# Synthetic Strategies to Colloidal Nanocrystals and Heterostructures

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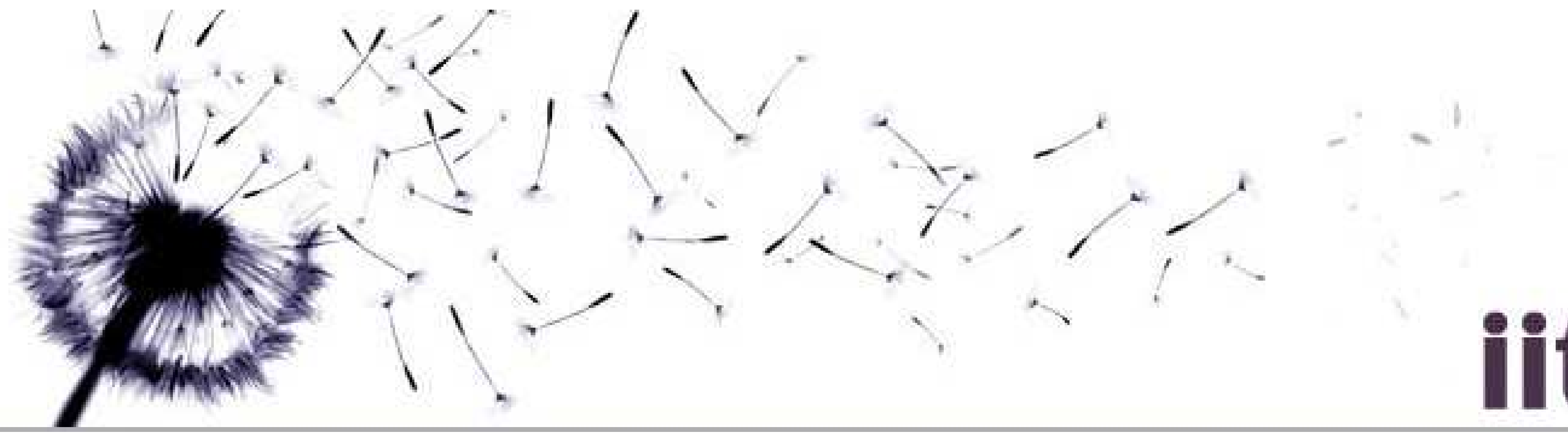
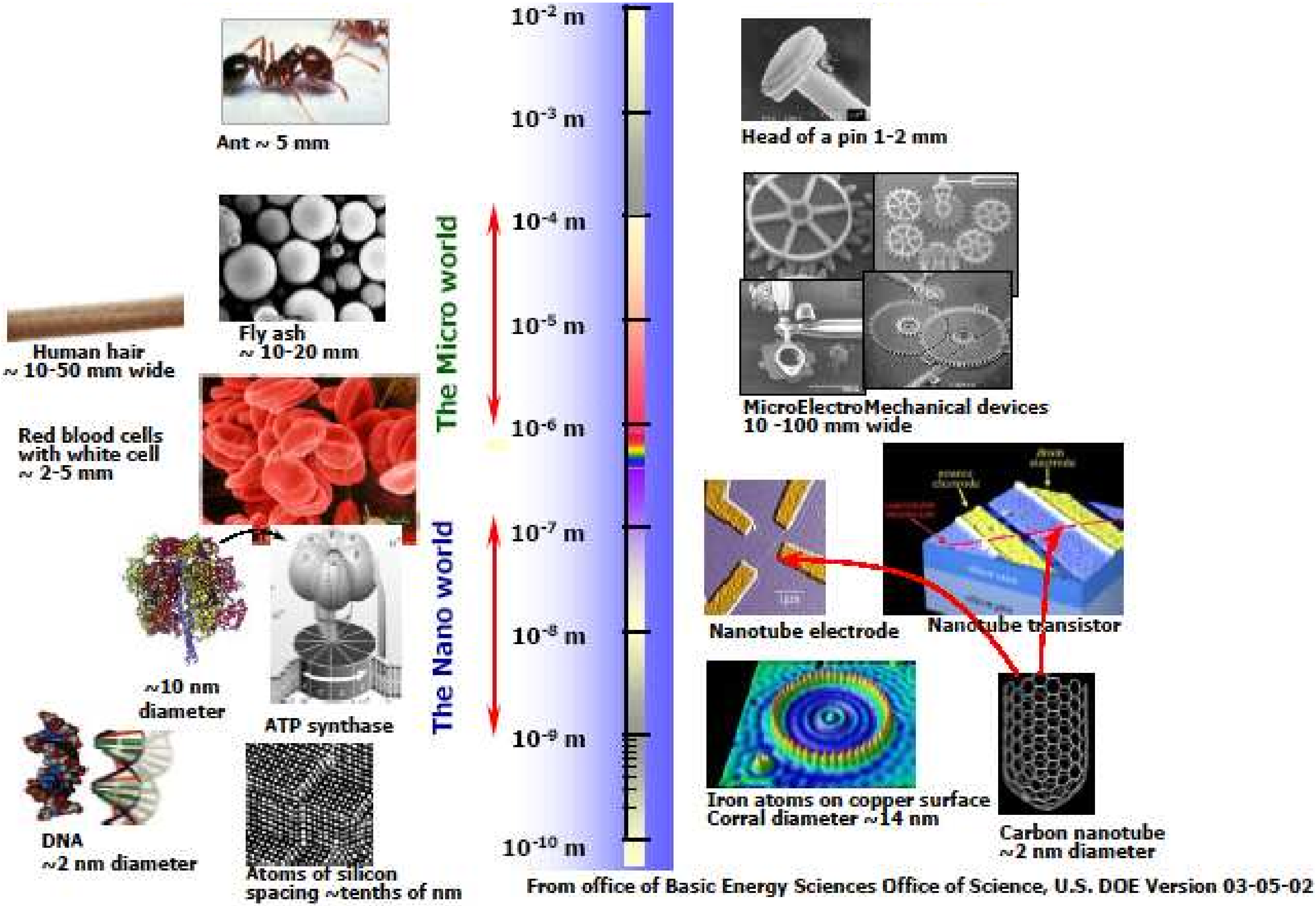


# Colloidal Nanocrystals and Heterostructures

## What are they?

Particles with a size of the order of nanometres.

| | | |
|---|---|---|
| Tera- | T | $10^{12}$ |
| Giga- | G | $10^{9}$ |
| Mega- | M | $10^{6}$ |
| Kilo- | k | $10^{3}$ |
| deci- | d | $10^{-1}$ |
| centi- | c | $10^{-2}$ |
| milli- | m | $10^{-3}$ |
| micro- | $\mu$ | $10^{-6}$ |
| nano- | n | $10^{-9}$ |
| pico- | p | $10^{-12}$ |



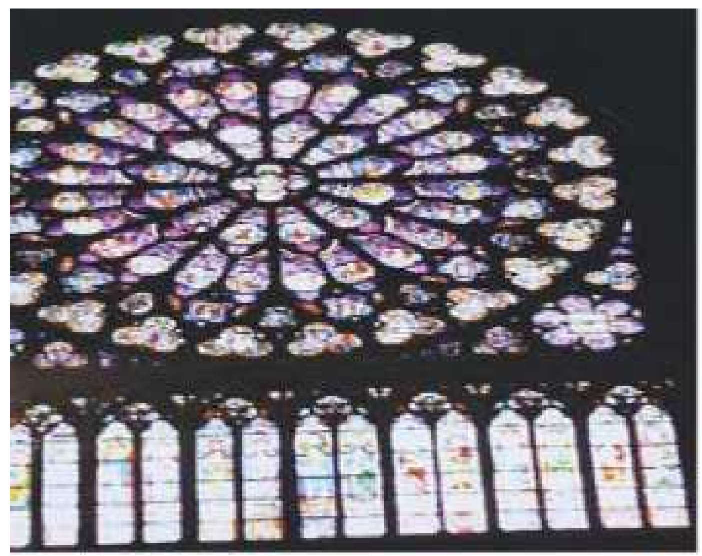
Ant ~ 5 mm
Fly ash
~ 10-20 mm
Human hair
~ 10-50 mm wide
Red blood cells
with white cell
~ 2-5 mm
~10 nm
diameter
ATP synthase
DNA
~2 nm diameter
Atoms of silicon
spacing ~tenths of nm
The Micro world
The Nano world
$10^{-2}$ m
$10^{-3}$ m
$10^{-4}$ m
$10^{-5}$ m
$10^{-6}$ m
$10^{-7}$ m
$10^{-8}$ m
$10^{-9}$ m
$10^{-10}$ m
Head of a pin 1-2 mm
MicroElectroMechanical devices
10 -100 mm wide
Nanotube electrode
Nanotube transistor
Iron atoms on copper surface
Corral diameter ~14 nm
Carbon nanotube
~2 nm diameter
From office of Basic Energy Sciences Office of Science, U.S. DOE Version 03-05-02

## Is Nanotechnology a completely new technology?

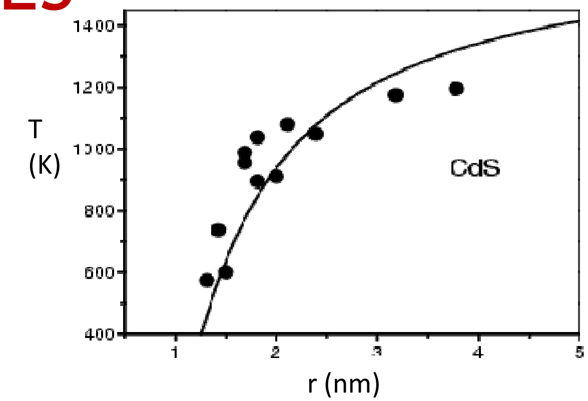
- as a science, nanotechnology is about 80 years old.
- nanofabrication has been used in the semiconductor industry for about 15 years.
- ultrafine chemicals have also been produced in bulk for a number of years.


Feature news

RENAISSANCE ARTISTS DECORATED POTTERY WITH NANOPARTICLES



# NOVEL AND USEFUL PROPERTIES




## THERMODINAMIC PROPERTIES

- decreasing of the melting point;

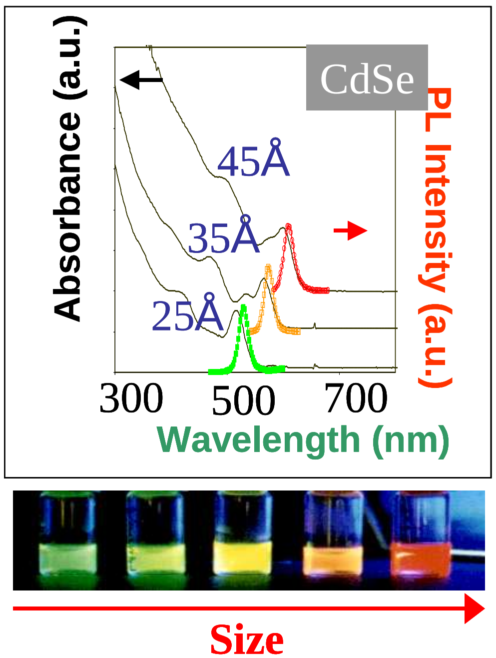
- increasing of pressure required for solid-solid transitions;

- crystalline phases unstable for extended solids

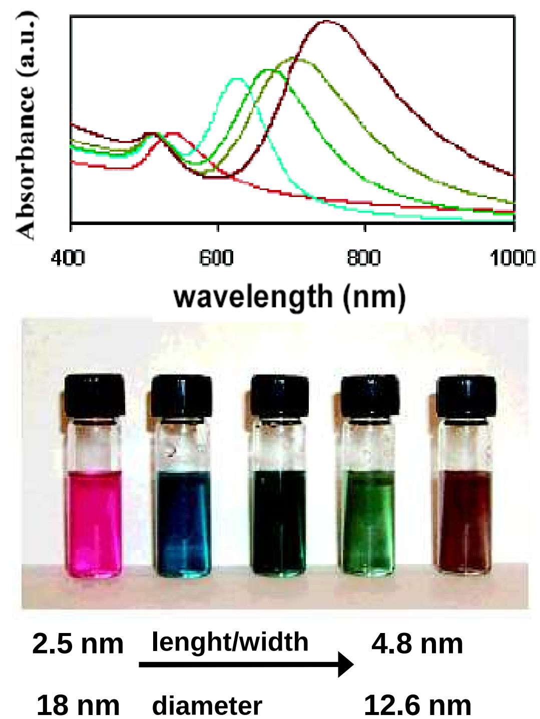
A SIGNIFICANT FRACTION OF ATOMS RESIDES AT THE SURFACE AND NOT IN THE BULK OF THE MATERIAL

# OPTOELECTRONIC PROPERTIES OF NANOCRYSTALS

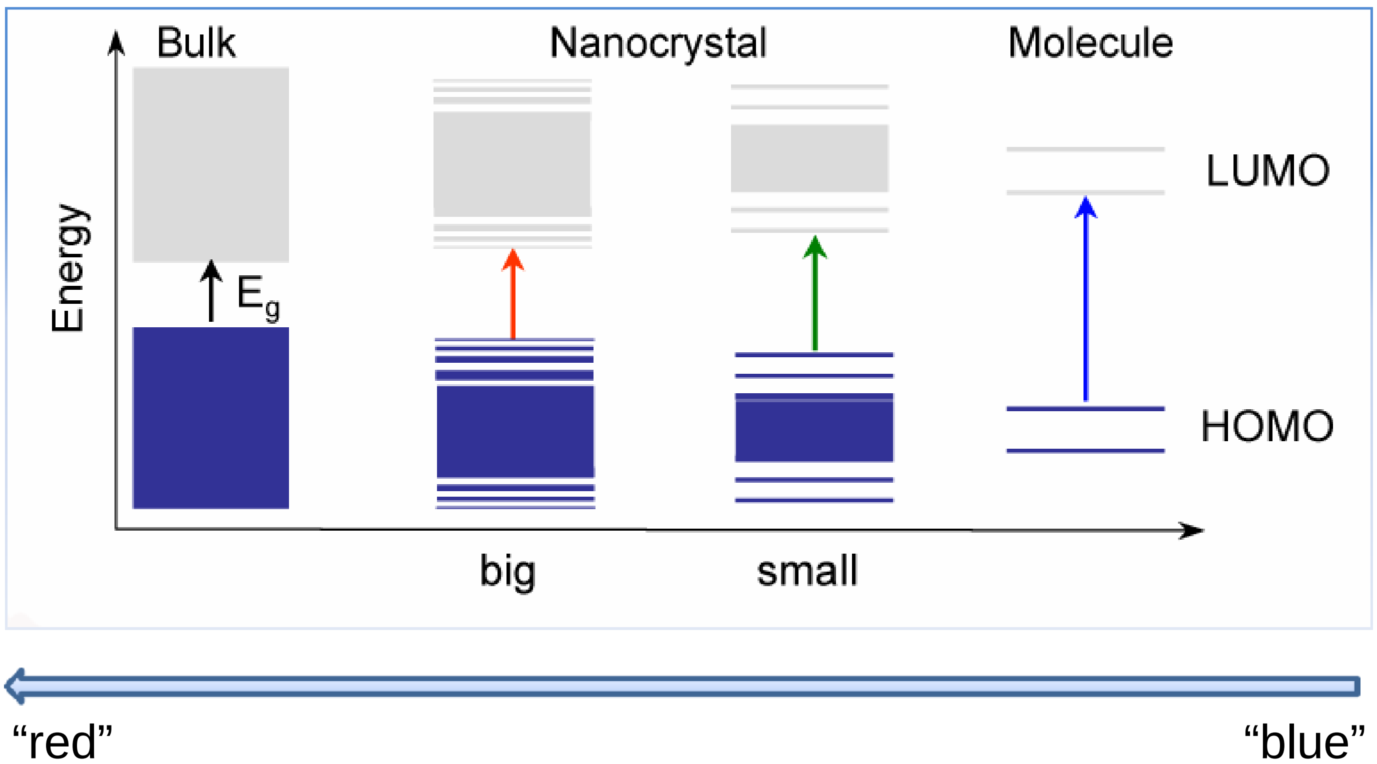
Optical transitions in semiconductors



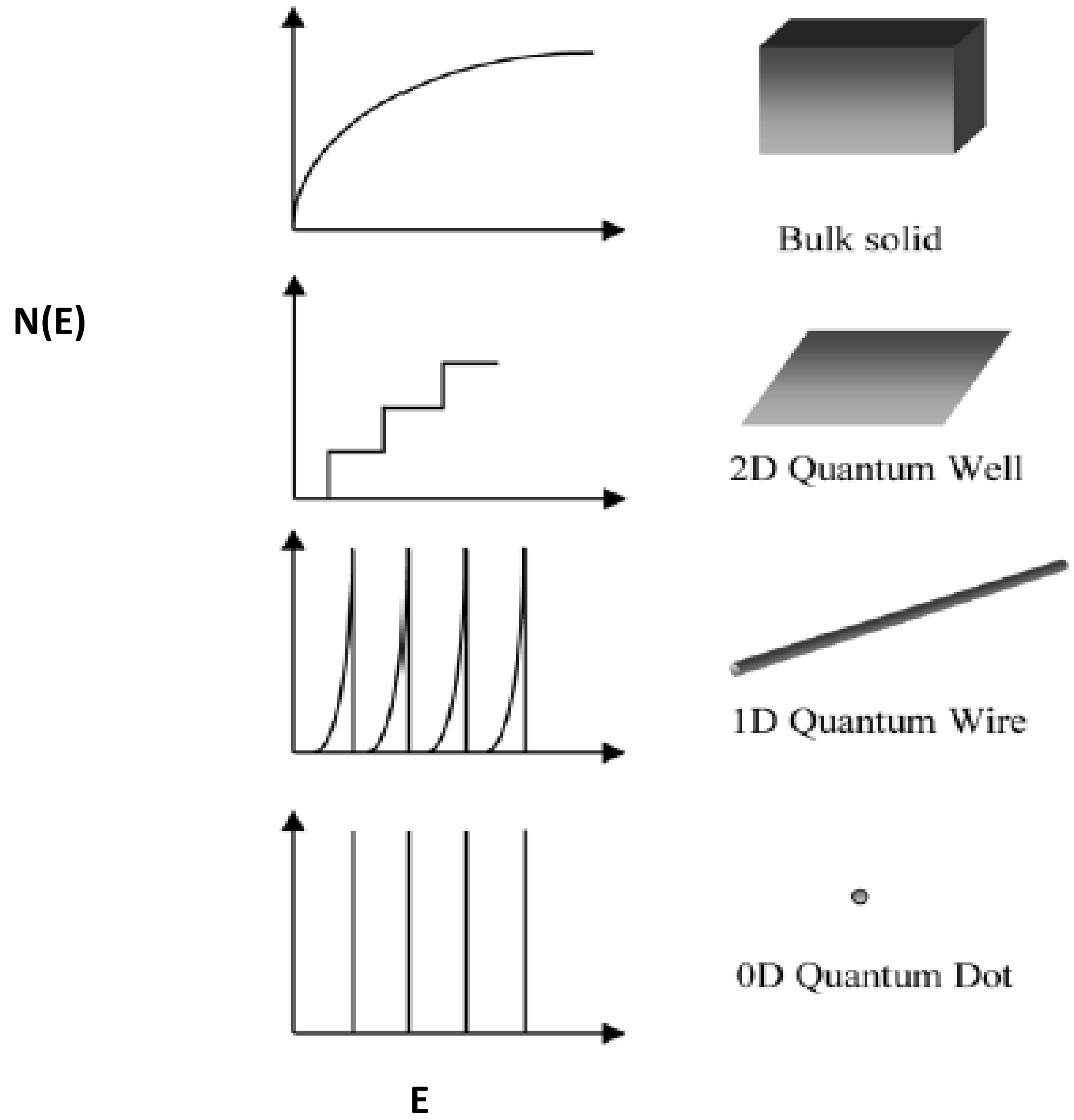

Absorption of metallic nanocrystals (Au NCs)



# ENERGETIC LEVELS OF A BULK SOLID, A NANOCRYSTAL AND A MOLECULE

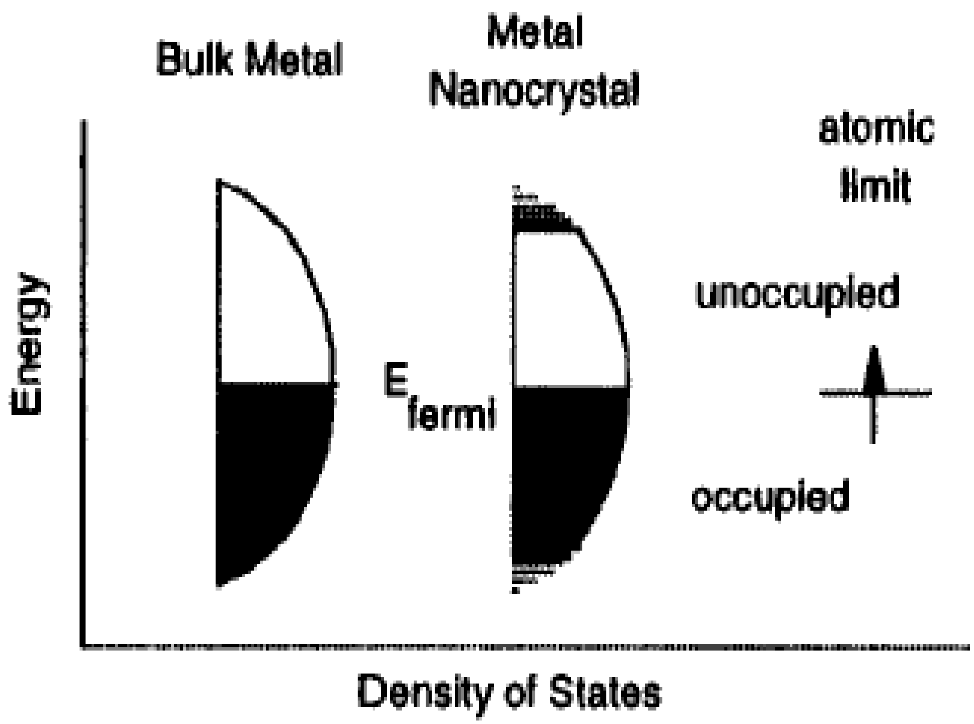


# QUANTUM CONFINEMENT

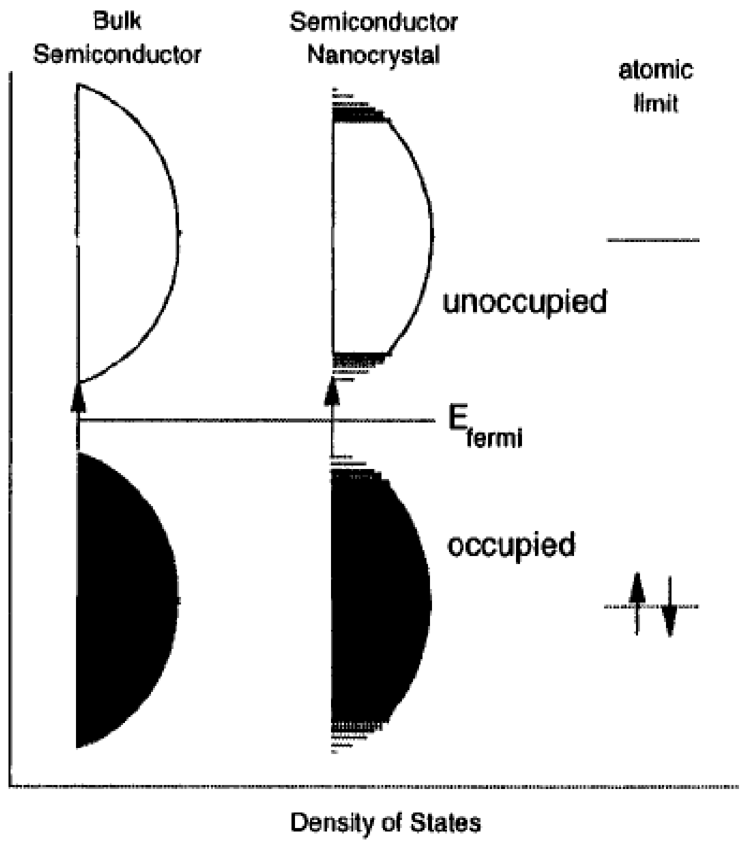



the charge carrier motion is restricted to a small material volume

METAL




SEMICONDUCTORS



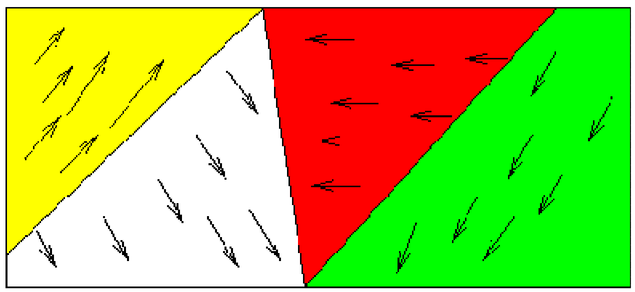

The red-ox potential can be tuned with the size of nanocrystals

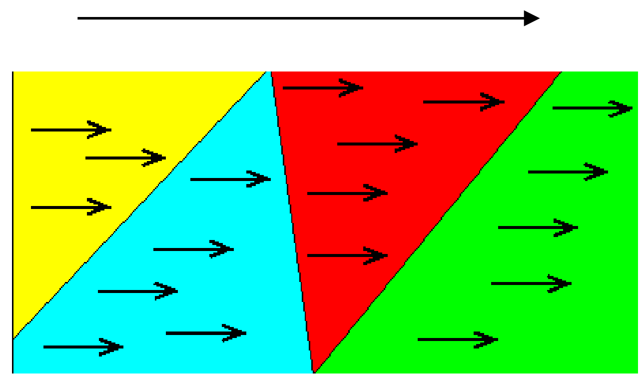
Usefull application of nanocrystals in Catalysis

# MAGNETIC PROPERTIES OF NCs

MAGNETIC FIELD

BULK:
Multidomain



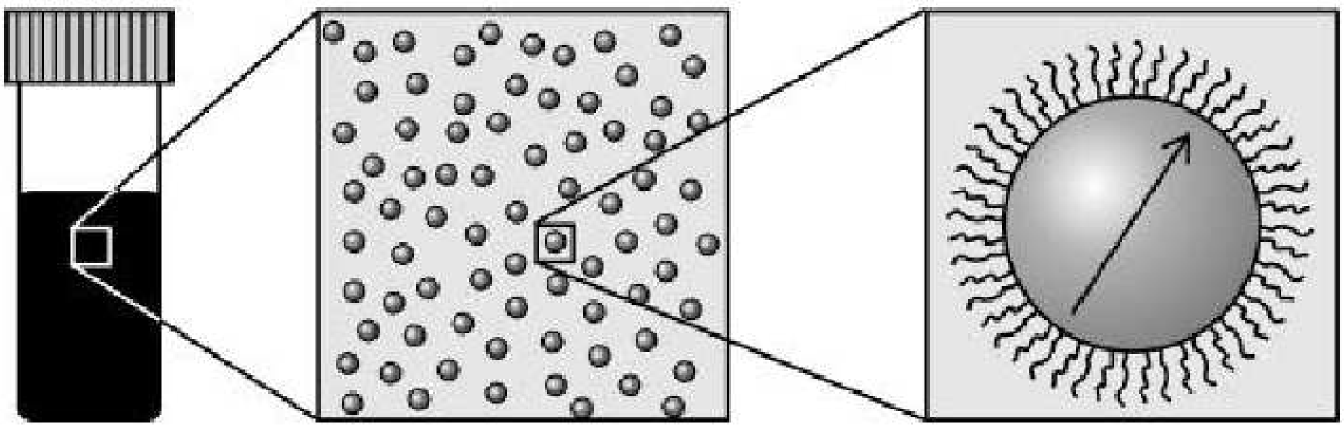


NANOCRYSTALS:
Single domain

Nanostructured ferromagnetic materials behave as single magnetic domain whose magnetization can be easily influenced by thermal fluctuations of the local environment, depending on the particle size and on a variety of surface effects.

# FERROFLUIDS

## Stable Colloidal Suspension of Magnetic Material (Nanoparticles) in a Liquid Carrier



Each Nanoparticle Constitutes a Single Magnetic Domain
- SuperParaMagnetism -

Applications: magnetic seals, lubricants, loudspeakers, dumpers, inks, medicine,...

## HOW ARE THEY SYNTHESIZED?

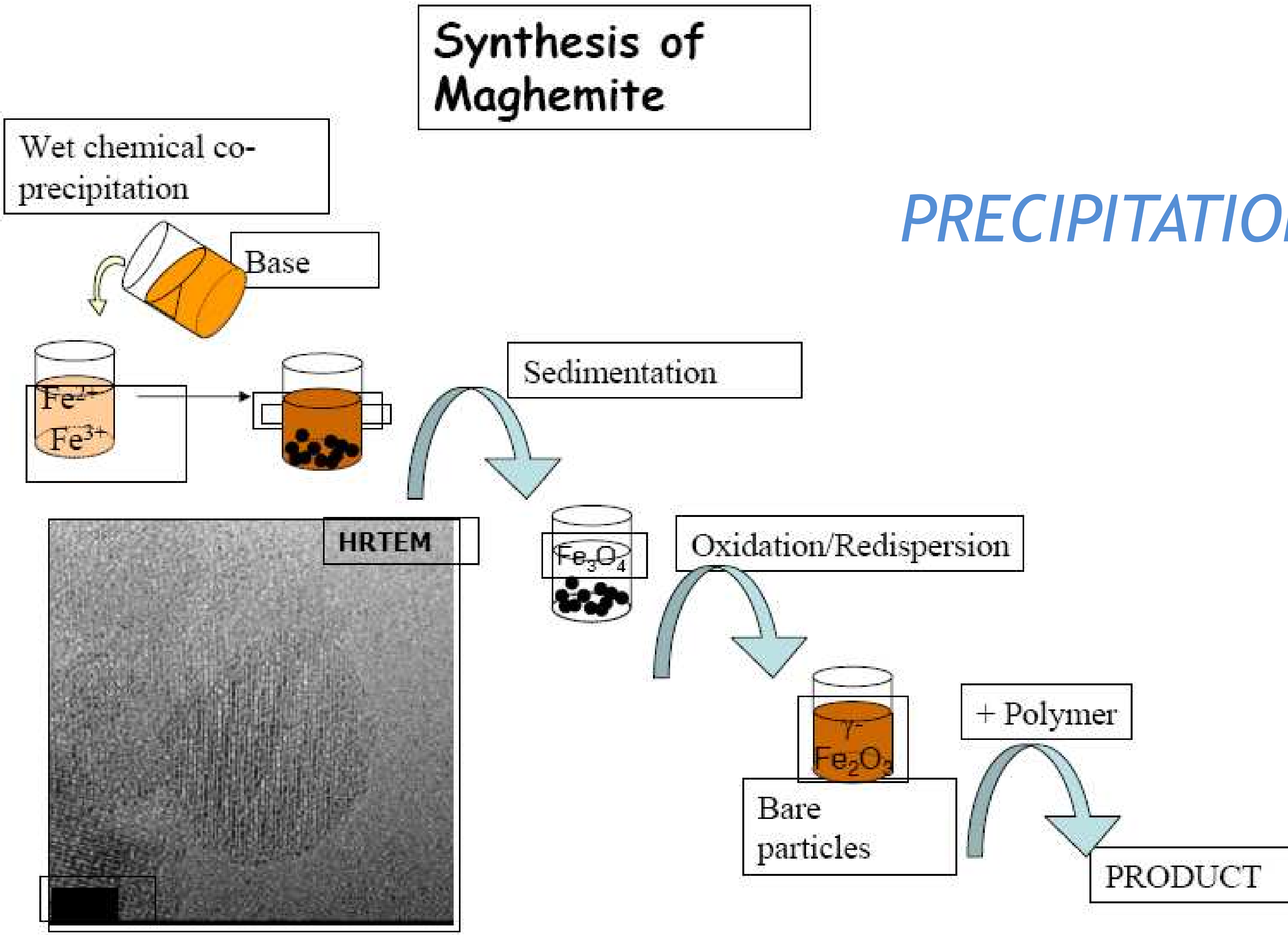
Several methods are possible, e.g.

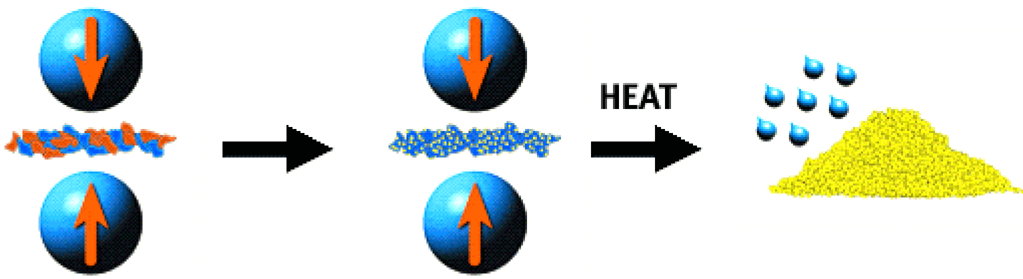
- Precipitation
- Milling
- Reduction
- Condensation

They can be synthesized in the solid, liquid or gaseous phase.

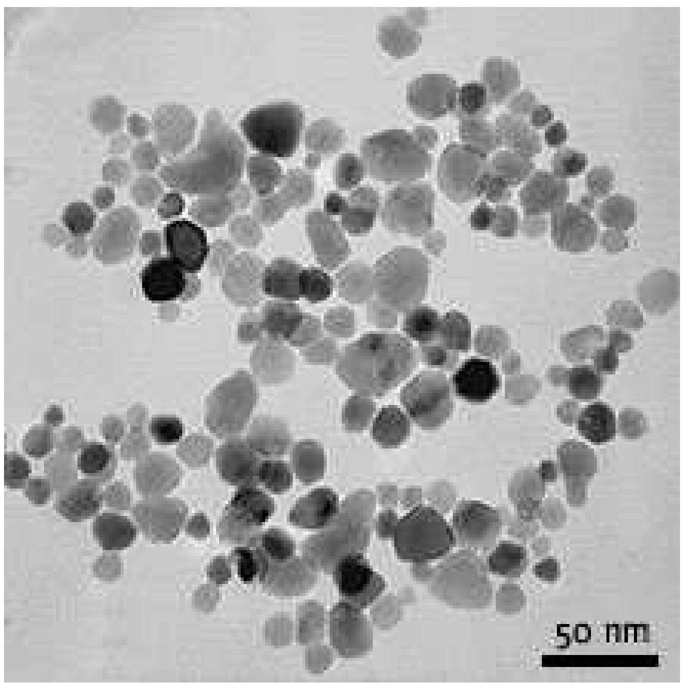
***SOME EXAPLES... >>***

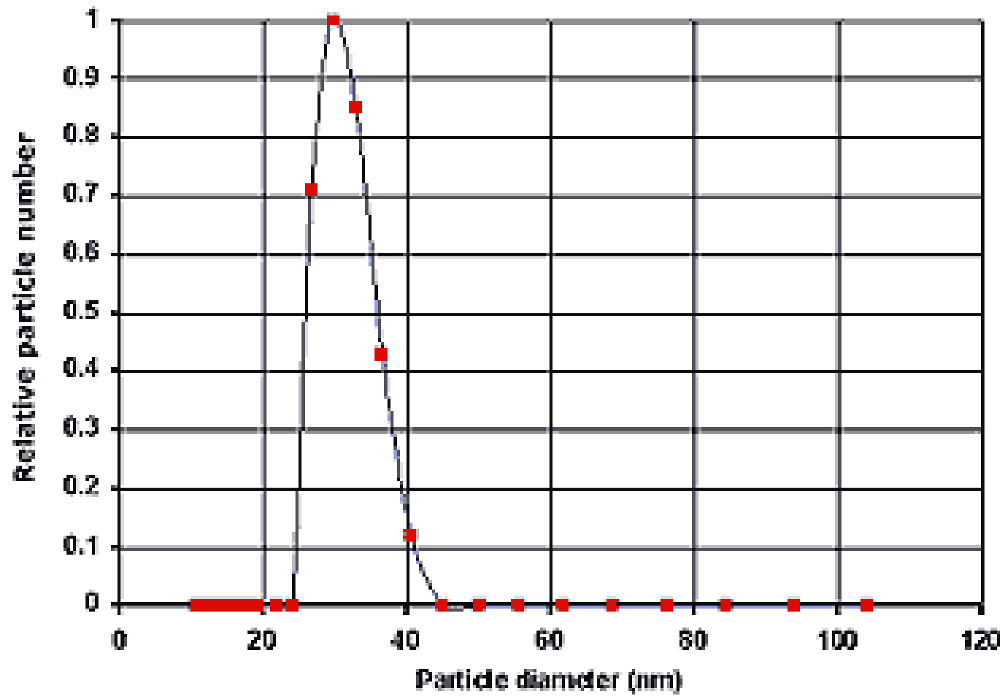
# PRECIPITATION





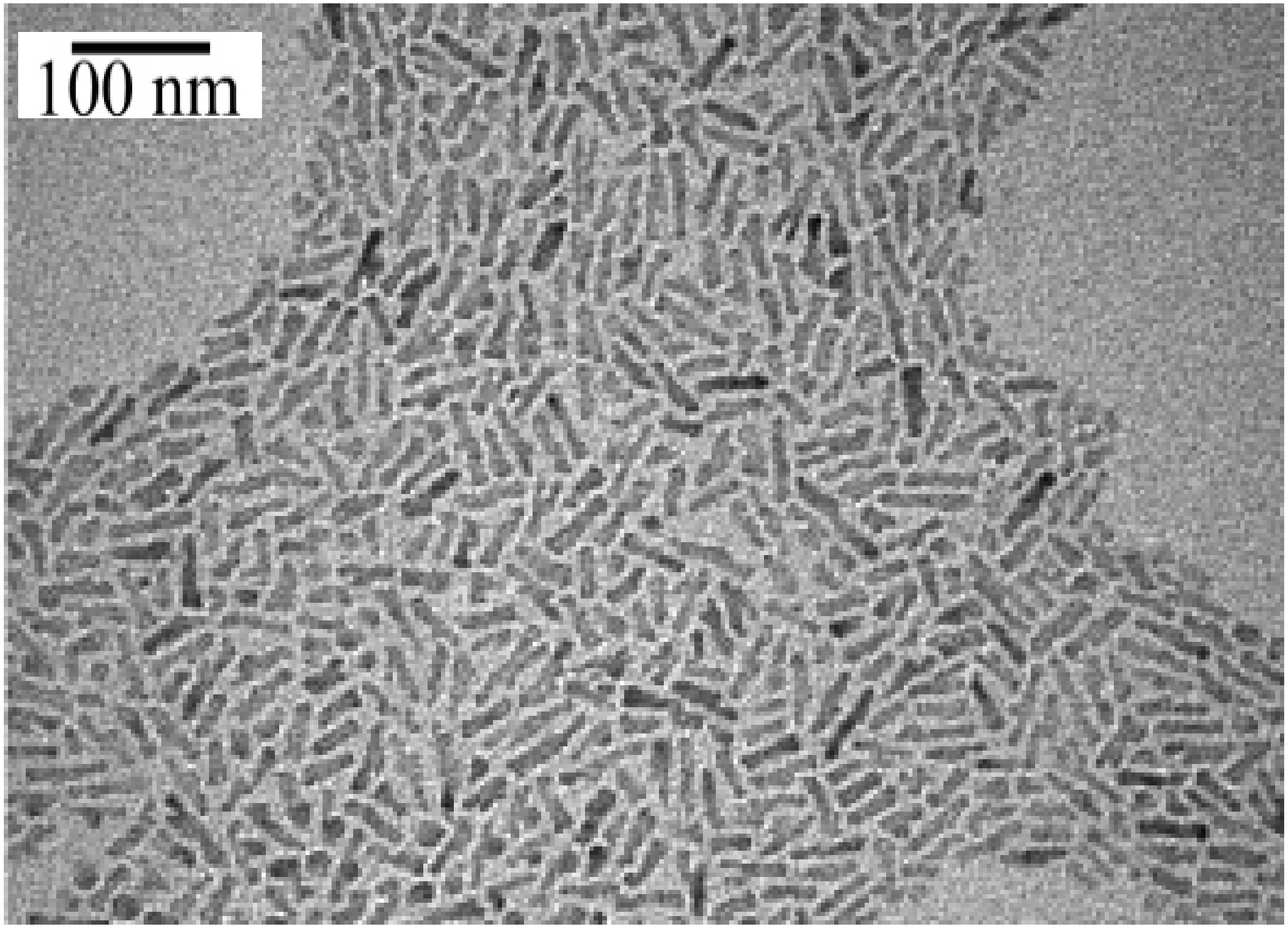

# *MILLING*




Transmission electron micrograph of ~30nm zinc oxide

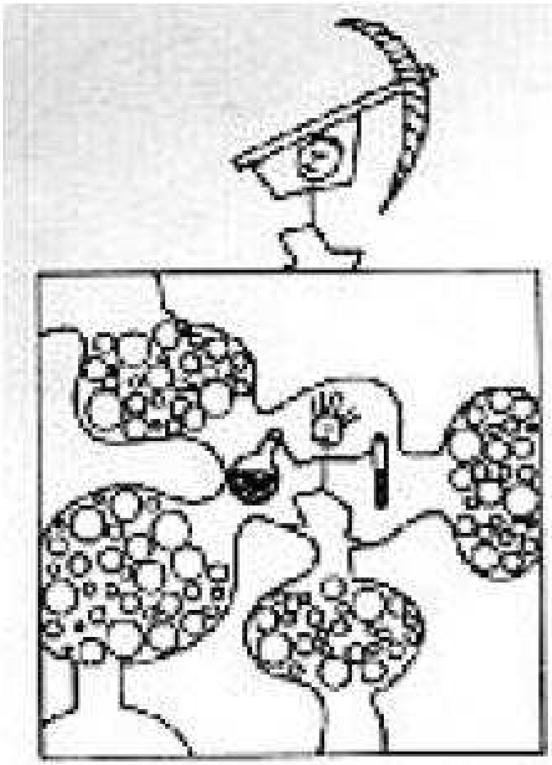
Particle size distribution curve for MCP ~30nm ZnO nanopowder showing a mean particle size of 30nm




$TiO_2$ Nanorods ≈ 10 nm

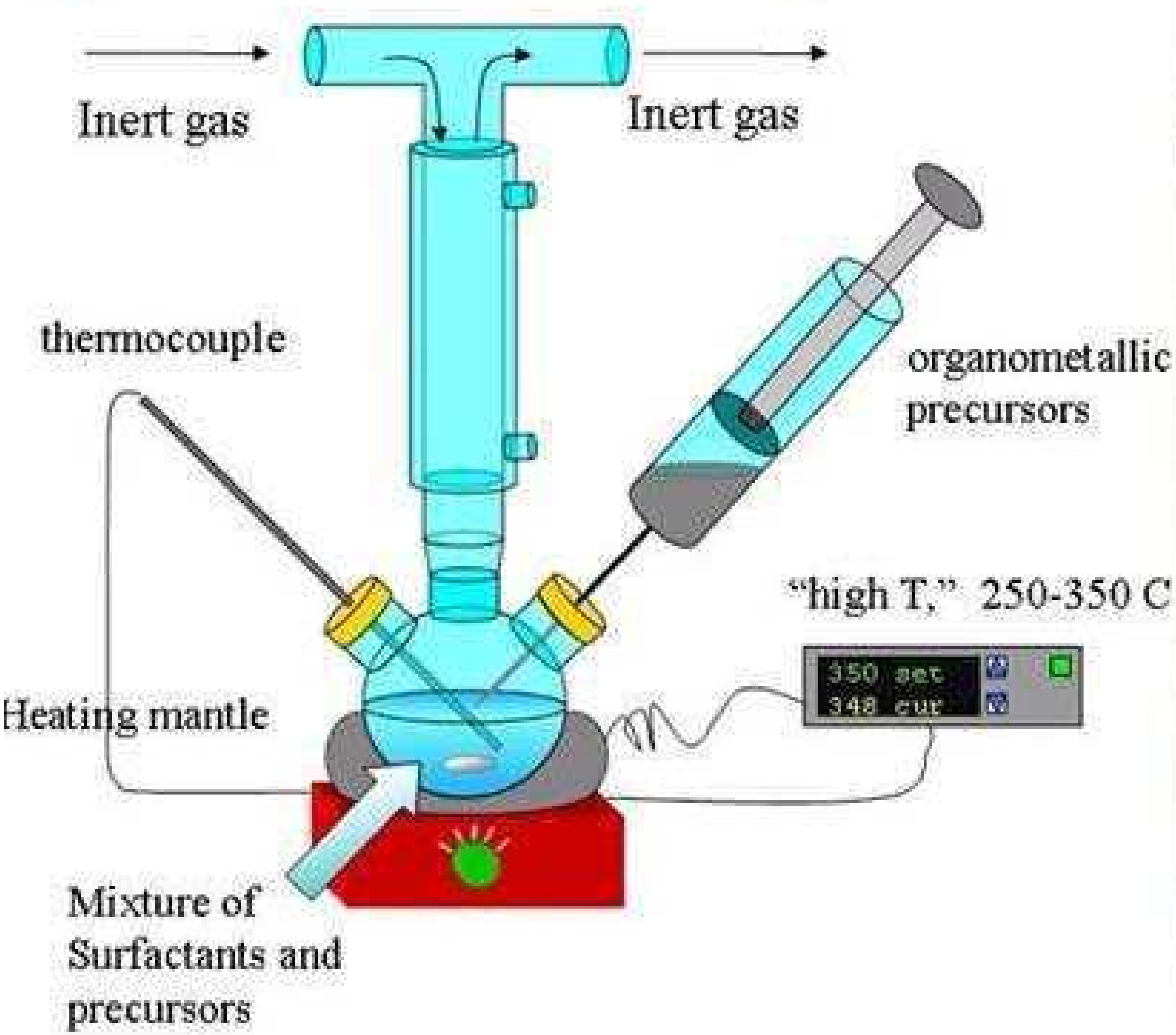
## “Nanochemistry and Nanophysics”

Nanochemistry can be described as a special discipline of inorganic or solid state chemistry. It focuses on the **synthesis** of nanoparticulate systems. The nanochemist can be considered to work towards this goal from the atom „up“, whereas the nanophysicist tends to operate from the bulk „down“:

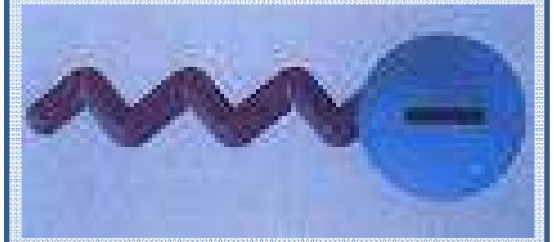


G. A. Ozin *Adv. Mater.* 4/10 (1992) 612ff.

# *“BOTTOM-UP” APPROACH: hot-injection method*



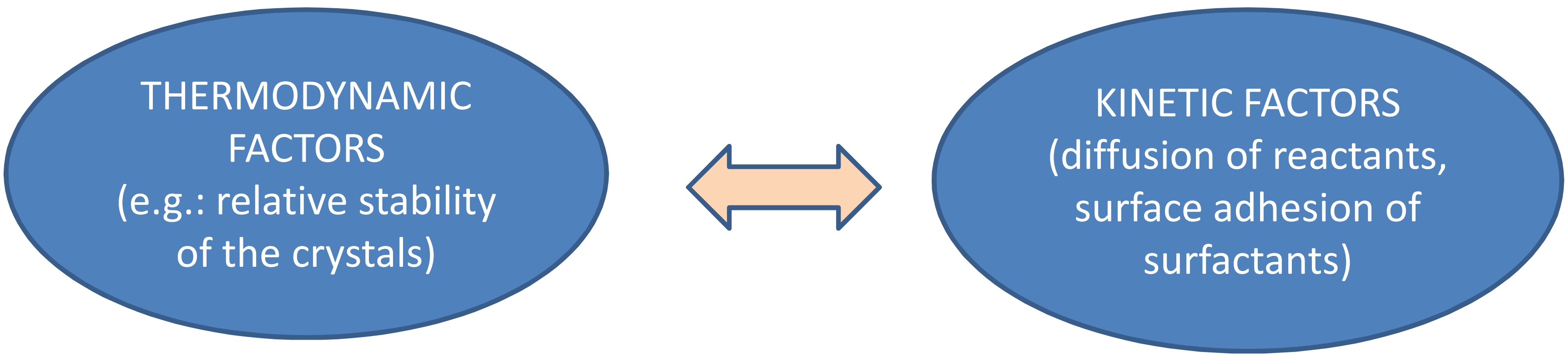

Surfactants are amphiphilic molecules composed of a polar head group and of one or more hydrocarbon chains with hydrophobic character.



They:

i) act as terminating or stabilizing agents insuring slow growth rate,
ii) prevent the agglomeration
iii) confer stability and processability

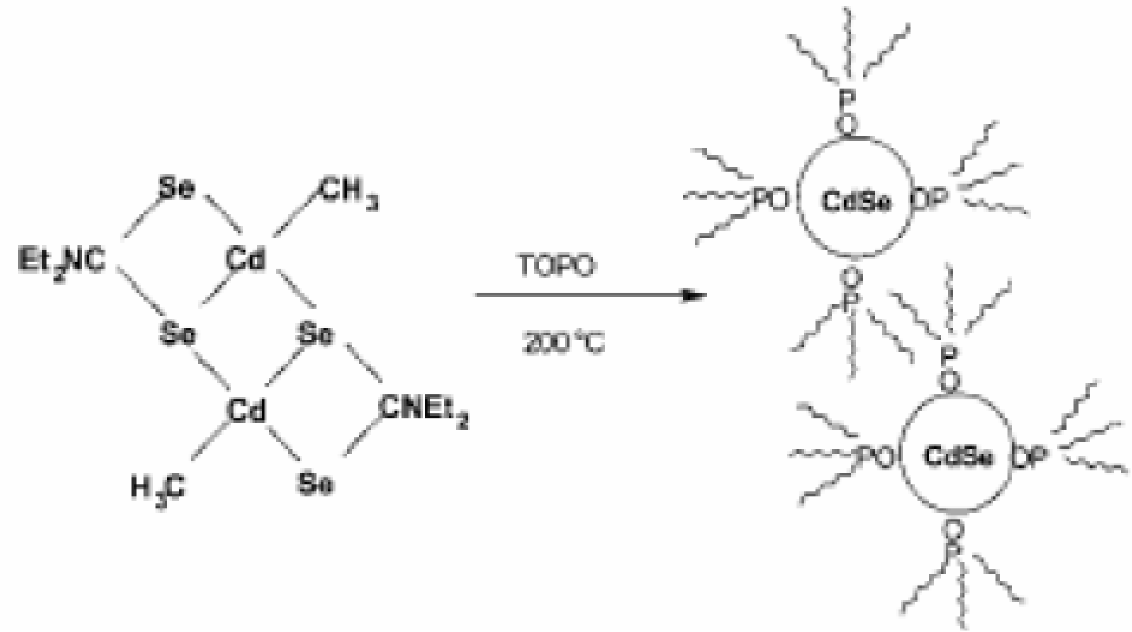
# SYNTHESIS OF NANOCRYSTALS




Experimental conditions to be controlled:

- ✓ nature and relative concentration of molecular precursors;
- ✓ catalysts;
- ✓ organic stabilizers;
- ✓ growth temperature

# Example CdSe

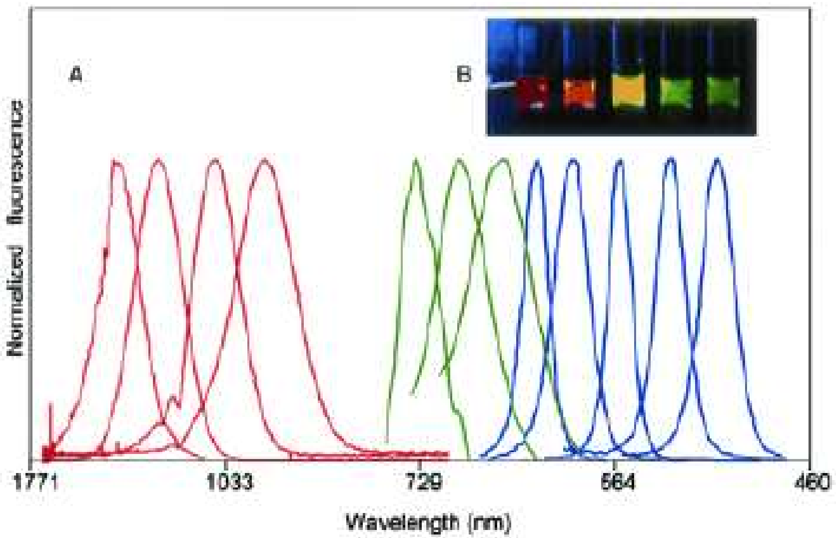



Preparation of semiconductor nanocrystallites:

Solutions of (CH3)2Cd and tri-*n*-octylphosphine selenide (TOPSe) are injected into hot tri-*n*-octylphosphine oxide (TOPO) in the temperature range 120-300 °C. This produced TOPO capped nanocrystallites of CdSe.

C. B. Murray and C. R. Kagan and M. G. Bawendi Annu. Rev. Mater. Sci. 2000. 30:545–610

# Quantum-dots

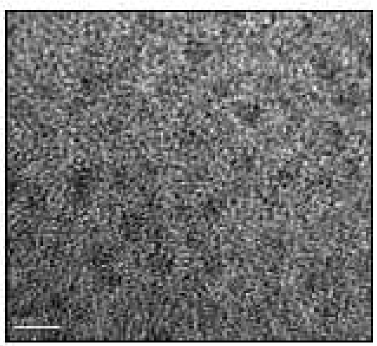



Size- and material-dependent emission spectra of several surfactant -coated semiconductor nanocrystals in a variety of sizes (**A**).
Blue series: different sizes of CdSe (Diameter : 2.1, 2.4, 3.1, 3.6, 4.6 nm)
Green series: InP nanocrystals (Diameter: 3.0, 3.5, and 4.6 nm)
Red series: InAs nanocrystals (Diameter: 2.8, 3.6, 4.6, 6.0 nm)
(**B**) A true-color image of a series of silica-coated core (CdSe)-shell (ZnS or CdS) nanocrystal probes in aqueous buffer, all illuminated simultaneously with a handheld ultraviolet lamp

Synthesis: There are many wet chemical methods of synthesis for semiconductor nanoparticles, a organic and an inorganic method are presented here:

$$Cd^{2+} + Se^{2-} \xrightarrow[\text{Stabilizer } L_n]{} CdSeL_n$$

**Optimized synthesis parameters:**
9<pH<12.5
Surfactant: Thioalcohols/Thioacids
Atmosphere: inert gas

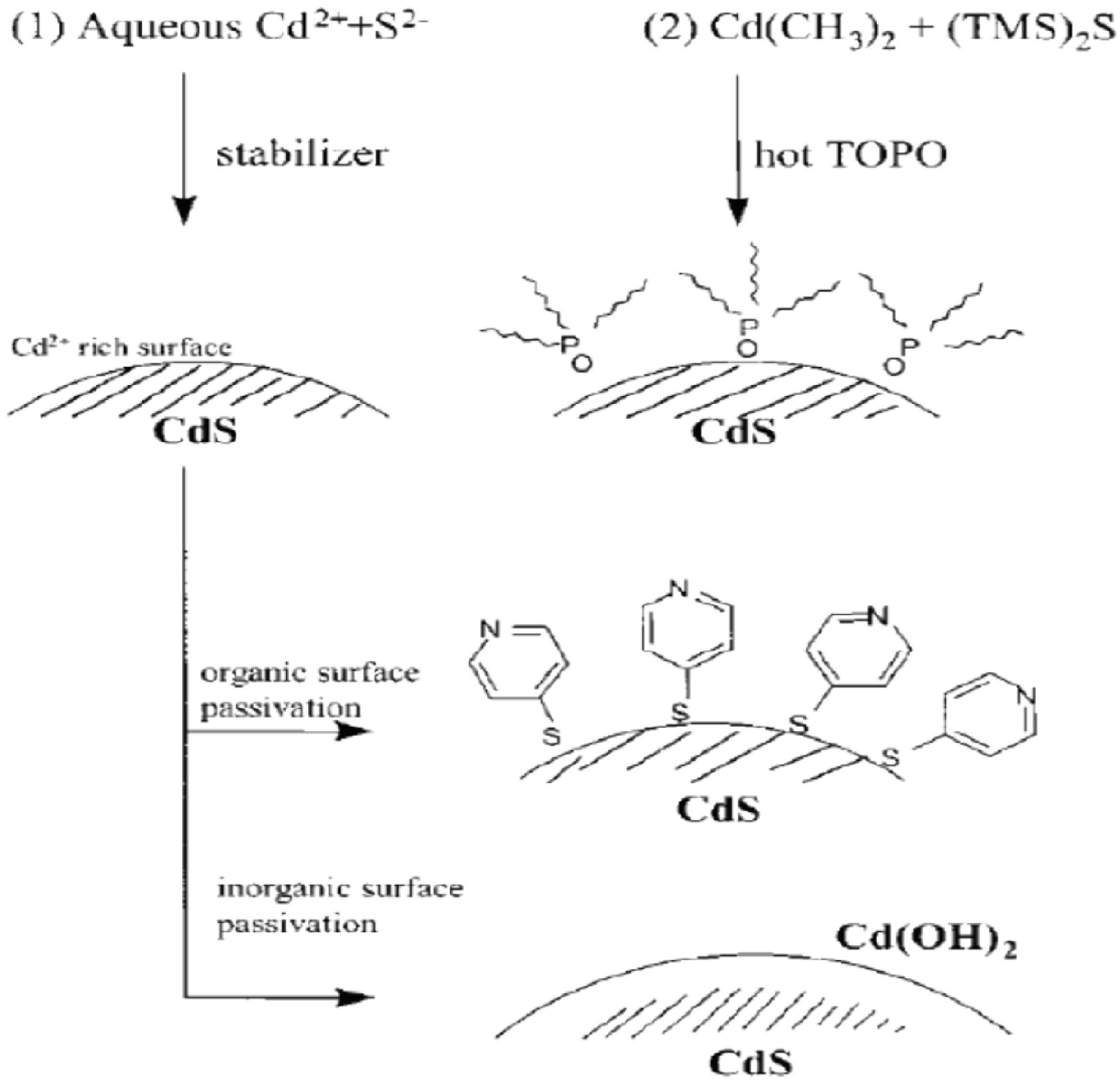


Transmission electron micrograph of CdSe

$$[Me_2Cd] + [(TMS)_2Se] \xrightarrow{\text{TOP/TOPO}} CdSe$$

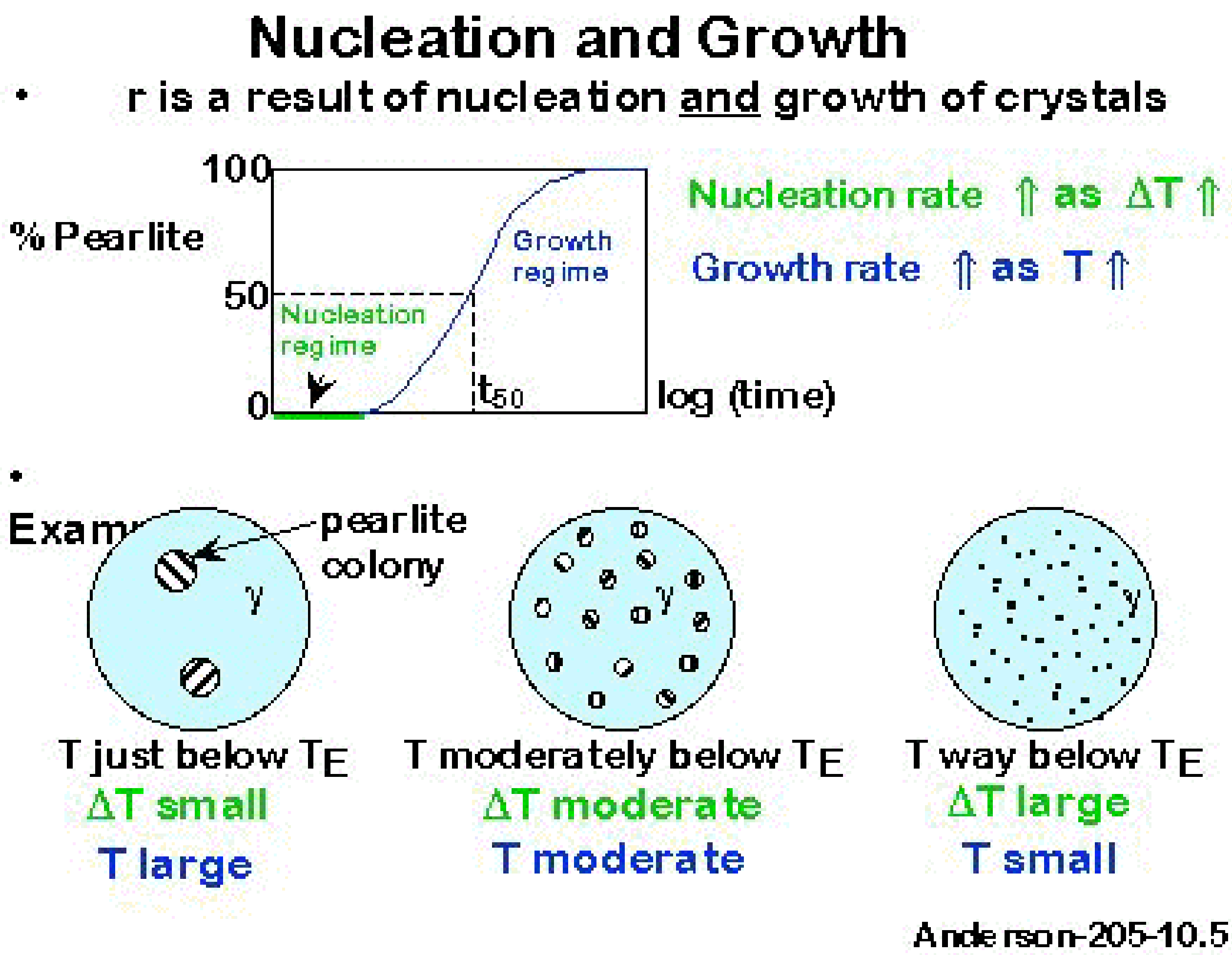
**Optimized synthesis parameters:**
230 < T < 260°C
Surfactant: TOP/TOPO
Atmosphere: inert gas

A. P. Alivisatos *J.Phys.Chem.* 100/31 (1996) 13226ff.



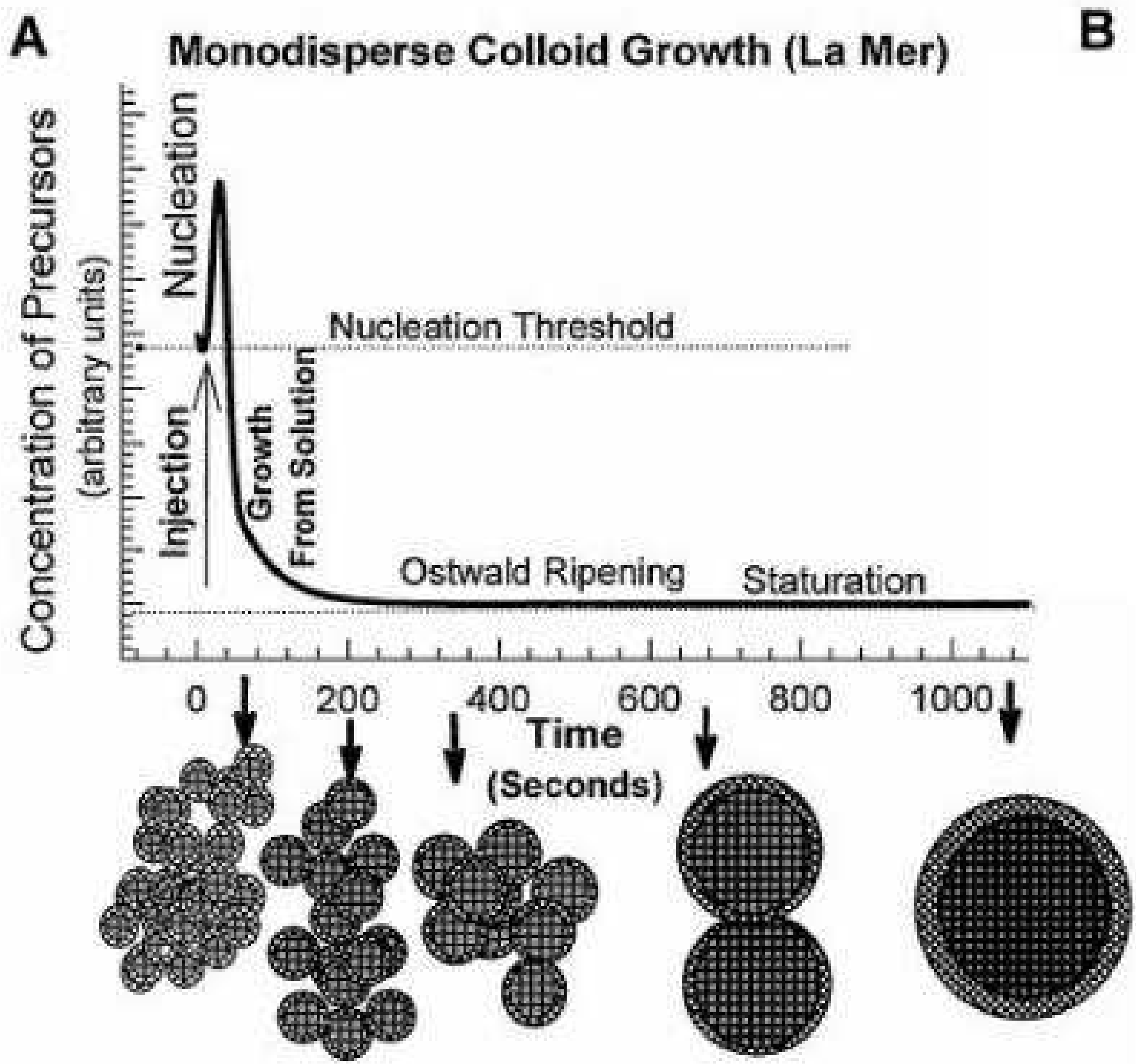
(1) Aqueous $Cd^{2+}+S^{2-}$
(2) $Cd(CH_3)_2$ + $(TMS)_2S$
stabilizer
hot TOPO
$Cd^{2+}$ rich surface
CdS
P
O
CdS
organic surface passivation
N
S
CdS
inorganic surface passivation
$Cd(OH)_2$
CdS

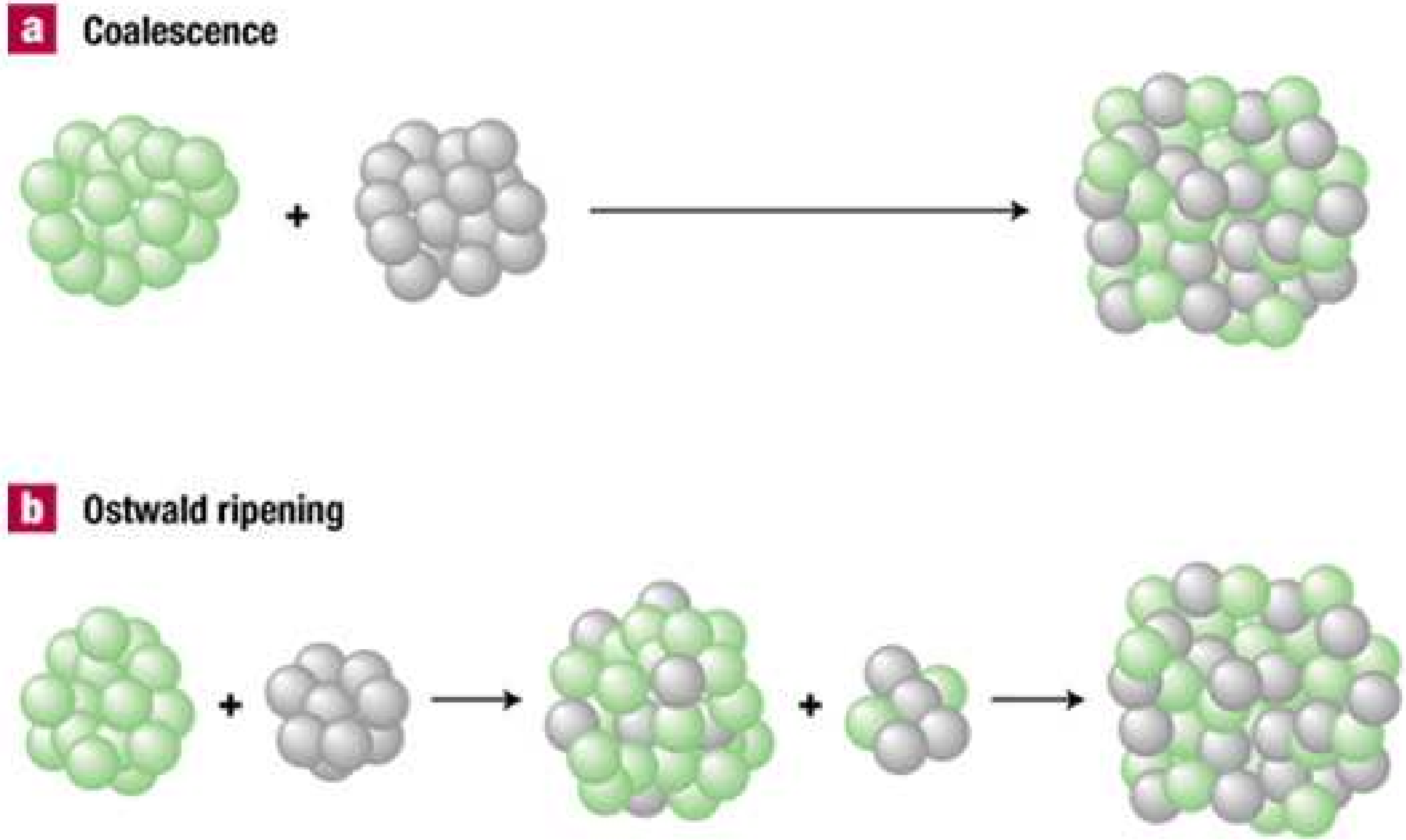
# *Size control*




*Ostwald ripening*

# Size control

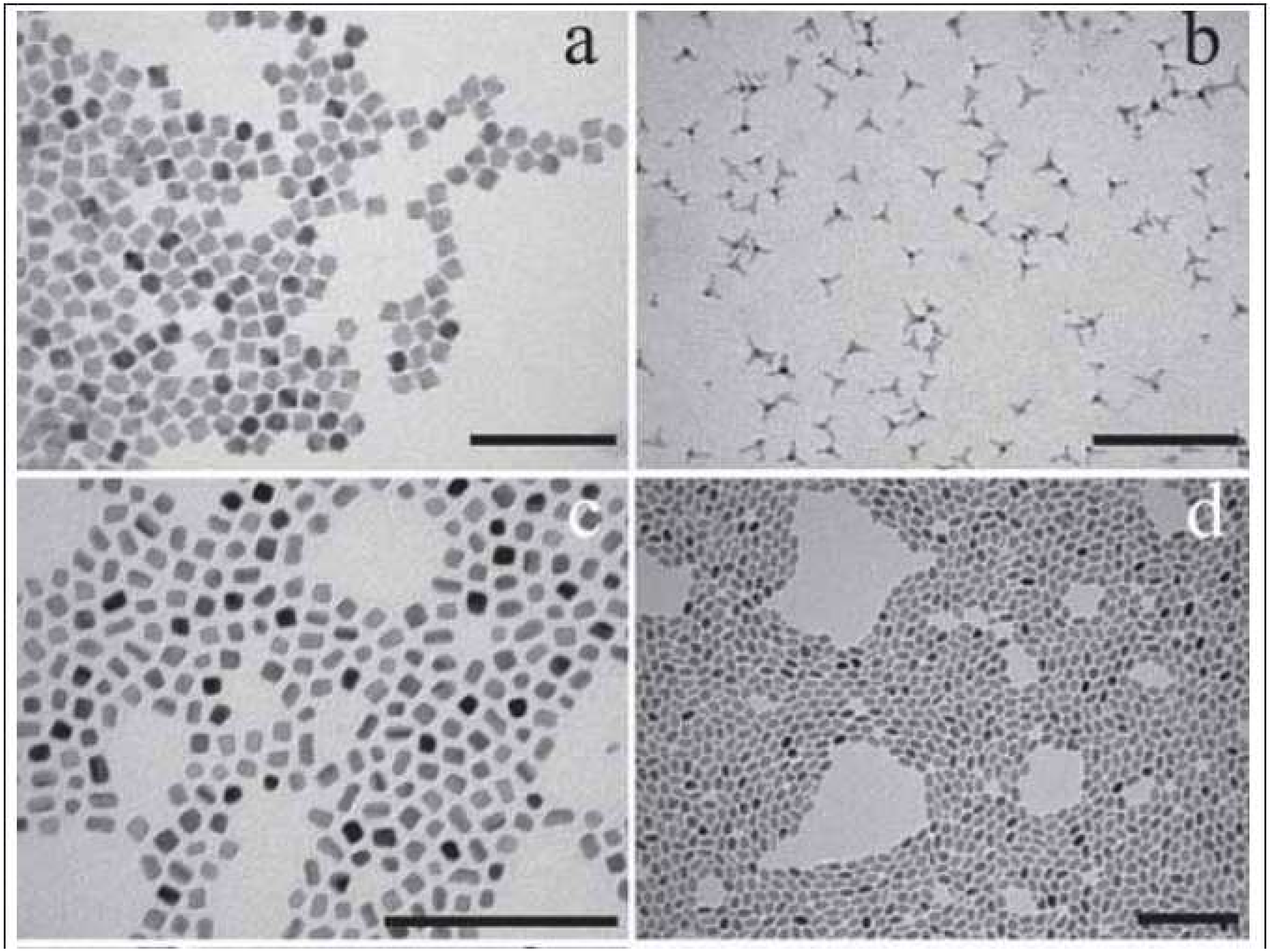



a
Coalescence
b
Ostwald ripening

# *Shape control*

$\gamma$-$Fe_2O_3$ tetrapods

Star-like PbSe




FePt faceted NCs

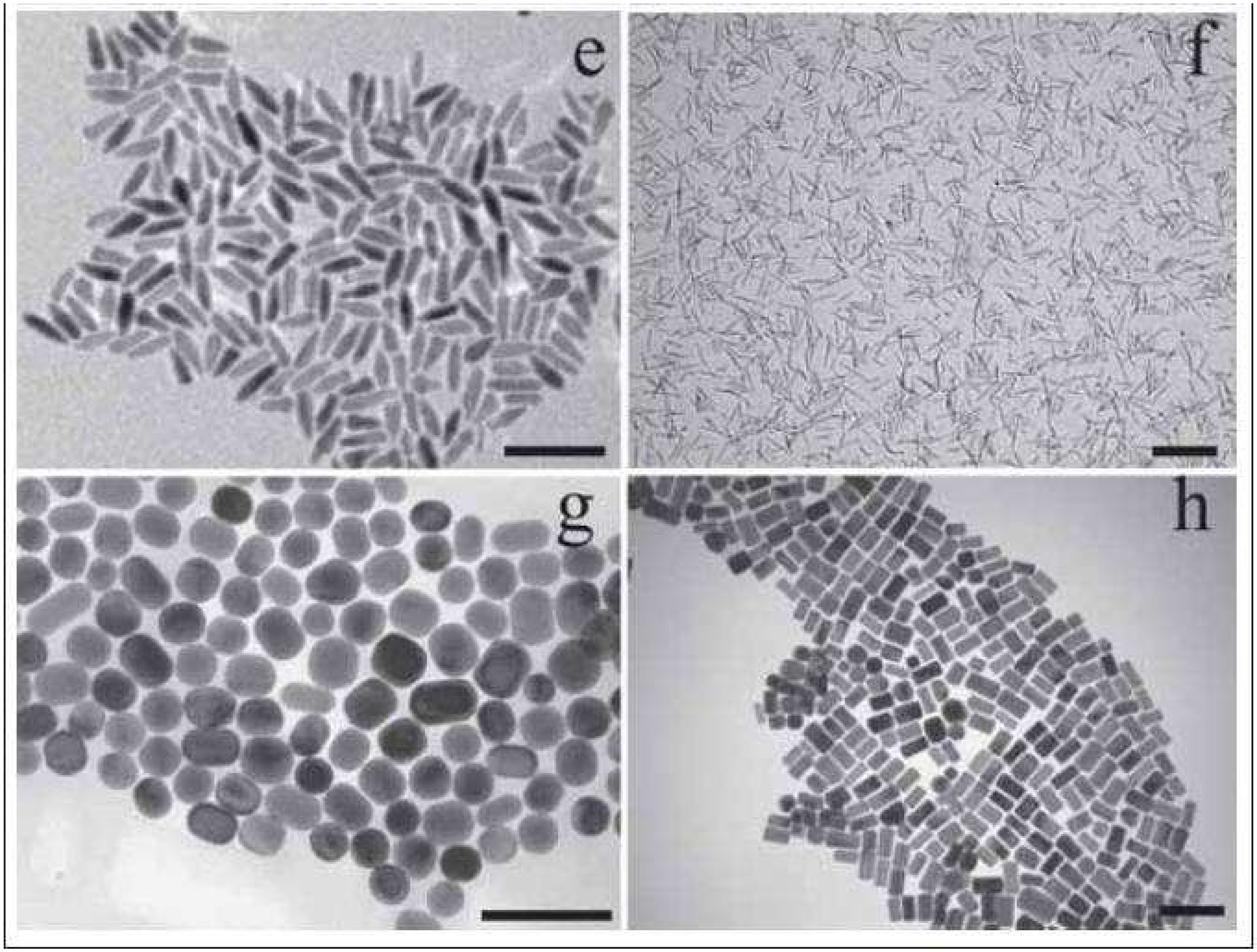
rise-shaped CdSe

Scale bar = 100 nm

# *Shape control*

Pencil-shaped CdS NCs

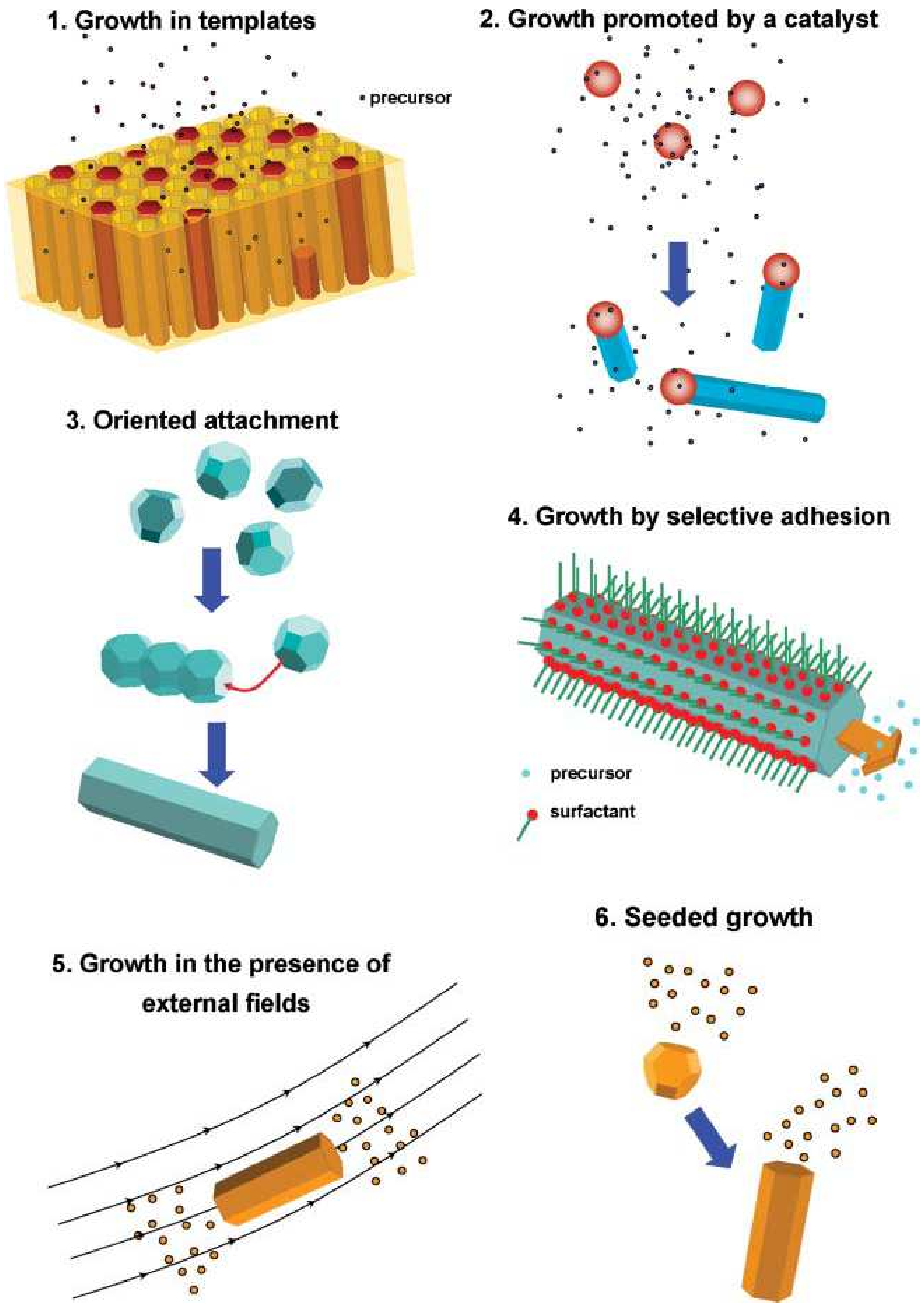
$TiO_2$ NCs




Ag spheroids

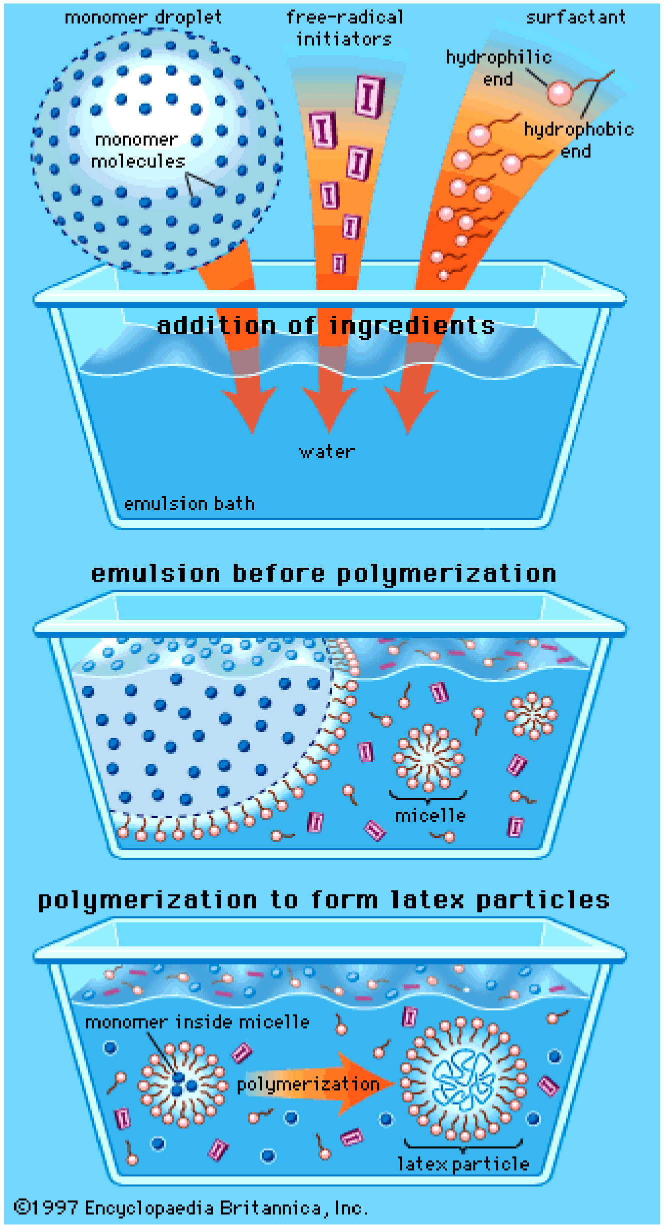
Rectangular-shaped Au nanorods

Scale bar = 100 nm

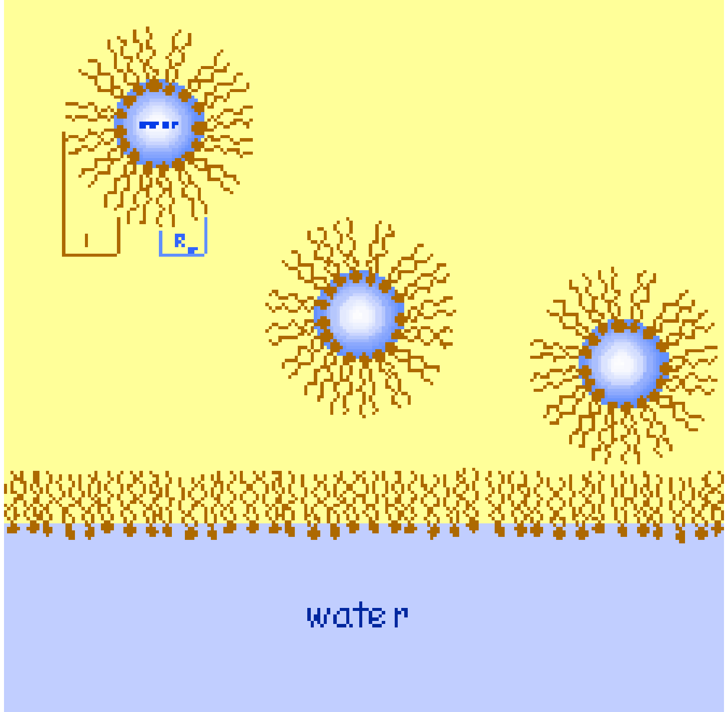



# STRATEGIES FOR SHAPE SELECTION

WATER




ORGANIC SOLVENT

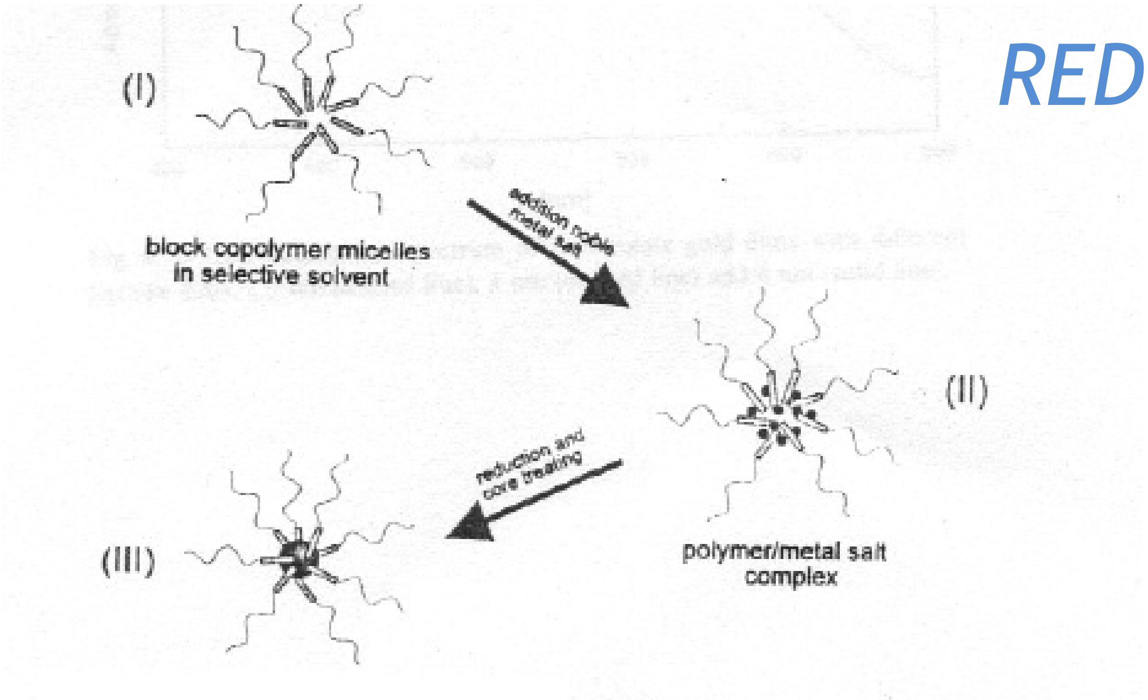



SURFACTANTS ACT BY:

❖ POSING PHYSICAL CONSTRAINS TO THE UNCONTROLLED NCs ENLARGEMENT DURING THE SYNTHESIS;

❖ COMPLEXING AGENT AVOIDING THE AGGREGATION OF THE NCs AFTER THE SYNTHESIS

# Gold particles in micelles



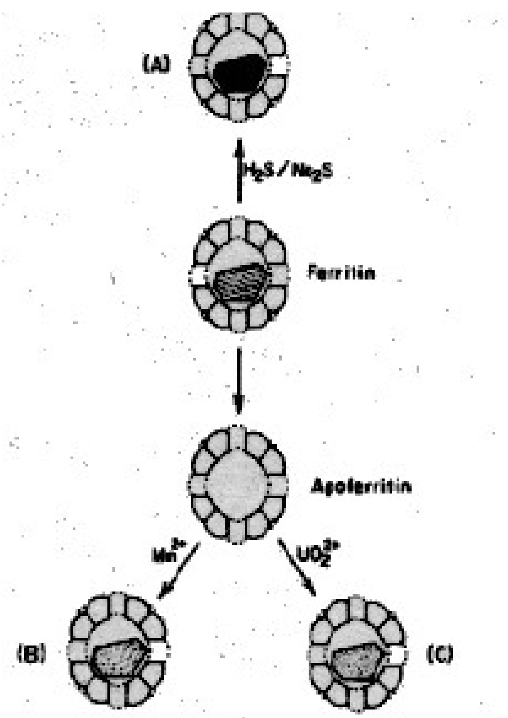

REDUCTION

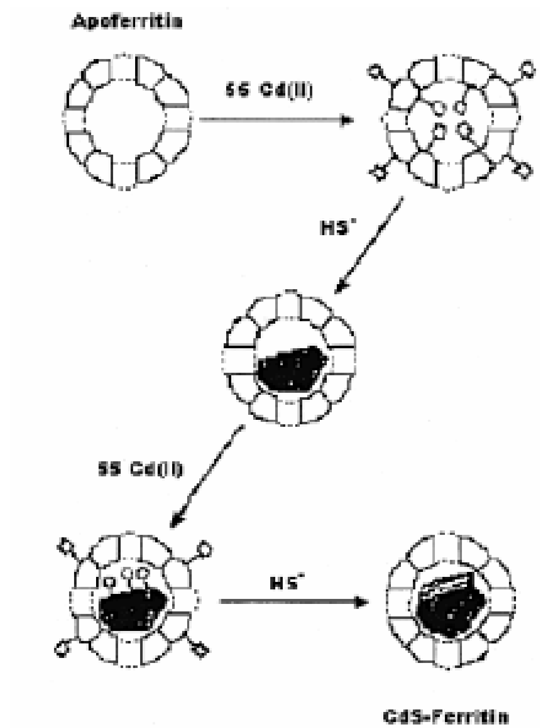
Synthesis: A-B diblock copolymer is used for micelle formation
Polymer: Poly(styrene-block-2-vinyl-pyridine)
Idea: An inorganic compound such as HAuCl4 is bound selectively to the Polyvinylpyridine block of the polymer and thus solubilized within the core of the micelle. Afterwards, the compound is transformed by chemical reaction to the metal.

J. P. Spatz, A. Roescher, M. Möller *Adv. Mater.* 8/4 (1996)

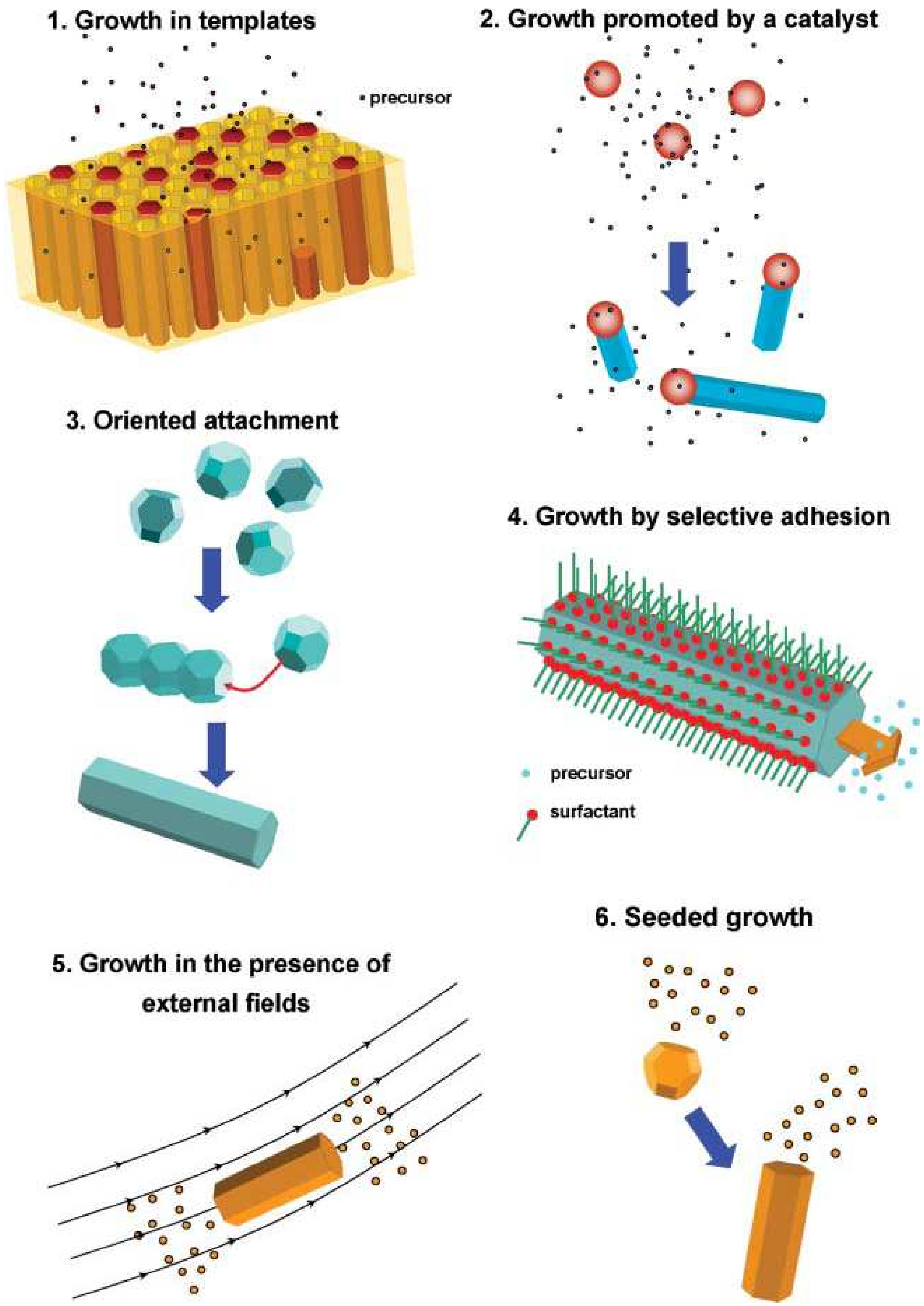
# Synthesis in a Structured Medium

A number of matrices have been used for the preparation of semiconductor nanoparticles including: zeolites, layered solids, molecular sieves, micelles/microemulsions, gels, polymers, and glasses. These matrices can be viewed as nano-chambers which limit the size to which crystallites can grow. The properties of the nanocrystallites are determined, not only by the confinements of the host material but also by the properties of the system, which include the internal/external surface properties of the zeolite and the lability of micelles.



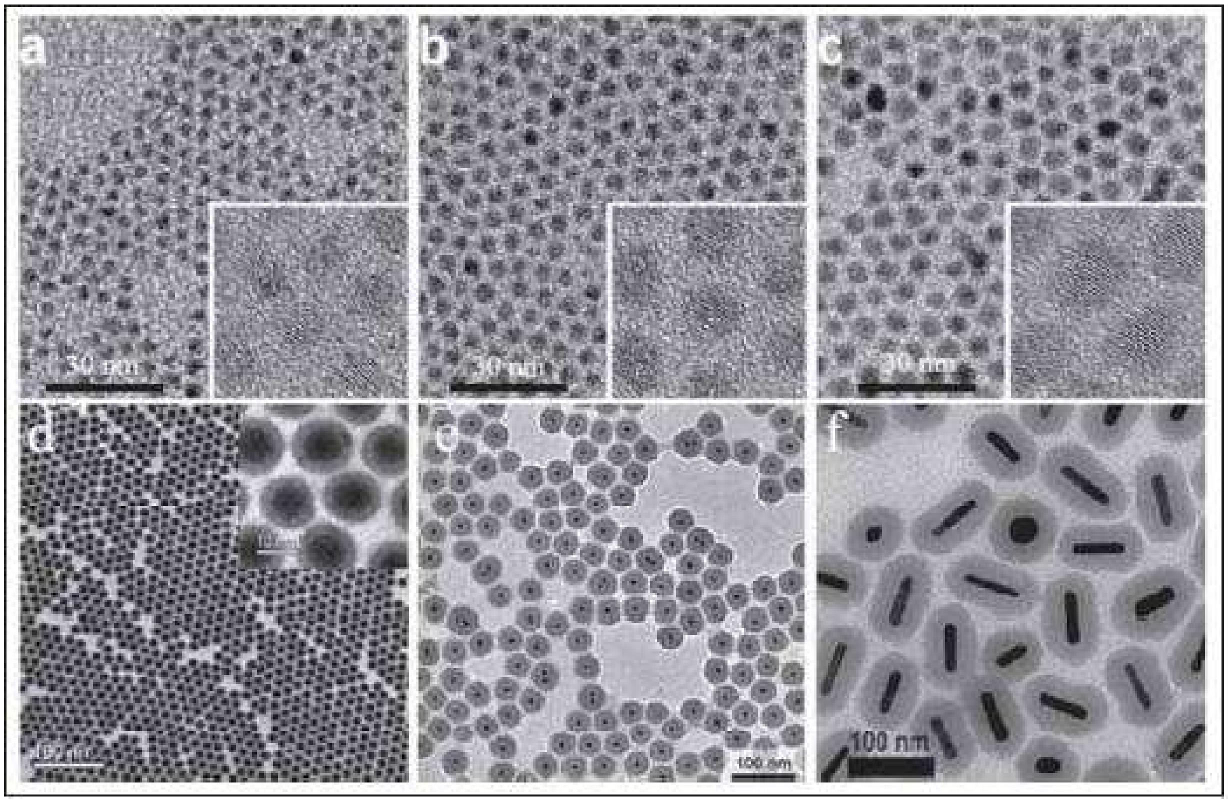

**Nanocrystalline Semiconductors: Synthesis, Properties, and Perspectives (review)** Tito Trindade et al. *Chem. Mater.* **2001,** *13,* 3843-3858




# STRATEGIES FOR SHAPE SELECTION

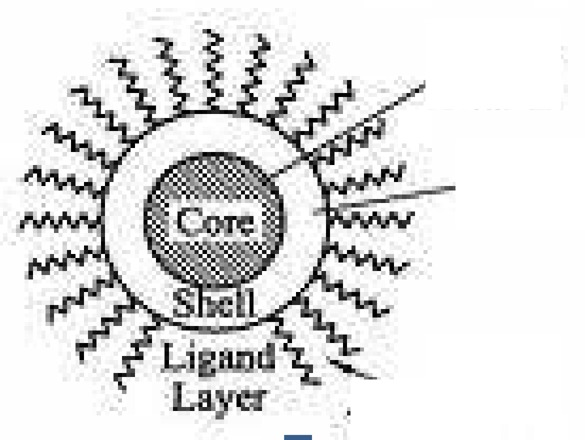
# HYBRID NANOCRYSTALS

a CdSe; b CdSe/CdS; c CdSe/CdS/ZnS




d $Fe/Fe_3O_4$; e $FePt/SiO_2$; f Au nanorods/$SiO_2$

*ONION-LIKE STRUCTURES*

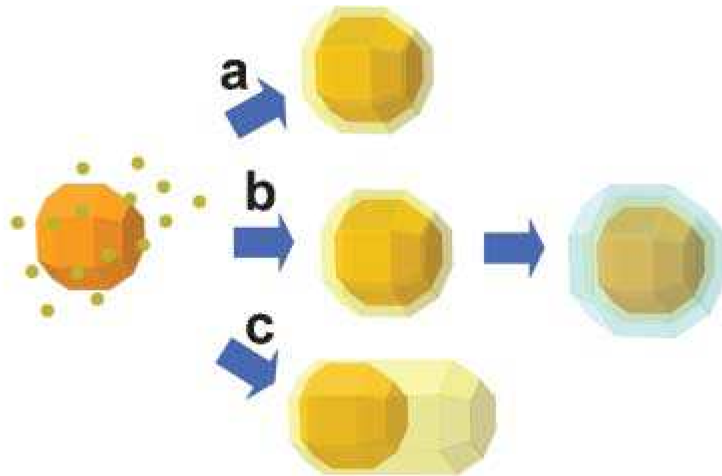



Large interphase between the two materials

Lattice constants do not differ significantly

# SKETCH OF POSSIBLE MECHANISMS FOR CORE–SHELL NANOCRYSTAL HETEROSTRUCTURES

1




GROWTH OF A SINGLE, A MULTIPLE OR AN ASYMMETRIC SHELL ON NANOCRYSTAL CORE

2

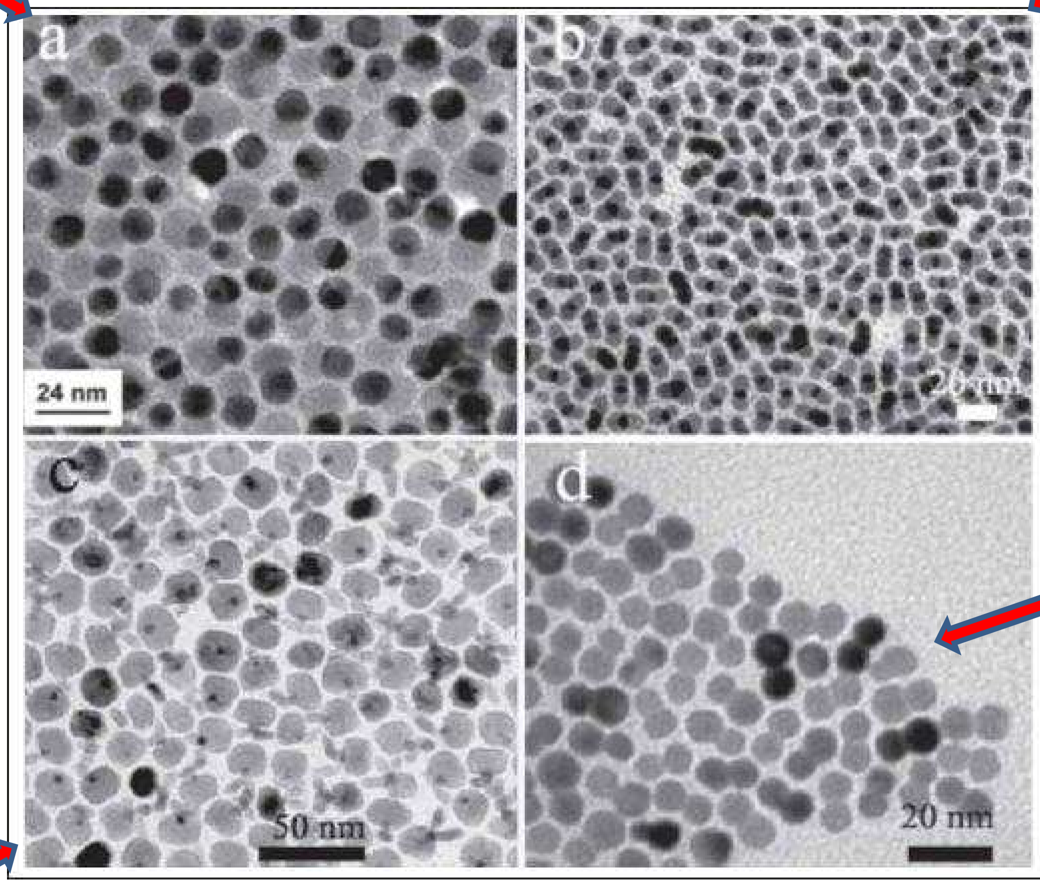

SHELL FORMATION FOLLOWING A REDOX REACTION WITH THE INITIAL CORE

3


FORMATION OF A UNIFORM SHELL UPON THERMAL ANNEALING OF AN INITIALLY AMORPHOUS AND/OR DISCONTINUOUS COATING

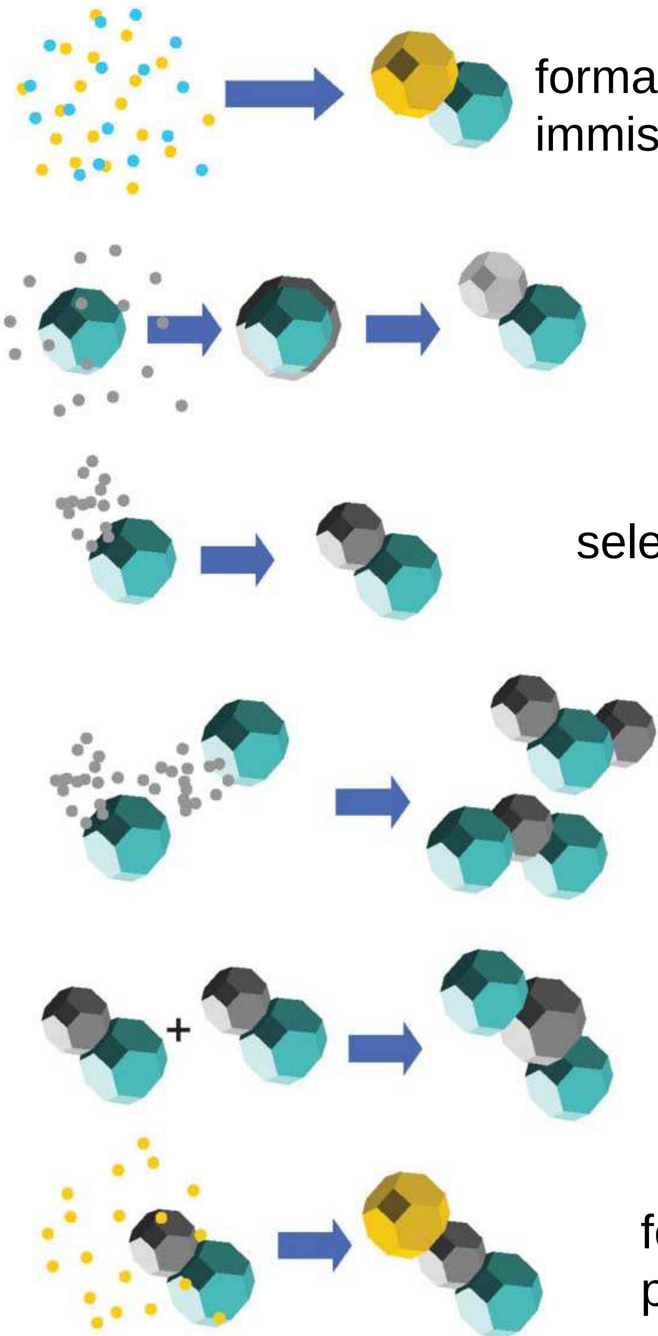
Dumbbell-like $Fe_3O_4$-Au dimers

Dumbbell-like PbS-Au-PbS ternary NCs




$CoPt_3$-Au dimers

PbSe nanorod- $Fe_3O_4$-Au ternary NCs



1 formation of a heterodimer by phase segregation of two immiscible materials

2 coalescence of an initially amorphous shell

3 selective nucleation on a starting seed

4 growth of a trimer upon formation of a domain which bridges two preformed NCs

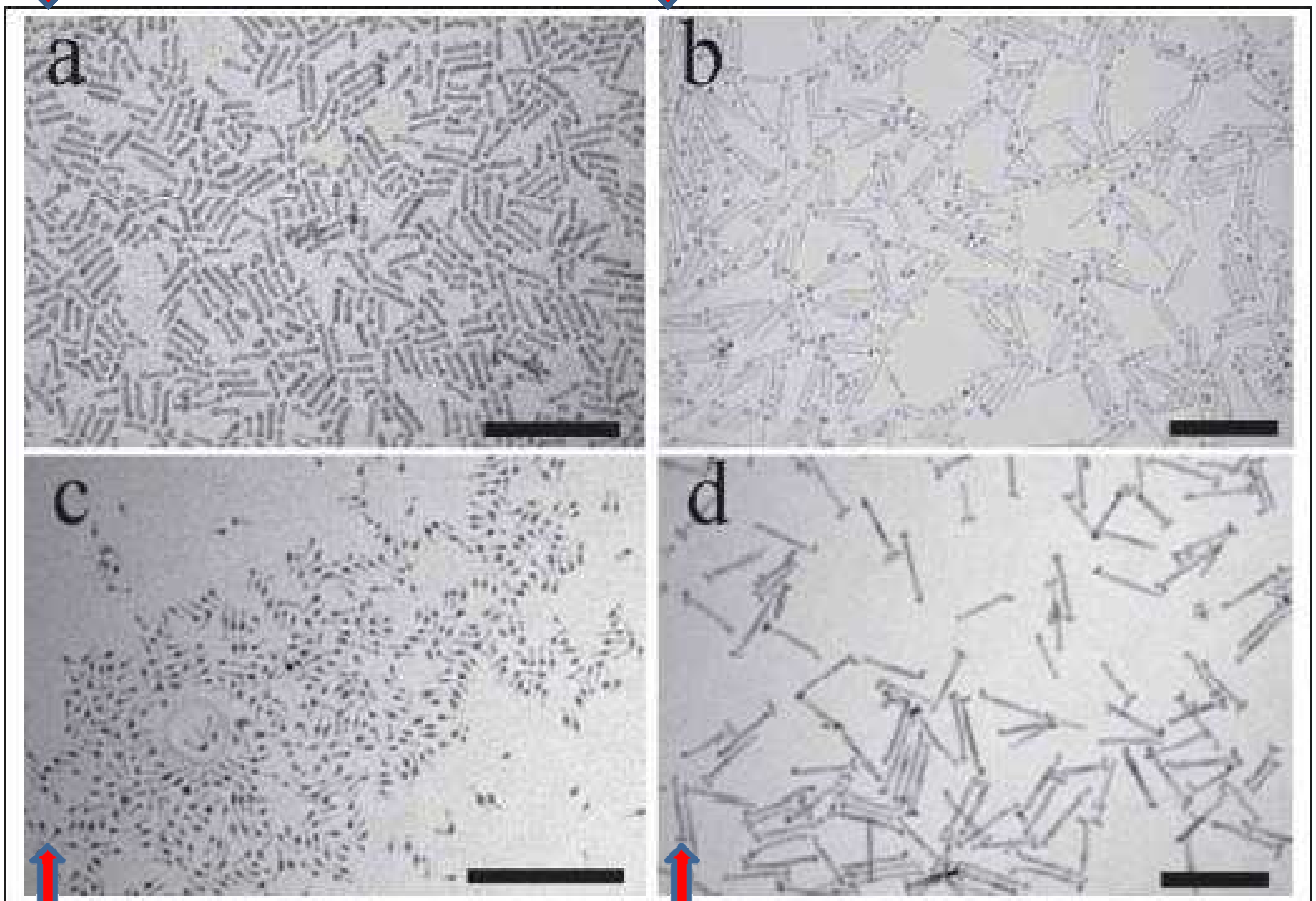
5 formation of a trimer by fusion of two reactive domains from distinct dimers

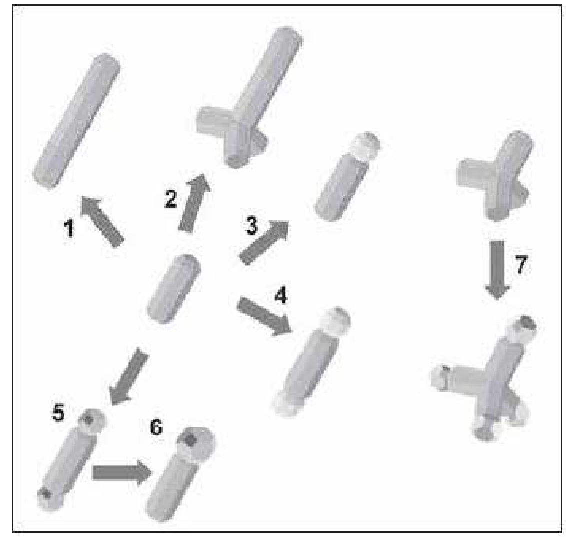
6 formation of a trimer by selective nucleation on a preformed heterodimer seed

Dumbbell-like CdSe nanorods with PbSe tips at the ends

Matchstick-like CdS nanorods with one PbSe tip

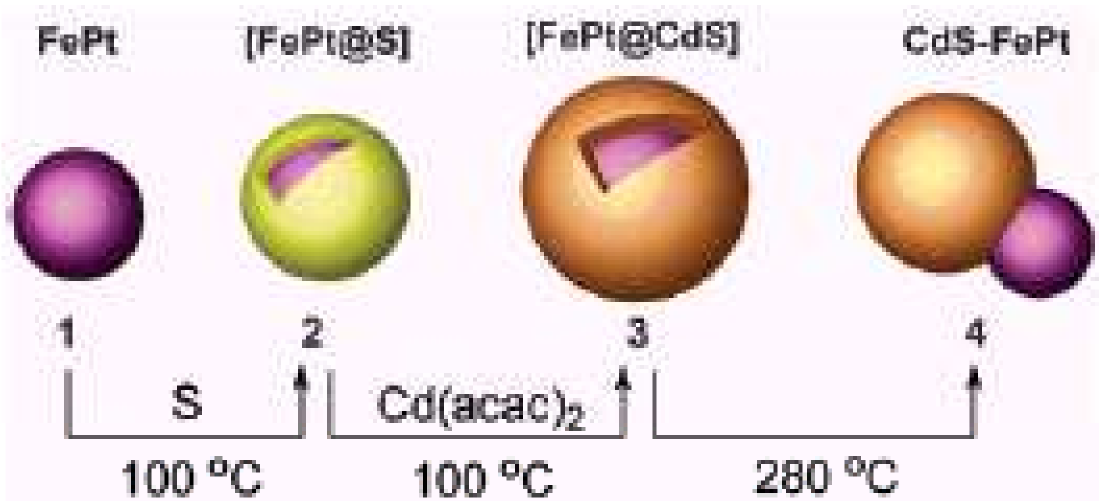
# *USE OF ROD-LIKE SEEDS*



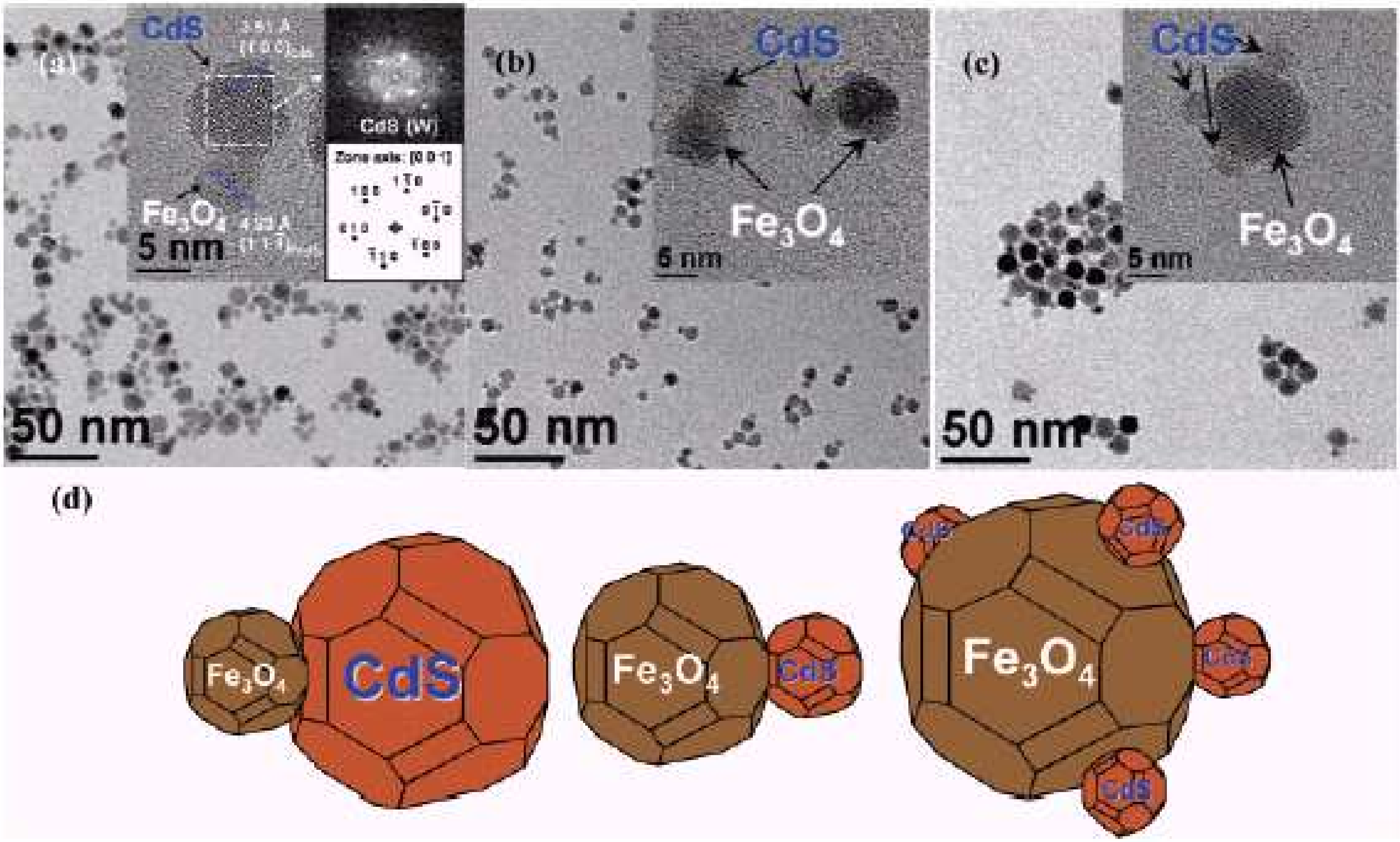

Matchstick-like CdSe nanorods with one Au tip

CdS Nanocrystals made of CdS rods with CdTe tip on one end and a branching point on the opposite end



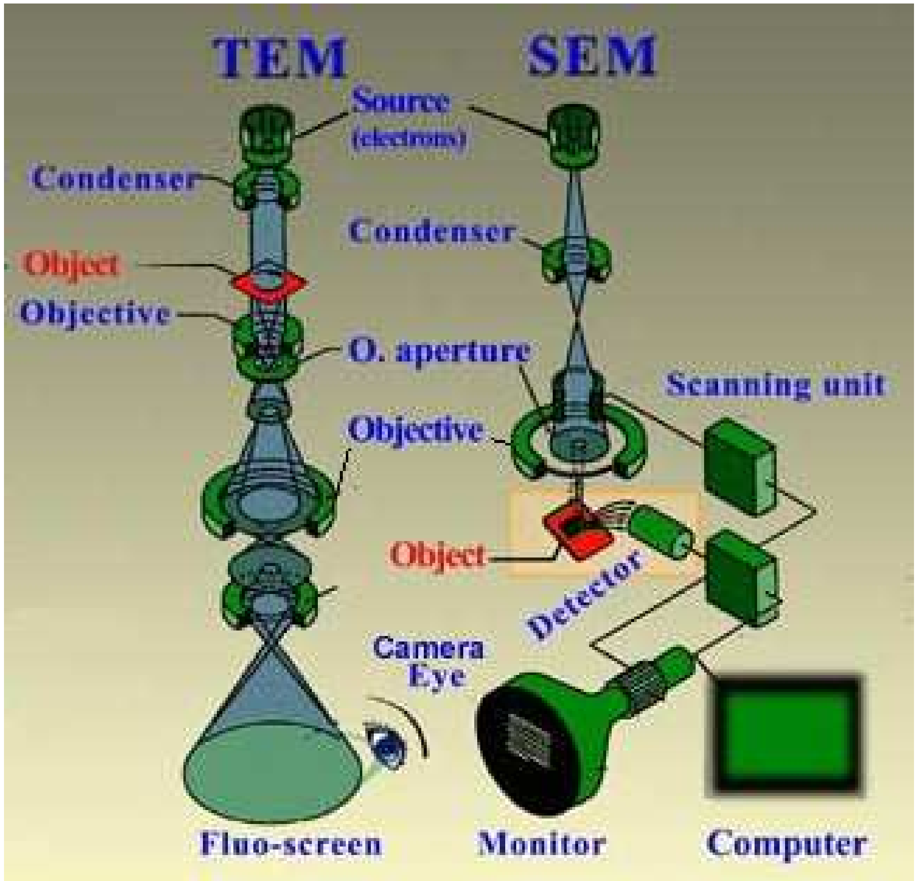

In DOE, TOPO, hexane-1,2-diol and $Cd(acac)_2$

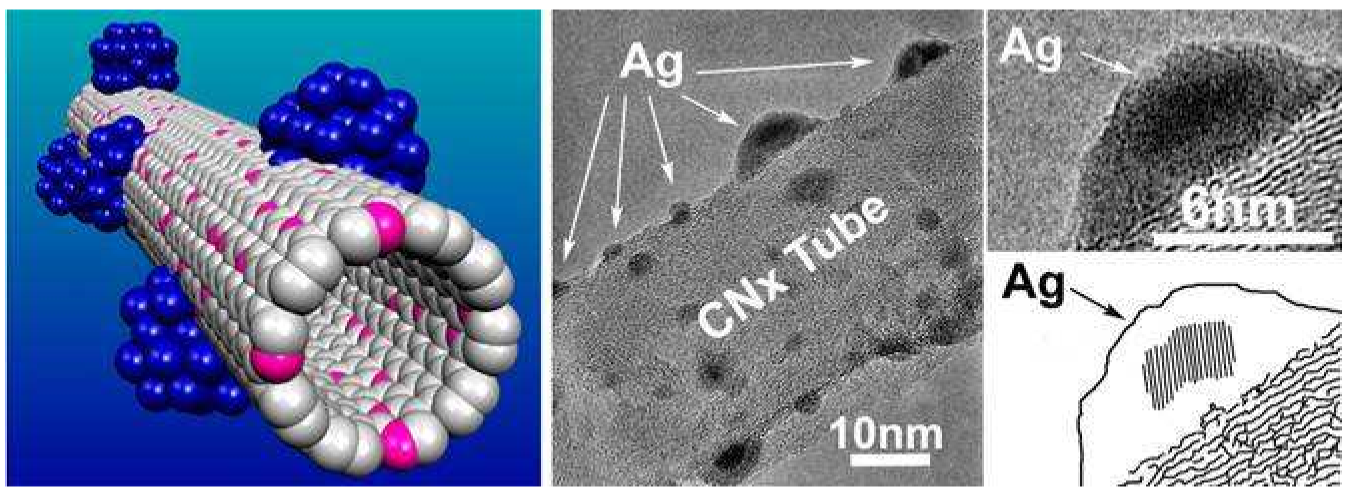
Bing Xu et. Al JACS **2004**, *126*, 5664

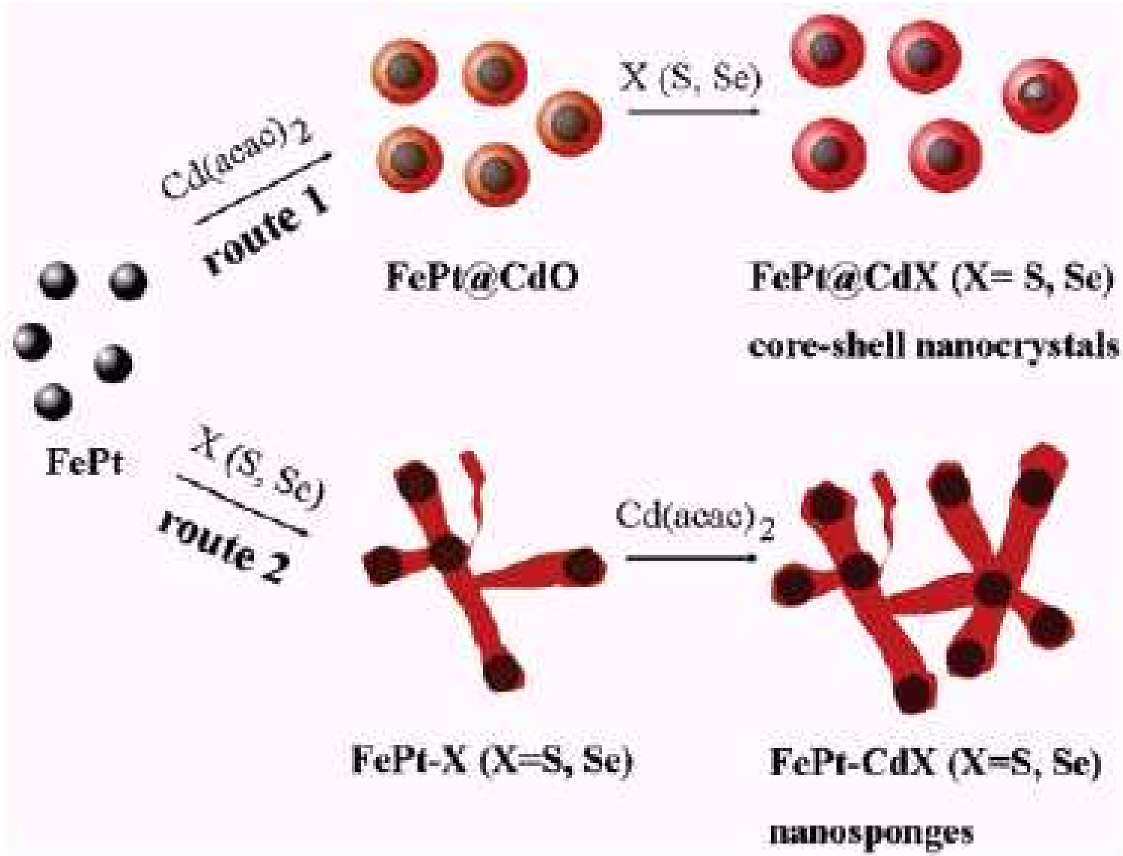



Moonsub Shim et al.Chem. Mater. **2006**, *18*, 6363

# TEM and SEM for hybrid NCs






Bing Xu et. Al. JACS 2007, *129*, 11930

# Nanoparticles

What are they used for?

The potential number of applications is enormous, e.g.
Adhesives, e.g. varied strength from “post it” to “solid weld”
Coatings, e.g. sunscreens now incorporate nanoparticles.
Medical, e.g. new methods of delivering drugs etc. etc.

Ultimately they will be applied in all industries just as micron-sized particles are used today.

*...WE’LL SEE THE NEXT TIME...>>*

# A GOOD NANOMATERIAL

- ✓ narrow size distribution;
- ✓ fewer internal defects;
- ✓ uniform surface;

✓ Well defined phisical properties, such as strong plasmon absorption for metal NCs or luminescence for semiconductor materials

Once the synthesis  is stopped by lowering the reaction temperature, a surfactant coating layer around the NCs remains tightly bound to their surface and guarantees their full solubility in a variety of organic solvents.

## REVIEWS

- Bio-Application of Nanoparticles, edited by Warren C.W. Chan, **2007** Landes Bioscience; Chapter 2 (P. D. Cozzoli and L. Manna)

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