

Nanoscience technology and advanced materials  
PHYS 6014

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**Lecture 2**

# Summary of last lecture's basics

What are the differences between matter at the nanoscale and the bulk?

What are the main properties of metal nanoparticles that they change at the nanoscale?

How the nanoparticle size and shape change affects their optical properties?

What are the differences between metal and semiconductor nanoparticles?

Name few applications of semiconductor nanoparticles.

# Outline

**Synthesis of nanoparticles–fundamentals**

**Functionalization of nanoparticles**

**Examples of synthetic protocols to produce nanoparticles of different sizes and shapes**

# Synthesis of nanoparticles–fundamentals

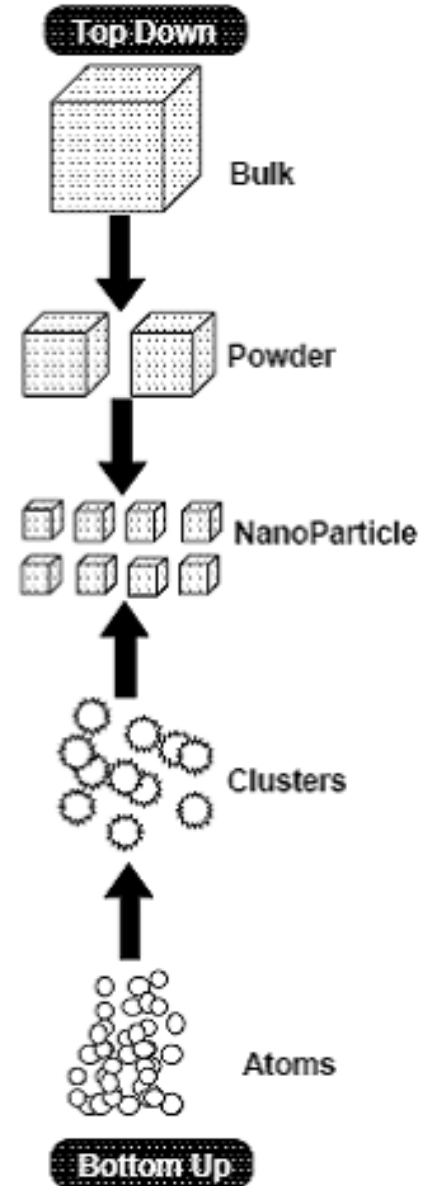
# Synthetic Approach

## Top-down approach

Physical and lithographic principles of microtechnology are used for the construction of nanometre scale objects.

## Bottom-up approach

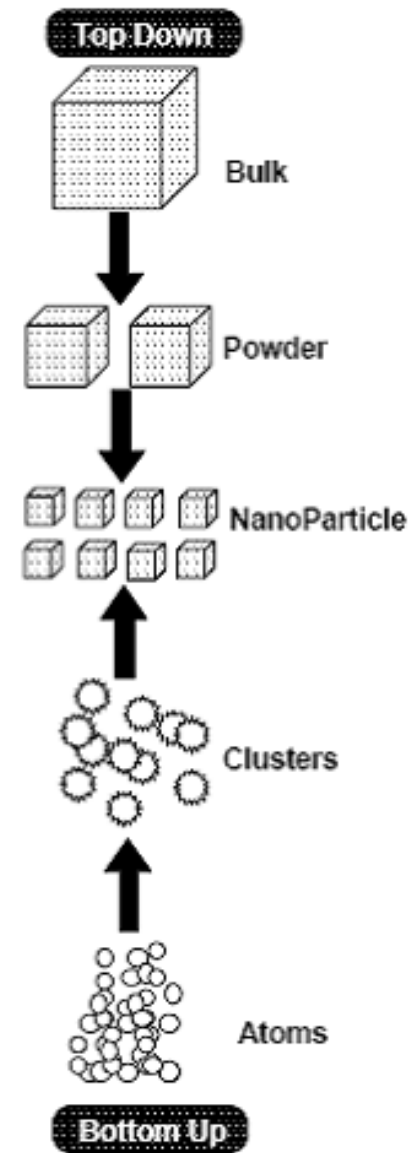
Ionic, atomic, or molecular units are assembled through various processes to form structures in the nanometer range.



Some examples of top down and bottom up approaches

*Top down approach:* Mechanical methods (e.g. Ball milling), thermal fabrication methods ( e.g. annealing), high energy and particle fabrication methods (e.g. laser ablation), chemical fabrication methods (e.g. etching), lithographic methods (e.g. electron beam lithography), natural fabrication methods (e.g. erosion).

*Bottom up approach:* Gas phase methods (e.g. chemical vapour deposition), non-biological liquid phase methods ( e.g. reduction of metal salts), bottom-up lithographic methods (e.g. STM writing), biological and inorganic methods (e.g. formation of DNA of sugars, phosphate and nucleosides).



bottom-up approach is driven mainly by  
the reduction of Gibbs free energy

$$\Delta G = \Delta H - T\Delta S$$



nanostructures and nanomaterials  
produced are in a state closer to a  
thermodynamic equilibrium state

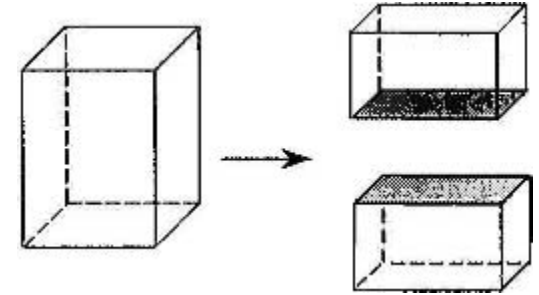
To have  $\Delta G$  as negative as possible,  $\Delta H$  should get small and  $\Delta S$  large

$\Delta H$  is related to the surface energy and  $\Delta S$  is related to the objects and  
the space that they occupy

# Surface energy

Surface energy is the energy required to create a unit area of surface

$$\gamma = \left( \frac{\partial G}{\partial A} \right)_{n,T,P}$$



A restoring force is needed to pull the surface atoms back to their original positions



$$\gamma = \frac{1}{2} N_b \varepsilon \rho_a$$

$\gamma \equiv$  surface energy

$\varepsilon \equiv$  bond strength

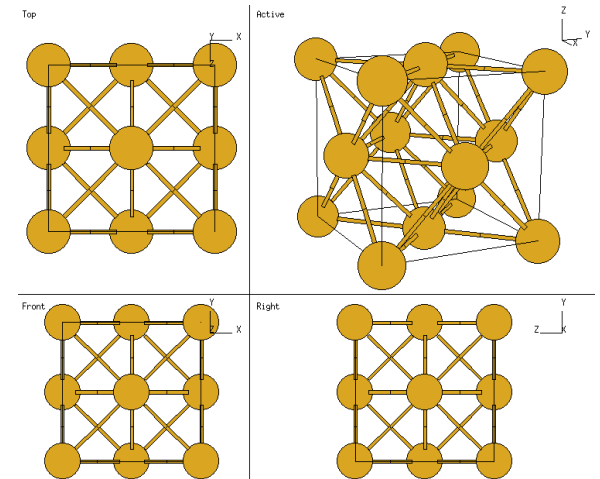
$N_b \equiv$  number of broken bonds

$\rho_a \equiv$  density of surface atoms

For an fcc structure with a lattice constant of  $a$ , the crystallographic face with the lowest surface energy is the 111.






$$\gamma \{111\}$$

$$\gamma_{\{111\}} = 2\sqrt{3} \frac{\varepsilon}{a^2}$$





# 'Magic' numbers

Full-shell "magic number" clusters					
Number of shells	1	2	3	4	5
Number of atoms in cluster	13	55	147	309	561
Percentage of surface atoms	92	76	63	52	45

$$\Delta G = \Delta H - T\Delta S$$

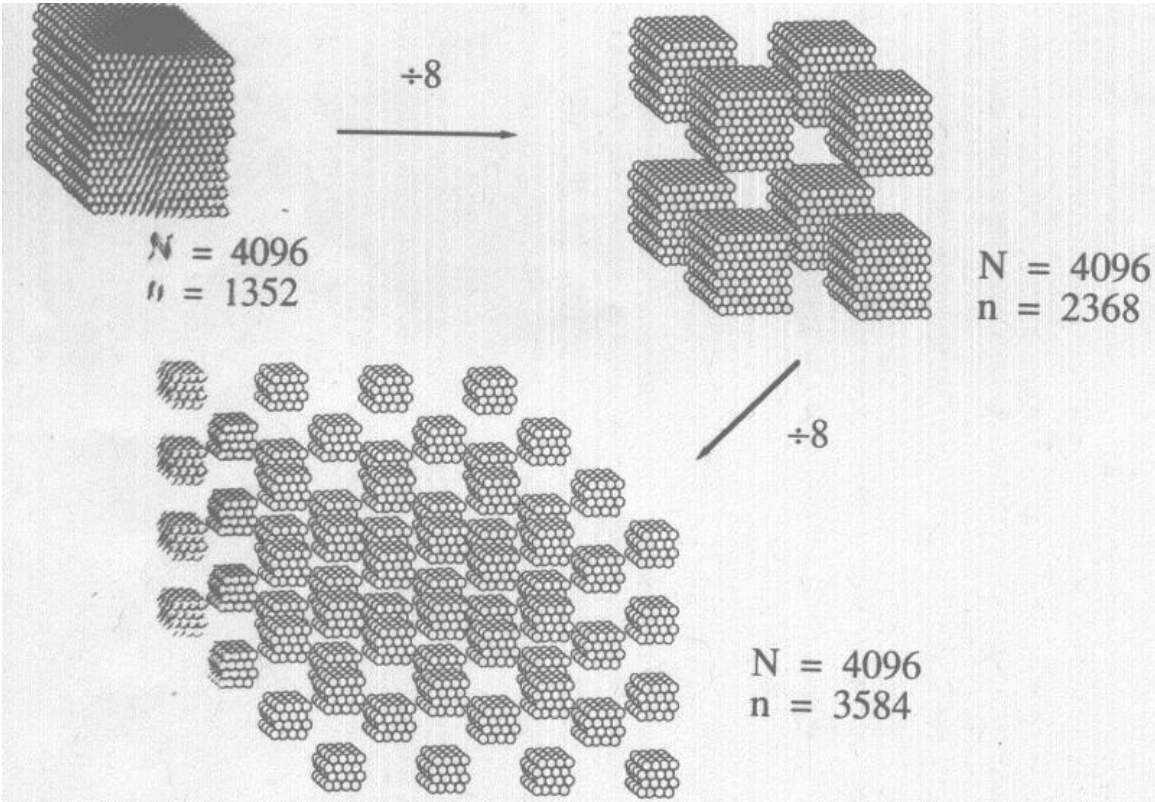
the surface energy can be reduced through:

- ⊙ surface restructuring through combining surface dangling bonds into strained new chemical bonds
- ⊙ surface relaxation, the surface atoms or ions shift inwardly which occur more readily in liquid phase than in solid surface due to rigid structure in solids
- ⊙ surface adsorption through chemical or physical adsorption of terminal chemical species onto the surface by forming chemical bonds or weak attraction forces such as electrostatic or van der Waals forces
- ⊙ composition segregation or impurity enrichment on the surface through solid-state diffusion

# Challenges to the synthesis of colloidal nanoparticles

Retain stability in solution of the as prepared nanoparticles (compensate the huge surface energy so that particles do not aggregate).

Identify ways to synthesize particles with narrow size distribution and good crystallinity.

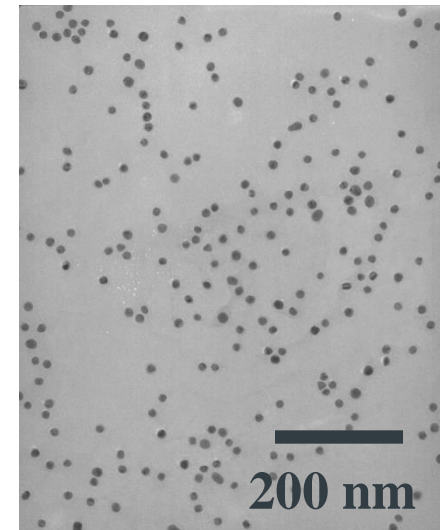


# A simple example of colloidal nanocrystal synthesis

**Aqueous Solution  
 $\text{NaAuCl}_4$**












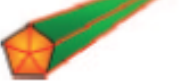




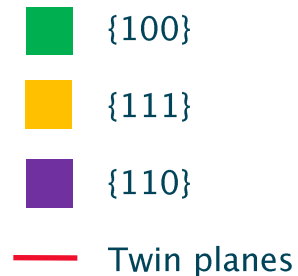
**Aqueous Solution  
Trisodium  
Citrate**



<i>Precursors</i>	<i>Formula</i>
Metal anode	Pd, Ni, Co
Palladium chloride	PdCl <sub>2</sub>
Hydrogen hexachloroplatinate IV	H <sub>2</sub> PtCl <sub>6</sub>
Potassium tetrachloroplatinate II	K <sub>2</sub> PtCl <sub>4</sub>
Silver nitrate	AgNO <sub>3</sub>
Silver tetraoxylchlorate	AgClO <sub>4</sub>
Chloroauric acid	HAuCl <sub>4</sub>
Rhodium chloride	RhCl <sub>3</sub>
<i>Reduction Reagents</i>	
Hydrogen	H <sub>2</sub>
Sodium citrate	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>
Hydroxylamine hydrochloride	NH <sub>4</sub> OH + HCl
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>
Carbon monoxide	CO
Phosphorus in ether	P
Methanol	CH <sub>3</sub> OH
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>
Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>
Sodium hydroxide	NaOH
Formaldehyde	HCHO
Sodium tetrahydroborate	NaBH <sub>4</sub>
Ammonium ions	NH <sub>4</sub> <sup>-</sup>

## Different nanocrystal morphologies

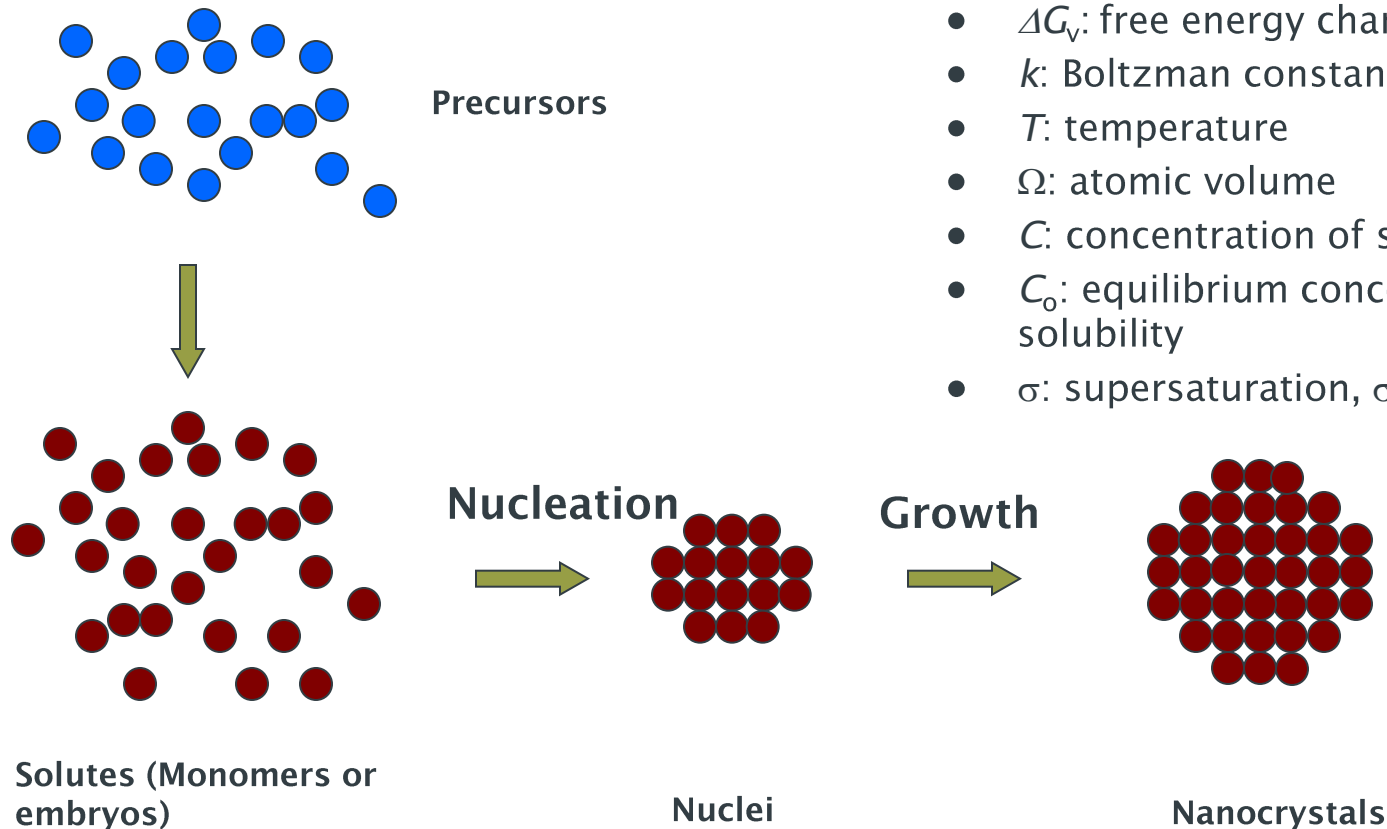
Structures	Shapes	Schematic drawings	Metals
single-crystal	perfect/truncated cube <sup>[4]</sup>		Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe
	perfect/truncated octahedron <sup>[4]</sup>		Pd, Ag, Au, Pt
	perfect/truncated tetrahedron <sup>[4]</sup>		Ag, Au, Pt, Rh
	rectangular bar		Pd, Ag, Pt
	octagonal rod		Pd, Au, Fe, Co, Ni
	rectangular or octagonal wire		Pb, In, Sn, Sb, Fe, Co
singly twinned	right bipyramid		Pd, Ag
	beam		Ag
multiply twinned	decahedron <sup>[4]</sup>		Pd, Ag, Au
	icosahedron <sup>[4]</sup>		Pd, Au
	five-fold twinned pentagonal rod		Pd, Ag, Au, Cu
	five-fold twinned pentagonal wire		Ag, Au, Cu
	triangular/hexagonal plate		Pd, Ag, Au, Cu, Pb, Bi, Co, Ni
	disc		Sn, Co



# Nanocrystal Synthesis: Nucleation and Growth

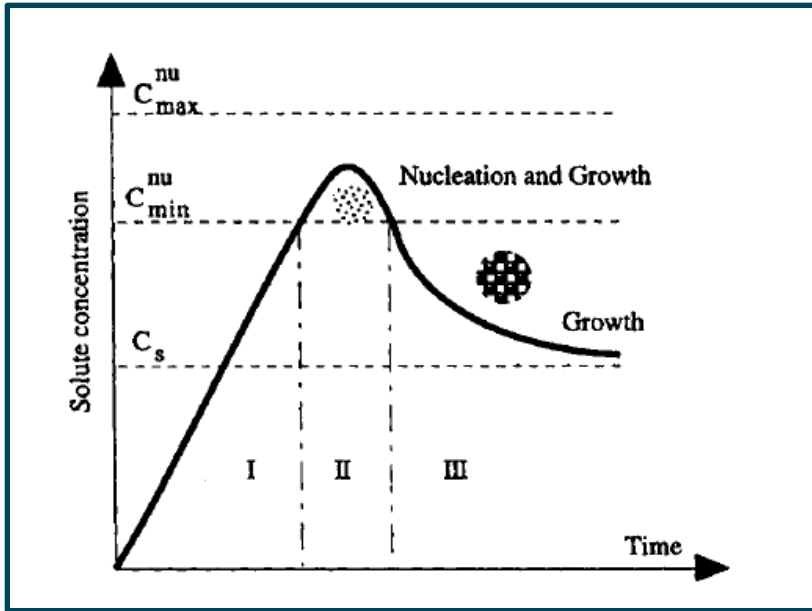
$$\Delta G_v = -\frac{kT}{\Omega} \ln(C/C_o) = -\frac{kT}{\Omega} \ln(1 + \sigma)$$

- $\Delta G_v$ : free energy change per volume
- $k$ : Boltzmann constant
- $T$ : temperature
- $\Omega$ : atomic volume
- $C$ : concentration of solute
- $C_o$ : equilibrium concentration or solubility
- $\sigma$ : supersaturation,  $\sigma = (C - C_o) / C_o$



Free energy decreases

# Nucleation and growth-schematically



I - the concentration of atoms steadily increases with time as the precursor is decomposed

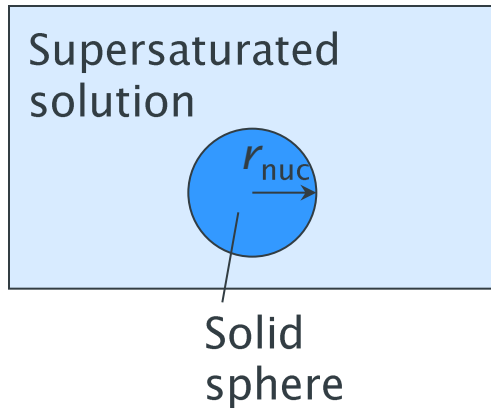
II - the concentration of atoms reaches a point of supersaturation, the atoms start to aggregate into small clusters (i.e., nuclei) via self- (or homogeneous) nucleation

These nuclei then grow in an accelerated manner and the concentration of atoms in solution drops

III - If the concentration of atoms drops quickly below the level of minimum supersaturation, no additional nucleation events will occur. With a continuous supply of atoms via ongoing precursor decomposition, the nuclei will grow into nanocrystals of increasingly larger size until an equilibrium state is reached between the atoms on the surface of the nanocrystal and the atoms in the solution



# Nucleation Process



$\Delta G_v$  ——— Free energy change per volume

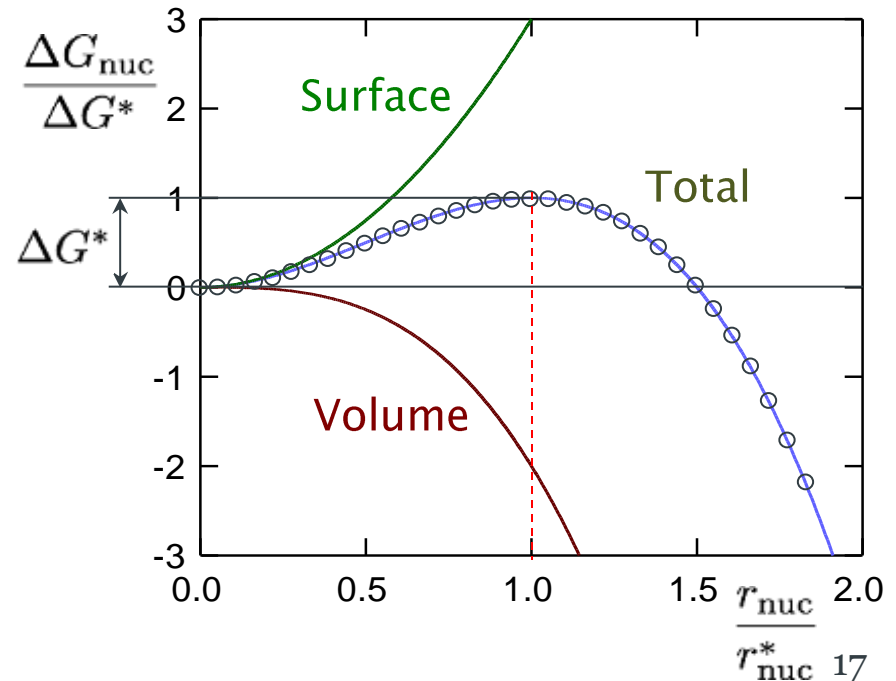
Free energy change for forming solid particle with radius  $r_{nuc}$ :

$$\Delta G_{nuc} = \underbrace{\Delta G_v \frac{4}{3} \pi r_{nuc}^3}_{\text{Volume}} + \underbrace{\gamma 4\pi r_{nuc}^2}_{\text{Surface}}$$

$$\frac{\partial \Delta G_{nuc}}{\partial r} \Big|_{r=r^*} = 0 = \Delta G_v 4\pi r^{*2} + 8\gamma\pi r^*$$

$$r^* = -\frac{2\gamma}{\Delta G_v}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2} \quad \text{critical free energy, nucleation barrier}$$



Nucleation rate: 
$$J = A \exp\left(\frac{-\Delta G^*}{kT}\right)$$
$$= \left(\frac{C kT}{3\pi\lambda^3\eta}\right) \exp\left(\frac{-\Delta G^*}{kT}\right)$$

- $\lambda$ : the diameter of the growth species (monomers)
- $\eta$ : viscosity of the solution
- $C$ : initial concentration

Fast nucleation is favored by:

High initial concentration (high supersaturation):  $C \uparrow$

Low viscosity:  $\eta \downarrow$

Low critical energy barrier  $\Delta G^* \downarrow$

High T (usually true, but not always because higher T leads to lower supersaturation )

Once a cluster has grown past a critical size, structural fluctuations become so energetically costly that the cluster becomes locked into a well-defined structure.

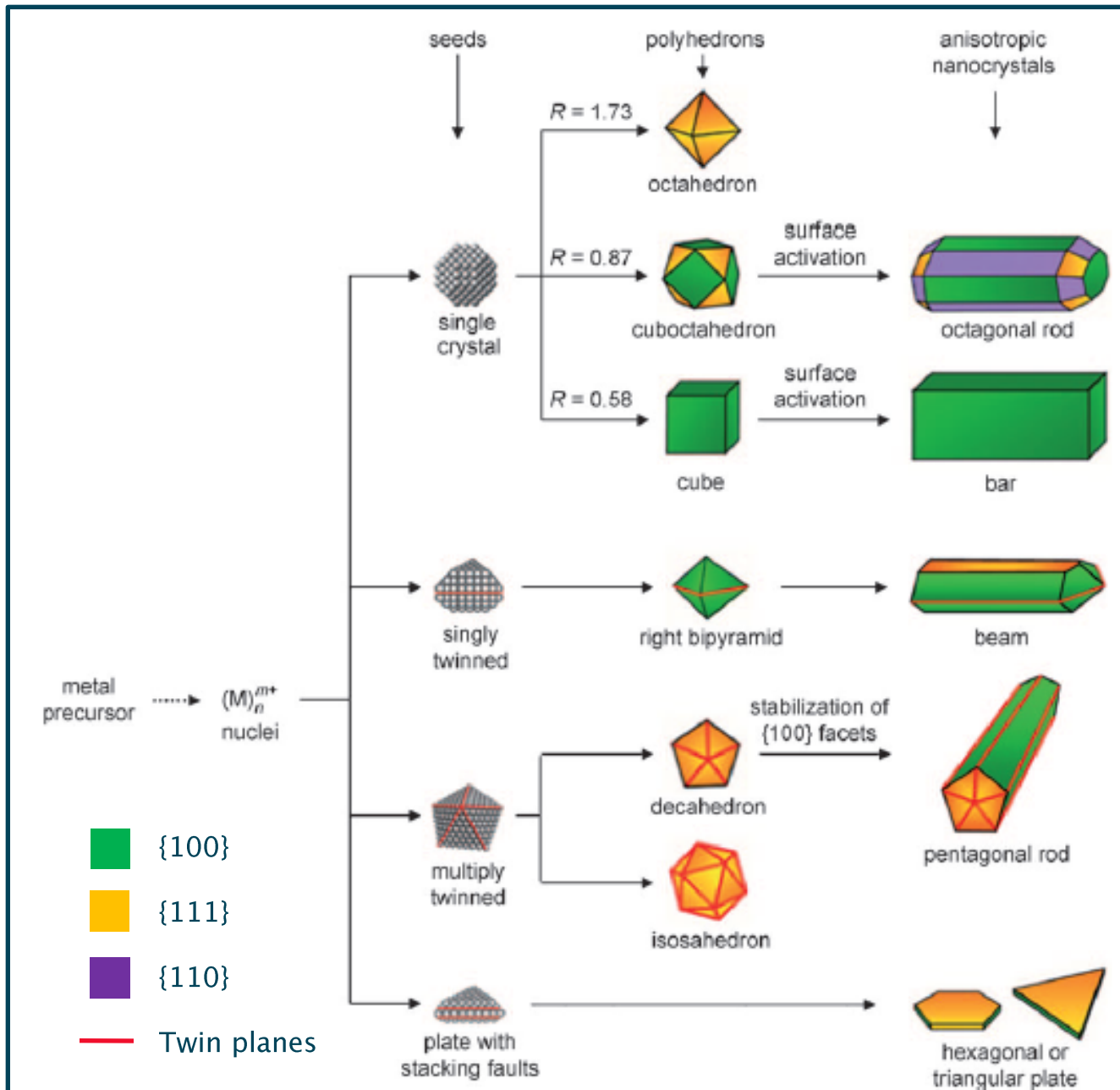
This critical point marks the birth of a seed

Structure of the seeds:

- ⊙ single-crystal
- ⊙ singly twinned crystal
- ⊙ multiply twinned crystal

# Evolution from nuclei to nanoparticles

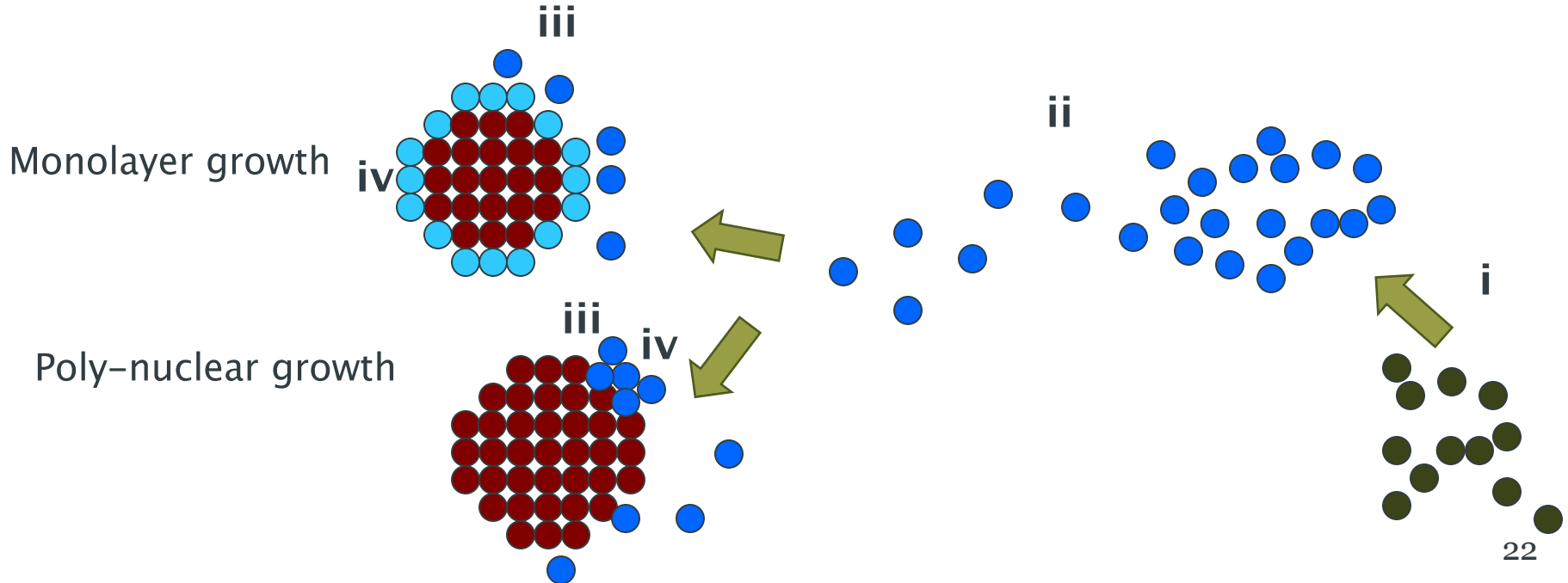
R is the ratio between the growth rates along the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions



# Growth rate of nanocrystals

- (i) generation of growth species
- (ii) diffusion of the growth species from bulk to the growth surface
- (iii) adsorption of the growth species onto the growth surface
- (iv) surface growth through irreversible incorporation of growth species onto the solid surface

Diffusion control growth–Surface control growth



What is the top-down and what is the bottom-up approach?

What drives the bottom-up chemical synthesis of inorganic colloidal nanocrystals?  
Suggest ways that the surface energy can be reduced.

For a fcc structure, which plane is more favorable energetically?

What are magic numbers?

Describe the nucleation and growth process. Calculate the critical free energy for the nucleation process?

Describe the nucleation and growth rate.

**Explain the top-down and the bottom up approach. What are their differences?  
Give two examples of production methods that involve these approaches.**

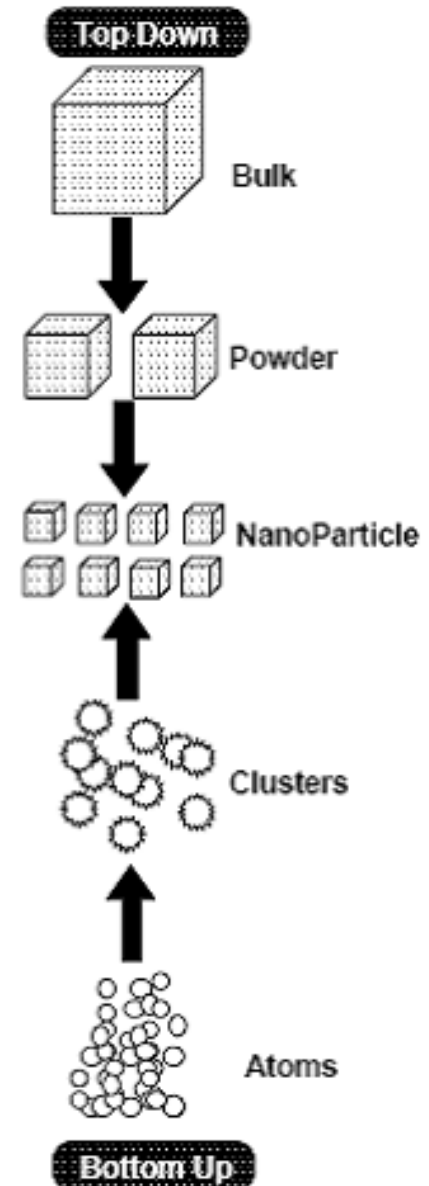
## Answer:

*Top down approach:* Physical and lithographic principles of microtechnology are used for the construction of nanometre scale objects from the bulk.

1. Mechanical methods (e.g. Ball milling–Production of nanoparticles by mechanical attrition to produce grain size particles. High energy ball milling uses steel balls to transfer kinetic energy by impact to the sample–Usually involved in the formation of ferroelectric barium titanate nanoparticles).
2. Lithographic methods (e.g. electron beam lithography–usually employed for the formation of nanoparticle patterns on surfaces. For example dimers of plasmonic nanorod antennas).

*Bottom up approach:* Ionic, atomic, or molecular units are assembled through various processes to form structures in the nanometer range.

1. Gas phase methods (e.g. chemical vapour deposition–Involves the formation of nanomaterials from the gas phase, usually at elevated temperatures, onto a solid substrate catalyst–for example the formation of carbon nanotubes).
2. Chemical liquid phase methods ( e.g. reduction of metal salts–for example the reduction of gold salt to gold nanoparticles using sodium borohydride),





# Surface stabilization

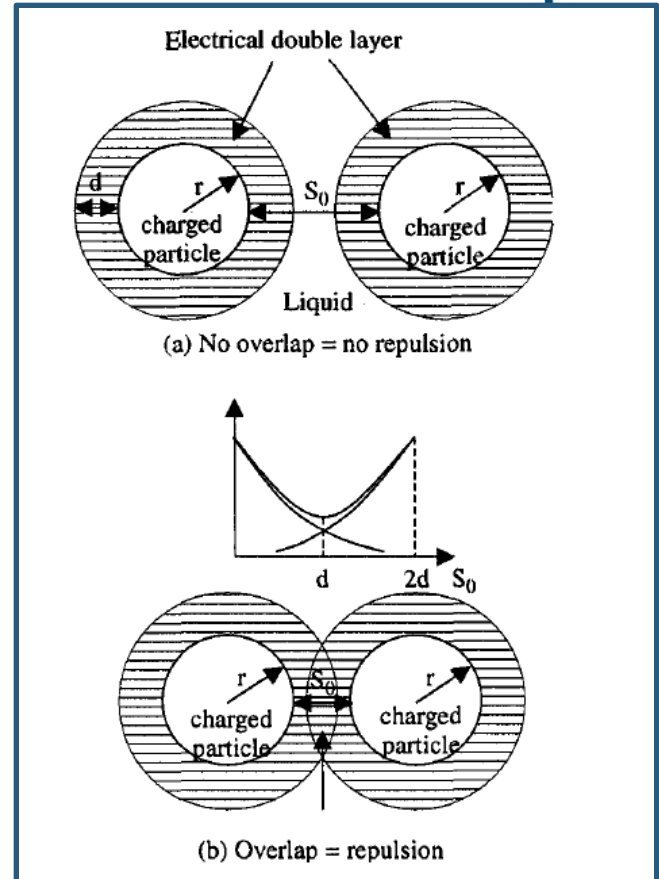
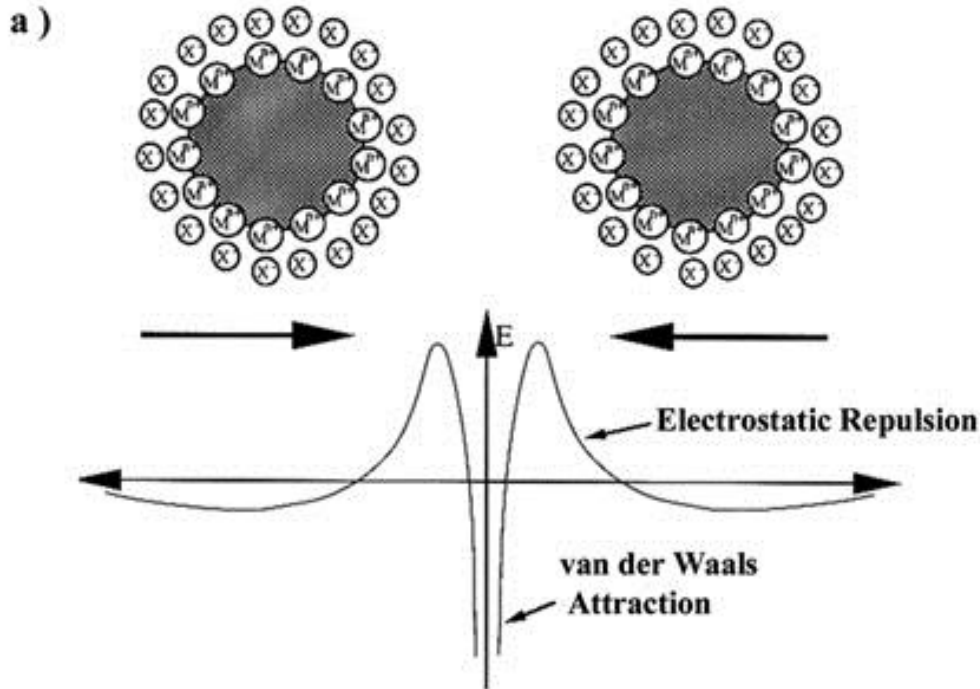
# Types of colloidal nanoparticle's stabilization

**Electrostatic stabilization**

**Steric stabilization**

**Electrosteric stabilization**

# Electrostatic Stabilization



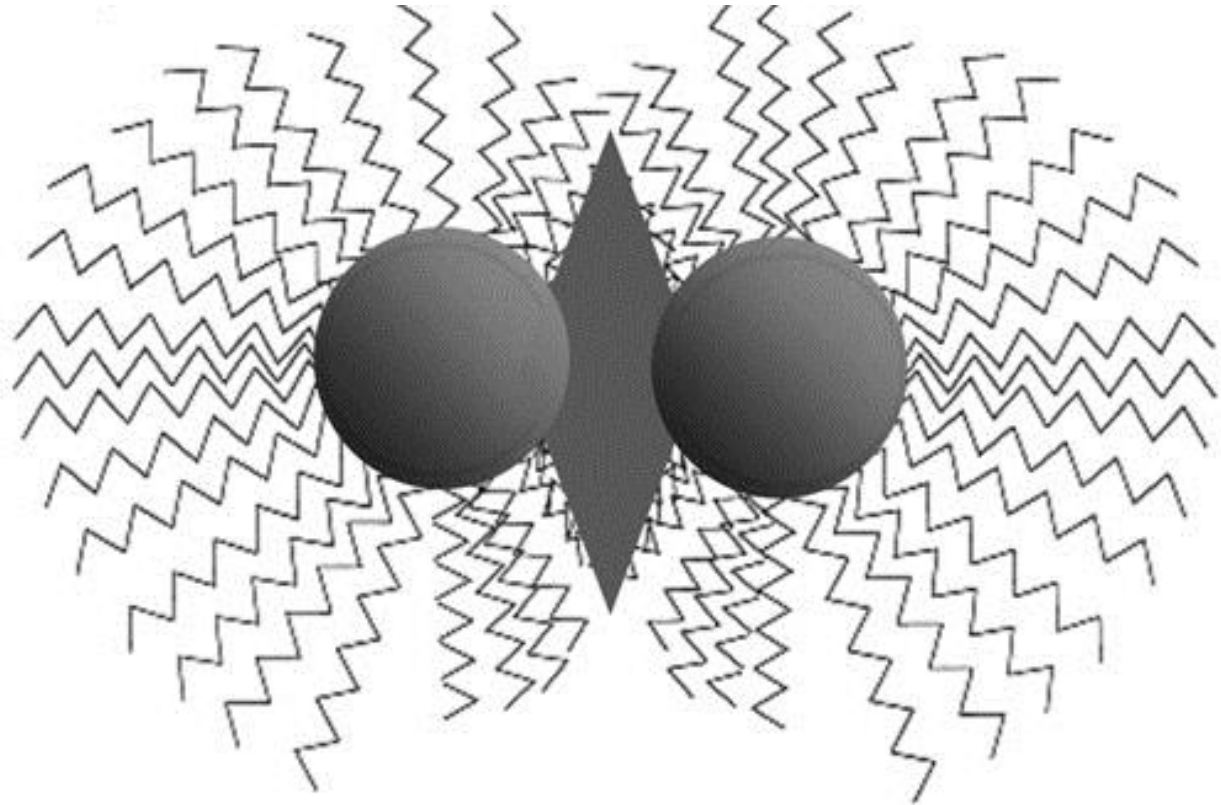
Repulsion due to electric potentials of two particles

Repulsion due to osmotic flow:

# • Steric Stabilization

$$\Delta S < 0$$

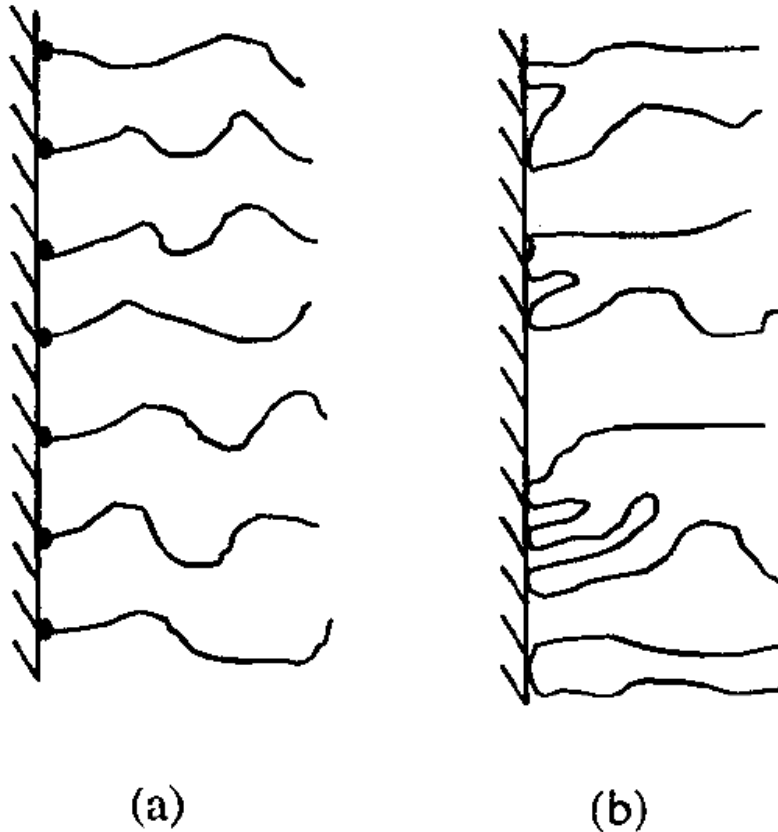
$$\Delta G = \Delta H - T\Delta S > 0$$



The physical basis for the steric stabilization is:

- i) A volume restriction effect arising from the decrease in possible configurations in the region between the two surfaces
- ii) An osmotic effect due to the relatively high concentration of adsorbed molecules in the region between the two particles

Type of interactions of the surfactant with the surface of the nanoparticle



(a)

(b)

a) Chemisorption – An anchored ligand which covalently binds to the surface of the nanoparticle (i.e. a thiol–gold bond or an amine–silver bond)

b) Physisorption – the ligand is adsorbed at the surface of the nanocrystal (i.e. hydrophobic, van der Waals interactions)

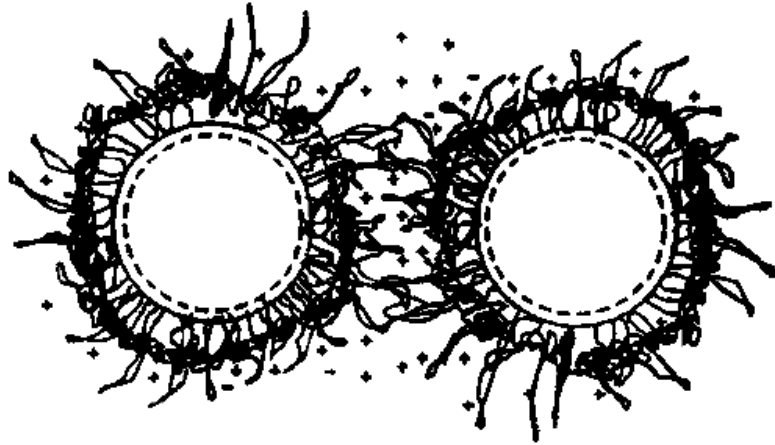
The stability of sterically stabilised nanoparticles depends on:

- i) Type of interaction of the ligands with the surface of nanoparticles
- ii) Solubility of the ligand/particle system (i.e. solvent polarity, temperature)
- iii) Degree of surface coverage of the ligands.

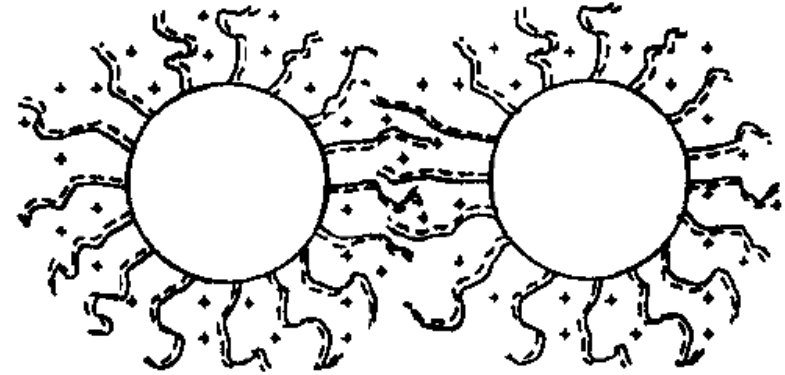
## Advantages of steric stabilization vs. electrostatic stabilization

- a) Particles with a high coverage of ligands are always re-dispersible
- b) Very high concentration of particles can be accommodated in a solution
- c) It is not electrolyte sensitive
- d) Particles can be well-dissolved in different solvents by appropriate choice of the stabilizer

# Electrosteric stabilization



(a)



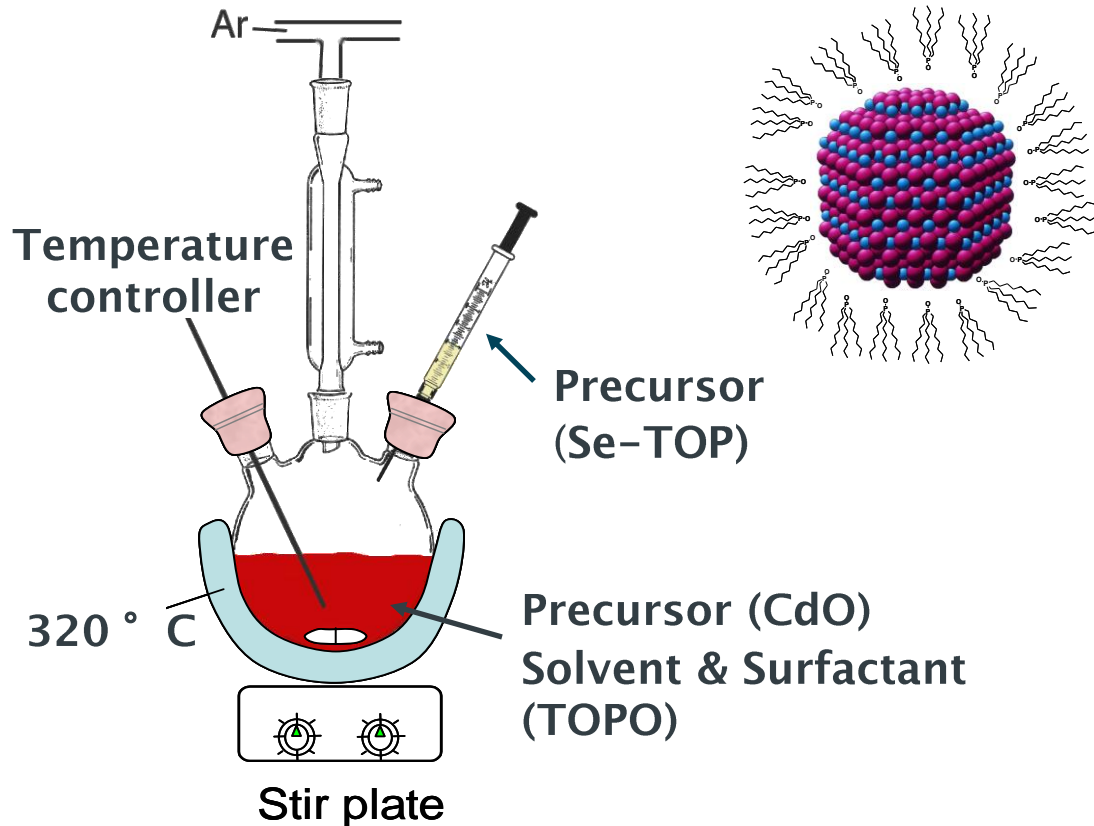
(b)

Schematic representation of electrosteric stabilization: (a) charged particles with nonionic polymers and (b) polyelectrolytes attached to uncharged particles.

# Examples of nanocrystal synthesis

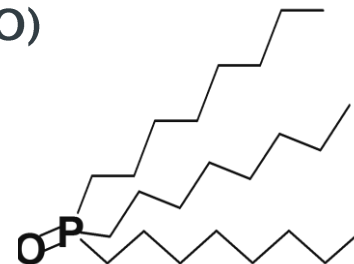


# CdSe Nanocrystal Synthesis–Thermal decomposition

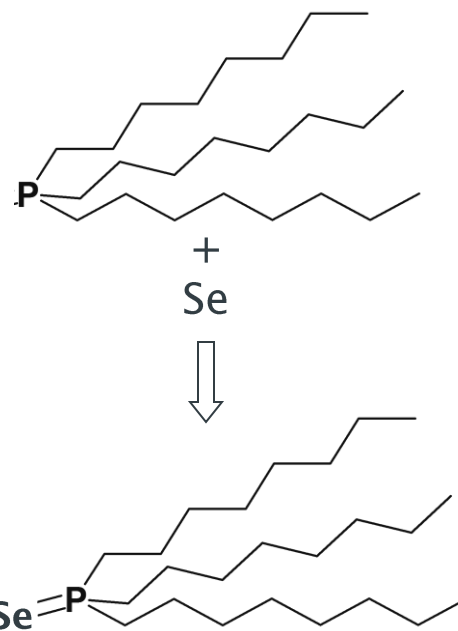


**Precursors:** CdO + Se-TOP  
**Surfactants:** TOPO, TOP, Alkyl amine  
**Solvent:** TOPO

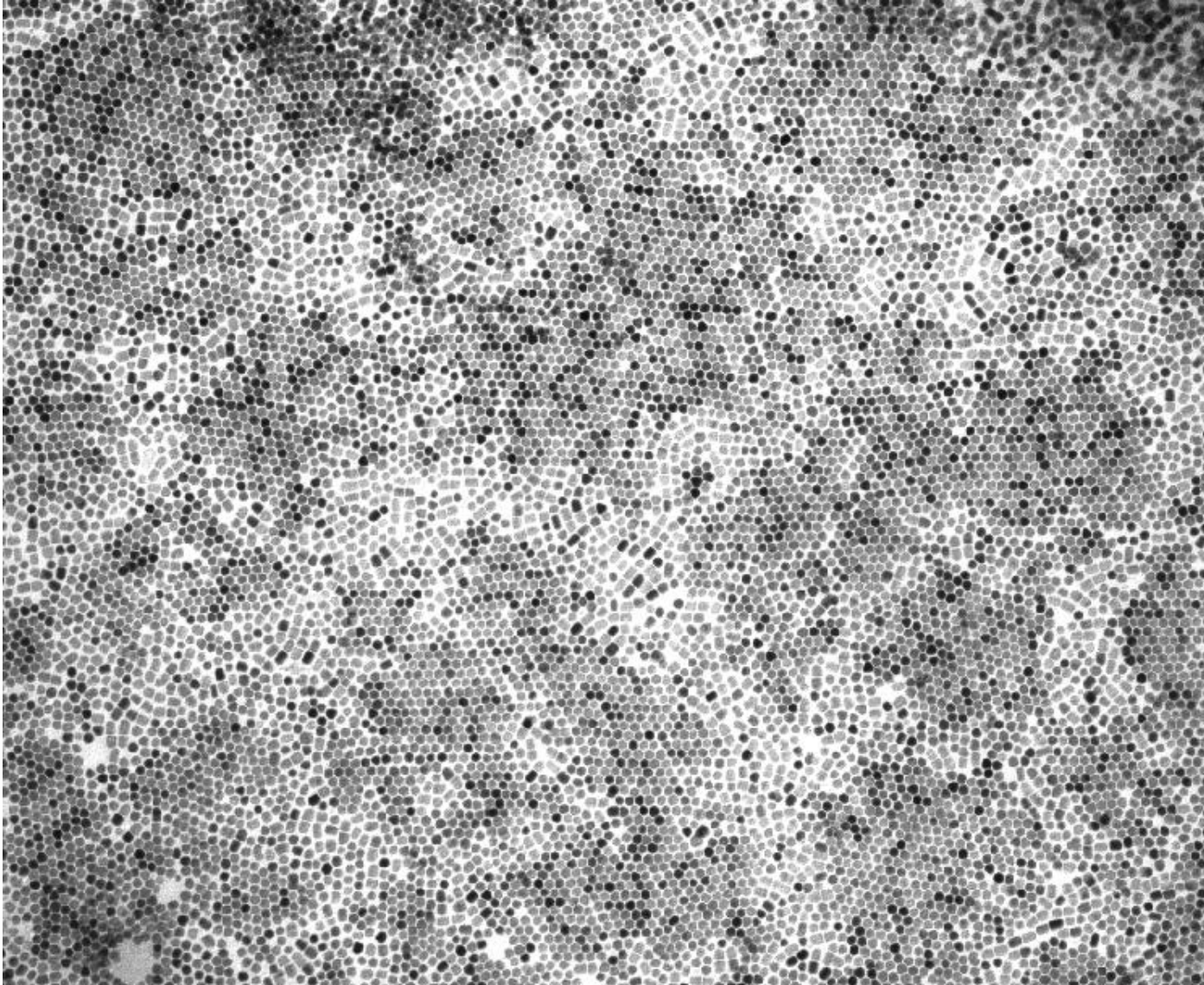
**Trioctylphosphine oxide (TOPO)**



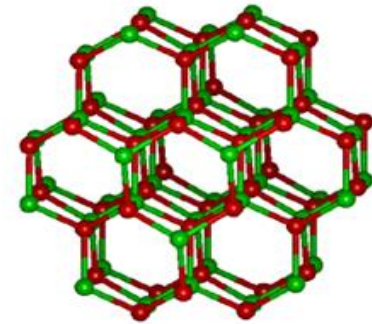
**Trioctylphosphine (TOP)**



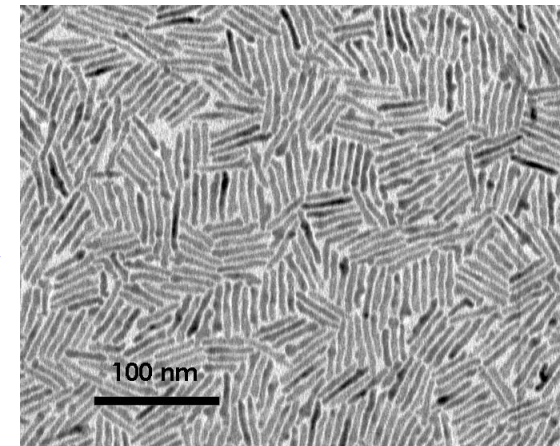
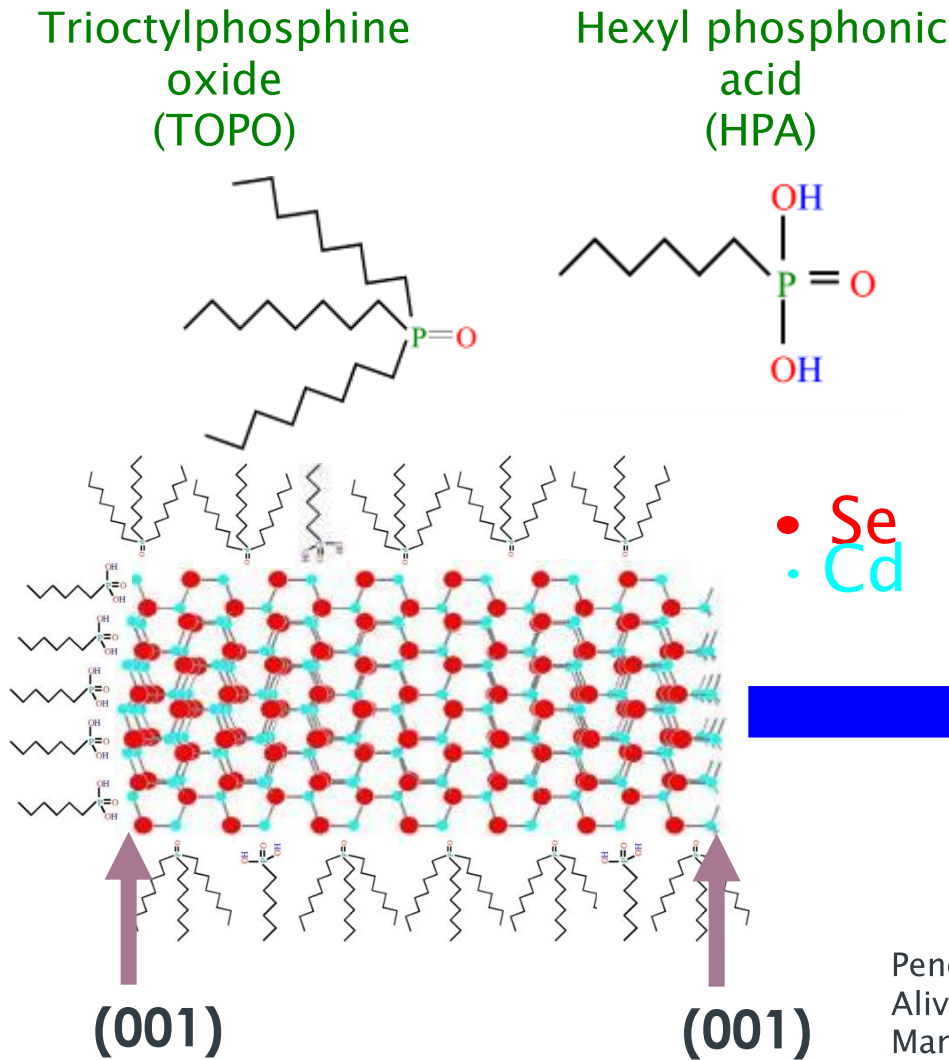
# A Wide Field View of 7-nm CdSe Nanocrystals



# Shape Control by Selective Adhesion of Surfactants



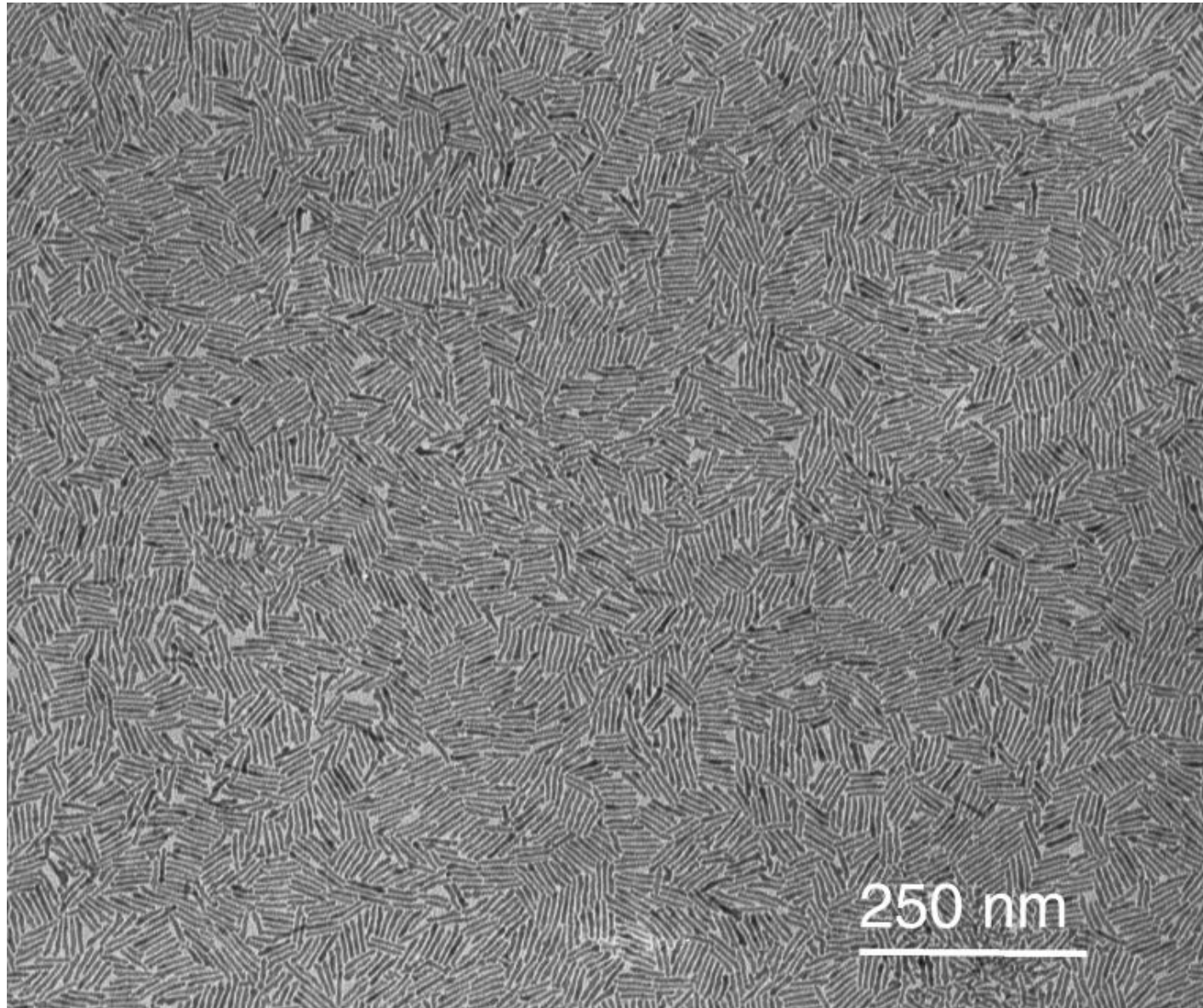
**Anisotropic Growth**



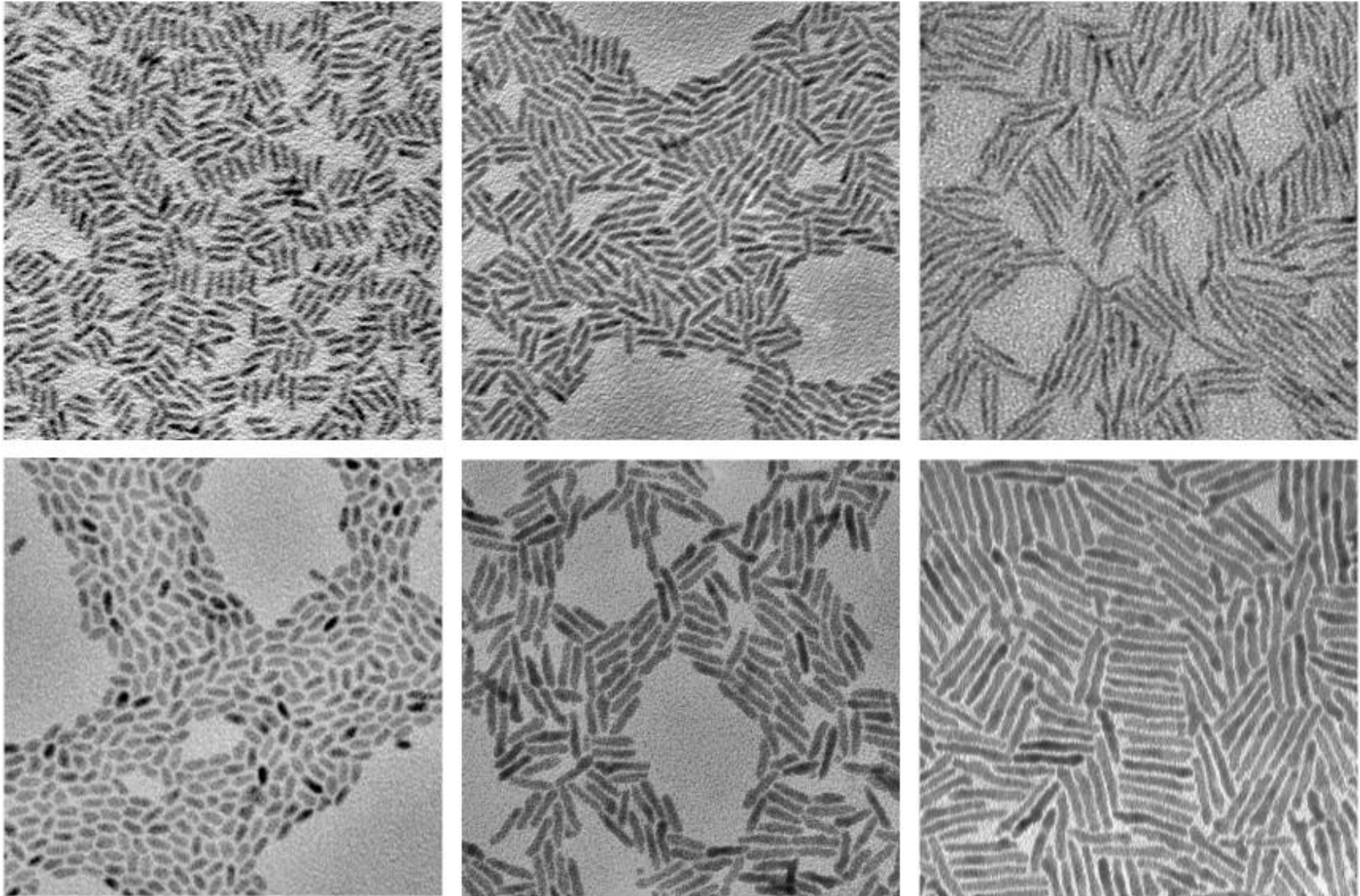
Peng, Manna, Yang, Wickham, Scher, Kadavanich, Alivisatos, *Nature* 2000, 404, 59.  
Manna, Scher, Alivisatos, *J. Am. Chem. Soc.* 2000, 122, 12700.

Surfactant binds selectively on crystal surfaces, changing surface energy

# Monolayer of 4x40 nm CdSe nanorods



# Control of Length and Diameter

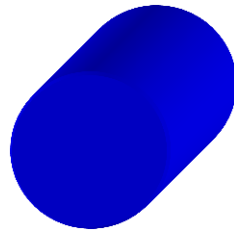
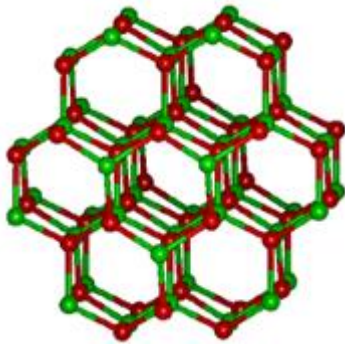


— 50 nm

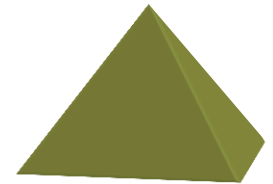
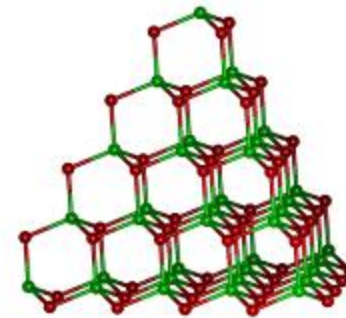
# Wurtzite and Zinc Blende Structures

- The stability of cubic zincblende and hexagonal wurzite structure is similar.
- Nucleation in zincblende structure, growth in wurzite structure.
- The (111) face of zinblende is equivalent to the (001) face of wurzite.

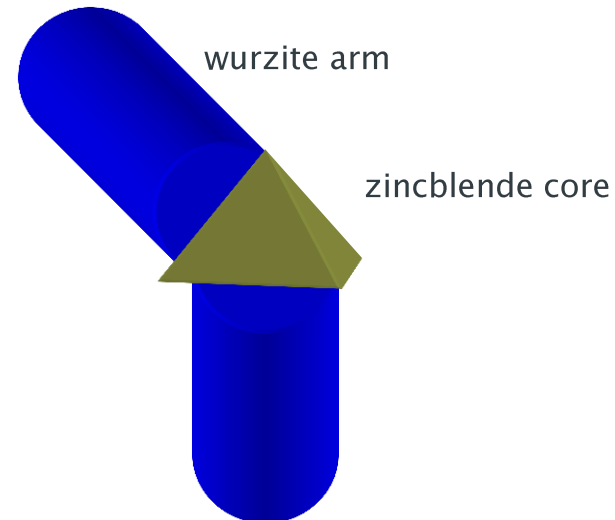
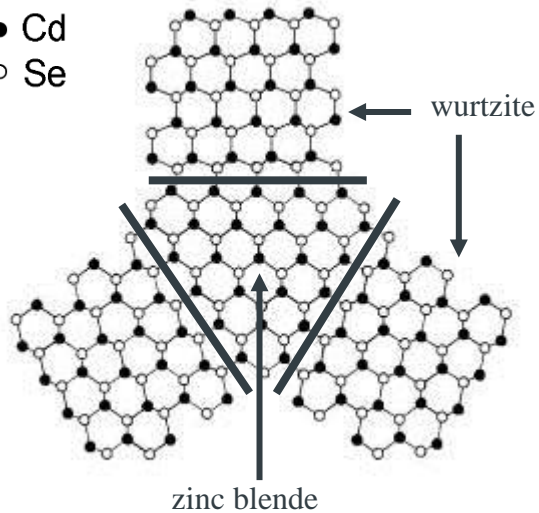
WZ



ZB



- Cd
- Se

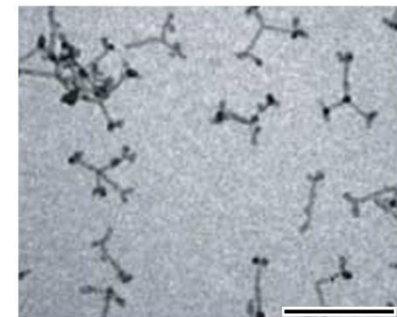
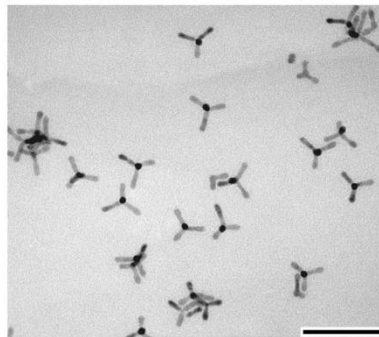
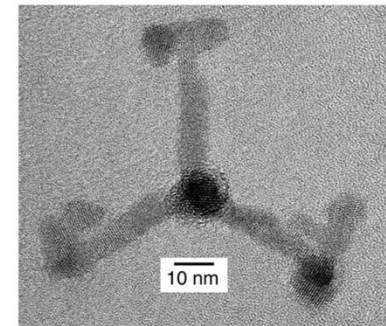
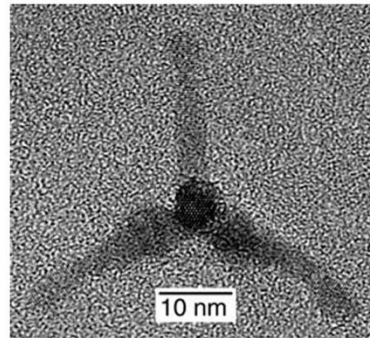
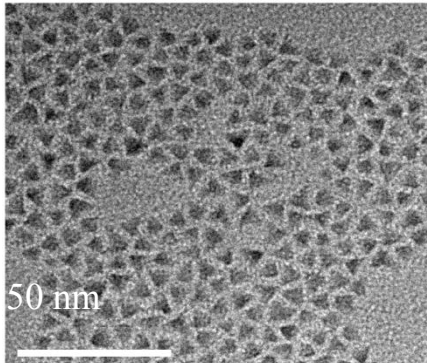
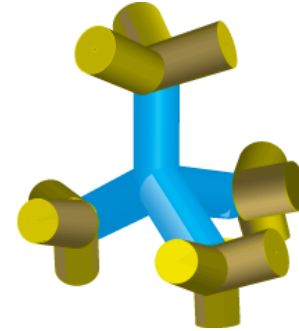
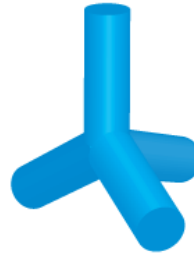


# Branching: CdTe Nano-tetrapod

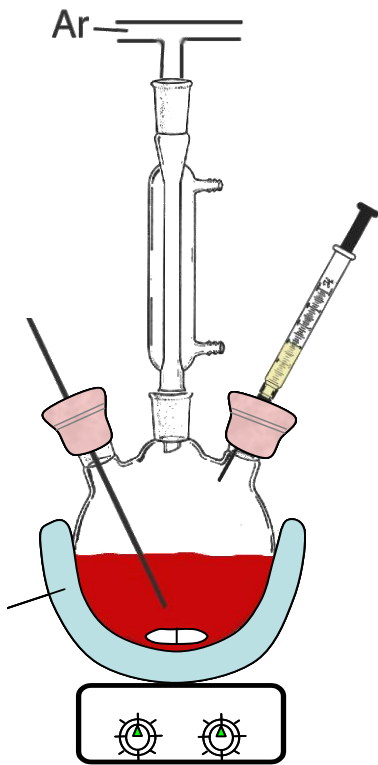
zinblende core



wurzite arm

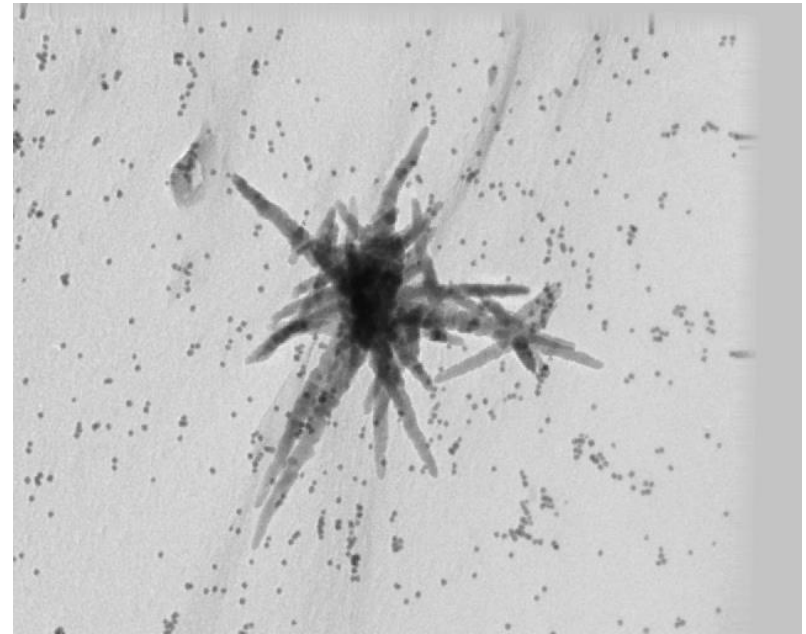
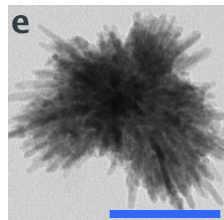
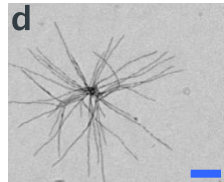
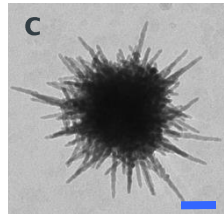
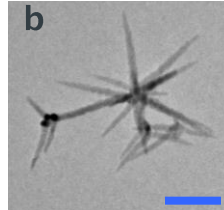
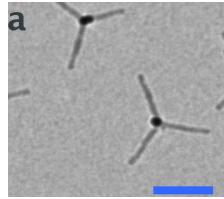


# Varying the reaction conditions



Stir plate  
Less amount of organics

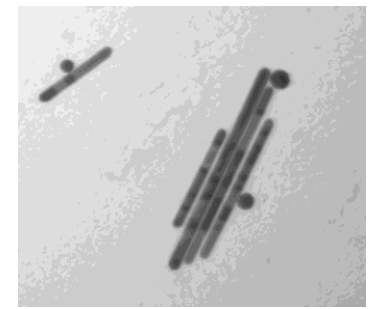
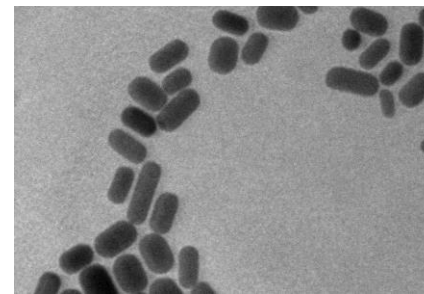
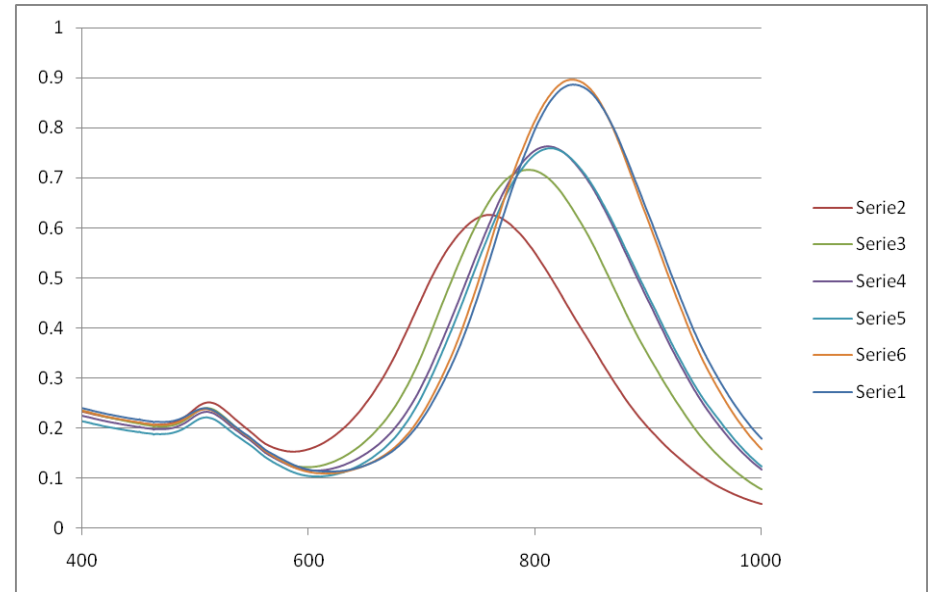
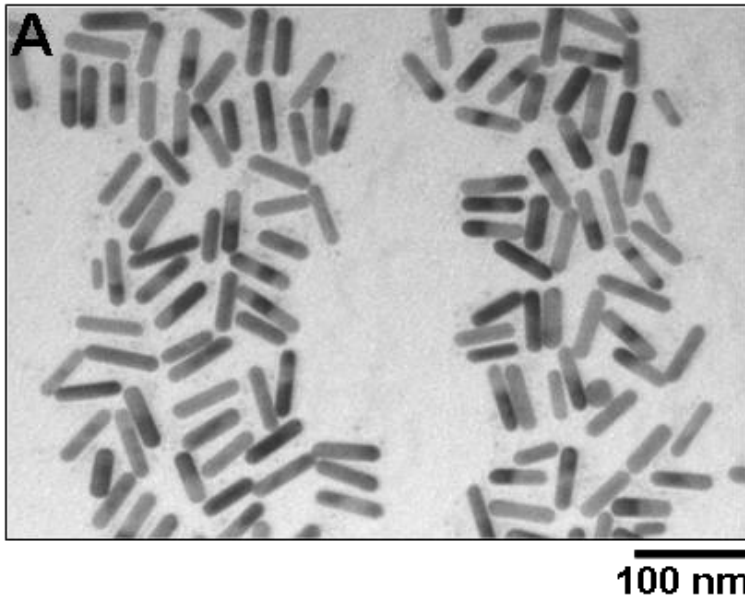
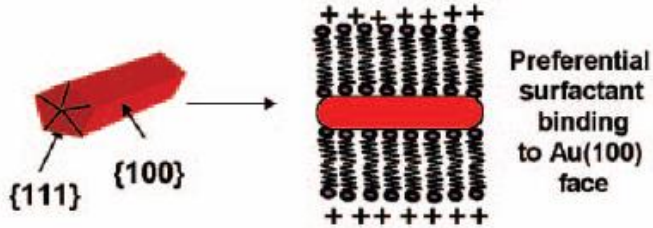
Se instead of Te





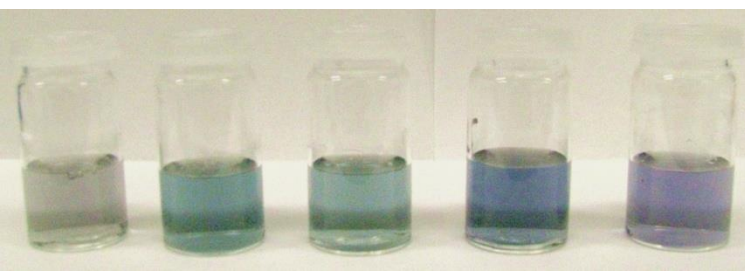
# Synthesis of gold nanorods-Seeding procedure

Surfactant as directing agent



50 nm

100 nm

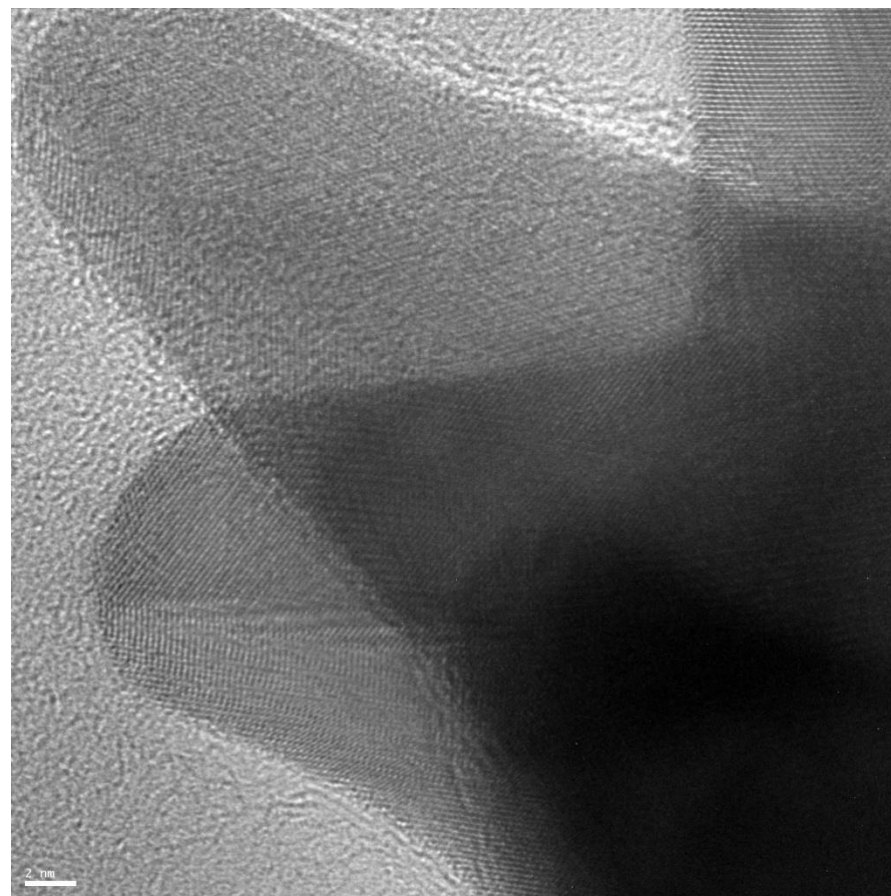
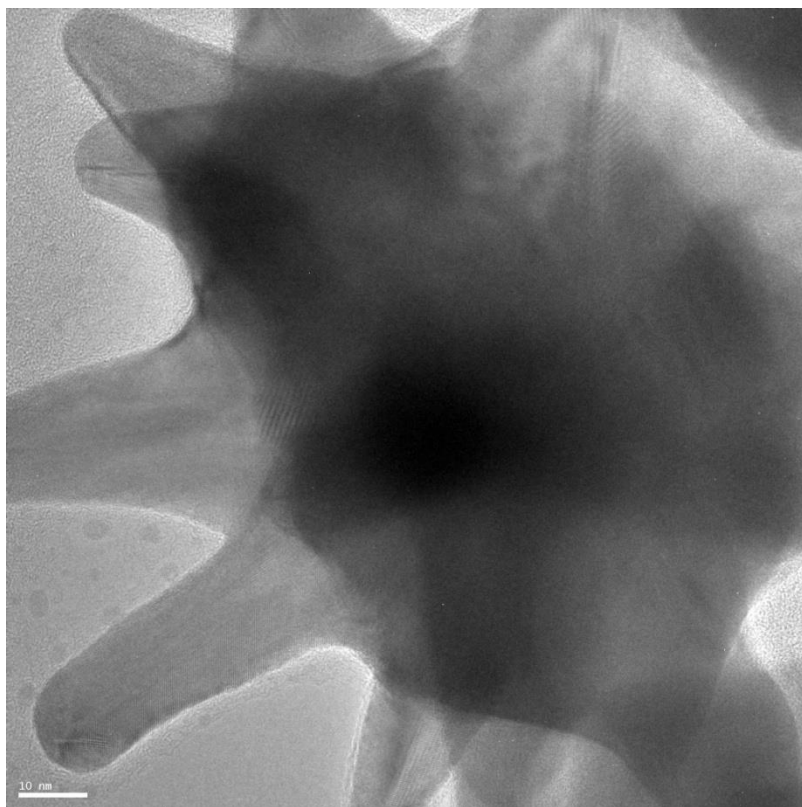


By changing the type of seeds, amount of reducing agents  
organics bind preferential to a particular crystallographic plane

perfect/truncated octahedron<sup>[4]</sup>



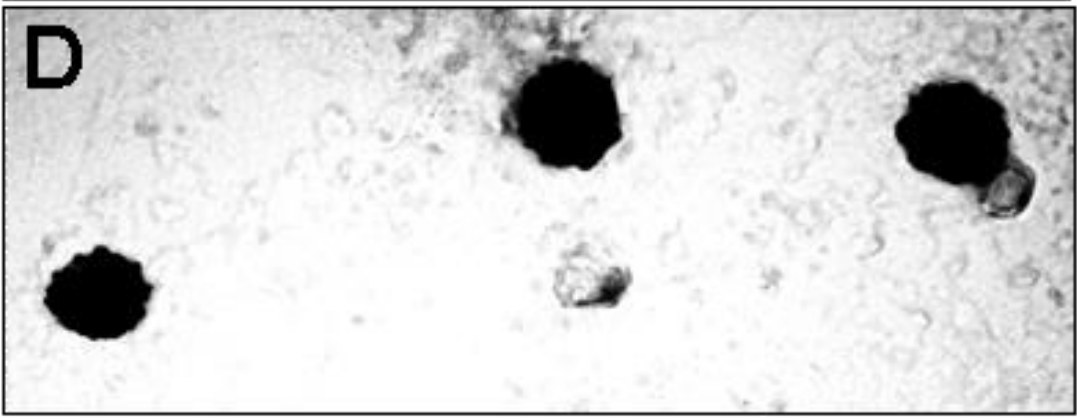
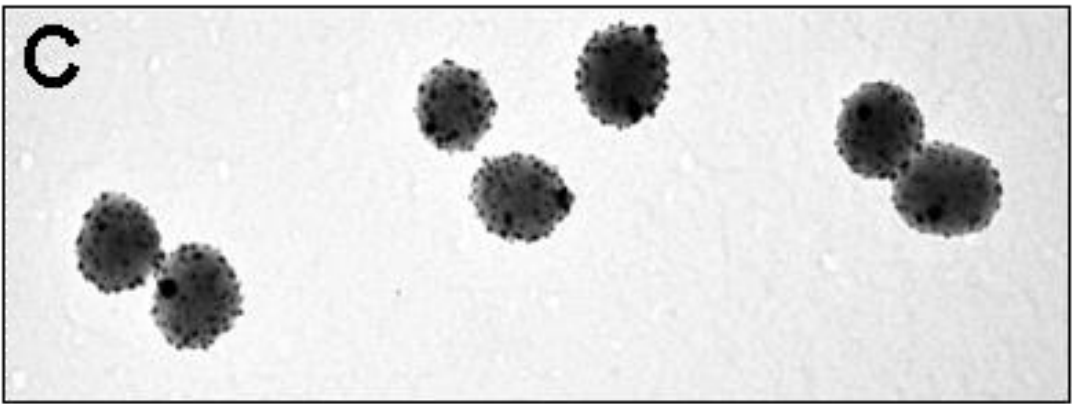
Pd, Ag, Au, Pt



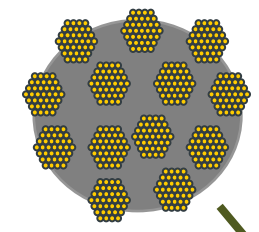
Kanaras group

*CrystEngComm*, 2010, 12 (12), 4312 – 4316

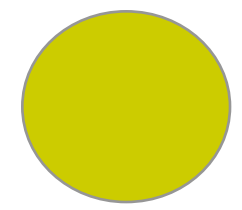
Seed-growth on a template



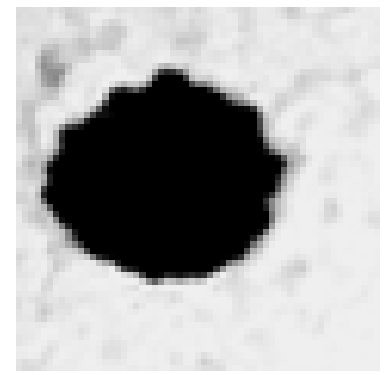
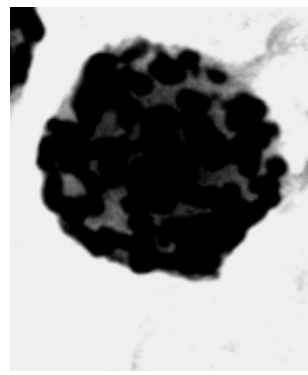
100 nm



Gold salt  
Reducing agent

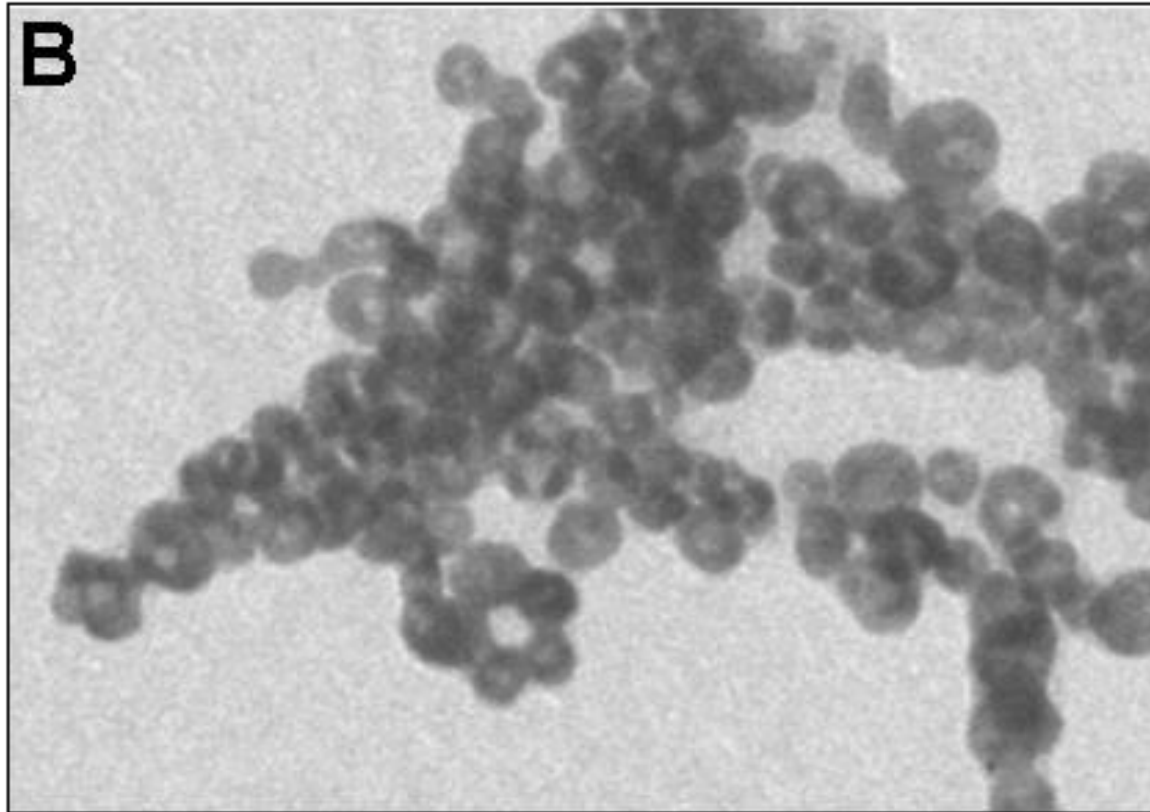


Gold shells grown on silica particles

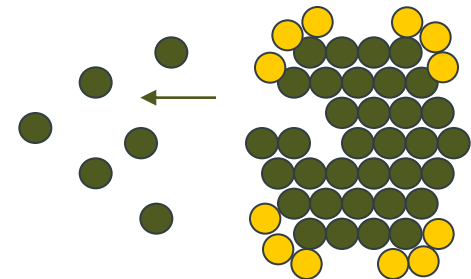
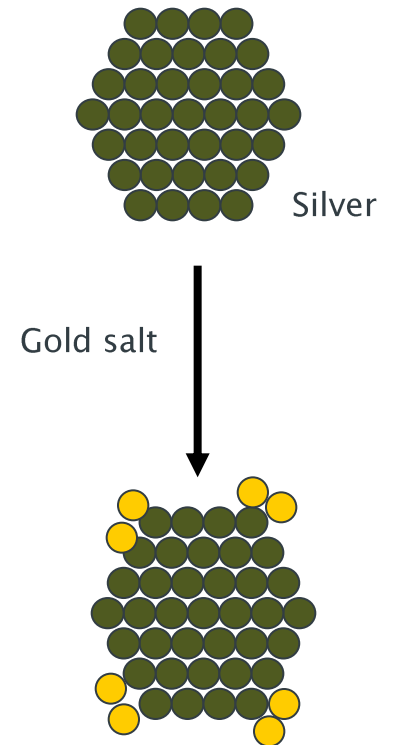
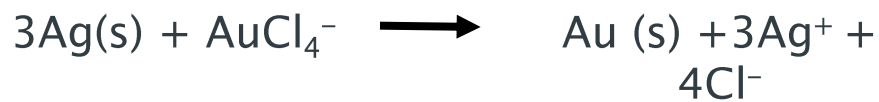


# Gold nanoshells

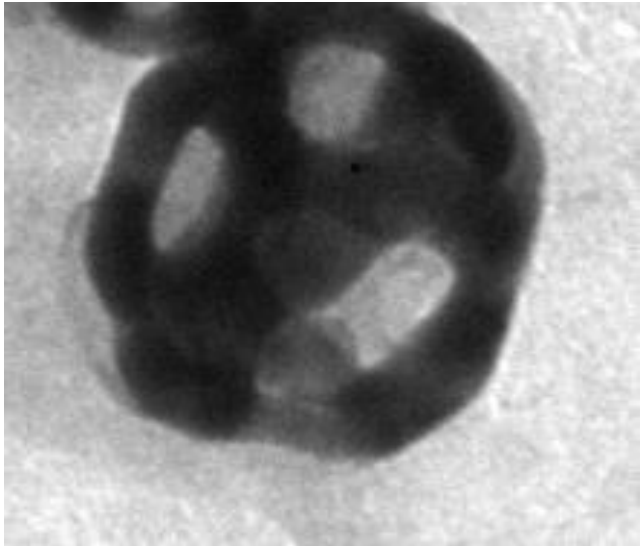
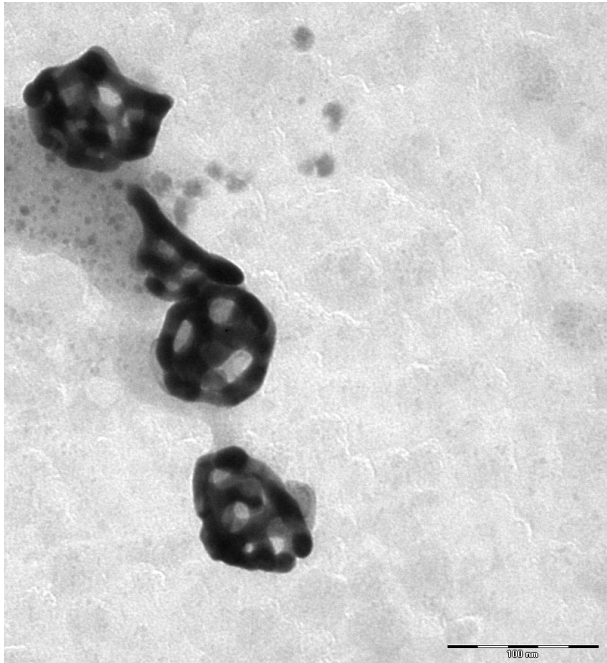
Galvanic replacement reaction



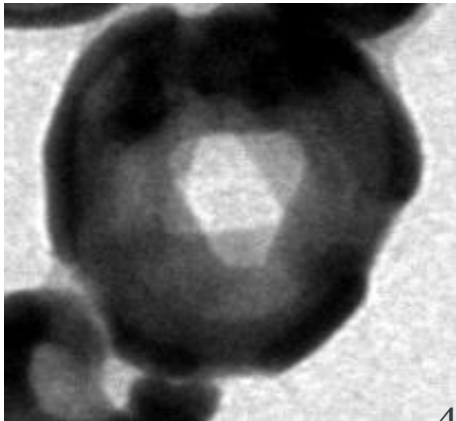
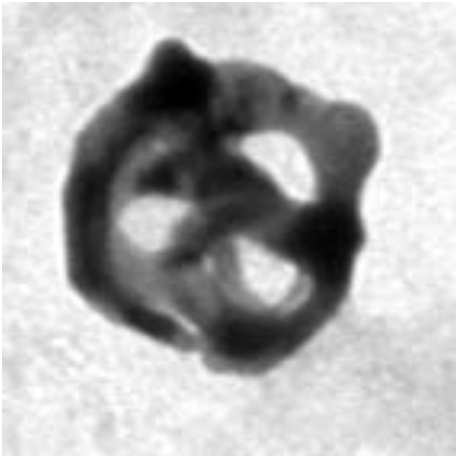
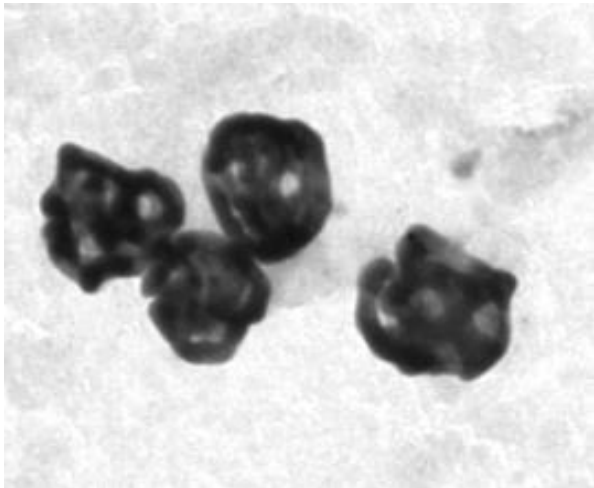
50 nm



# Nanocages



Nanocage size is about 80 nm



Name the different ways that nanoparticles are stabilised in solution and explain them. Which type of stabilization is the ideal one to avoid aggregation ?

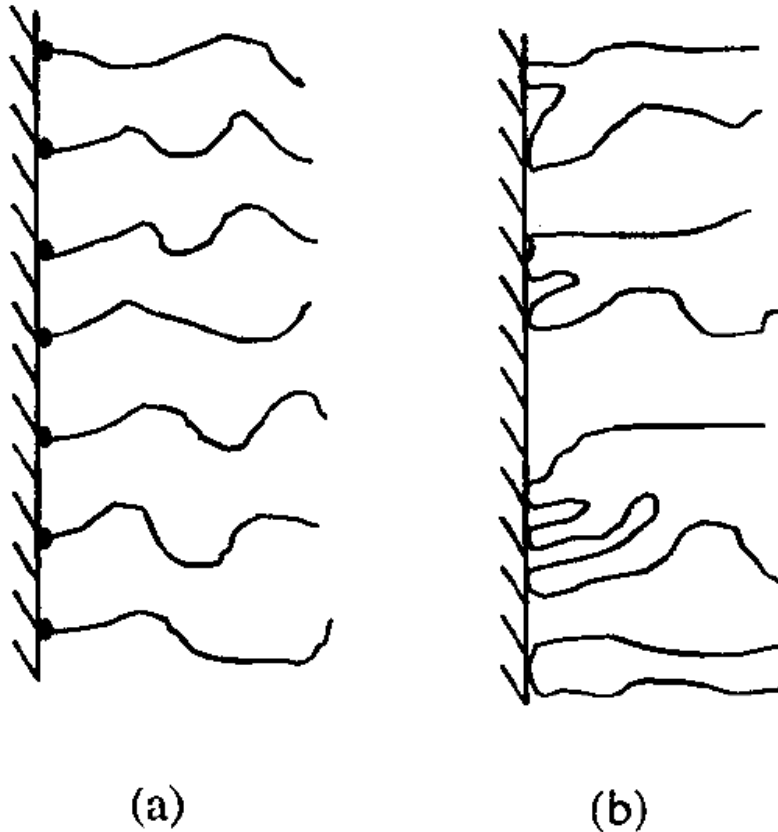
Give two examples of nanocrystal synthesis based on thermal decomposition and explain. How the shape of CdSe nanocrystals to nanorods can be controlled?

Explain one example of nanoparticle synthesis that involves a seeding procedure.

What is a galvanic replacement reaction and what types of nanoparticles we could synthesize?

**Name two ways that a surfactant can interact with the nanoparticle surface**

Answer:

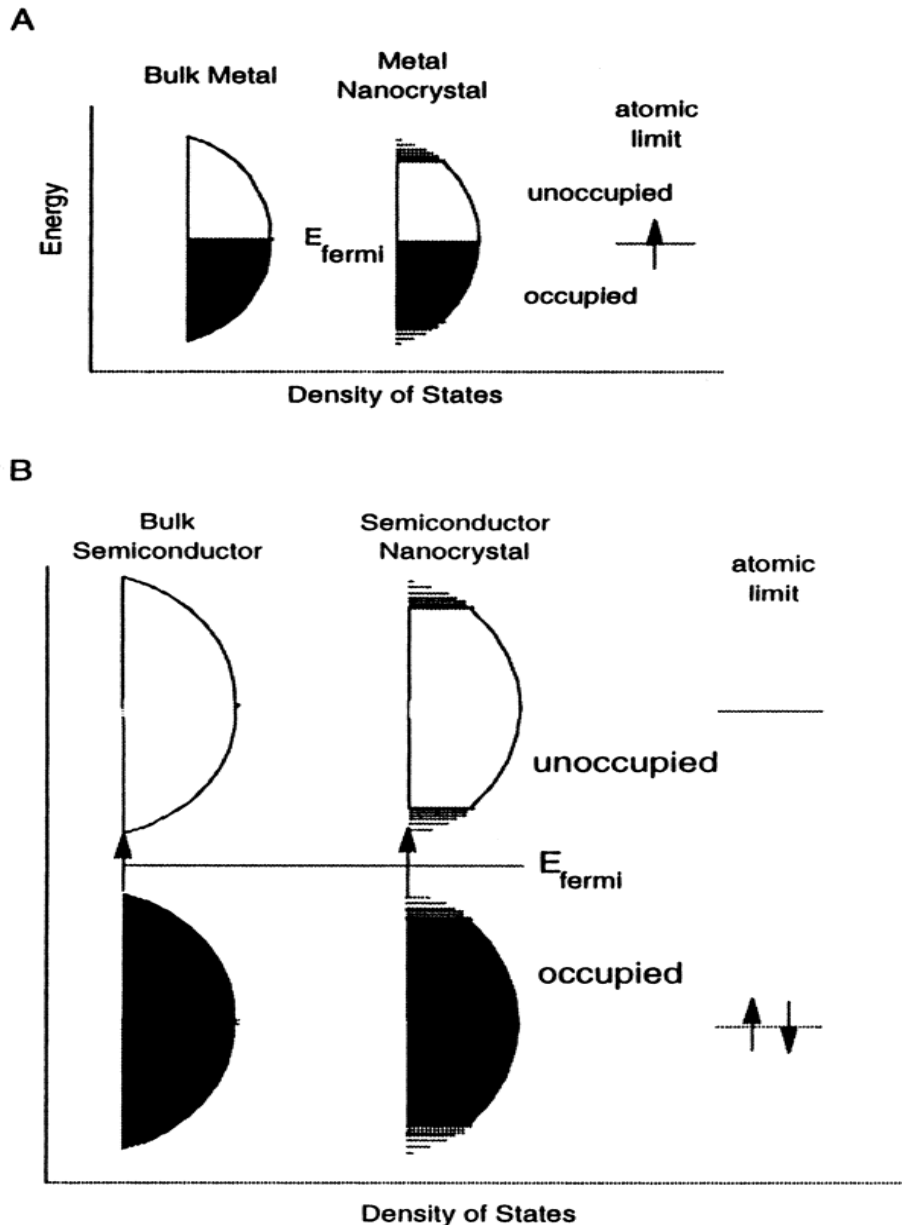


- a) Chemisorption - An anchored ligand which covalently binds to the surface of the nanoparticle (i.e a thiol-gold bond or a amine-silver bond)
- b) Adsorption- the ligand is adsorb at the surface of the nanocrystal (i.e. hydrophobic, van der Waals interactions)



**What is the difference between metal and semiconductor nanoparticles?  
Draw a graph and explain.**

# Answer:



In any material, there will be a size below which there is substantial variation of fundamental electrical and optical properties with size, which will be seen when the energy level spacing exceeds the temperature. For a given temperature, this occurs at a very large size in semiconductors, as compared to metals. This can be understood by considering that the bands of a solid are centered about atomic energy levels, with the width of the band related to the strength of the nearest neighbor interactions. As a function of increasing size, the center of a band develops first and the edges develop last. Thus, in metals, where the Fermi level lies in the center of a band, the relevant energy level spacing is still very small, and at temperatures above a few kelvin, the electrical and optical properties more closely resemble those of a continuum, even in relatively small sizes (tens or hundreds of atoms). In semiconductors, however, the Fermi level lies between two bands, so that the edges of the bands dominate the low-energy optical and electrical behavior. Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10 000 atoms.