Department of Inorganic Chemistry

Fritz Haber Institute

Max Planck Society

SYNTHESIS, DOPING AND SIZE EFFECTS OF INORGANIC NANOPARTICLES

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06th November 2009

Lecture Series
Heterogeneous Catalysis

We are targeting inorganic nanocrystals – solid crystalline matter

The crystalline state of matter is characterized by a distinct structural rigidity and virtual resistance to deformation (*i.e.* changes of shape and/or volume)

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Solids are formed in the course of crystallization process

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Crystallization is the (natural or artificial) process of formation of solid crystals precipitating from a solution, melt or more rarely, deposited directly from a gas.
It is also known as a process of mass transfer of a solute from the liquid solution to a pure solid crystalline phase.

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The crystallization proceeds in two major events, nucleation and crystal growth.

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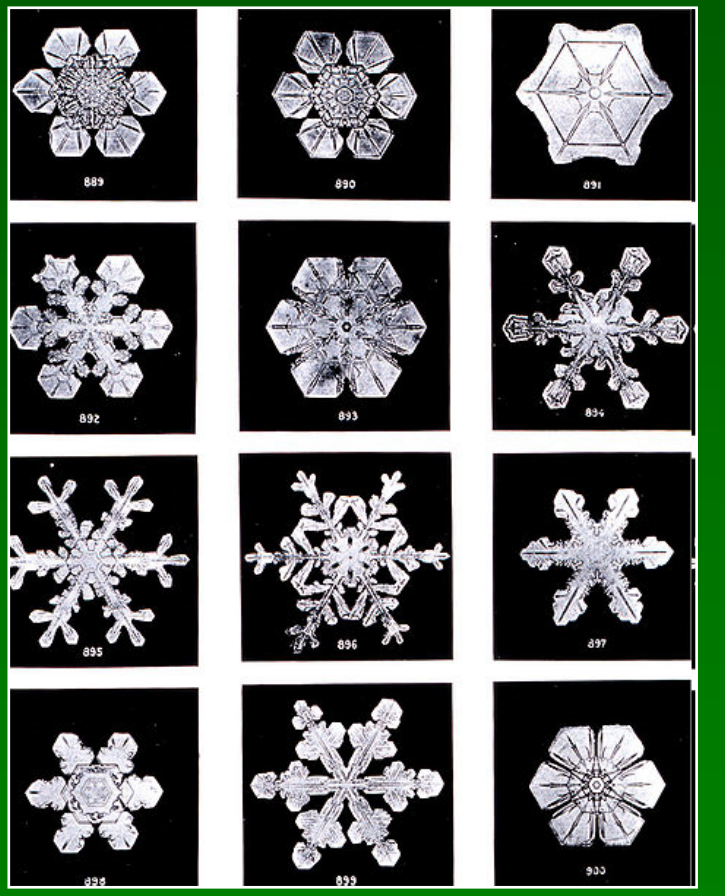
By conditioning crystallization, we could control size and shape of a given solid



Snow flakes

Nucleation → the extremely localized budding of a distinct thermodynamic phase

Nucleation of CO_2 bubbles around a finger

Some examples of such phases:

- gaseous bubbles,
- crystals,
- glassy regions,
- liquid droplets

Most nucleation processes are physical, but a few examples of chemical nucleation do exist.

For instance, reaction of Diet Coke and mint Mentos candies (so called Mentos eruption)

Mechanics of Nucleation

- Nucleation normally occurs at nucleation sites:
  - -. surfaces contacting the liquid or vapor
  - -. suspended particles (dusts)
  - -. minute bubbles…

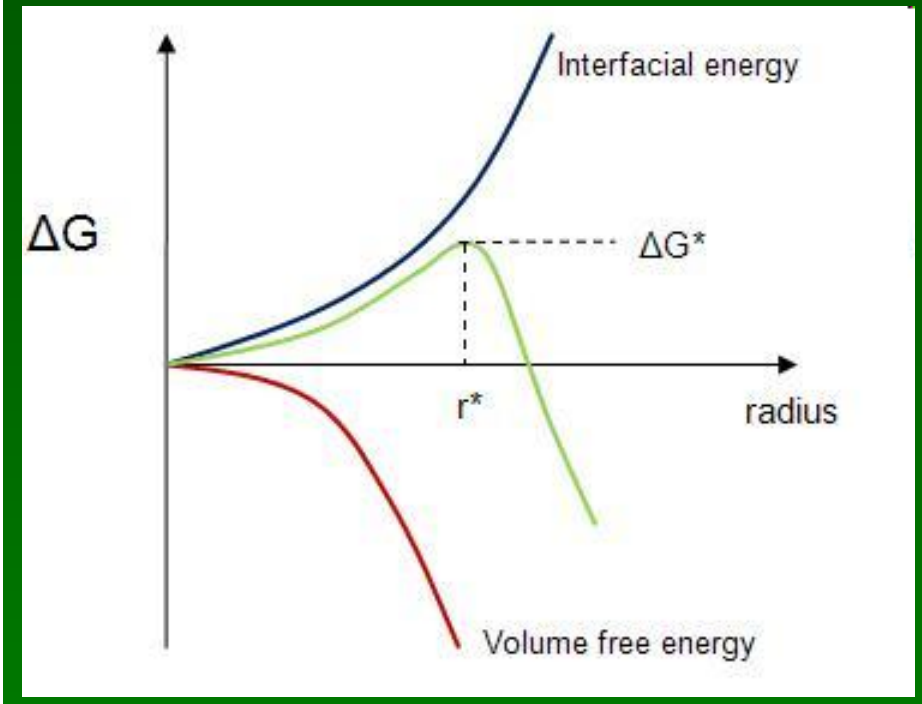
  This is called *heterogeneous nucleation*

- Nucleation which is not surface catalyzed is called *homogeneous nucleation*

- The driving force for *homogeneous nucleation* is supersaturation under supercooling condition.
- During nucleation the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (concentrated in a small region)
- The clusters which reach a critical size r^* become stable nuclei. If no, they redissolve
- Nuclei are characterized by arranged atoms in a defined and periodic manner forming the internal crystal structure (not the same as classic crystal structure)

Mechanics of Homogeneous Nucleation

For spherical cluster



$$\Delta G = \frac{4}{3}\pi r^3 G_v + 4\pi r^2 \sigma$$

Competition between energy gain of creating a new volume & the energy loss due to surface tension of the new interface.

$$\frac{dG}{dr} = 0 \rightarrow r^* = -\frac{2\sigma}{G_v}; \Delta G^* = \frac{16\pi\sigma^3}{3(G_v)^2}$$

Addition of new molecules to clusters larger than r^* releases, rather than costs, available work → growth of the cluster is no longer limited by nucleation, perhaps, by diffusion or by reaction kinetics

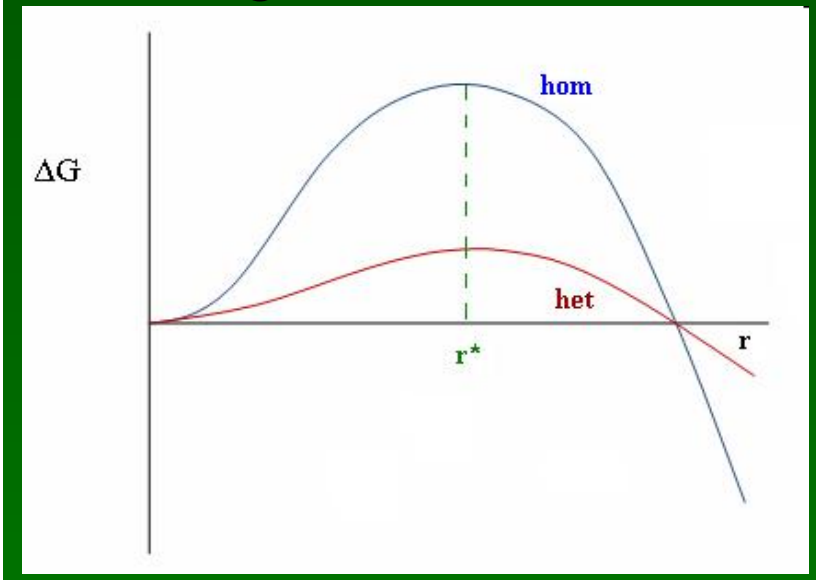
After reaching free energy ΔG^* needed to form r^*, the phase transformation becomes more and more favorable, allowing progressively smaller nuclei to become viable. Further, a greater degree of supercooling favors phase transformation, and we can relate ΔG to supercooling and find r^* and ΔG^* as a function of ΔT

$$r^* = \frac{2\sigma T_m}{\Delta H_s}\frac{1}{\Delta T} \Leftrightarrow \Delta G^* = \frac{16\pi\sigma^3 T_m^2}{3\Delta H_s^2}\frac{1}{(\Delta T^2)}$$

The greater the supercooling, the smaller the critical radius and the less energy needed to form it.

Mechanics of Heterogeneous Nucleation & Nucleation Rate

Heterogeneous nucleation occurs in vast cases *cf.* homogeneous nucleation

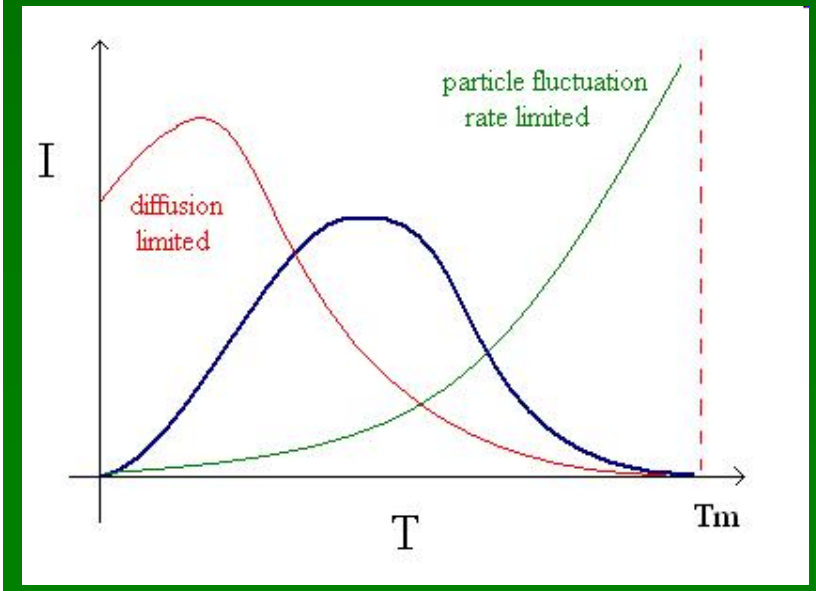


Simply put, on the nucleation sites the effective surface energy is lower, thus diminishing the free energy barrier and facilitating nucleation.

Surfaces promote nucleation because of wetting – contact angles greater than zero between phases encourage particles to nucleate.

$$\Delta G_{heterogeneous} = \Delta G_{homogeneous} \cdot f(\theta)$$

$$f(\theta) = \tfrac{1}{2} + \tfrac{3}{4}\cos\theta - \tfrac{1}{4}\cos^3\theta$$



The nucleation rate *I is* determined by competition between rate of diffusion and fluctuation of molecules.

At low T, nucleation rate is dominated by diffusion, as temperature increases, molecular fluctuations increase, and molecules tend to escape from the nucleus, causing a decreased rate of nucleation

Crystal Growth

- After initial stage of *homogeneous* or *heterogeneous nucleation*, next a major stage of a crystallization process take place → crystal growth

- Crystal growth – is a subsequent growth of the nuclei, achieved the critical cluster size, *via* addition of new atoms, ions, or polymer strings into the characteristic arrangement of a crystalline Bravais lattice.
- Perfect crystals would only grow exceedingly slowly due to the discontinuity in the chemical potential when one structural motif is complete.
- Real crystals grow fast because they contain defects (dislocations, *etc.*), which provide the necessary growth points, thus catalyzing structural transformation and long-range order formation

Under supersaturation conditions nucleation and growth occur simultaneously

↓

Controlling the conditions, we could control nucleation or growth being predominant over the other, in this way, crystals with different sizes and shapes can be generated

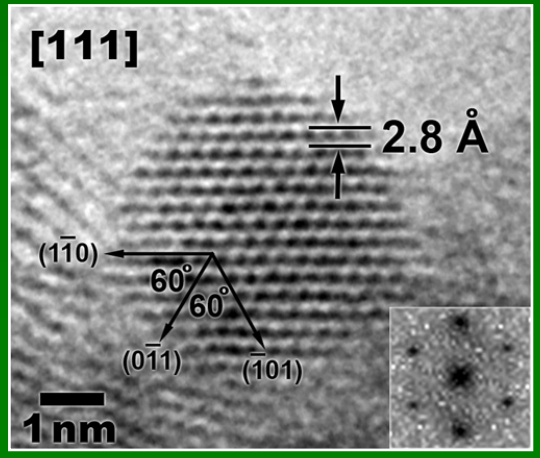
↓

Crystallization is complete once the supersaturation is exhausted

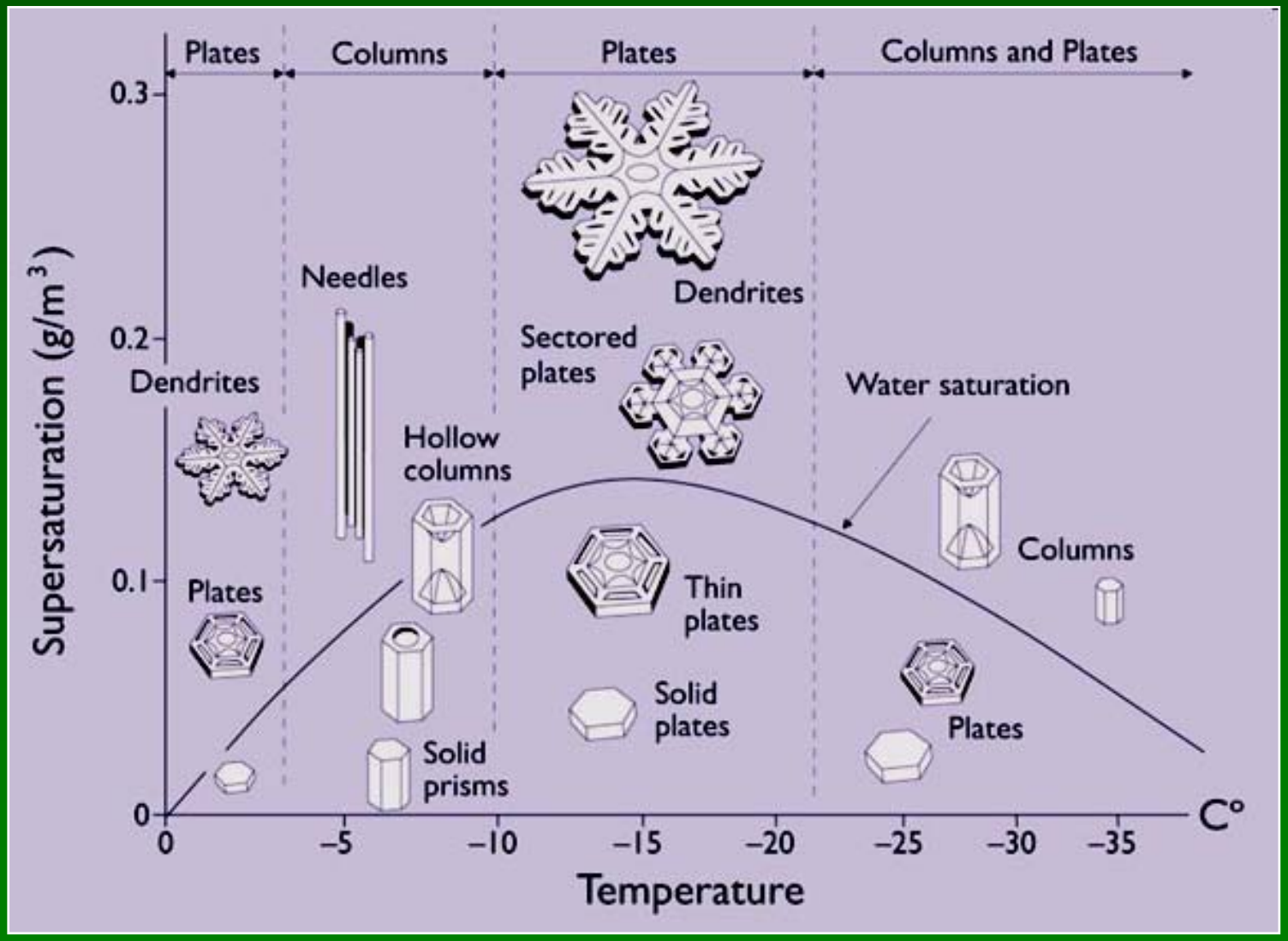
What is NANO ! ? !

NANO → 10^{-9} m (from Greek νάνος (nanos) → " dwarf ")

An engineered *nanoparticle (NP) or nanocrystal (NC)* may be defined as any intentionally produced particle that has a characteristic dimension from 1 to 100 nm and that shows properties that are not found in bulk samples of the same material.



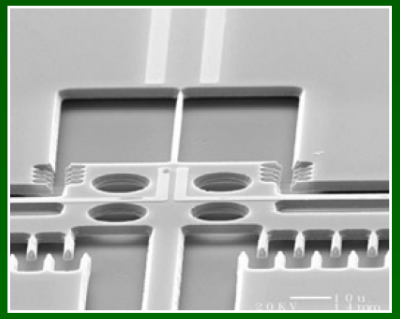
Control over shape and size by conditioning crystallization



Shape of snowflakes depends on the temperature and supersaturation at which they form

Approaches to Nanoscaled Structures

Microelectromechanical systems (MEMS)



Millimeter

Micrometer

Nanometer

Angstrom

Top Down

Bulk materials

Thin films

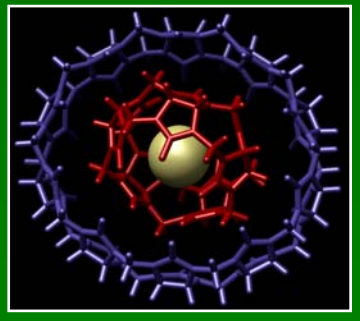
Heterostructures

Lithographic wiers

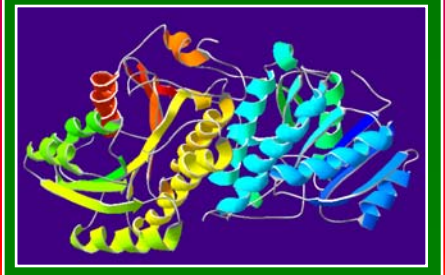
Quantum dots

Dip-Pen Nanolithography

Supramolecular complex



Alcohol dehydrogenases



Nanocrystals

Molecular Wiers DNA

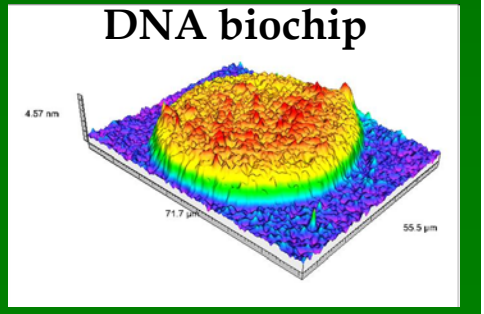
Proteins

Molecules

Atoms

Bottom Up

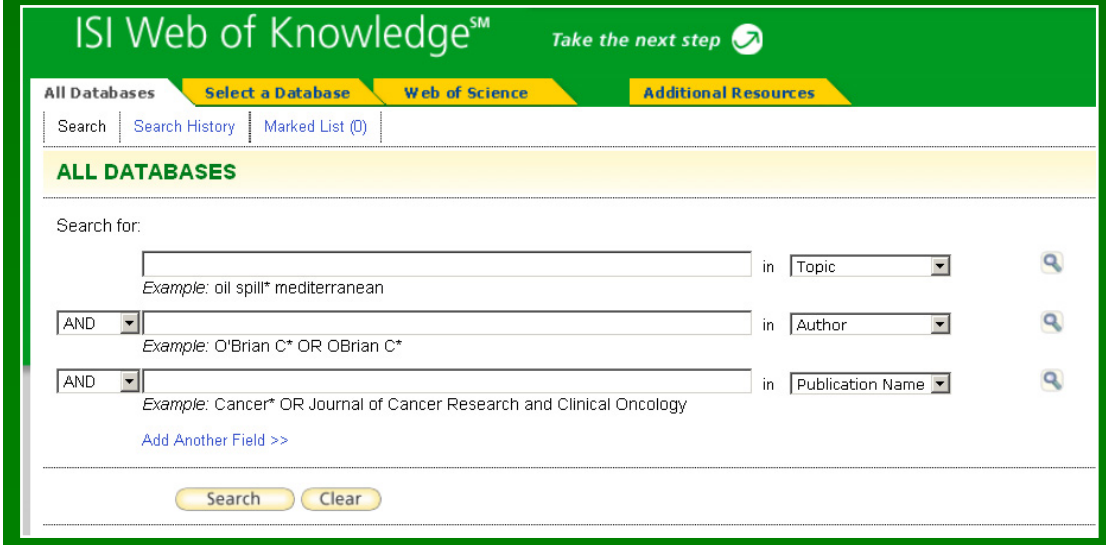
DNA biochip

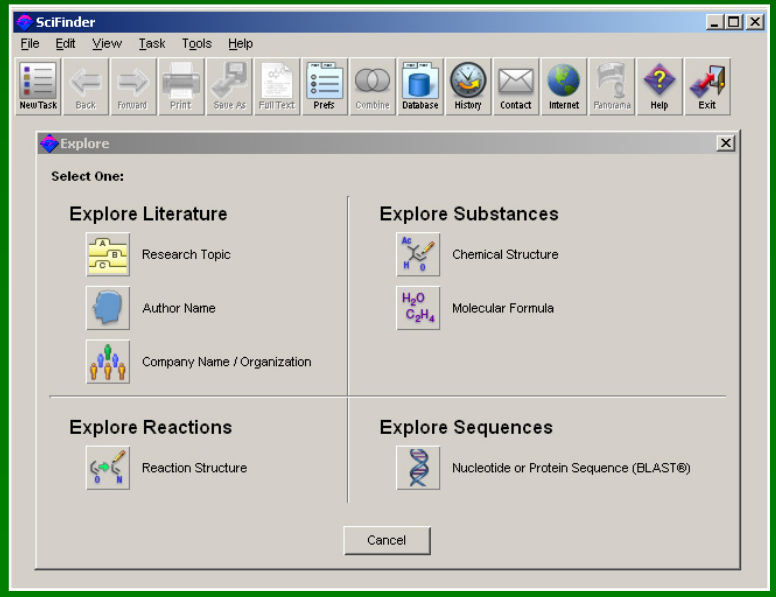


Synthesis of Nanoparticles

- Vast sea of the literature available, which describes NPs synthesis

- Principles for selection/elaboration of a synthesis method:
  - -. Easy and cheap
  - -. Reproducible
  - -. Quality of the NPs (monodispersity, perfection, purity)
  - -. Possibility to achieve control over phase, shape and size
  - -. Feasibility of large-scale production
  - -. *etc.*



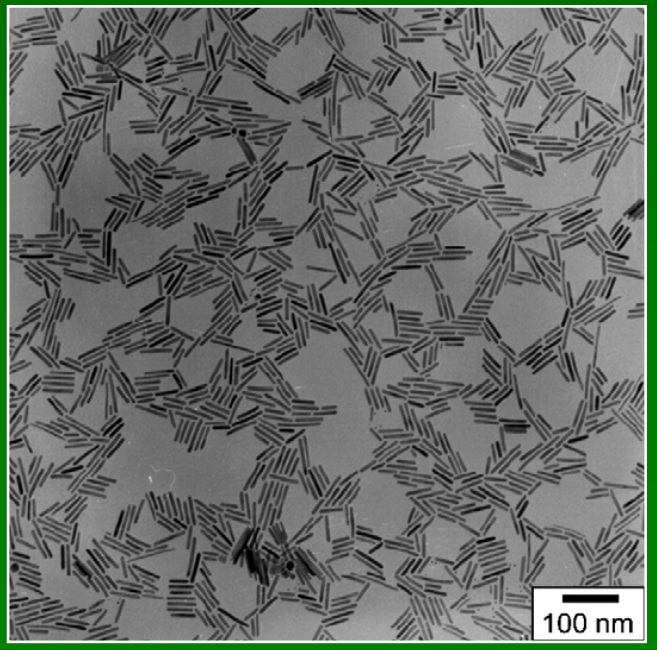


Methods in Nanoparticles Synthesis

- We will take into account only chemical approaches to NPs
- Basically there are 3 chemical methods to obtain NPs:
  -. Kinetic control of nucleation and growth of the particles, typically by control the degree of supersaturation applying non-equilibrium techniques
  -. Electrostatic stabilization of NPs in (aqueous) suspension
  -. Introduction of spatial constraints, also called *synthesis in nanoreactors*

ꕥ Nanocrystals are typically synthesized in the solution phase using a shell of organic ligands such as alkanethiols, alkylamines, or phosphonic acids to stabilize the surface.

ꕥ The choice of ligand, solvent, and reaction conditions can influence both the size and morphology of the resulting crystals.



Synthesis of Metal Nanoparticles: Chemistry

∞ Bottom-up approach from molecular precursors:

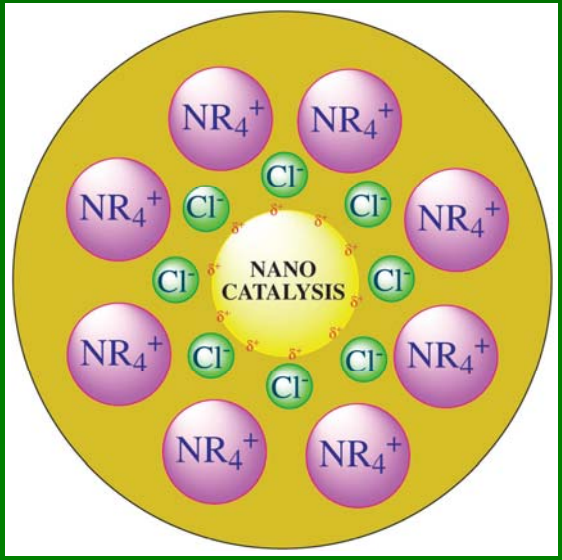
$$MX_n(NR_4)_m + (m\text{-}n)Red \xrightarrow{TFT} M_{NP} + (n\text{-}m)Red^+X^- + m(NR_4^+X^-)$$

M = Metal from Group 8–10

X = Cl^- or Br^-

R = $C_{4\text{-}12}$ alkyl

Red = M'H with M'=H, Li, $LiBEt_3$, $NaBEt_3$, $KBEt_3$



"*Electrosteric*" (that is electrostatic and steric) stabilization of metal NPs obtained by reduction of a metal chloride salt in the presence of a tetra-*N*-alkylammonium cations.

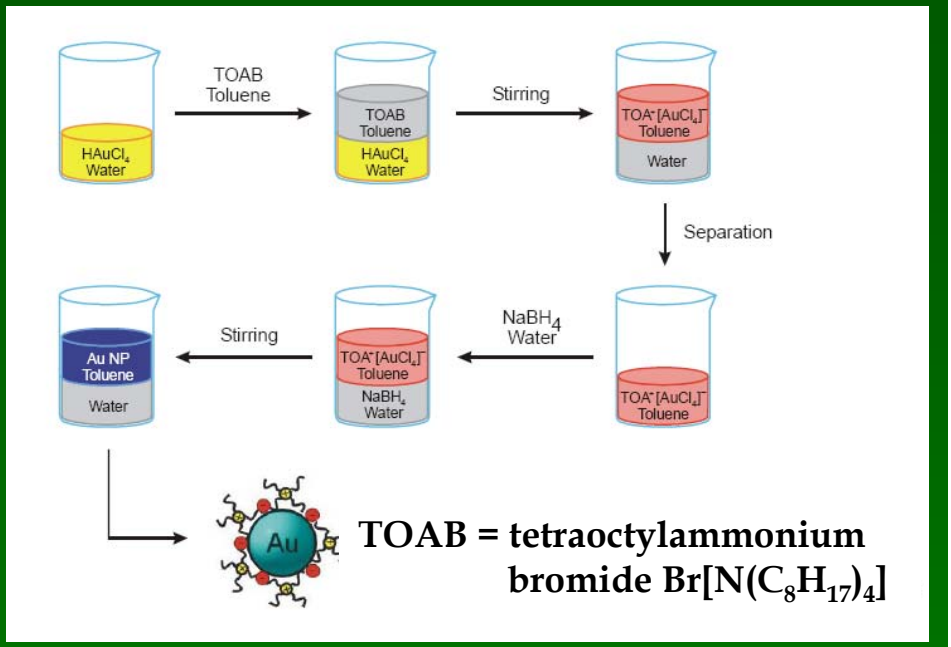
The halide anions provide the *electrostatic stabilization* and the tetrabutylammonium cations the *steric* one

Angew. Chem. Int. Ed. 2005, 44, 7852 – 7872

Synthesis of Metal Nanoparticles: Chemistry

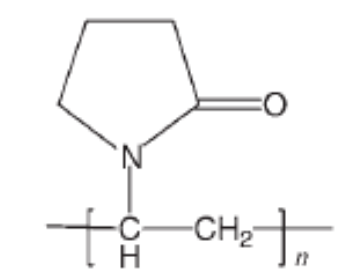
a) Reduction of metal precursor ($HAuCl_4$, Na_2PdCl_4) by $NaBH_4$ in a biphasic organic solvent/water system in the presence of the phase-transfer reagent tetraoctylammonium bromide

b) Next, formed NP must be stabilized (electrostatic-, steric-, electrostericly)



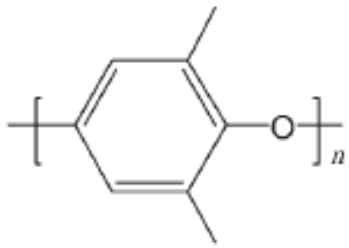
TOAB = tetraoctylammonium bromide $Br[N(C_8H_{17})_4]$

Polymer stabilizers:



PVP

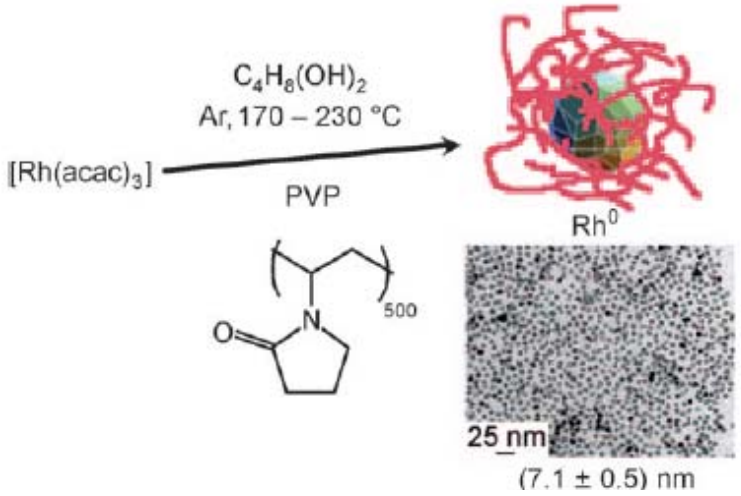
poly(vinylpyrrolidone)



PPO

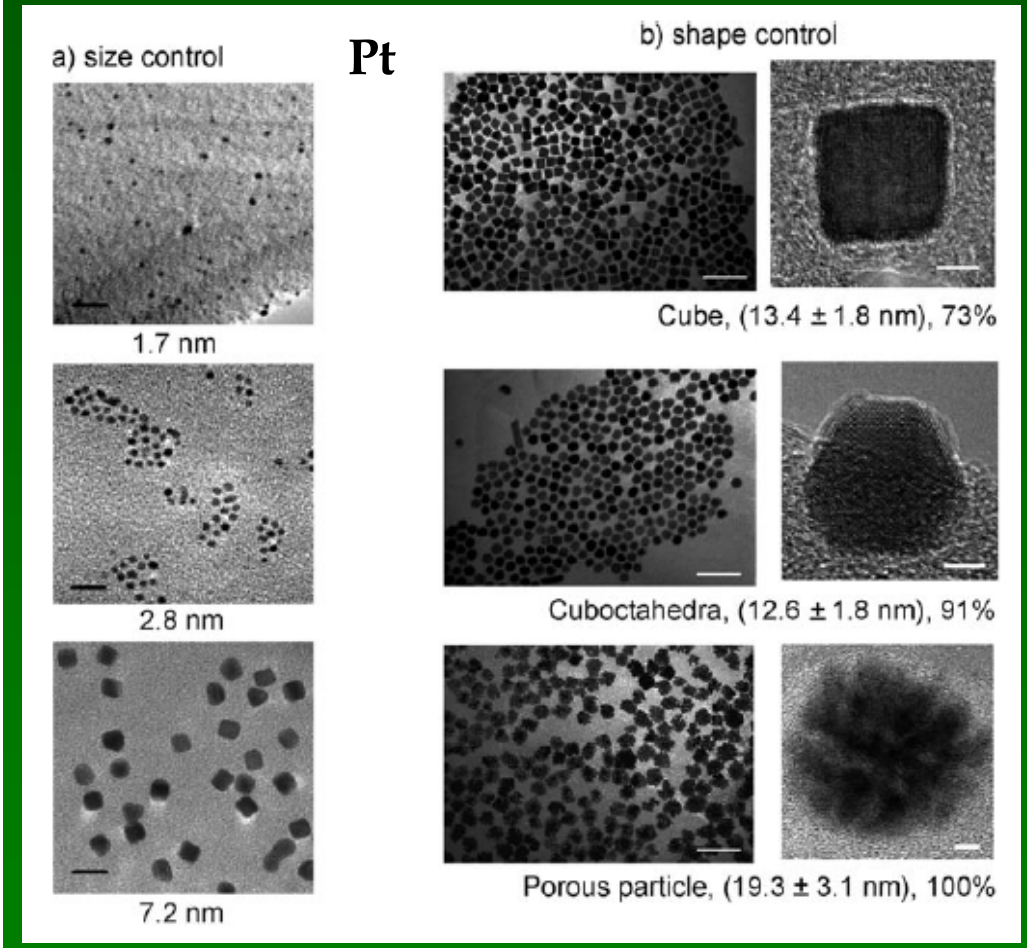
poly(2,5-dimethylphenylene oxide)

Angew. Chem. Int. Ed. 2005, 44, 7852 – 7872



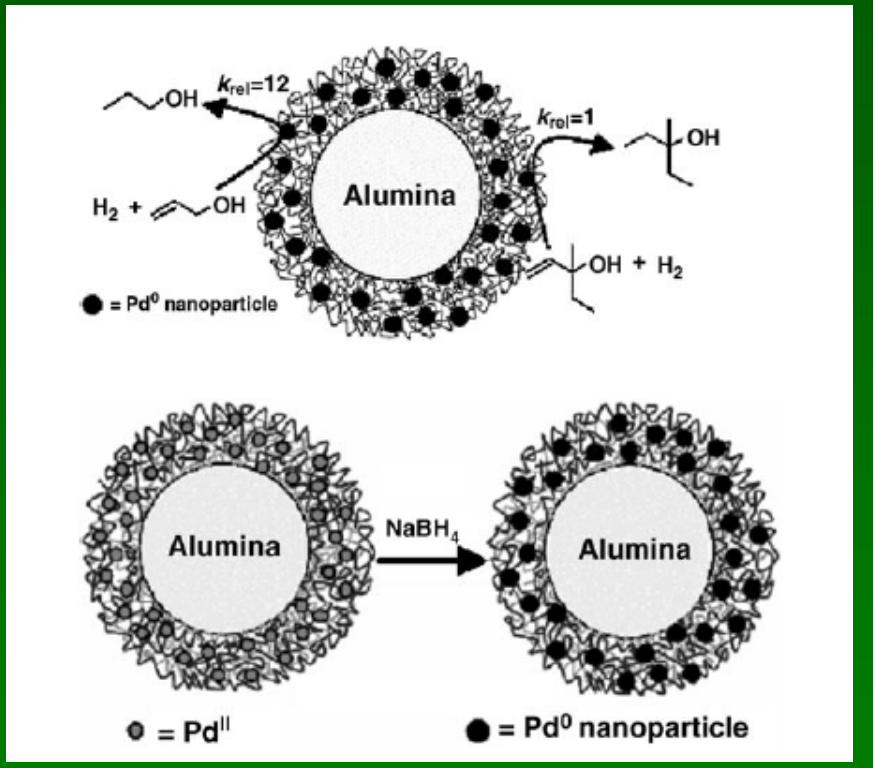
Angew. Chem. Int. Ed. 2008, 47, 9212 – 9228

Synthesis of Metal Nanoparticles: Control over Size & Shape



Size and shape can be controlled by changing the monomer concentration

Angew. Chem. Int. Ed. 2005, 44, 7852 – 7872

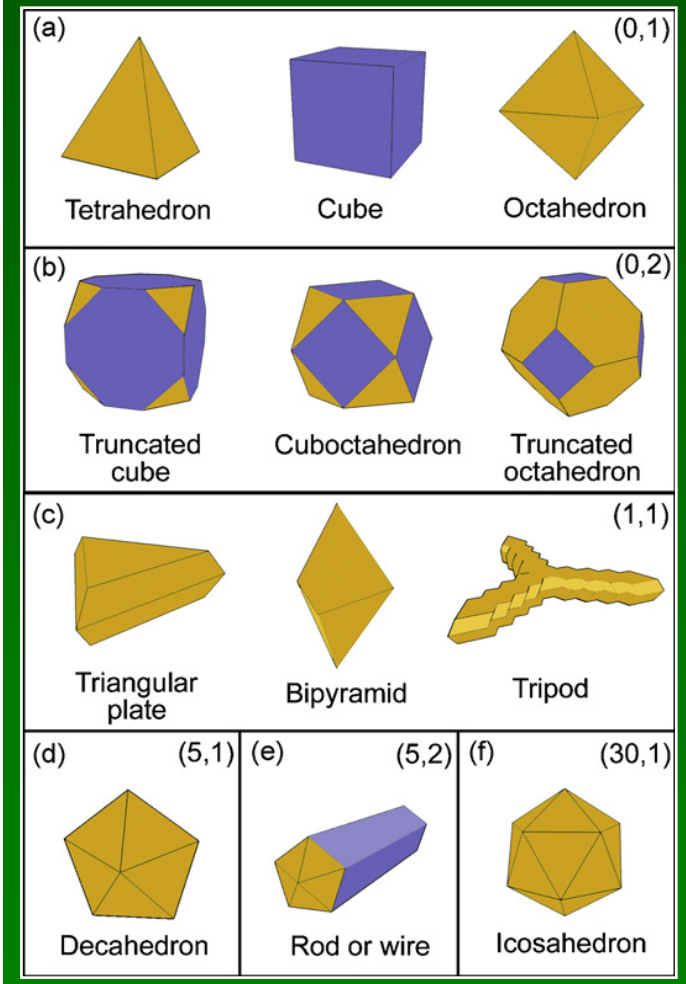


Principle of the formation of Pd NPs in multilayer olyelectrolyte films for selective hydrogenation

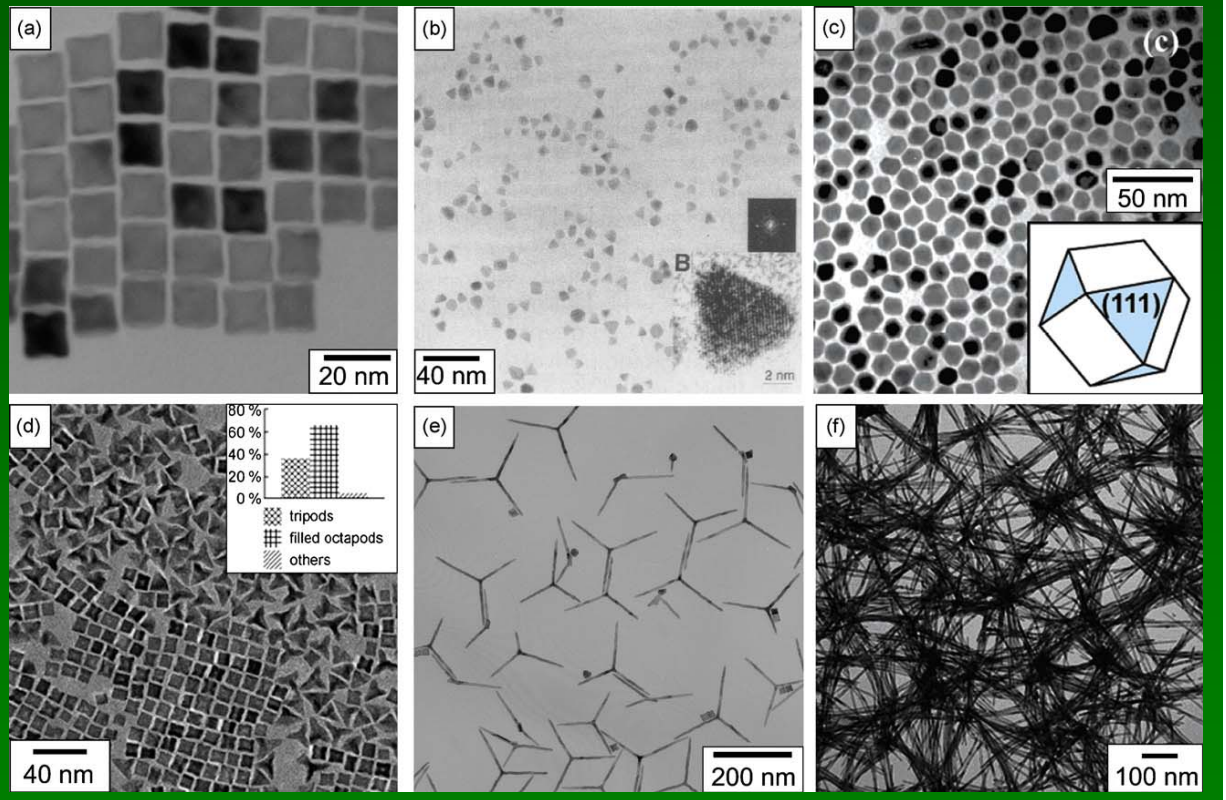
Angew. Chem. Int. Ed. 2008, 47, 9212 – 9228

Synthesis of Metal Nanoparticles: Control over Shape

Way to control: variation of precursor, reductant, surfactant, additive and conditioning



Selective possible shapes of Pt nanoparticles

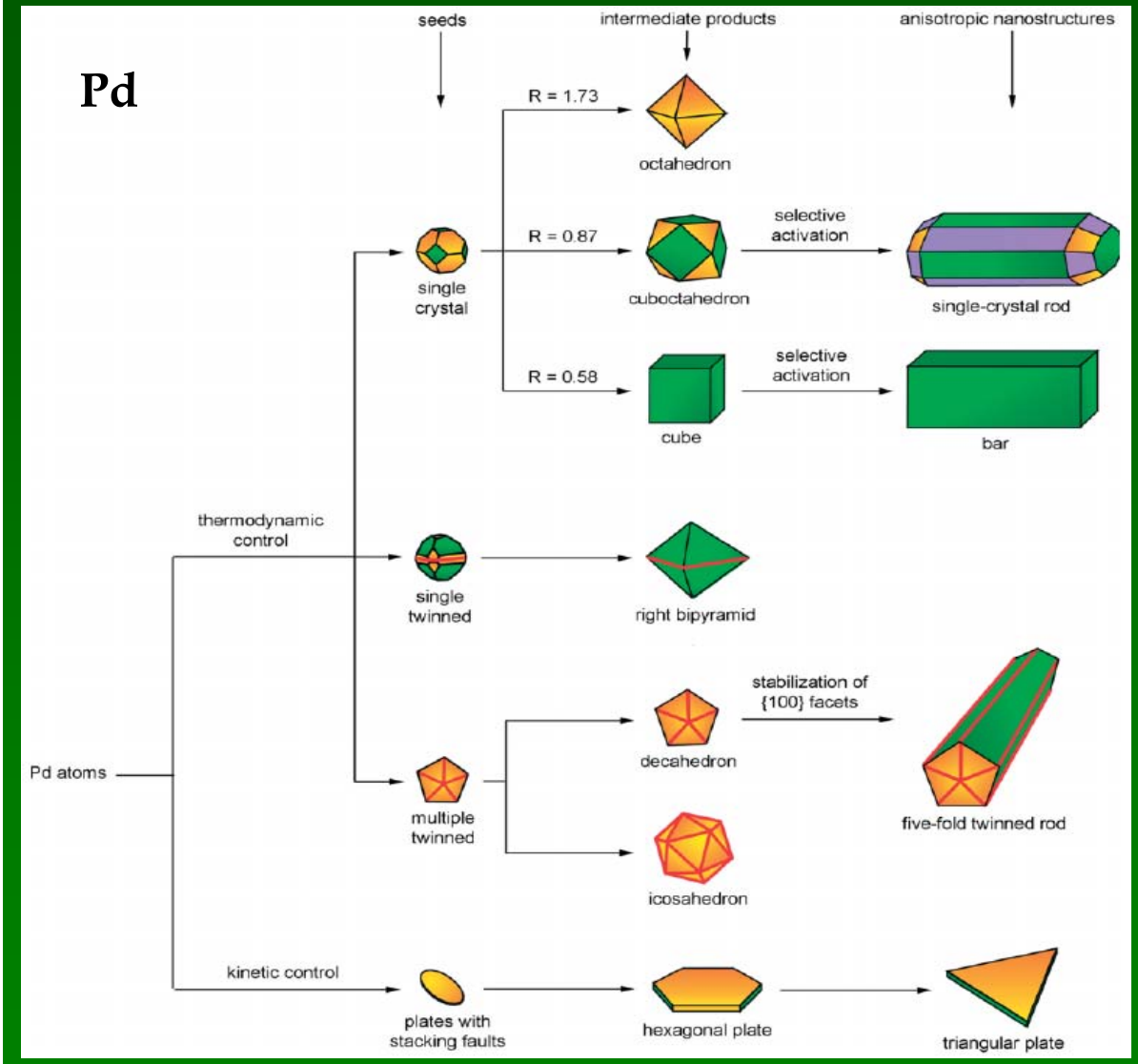


TEM images of Pt nanostructures with different shapes

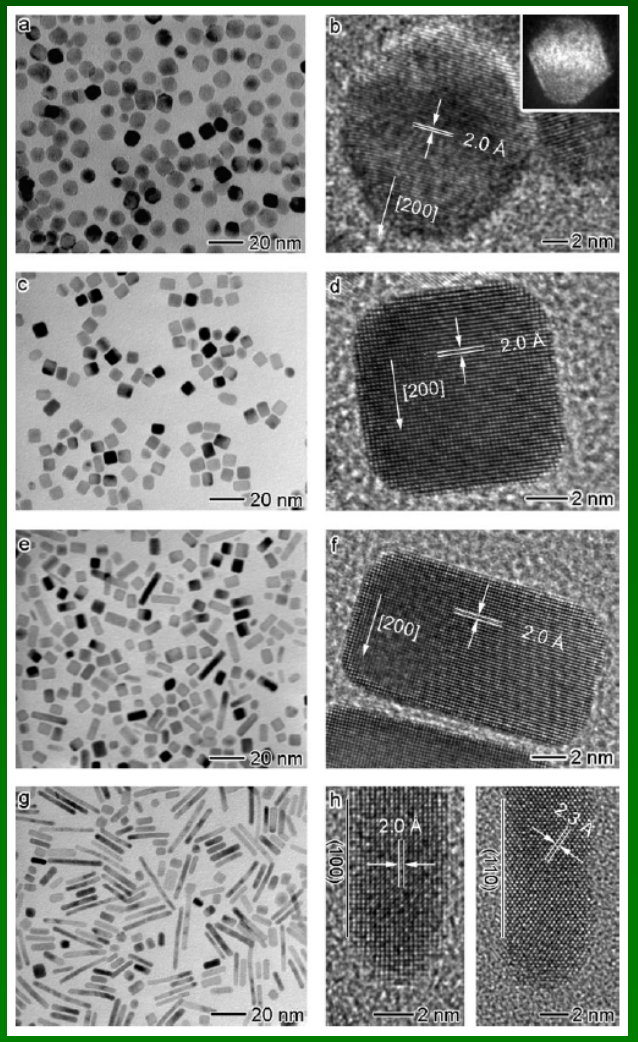
Nano Today 2009, 4, 143–164

Synthesis of Metal Nanoparticles: Control over Shape

Way to control: variation of precursor, reductant, surfactant, additive and conditioning



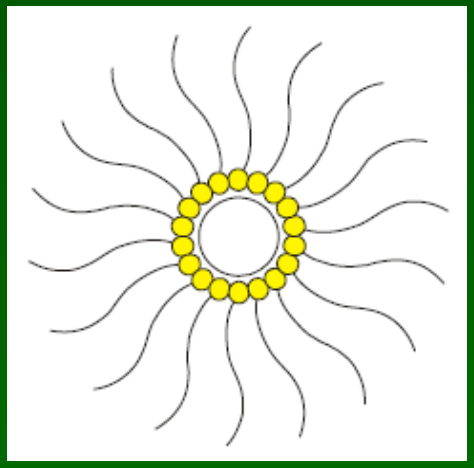
Reaction pathways that lead to Pd nanostructures with different shapes



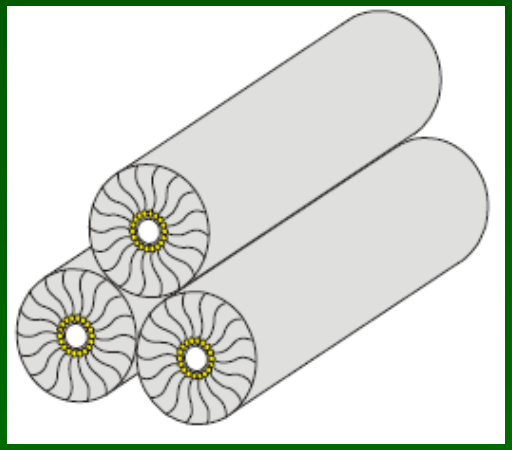
TEM images of differently shaped Pd

Adv. Mater. 2007, 19, 3385–3391

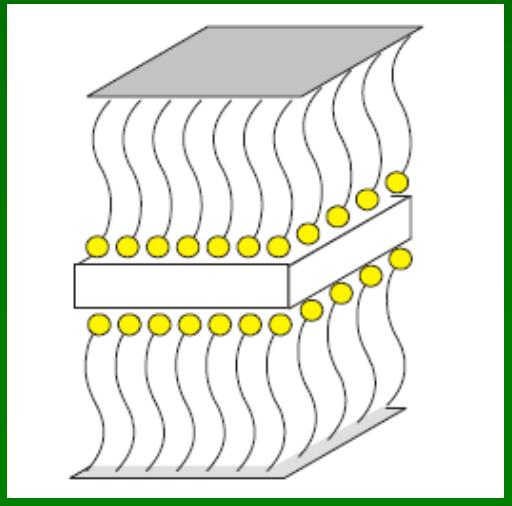
Synthesis in Nanoreactors



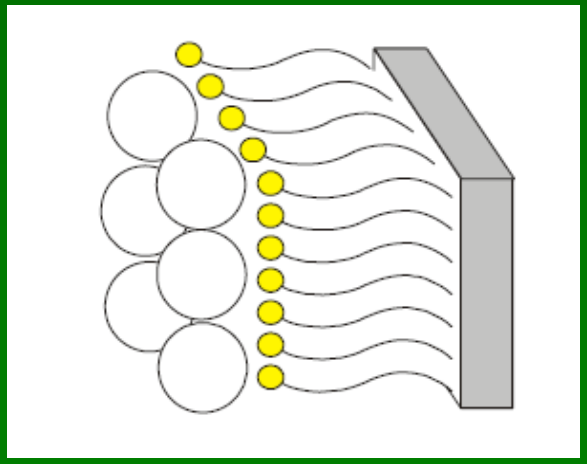
Reverse micelles



Liquid-crystals



Self-assembled layers



Langmuir–Blodgett film

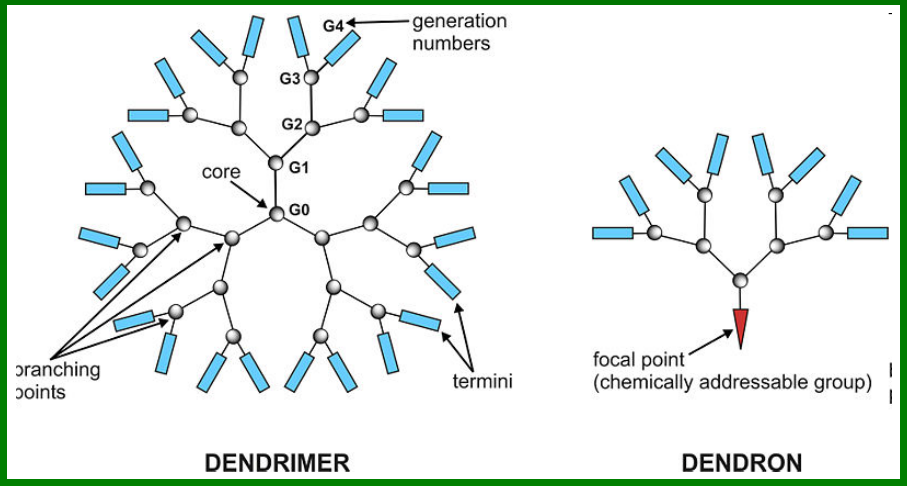
Synthesis in Nanoreactors: Nanoparticles Growth within Dendrimers

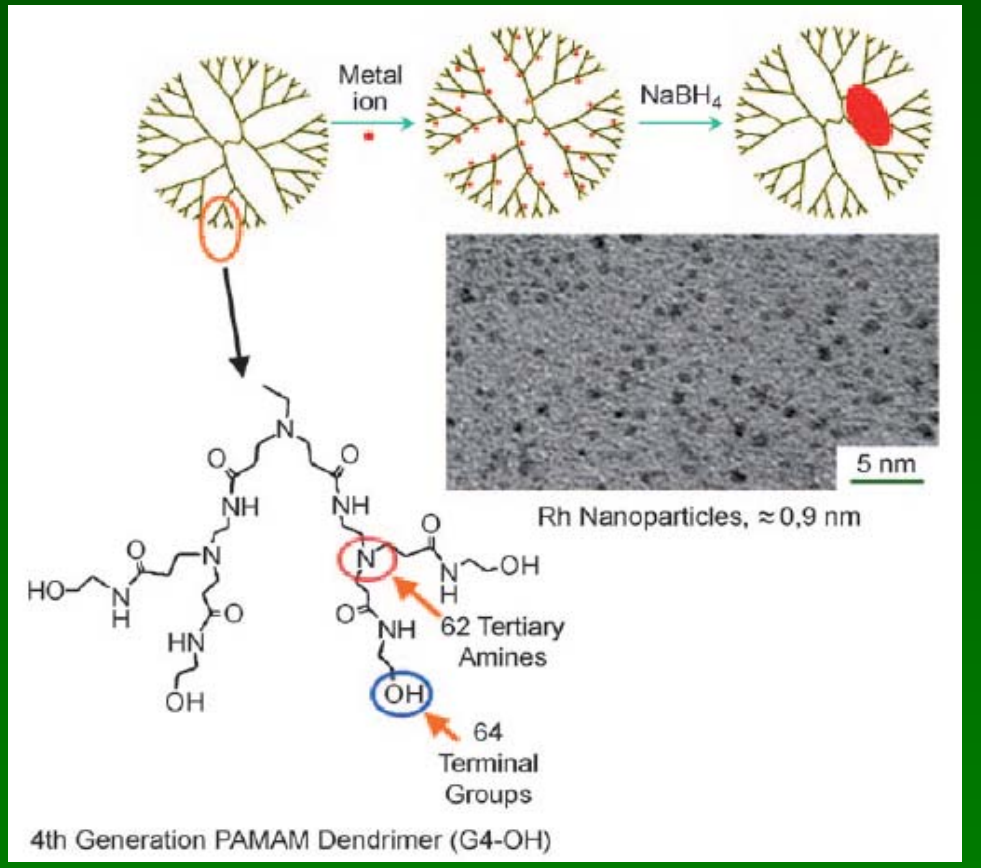
Poly(amidoamine)s (PAMAMs) are the most popular dendrimers used in the synthesis of metal nanoparticles

PAMAMs bind limited number of metal cations - Cu, Ag, Au, Pt, Pd

Driving force for encapsulation includes electrostatic, steric confinement, covalent bonds

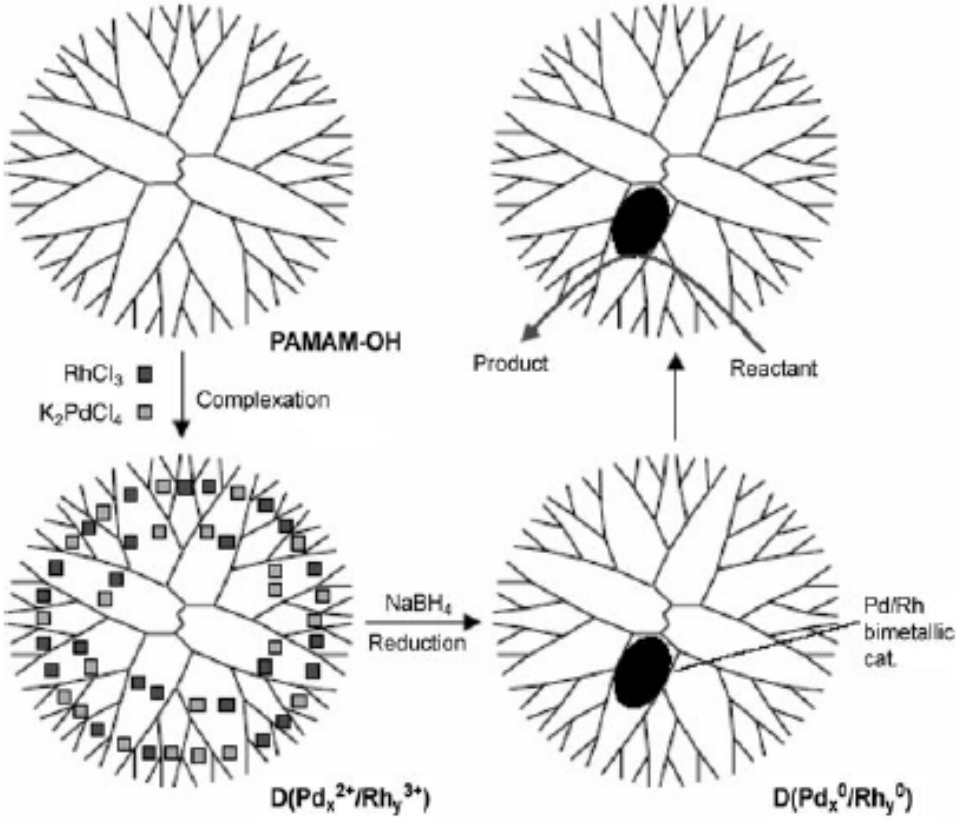
NPs as smaller as 1 nm



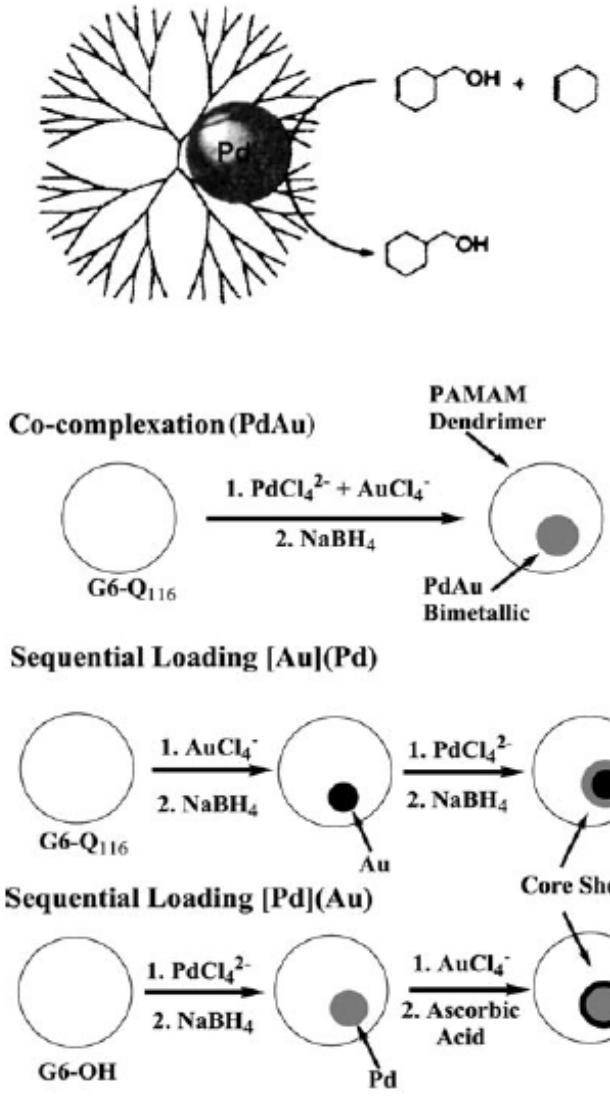


Angew. Chem. Int. Ed. 2008, 47, 9212 – 9228

Synthesis in Nanoreactors: Nanoparticles Growth within Dendrimers



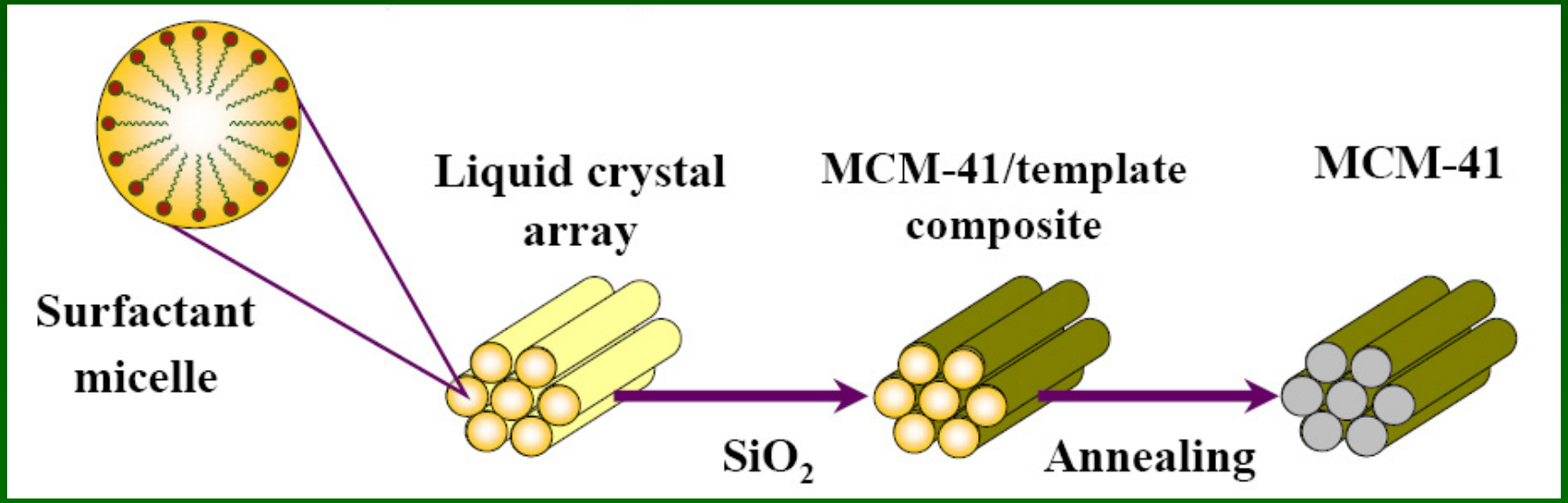
Complexation of a metal cation to the inner nitrogen atoms of tertiary amines, then reduction to metal(0) by $NaBH_4$, and aggregation giving the NPs inside the dendrimer

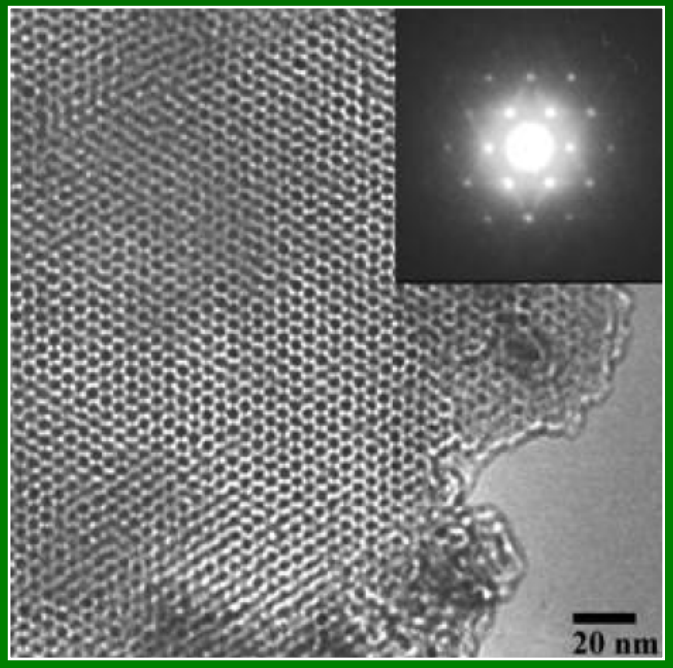


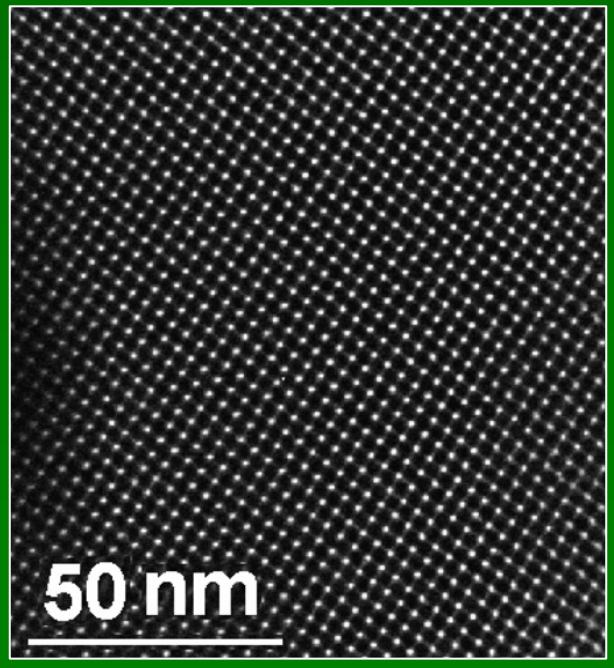
Modes of synthesis of PAMAM-dendrimer-encapsulated heterobimetallic Pd–Au NPs

Angew. Chem. Int. Ed. 2005, 44, 7852 – 7872

Synthesis in Nanoreactors: Liquid-Crystals Templating

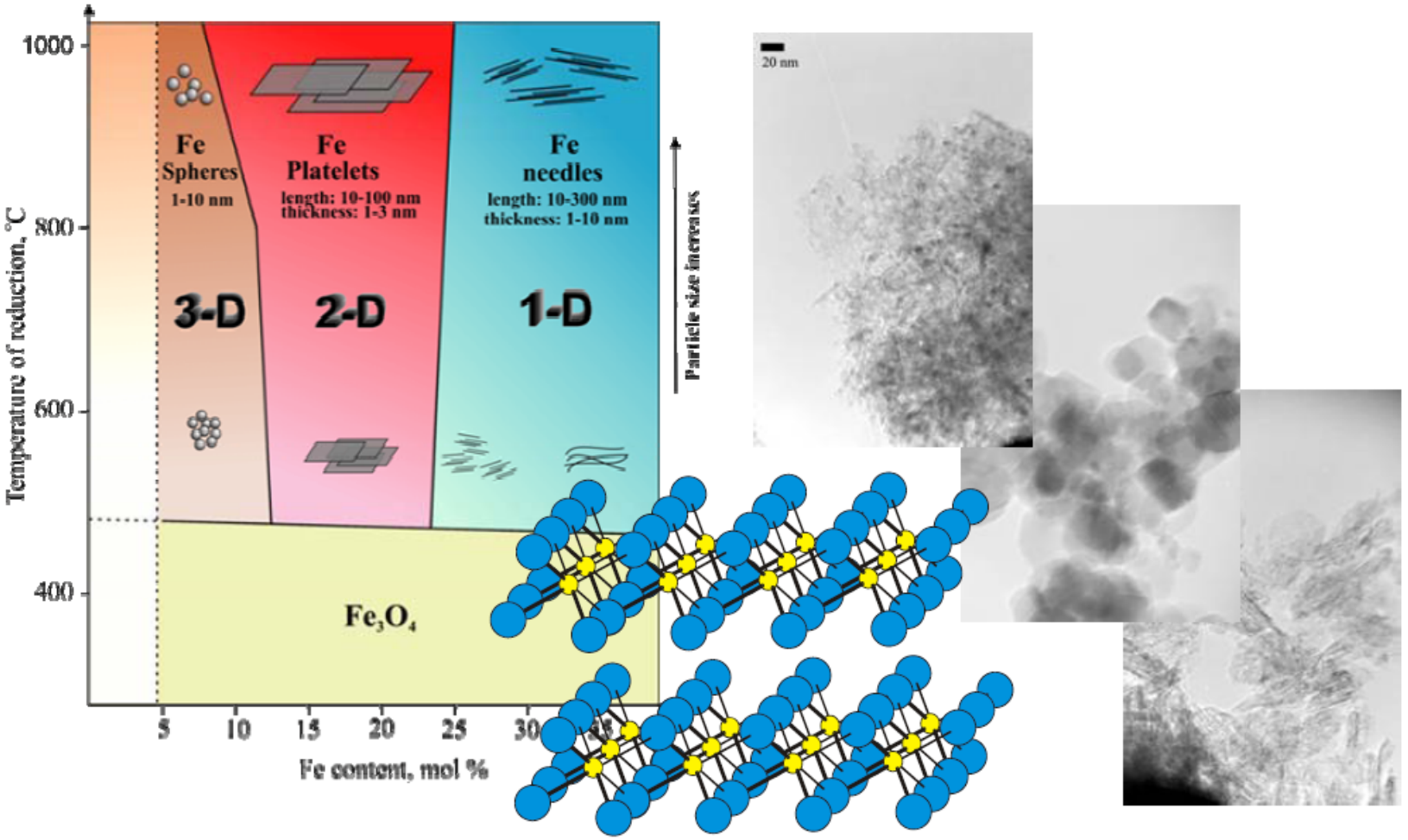






Synthesis in Nanoreactors: Layered Double-Hydroxyde (LDH)

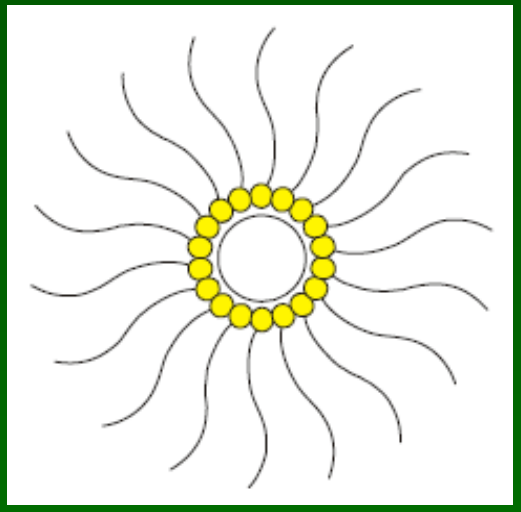
Most famous LDH is hydrotalcite with general formula
$(Mg_6Al_2(CO_3)(OH)_{16} \cdot 4(H_2O)$



Synthesis in Nanoreactors: Reverse Micelles

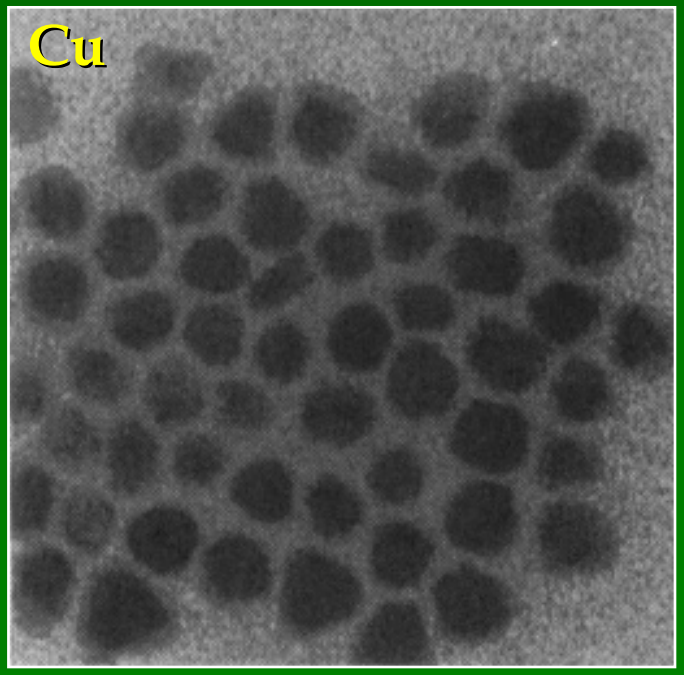
Spherical water in oil droplets:

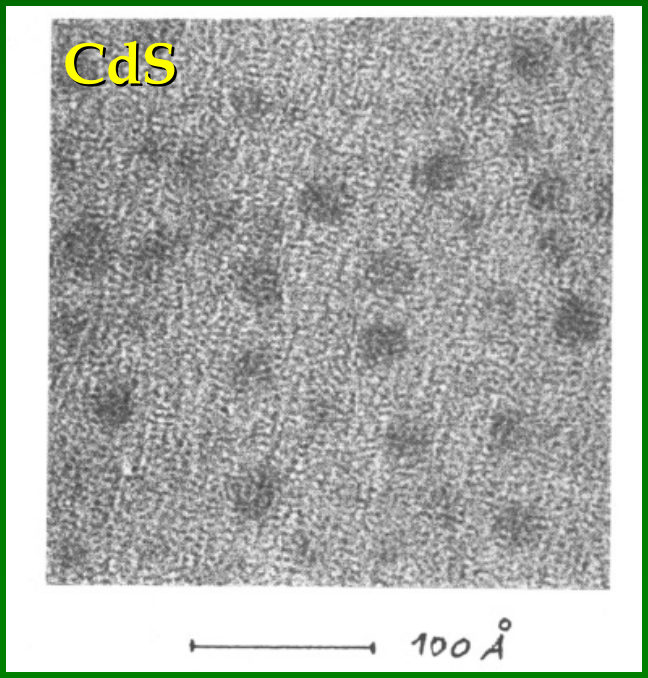
- surfactant is metal (II) bis(2-ethylhexyl) sulfosuccinate
- size of water unit determined by relative concentration of surfactant



ꕥ Reduction of metal cations gives metal NPs

ꕥ Precipitation gives complex NPs, *e. g.* CdS (~)



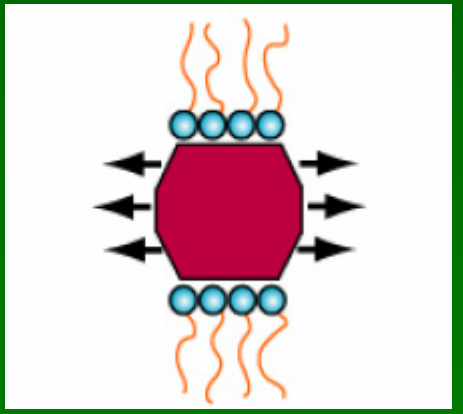


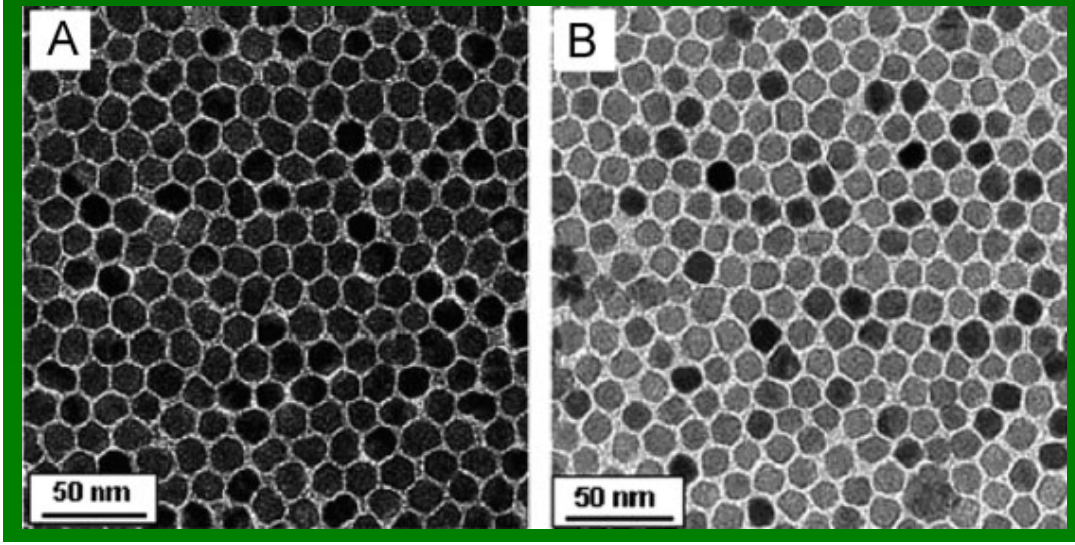
J. Phys. Chem. 1993, 97, 6961-6973

Synthesis of NP using Capping Agent (Polymer Emulsification)

Composition	Crystal structure	Diameter [nm]	Capping agent [a]
Fe	bcc	3.0–9.3	OA, LA, HAc, HAm
ε-Co	fcc	3.5–17	OA, LA, TOP
Co	hcp	2.0–12	OA, TOP, TBP, TOPO
Ni	fcc	5.0–13	OA, TOA, TOPO
FePt	fcc, fct	3.0–17	OA, OAm
CoPt	fcc, fct	7.0	ACA, HDA
γ-Fe_2O_3	fcc	3.0–25	OA, SA
Fe_3O_4	fcc	8.0–30	OA
CoO	fcc	~8	TOP
$CoFe_2O_4$	fcc	2.0–12	OA

Adamantanecarboxylic acid (ACA), hexadecylamine (HDA), hexanoic acid (HAc), hexylamine (HAm), lauric acid (LA), oleic acid (OA), trioctylamine (TOA), oleylamine (OAm), stearic acid (SA), trioctylphosphine (TOP), trioctylphosphine oxide (TOPO)





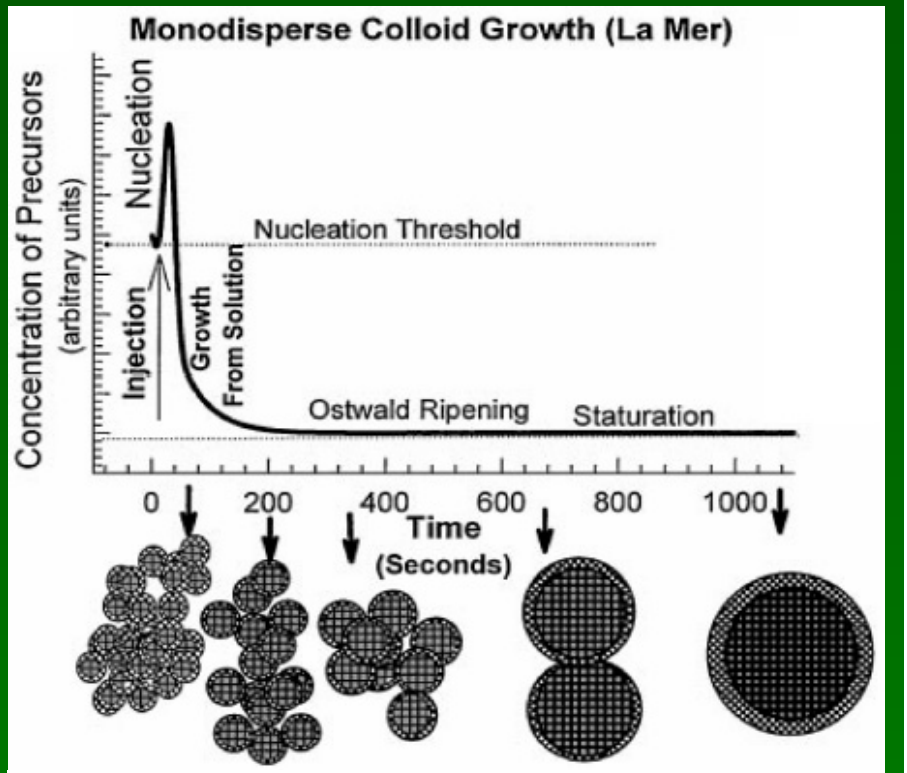
TEM image of A) $CoFe_2O_4$ and B) $MnFe_2O_4$ nanoparticles 14 nm in diameter
Both samples were prepared using the seed-mediated growth method

Adv. Mater. 2007, 19, 33–60

Arrested Precipitation

The stages of nucleation and growth for the preparation of monodisperse NCs in the framework of the *La Mer* model

As NCs grow with time, a size series of NCs may be isolated by periodically removing aliquots from the reaction vessel

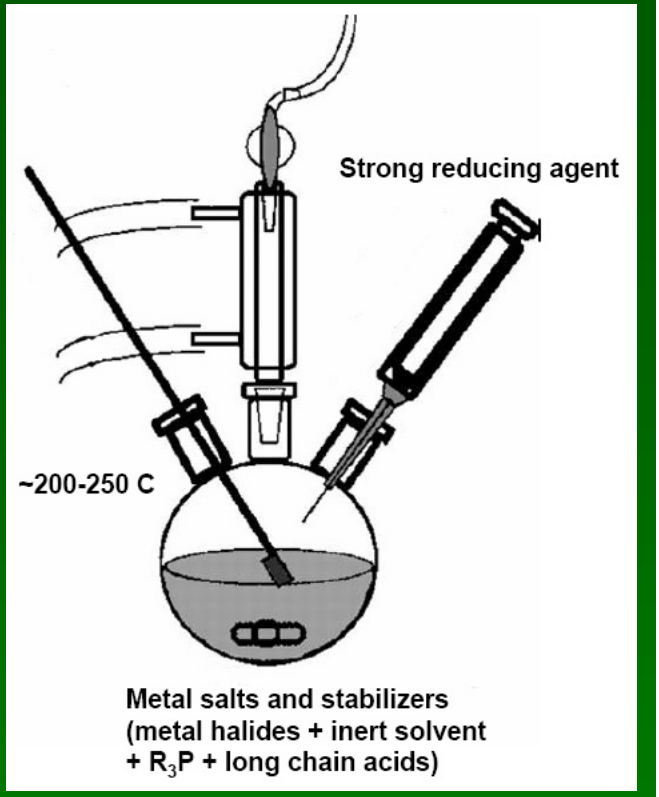


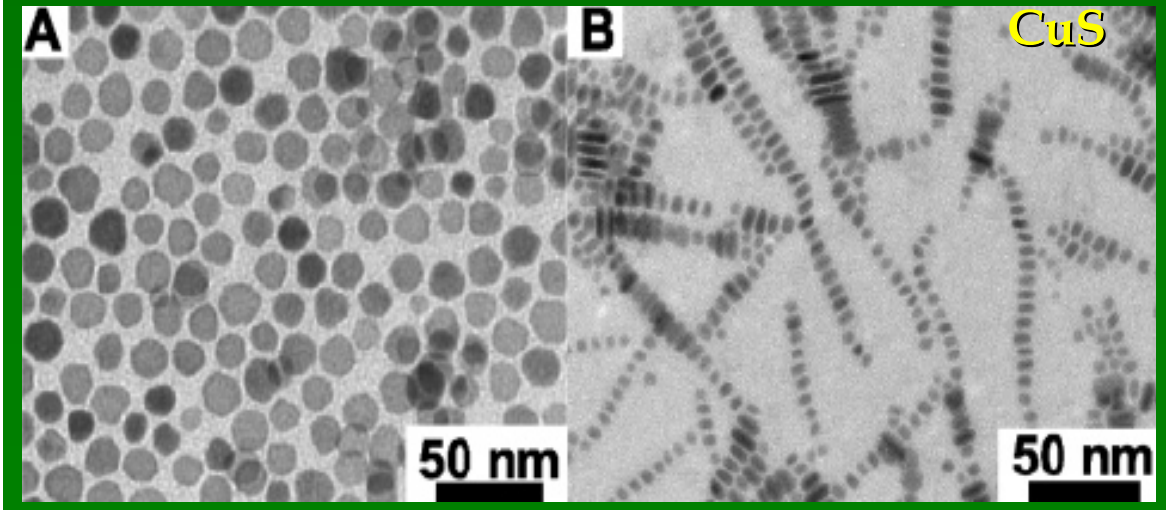
Chem. Rev. 1992, 92, 1709-1727

Ostwald ripening: when a phase precipitates out of a solid, energetic factors will cause large precipitates to grow, drawing material from the smaller precipitates, which shrink

Arrested Precipitation

- Aqueous reduction of metal salts (Ag, Au) in presence of citrate ions
  - -. Chemisorption of organic ligands for handling
  - -. Particle size distribution varies > 10%
- II-IV MX NPs (M = Zn, Cd, Cu, Hg; X = S, Se, Te)
- Metal alkyls [$Cd(CH_3)_2$] + organophosphine chalcogenides tri-*n*-octylphosphine selenide
- Phosphone(tri-*n*-octylphosphine oxide) binding to M controlled by *T*
- Ostwald ripening allows control over size

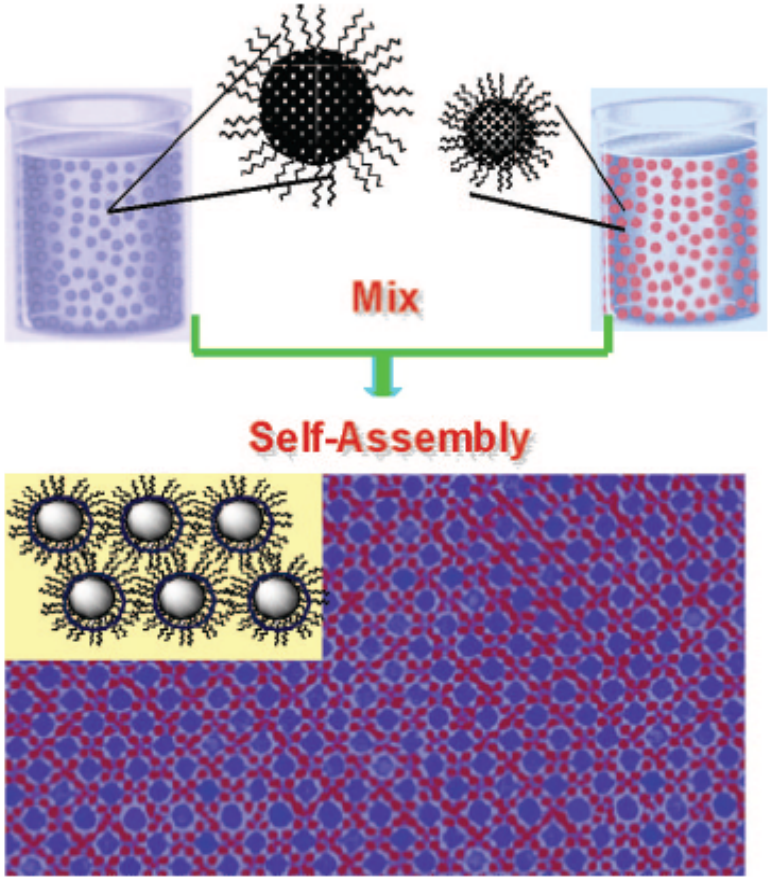




Chem. Mater. 2001, 13, 3843-3858
Langmuir 2005, 21, 9451-9456

Assembled Nanostructures: Nanocrystal Superlattices

Formation of a binary nanocrystal superlattice through van der Waals and dipole or induced dipole interactions between NPs

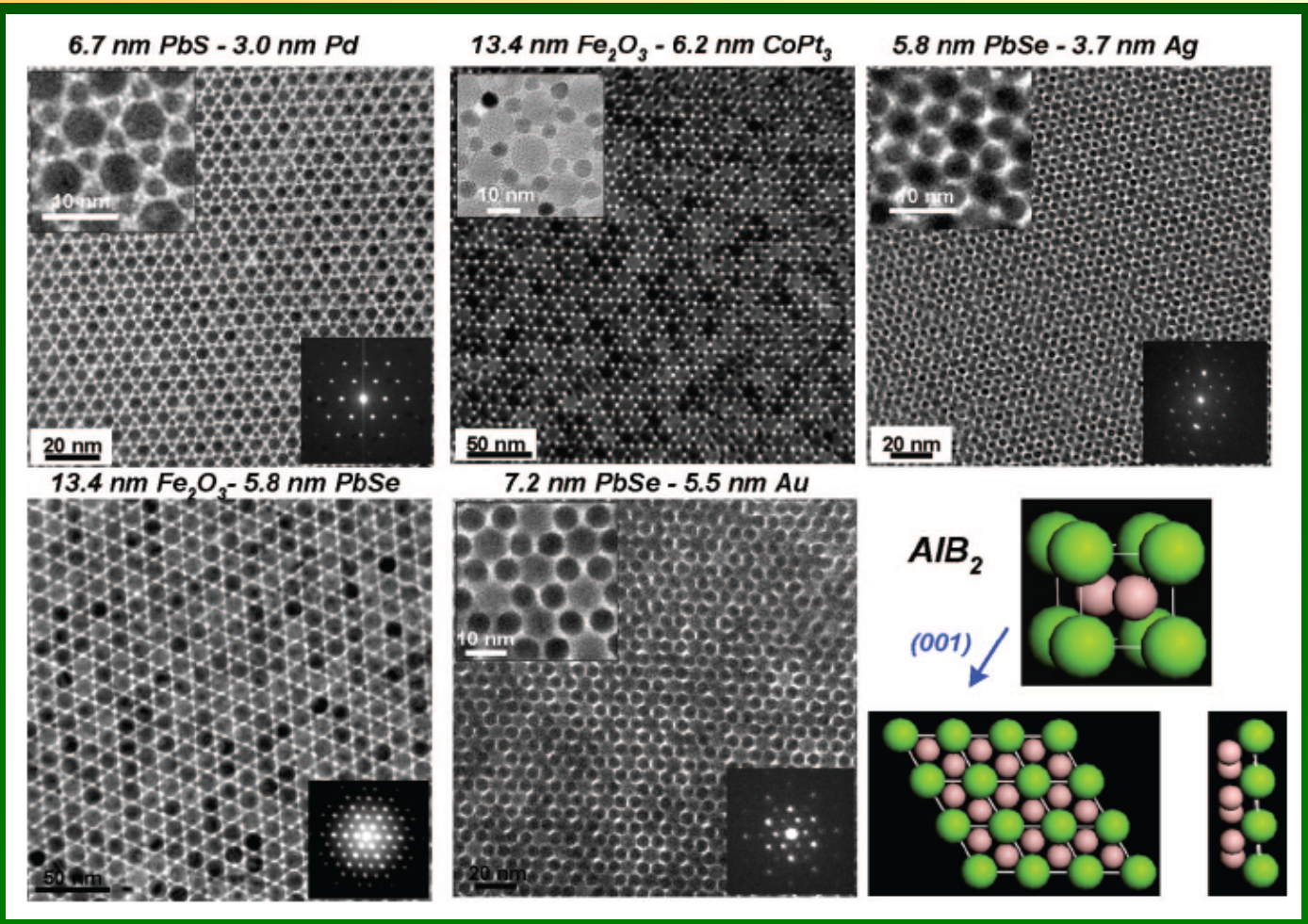


ACS Nano, 2009, 3, 244-255

As-assembled materials offer the ability to tune component properties, lattice parameters, and thus coupling of physical properties through the careful selection and assembly of building blocks

Assembled Nanostructures: Nanocrystal Superlattices

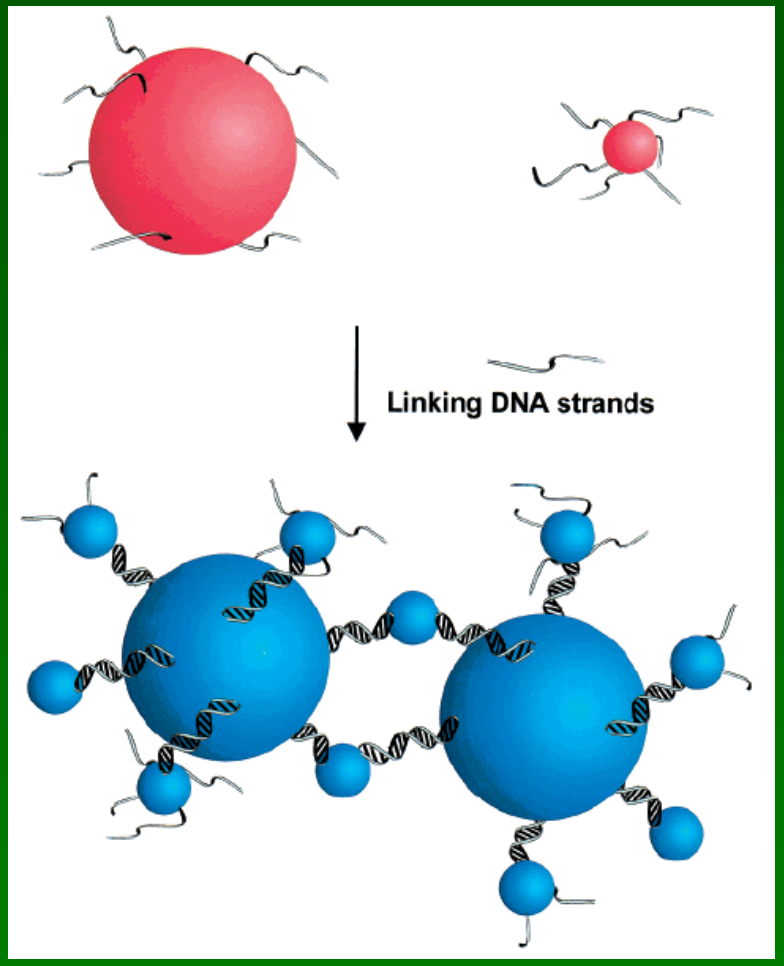
Examples of a series of binary superlattices with stoichiometries of one large particle for each two small particles

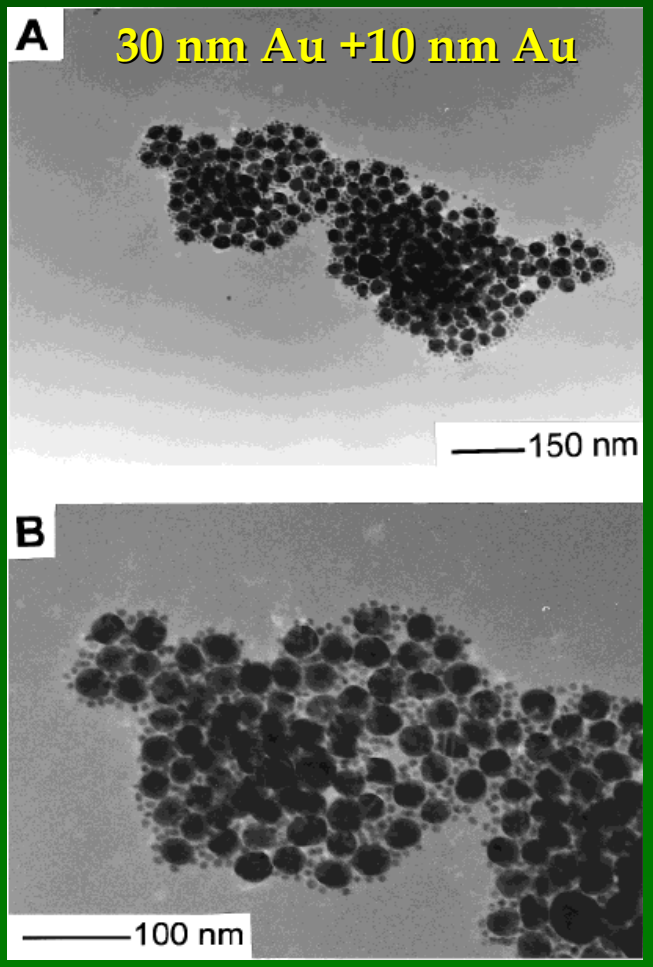


A wide range of semiconducting, metallic, magnetic, and plasmonic building blocks can be captured, while retaining a constant stoichiometry and symmetry.
With dozens of monodisperse building blocks available, tunable in size increments as little as one atomic layer, and with more than 25 binary crystal structures, the available combinations to explore are in the order of tens of thousands

ACS Nano, 2009, 3, 244-255

Assembled Nanostructures: DNA-based assemble

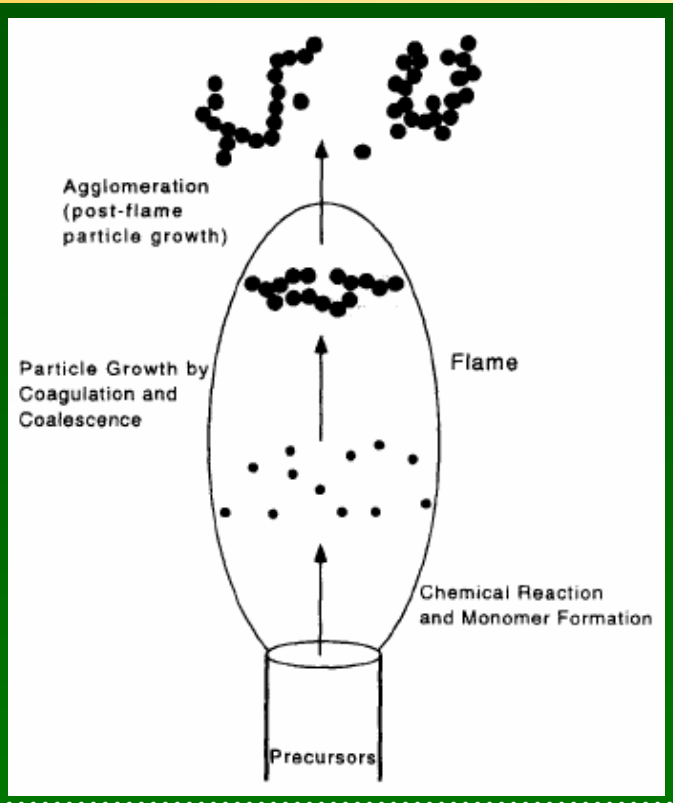




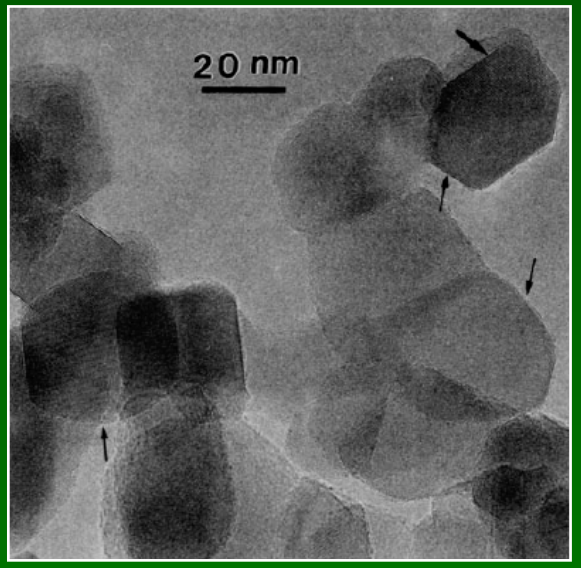
- Au nanostructures assembled by DNA hybridization:
  - -. Functionalize large and small Au NPs with different DNA strands
  - -. Introduction of linker strand that contains complementary sequence to those on large and small Au NPs

Inorg. Chem. 2000, 39, 2258-2272

Gas-Phase Chemical Preparation: Flame Synthesis



TiO_2 P-25 (DEGUSSA)

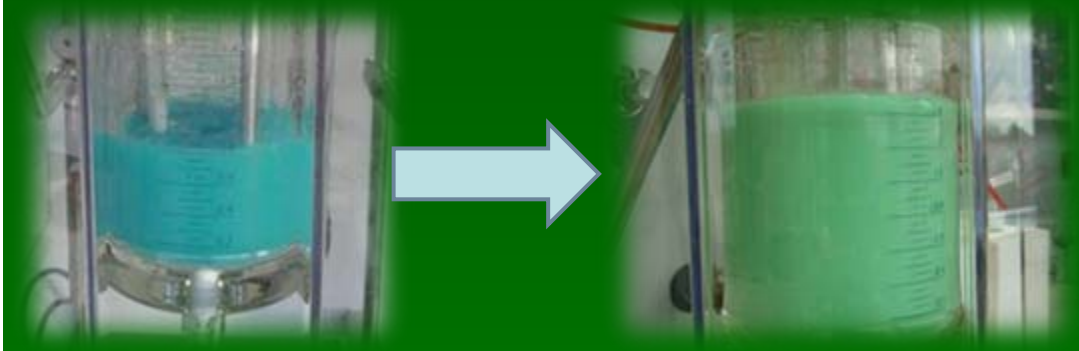


$$TiCl_4(g) + 2H_2O(g) = TiO_2(s) + 4HCl(g)$$

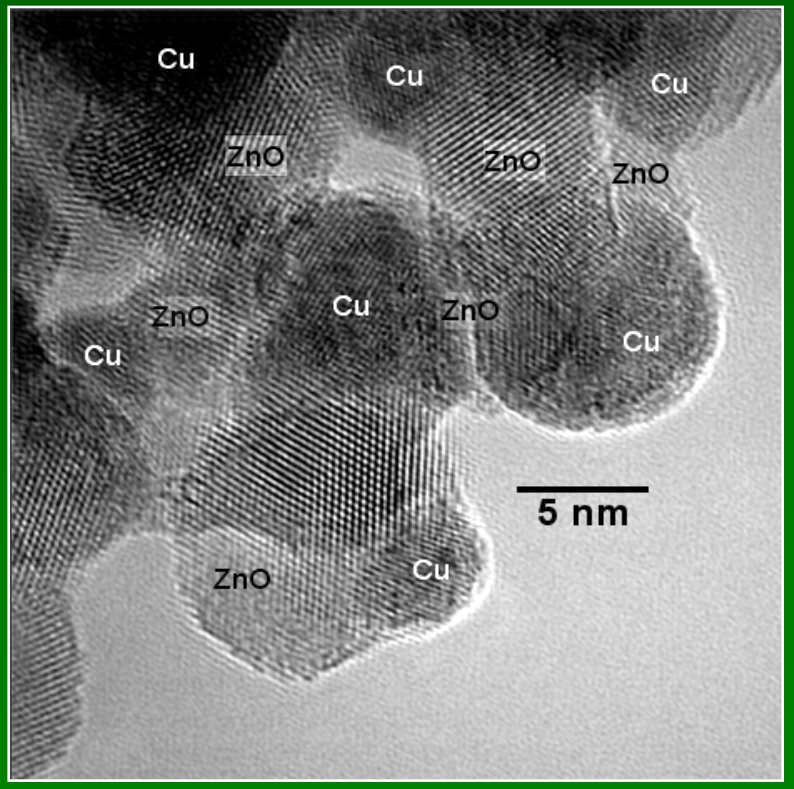
- Requires fuels for combustion as heat supply
- Evaporation and chemical reaction of precursors in a flame produced by fuel combustion
- The most commercially successful process - ~10^6 tons/year of carbon black and metal oxides(SiO_2, TiO_2, Al_2O_3)
- Difficult to control the process
- Flame temperature: 1000-2400°C, residence time in flame: 10-100ms

Wet Chemical Preparation: Co-Precipitation

- Co-Precipitation (Cu^{2+}, Zn^{2+} nitrates + Na_2CO_3)
- Aging



- Washing
- Drying
- Calcination
- Reduction



$H_2 / CO / CO_2$ → Methanol H_3COH

Wet Chemical Preparation: Sol-Gel Processing

Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid.

<u>Precursors</u>

- Metal alkoxides, $M(OR)_Z$, in organic solvent

  where M = Si, Ti, Zr, Al, Sn, Ce

  OR = an alkoxy group

- Metal salts (chloride, oxychloride, nitrate…) in aqueous solution

  much cheaper and easier to handle

  reactions: more difficult to control

<u>Basic mechanism</u>

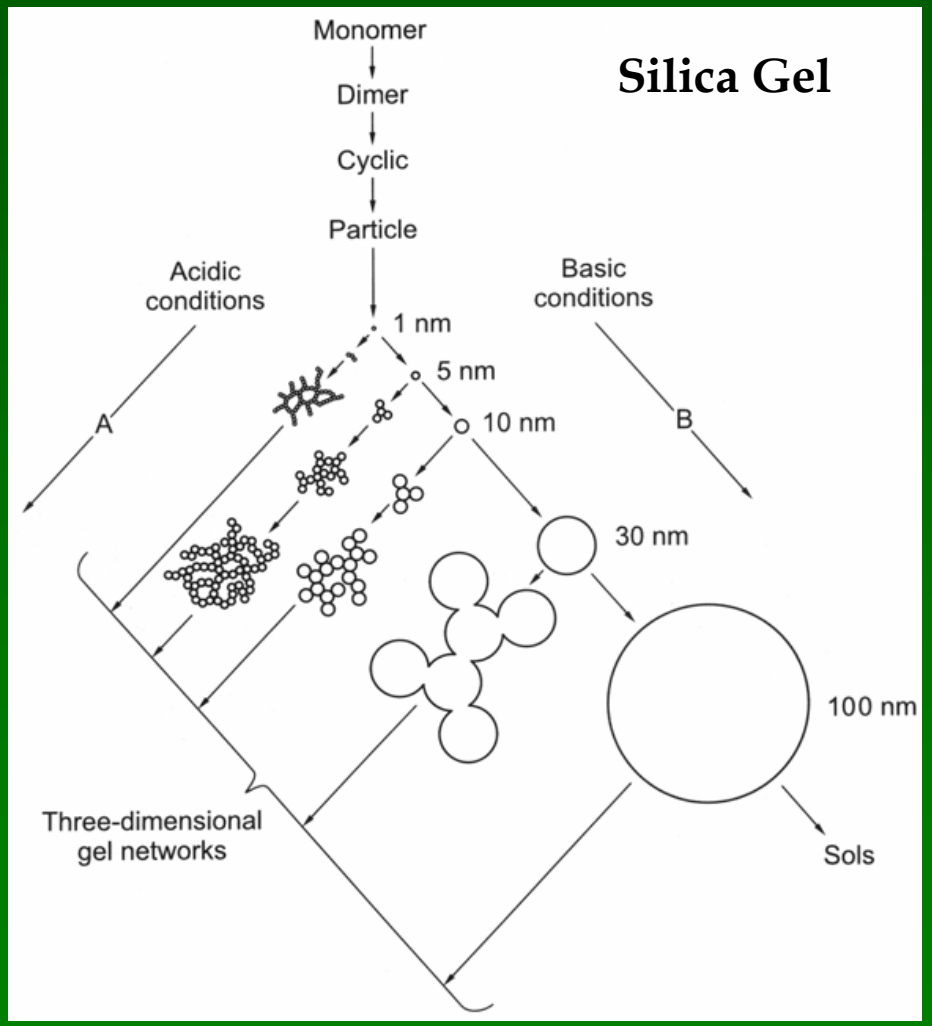
- Hydrolysis $M\text{-}OR + H_2O = M\text{-}OH + ROH$
- Polycondensation

  $M\text{-}OH + RO\text{-}M = M\text{-}O\text{-}M + ROH$

  $M\text{-}OH + HO\text{-}M = M\text{-}O\text{-}M + H_2O$
- Occurs sequentially and in parallel

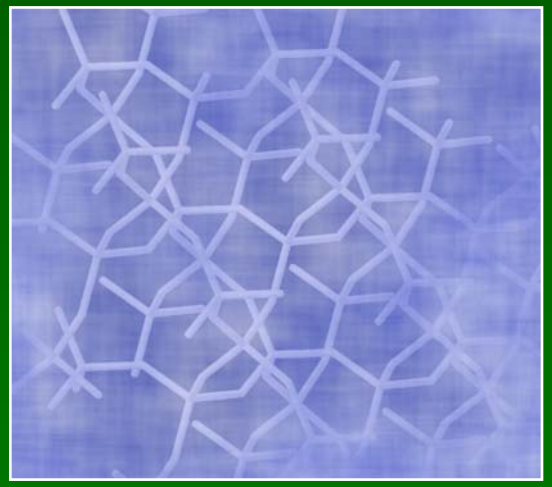
<u>Characteristics of sol-gel processes</u>

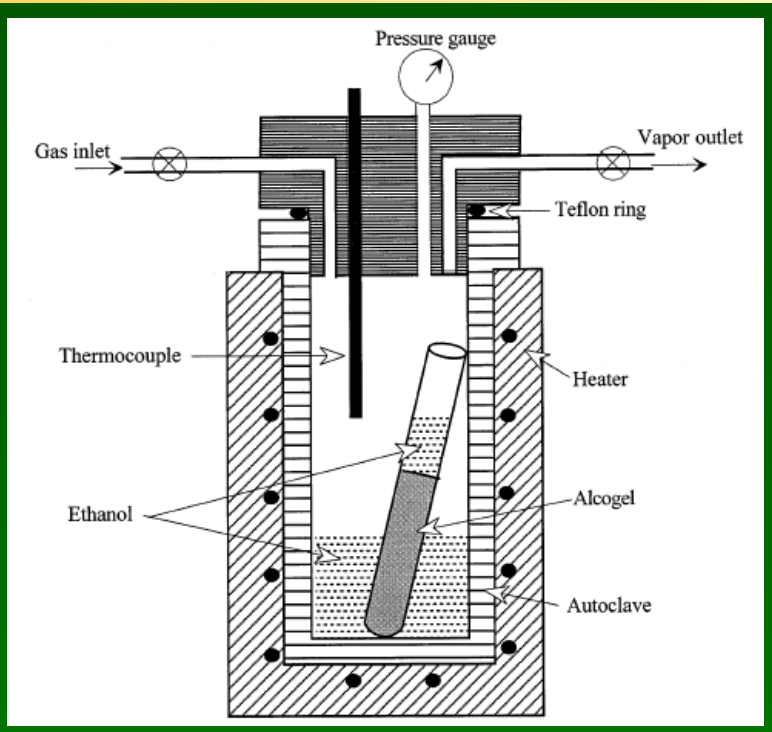
- Low processing temperature
- Molecular-level homogeneity

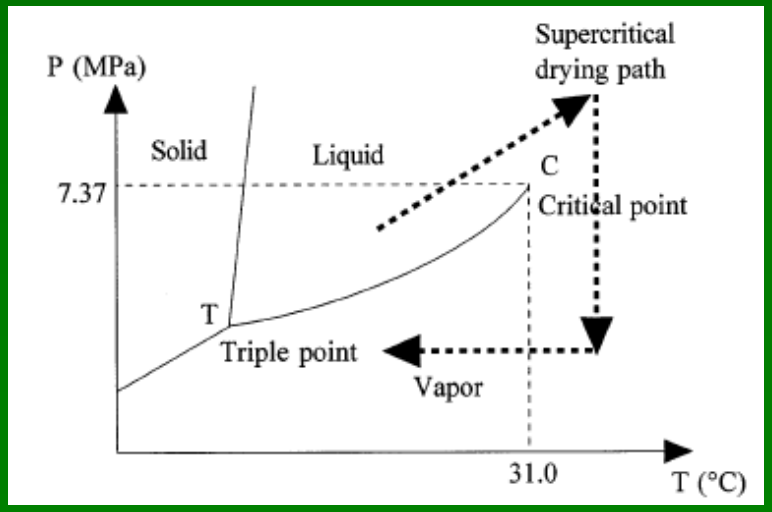


Sol-Gel Processing: Silica Aerogels

Wet-gel

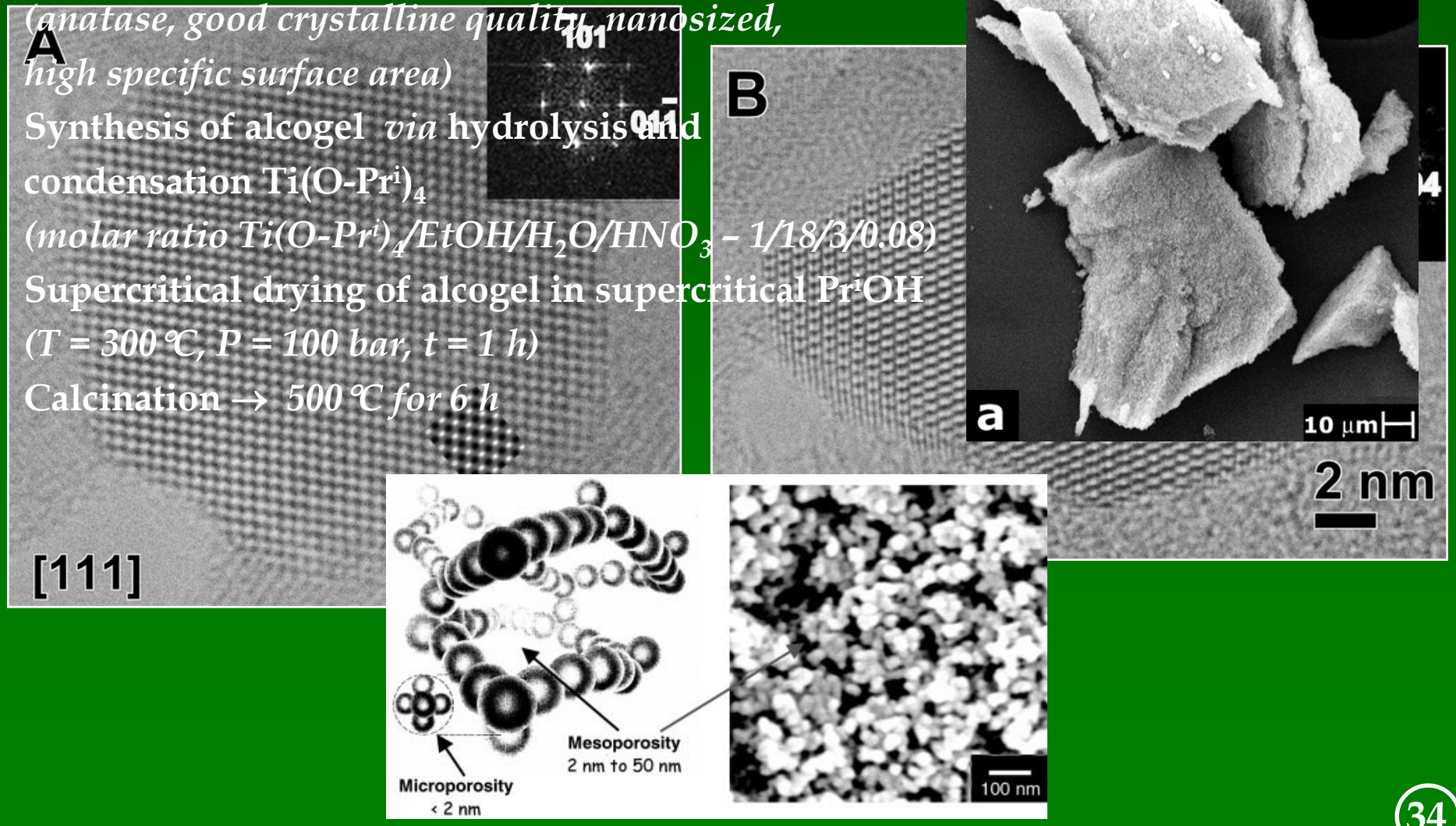






Sol-Gel Processing: Metal Oxide Aerogels

Photocatalytic TiO_2 should be specially structured
(anatase, good crystalline quality, nanosized, high specific surface area)
Synthesis of alcogel *via* hydrolysis and condensation $Ti(O\text{-}Pr^i)_4$
(molar ratio $Ti(O\text{-}Pr^i)_4/EtOH/H_2O/HNO_3$ – 1/18/3/0.08)
Supercritical drying of alcogel in supercritical Pr^iOH
(T = 300 ℃, P = 100 bar, t = 1 h)
Calcination → *500 ℃ for 6 h*



J. Photochem. Photobiol. A: Chem. 2005, 172, 19 @ J. Phys. Chem. B 2005, 109, 20303

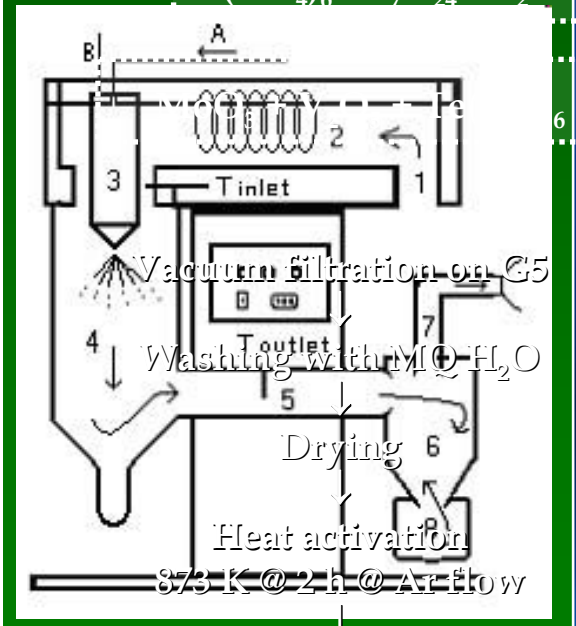
The Miracle of Instant Coffee ☺

Spray-Drying Technique

Spray-drying is a method of producing a dry powder from a liquid or slurry by rapidly drying with a hot gas

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O + NH_4VO_3 + Te(OH)_6 + NH_4[NbO(C_2O_4)_2]\cdot 8.8H_2O \rightarrow$ orange SLURRY

$+ NH_4[NbO(C_2O_4)_2]\cdot 8.8H_2O + C_2H_2O_4\cdot 2H_2O \rightarrow$ ox[illegible]c complex solution



Vacuum filtration on G5

↓

Washing with MQ-H_2O

↓

Drying

↓

Heat activation

873 K @ 2 h @ Ar flow

↓

~54 g of M1 in one run
Yield ~41%

Calcination
548 K @ 1 h @ Air flow

↓

Crystallization/Activation
873 K @ 2 h @ Ar flow

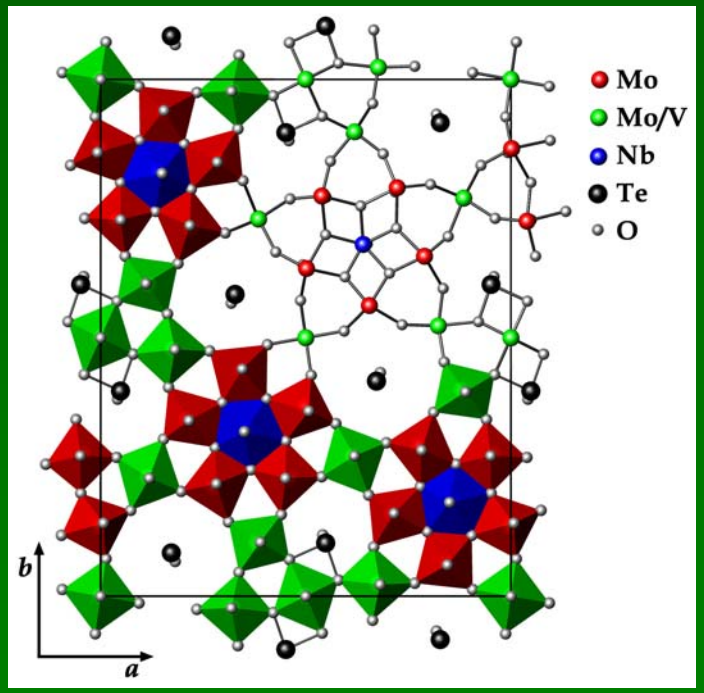
↓

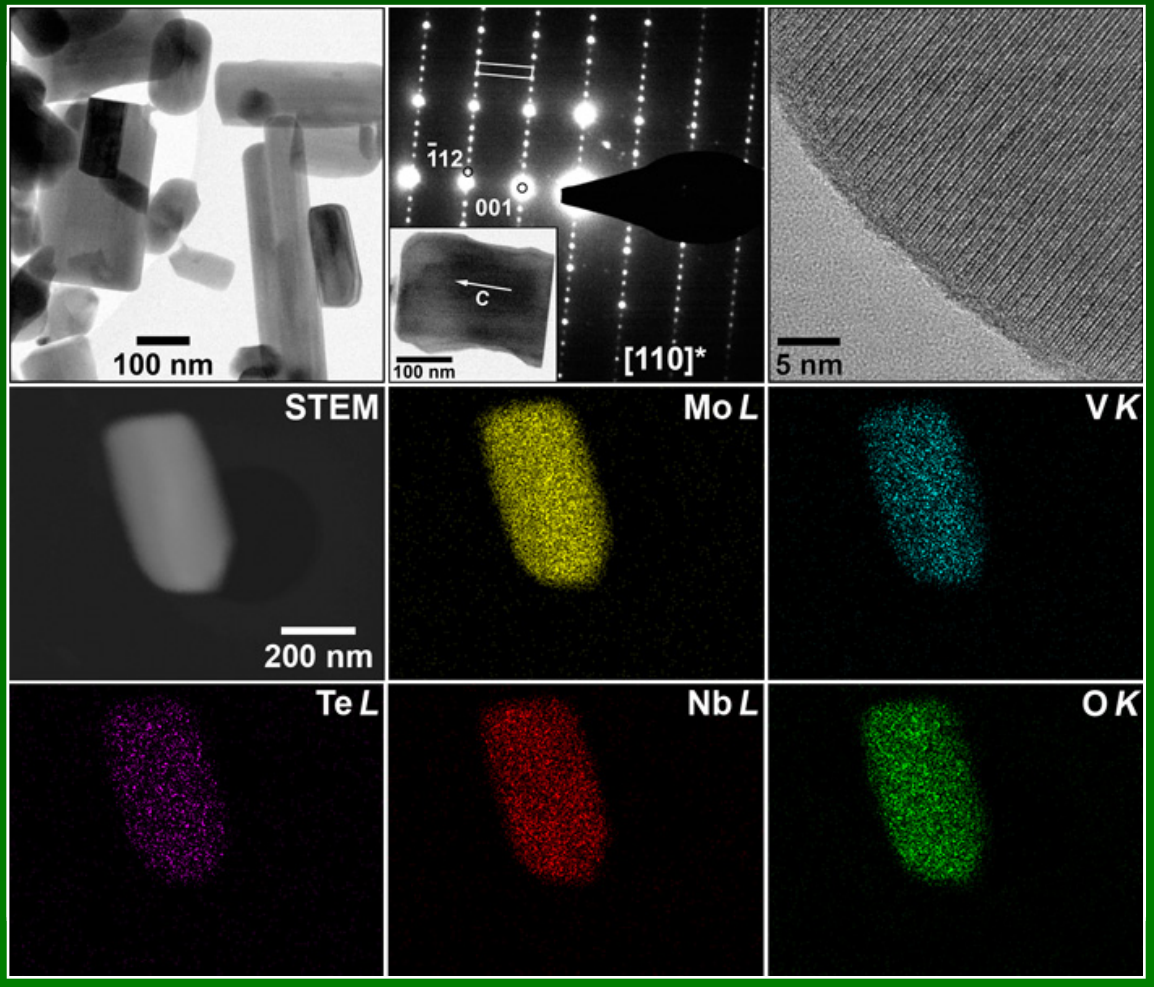
15% H_2O_2 washing
S/L ratio 0.04 g/mL
24 h @ 400 rpm

Spray-Drying

Spray-Drying Technique

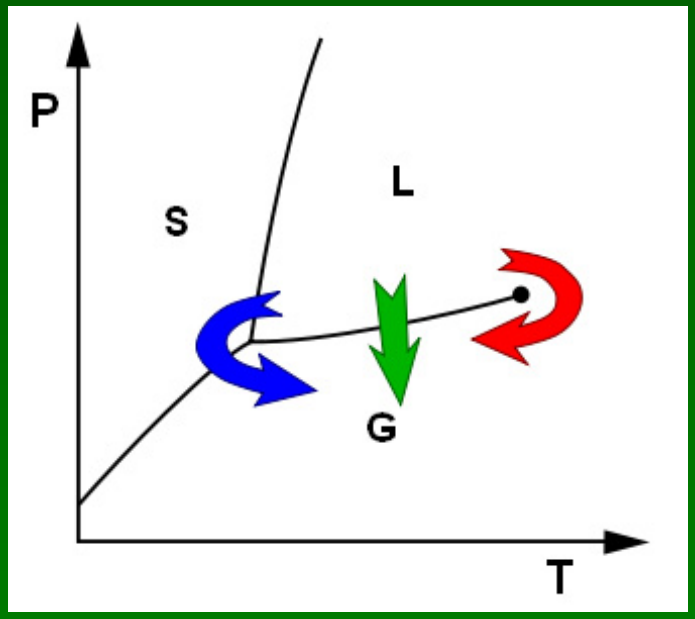
M1 Phase $Mo_{7.8}V_{1.2}NbTe_{0.937}O_{28.9}$





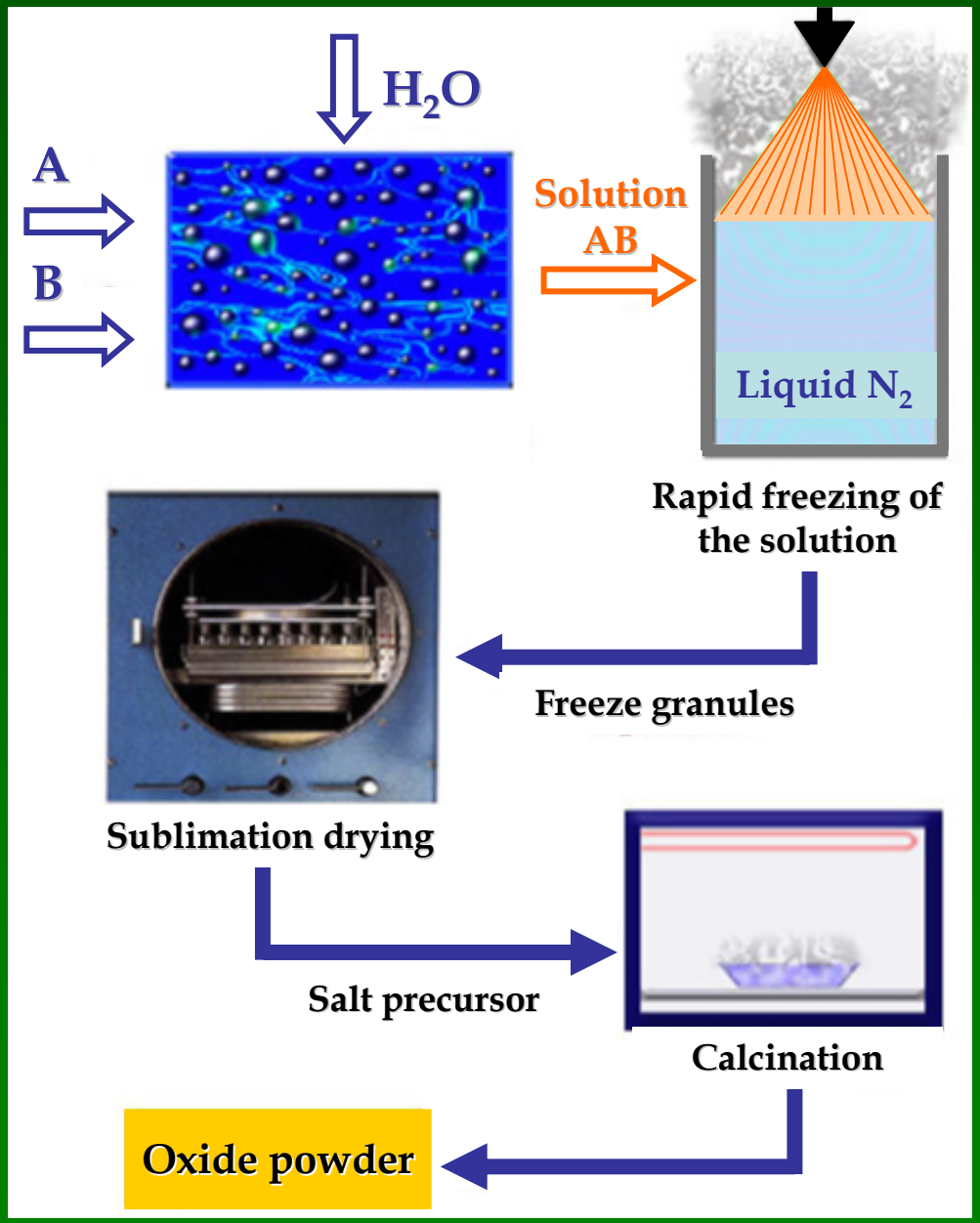
Freeze-Drying Technique

Freeze-drying works by freezing the material and then reducing the surrounding pressure and adding enough heat to allow the frozen water in the material to sublime directly from the solid phase to gas



In a typical phase diagram, the boundary between gas and liquid runs from the triple point to the critical point. Freeze drying (blue arrow) brings the system around the triple point, avoiding the direct liquid-gas transition seen in ordinary drying (green arrow).

Freeze-Drying Technique



$La_{0.7}Ca_{0.3}MnO_3$

J. Eur. Ceram. Soc. 2000, 20, 2047

Hydrothermal Synthesis

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures

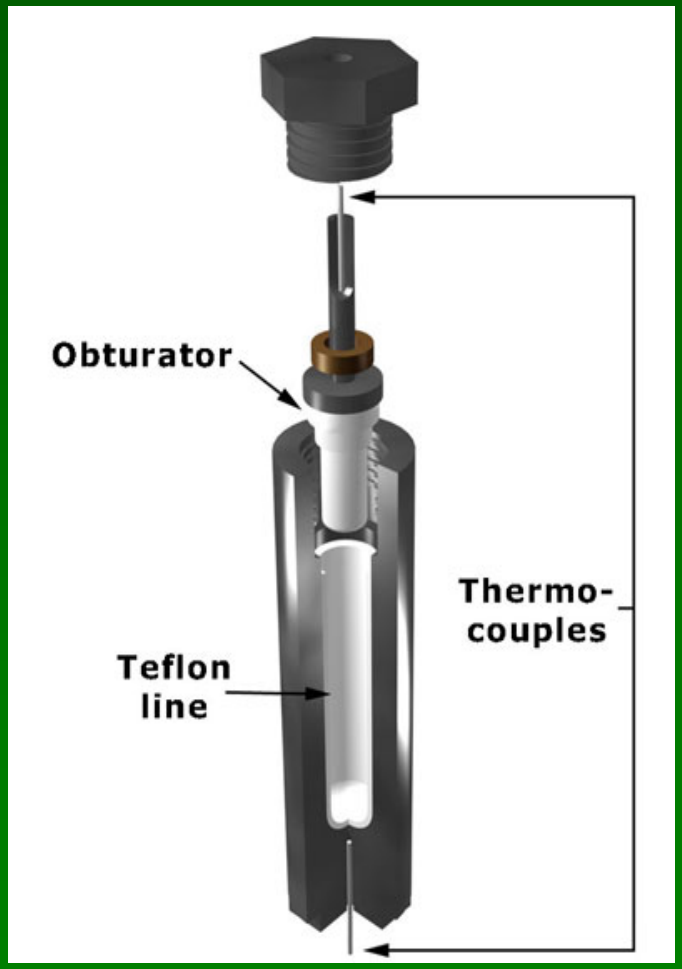
Precursors:

Amorphous gel $TiO_2 \cdot nH_2O$

$TiOSO_4$ (0.25 & 0.44 M)

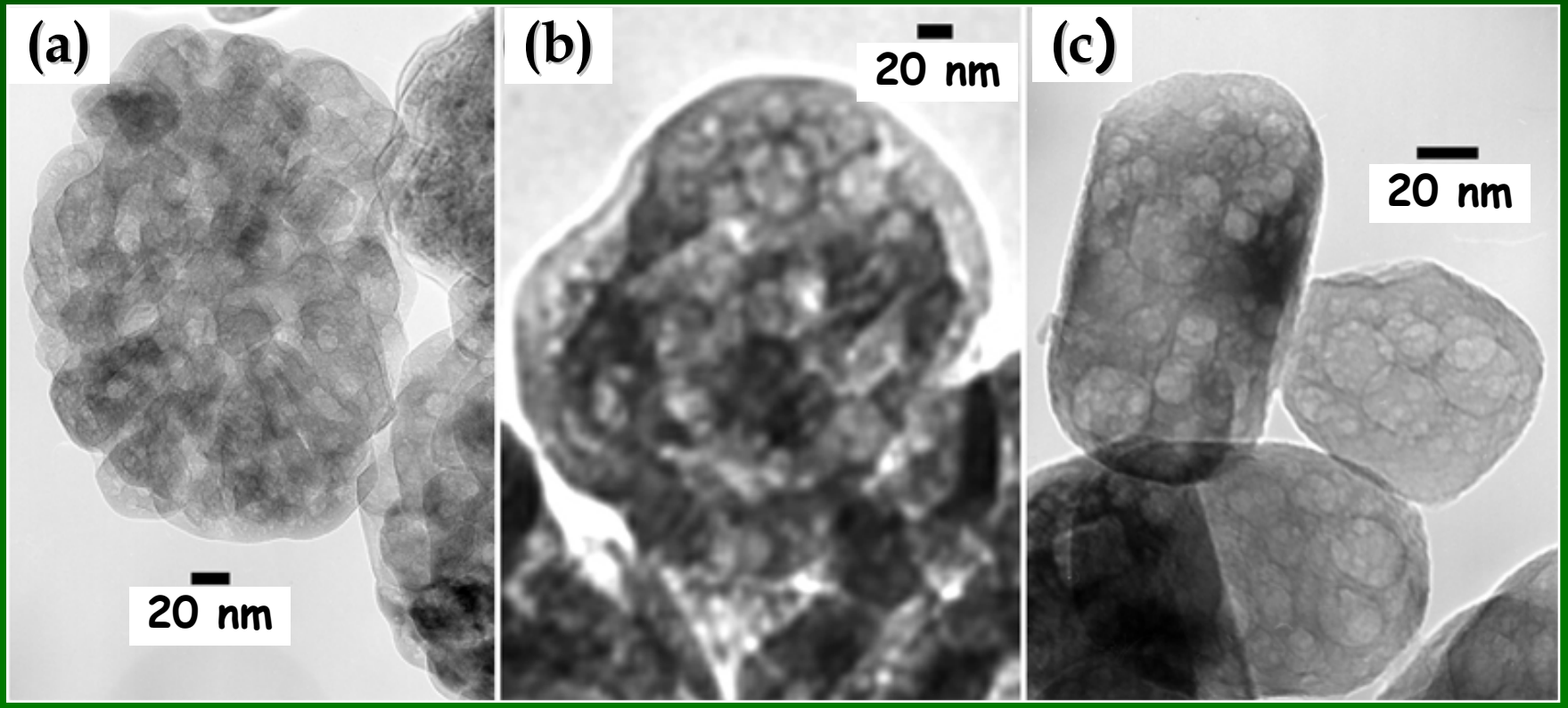
$TiO(NO_3)_2$ (0.25 & 0.50 M)

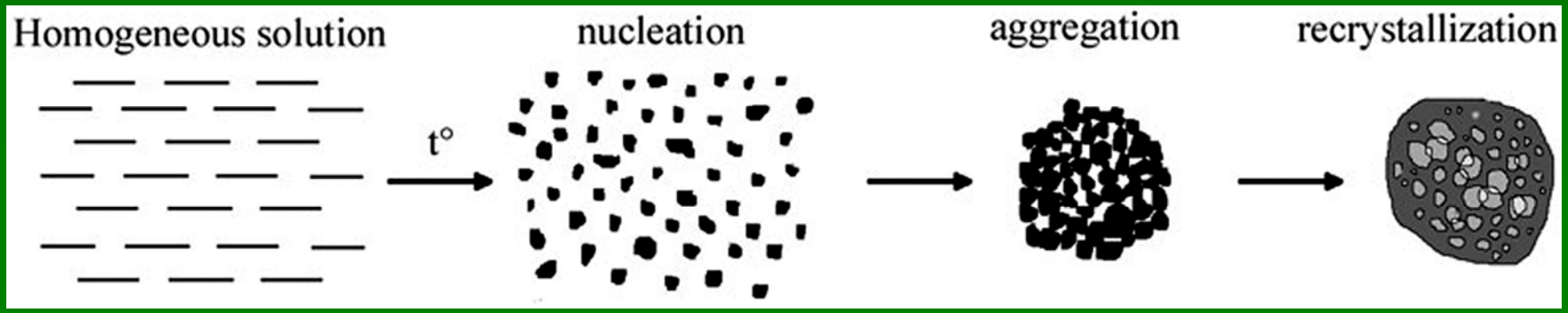
$H_2TiO(C_2O_4)_2$ (0.07 & 0.28 M)



Hydrothermal Synthesis

$$H_2[TiO(C_2O_4)_2] + H_2O \longrightarrow (a, r)\text{-}TiO_2\downarrow + 2H_2C_2O_4$$

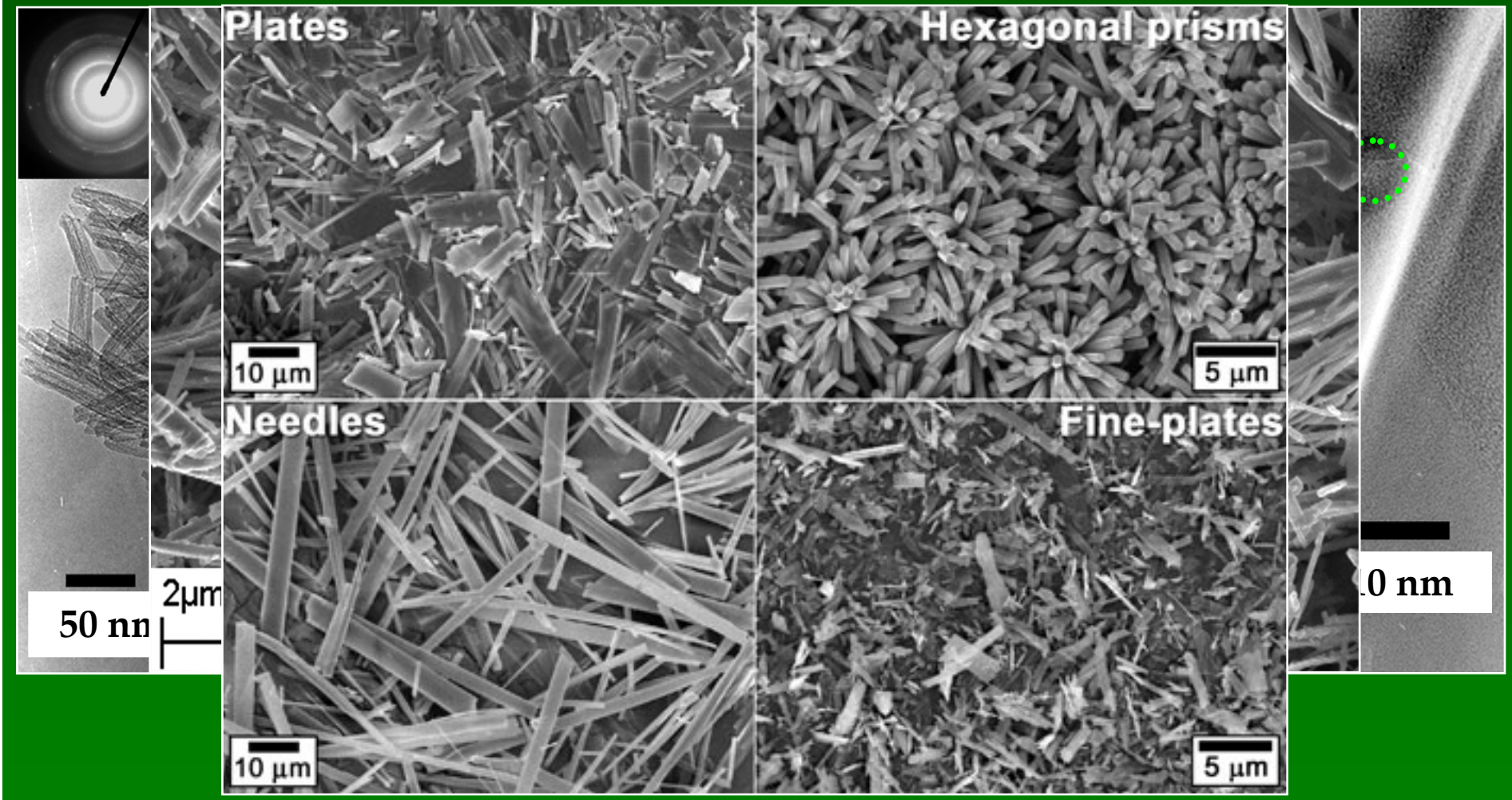




Chem. Phys. Lett. 2004, 388, 411

Hydrothermal Synthesis

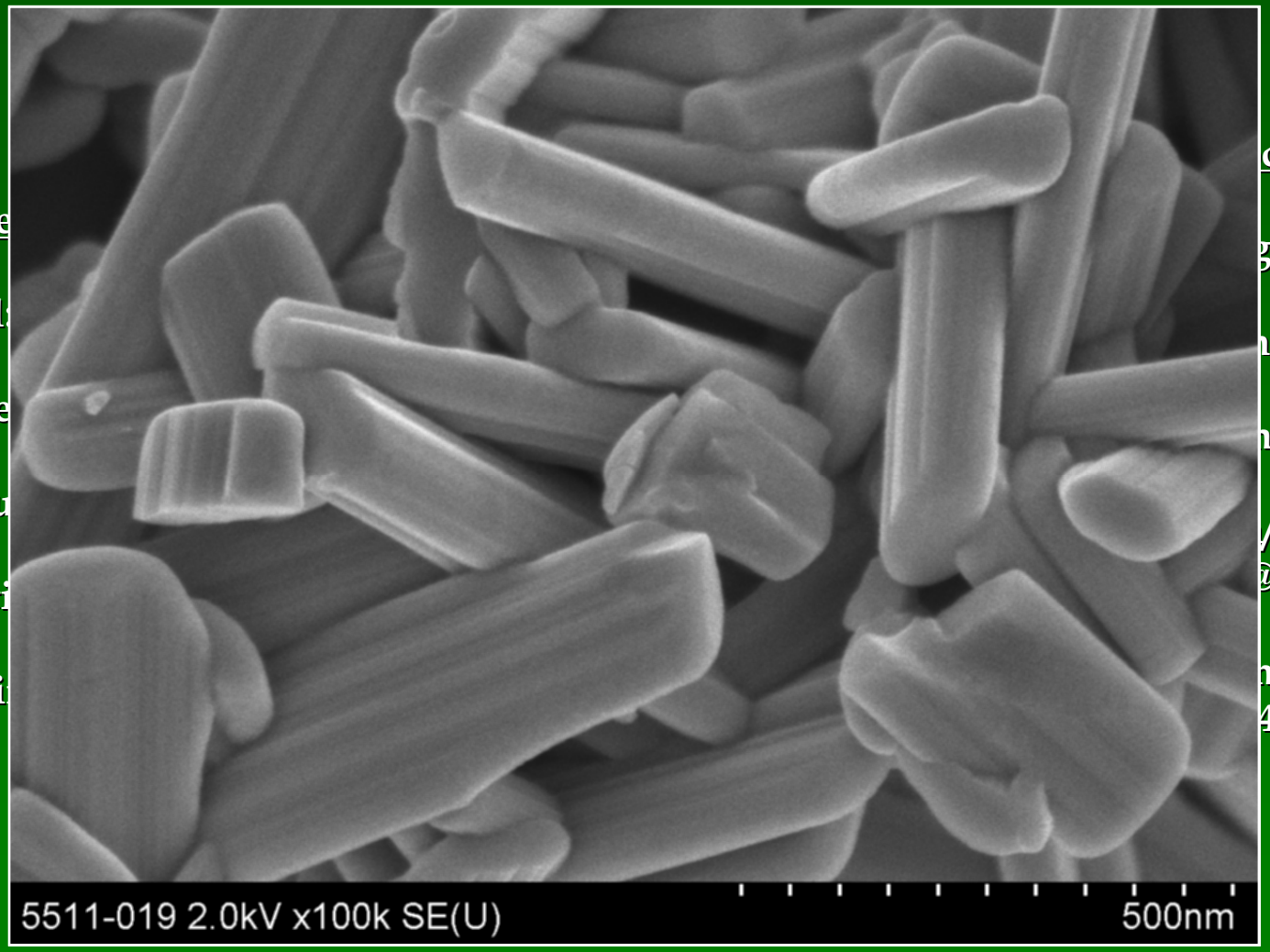
Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$



J. Phys. Chem. B 2006, 110, 4030 @ Cryst. Growth Des. 2009, 9, 466

Hydrothermal Synthesis

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O + VOSO_4\cdot 5H_2O + Te(OH)_6 + NH_4[NbO(C_2O_4)_2]\cdot 8.8H_2O \rightarrow$ M1 phase $Mo_1V_{0.27}Te_{0.1}Nb_{0.1}O_{3.8}$



cessing:

Hydrothe

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Material

n MQ H_2O

Tempe

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Pressu

/Activation

Durati

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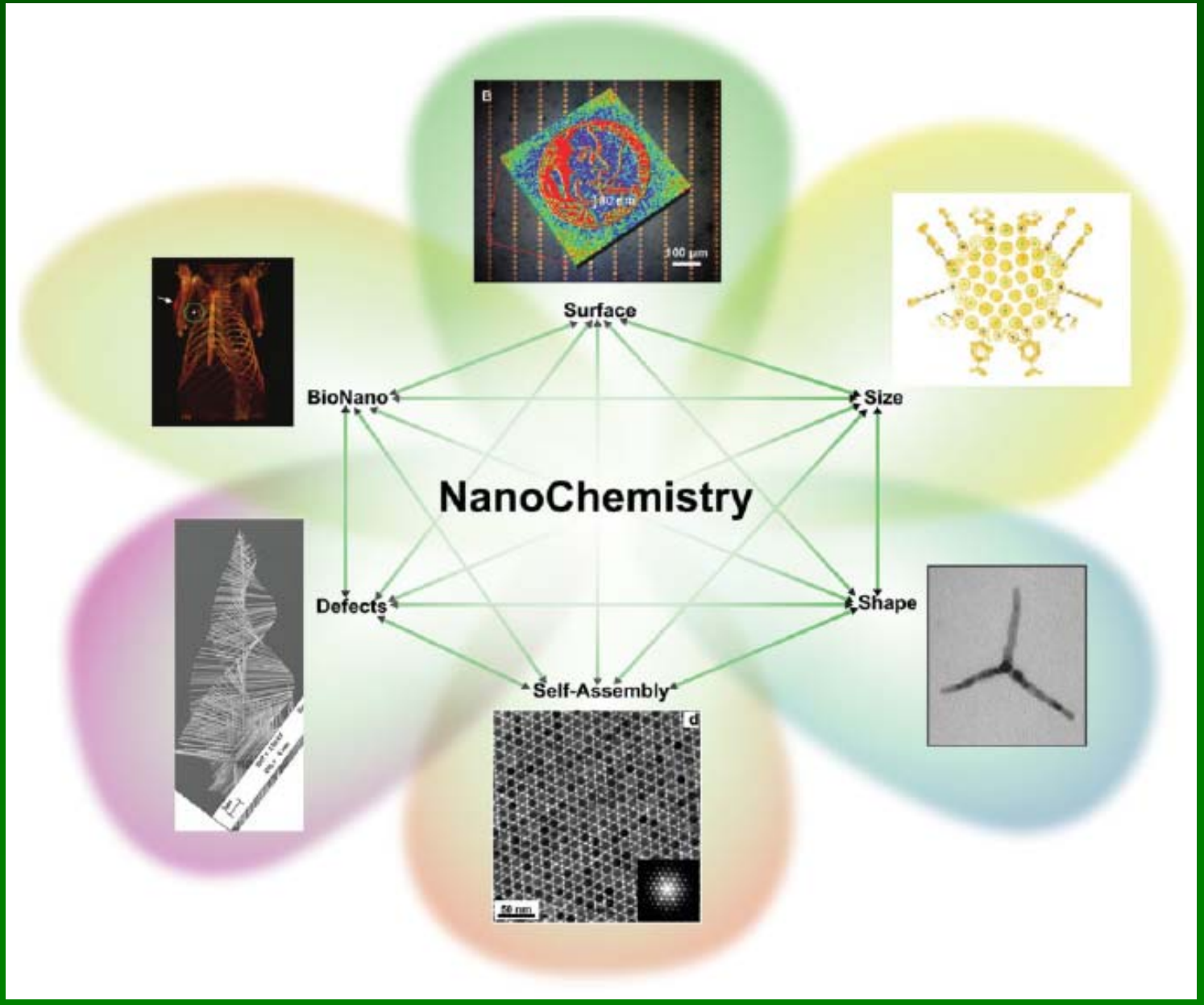
Stirri

n one run

47%

Why NANO?

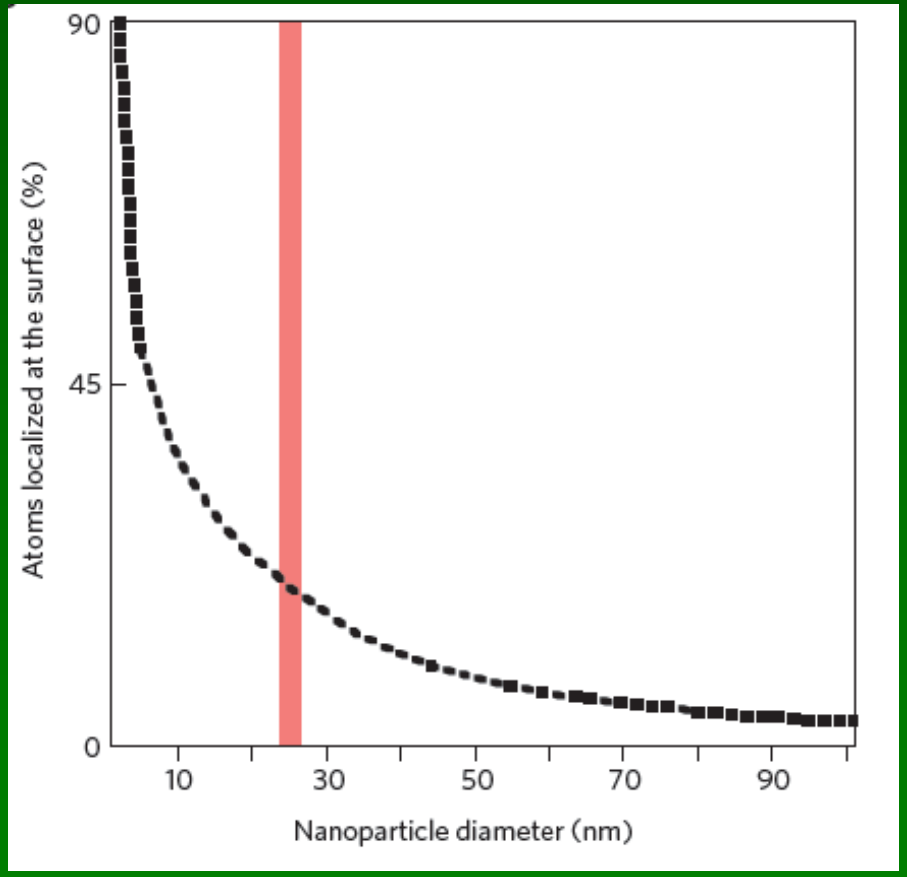


Small 2009, 5, 1240–1244

Appealing Features of Nanoparticles

!!! Nanocrystal has properties that are not shared by non-nanoscale particles with the same chemical composition !!!

- NPs below 20–30 nm in size are characterized by an excess of energy at the surface and are thermodynamically unstable
- Crystallographic changes may occur to stabilize them (*i.e.*, lattice contraction or deformation, the appearance of defects, rearrangements of the surface atoms or changes in morphology)
- These unique nanoscale features affect the interfacial reactivity and the intrinsic properties of nanoparticles

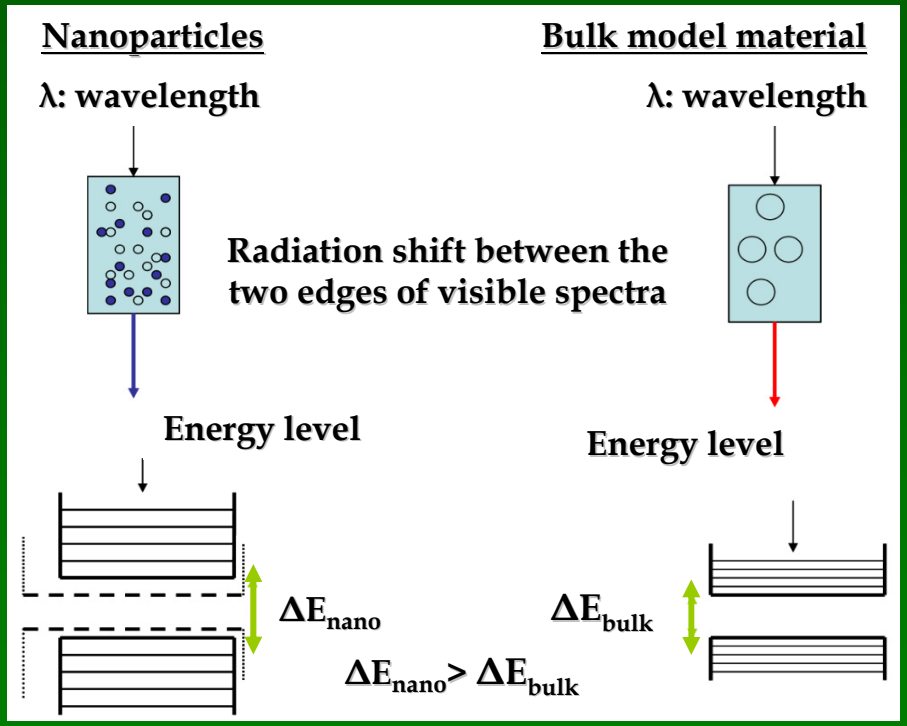


The % of atoms localized at the surface of a nanoparticle as a function of the nanoparticle ∅

Nat. Nano. 2009, 4, 634

Quantum Confinement

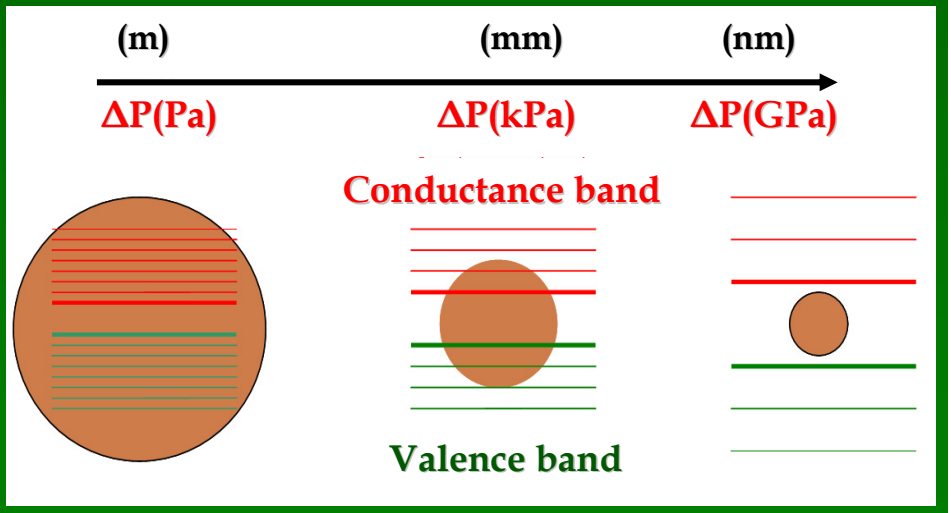
In small nanocrystals, the electronic energy levels are not continuous (as in the bulk) but discrete (finite density of states), because of the confinement of the electronic wavefunction to the physical dimensions of the particles. This phenomenon is called quantum confinement and therefore nanocrystals are also referred to as quantum dots (QDs).



Quantum confinement is responsible for the increase of energy difference between energy states and band gap. A phenomenon tightly related with the optical and electronic properties of the materials.

The Young-Laplace equation:

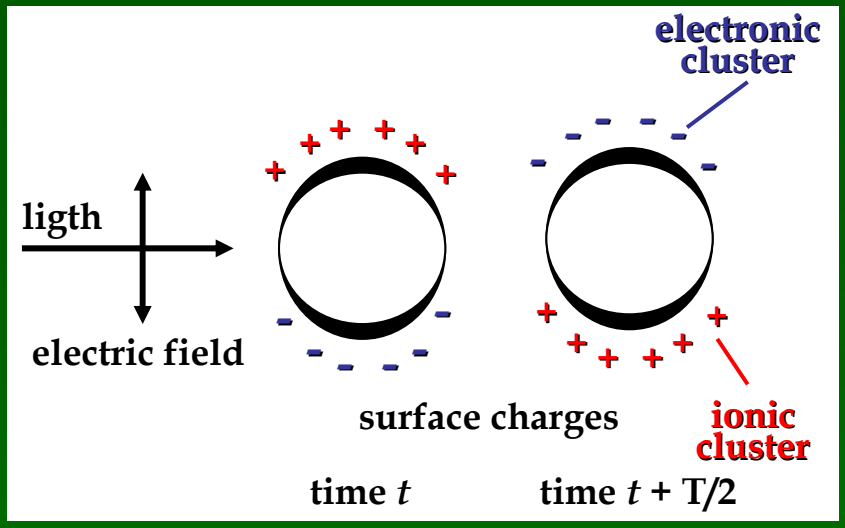
$$\Delta P = \gamma \nabla \hat{n} = 2\gamma H = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

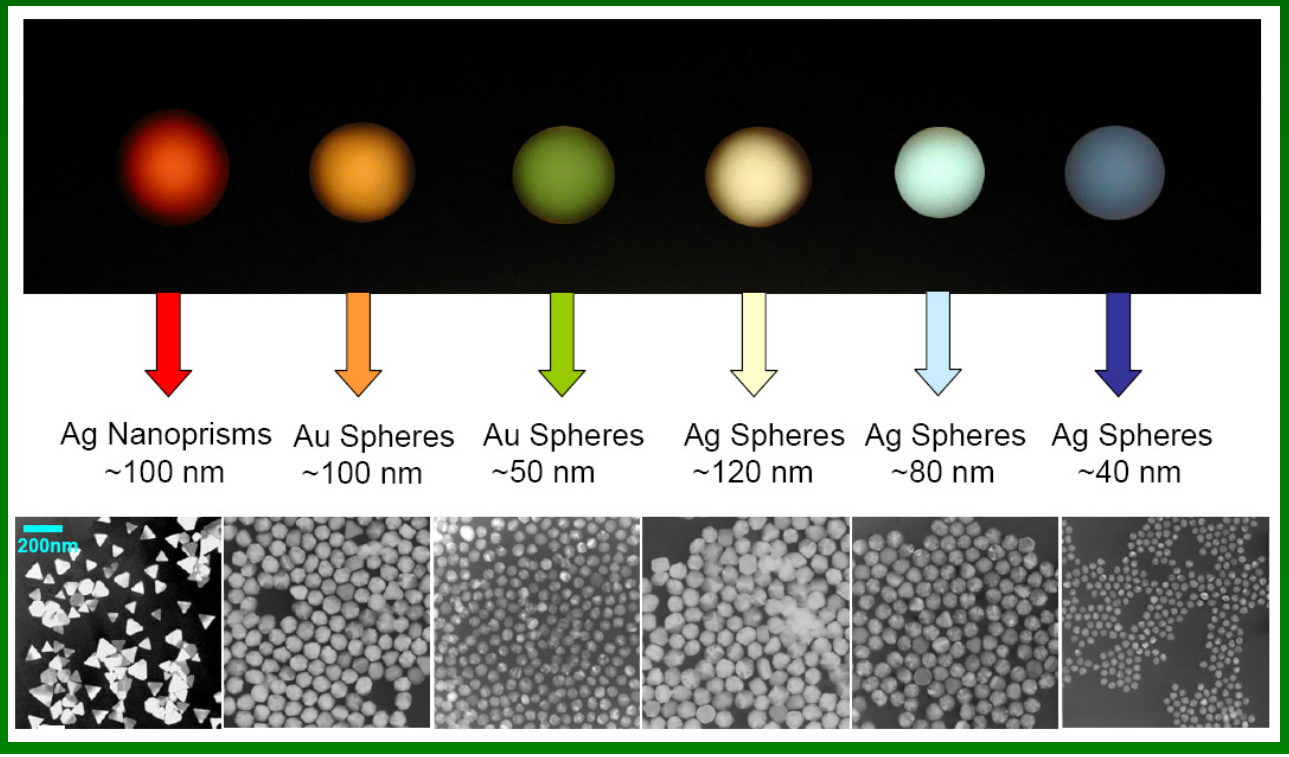


The Young-Laplace law provides evidence on how Pressure drop advances from scale to scale. Size-dependent γ is strongly related to dissolution and phase transformation of NPs

Size-Dependent Optical Properties of Metal Nanoparticles

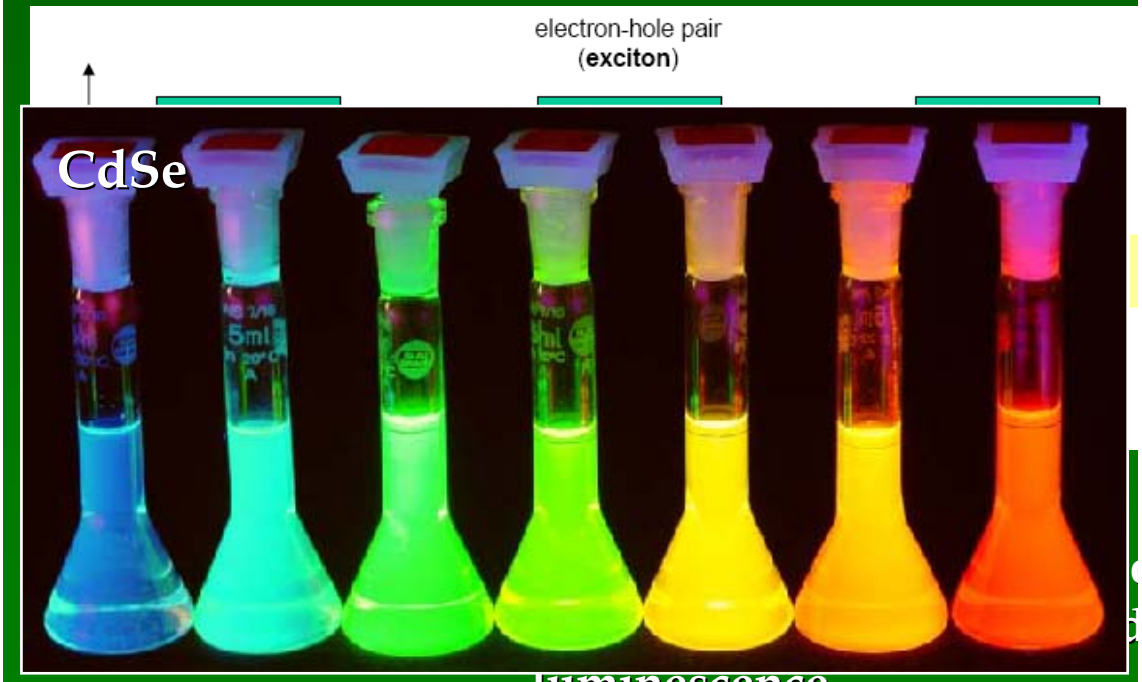
- Quantum confinement occurs when the electrons motion is limited by the size of the NP
- The UV-visible absorption is determined by the surface plasmon resonance (SPR), which is size and shape dependent
- Optical excitation of the SPR gives rise to the surface plasmon absorption

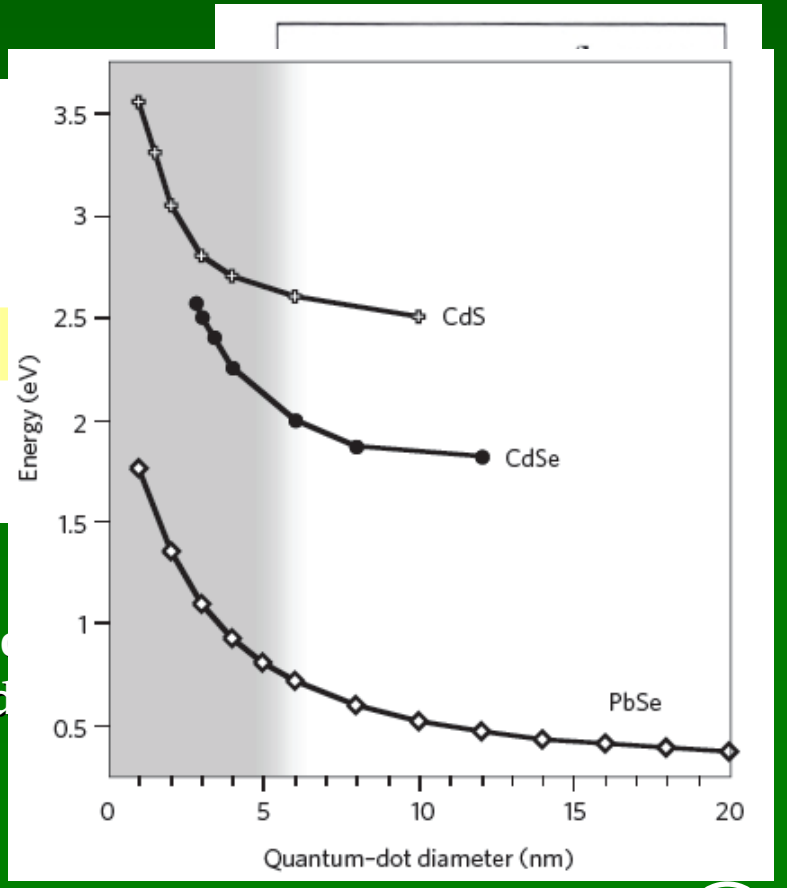




Size-Dependent Optical Properties of Semiconductor NPs (QDs)

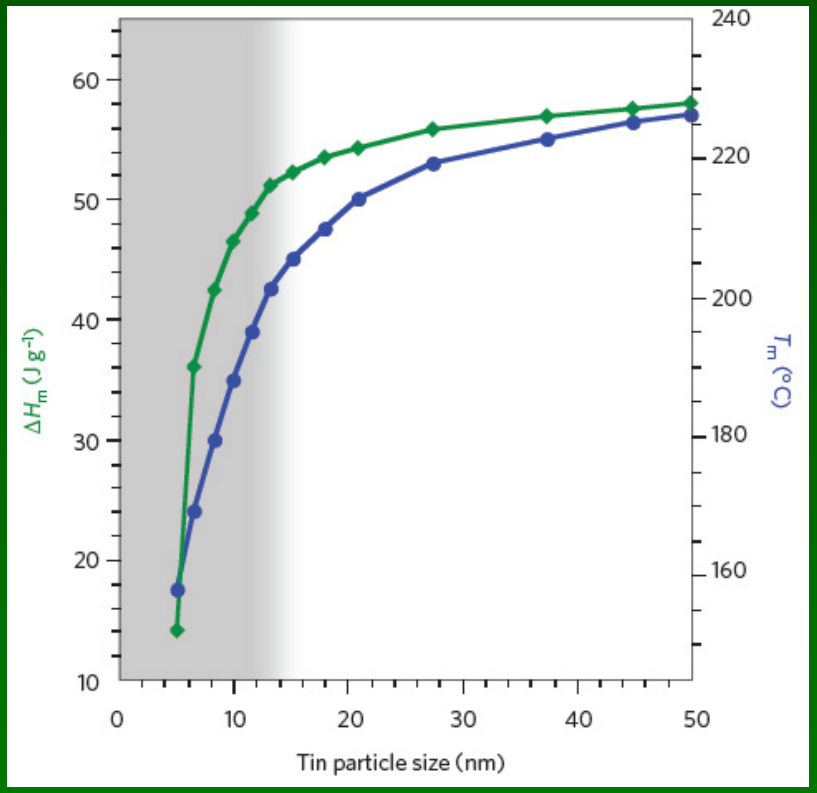
- Quantum confinement occurs when the radius of the NP is comparable to the exciton's Bohr radius
- The UV-visible absorption is determined by the band edge transition, which is strongly size and shape dependent (bandgap energy increases as the size decreases) and hence highly tunable





Phys. Rev. B 1996, 53, 16338

Size-Dependent Thermodynamics

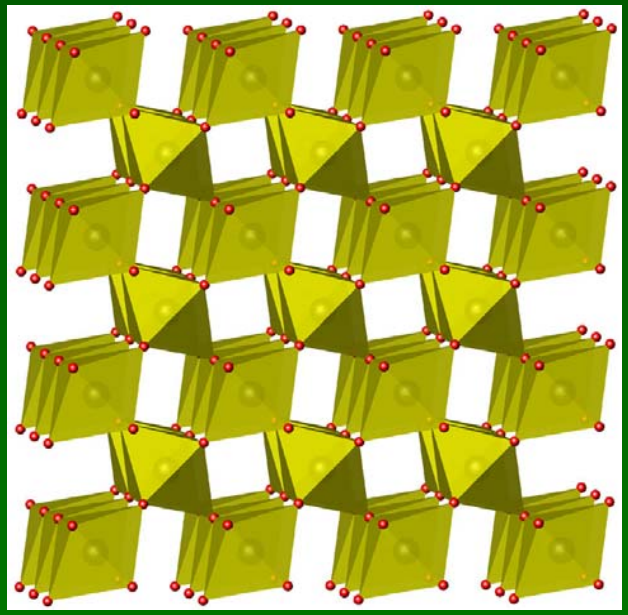


The melting point of Sn nanoparticles can be reduced down to 120°C by decreasing their diameters from 100 nm to 10 nm, with an exponential drop for sizes below 15 nm. Moreover, the normalized heat of fusion, ΔH_m, behaves in a similar way, whereas it is assumed to be constant in classical thermodynamics. This enhancement is attributed to an increasing fraction of lattice defects and irregularities in the crystalline structure of the nanoparticles

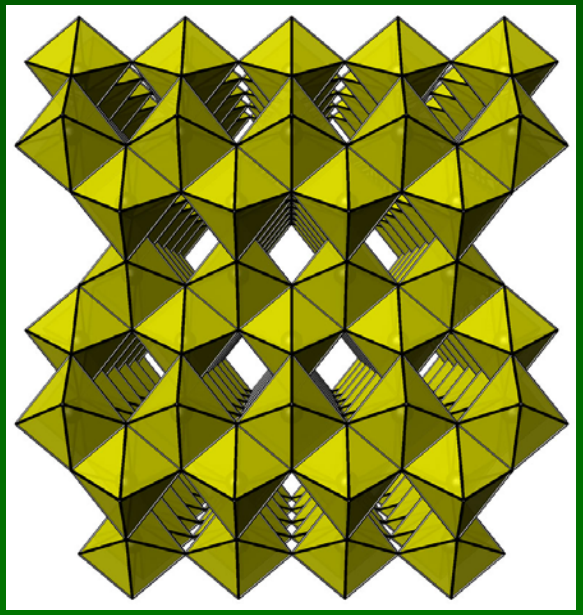
Phys. Rev. B, 2000, 62, 10548; Thermochim. Acta 2007, 463, 32

Size-Dependent Crystallinity

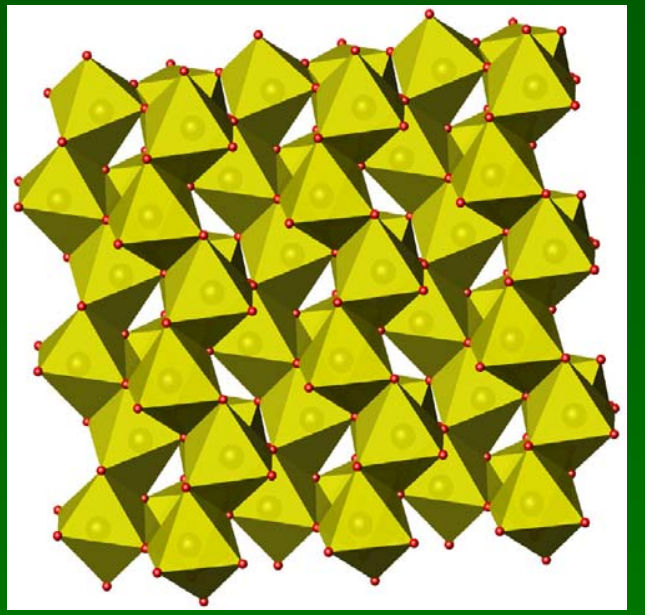
Rutile TiO_2
surface enthalpies 2.2 ± 0.2 J/m^2



Anatase TiO_2
1.0 ± 0.2 J/m^2



Brookite TiO_2
0.4 ± 0.1 J/m^2



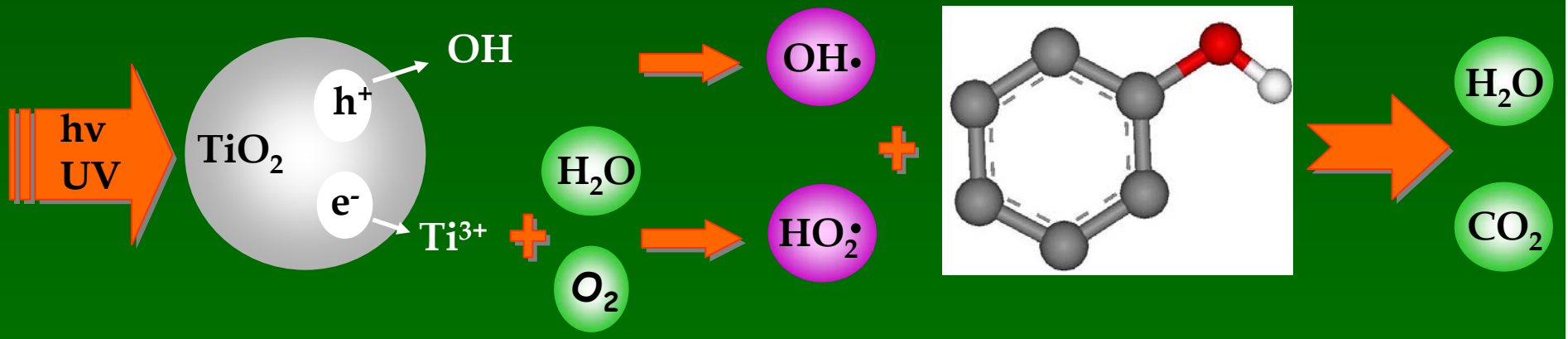
If surface tension γ is increased, the pressure inside particles increases and the phase-transition temperature decreases

- 10 nm ZrO_2 particle monoclinic phase is transformed to the tetragonal one at room temperature, whereas in bulk ZrO_2 it happened at 1100°C
- It has been proposed that the surface enthalpies of the three TiO_2 polymorphs are sufficiently different that crossover in thermodynamic stability can occur under conditions that preclude coarsening, with anatase and/or brookite stable at small size

J. Phys. Chem. B, 2000, 104, 3481 @ Phys. Rev. B, 1995, 51, 6135

Size-Dependent Photocatalytic Activity of TiO_2

TiO_2 NPs favored *anatase* phase, which is more effective in the production of hydroxyl radicals and the subsequent decomposition of organic compounds *cf.* rutile or brookite



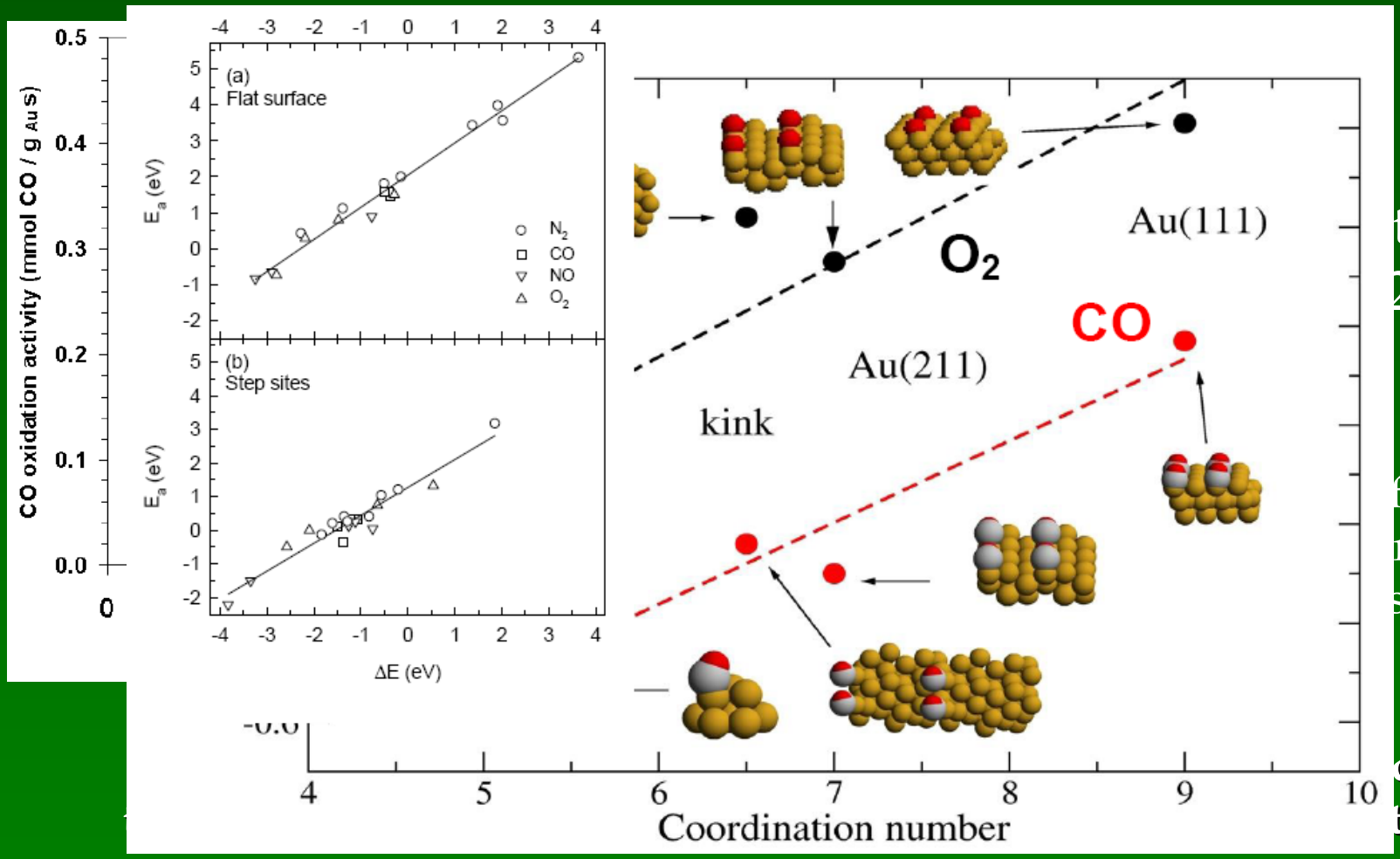
Size-dependent photocatalytic activity does not increase monotonically with decreasing size but rather passes through a maximum below 100 nm.

-. For trichloroethylene ~7 nm
-. For chloroform ~11 nm
-. For phenol~25 nm

These optimum sizes are thought to result from competing effects of the particle size on light absorption and scattering efficiency, chargecarrier dynamics and specific surface area

J. Catalys., 2000, 192, 185 @ Nanostruct. Mater., 1997, 9, 583 @ J. Catalys. 2002, 212, 145

Size-Dependent Catalytic Activity of Gold



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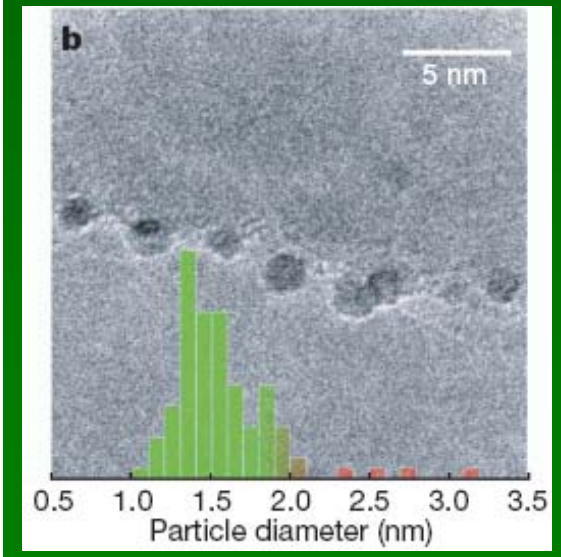
Low coordinated atoms in the nanoparticle are the key to catalytic activity
Oxygen penetration from support to Au NP surface

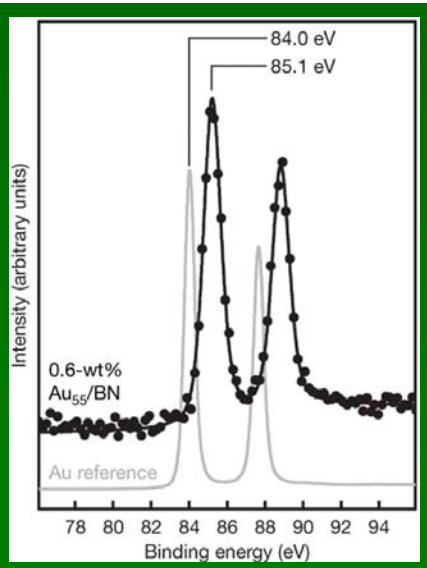
J. Catal. 2004, 223, 232

Size-Dependent Catalytic Activity of Gold

Table 1 | Catalytic results of the partial oxidation of styrene using O_2 alone for supported Au_{55} and comparison catalysts prepared by various techniques.

Catalyst	Prep.*	Exact loading† (wt%)	Mean Au size‡ (nm)	Conversion (%)	Selectivity (%)		
					Benzaldehyde	Styrene epoxide	Acetophenone
0.6-wt% Au_{55}/BN	Au_{55}	0.63	1.6	19.2	82.3	14.0	3.9
0.6-wt% Au_{55}/SiO_2	Au_{55}	0.67	1.5	25.8	82.1	12.0	5.7
0.6-wt% Au_{55}/SiO_2 recycled 1	Au_{55}	0.67	—	21.4	69.2	23.7	7.1
0.6-wt% Au_{55}/SiO_2 recycled 2	Au_{55}	0.67	—	15.9	63.7	27.1	9.2
6-wt% Au/SiO_2	Au_{55}	6.35	3.0	Trace	Trace	—	—
0.6-wt% Au/SiO_2	PVP	—	4.0	Trace	Trace	—	—
1-wt% Au/C	ME	—	17.0	No reaction	—	—	—
5-wt% Au/SiO_2	IW	—	>30	No reaction	—	—	—





Catalytic activity is quenched once the Au NPs ≥ 2 nm

- A shift (of 1.1 eV) in the $4f_{7/2}$-electron apparent binding energy of gold NPs
- An increase in the 3*d*-electron density of the gold atoms and the onset of reactivity with oxygen in air

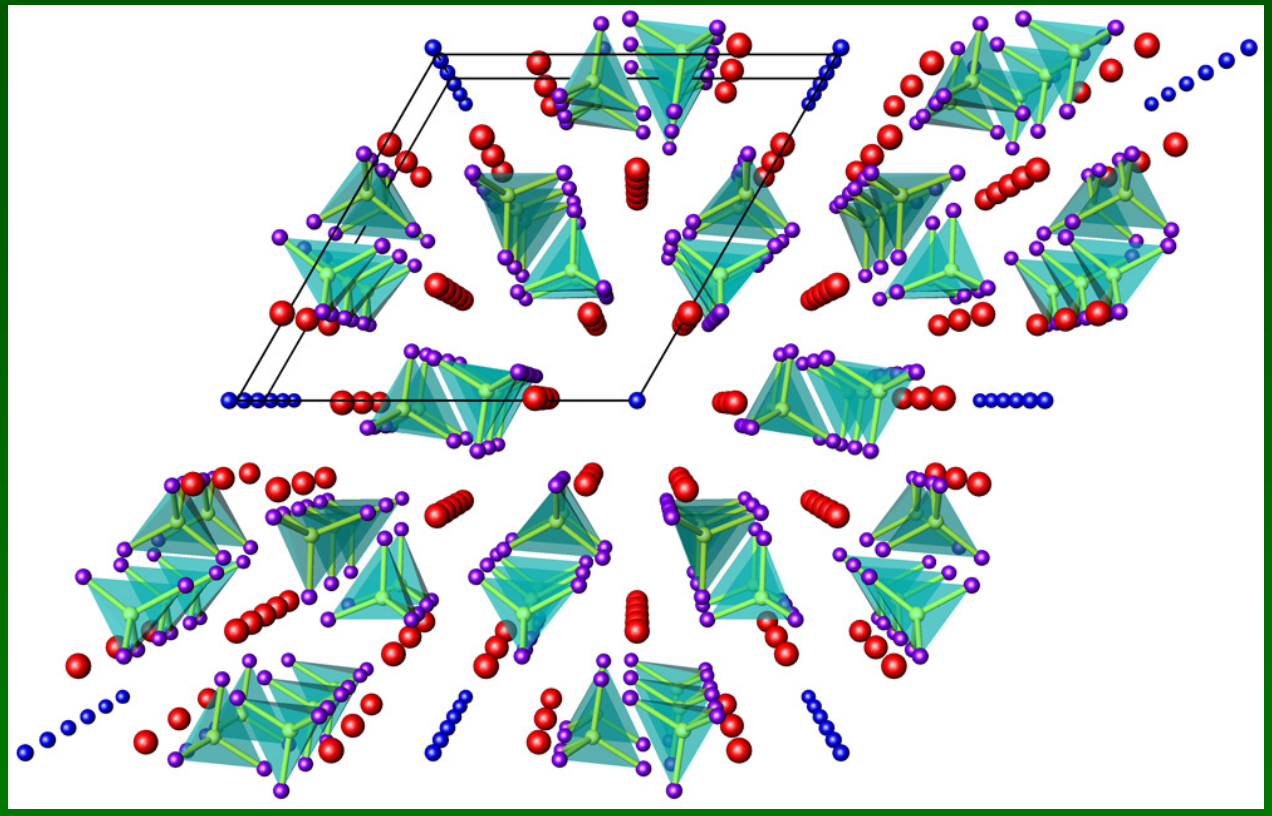
These facts suggest that the size-dependent alteration of electronic structure gives rise to unusual catalytic properties.

Nature 2008, 454, 981 @ J. Catalys. 2006, 240, 222

Doping Nanocrystals

Doping is the intentional introduction of impurities into a material in order to control the properties of the materials

Types of Doping: Cation and Anion

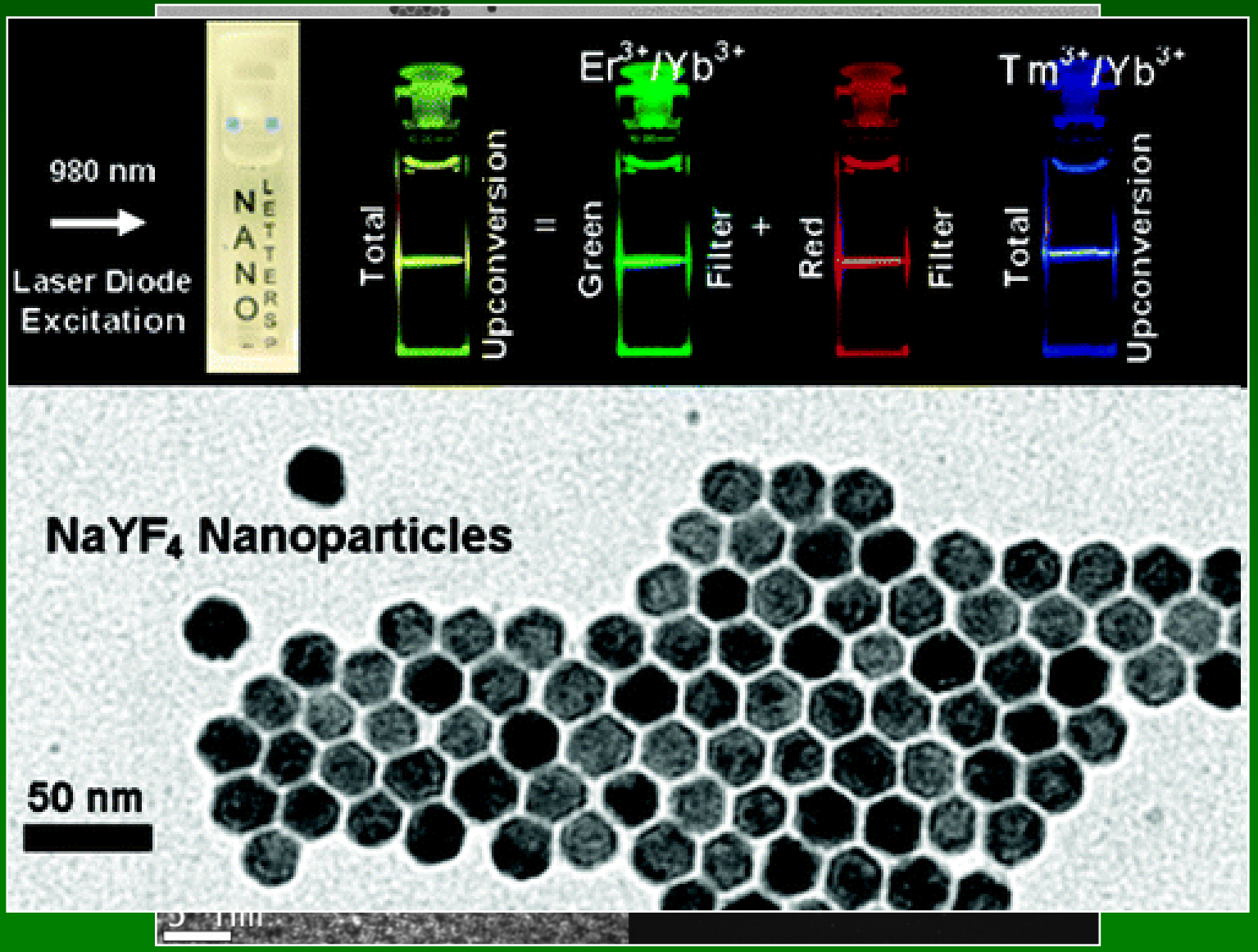


Schematic representation of the hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ structure along the [001] axis

Ca atoms: red, P atoms: yellow; O atoms belonging to PO_4 tetrahedra: violet; O atoms from hydroxyl groups: blue.

Cryst. Growth Des. 2009, 9, 466

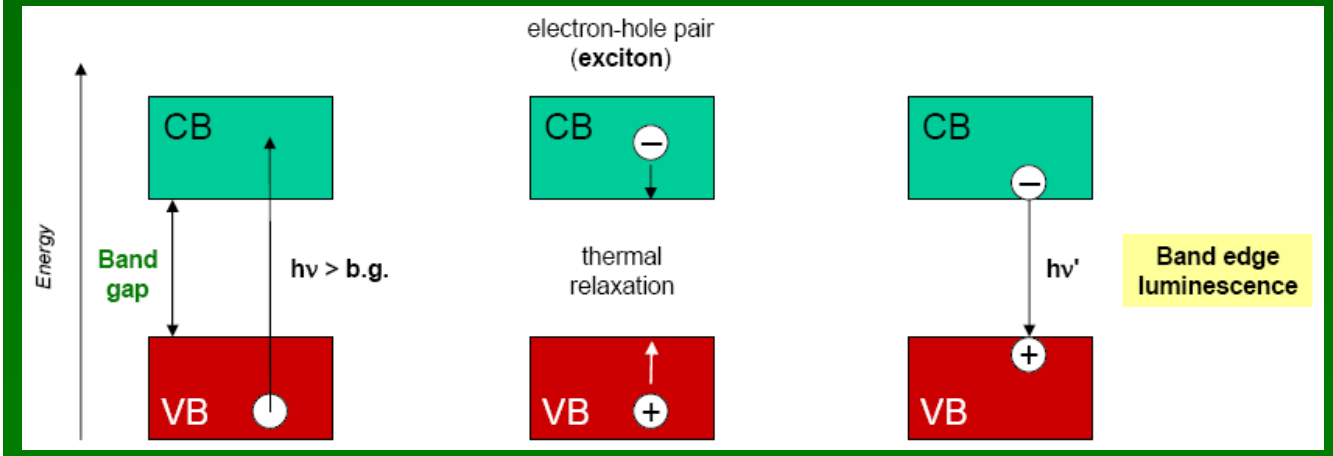
Upconverting NaYF4: Er^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+}

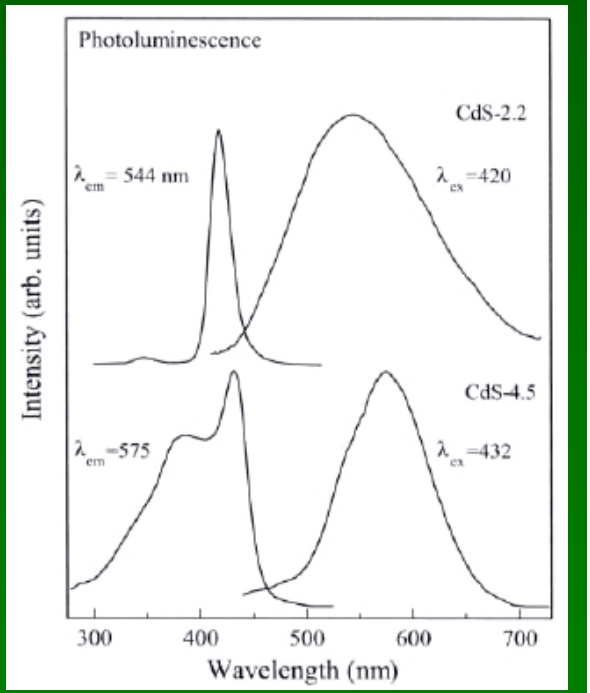


Nano Lett. 2007, 7, 847

Dopped Quantum Dots (QDs)

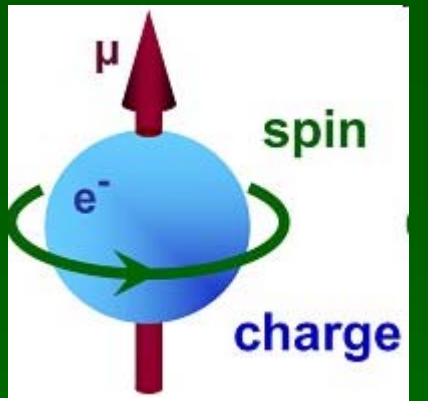
Defect (red-shifted) emission: large stokes shift, broad, controllable by chemical means, *i.e.* doping





Photoluminescence arises from recombination of the CB electron with the VB hole and is called band edge luminescence

Diluted Magnetic Semiconductors

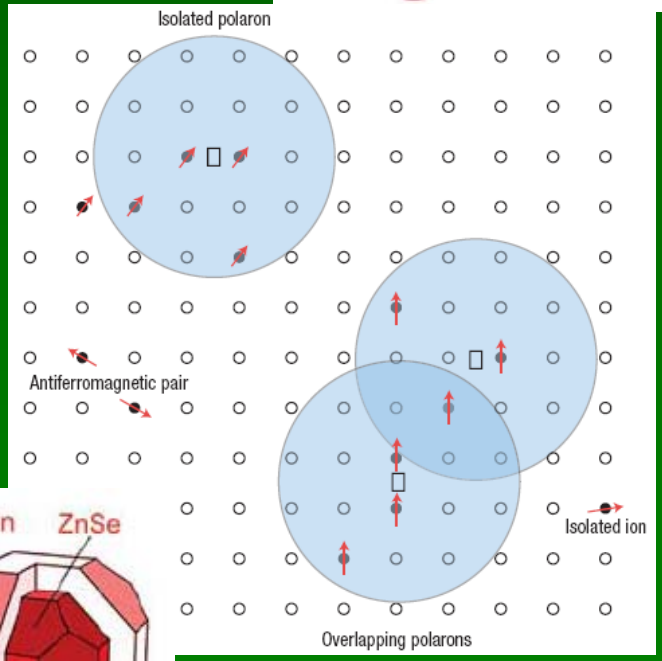


Diluted magnetic semiconductors (DMS):
allow control of quantum spin-state
Traditional semiconductors doped with transition metals
Why "Dilute" ?→ Small doping concentration (a few %)

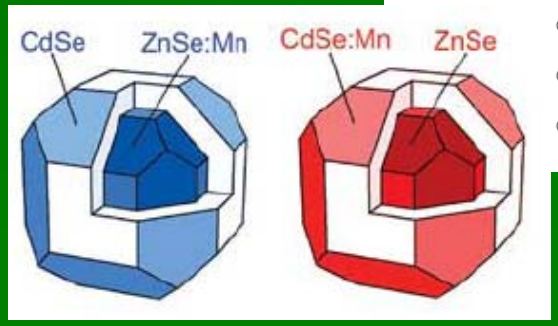
Why "Magnetic" ? → Display ferromagnetisation

Why "Semiconductor" ? → Shows semiconducting properties (not so principle)

Spintronic devices:
change their electrical resistance depending on applied magnetic field direction



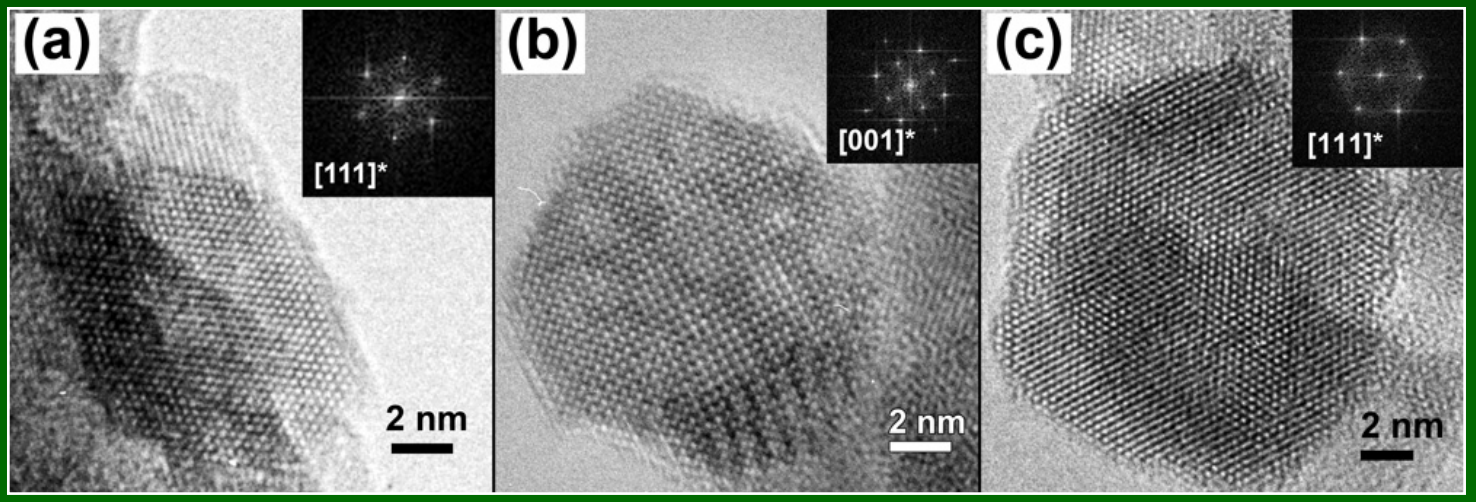
Applications:
- spin-based transistor
- magnetic random access memory

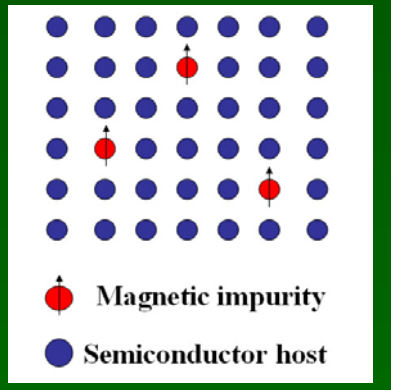


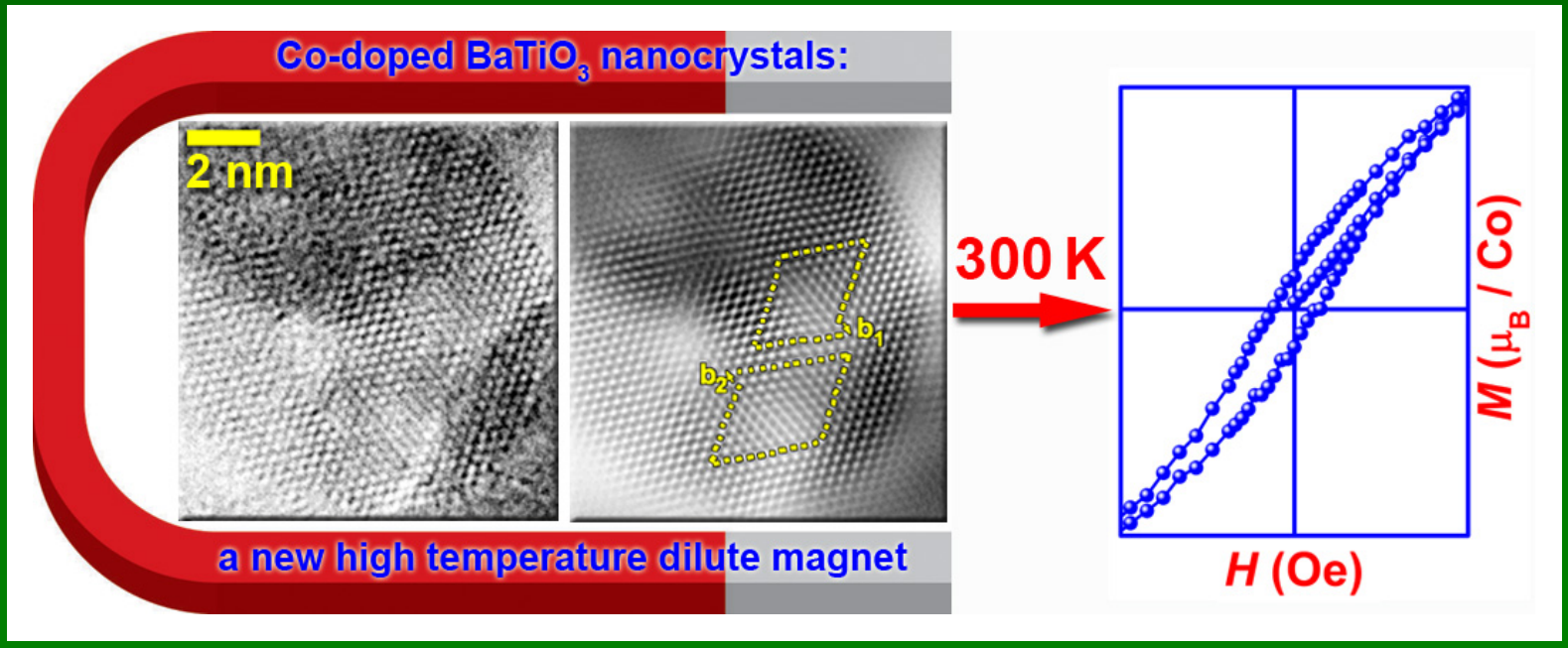
Materials:
Mn-doped ZnSe, CdTe & CdS
Mn-doped GaAs & InSb
Co-doped TiO_2 & ZnO

Appl. Phys. Lett. 1996, 69, 363 @ Nat. Mater. 2005, 4, 173

Co-doped $BaTiO_3$ particles: New DMS







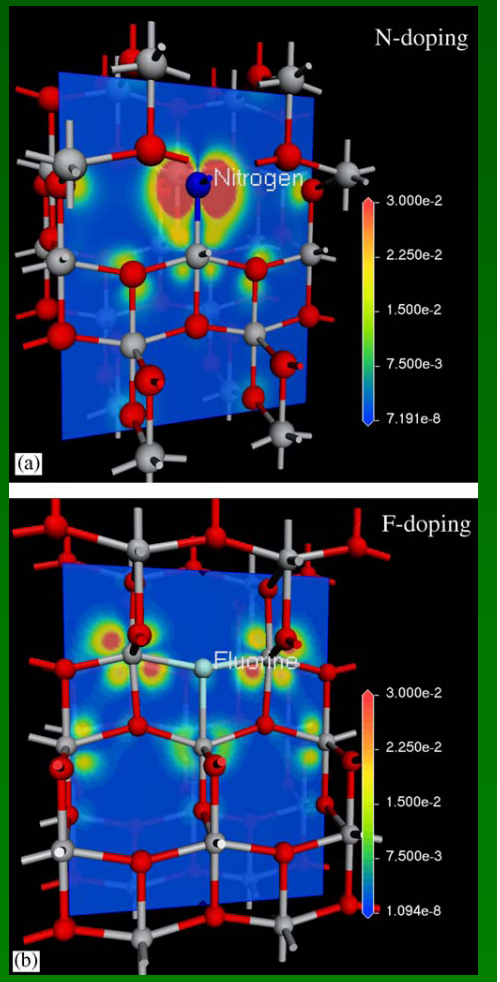
Anion doping of TiO_2 for Photocatalysis

TiO_2 is routinely modified by means of N, F, C, S, *etc.* anion doping to improve photocatalytic activity under visible light

-. **Band gap narrowing:** It was found N 2_p state hybrids with O $2p$ states in anatase TiO_2 doped with nitrogen because their energies are very close, and thus the band gap of N-TiO_2 is narrowed and able to absorb visible light.

-. **Impurity energy level:** It was stated that TiO_2 O sites substituted by N atom form isolated impurity energy levels above the valence band. Irradiation with UV light excites electrons in both the VB and the impurity energy levels, but illumination with visible light only excites electrons in the impurity energy level.

-. **Surface modification:** It was observed the creation of surface O vacancies, the enhancement of surface acidity and the increase of Ti^{3+} cations.



Catal. Today 2009, 147, 1 @ J. Solid State Chem. 2005, 178, 3293

Concluding Remarks & Prospects

"Fighting Cancer with Magnetic Nanoparticles"
developed by the spin-off of the Charité Hospital of the Charité–Universitätsmedizin called MagForce Nanotechnologies AG