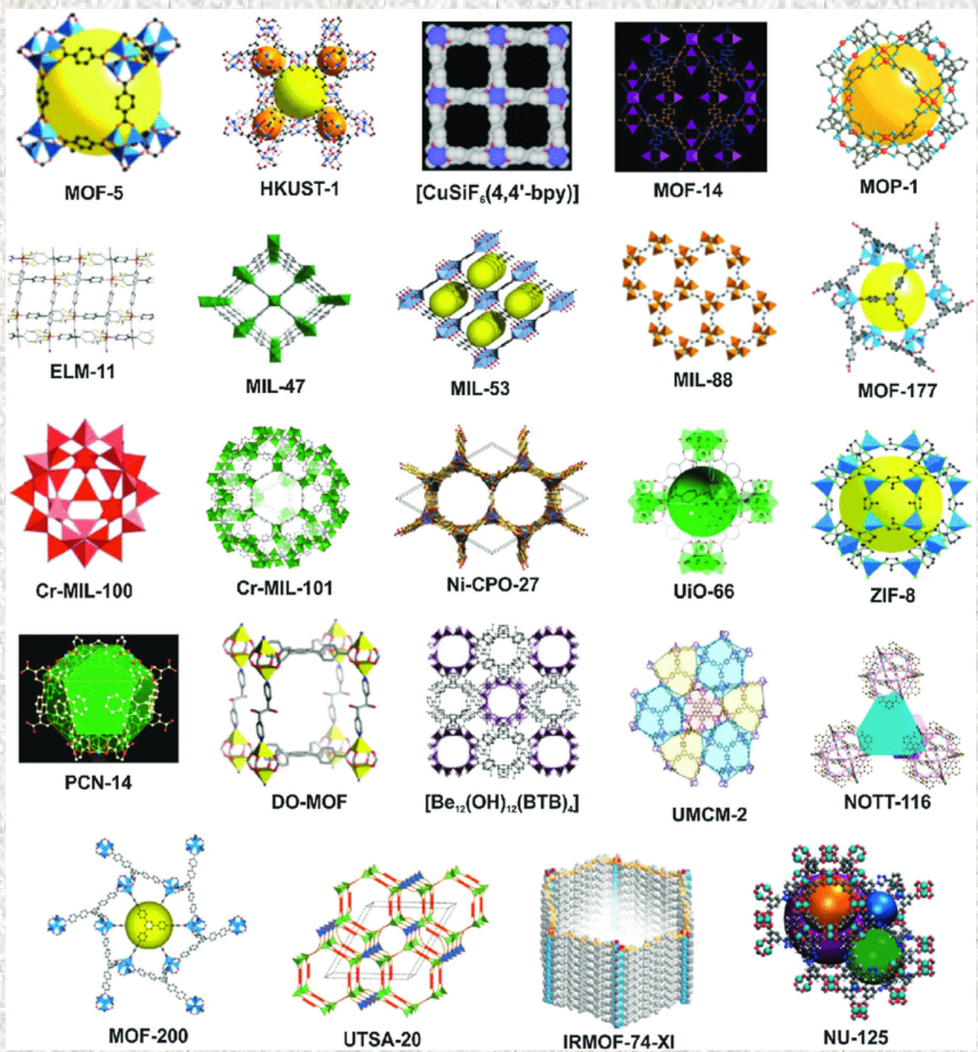
# Metal-Organic Frameworks (MOFs)

- organic-inorganic hybrids
- crystalline
- porous

A regular array of positively charged metal ions (nodes ) surrounded by organic molecules (linkers)

A repeating cage-like structures

An extraordinarily large internal surface area



# 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 $\rightarrow$ $\beta$-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)

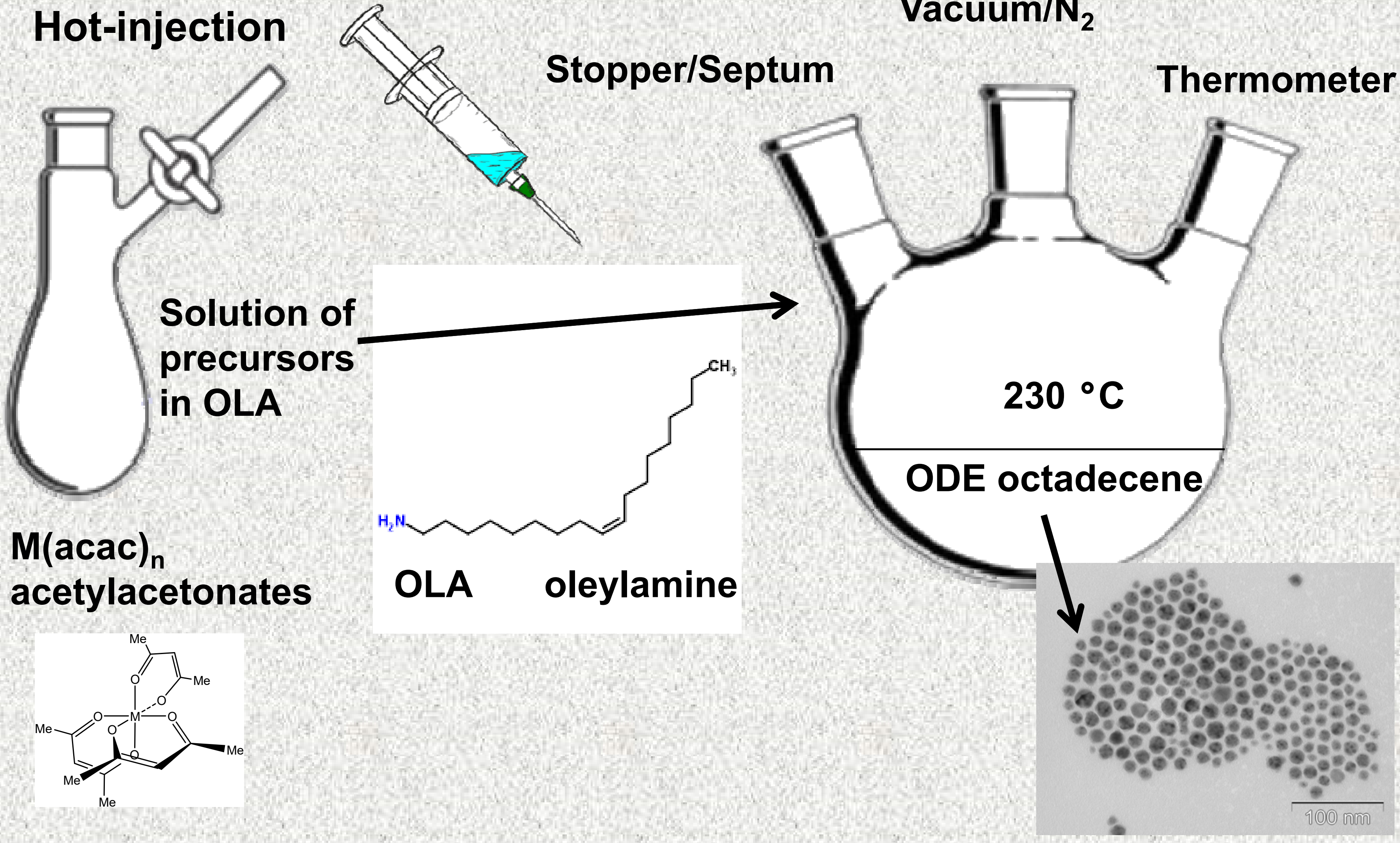
$Si(OEt)_4 + Ag^+$ or $Cu^{2+} + H_2O \rightarrow$ $SiO_2/Ag^+/Cu^{2+}$ metal-impregnated gel

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

# Bottom-up Synthesis

**Thermal decomposition of precursors**

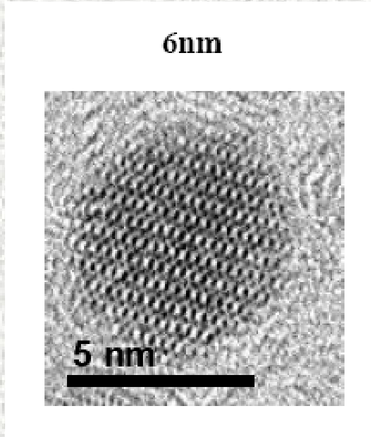
**Hot-injection**



# Thermal Decomposition of Precursors

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

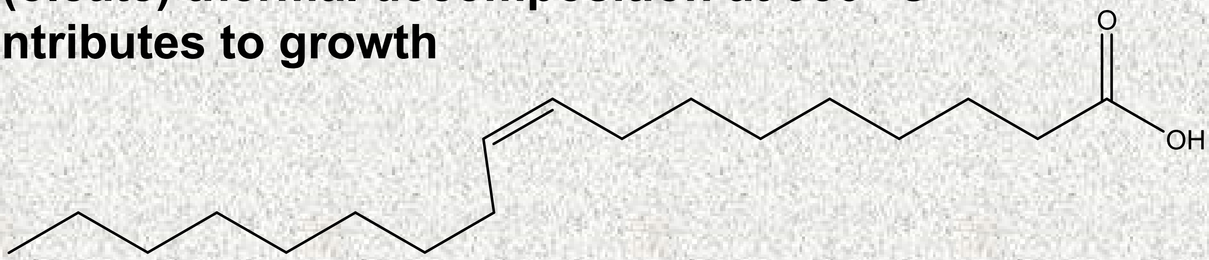
6 nm




**Separation of nucleation and growth**

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

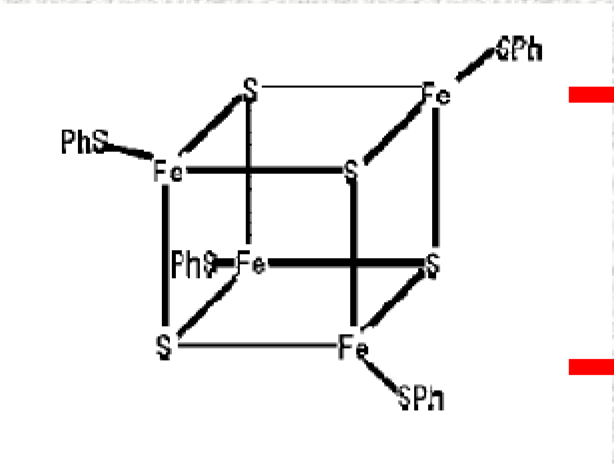
**Fe(oleate) thermal decomposition at 350 $^{o}$C contributes to growth**



# Thermal Decomposition of Precursors

## Phase Control

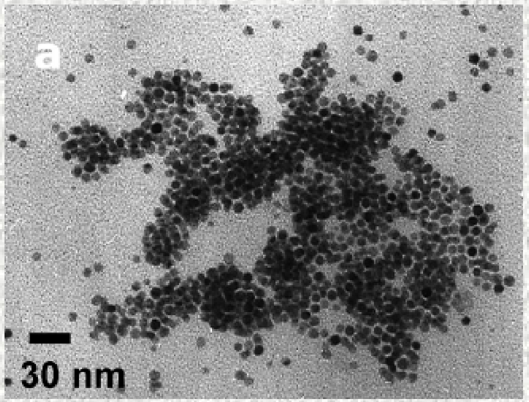
$[N^{n}Bu_4]_2[Fe_4S_4(SPh)_4]$



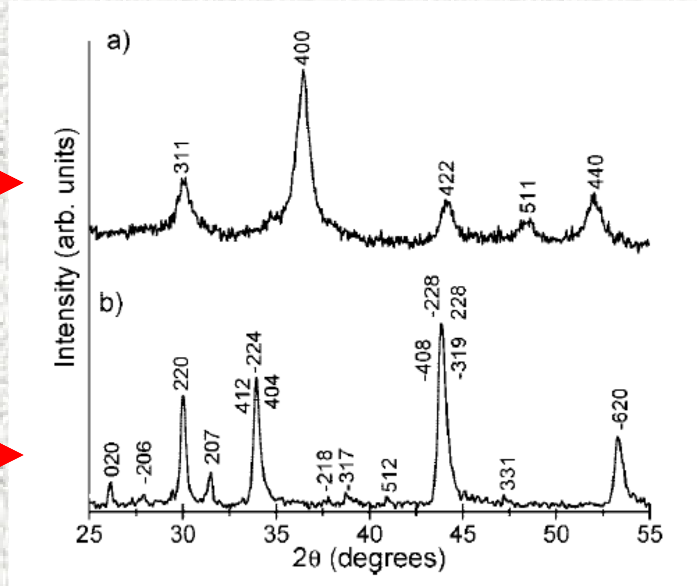

**Thermolysis**

**180 °C**
**in octylamine**

**200 °C**
**in dodecylamine**



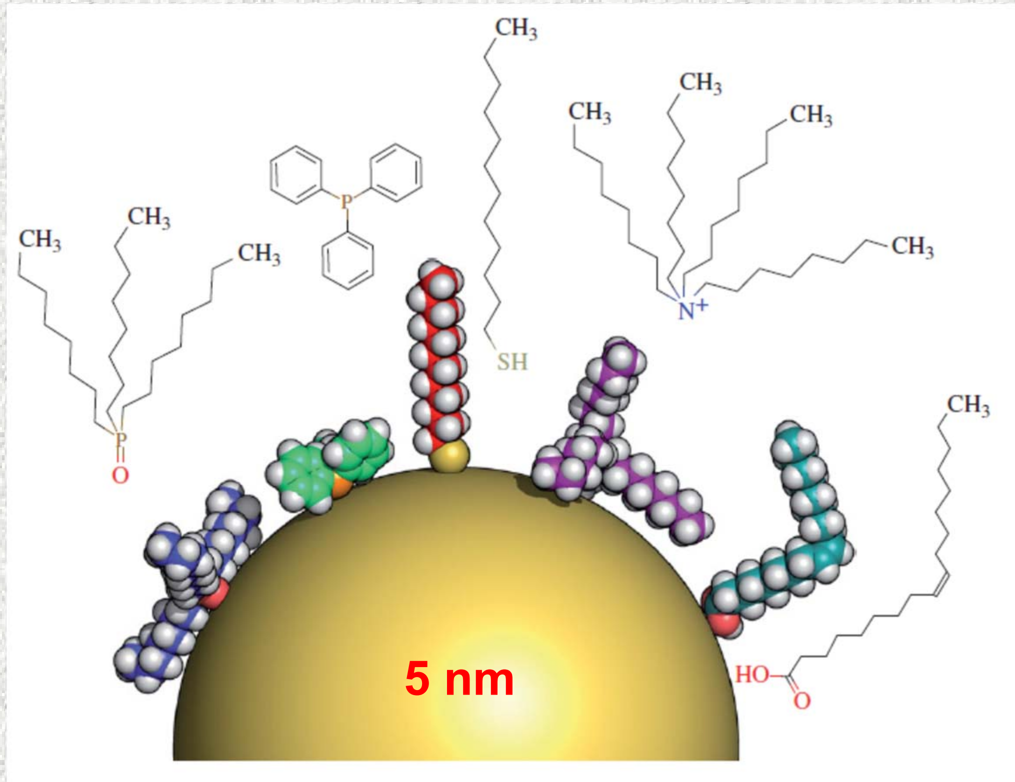

## pyrrhotite $Fe_7S_8$




## greigite $Fe_3S_4$

**thiospinel, the sulfide analogue of magnetite**

# 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)

# LaMer Mechanism

## Hot-injection synthesis

1) Monomer formation

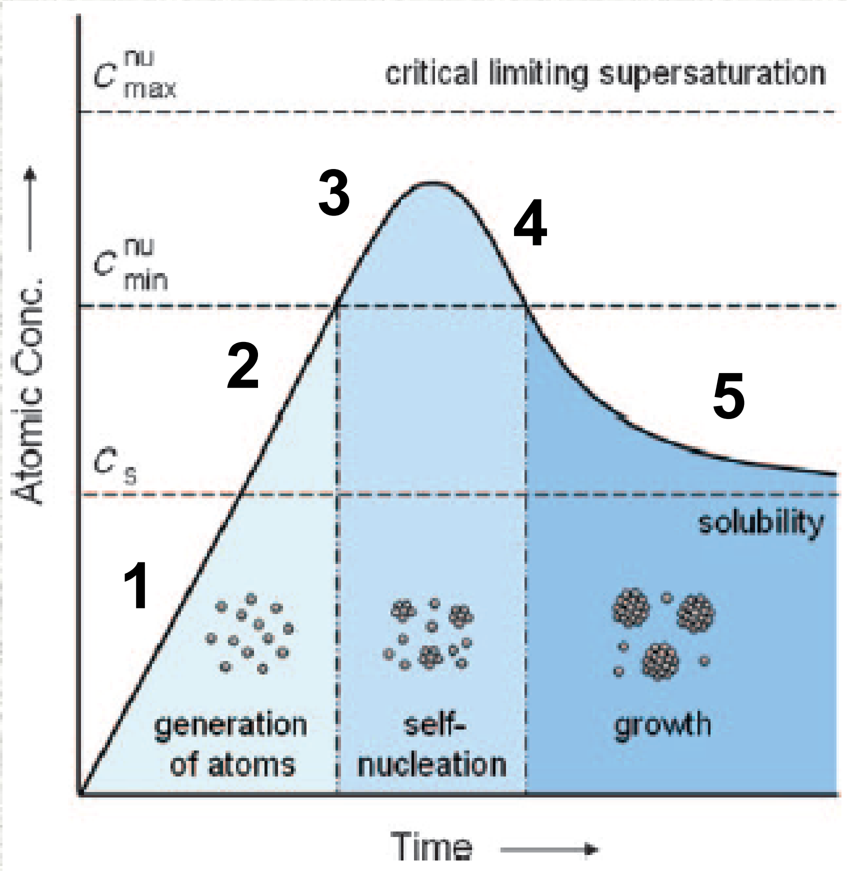
2) Supersaturated solution

3) Burst of nucleation

4) Depletion of monomer

5) Slow growth of particles without additional nucleation

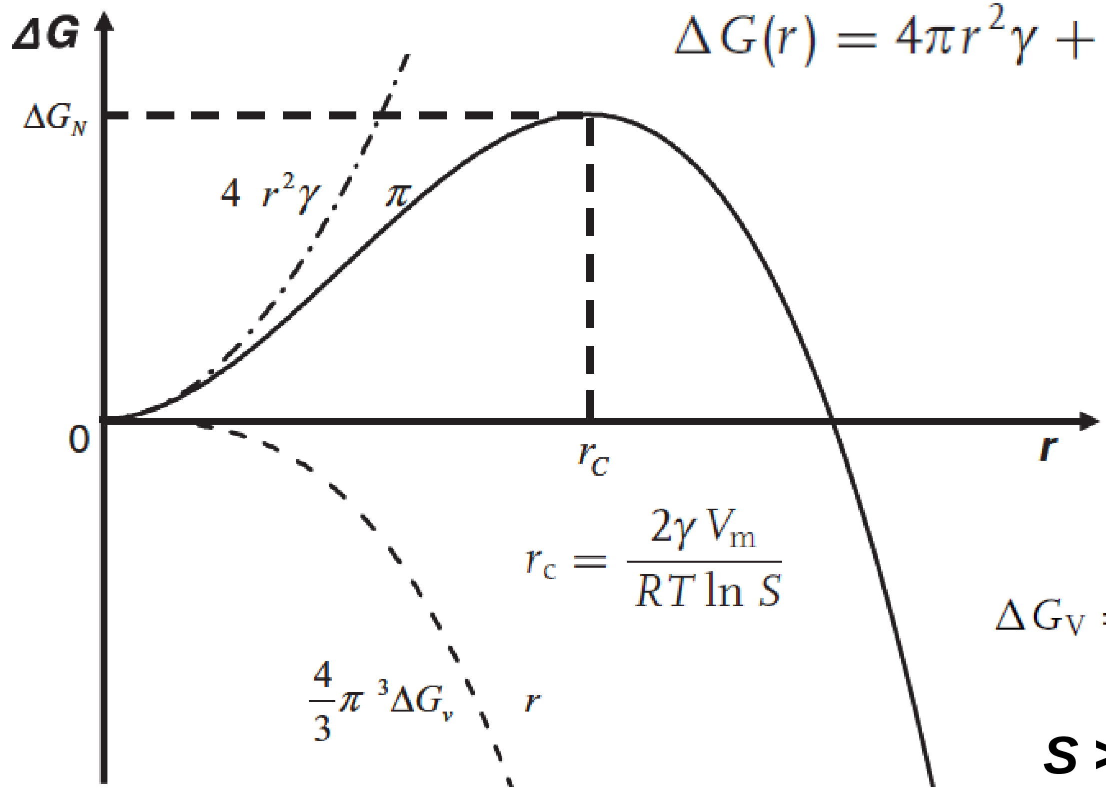
**Separation of nucleation and growth - monodisperse**



# Bottom-up Synthesis

## Crystallization free energy

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




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

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

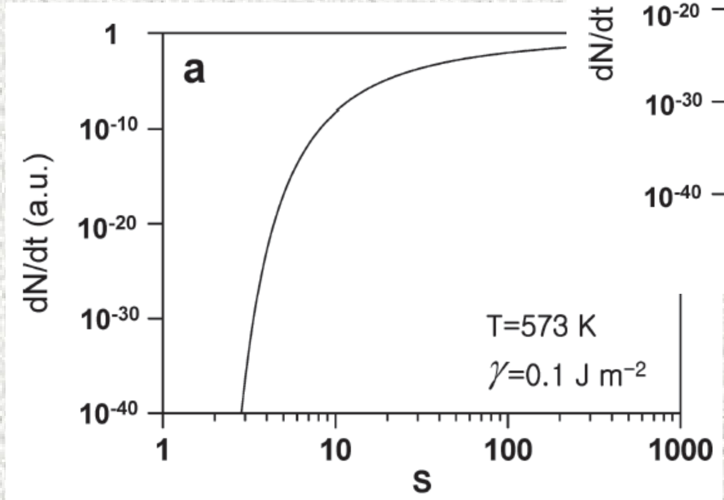
***S* > 1 supersaturation**

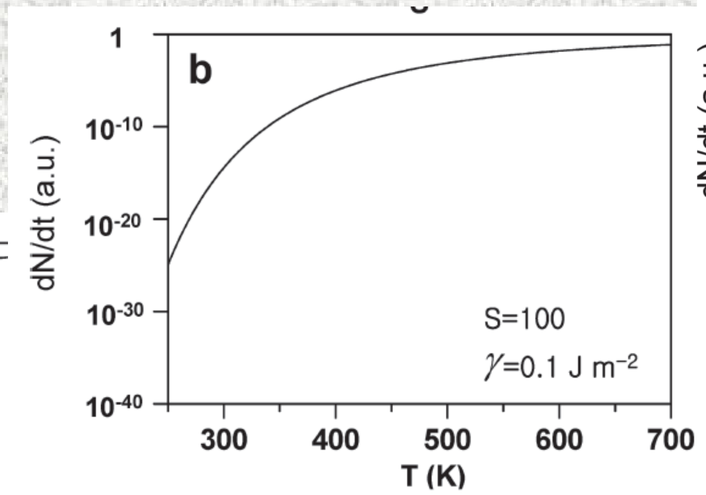
# Bottom-up Synthesis

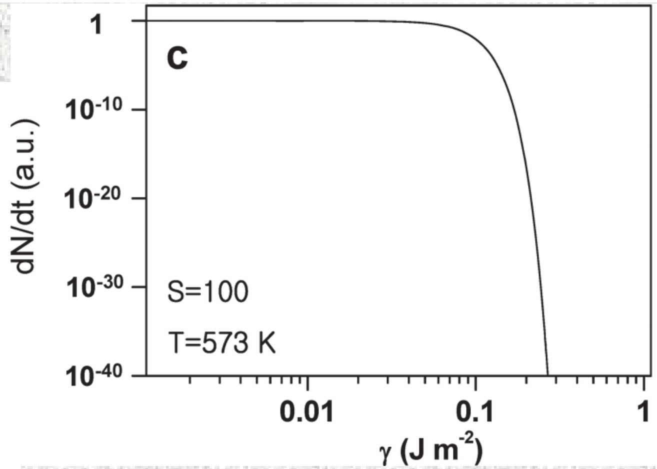
**Nucleation rate**

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

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



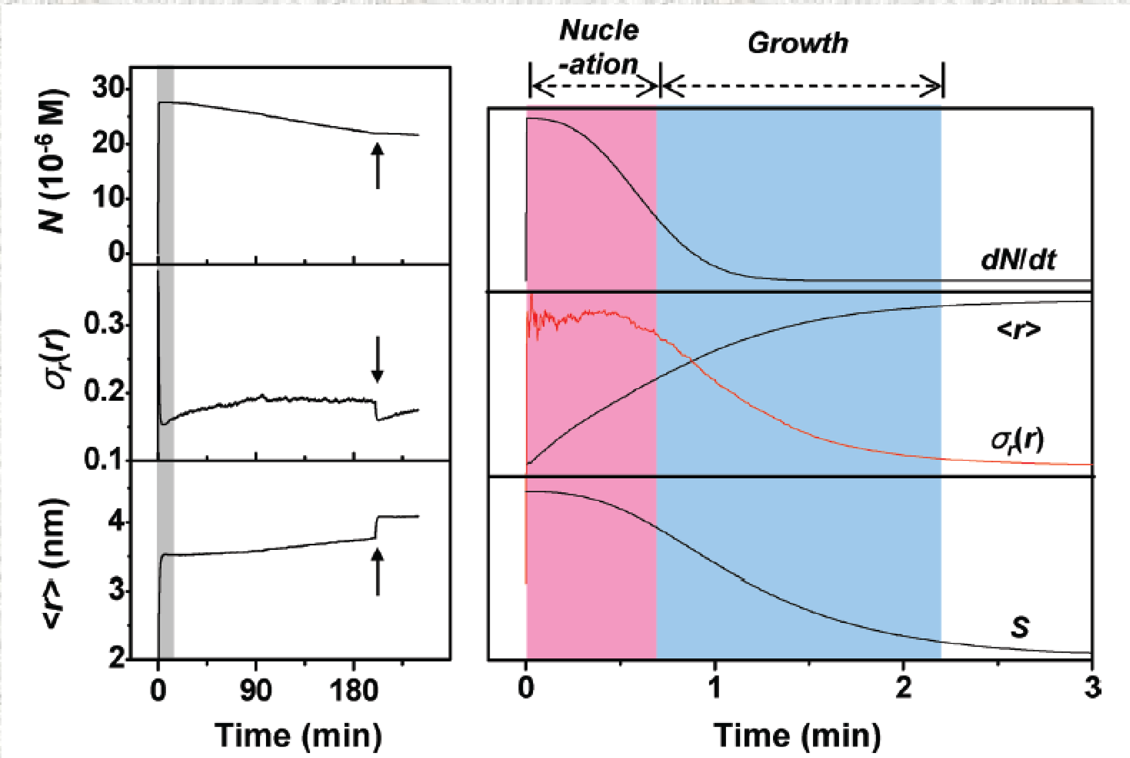




$V_m = 3.29 \times 10^{-5}\ m^3\ mol^{-1}$ (CdSe)

# Bottom-up Synthesis

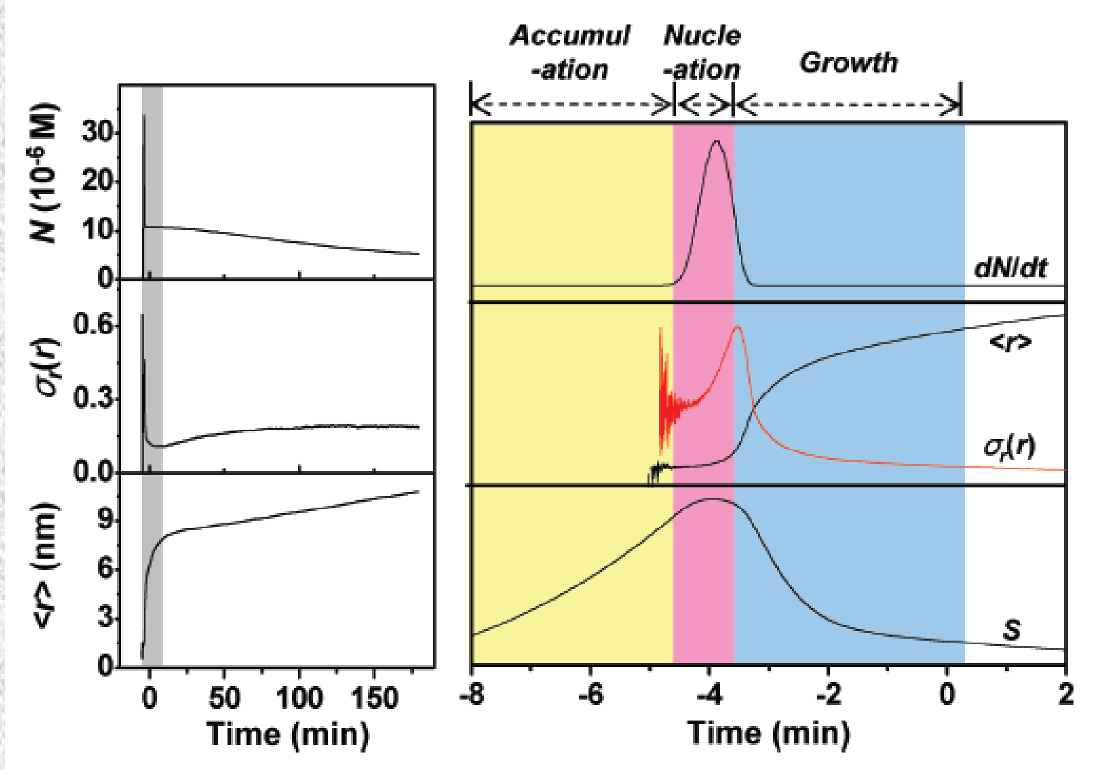
**Hot-injection**




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

# Bottom-up Synthesis

**Heat-up**

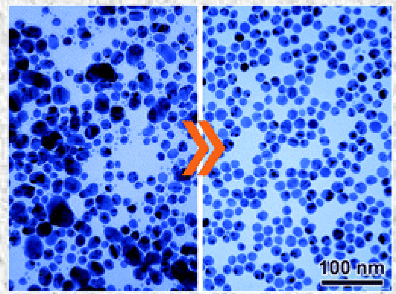



***N*** **= the number concentration of the nanocrystals**
**σ(** ***r*** **) = relative standard deviation of their radii r**
**<** ***r*** **> = mean radius**
***dN*** **/** ***dt*** **= nucleation rate**

# 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**

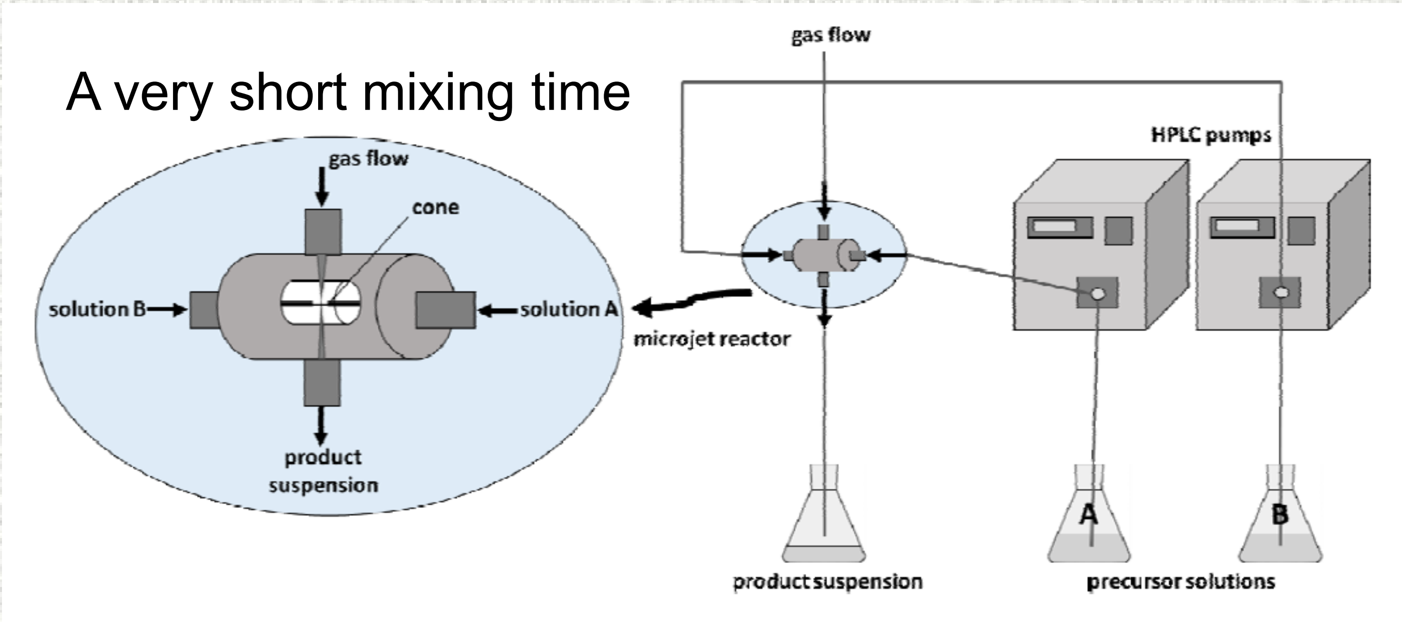
Slow continuous nucleation - Fast autocatalytic surface growth

**Seed-mediated Mechanism**

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

# Continuous Synthesis of Inorganic Nanoparticles

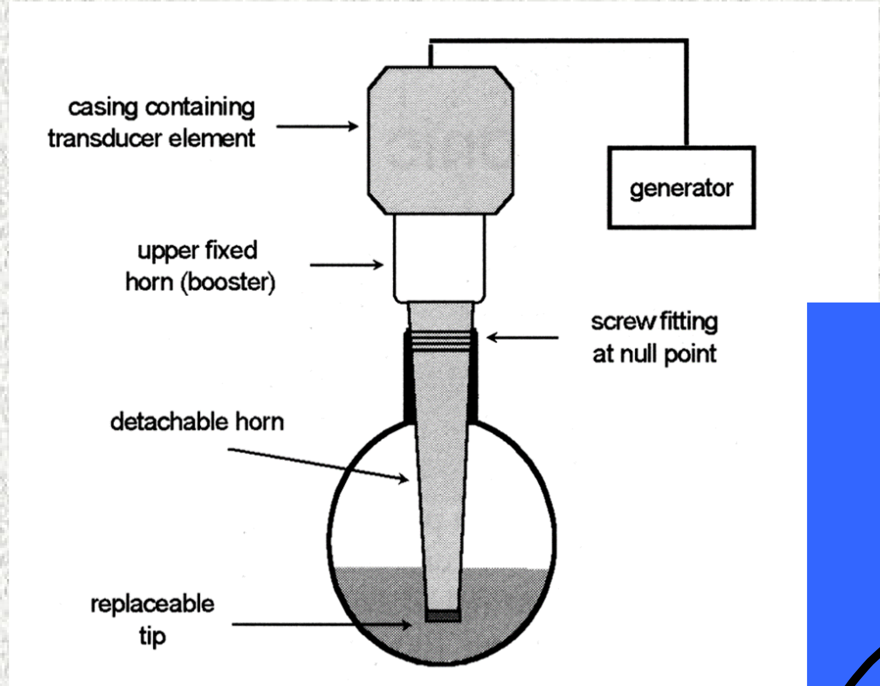
Rapid mixing of two precursor solutions and the fast removal of the nuclei from the reaction environment



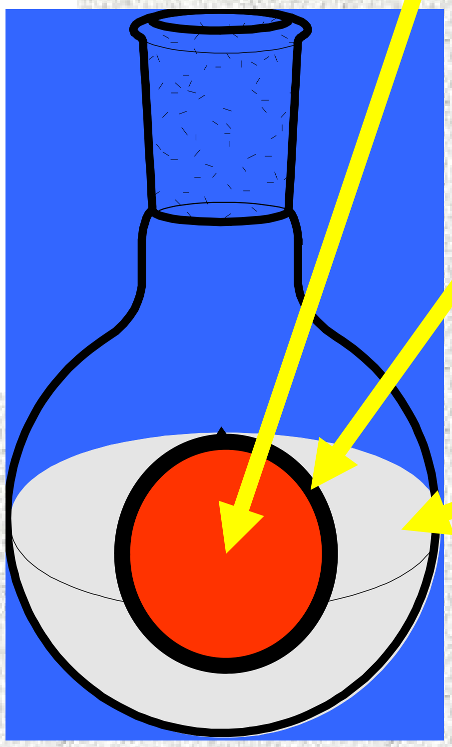

Transport from the reactor to a tubing for the particle growth
The length of tubing up to the collection vessel influences the particle growth

# Bottom-up Synthesis

## Sonocative decomposition of precursors




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



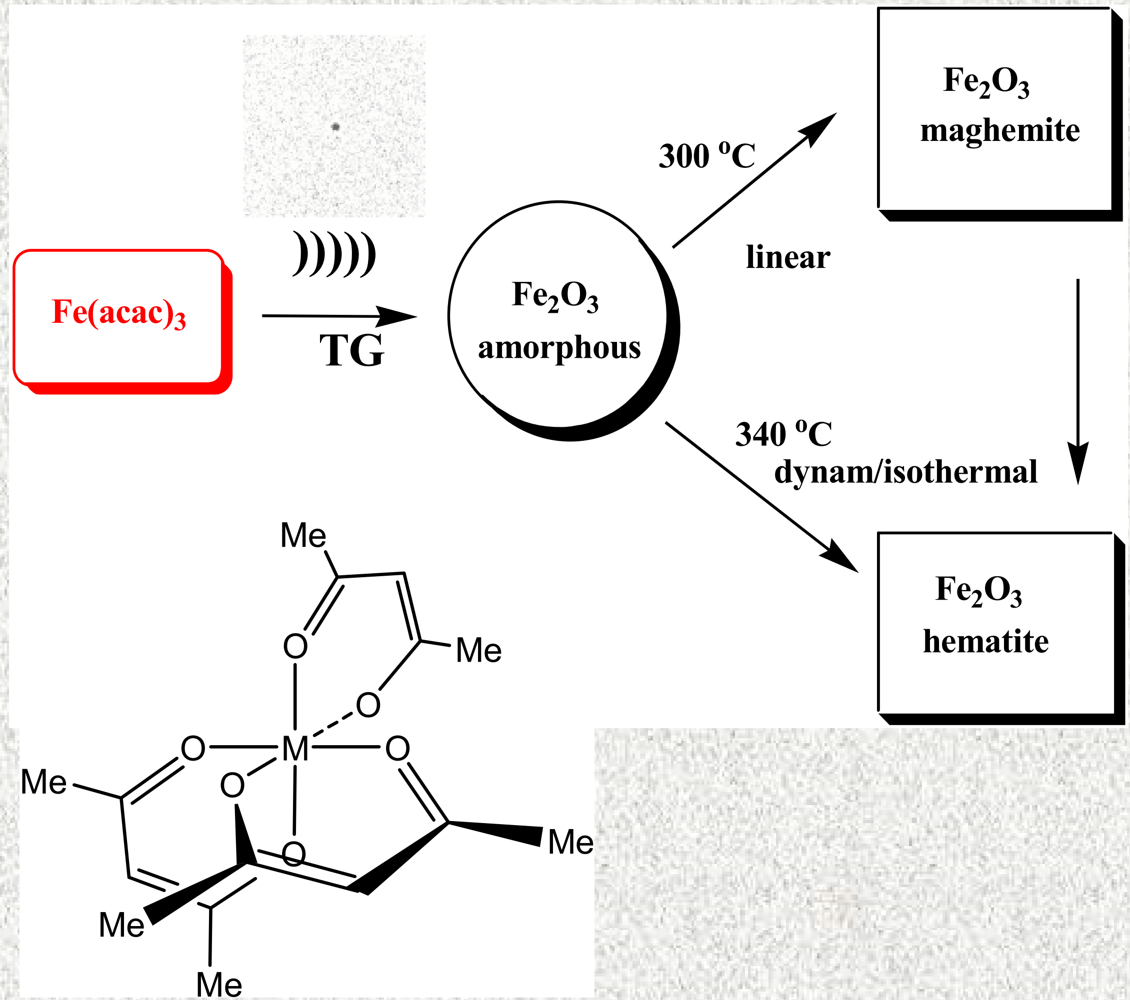
**Surrounding liquid layer**
**2000 °C**

**Bulk liquid**
**shock waves**
**shear forces**

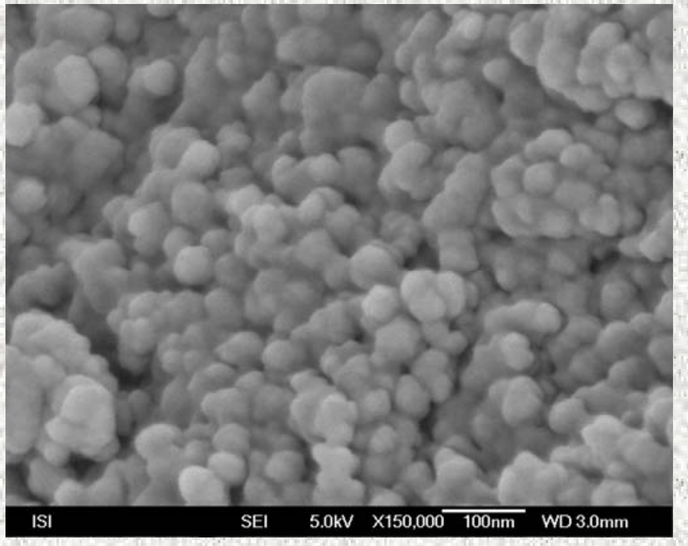
**Cavitation**
**creation, growth, and implosive collapse of bubbles in a liquid**

# Bottom-up Synthesis

## Sonocative decomposition of precursors




**Particle size 20 - 30 nm**
**Spherical shape**
**Uniform size distribution**



# Borohydride Reduction

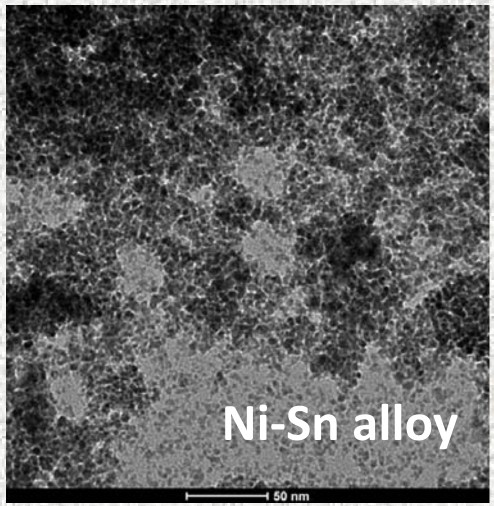
**Reduction of Metal Ions**
**Manhattan Project**

**$NaBH_4$**
**$BH_3NH_2tBu$**
**$NR_4[BEt_3H]$**

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

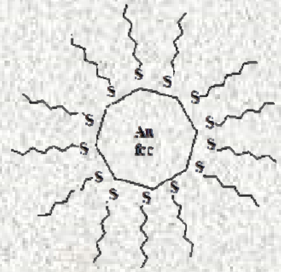
$TiCl_4 + 2\ NaBH_4 \rightarrow TiB_2 + 2\ NaCl + 2\ HCl + H_2$

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




**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, ….**

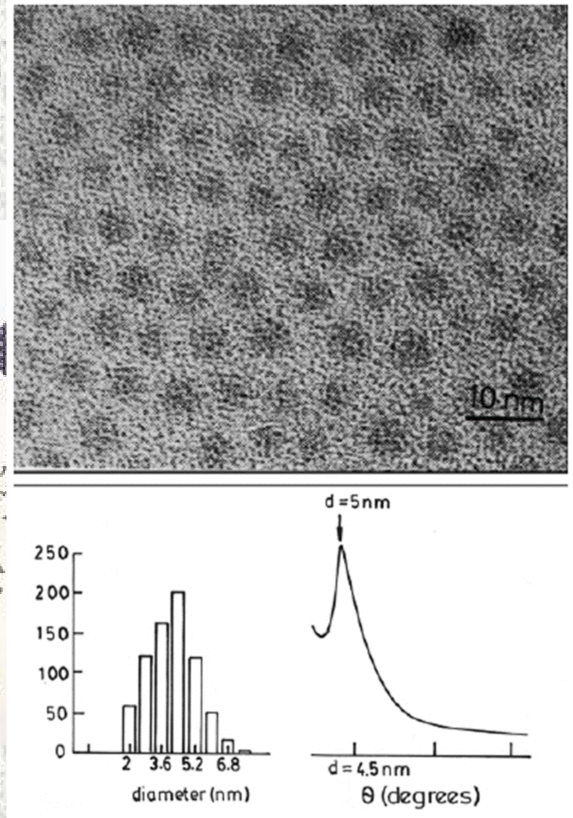
# Borohydride Reduction

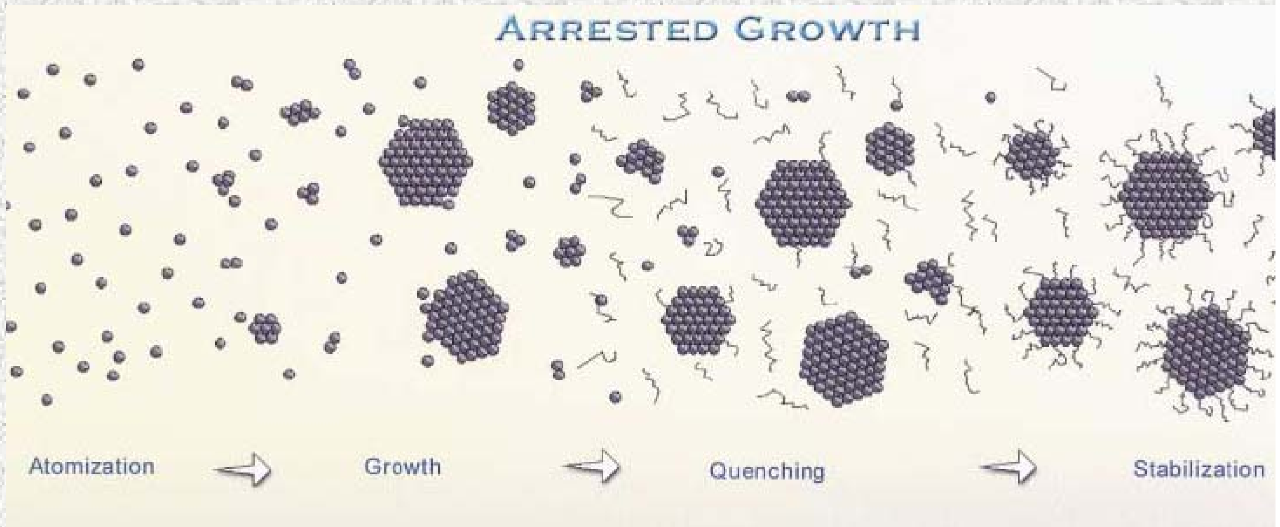


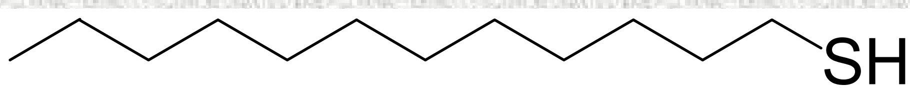

**Au colloidal particles**

**$HAuCl_4$ + $NaBH_4$ 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

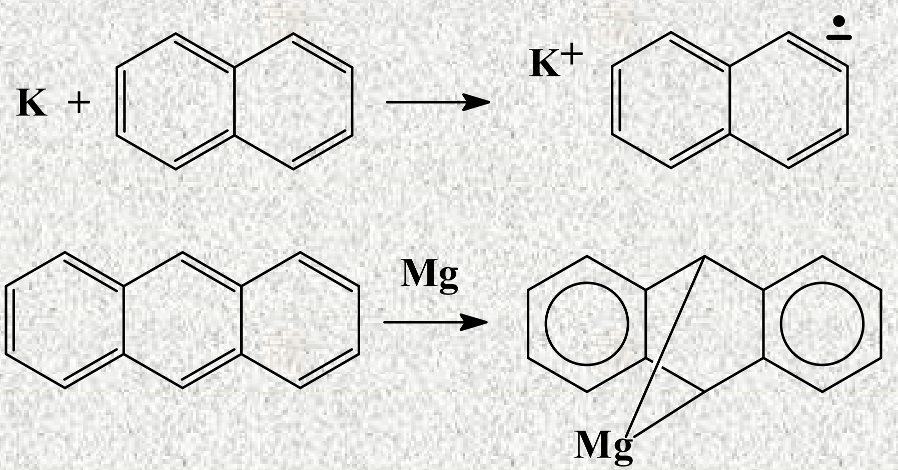
**Solvents: dry anaerobic diglyme, THF, ethers, xylene**

**$NiCl_2$ + 2 K → Ni + 2 KCl**

**$AlCl_3$ + 3 K → Al + 3 KCl**

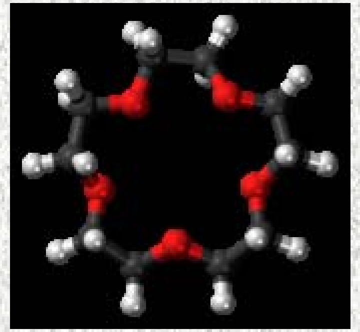
**Reduction by Glycols or Hydrazine**

**"Organically solvated metals"**



# Bottom-up Synthesis

**Alkalide Reduction**



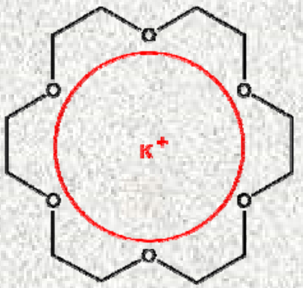
$$13\ K^+(15\text{-crown-}5)_2Na^- + 6\ FeCl_3 + 2CBr_4$$

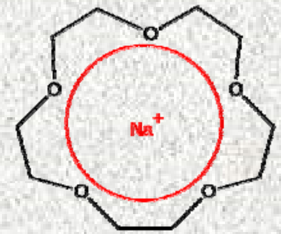
$$\Big\downarrow \text{THF},\ -30\ °C$$

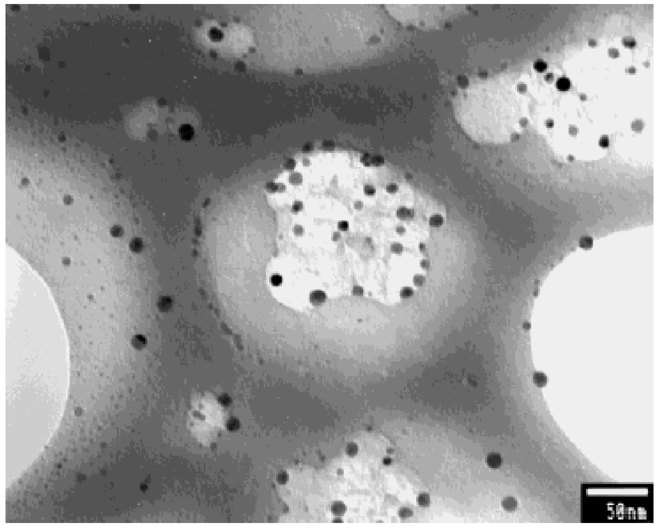
$$2\ Fe_3C\ (\text{nano}) + 13\ K(15\text{-crown-}5)_2Cl_{0.43}Br_{0.57} + 13\ NaCl$$

**Anealed at 950 °C / 4 h**

**$Fe_3C$: 2 – 15 nm**



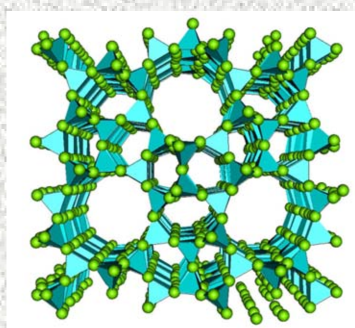
# Reactions in Porous Solids

Zeolites, Mesoporous materials

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

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

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



Ship-in-the-Bottle Synthesis

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

Ru(III)-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

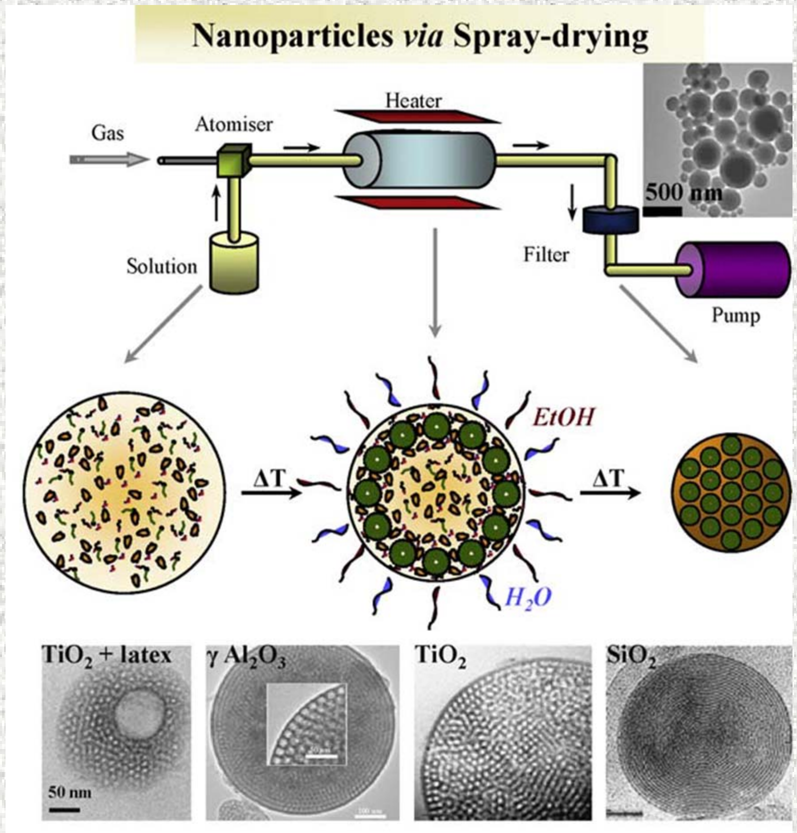
# Bottom-up Synthesis

**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**

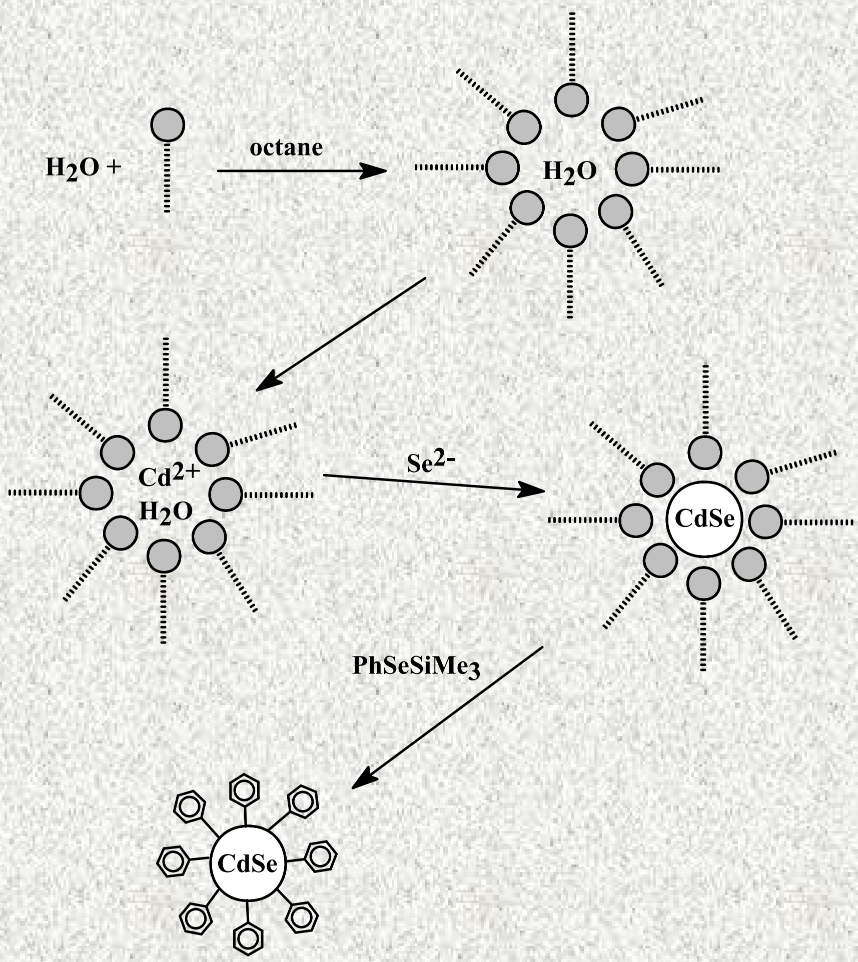


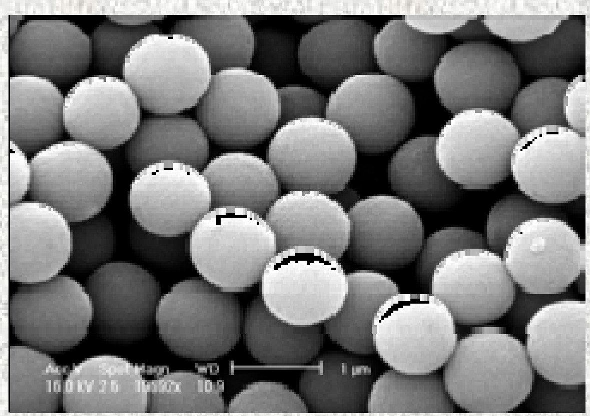

$$3\ Gd(NO_3)_3 + 5\ Fe(NO_3)_3 \rightarrow Gd_3Fe_5O_{12} + 6\ O_2 + 24\ NO_2$$

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

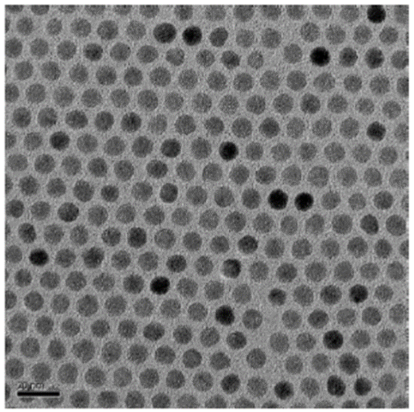
# Bottom-up Synthesis

## Inverse micelles

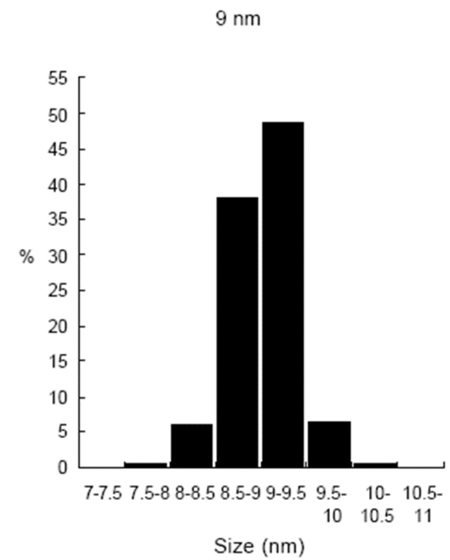


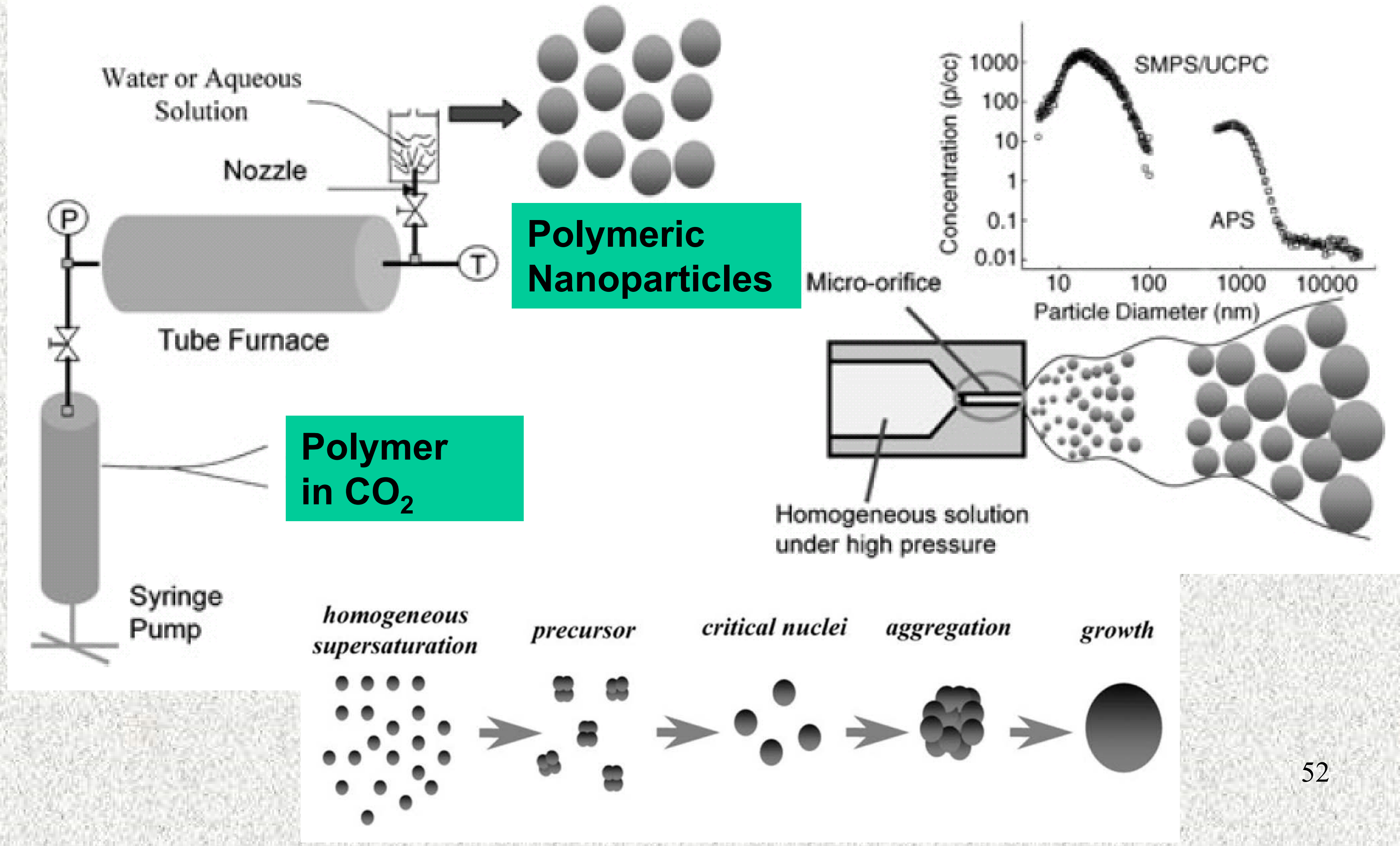
## Size distribution histogram



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



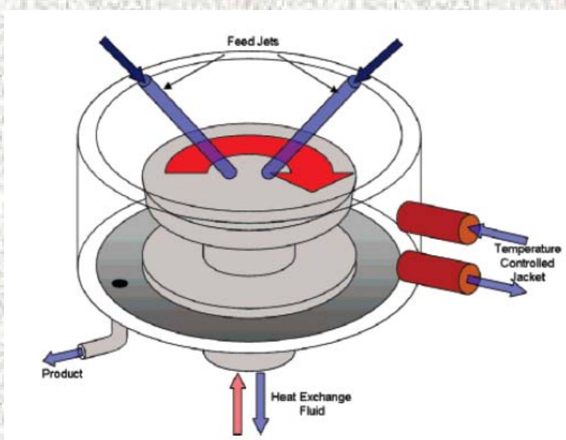
# Rapid Expansion of Supercritical Fluid Solution



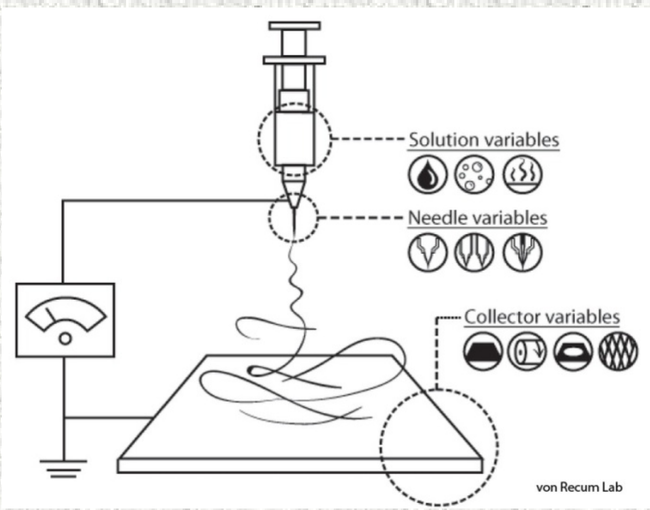
# Spinning Disc Processing SDP

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 $\mu$m) 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%

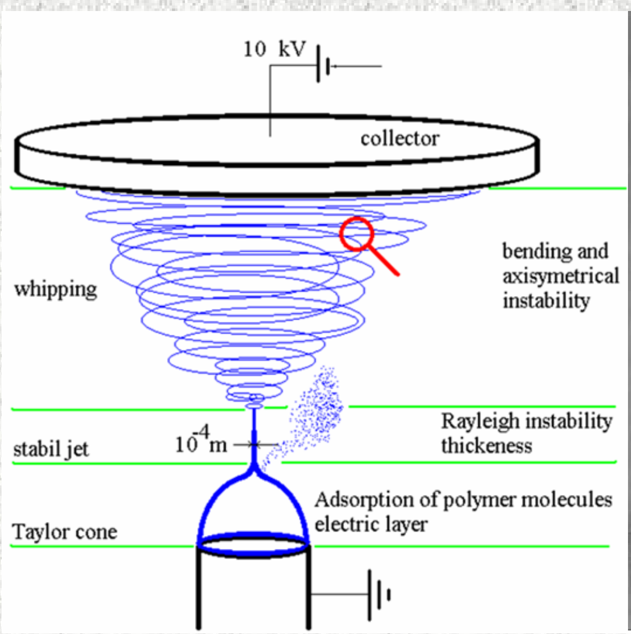


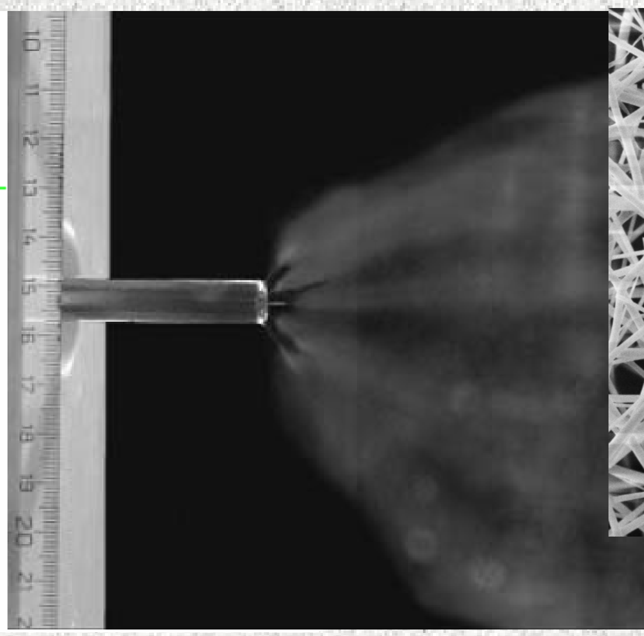
# Electrospinning

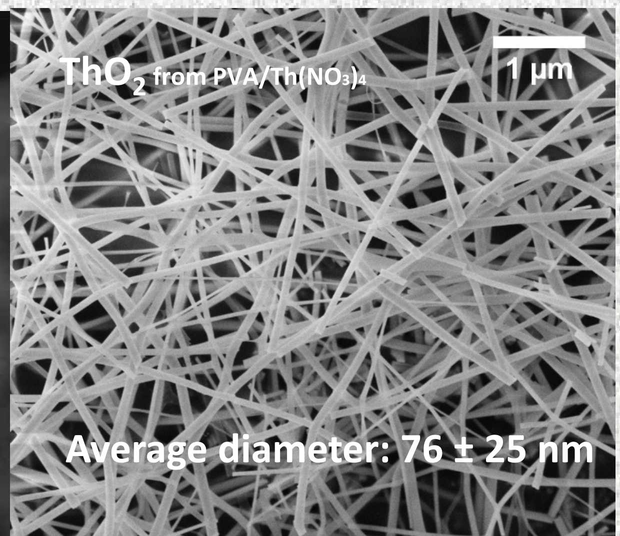



**Parameters**

- **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

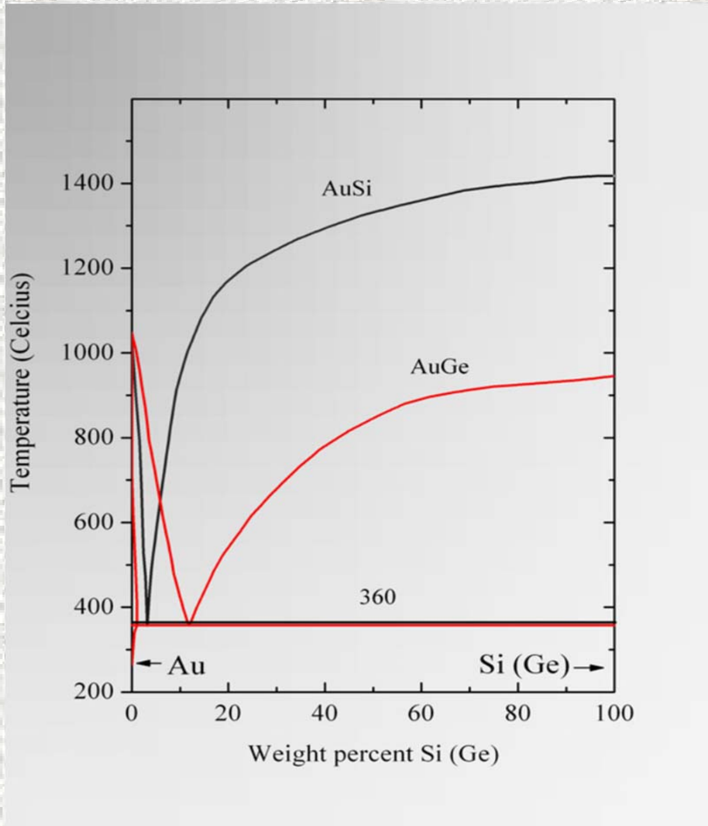
Metal catalyst nanoparticles - Au(s) – (1)

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)

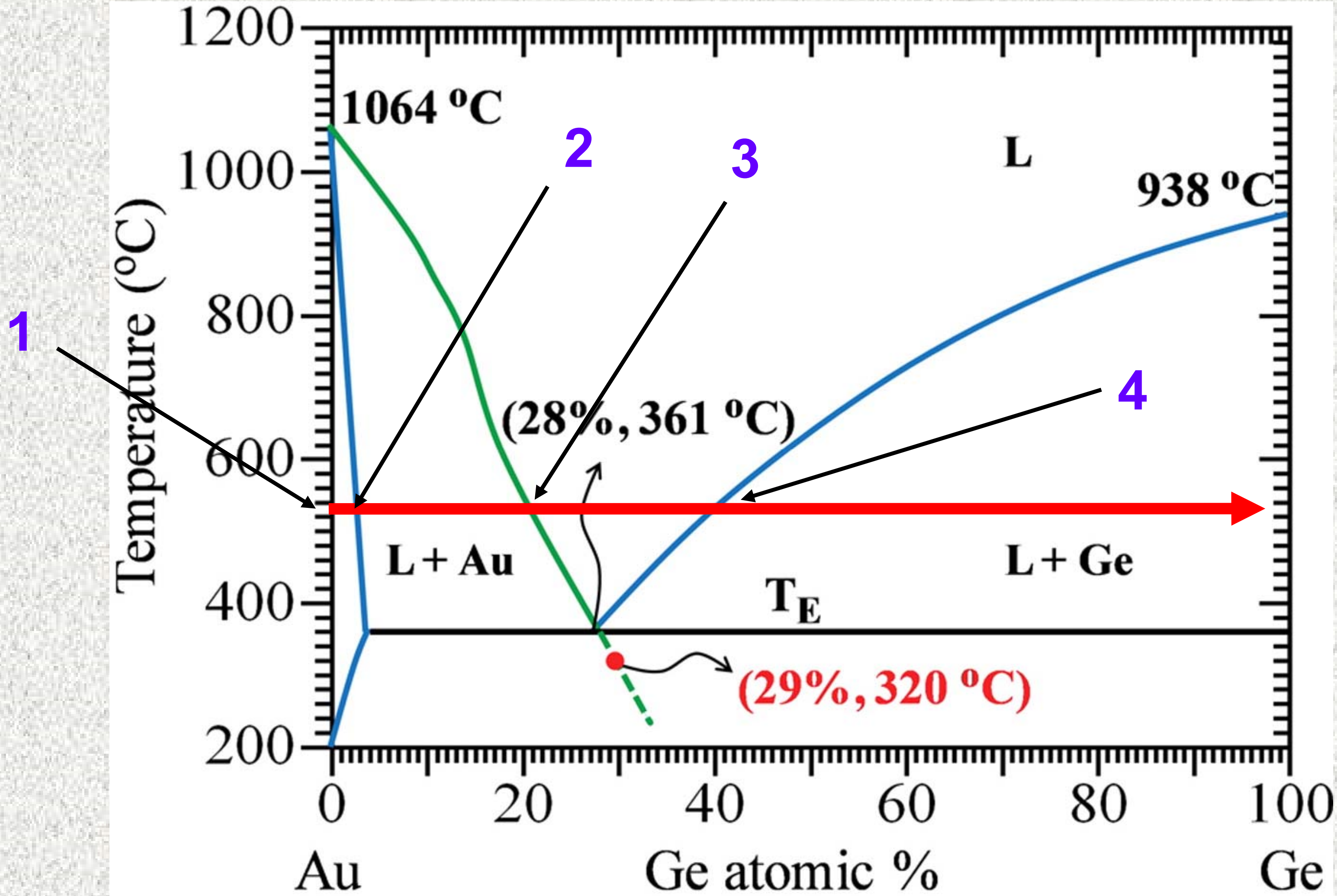
A liquid phase appears (3), melts to a droplet
The droplet becomes supersaturated with Ge

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

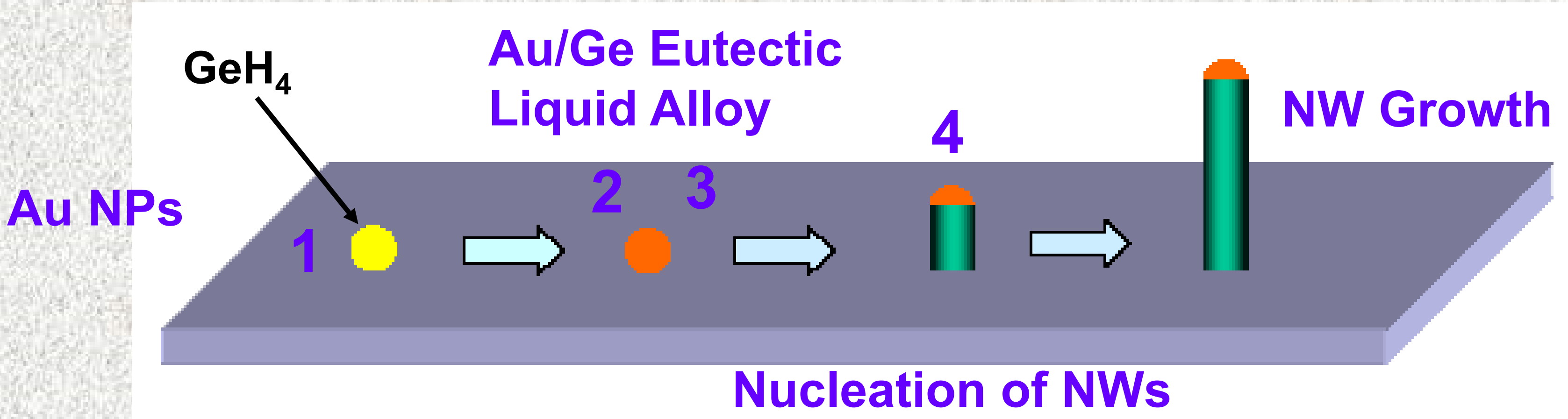


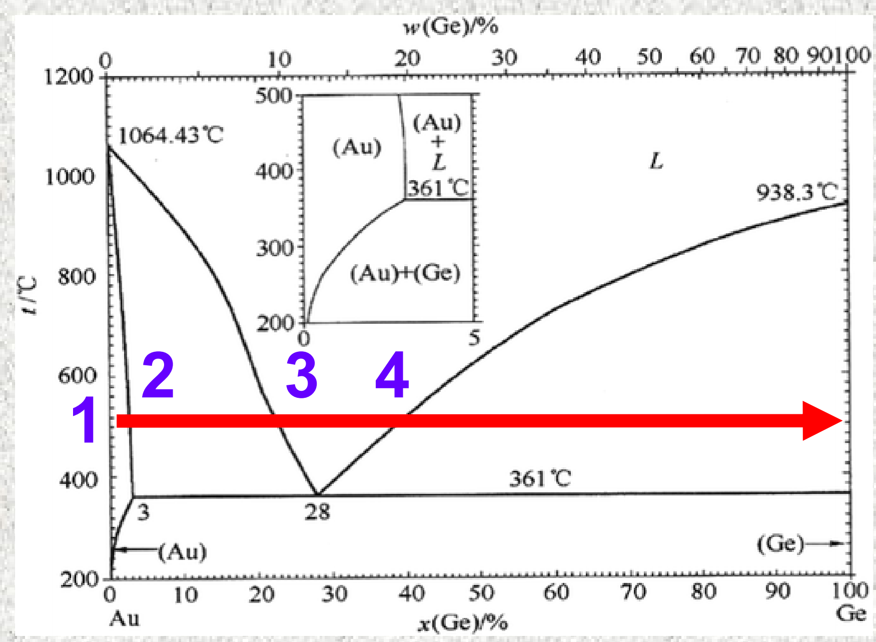

Eutectic 360 °C
Au (mp 1064 °C)
Si (mp 1410 °C)
Ge (mp 938 °C)

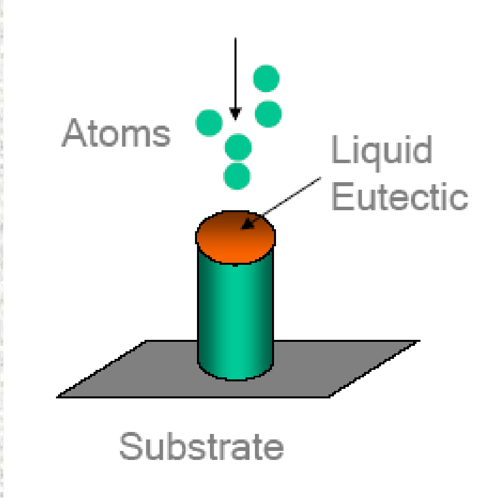
# Vapor-Liquid-Solid (VLS) Growth



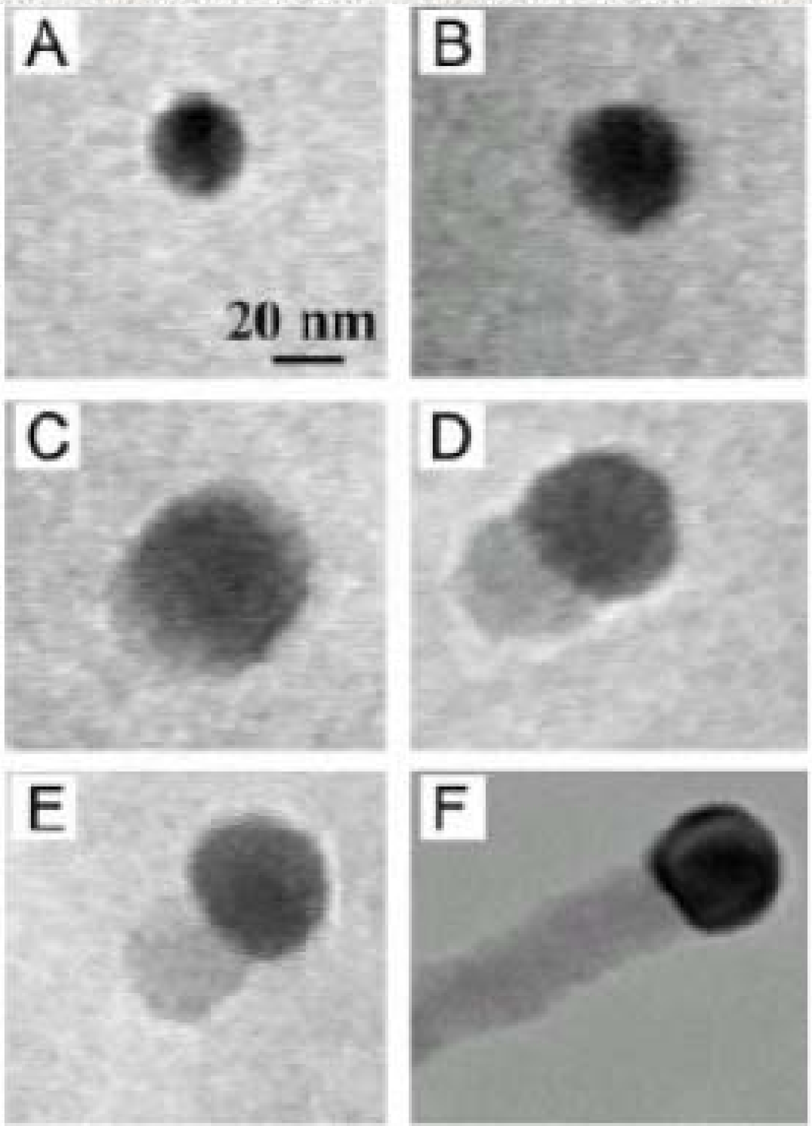
# Vapor-Liquid-Solid (VLS) Growth



# 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**

# Combustion-based Methods

– **Solution-combustion synthesis (SCS)** of nanosized powders initial reaction medium is an aqueous solution

– **Salt-assisted combustion reaction (SACR)** of nanomaterials initial reactants are in a solid state (condensed phase combustion)

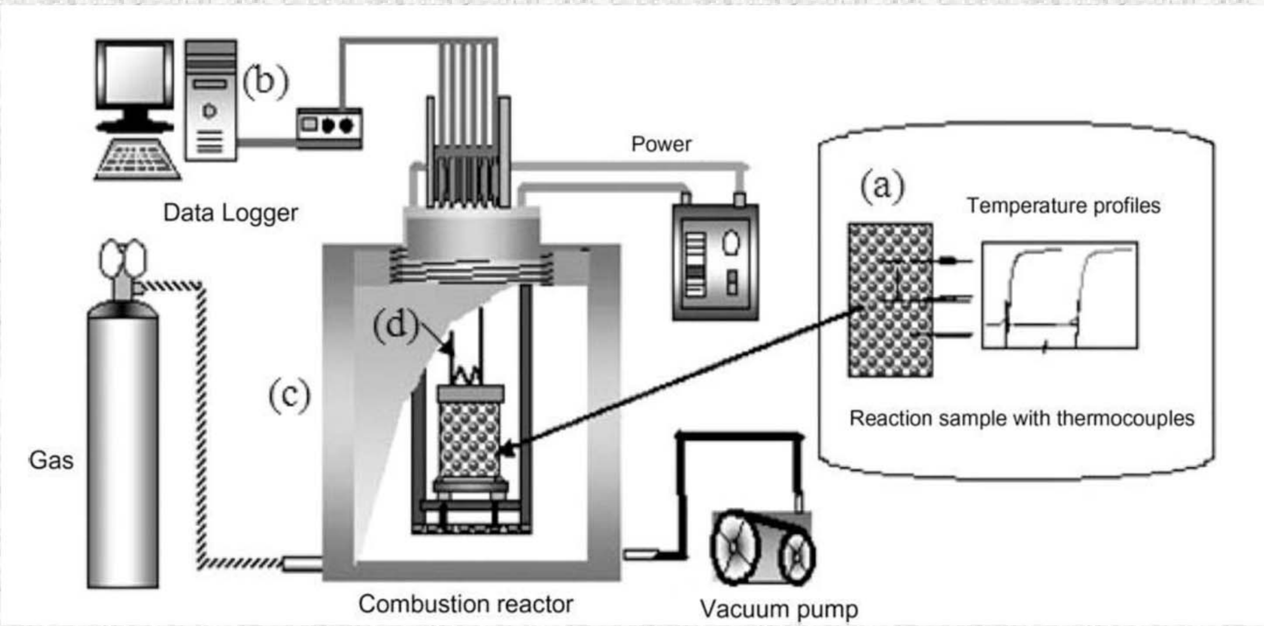
The solution-combustion synthesis involves a self-sustained reaction in a homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine and hydrazides)

Depending on the type of the precursors, as well as on conditions used for the process organization, SCS may occur by either volume or layer-by- layer propagating combustion modes

# Combustion-based Methods

**Salt-assisted combustion reaction**

A thermocouples
B data logger
C combustion reactor
D initiated by an electrically heated Ni-Cr wire
The reaction by-products are leached out using HCl-water



# 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

**Ball Milling**

$$WO_3 + 3\ Mg \rightarrow W + 3\ MgO$$

**A vibratory ball mill (Spex 8000 mixer-mill) under Ar at r.t.**

**Carbon steel balls (diameter: about 8 mm)**

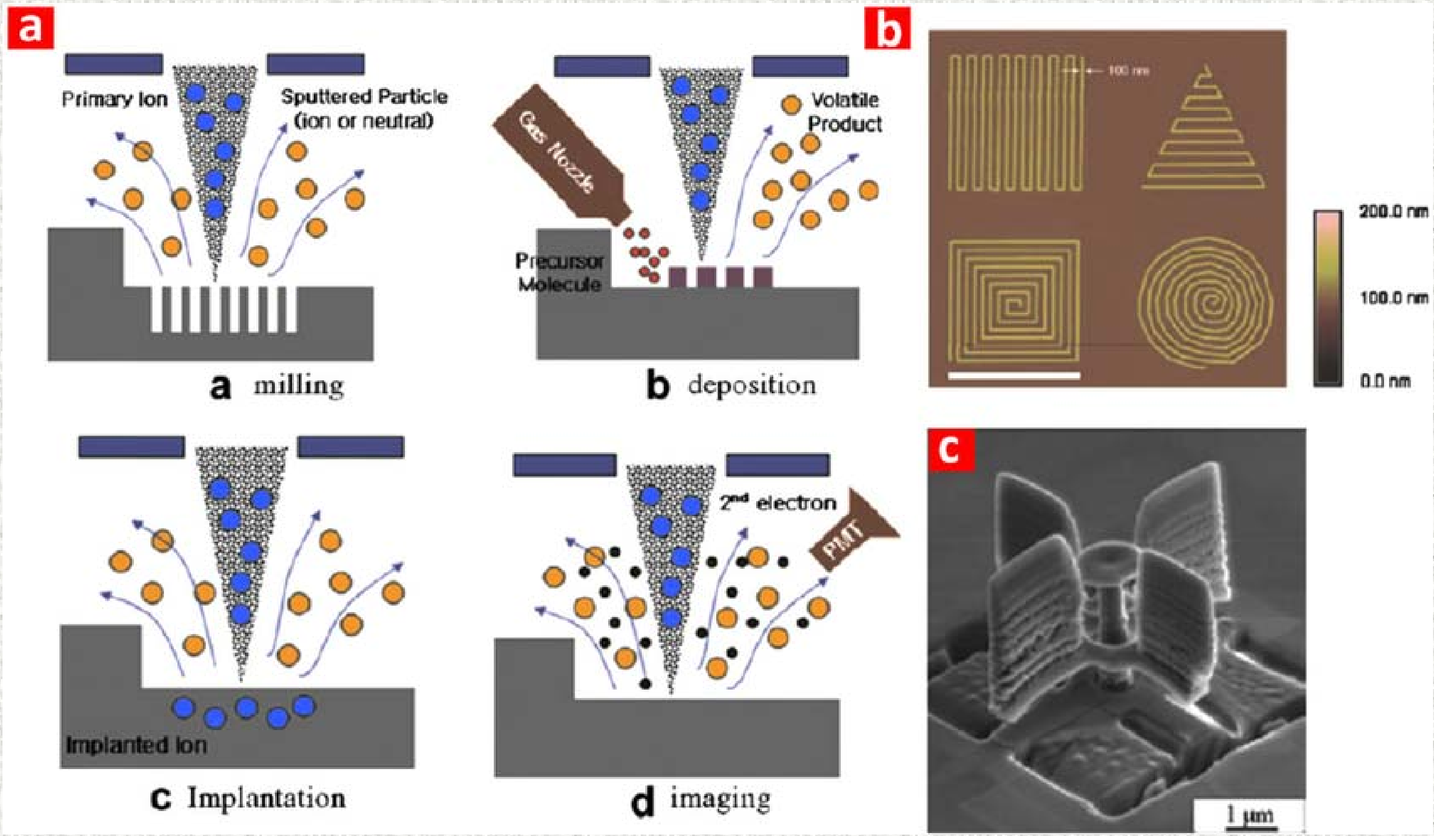
**A ball-to-powder weight ratio of 24:1**

**Leached using 2.0 M HCl, 2 h stirred**

# Top-down Synthesis: Bulk Down

## 🛠Lithographic Techniques

✧electron beam and focused ion beam (FIB) lithography



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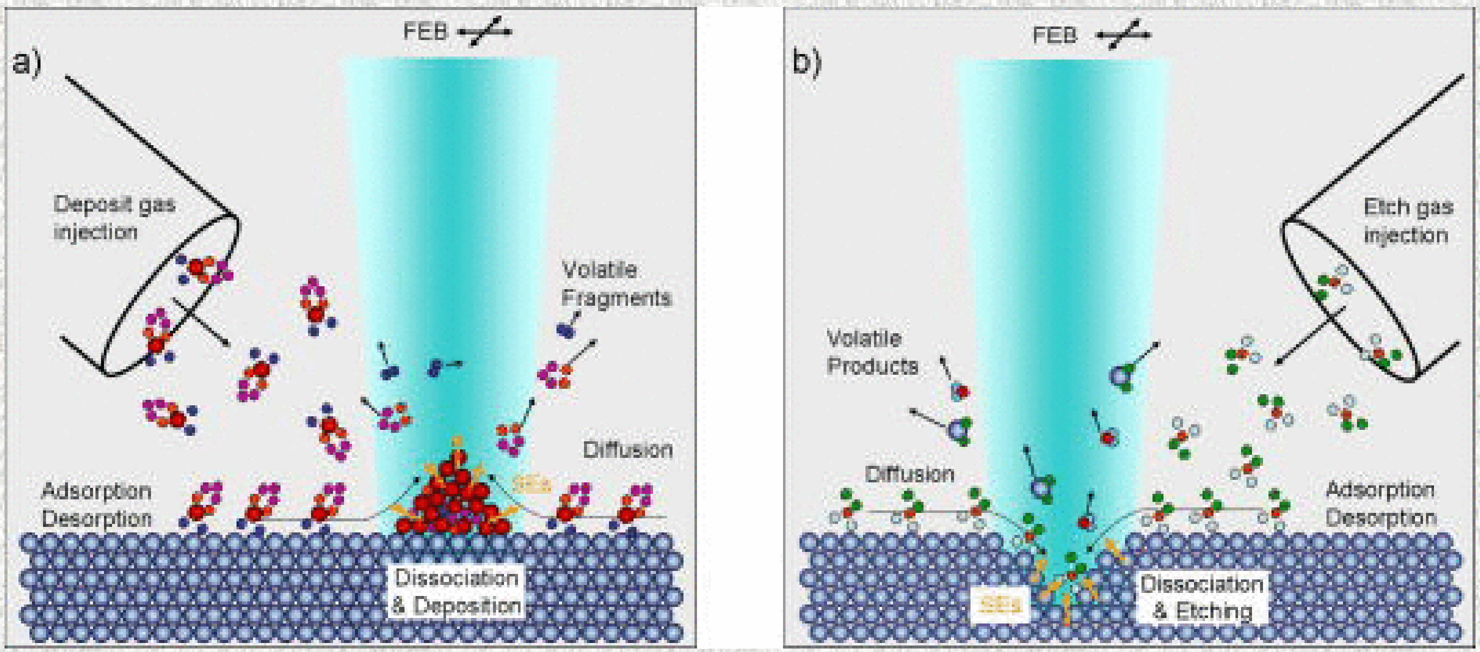
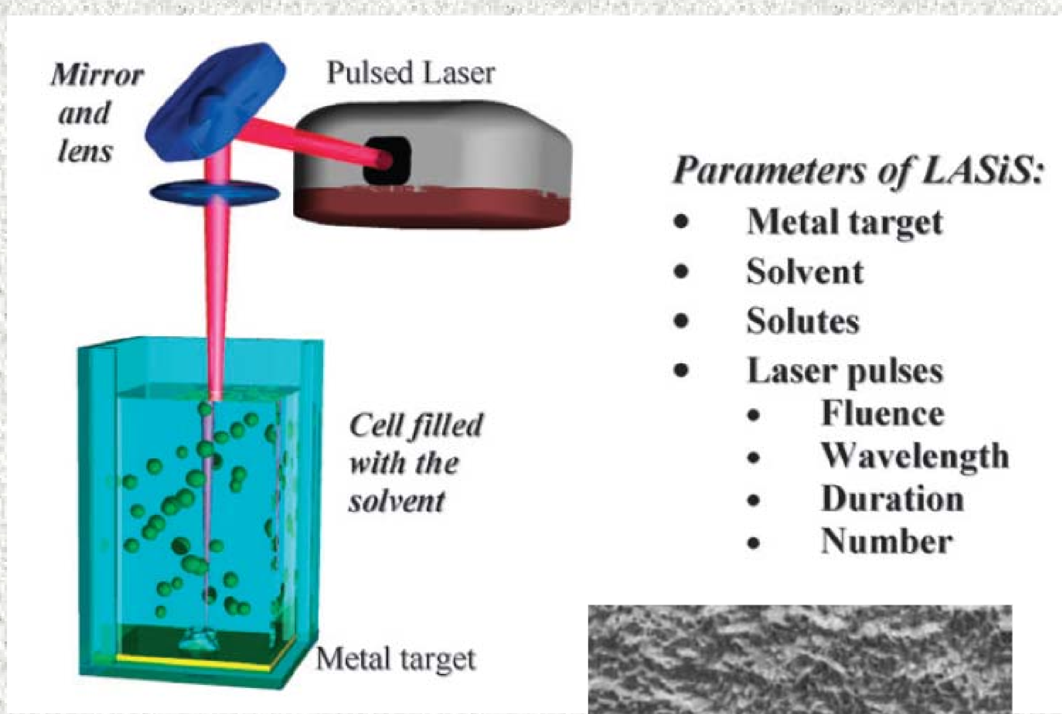
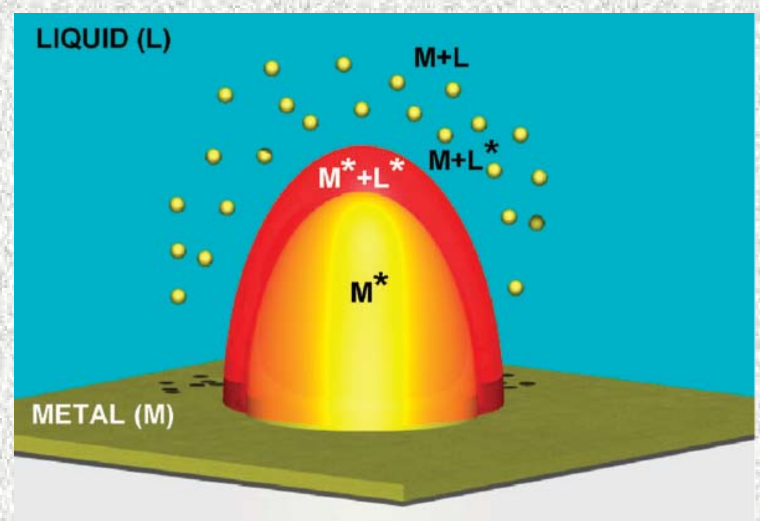


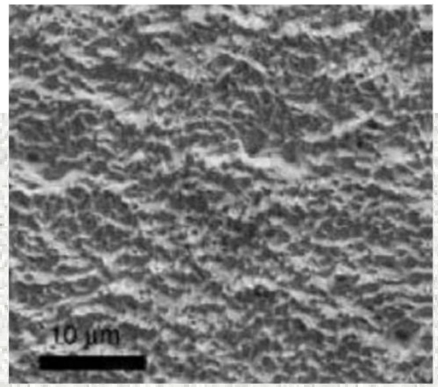
# Top-down Synthesis

## Laser ablation synthesis in solution



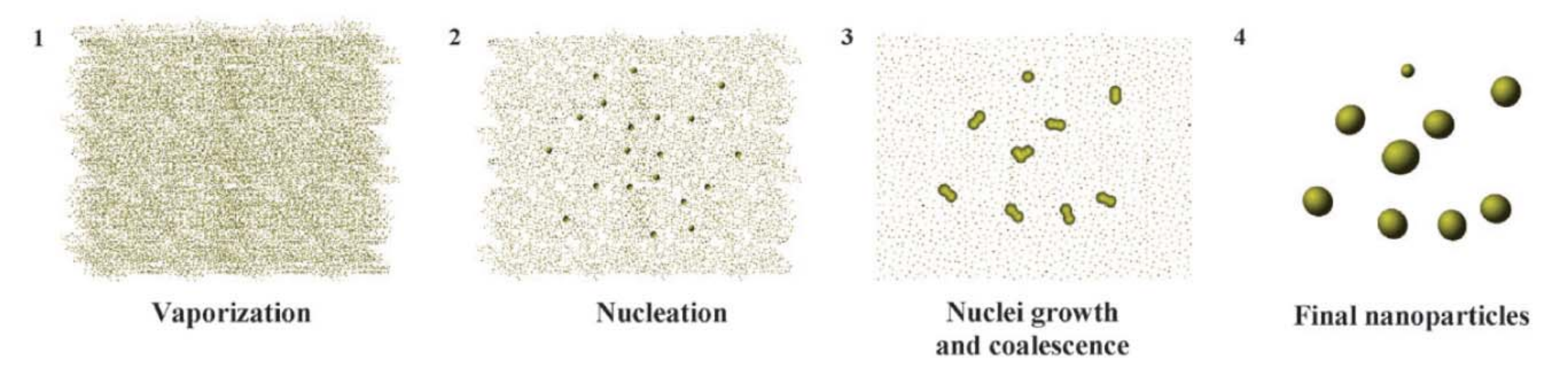




SEM image of Pt target after ablation at 355 nm for 15 min at 14 J/$cm^2$

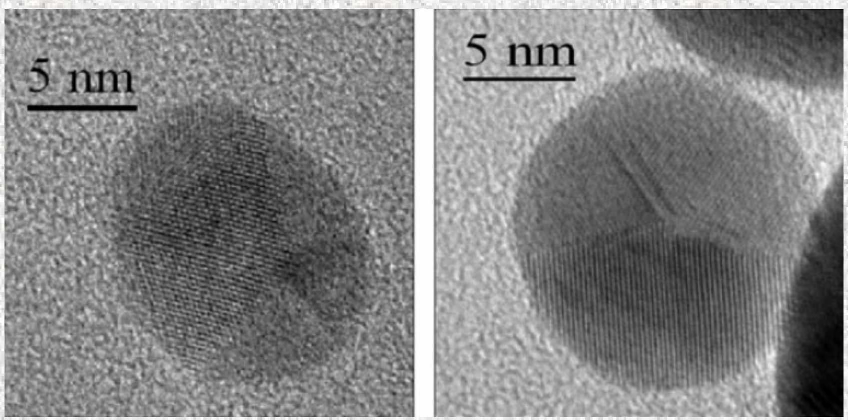


# Top-down Synthesis

## Laser ablation synthesis in solution

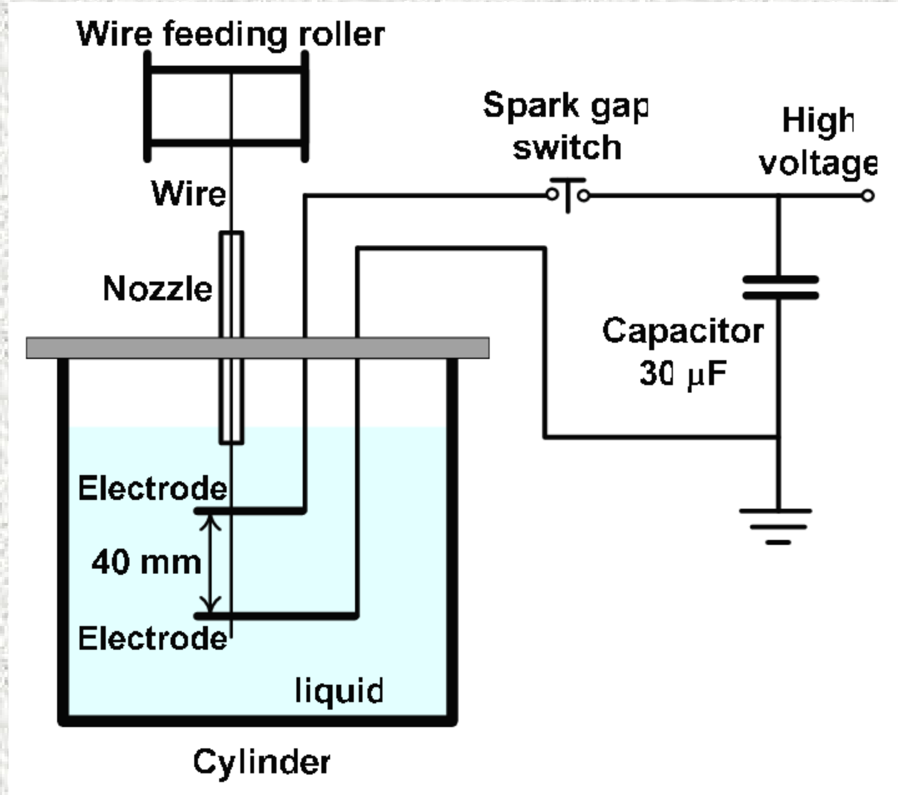



HRTEM images of AgNP (left) and AuNP (right) obtained by LASiS in DMF and water, respectively



# Exploding Wire Method

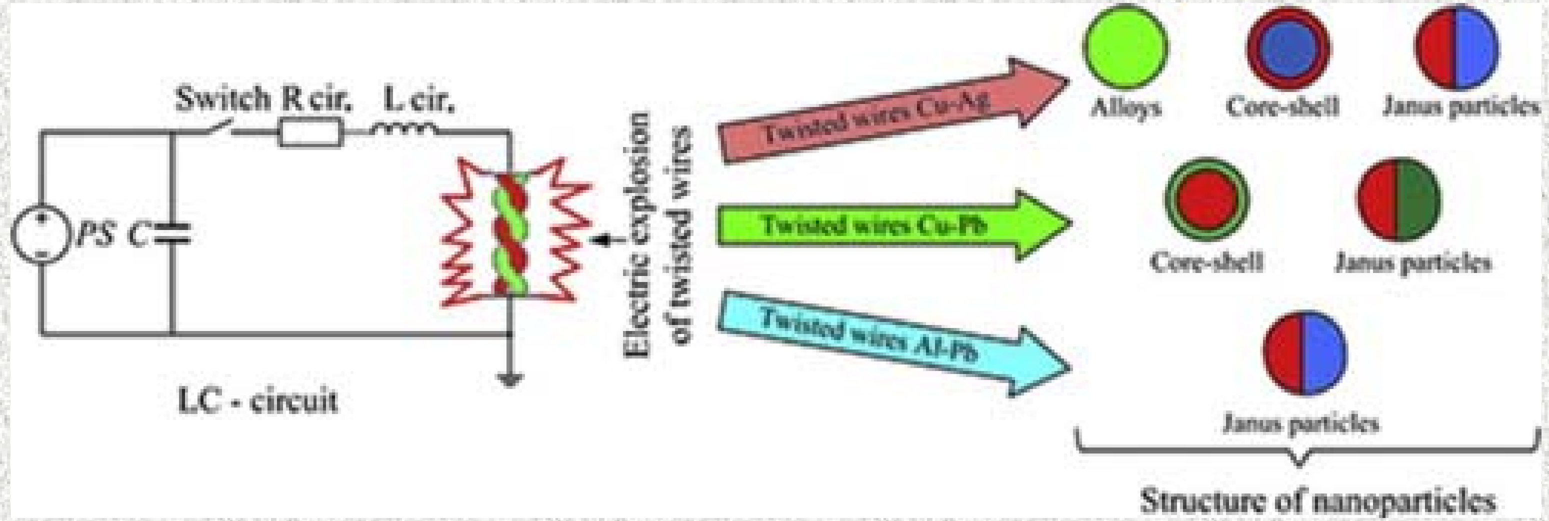
Thin wire: Au, Al, Fe, Pt (diam. $<$ 0.5 mm)
The capacitor - an energy consumption 25 kWh/kg
A pulse of current density $10^4 - 10^6$ A/mm$^2$
Temperatures ~100 000 K
Time $10^{-8}$ to $10^{-5}$ seconds



# Exploding Wire Method

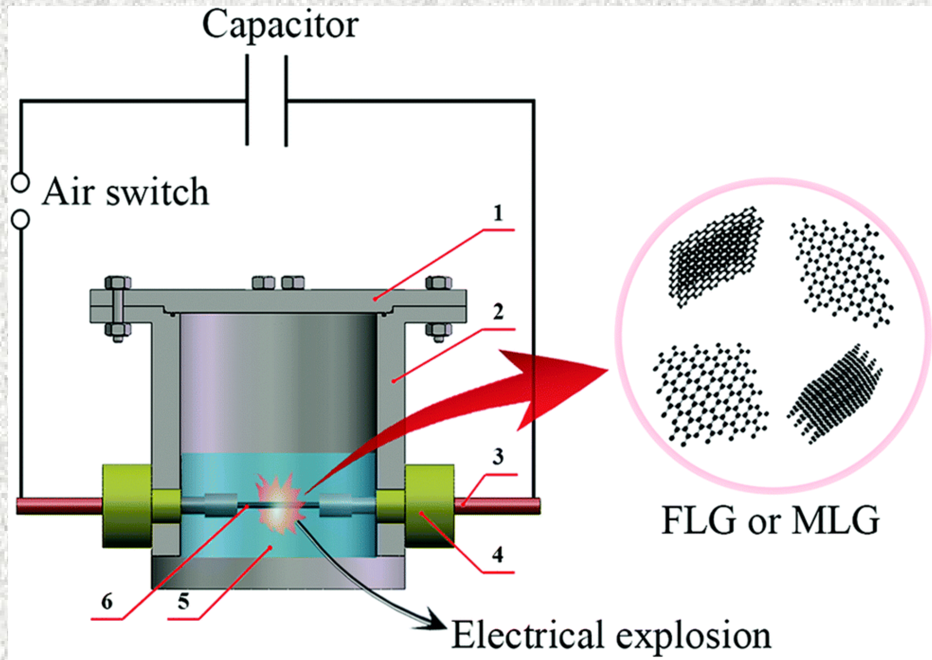
- A **current**, supplied by a **capacitor**, is carried across a wire
- The current heats up the wire - **ohmic heating**
- The metal **melts** to form a broken series of imperfect spheres – **unduloids**
- The current rises fast - the liquid metal has no time to move out of the way
- The unduloids **vaporize**, the metal vapor creates a lower resistance path, allowing an even **higher current** to flow
- An **electric arc** is formed - turns the vapor into **plasma** – a bright flash of light
- The plasma is allowed to expand freely, creating a **shock wave**
- **Electromagnetic radiation** is released in tandem with the shock wave
- The shock wave pushes liquid, gaseous, and plasmatic metal outwards, breaking the circuit and ending the process

# Exploding Wire Method



# Exploding Wire Method

Synthesis of carbon nanodots, graphite nanoflakes, few-layer and multilayer graphene




The electrical explosion chamber, 1 – lid, 2 – stainless steel cylindrical container, 3 – copper electrodes, 4 – insulation blocks, 5 – distilled water, 6 – high purity graphite sticks

# Exploding Wire Method

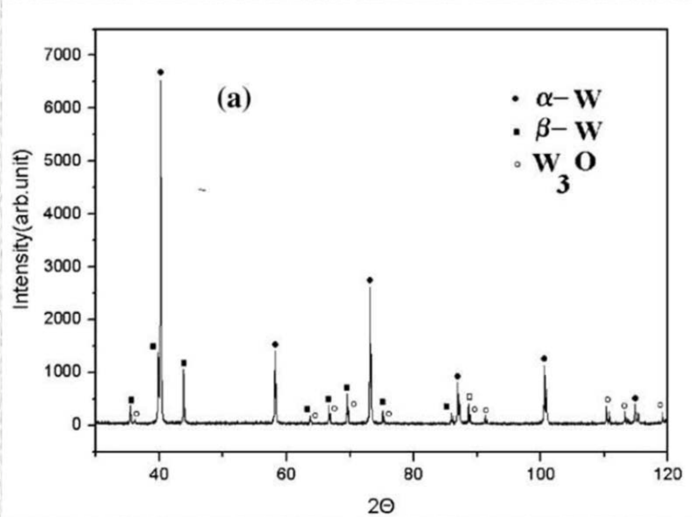
**The synthesis of W NPs**

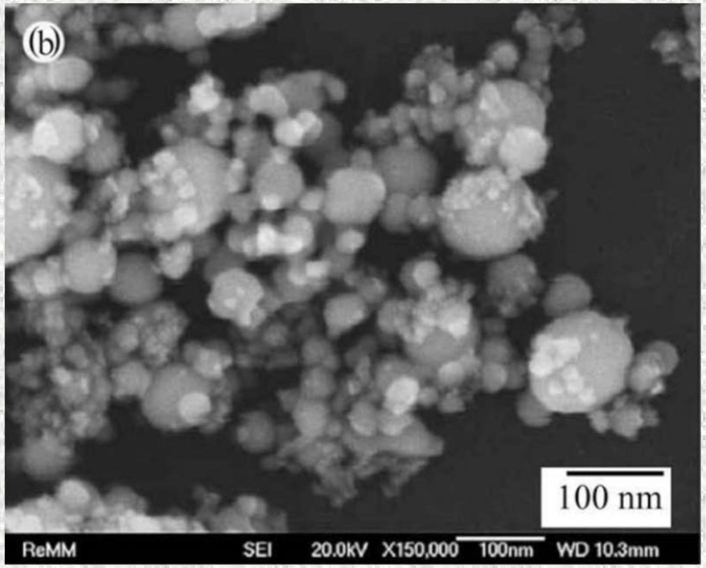
An explosion chamber, a powder collector and an electric circuit
W wire, 0.27 mm in diameter
The explosion by a pulsed electric plasma in an Ar atmosphere
A high-voltage source (5–30 kV)
A current pulse of several thousands Amps

The surface of W nanopowder was passivated at r.t. in Ar gas by air (0.1 vol.%)

XRD analysis showed three phases:
$\alpha$-W, $\beta$-W and $W_3O$

The particles have a spherical shape and a diameter between 20 and 200 nm



# Dictionary of Used Terms

Galvanic replacement = cementace
Interdigitating = prostupující, propletené
Corral = ohrada
Unduloid =