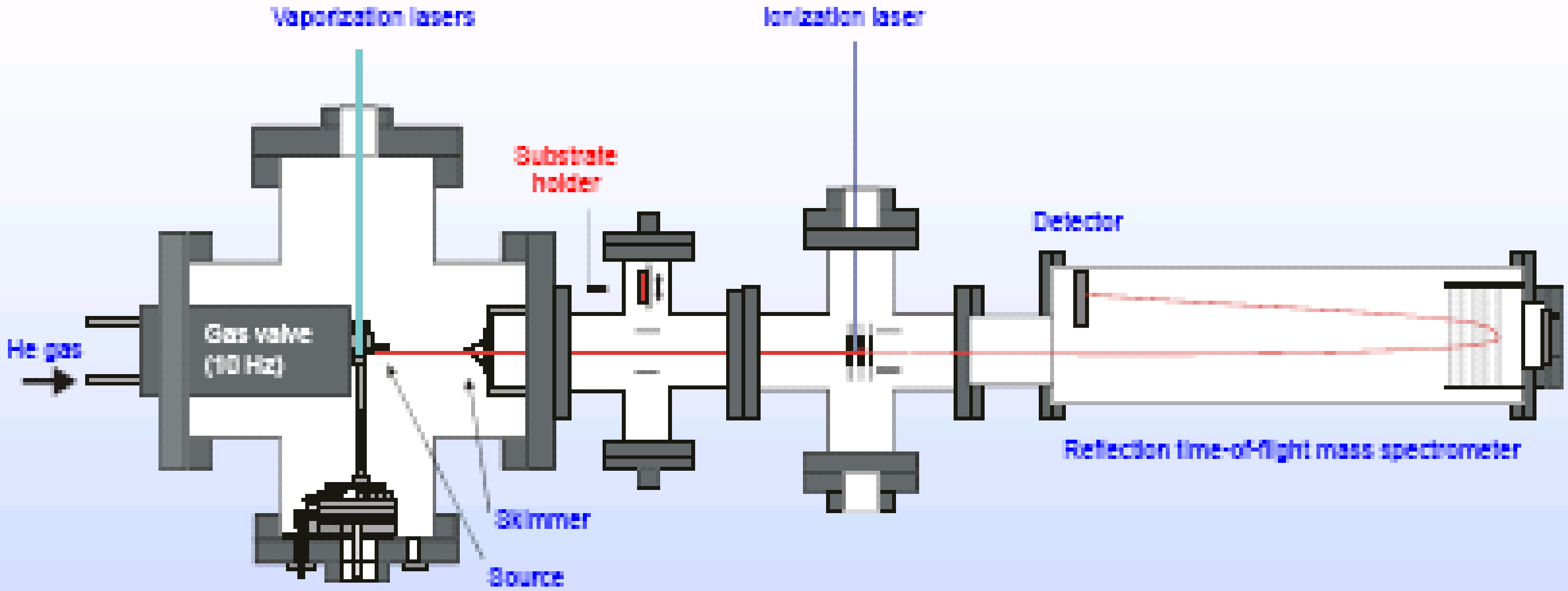
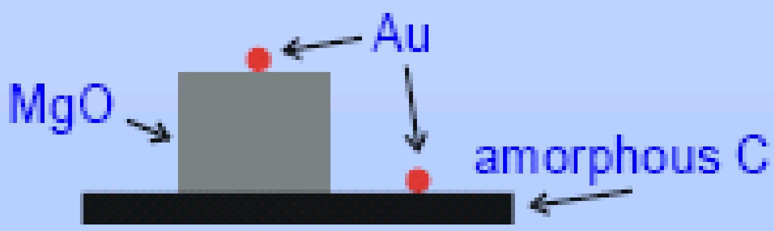
# Nanoparticle Synthesis
# Lecture 2

# Metallic clusters: laser vaporization

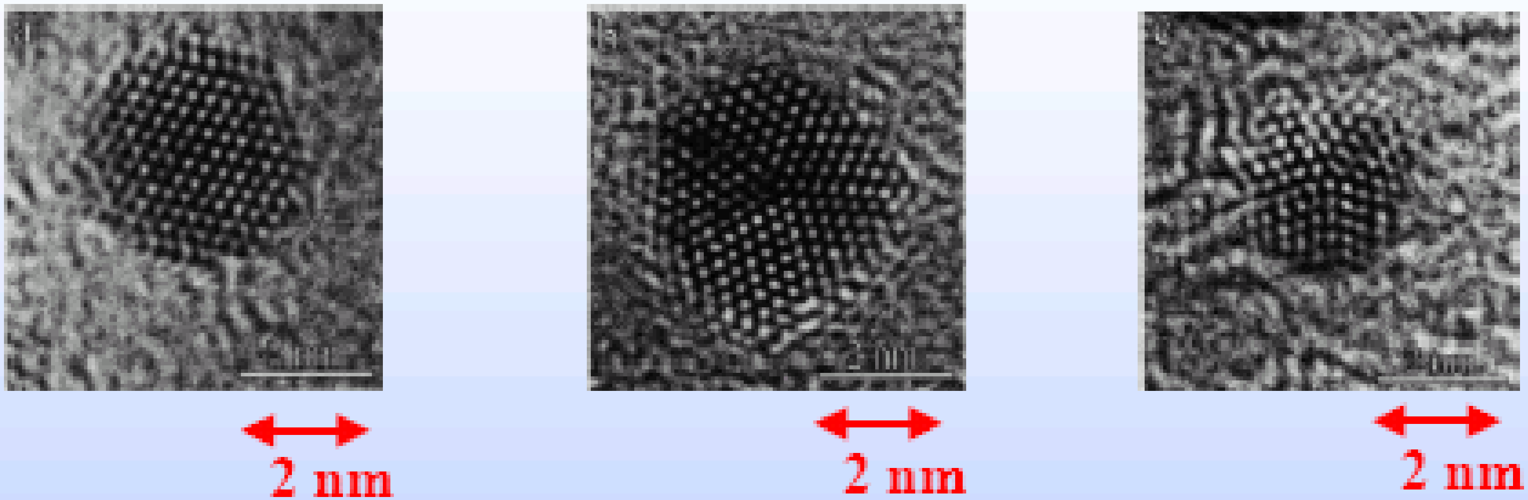



Low kinetic energy: $E_{kin} \approx 0.4$ eV/atom



# Metallic clusters on amorphous C

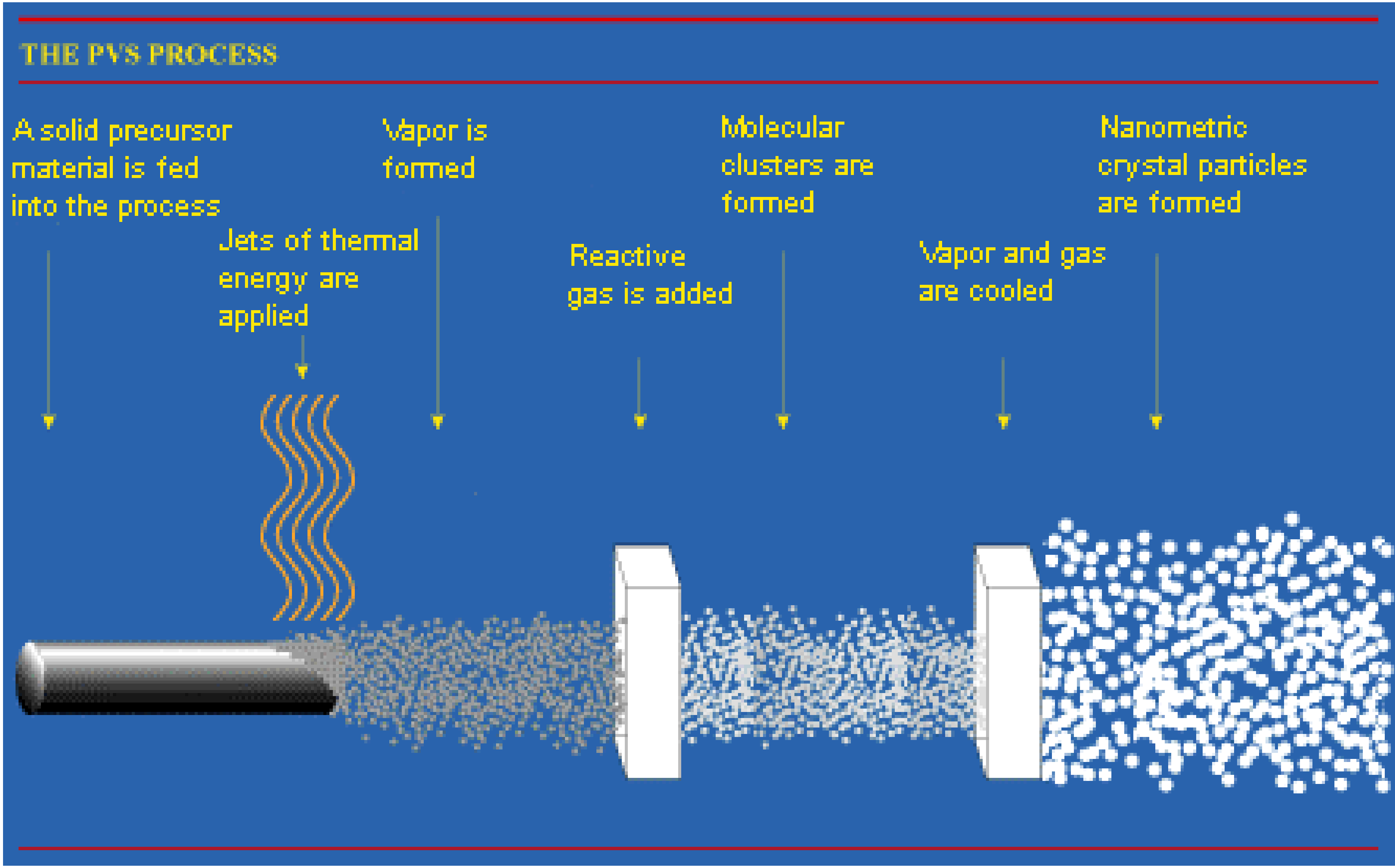
## HRTEM imaging



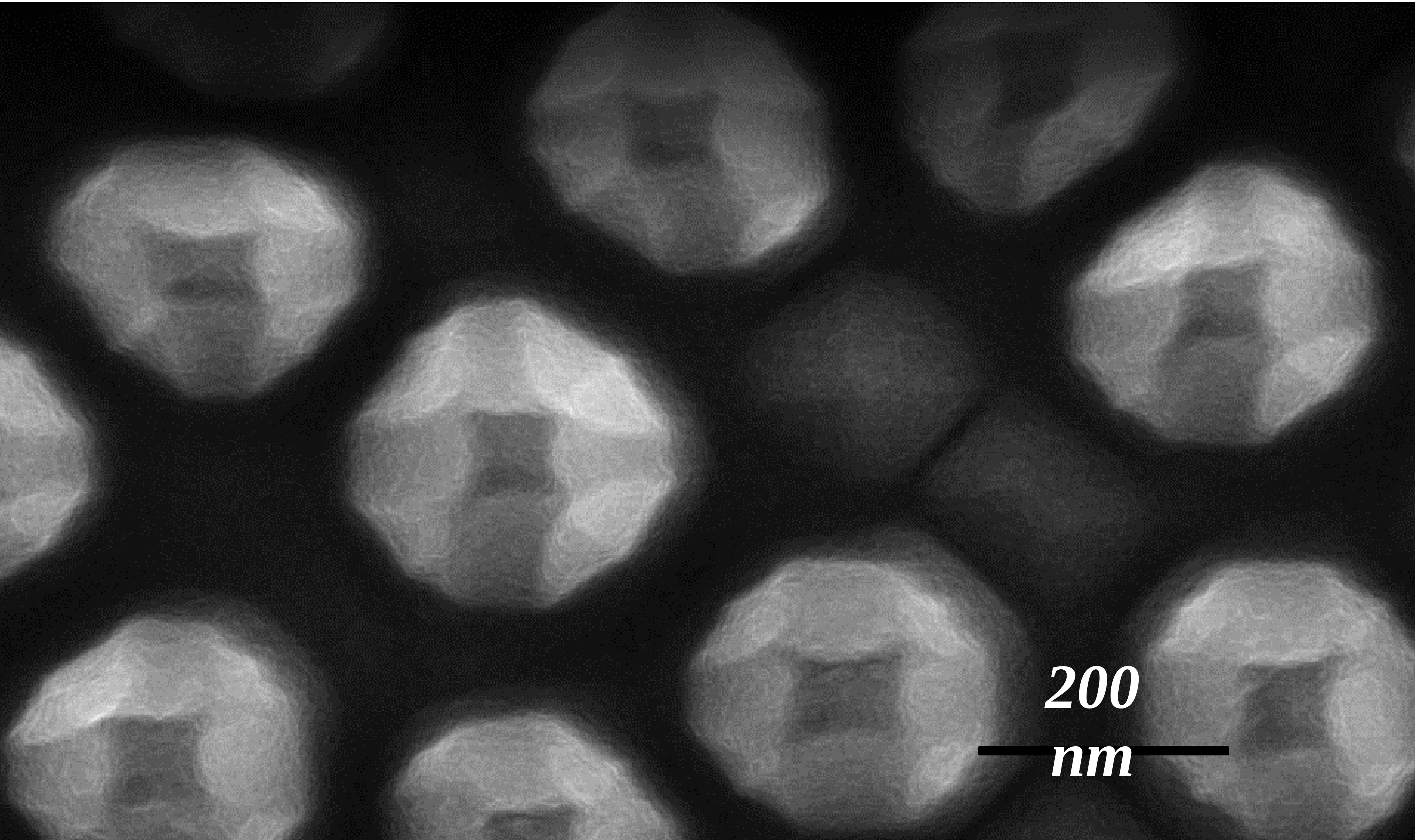

Cuboctahedra, decahedra, icosahedra

Equilibrium shapes of free Au clusters

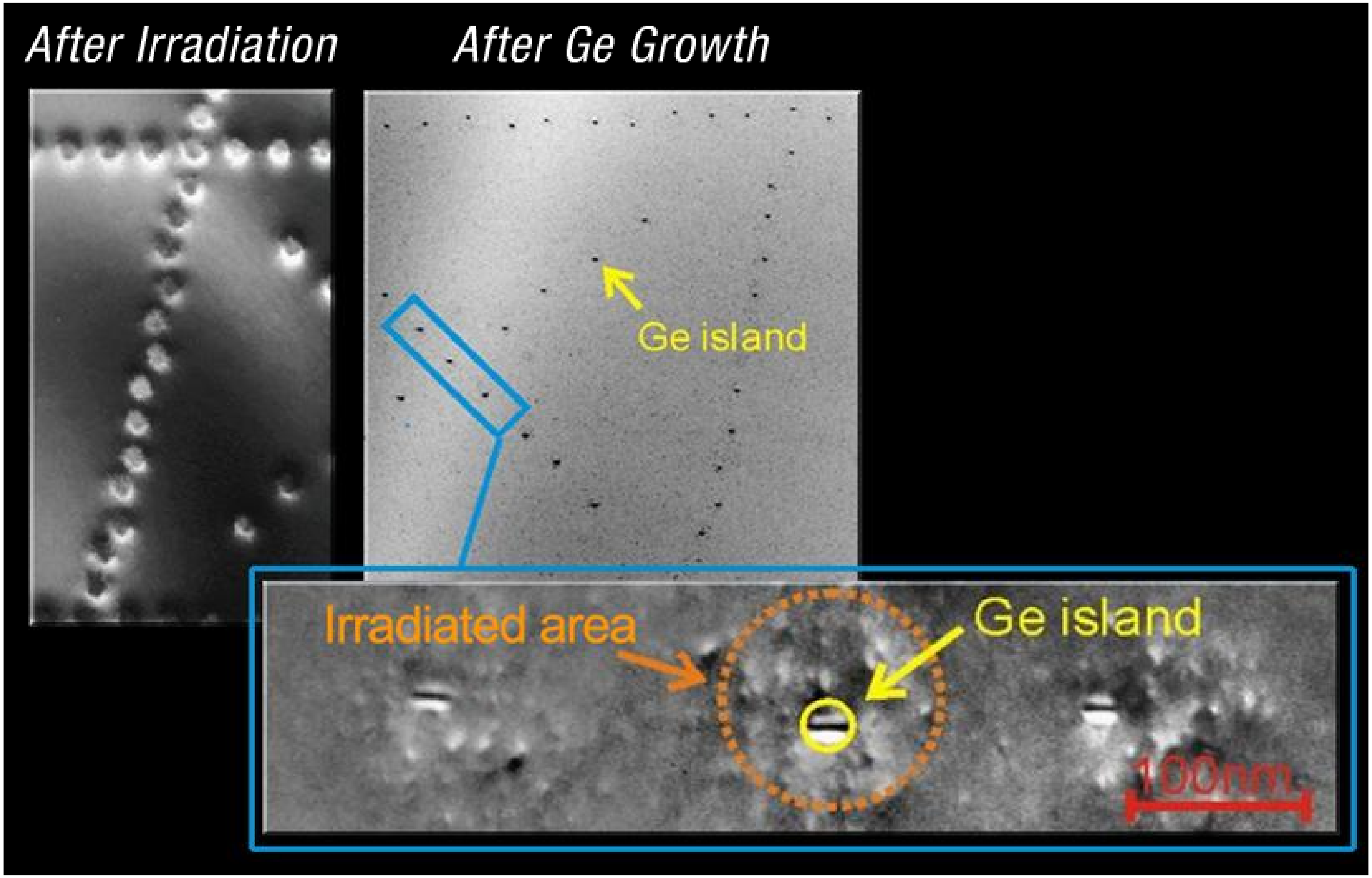
Amorphous substrate: no change of cluster size or shape


THE PVS PROCESS
A solid precursor material is fed into the process
Jets of thermal energy are applied
Vapor is formed
Reactive gas is added
Molecular clusters are formed
Vapor and gas are cooled
Nanometric crystal particles are formed

# Silicon Germanium Quantum Dots

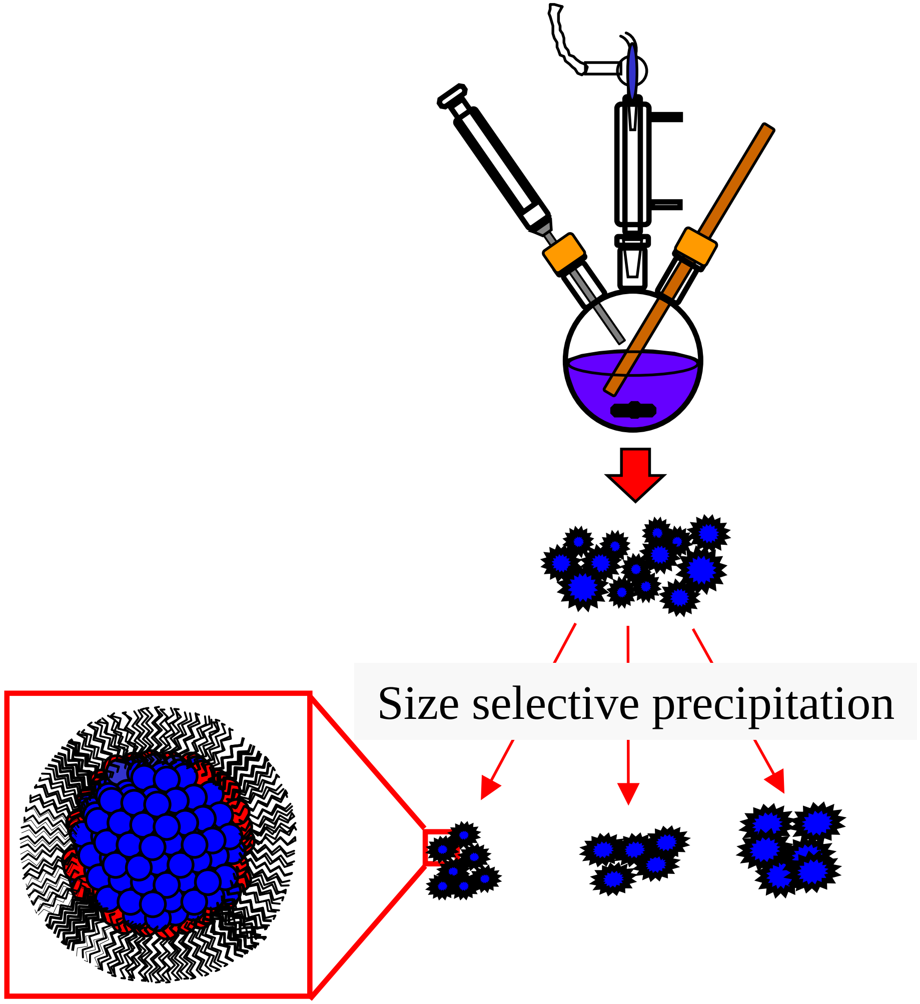


# Precise Placement of Quantum Dots



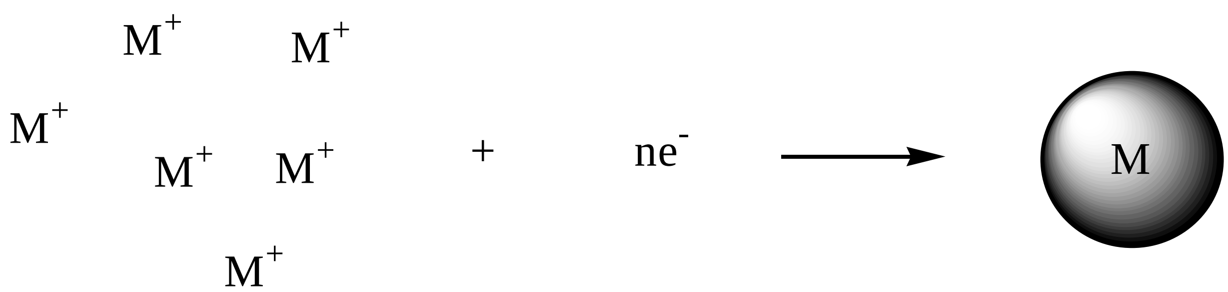
# Synthesis and Characterization of Monodisperse Nanoparticles

C. B. Murray IBM



# Metallic Nanoparticle Synthesis

$$M^{+} \quad + \quad \text{Reductant} \longrightarrow \text{Nanoparticle}$$




M = Au, Pt, Ag, Pd, Co, Fe, etc.

Reductant = Citrate, Borohydride, Alcohols

Shipway, A.N.; Katz, E.; Willner, I. *CHEMPHYSCHM*. **2000**, 1, 18-52.

# Control Factors

**Average Size**

Reductant Concentration

Stirring Rate

Temperature

**Size Distribution**

Rate of Reductant Addition

Stirring Rate

Fresh Filtered Solutions

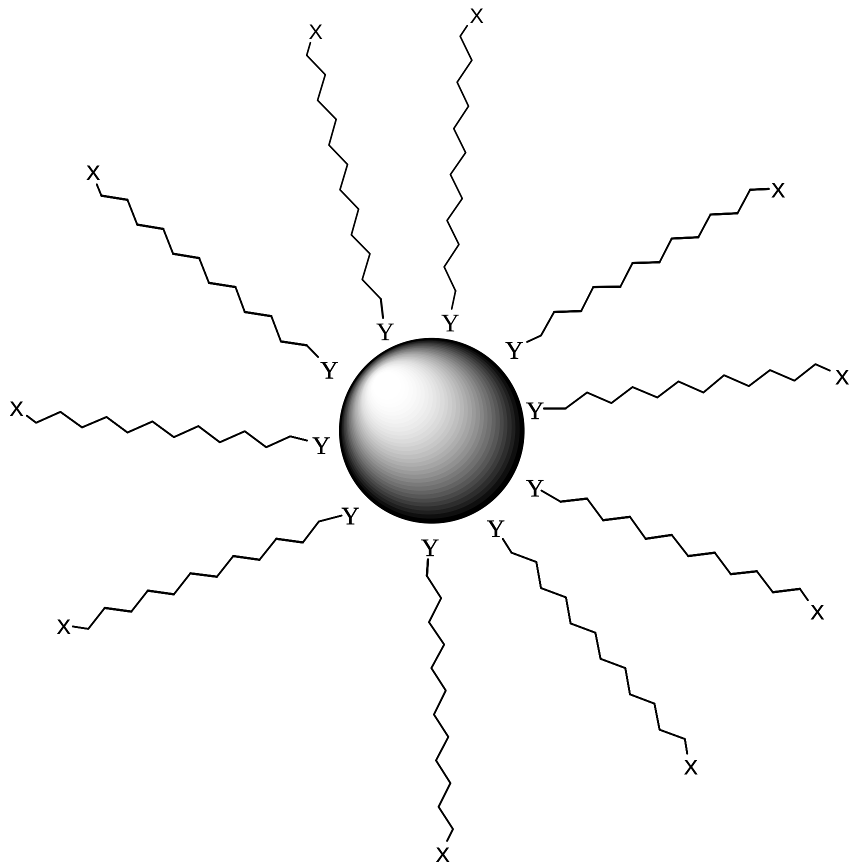
**Stabilization**

Solution Composition

Hayat, M. A. , Ed., *Colloidal Gold: Principles, Methods, and Applications*; Academic Press: San Diego, 1989; Vol 1.

# Functionalized Reductions

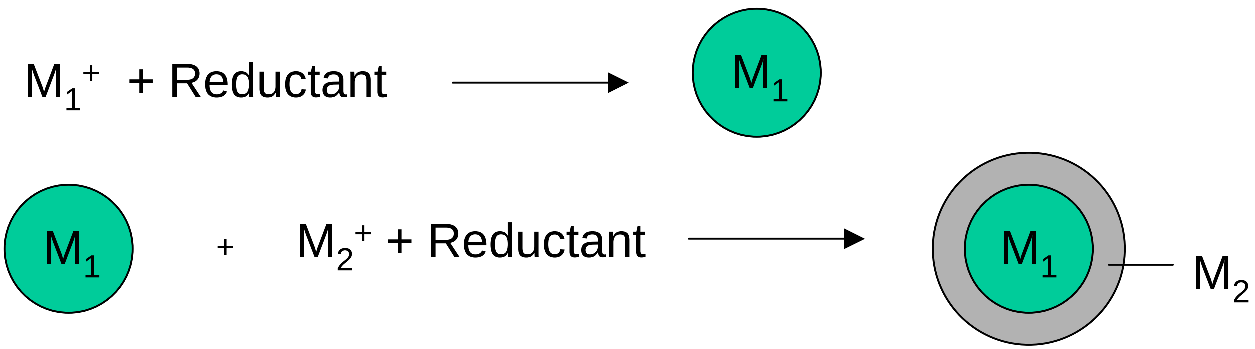
$M^+$ + Reductant → Functionalized Nanoparticle
Surfactant



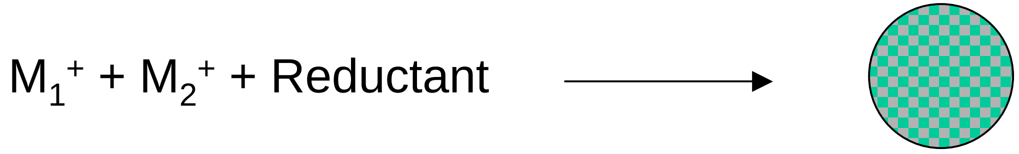

Shipway, A.N.; Katz, E.; Willner, I. *CHEMPHYSCHM*. **2000**, 1, 18-52.

# Bimetallic Nanoparticle

**Core-Shell**

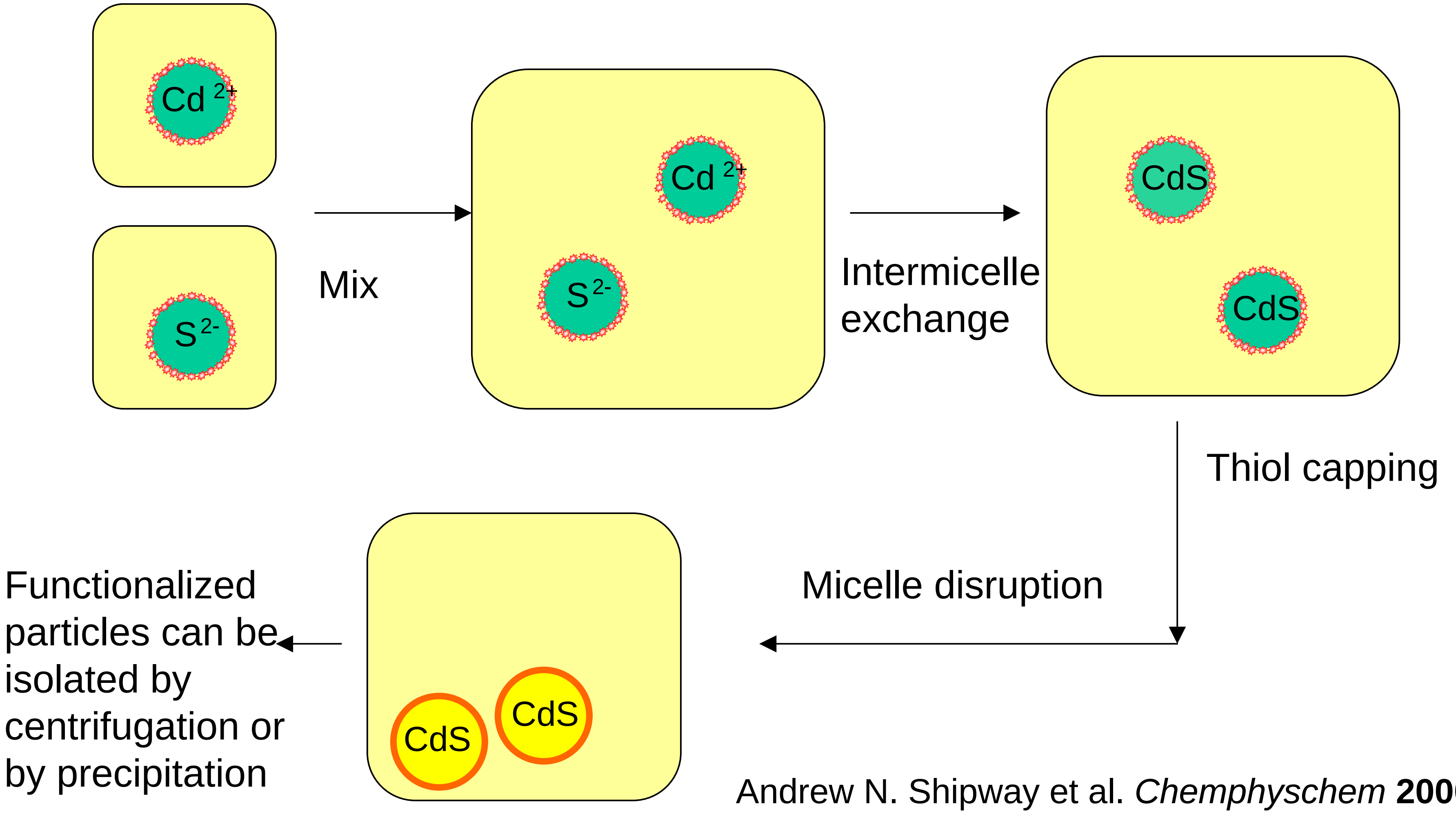



**Mixed Alloy**



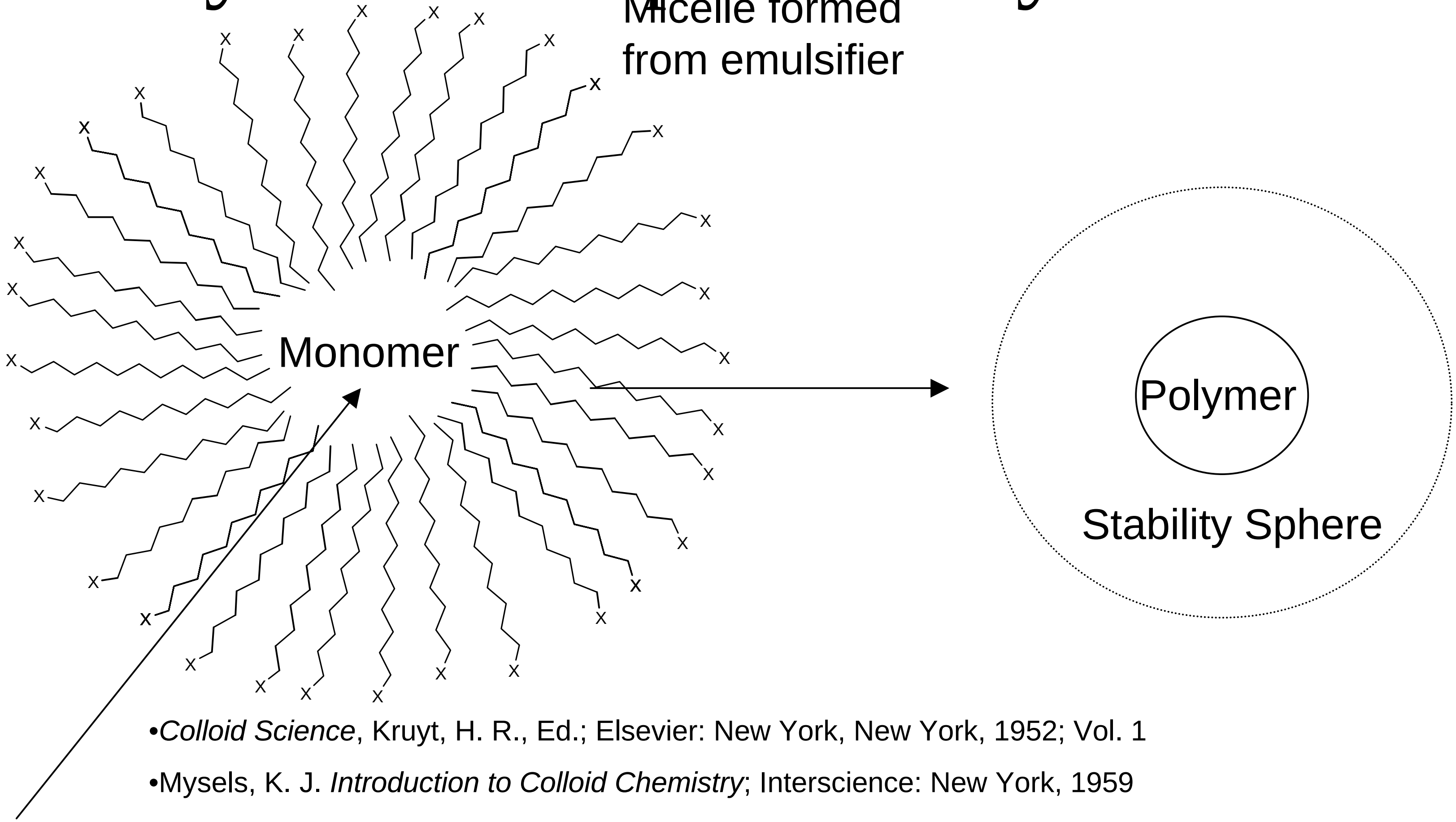

Toshima, N.; Yonezawa, T. *New Journal of Chemistry* **1998**, 1179-1201.

# Semiconductor nanoparticles




Andrew N. Shipway et al. *Chemphyschem* **2000**, 1, 18-52

# Polymer Nanoparticle Synthesis




•*Colloid Science*, Kruyt, H. R., Ed.; Elsevier: New York, New York, 1952; Vol. 1

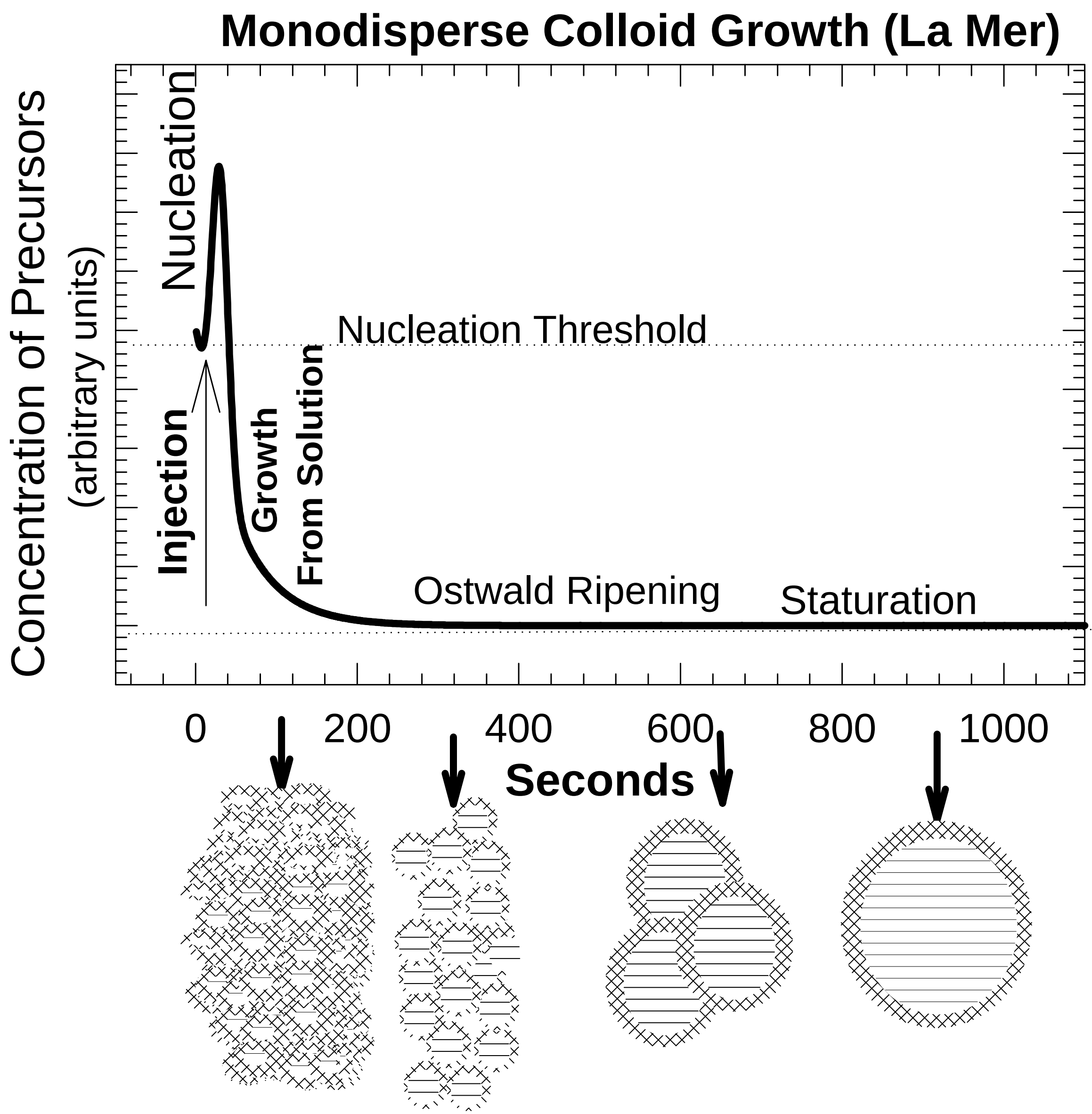
•Mysels, K. J. *Introduction to Colloid Chemistry*; Interscience: New York, 1959

•Irja Piirma, Ed., *Emulsion Polymerization*; Academic Press: New York, 1982

•Eliseeva, V. I.; Ivanchev, S. S.; Kuckanov, S. I.; Lebedev, A. V. *Emulsion Polymerization and its Applications in Industry*; Plenum: New York, 1981

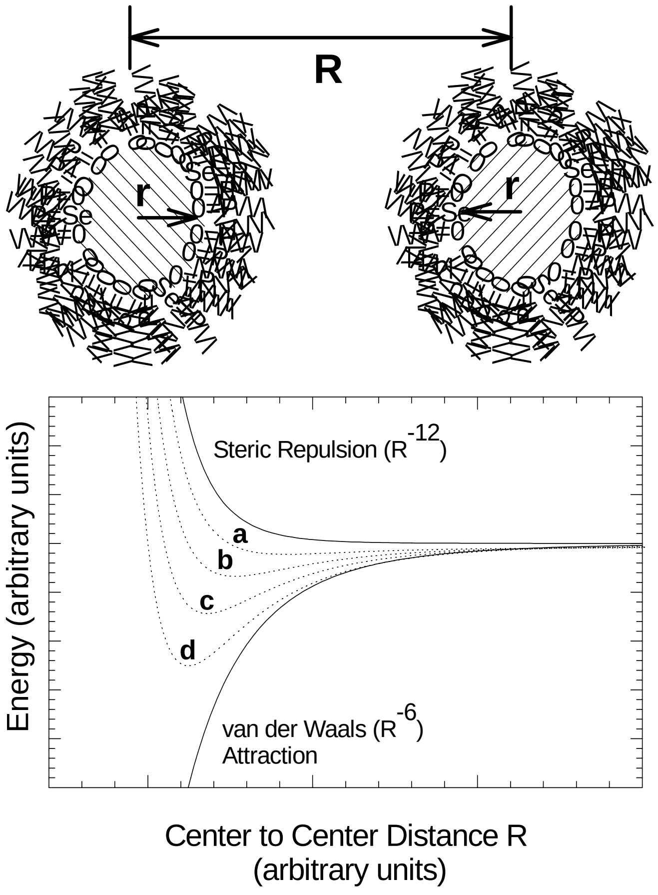
•Bovey, F. A.; Kolthoff, I. M.; Medalia, A. I.; Meehan, E. J. In *High Polymers*; Mark, H., Melville, H. W., Marvel, C. S., Whitby, G. S., Eds.; Interscience: New York, 1955; Vol. IX

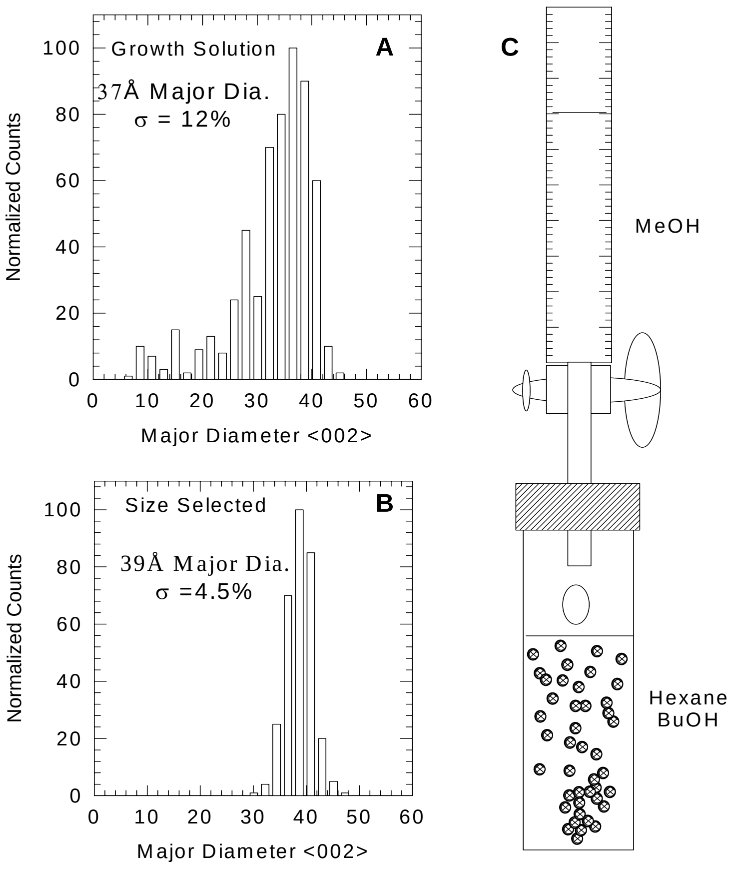
**A**



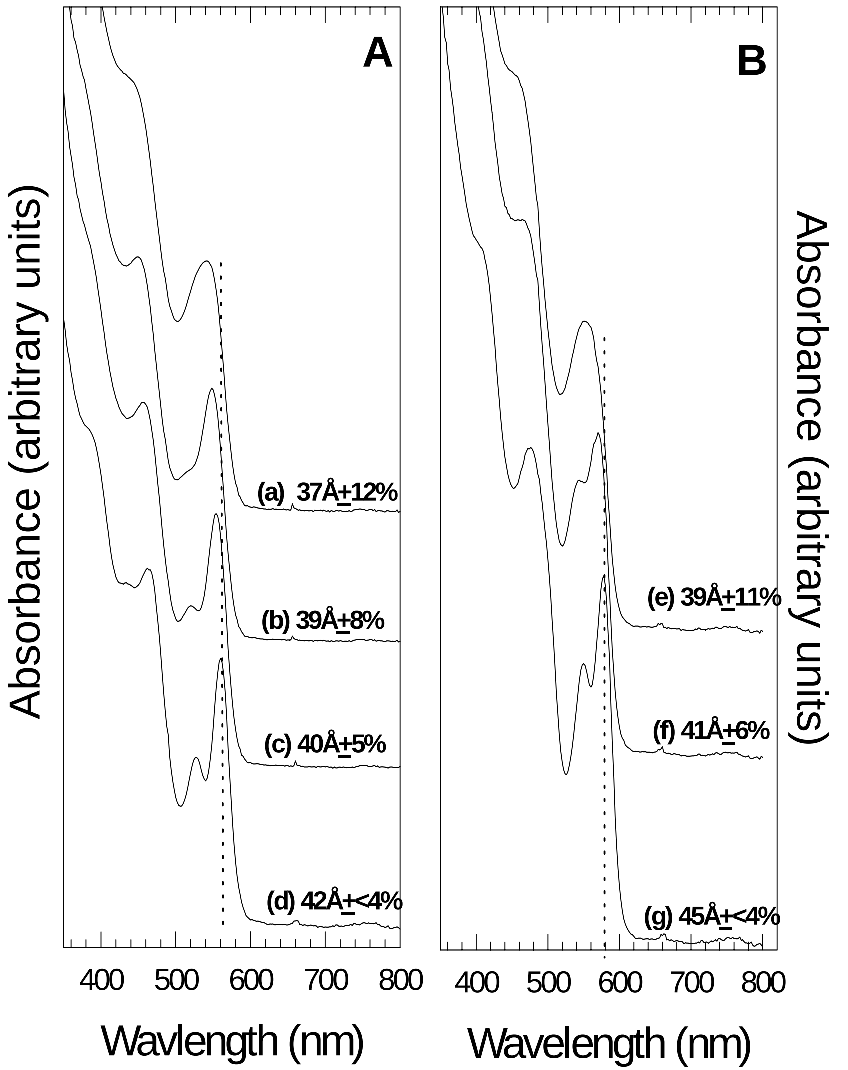
Monodisperse Colloid Growth (La Mer)
Concentration of Precursors
(arbitrary units)
Nucleation
Nucleation Threshold
Injection
Growth
From Solution
Ostwald Ripening
Staturation
0
200
400
600
800
1000
Seconds

# Size selective processing:



# Results of size selected Percipitation



# Gold COLLOIDS

## Preparation of $2.5 \times 10^{-4}$ M Gold Colloids (Sodium Citrate Reduction Method)

1. Make a solution of ~$5.0 \times 10^{-3}$M $HAuCl_4$ in water. (0.1699 g $HAuCl_4$ in 100 mL deionized $H_2O$)
2. Take 1 mL of that solution and add it to another 18 mL of $H_2O$.
3. Make a solution of 0.5% sodium citrate (0.25g in 50 mL of $H_2O$).
4. Heat the 19 mL solution of $HAuCl_4$ until it begins to boil.
5. Add 1 mL of 0.5% sodium citrate solution, as soon as boiling commences.
6. Continue heating until colour change is evident (pale purple).
7. Remove the solution from the heating element and continue to stir until it has cooled to room temperature.
8. Top the solution up to 20 mL to account for boiling.

348 Jpn. J. Appl. Phys. Vol. 40 (2001) Pt. 1, No. 1 G. TSUTSUI *et al.*

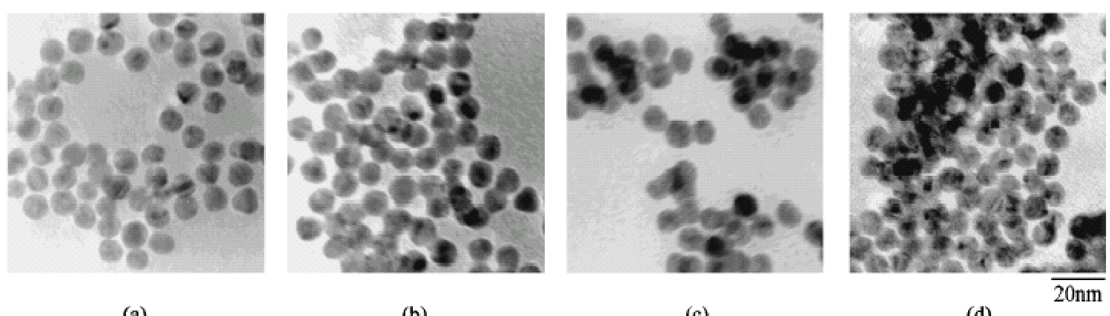



Fig. 5. TEM images of the 8.3-nm-diameter colloidal gold particles in (a) water, (b) ethanol, (c) chloroform, and (d) benzene.

*This is an old method (refereed as Turkevich method) which yields fairly uniform size colloids with diameter of 15-20 nm. See reference Turkevich, J.;Stevenson, P. L.;Hillier, J.Discuss. Faraday Soc. 1951, 11, 55*

## Preparation of 1.0 x $10^{-3}$M Ag Colloids (Sodium Citrate Reduction Method)

1. Make a solution of ~ 5.0 x $10^{-3}$M $AgNO_3$ in water. (0.0425 g in 50 mL deionized $H_2O$).
2. Take 25 mL of that solution and add it to another 100 mL of $H_2O$ (now ~1.0 x $10^{-3}$M).
3. Make a solution of 1% sodium citrate (0.5 g in 50 mL of $H_2O$).
4. Heat the 125 mL solution of $AgNO_3$ until it begins to boil.
5. Add 5 mL of 1% sodium citrate solution, as soon as boiling commences.
6. Continue heating until a colour change is evident (pale yellow).
7. Remove the solution from the heating element and continue to stir until it has cooled to room temperature.
8. Top the solution up to 125 mL to account for boiling.

This method yields relatively large size silver nanocrystallites with a diameter of 60-80 nm and exhibits abs. max. ~420 nm. See reference *J. Phys. Chem. B*, 1998, *102*, 3123

*(Note: Use of Sodium Borohydride as a reductant can give smaller size silver nanoparticles with plasmon absorption around 380 nm. Presence of citric acid or polyvinyl alcohol can provide additional stability to these colloids)*

## Preparation of Gold Particles in Toluene:

A.Hydrogen tetrachloroaurate (30 mL of 30 mM, in water).

Mass = 393g/mol ´ 0.03 M ´ 30mL/1000mL = 0.3537g of $HAuCl_4$ in 30mL of $H_2O$

B. Tetraoctyl ammonium bromide (80 mL in 50 mM, in toluene).

Mass = 546.8g/mol ´ 0.05 M ´ 80ml/1000mL = 2.187g of TOAB in 80mL of toluene

1.Prepare 2.19 g of tetraoctyl ammonium bromide in 80 mL of toluene.

2.Add solution prepared in step 1. to a solution of hydrogen tetrachloroaurate (0.3537 g in 30 mL of $H_2O$).

3.Stir for 10 min.

4.Vigorously stir reaction mixture and add $NaBH_4$ (0.38 g in 25 mL of $H_2O$) dropwise over a period of ~30 min. (Ensure that organic and aqueous phases are being mixed together).

5.Stir solution for an additional 20 min.

6.Extract organic phase and wash once with diluted $H_2SO_4$ (for neutralization) and five times with distilled water.

7.Dry organic layer with $Na_2SO_4$.

For platinum particles substitute dihydrogen hexachloroplatinate (IV) ($PtCl_6 . H_2O$) for $HAuCl_4$ and for iridium particles substitute $H_2IrCl_6 . 4H_2O$ for $HAuCl_4$.

Yields highly concentrated gold colloidal suspension with particle diameter in the range of 5-10 nm. Can be suspended in both polar and nonpolar solvents.

Adopted from the reference Brust, M.;Walker, M.; Bethell, D.;Schffrin, D. J. Whyman, R., *J. Chem. Soc., Chem. Commun.*, 1994, 801-802 and George Thomas, K.Kamat, P. V. *J. Am. Chem. Soc.* 2000, *122*, 2655

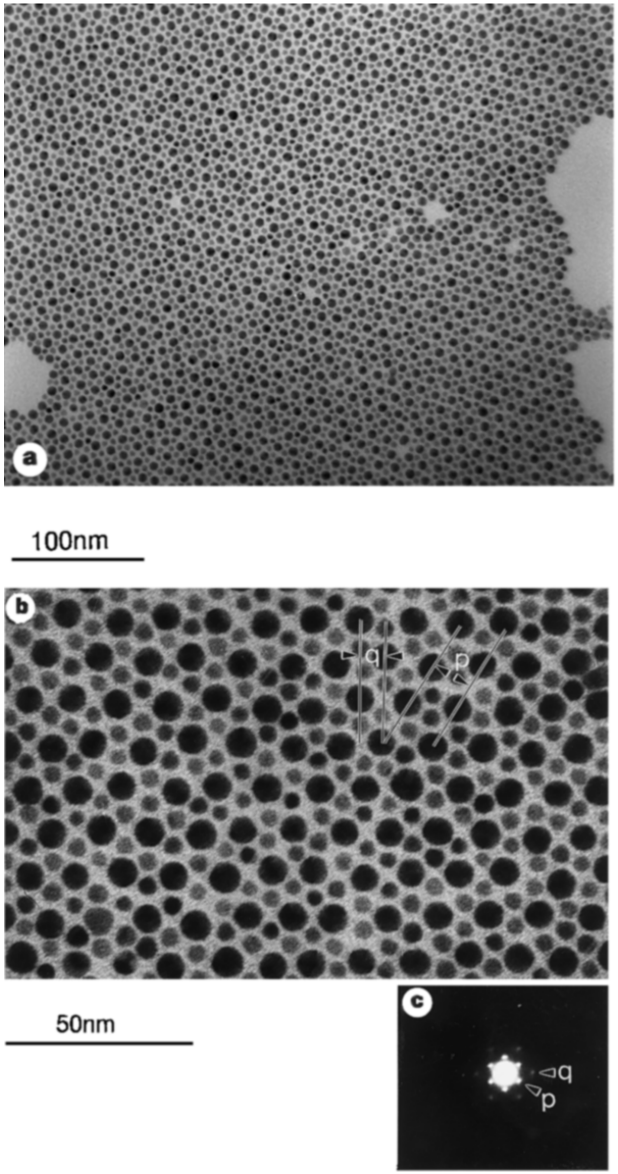
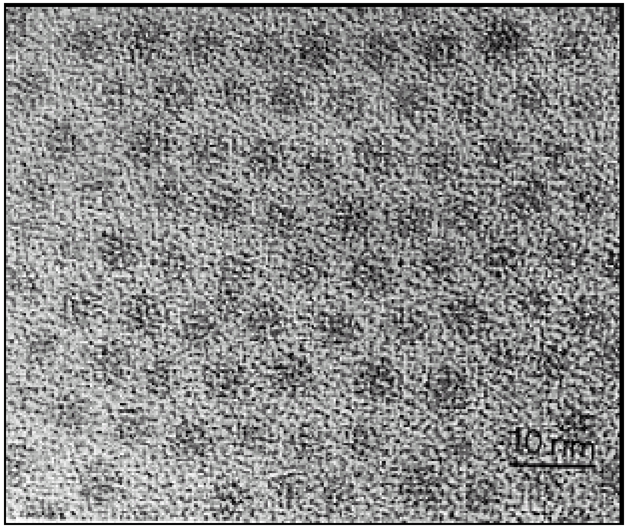



**Figure 1** An ordered raft comprising Au nanoparticles of two distinct sizes with $R_B/R_A$ 0.58. Shown are electron micrographs at low (**a**) and higher (**b**) magnification. **c**, The low-angle superlattice electron diffraction pattern obtained from this bimodal raft structure.

# Thiol Stabilized Gold Nanocrystals



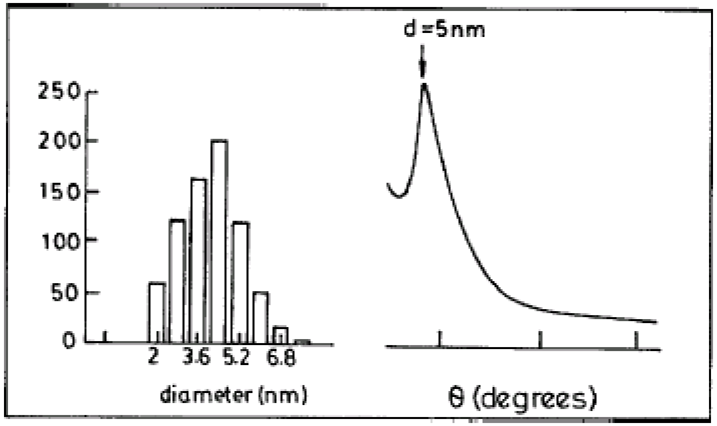




**Fig. 5** 2D array of thiol-derivatized Au particles of 4.2 nm mean diameter. Histograms indicating particle size distribution is given. XRD pattern from this array is also shown.

## Silver Nanocrystal Preparation in Organic Medium

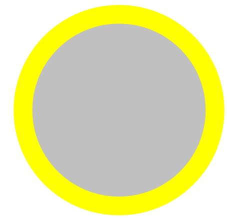
Modification of method found in source: Korgel, B.A.; Fullam, S.; Connolly, S.; Fitzmaurice, D. *J. Phys. Chem. B* **1998**, *102*, 8379-8388. (The method described in this paper yields a precipitate of AgBr in the initial extraction process)

1. Prepare ~5.0M $NaNO_3$ in deionized water (12.749g $NaNO_3$ in 30mL $H_2O$).
2. Prepare ~50mM TOAB in toluene (1.367g tetraoctylammonium bromide in 50mL toluene).
3. Add the TOAB/toluene solution to the $NaNO_3$/water solution.
4. Stir vigorously for 1 hour (to remove $Br^-$ ions from solution and prevent the formation of AgBr when $AgNO_3$ is added).
5. Extract organic phase and set aside. Discard aqueous phase.
6. Prepare ~30mM $AgNO_3$ in water (0.0764g $NaNO_3$ in 14mL $H_2O$).
7. Add 7.5mL of 30mM $AgNO_3$ solution to the organic solution.
8. Stir vigorously for 45 minutes.

Part 2 of Silver Nanocrystals Synthesis.

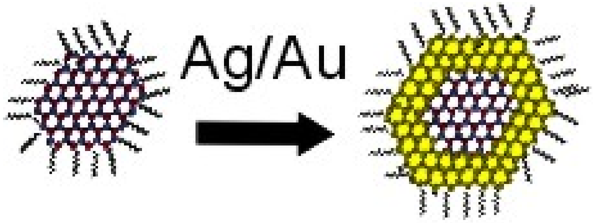
9. Extract organic phase (discard aqueous layer).
10. Add 0.16mg (~0.189mL) of 1-dodecanethiol to organic solution (to cap the silver)
11. Stir vigorously for 15 minutes.
12. Meanwhile, prepare ~0.4M $NaBH_4$ in water (0.3783g $NaBH_4$ in 24mL $H_2O$).
13. Add 6.25mL of the $NaBH_4$,dropwise over a 35min. period, to the solution containing the silver (organic layer), while stirring vigorously.
14. Stir for ~15 hours (overnight).
15. Extract organic layer (discard aqueous layer).
16. Wash organic layer 3 times with dilute ethanol.
17. Allow to settle, and extract organic layer.
18. Store is closed container.

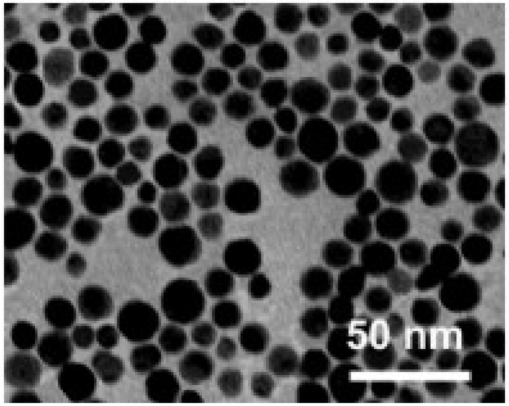
**Preparation of Au Capped Ag**

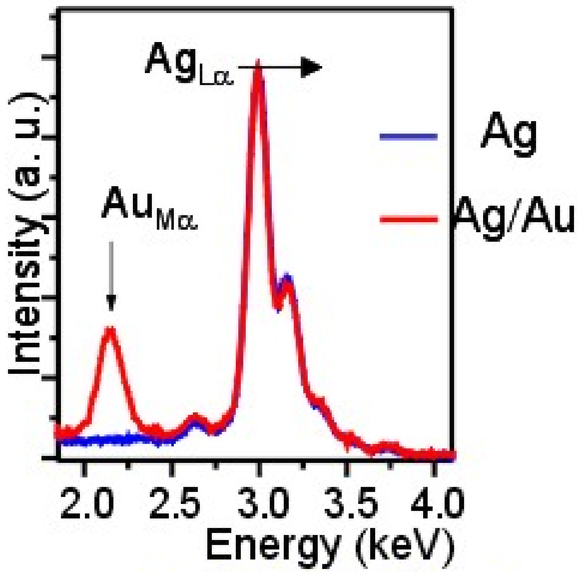


1.Take 125 mL of 1.0 x $10^{-3}$M solution of Ag colloids and add 12,5 mL $H_2O$.

2.Heat this solution until it comes to a boil and then add the appropriate amount of 5.0 x 10-3M $HAuCl_4$. (For example: 50µ L, 100µ L, 150µ L, 300µ L, and 500µ L)



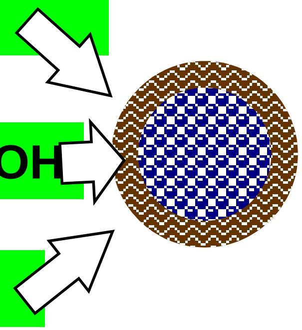

Ag:Au about 5.2 : 1.

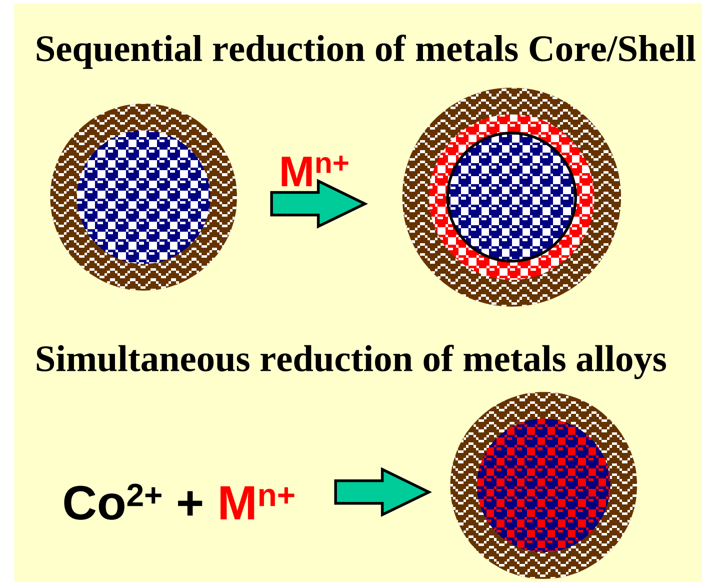
# Synthesis of Transition Metal Nanocrystals

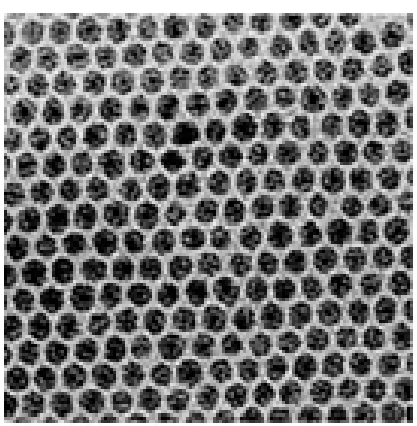
$Co^{2+}$ + $(Et)_3BH$ + $R_3P$ + $C_{17}H_{19}COOH$
250C Na$^{+}$Napth$^{-}$

$Co^{2+}$ + C16(OH)2+$R_3P$ + $C_{17}H_{19}COOH$

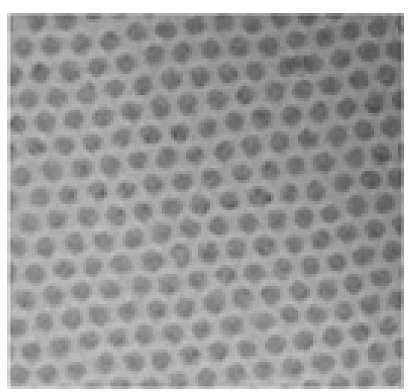
$Co_2(CO)_8$ + $R_3P$ + $C_{17}H_{19}C00H$



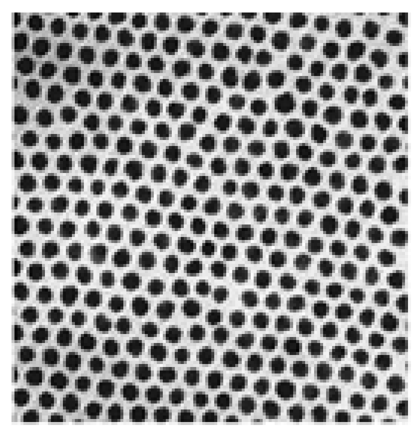


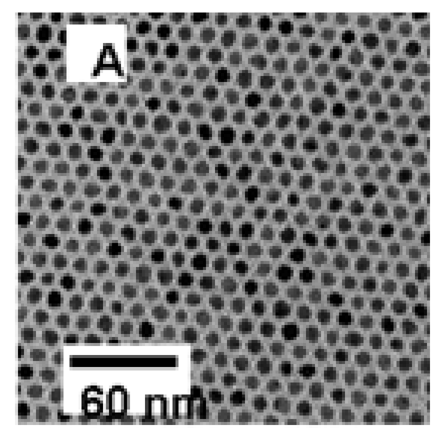
Co 8 nm



Ni 9 nm

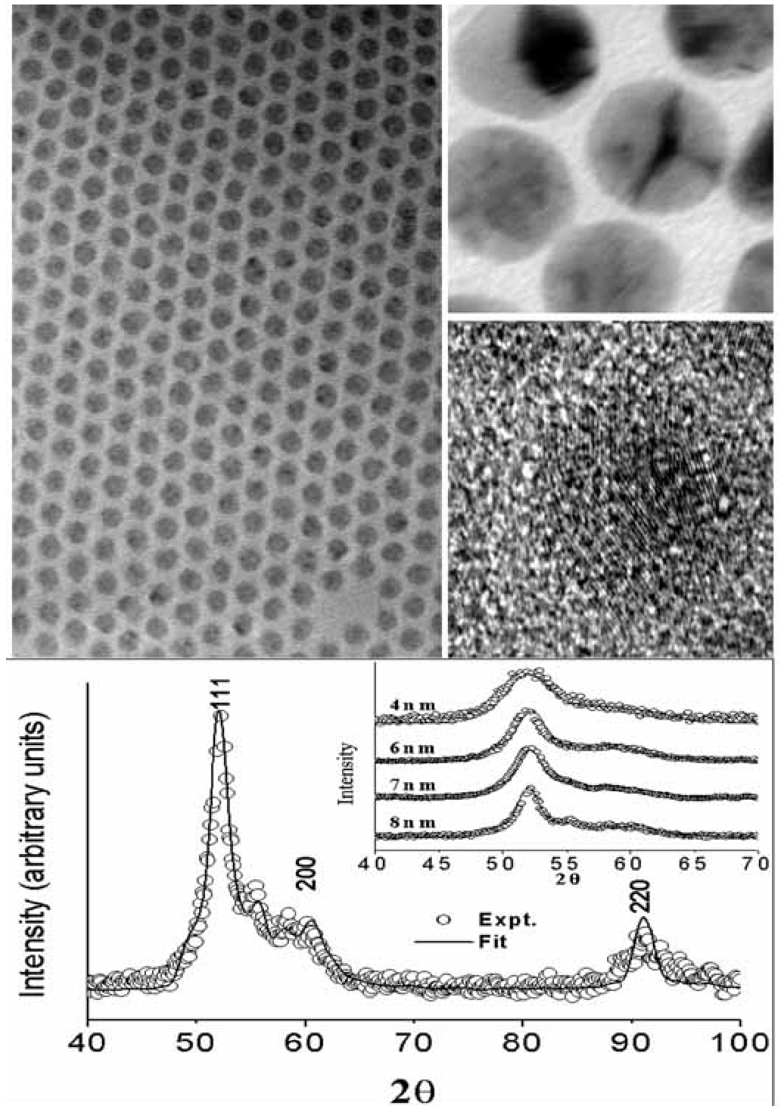


Co/Ni 9 nm




FePt 4 nm

# CobaltNanocrystal Synthesized by decomposition of Cobalt Carbonyls



# Organometallic syntheis of the II-VI Semiconductor Nanocrystals

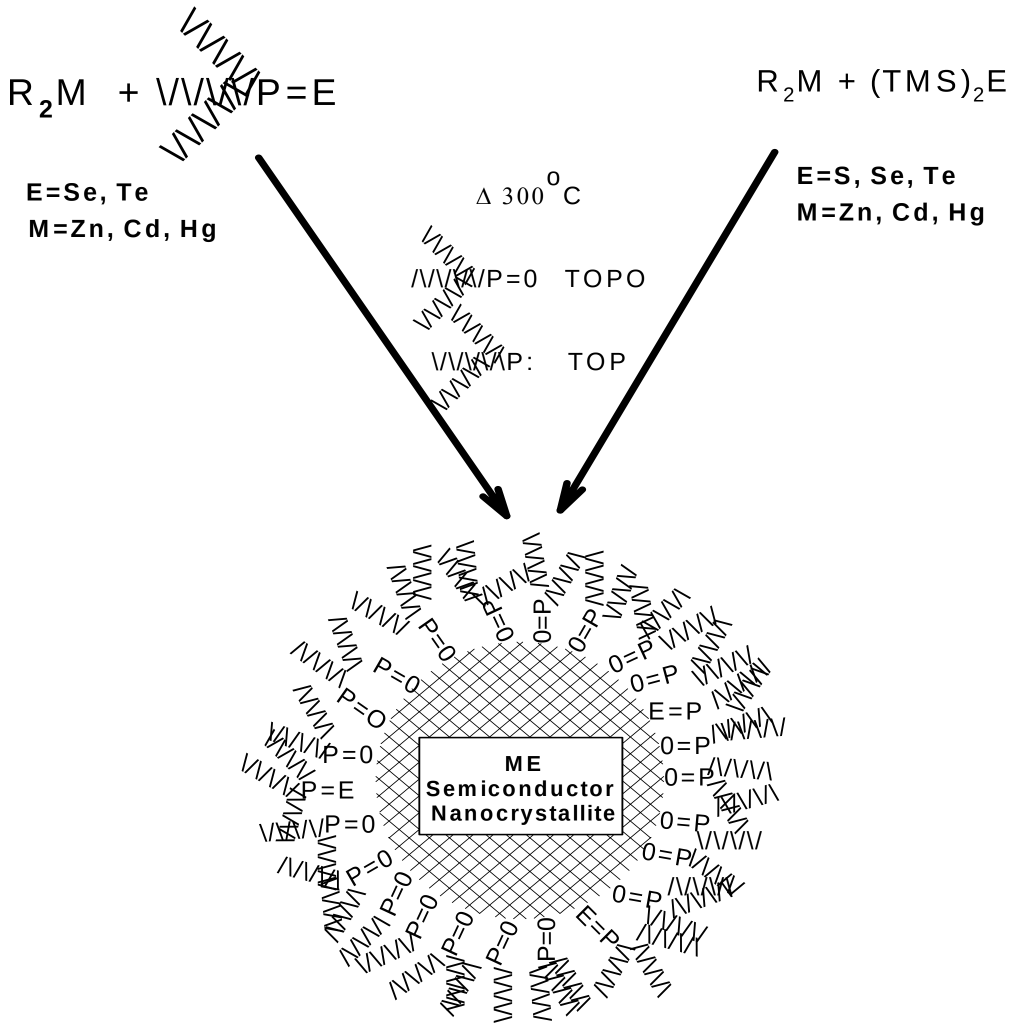
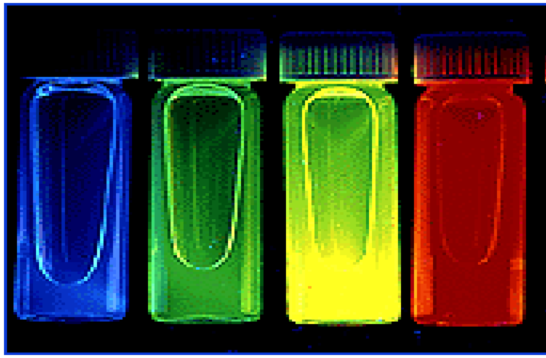
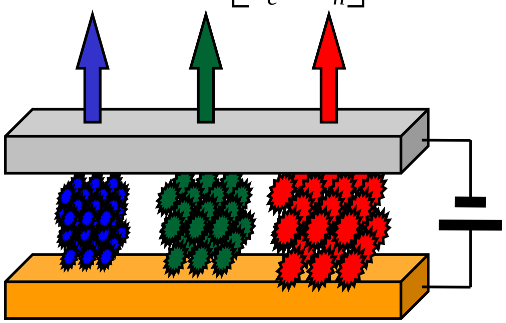


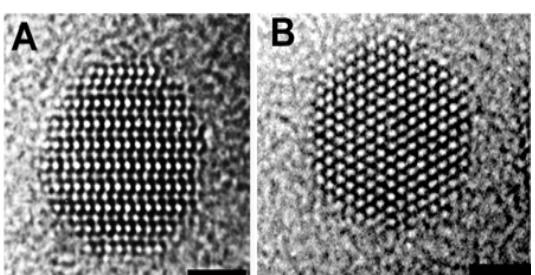

**FIG. 2.1** Cartoon of the reaction scheme for the production of monodisperse II-VI nanocrystallites by rapid pyrolysis in coordinating solvents.

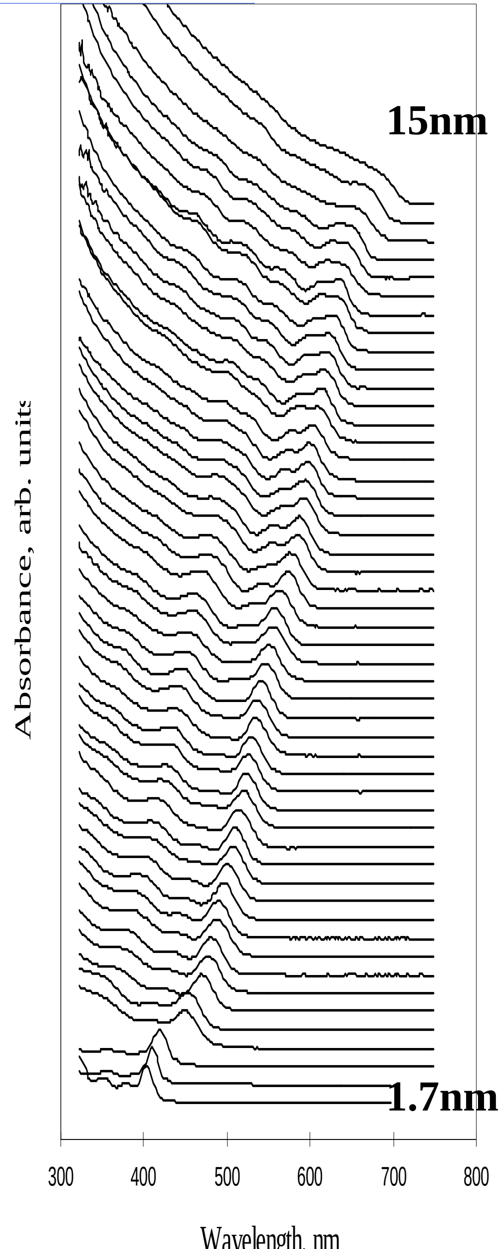
# Colloidal CdSe Nanocrystals (Quantum dots).



$$E^* = E_{bg} + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon R}$$





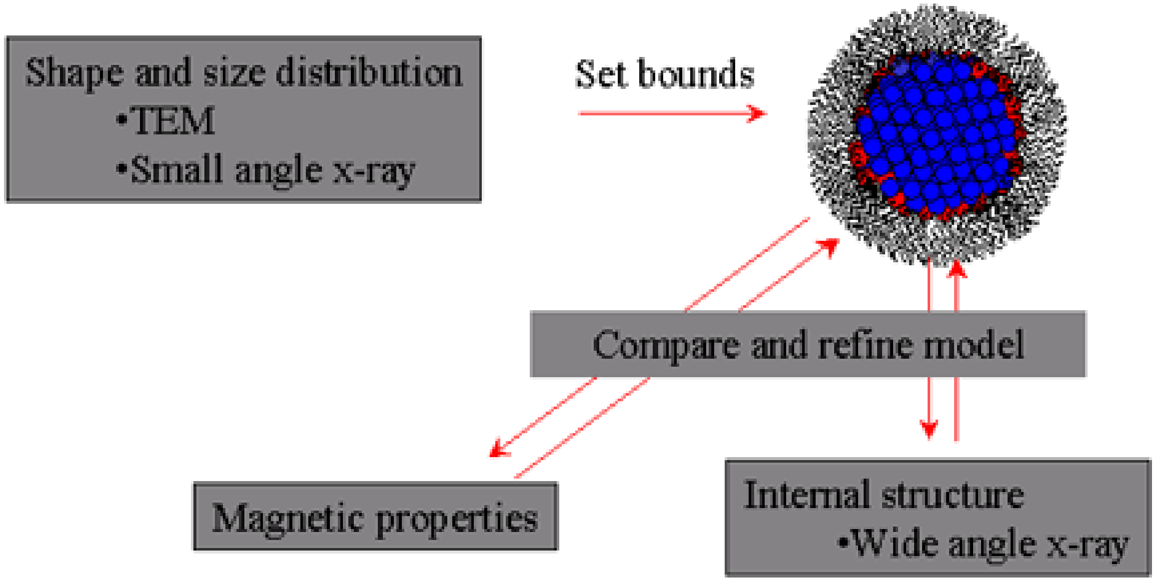





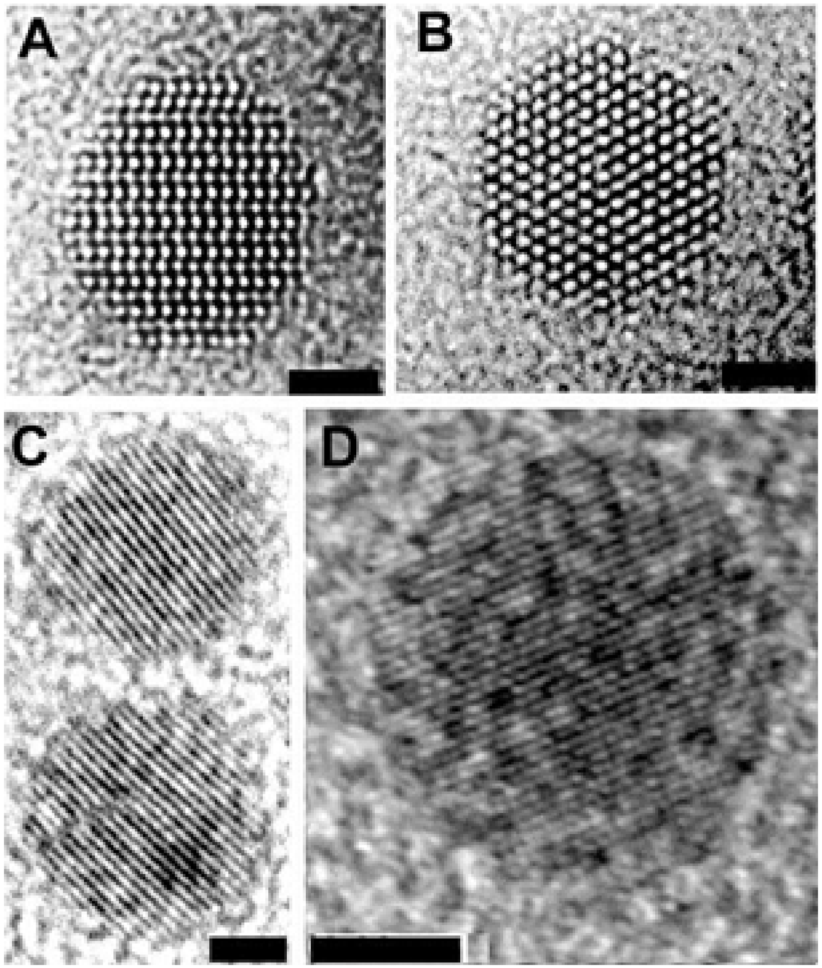
**5 nm σ <5% CdSe Nanocrystals**

# Atomistic approach to structural characterization

- Nanoparticles are measured using a wide variety of techniques
- Standard approach
  - Specific modeling for each measurement.
  - Difficult to produce single unified model.
- Atomistic approach
  - Model of nanoparticle built up atom-by-atom.
  - Single model used for each technique.
  - Self-consistent, systematic and extensible methodology.



# High Resolution TEM Images reveal internal lattice.

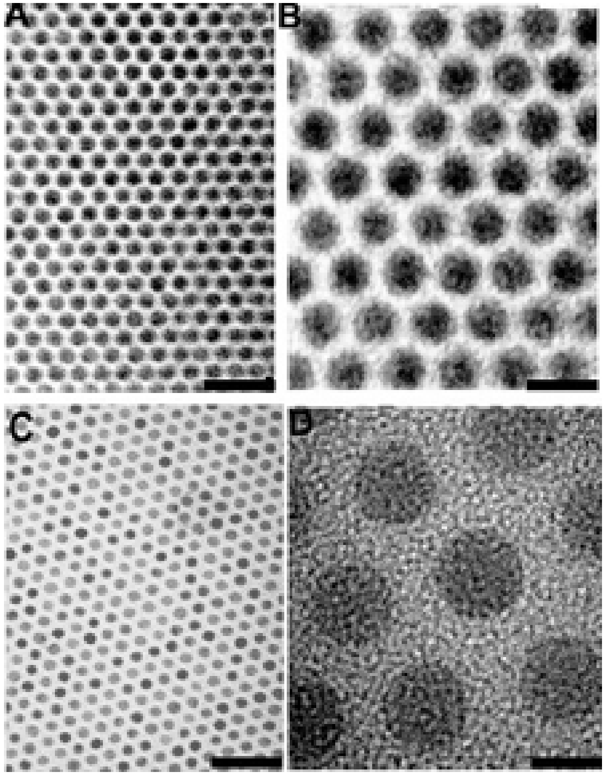



A & B CdSe

C CdTe

D Cobalt

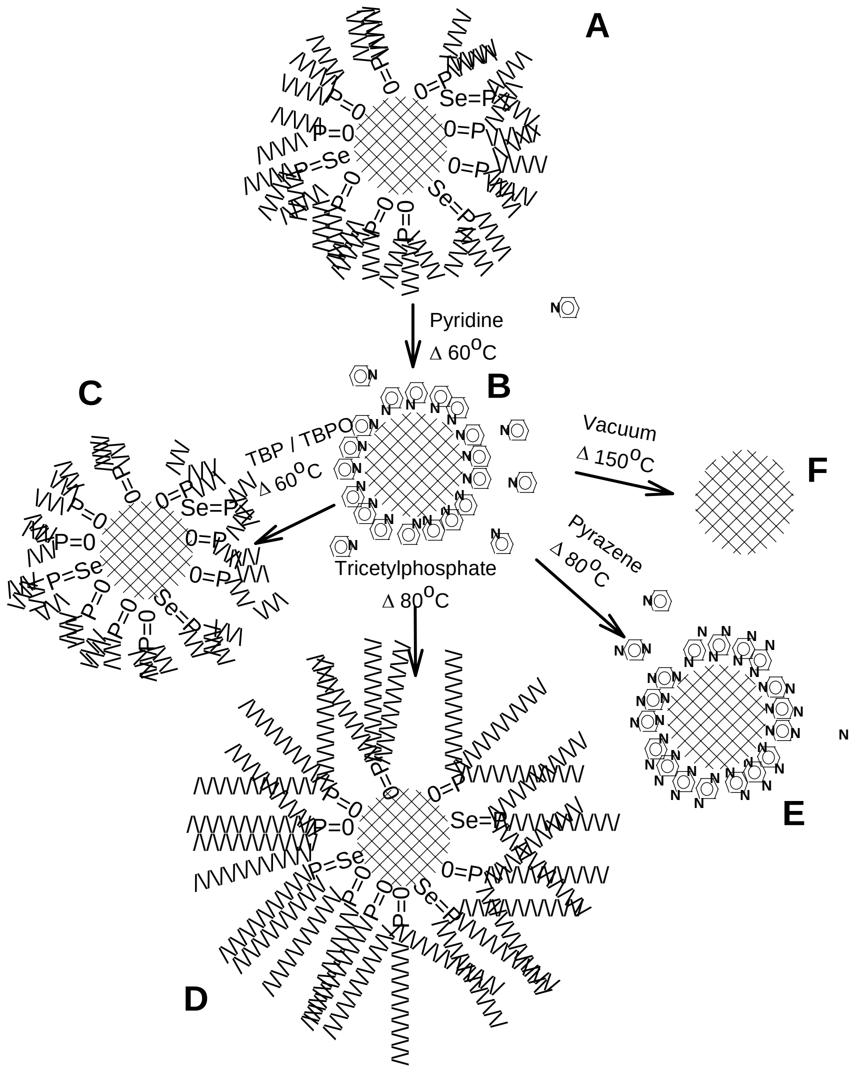
Low Mag TEM allows determination of average size and shape:




CdSe

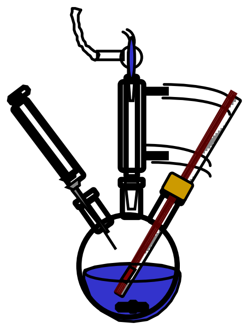
Cobalt

# Cap exchange to modify surface:

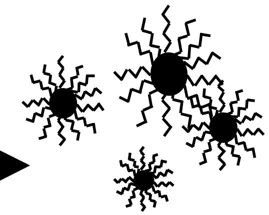


# Wet Chemical Synthesis of PbSe Nanocrystals and Superlattices

**Synthesis**



**$Pb(OAc)_2 + R_3PSe$** —— oleic acid, $R_3P$, T=150 C ——→

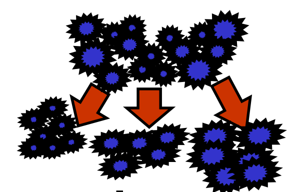


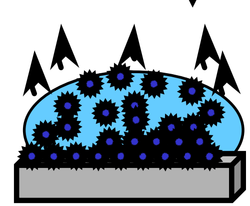
R= octyl

**PbSe**

**Size Selective Processing**

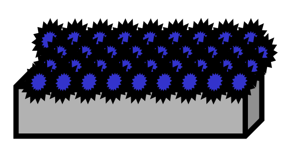
**Size selective precipitation in solvent/ non solvent pairs like hexane-methanol**



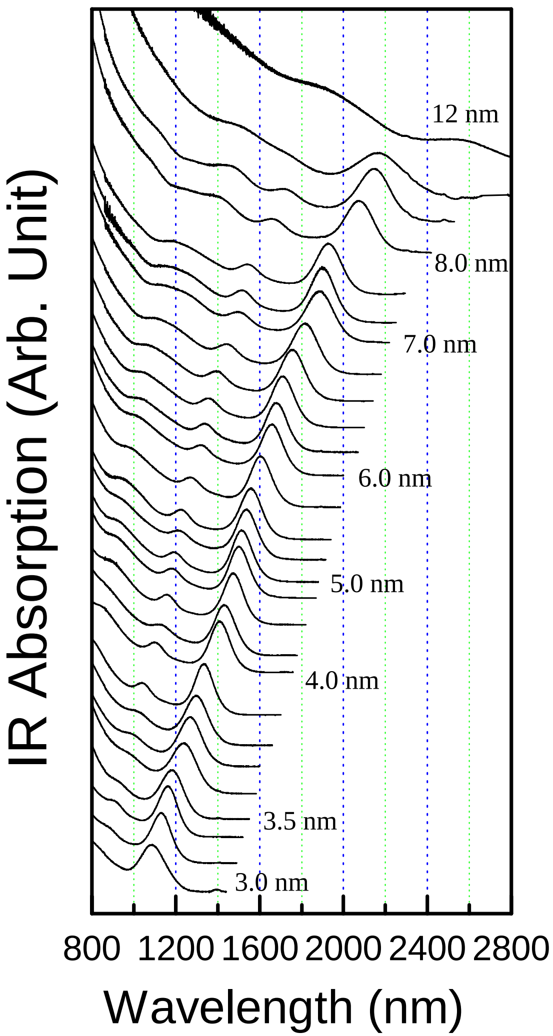


**Self Assembly**

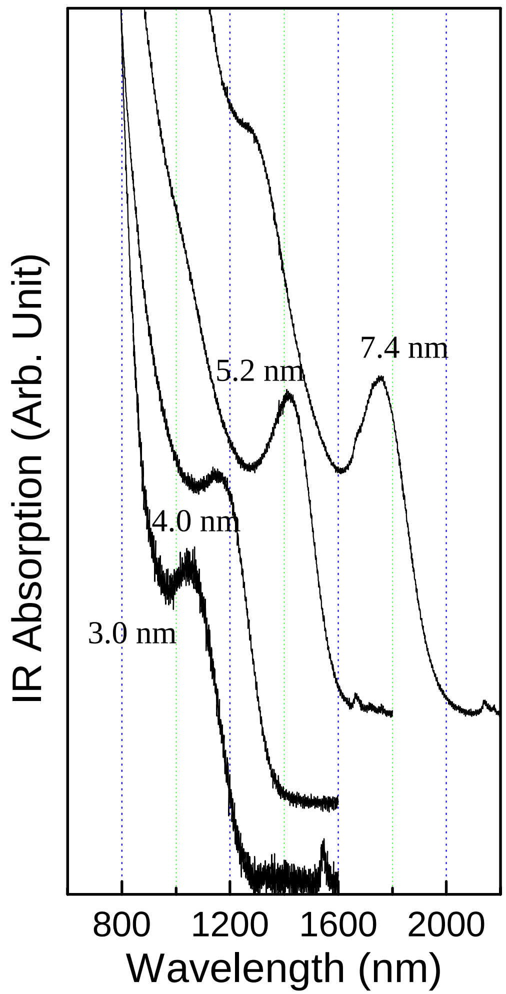
**Evaporation of the solvent**



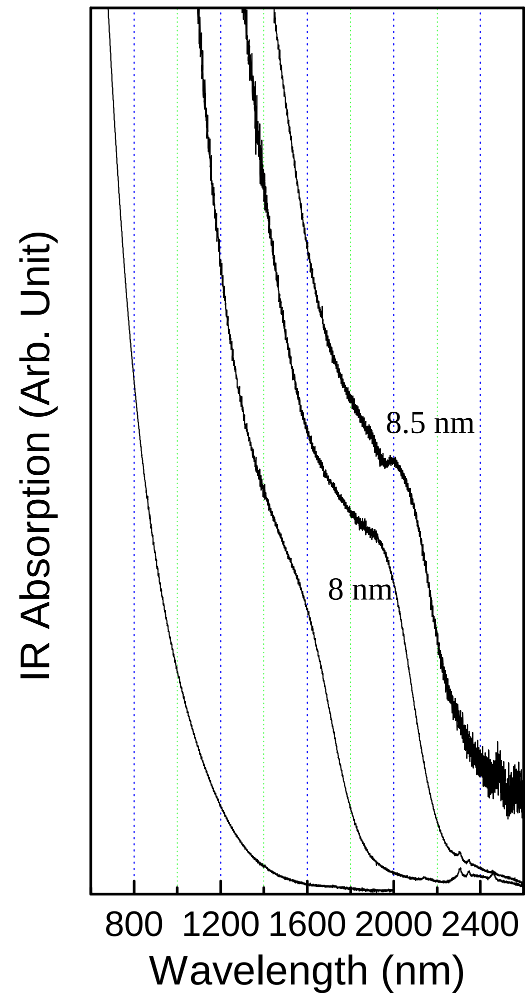
# IR Absorption of Lead Chalcogenides NCs




PbSe

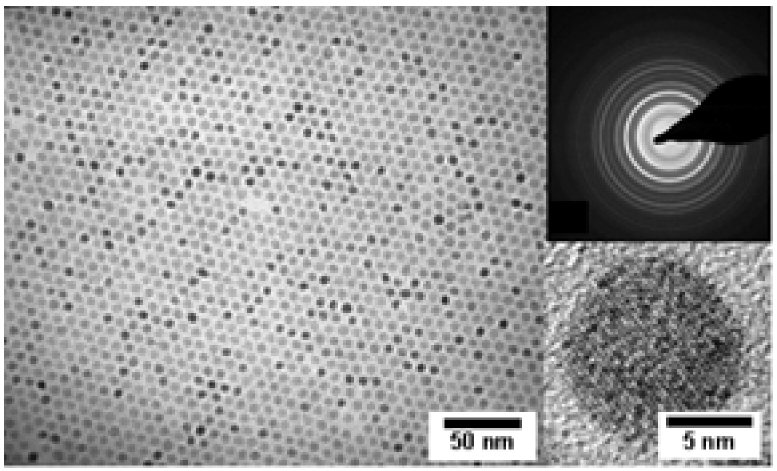


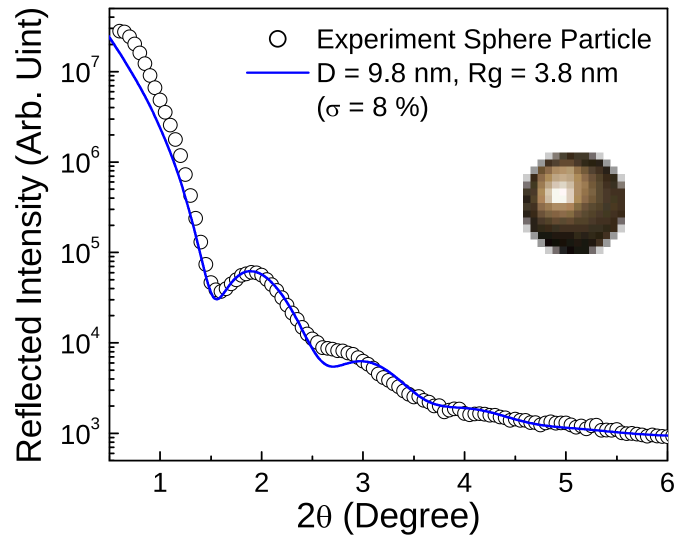

PbS

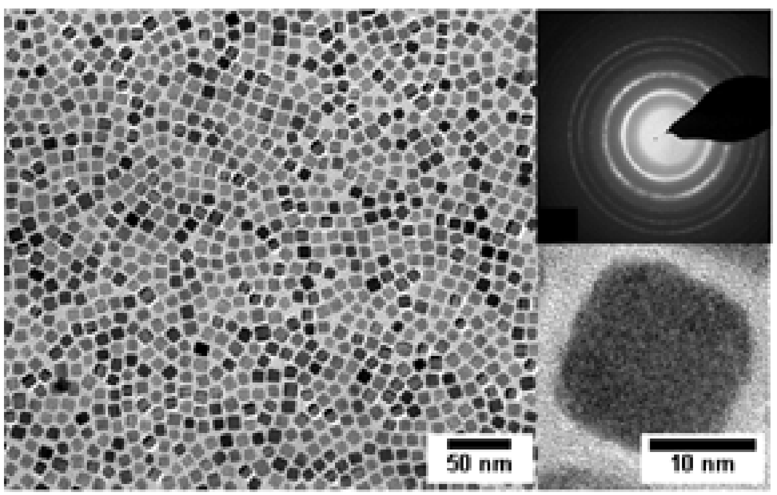


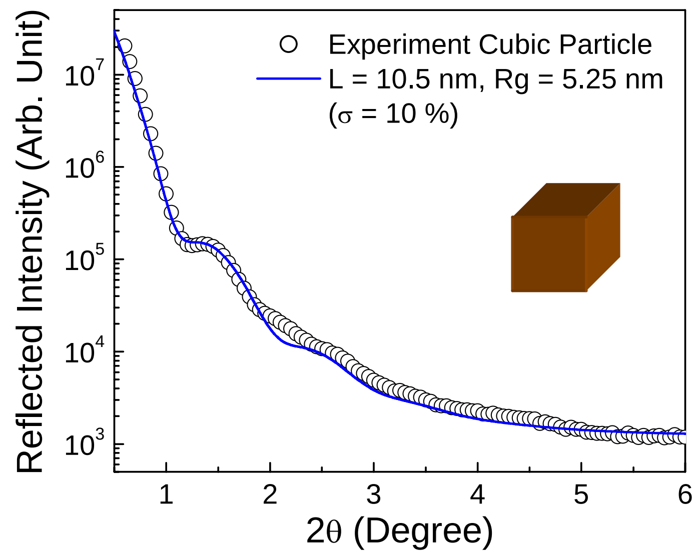

PbTe

# Shape Change from Sphere to Cubic and SAXS in Polymer Matrix



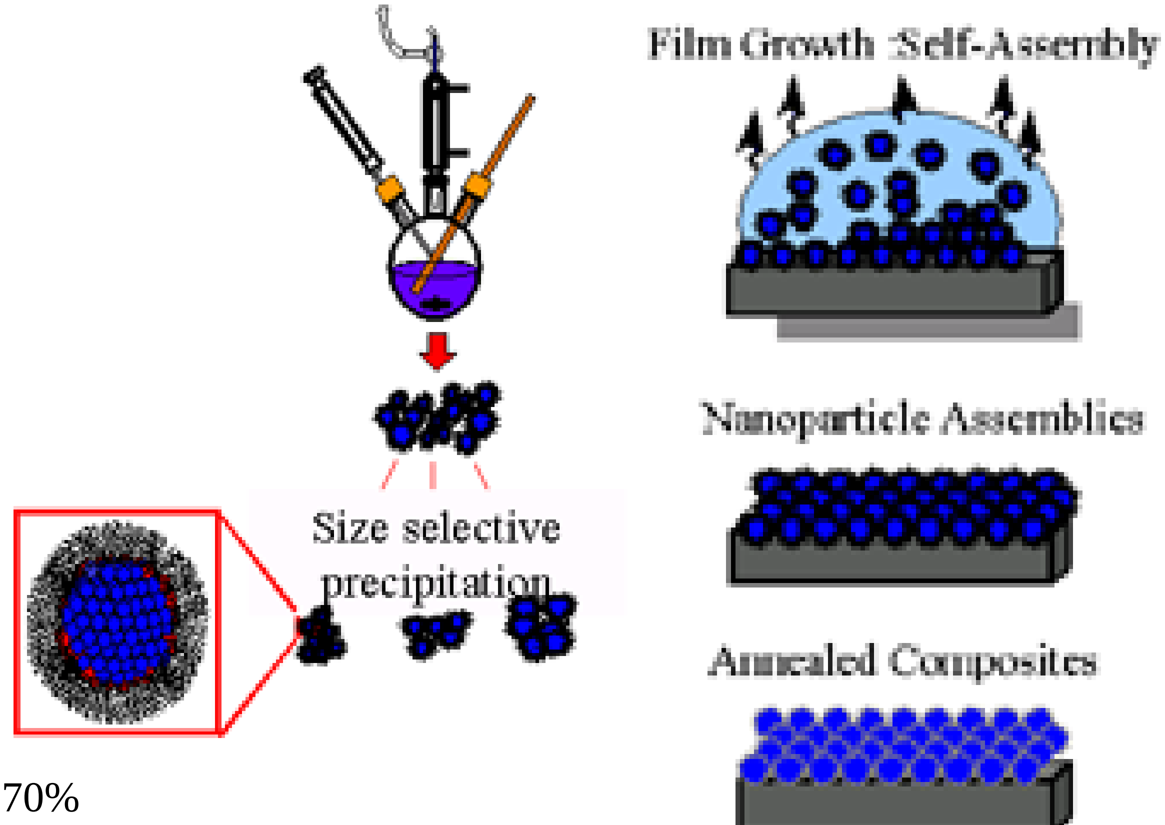




K.-S. Cho, W. Gaschler

# Ferroic Nanoparticles: synthesis and self-assembly into Ferroic Nanocomposites

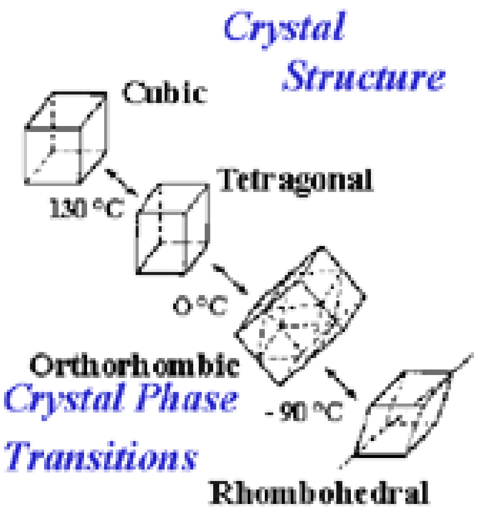
Target ferroelectrics:
BaTiO3
SrTiO3
BaSrTiO3
Future targets Niobdates



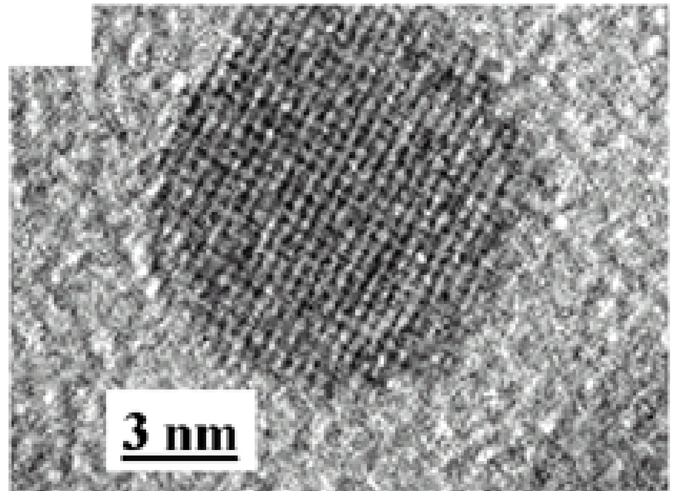

**DARPA supported personnel:**
Visiting Scientist Franz Redl 70%
Staff: C.B Murray 5%
Additional costs covered by IBM

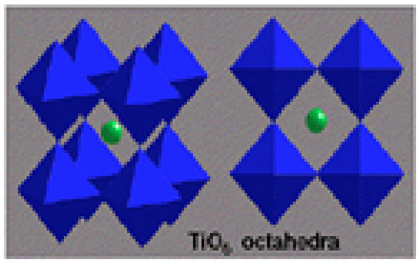
# Ferroelectric Nanocrystals $BaTiO_3$

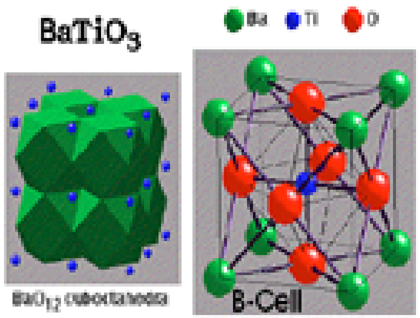
**Synthesis of Mg Quantities complete in Q2**

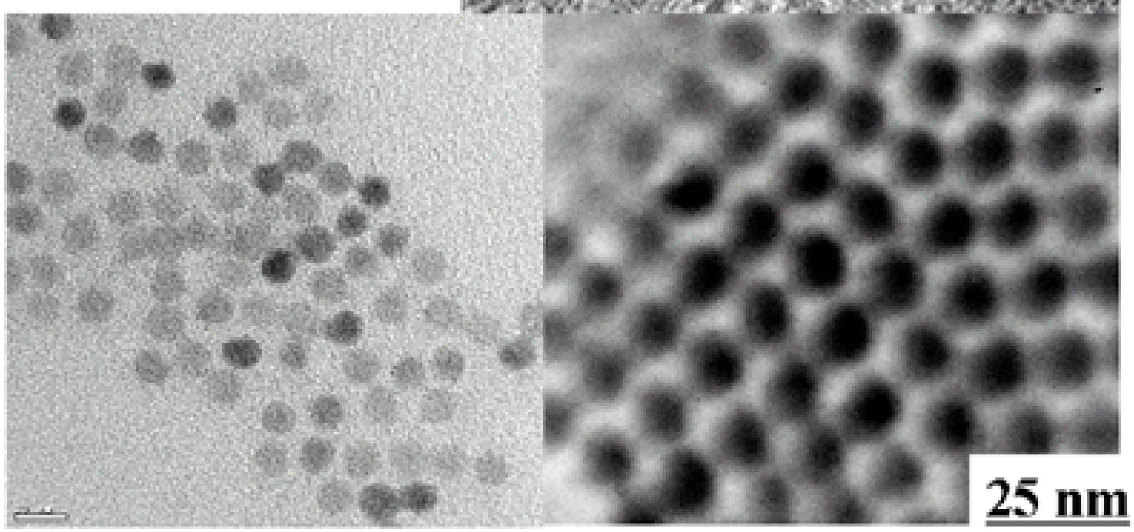



Challenge for Q3 to extend synthesis extend to SrTiO3.

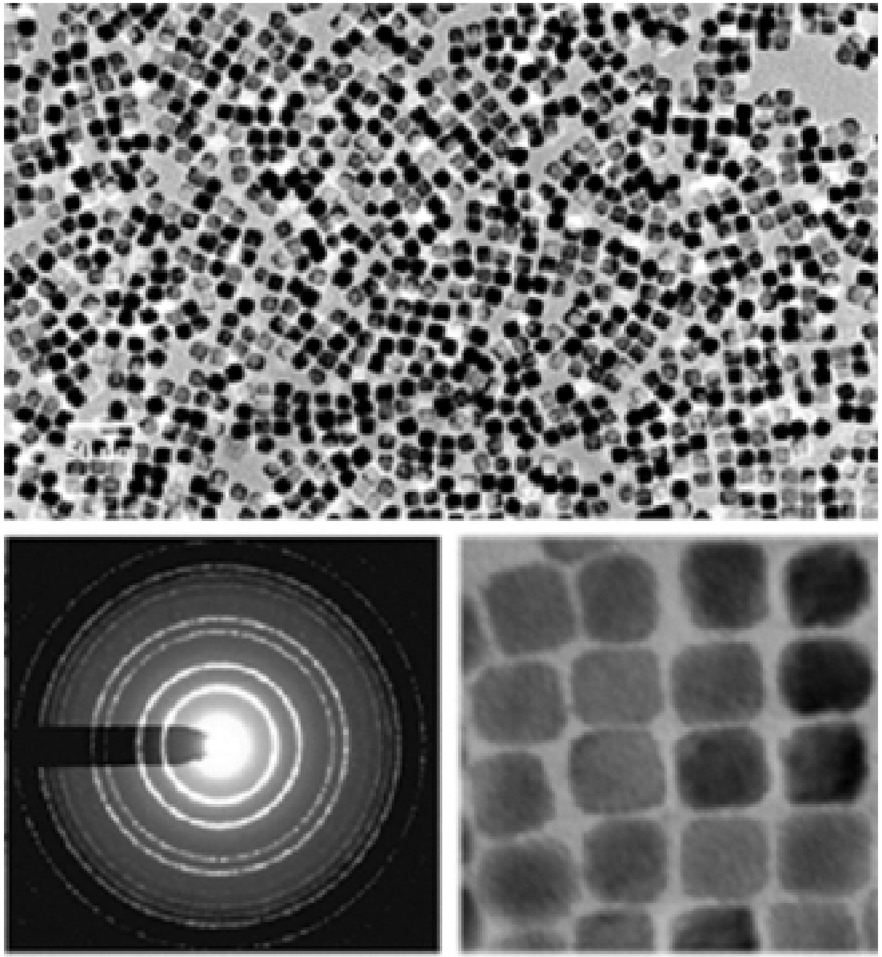


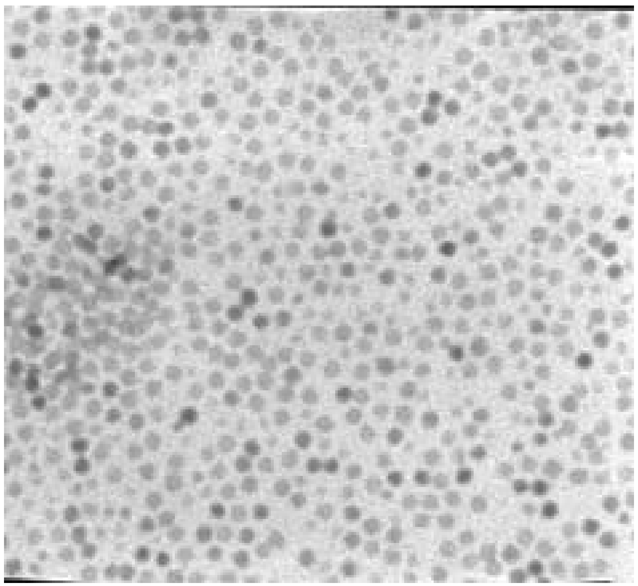



12 nm SrTiO3 for Strontium titanium isopropoxide
Milligram quantities preparation complete Q3 but mixed BaSrTiO3 takes a couple more months.



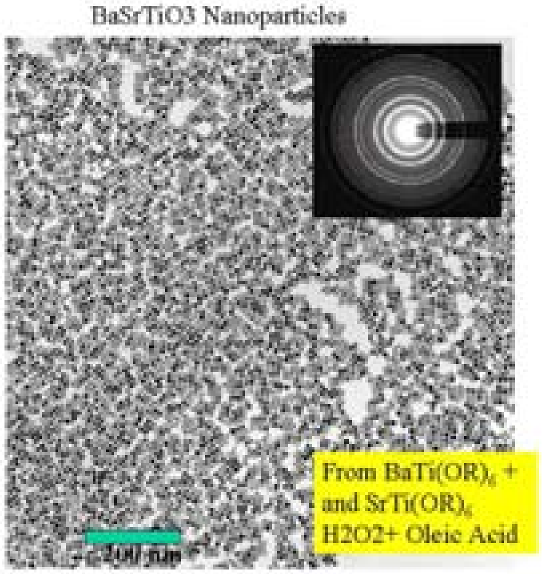
Mixed BaSrTiO3 Nanoparticles
Milligram Quantities complete Q5.

BaSrTiO3 synthesis from injection of
Individuale Ba and Sr alcoxide precursors.



**average size 8 nm**
**Bimodal population**
**(Most runs look worse)**

React Ba and Sr precursors to make mixed alcoxide prior to initiating growth



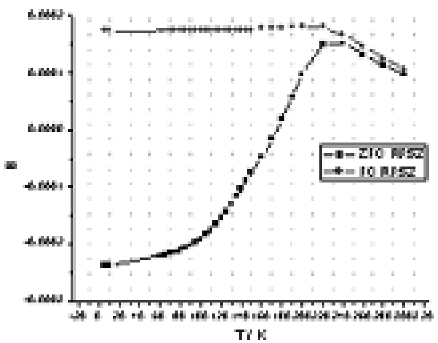
# Synthesis and Characterization of Iron Oxide Nanoparticle

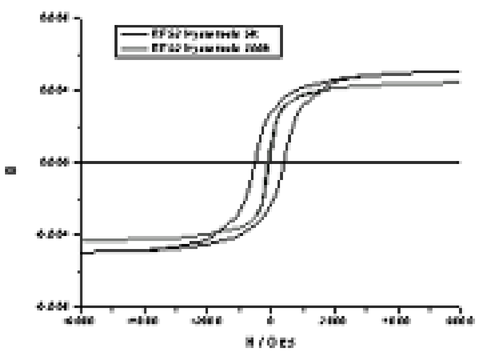
$Fe(CO)_5 \xrightarrow[\text{100-290 C}]{\text{octyl ether, oleic acid}} \text{Fe-NC} \xrightarrow{(CH_3)_3N\text{-}O} \gamma\text{-}Fe_2O_3\text{-NC}$

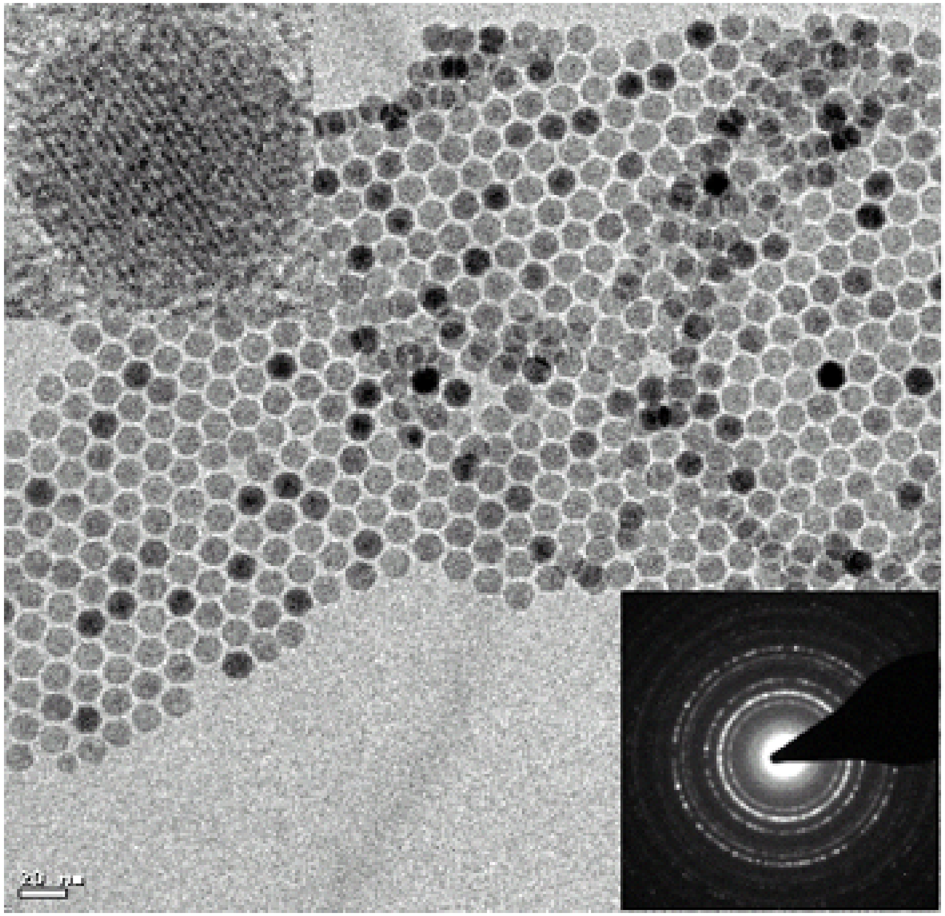
Fe-NC ↓ oxydation in air

$FeO \xrightarrow{\Delta T} Fe + Fe_3O_4$

*narrow sizedistribution of maghemite particle tuning of physical (e.g. magnetic) properties.*
*RF & Micrwave*
*Bio applications.*

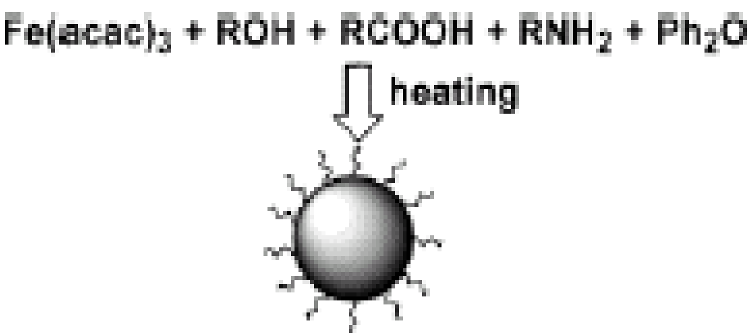


# Fe3O4 Nanocrystals

(Sun and Zeng)



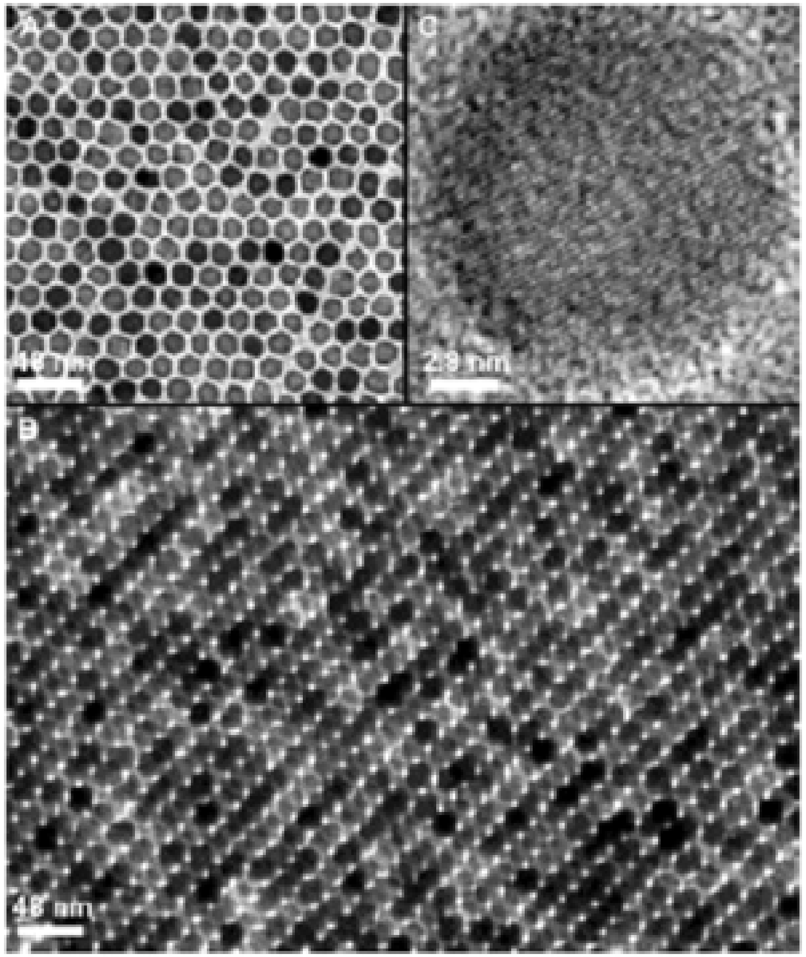
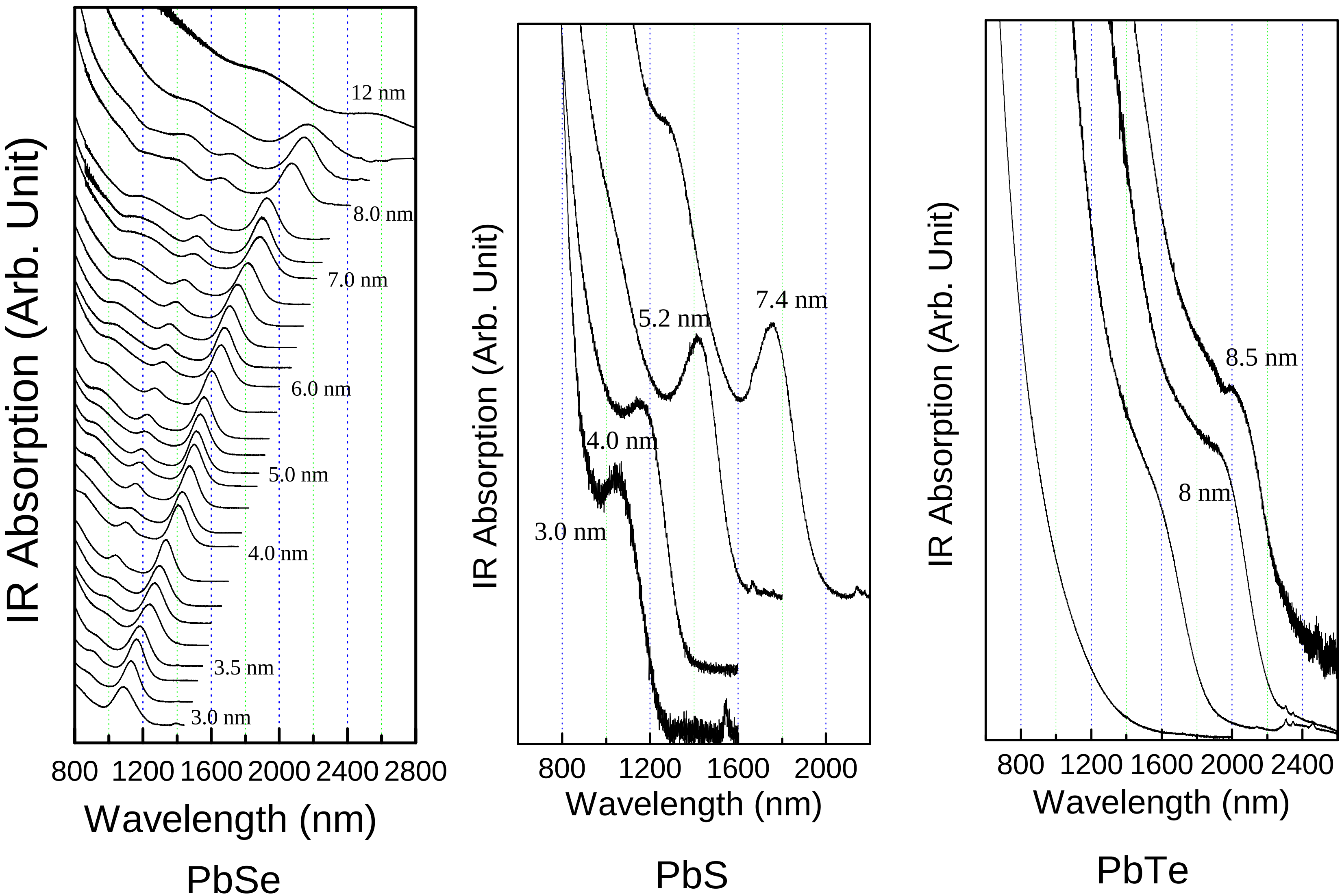



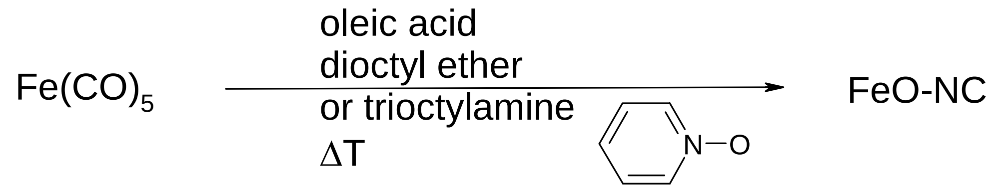

*Figure 1.* TEM bright field image of 16-nm $Fe_3O_4$ nanoparticles deposited from their dodecane dispersion on amorphous carbon surface and dried at 60 °C for 30 min: (A) a monolayer assembly, (B) a multilayer assembly, (C) HRTEM image of a single $Fe_3O_4$ nanoparticle. The images were acquired from a Philips EM 430 at 300 KV.

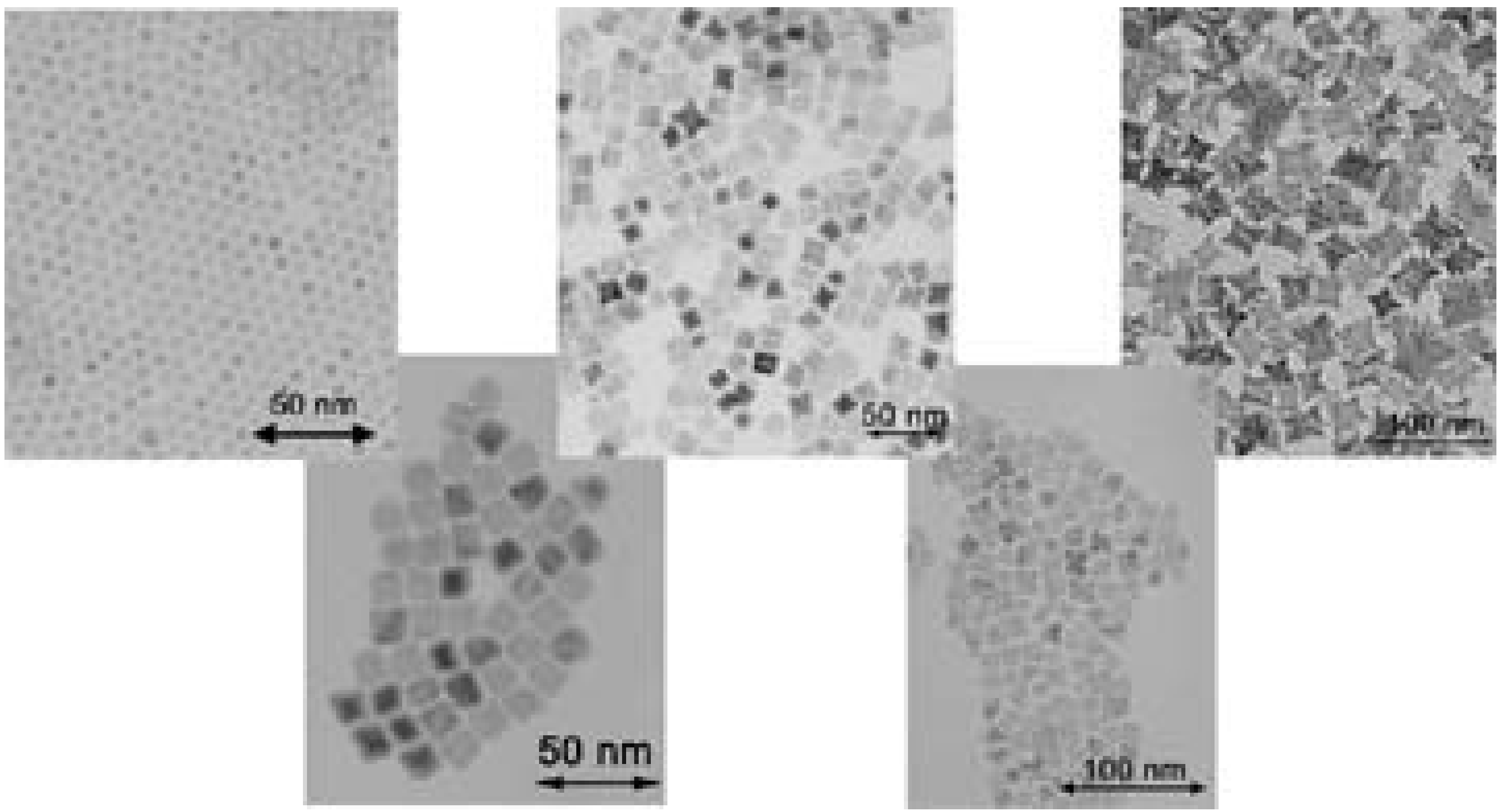
## IR Absorption of Lead Chalcogenides NCs



# Shape selective synthesis of wuestite

Substitute trimetylamine N-oxide with pyridin N-oxide



## Ag Nanocubes contd...

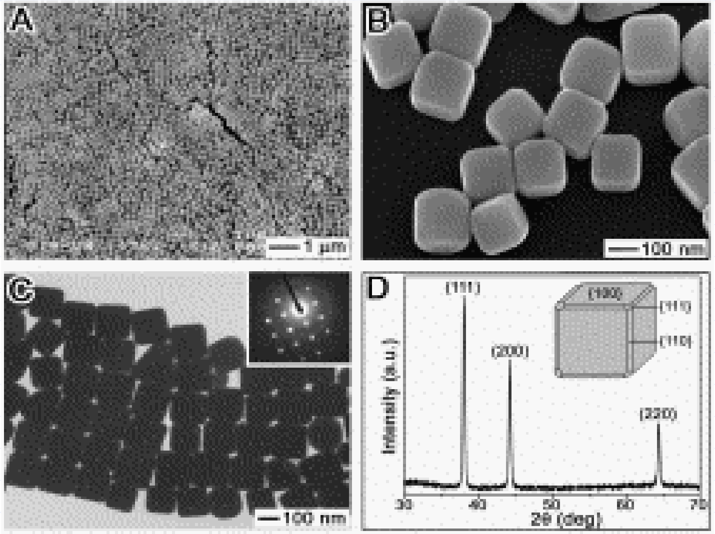



Fig.1

(**A**) Low &

(**B**) High magnification SEM images (B) was taken at a tilting angle of 20°

(**C**)TEM image

(**D**) XRD pattern

# Gold nanoboxes:

- Ag nanocubes were used to generate gold nanoboxes
- $3Ag(s) + HAuCl_4(aq) \longrightarrow Au(s) + 3AgCl(aq) + HCl(aq)$
- Black hole represents pinholes
- No gold had been deposited
- Order of faceting is {110}, {100}, {111}
- Free energies are associated with it
- Each nanobox is a single crystal

# Gold Nanoboxes contd…

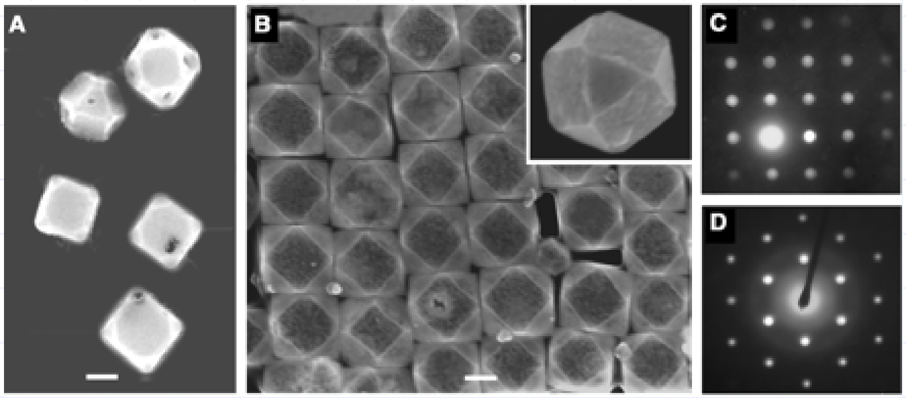



Fig3. SEM images of gold nanoboxes

(A) 0.3 ml and

(B) 1.5 ml of aqueous $HAuCl_4$ solution

Electron diffraction patterns

(c) Square facets{100}

(D) Triangular facets{111}