

0 D nanoparticles

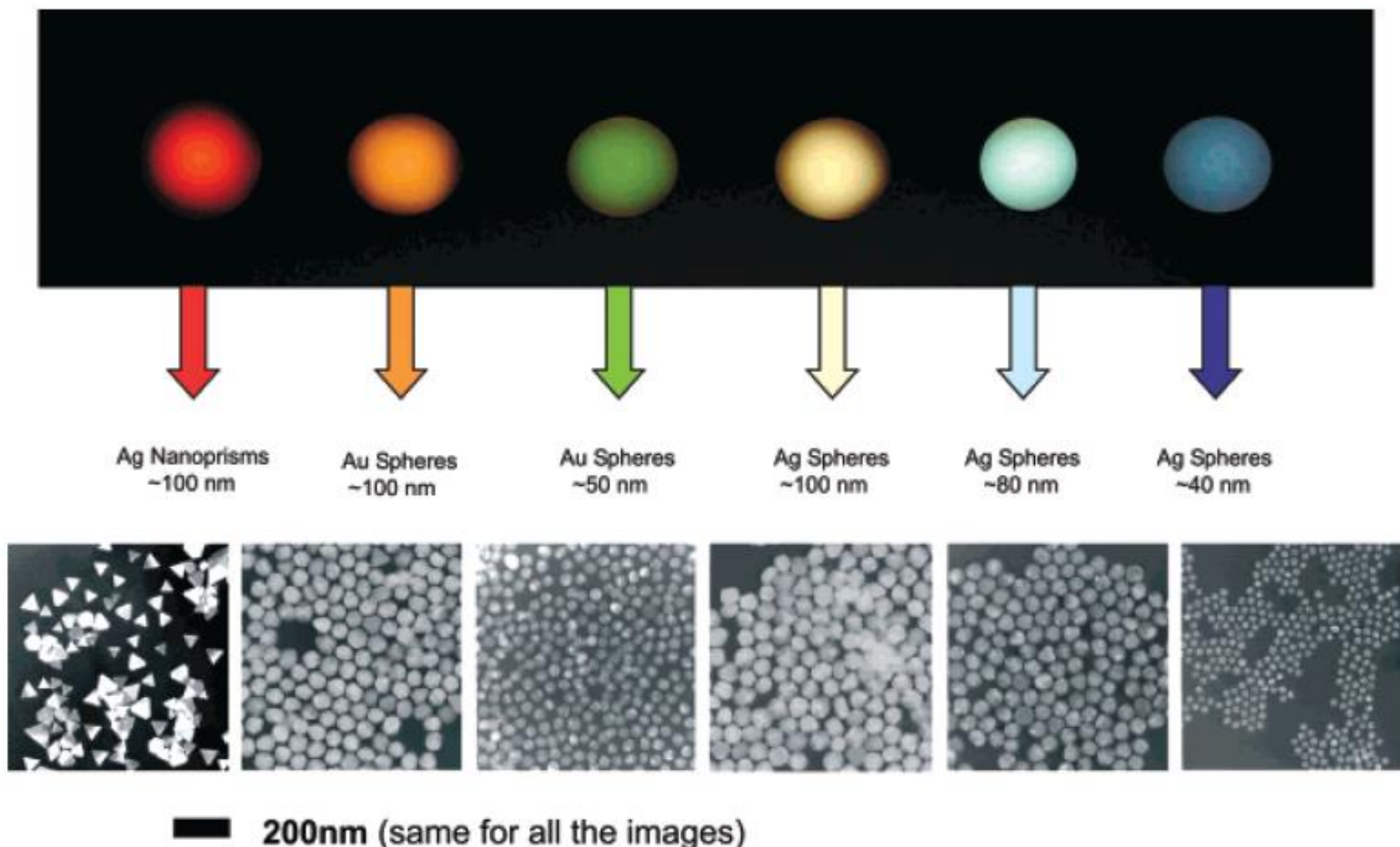
CML102

Contents

- Metal NPs
 - Au NPs
 - Pt NPs
 - Ag NPs
- Semiconductor NPs (Quantum Dots)
- Sol-gel method – oxides
- Heterostructures
 - SILAR
 - cALD
 - Cation exchange



Metal nanoparticles (NPs)



Synthesis of metal NPs

- General method – reduction of metal complexes
- for monodispersity – low conc, polymer
- precursors – elements, inorganic salts, metal complexes – Ni, Co, HAuCl_4 , H_2PtCl_6 , RhCl_3 , PdCl_3 ...
- reduction reagents – sodium citrate, H_2O_2 , $\text{NH}_2\text{OH} \cdot \text{HCl}$, citric acid, CO, P, H_2 , HCHO, CH_3OH , Na_2CO_3 , NaOH ...
- polymers – PVA, sodium polyacrylate

Table 3.1. Summary of precursors, reduction reagents and polymer stabilizers.

<i>Precursors</i>	<i>Formula</i>
Metal anode	Pd, Ni, Co
Palladium chloride	PdCl_2
Hydrogen hexachloroplatinate IV	H_2PtCl_6
Potassium tetrachloroplatinate II	K_2PtCl_4
Silver nitrate	AgNO_3
Silver tetraoxylchlorate	AgClO_4
Chloroauric acid	HAuCl_4
Rhodium chloride	RhCl_3
<i>Reduction Reagents</i>	
Hydrogen	H_2
Sodium citrate	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$
Hydroxylamine hydrochloride	$\text{NH}_4\text{OH} + \text{HCl}$
Citric acid	$\text{C}_6\text{H}_8\text{O}_7$
Carbon monoxide	CO
Phosphorus in ether	P
Methanol	CH_3OH
Hydrogen peroxide	H_2O_2
Sodium carbonate	Na_2CO_3
Sodium hydroxide	NaOH
Formaldehyde	HCHO
Sodium tetrahydroborate	NaBH_4
Ammonium ions	NH_4^+
<i>Polymer stabilizers</i>	
Poly(vinylpyrrolidone), PVP	
Polyvinylalcohol, PVA	
Polyethyleneimine	
Sodium polyphosphate	
Sodium polyacrylate	
Tetraalkylammonium halogenides	



Turkevich method – Au NPs

- HAuCl_4 in water $\sim 2.5 \times 10^{-4}$ M, 20 ml
- Add 1 ml 0.5% sodium citrate into boiling solution
- color changes
- ~ 20 nm diameter NPs
- large number of nuclei
 - small size
 - narrow size distribution

Gold Bull. **18**, 86 (1985)

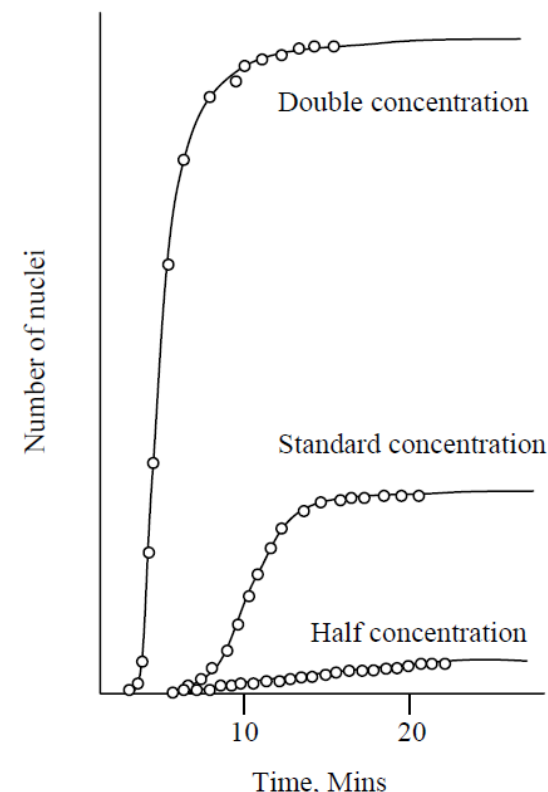
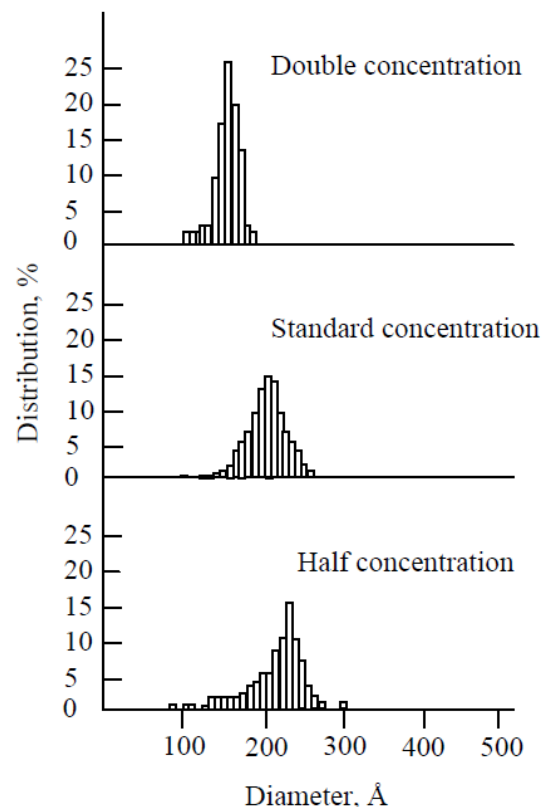
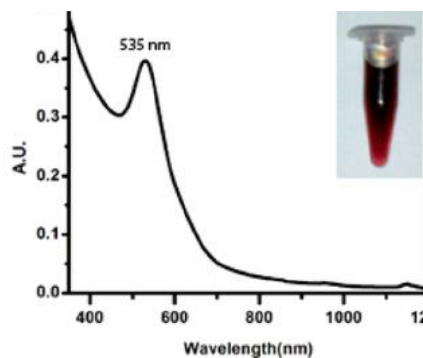
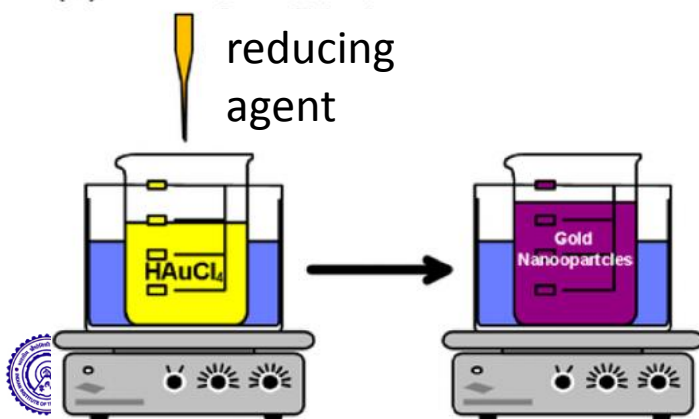


Fig 3.9 (left) Particle size distribution curves of gold sol prepared at different concentrations (right) Nucleation rate curves for gold sols prepared at different concentrations

(A)



Influence of reducing agents

- strong reducing agent → fast reaction rate → small NPs
- weak reducing agent → slow reaction rate → large NPs
 - if slow reaction leads to continuous formation of nuclei → wide size distribution
 - if no more nuclei formed → slow reduction → diffusion-limited growth → narrow size distribution
- morphology control
 - (a) sodium citrate
 - (b) citric acid
 - (morphology control possible by pH too)

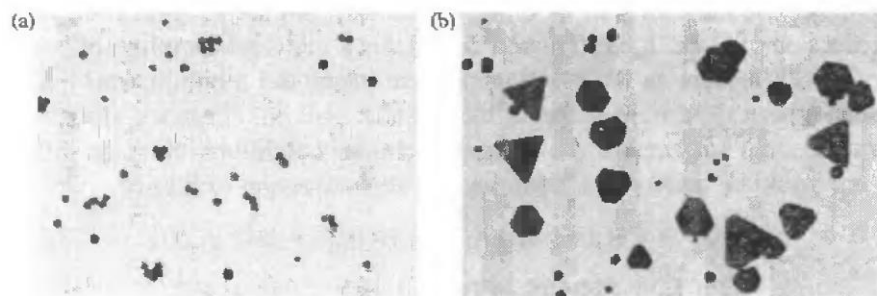
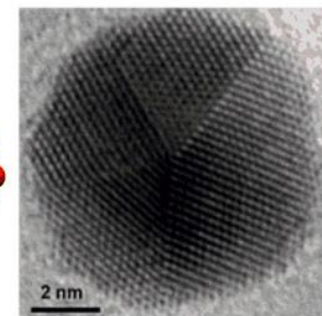
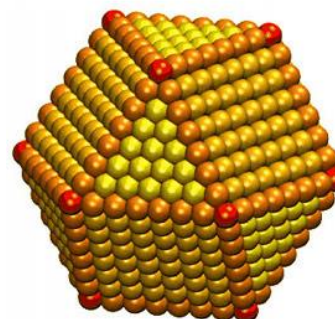


Fig. 3.10. SEM micrographs of gold nanoparticles prepared with sodium citrate (a) and citric acid (b) as reduction reagents, respectively, under otherwise similar synthesis conditions. [W.O. Miligan and R.H. Morriss, *J. Am. Chem. Soc.* **86**, 3461 (1964).]

Table 3.2. Comparison of average sizes of Au nanoparticles synthesized using various reduction reagents, all in nanometer.²⁷

<i>Reduction reagents</i>	436 nm*	546 nm*	<i>XRD</i> [#]	<i>SEM</i>
Sodium citrate	29.1	28.6	17.5	17.6±0.6
Hydrogen peroxide	25.3	23.1	15.1	15.7±1.1
	31.0	31.3	18.7	19.7±2.6
Hydroxylamine hydrochloride			37.8	22.8±4.2
Citric acid	23.5	22.8		12.5±0.6
Carbon monoxide	9.1	7.4	9.0	5.0±0.5
	15.3	15.3	9.8	7.5±0.4
	18.9	18.3	13.1	12.2±0.5
Phosphorus			13.9	8.1±0.5
			21.0	15.5±1.7
			29.6	25.6±2.6
			36.9	35.8±9.7

* The particle sizes are determined using light scattering with the indicated wavelengths.

[#] The particle sizes are determined based on X-ray diffraction line broadening.

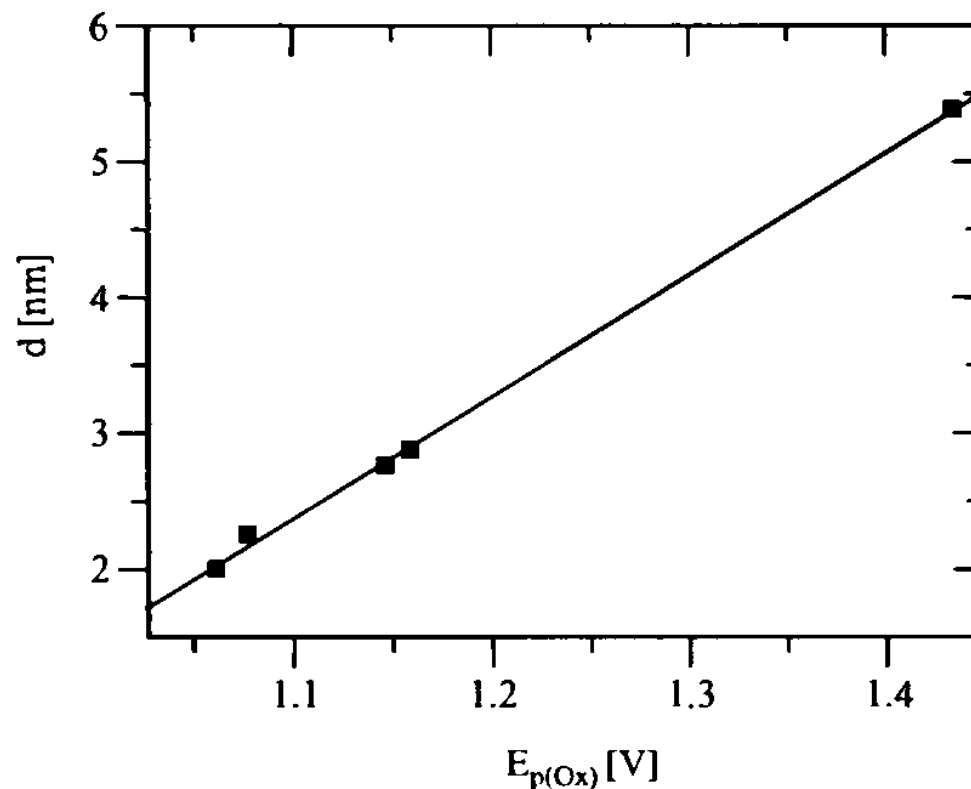
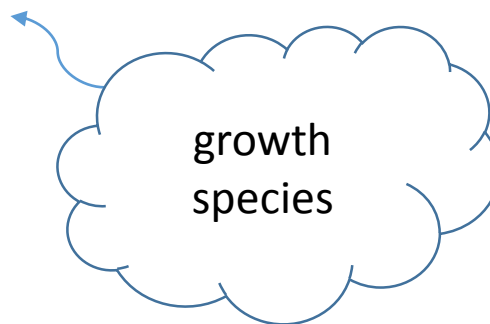
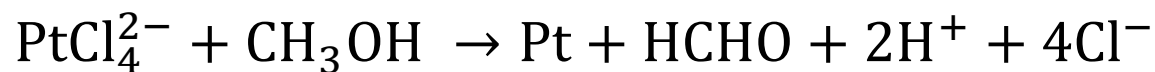
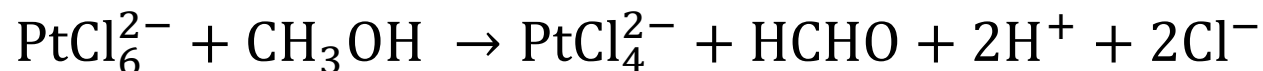


Fig. 3.11. The particle size of Pd colloids as a function of peak potentials of reduction reagent, carboxylates, in which smaller peak potentials mean stronger reduction reagents. [M.T. Reetz and M. Maase, *Adv. Mater.* **11**, 773 (1999).]

Pt synthesis using aq. MeOH – role of byproduct conc

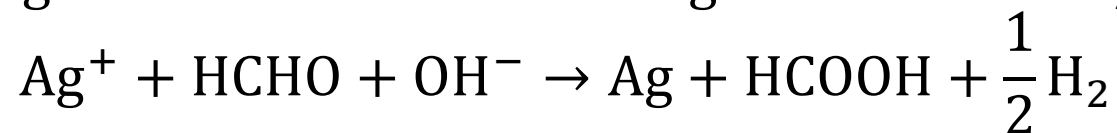
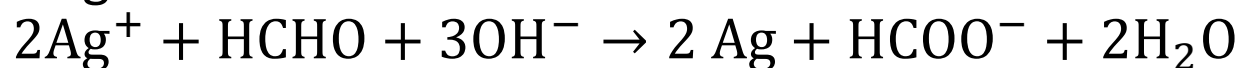
- Add high Chloride ion conc.



- reverse reaction favoured
- increase polymer conc.
 - diffusion control

Ag NPs – role of reactant conc.

- Reduction of Ag^+



use only NaOH $\rightarrow$ large particles

add $\text{Na}_2\text{CO}_3 \rightarrow$ reduces pH $\rightarrow$ controls size

PVP/PVA stabilized

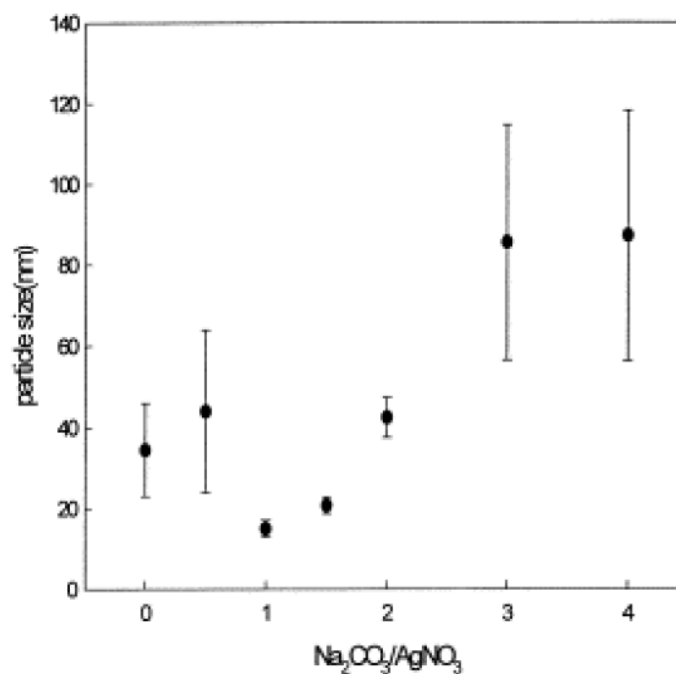


Fig. 3.12 Effect of $[\text{Na}_2\text{CO}_3]/[\text{AgNO}_3]$ ratio on silver average size and its standard deviation (other conditions: $[\text{AgNO}_3] = 0.005\text{M}$, $[\text{HCHO}]/[\text{AgNO}_3] = 4$, $[\text{NaOH}]/[\text{AgNO}_3] = 1$, $\text{PVP}/[\text{AgNO}_3] = 9.27$).

effect of polymer stabilizer/capping agent/ligand

- strong adsorption on growth sites → slow growth
- interact with solute, catalyst, solvent
 - PVP is a weak acid and combines with OH^- ions
- amount of polymer can change the shape
 - Pt ions: Na polyacrylate 1:1 → cubic NPs, 5:1 → Td NPs
 - growth rate of $\{111\}$ and $\{100\}$ facets of Pt nuclei is affected

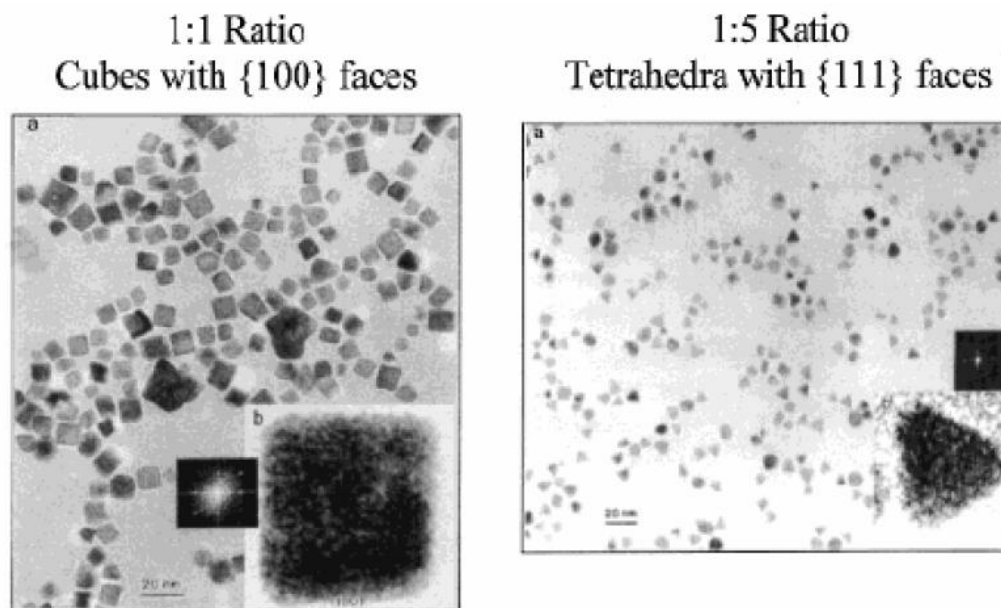
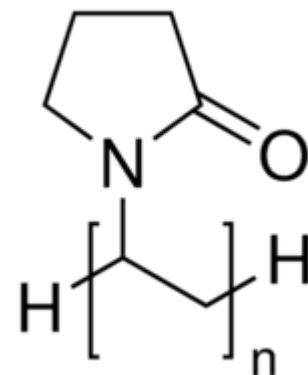


Fig. 3.13 Pt nanoparticles synthesized in colloidal solution and having different shapes (11 nm cubes on the left and ~7 nm tetrahedrons on the right). The potential use of these nanoparticles for different types of catalyses drives our research interest in these particles.

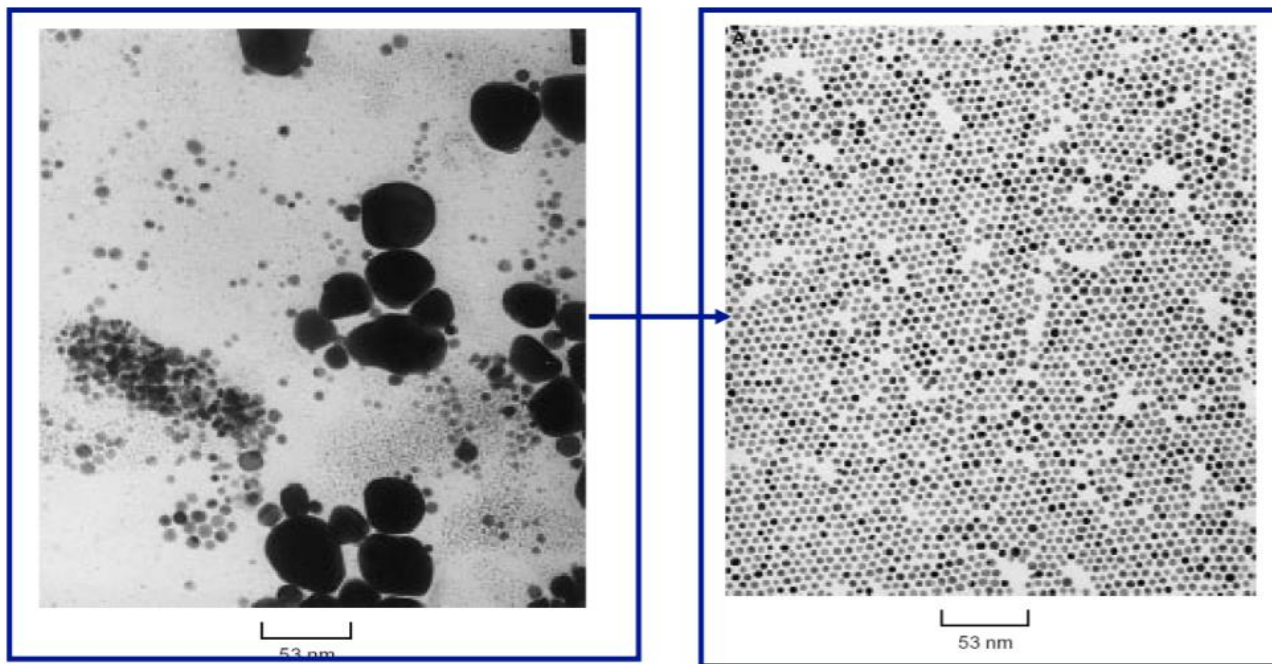
Digestive Ripening

large particles break apart and small particles increase in size

Electrostatic interaction

Uniform and Narrow size distribution
modification of the particle surface

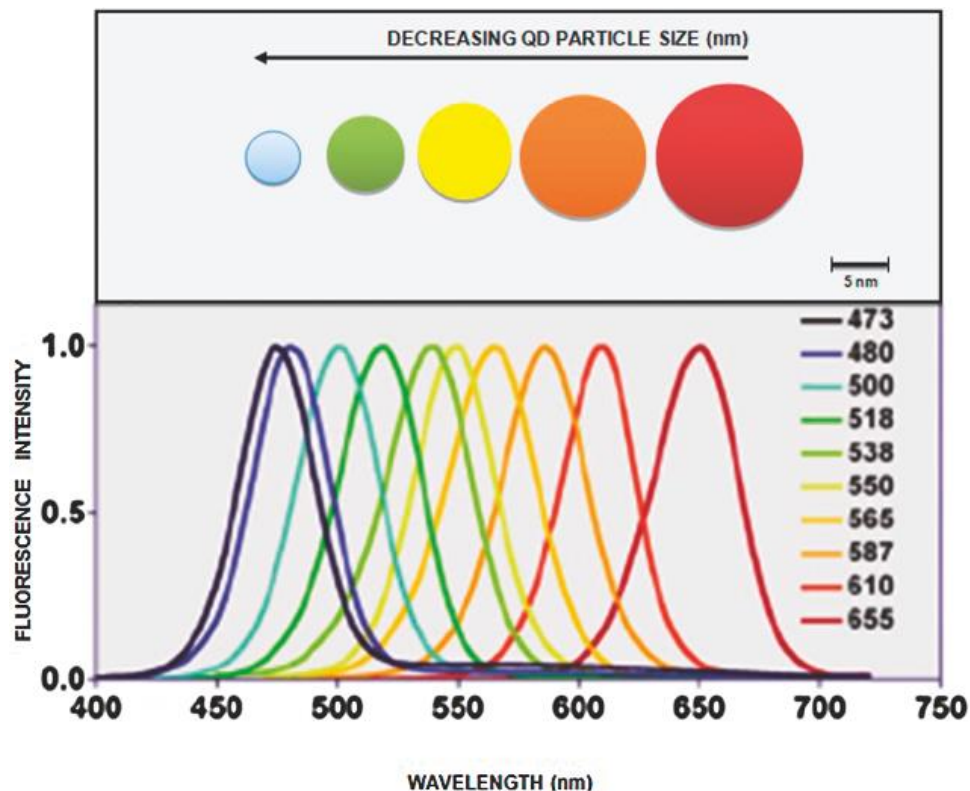
Thiols (C8 –C16) : **digestive ripening agents**



1. X.M. Lin, C.M. Sorensen and K.J. Klabunde *Journal of Nanoparticle Research* 2000, 2, 157–164
2. S. Stoeva, K. J. Klabunde, C. M. Sorensen, and I. Dragieva, *J. Am. Chem. Soc.*, 2002, 124, 2305-2311

Semiconductor Nanocrystals (NCs) or Quantum dots (QDs)

- quantum size effects
- tunability of band gap
- LEDs – QD vision, Samsung
- solar cells
- bio-labeling



CdSe synthesis

- TOPO at 300 C + Me₂Cd + TOPSe injection, temp drops, control temp
- methanol for flocculation, redisperse in butanol
- size selected precipitation

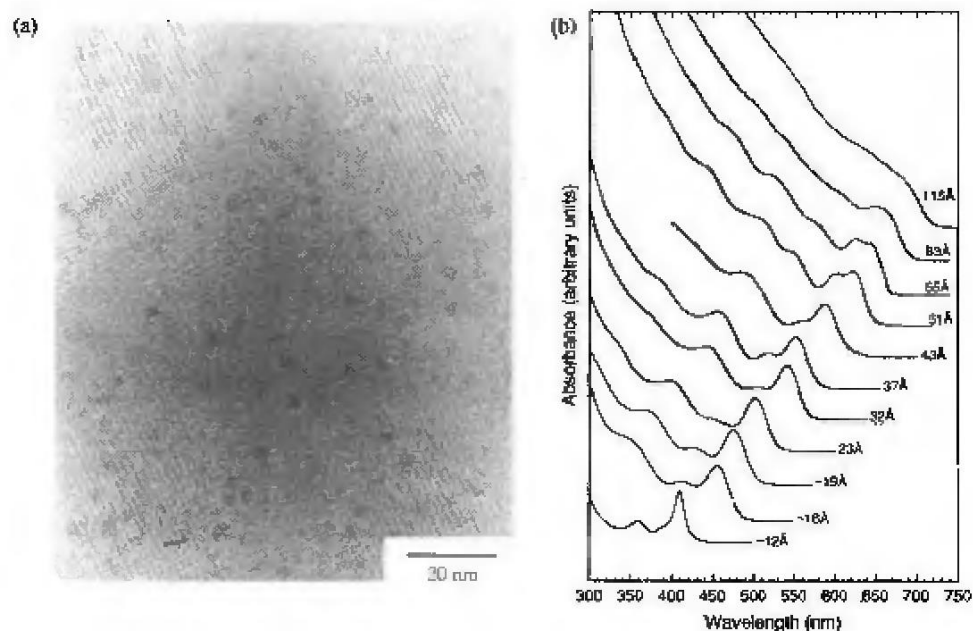


Fig. 3.15. (a) A near monolayer of 51 Å diameter CdSe crystallites showing short-range hexagonal close packing. (b) Room temperature optical absorption spectra of CdSe nanocrystallites dispersed in hexane and ranging in size from ~12 to 115 Å. [C.B. Murray, D.J. Norris, and M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).]

x-ray diffraction – broadening

- Scherrer equation

$$D = \frac{4}{3} \frac{0.9\lambda}{\beta \cos \theta}$$

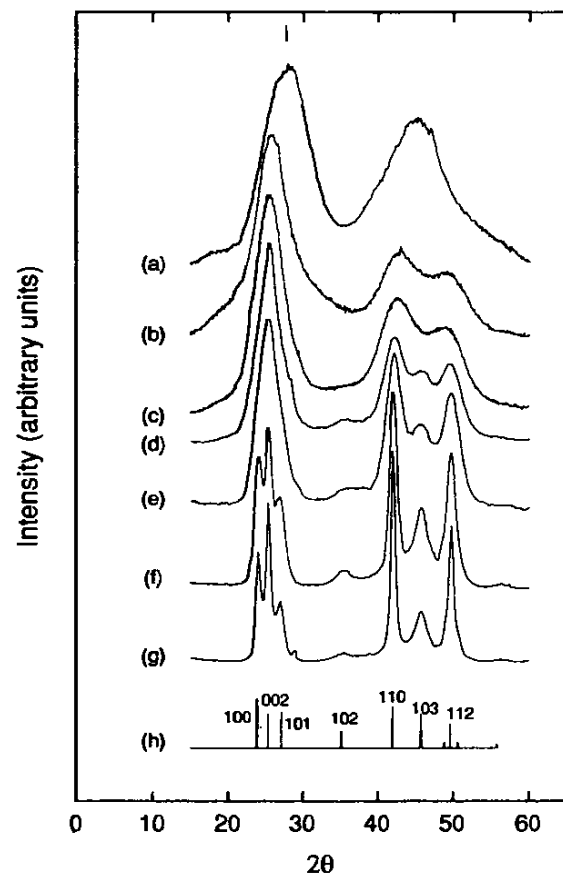


Fig. 3.16. Powder X-ray diffraction spectra of (a) 12, (b) 18, (c) 20, (d) 37, (e) 42, (f) 83 and (g) 115 Å diameter CdSe nanocrystallites compared with the bulk wurtzite peak positions (h). [C.B. Murray, D.J. Norris, and M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).]

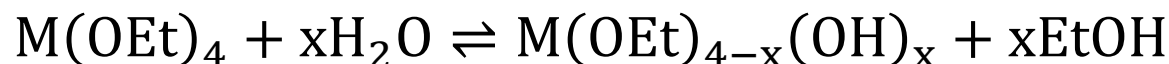
Thermal decomposition at high T - GaP

- $\text{GaCl}_3 + \text{P}(\text{SiMe}_3)_3 \xrightarrow{\text{toluene, r.t.}} [\text{Cl}_2\text{GaP}(\text{SiMe}_3)_2]_2$
- $\text{InClC}_2\text{O}_4 + \text{P}(\text{SiMe}_3)_3 \xrightarrow{\text{toluene, r.t.}} \text{precursor}$
- heat the precursors in TOP/TOPO for several days $\rightarrow$ 2-6 nm particles, zinc blende structure
- MeOH to ppt
- Long chain stabilizers
 - hexadecylamine (HDA), octadecylamine (ODA), oleylamine (OLA)
 - oleic acid (OA), stearic acid (SA), myristic acid

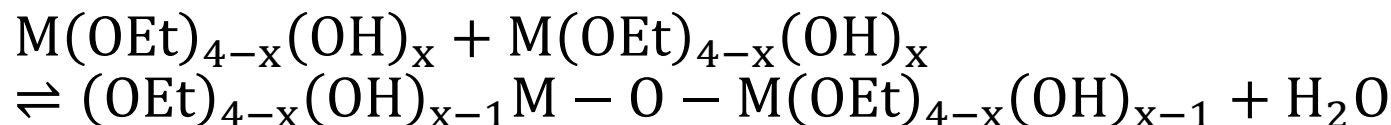


Sol-gel synthesis

- hydrolysis



- condensation



- results in nanoscale clusters with organic ligands
- hydrolysis and condensation can occur sequentially or in parallel
- rates of reactions of the two materials
 - extent of charge transfer
 - ability to expand coordination number
- reactivity inc. as ionic radius inc.
- multicomponent materials

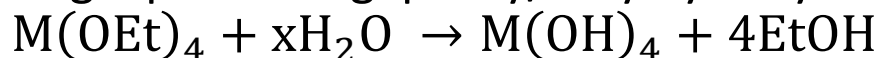
Table 3.3. Electronegativity, χ , partial charge, δM , ionic radius, r , and coordination number, n , of some tetravalent metals.⁷⁷

Alkoxide	χ	δM	$r(\text{\AA})$	n
Si(OPr ⁱ) ₄	1.74	+0.32	0.40	4
Ti(OPr ⁱ) ₄	1.32	+0.60	0.64	6
Zr(OPr ⁱ) ₄	1.29	+0.64	0.87	7
Ce(OPr ⁱ) ₄	1.17	+0.75	1.02	8

where OPrⁱ is OCH₂CH₂CH₃

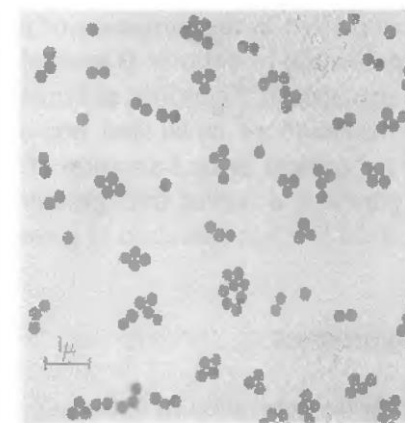
– heterocondensation

- different organic ligands (bulkier → slower, Si(OC₂H₅)₄ < Si(OCH₃))
- modify coordination state of alkoxide with a chelating agent e.g. acac
- multiple step sol-gel processing. partly/fully hydrolyze less reactive first



Forced hydrolysis – Silica spheres (Stober process)

- metal salt solutions – hydrolyze
- inc. temp. to deprotonate the attached H_2O
 - more intermediate hydroxide at high T
 - results in supersaturation $\rightarrow$ nucleation of MO
- NH_3 as catalyst, alcohols as solvents, H_2O for hydrolysis + add Silicon alkoxides with vigorous stirring $\rightarrow$ 50 nm – 2 μm sized particles
- reaction rate depends on
 - solvents
 - smallest particles in MeOH – fast reactn, large in n-BuOH – slow reactn
 - precursors – alkyl chains
 - short ligands favour faster reactn $\rightarrow$ small sizes
 - amount of water
 - NH_3
 - linear structures and not 3D in absence of ammonia
- Stober et al. J. Colloid Interf. Sci. **26**, 62 (1968)



Forced hydrolysis - α -Fe₂O₃

- mix FeCl₃ solution with HCl. Dilute it.
- add mixture to preheated water at 95-99 °C with constant stirring.
 - keep sealed for 24 hrs.
 - high T favours fast hydrolysis → high supersaturation → large # of nuclei
 - quench in cold water.
- dilution before heating – v. imp. to ensure
 - controlled nucleation
 - diffusion limited growth
- long aging would lead to Ostwald ripening – narrow size distribution
- metal acac + 1,2-hexadecanediol → MFe₂O₄ (M=Fe, Co, Mn) NPs 3-20 nm
 - magnetic studies



Effect of anions

Cl⁻ ions
hematite or akageneite

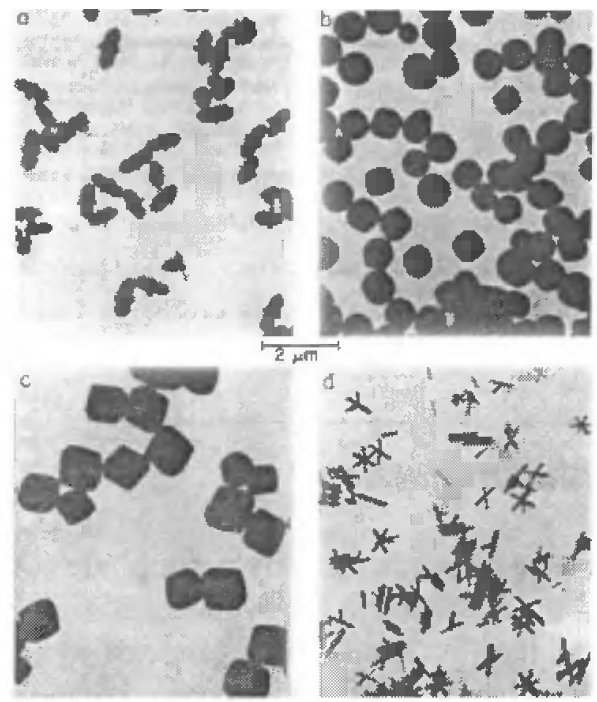


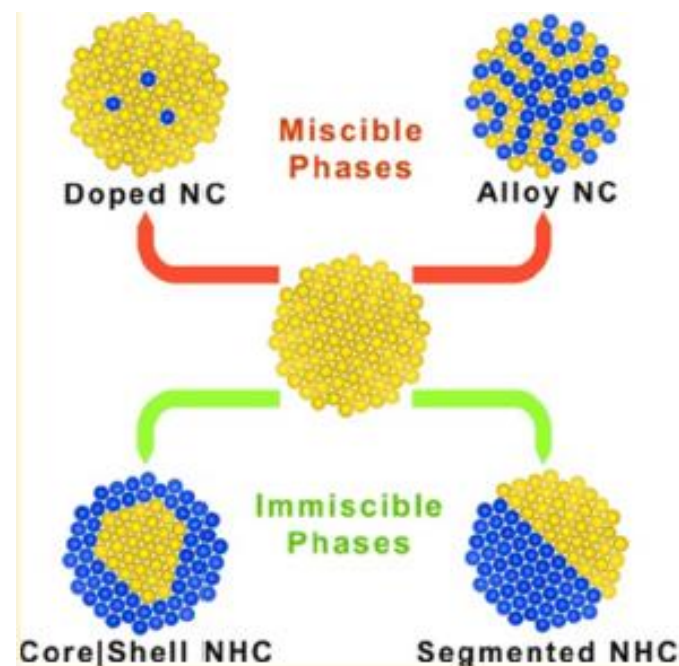
Fig. 3.20. TEM images of various iron oxide and iron hydroxide nanoparticles obtained from solutions of FeCl₃ and HCl under various conditions listed in Table 3.4. [E. Matijević, *J. Colloid Interf. Sci.* **58**, 374 (1977).]

Table 3.4. A summary of synthesis parameters including temperature and time of aging are used to obtain α-Fe₂O₃ (A, B, and C) or β-FeO(OH) nanoparticles shown in Fig. 3.19.^{88,89}

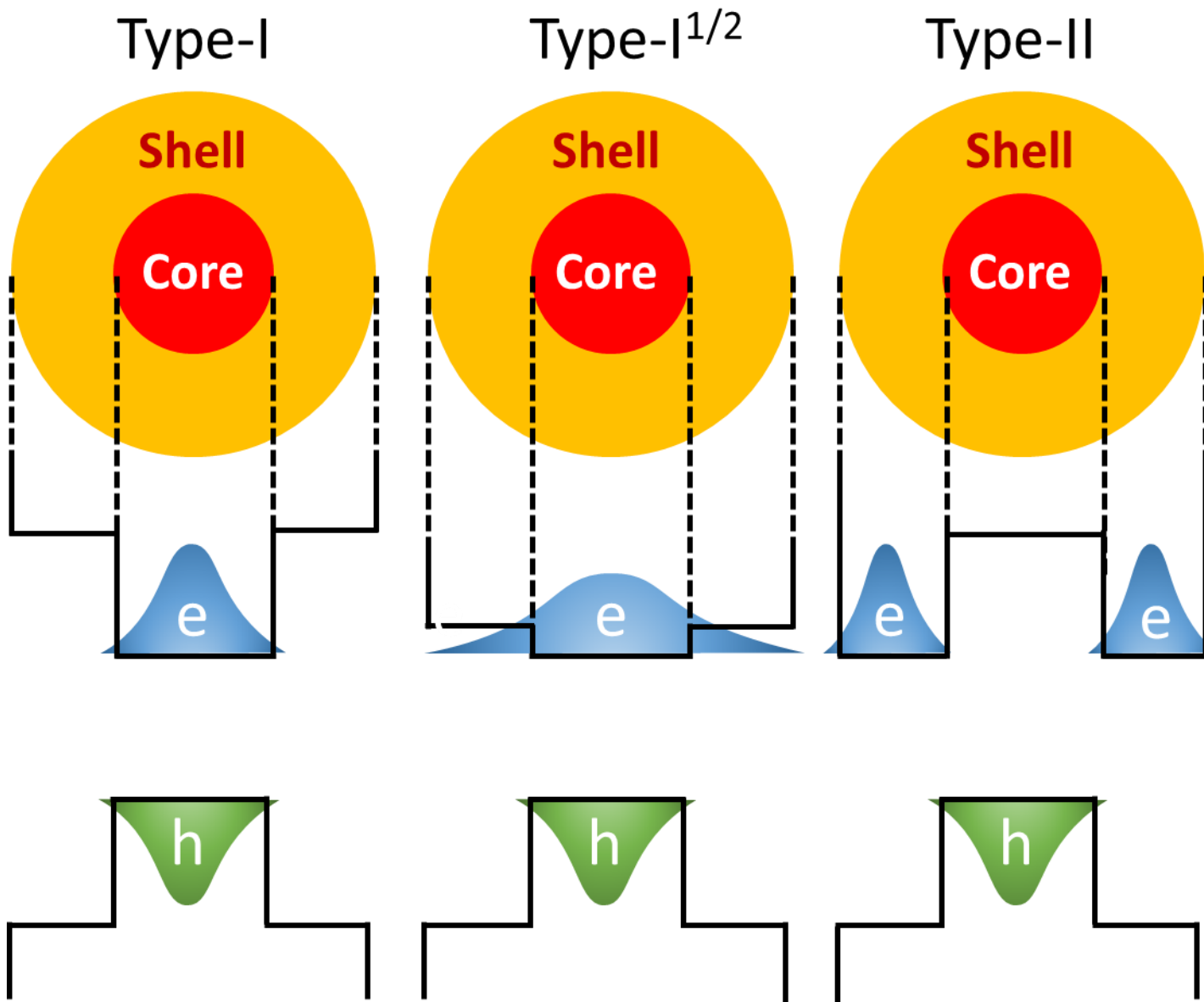
	<i>Fe³⁺</i> (M)	<i>Cl⁻</i> (M)	<i>Initial pH</i>	<i>Final pH</i>	<i>Temp</i> (°C)	<i>Time</i>
A	0.018	0.104	1.3	1.1	100	24 hr
B	0.315	0.995	2.0	1.0	100	9 days
C	0.09	0.28	1.65	0.88	100	24 hr
D	0.09	0.28	1.65	0.70	100	6 hr

core shell

- type I
- type II
- SILAR
 - Peng et al. Chem Mater (2003)
- cALD
 - JACS 134, 18585
- cation exchange
 - Chem Rev. 116, 10852 (2016)

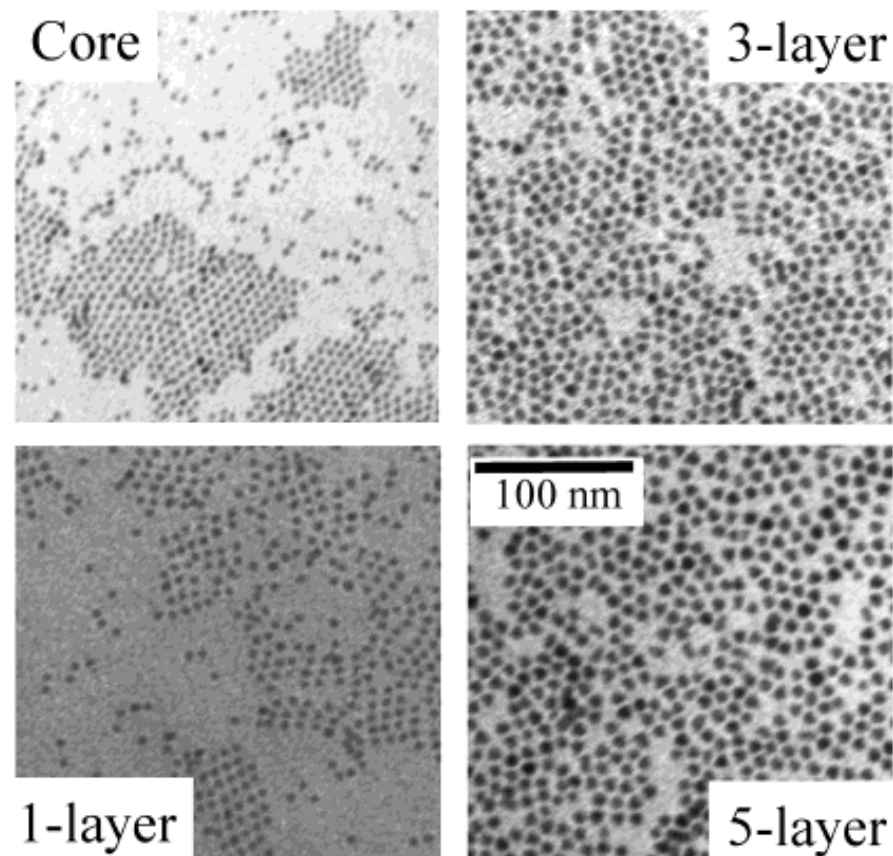
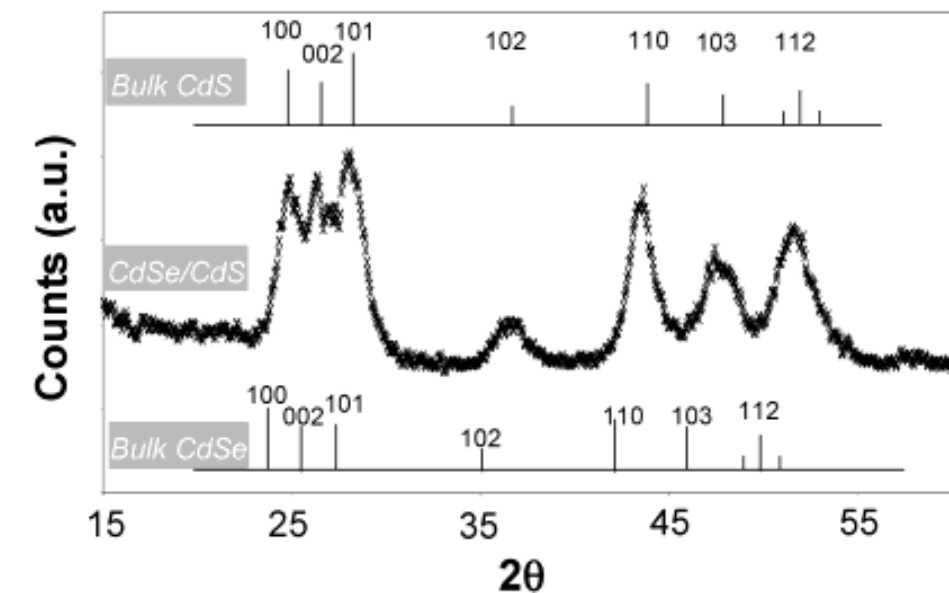


Heterostructures



SILAR – successive ion layer adsorption and reaction

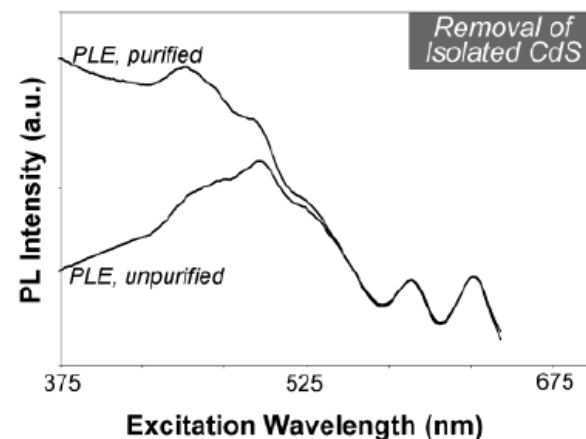
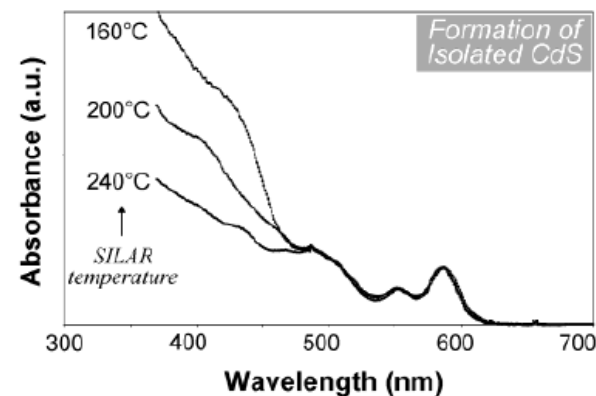
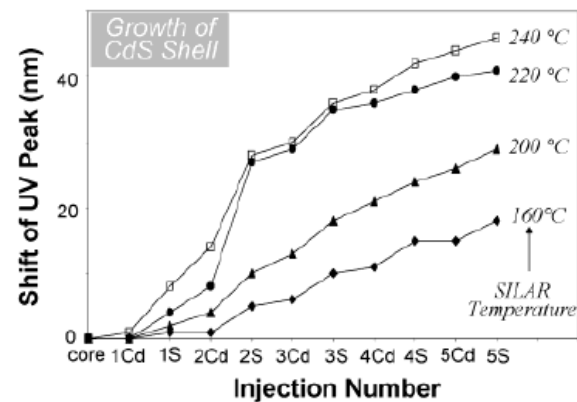
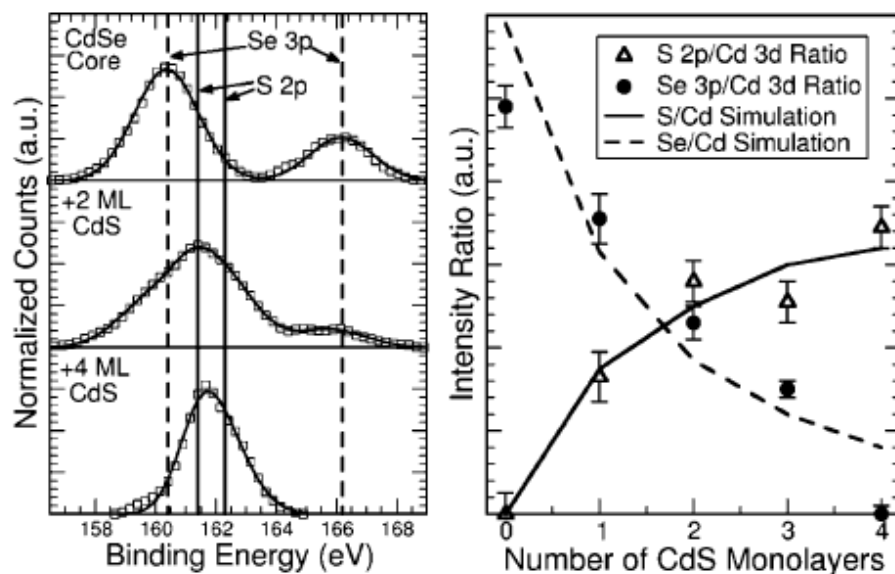
- CdS on CdSe cores
- lattice mismatch $\sim 5\text{-}6\%$



Peng et al. Chem Mater (2003)

SILAR – successive ion layer adsorption and reaction

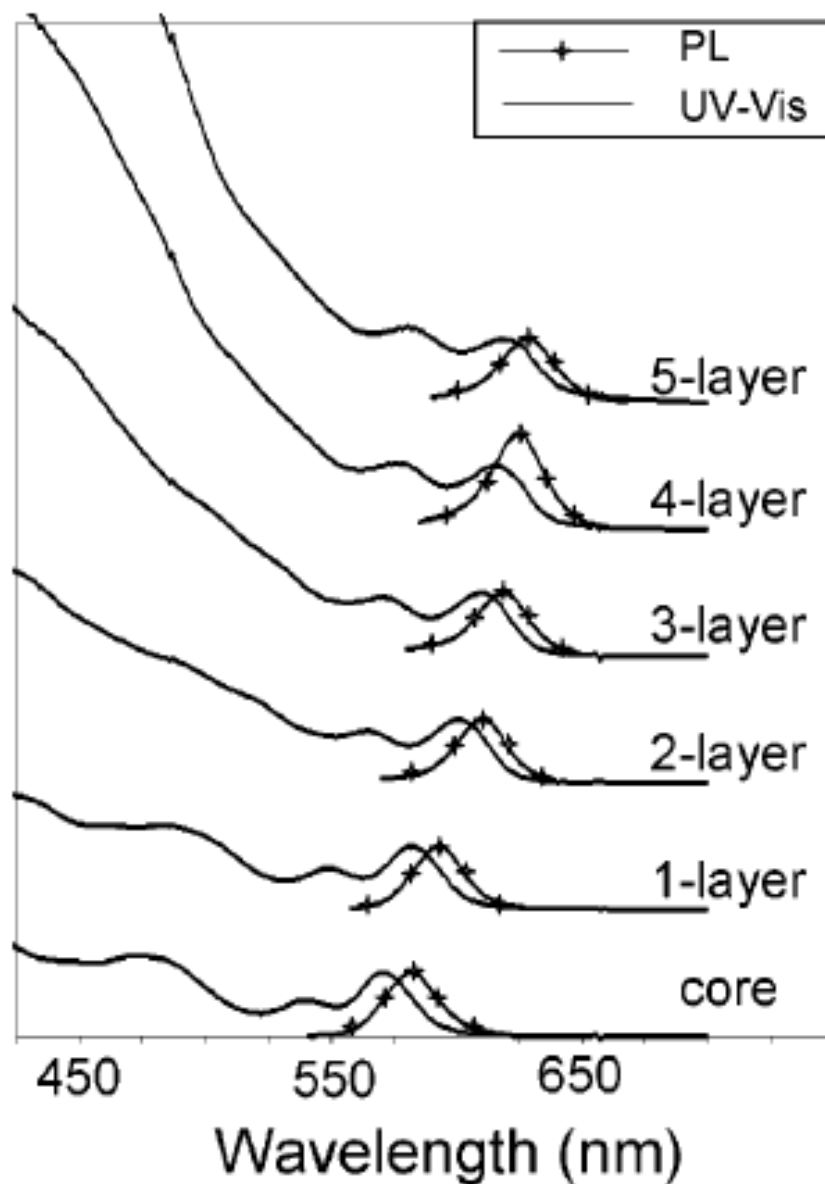
- Increasing S



- Optimization of SILAR temperature →

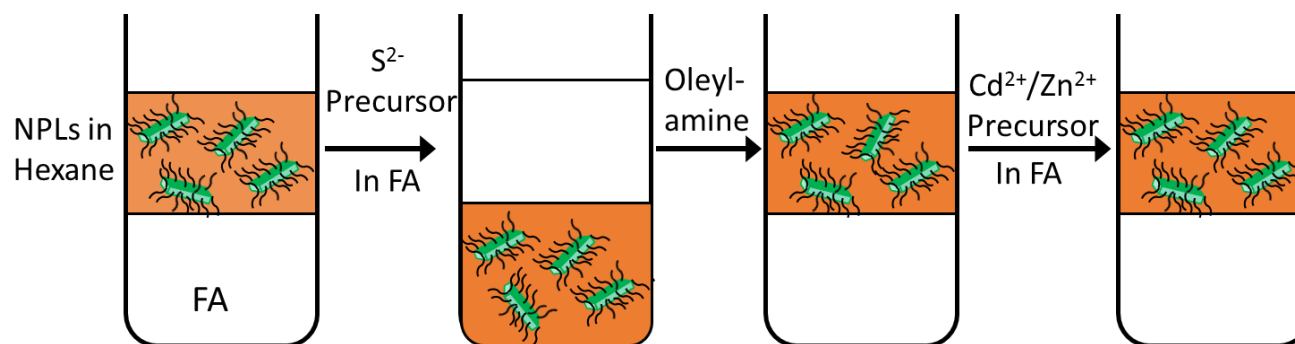


SILAR – growth of CdS on CdSe



Colloidal Atomic Layer Deposition (cALD) Technique

- Room temperature
- Based on self-limiting half reactions.
- Phase transfer of NCs or molecular precursors between immiscible nonpolar and polar phases.
- The phase transfer allows removal of unreacted molecular precursors and prevents accumulation of the reaction by-products.

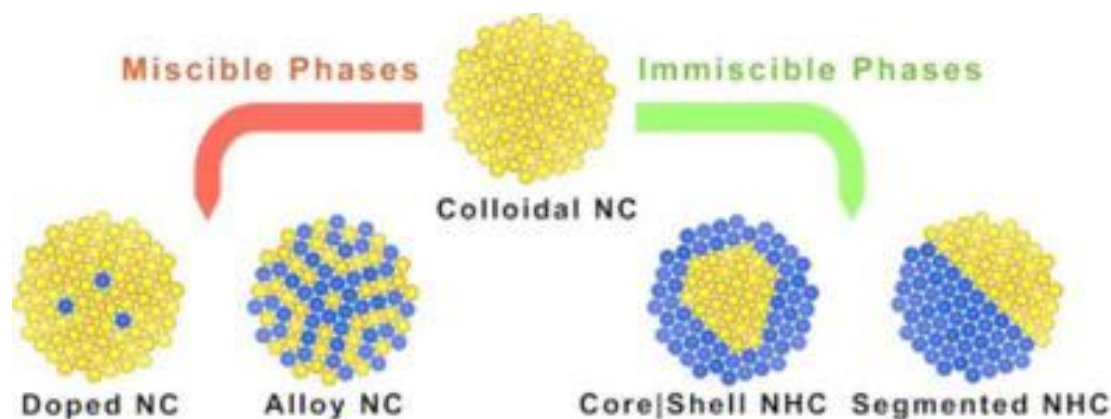


NCs: Nanocrystals, FA: Formamide

J. Am. Chem. Soc., **2012**, *134*, 18585–18590

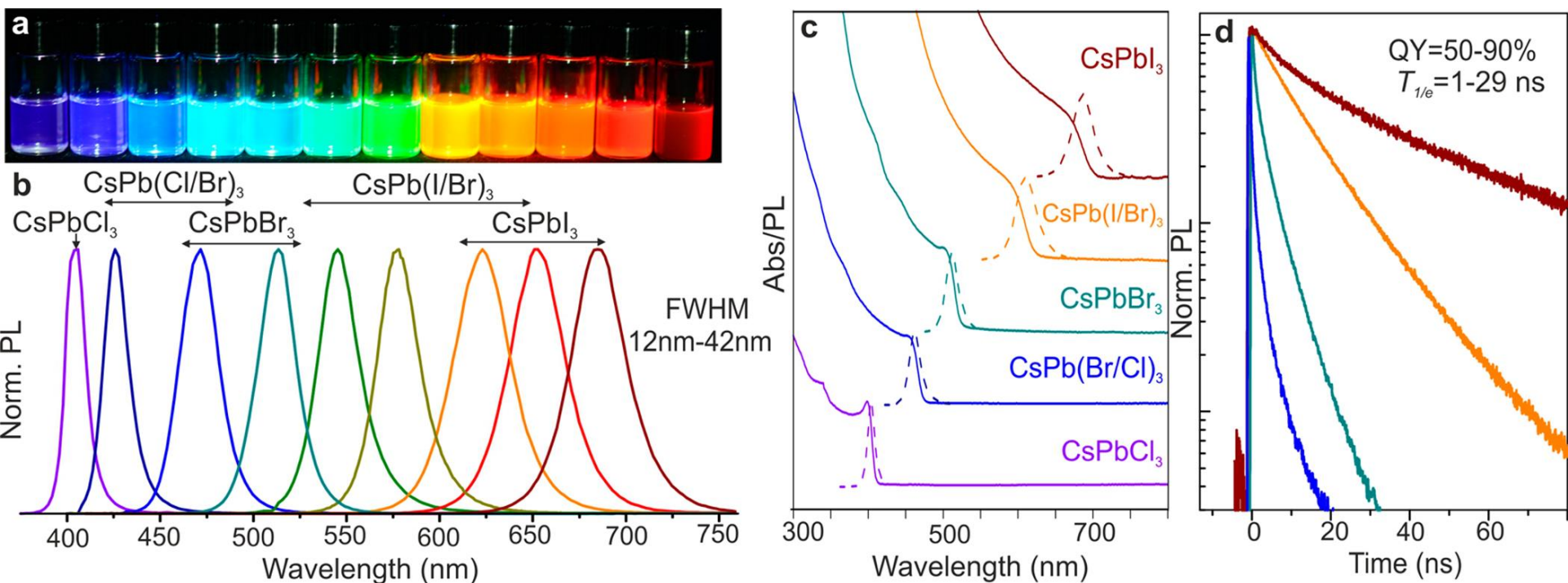
cation exchange (CE)

- transformations of nanomaterials driven by cation exchange
- II-VI, I-III-VI, IV-VI semiconductors
- replacement of cations
 - preserves the original anion sublattice (with slight rearrangement sometimes)
 - cations are usually smaller and thus can diffuse in and out of the anion lattice
- NCs, NRs, NPLs, NWs possible
- partial CE possible



Chem. Rev. **116**, 10852 (2016)

anion exchange – an example



Nanolett. **15**, 3692 (2015)



Thermodynamics of CE

- $AX(s) + B^+(sol) \rightarrow BX(s) + A^+(sol)$
- A-X dissociation, B-X association, B^+ desolvation, A^+ solvation – need to know the energies involved
- not much entropic change. Each A^+ solvated = B^+ desolvated
- **association and dissociation** = lattice energy

$$\Delta H_{latt} = -\frac{NMz_+z_-e^2}{r^+ + r^-} (1 - 1/n)$$

- as size inc. ΔH_{latt} dec. $MS > MSe > MTe$
- use bond dissociation energy in absence of knowledge of lattice energy
 - $A - X \rightarrow A + X$

- **Solvation and desolvation energies**

- proper solvent and ligands necessary – HSAB
 - F, O, N – hard, P, Cl, S – soft bases
 - Zn^{2+} Cd^{2+} hard acids, Cu^+ Pb^{2+} Ag^+ soft
- K_{sp}
 - aqueous solubility, $\Delta G^0 = \Delta G_f^0(M^+, aq) + \Delta G_f^0(A^-, aq) - \Delta G_f^0(MA, s)$
 - $\ln K_{sp} = -\Delta G^0/RT$
 - e.g. CdS or CdSe gets exchanged with Pb^{2+} , Ag^+ , Cu^+ , Cu^{2+} , Hg^{2+} in water
 - $S^{2-} > Se^{2-} > Te^{2-}$



Thermodynamics of CE ...

- ligands
 - water/alcohol good to extract hard acids and insert soft acids
 - extract soft – Cu^+ , Ag^+ , Pb^{2+} and replace with harder ones such as Cd^{2+} , Zn^{2+} , In^{3+} , Sn^{2+} , Sn^{4+} in metal chalcogenides and pnictides using TOP, TBP or carboxylates as soft bases
 - remove Cd^{2+} using amine Cd-Oleylamine

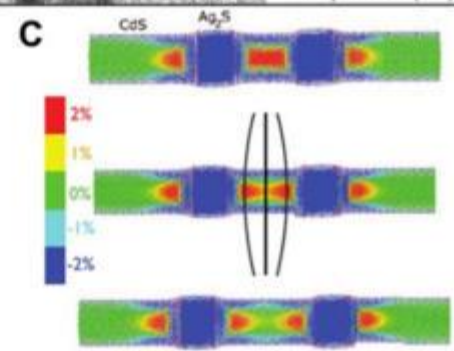
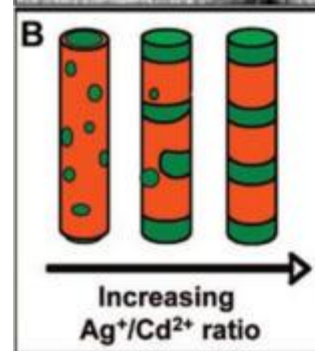
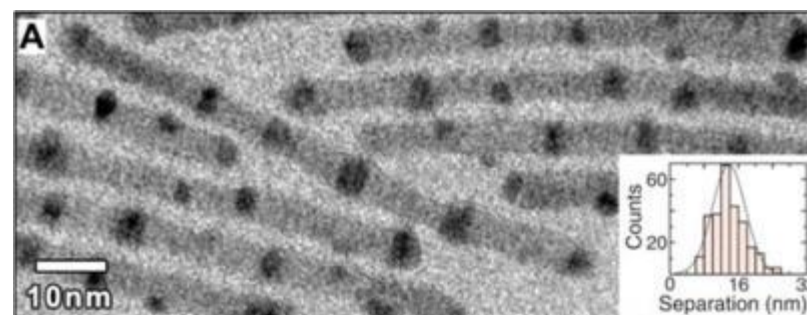
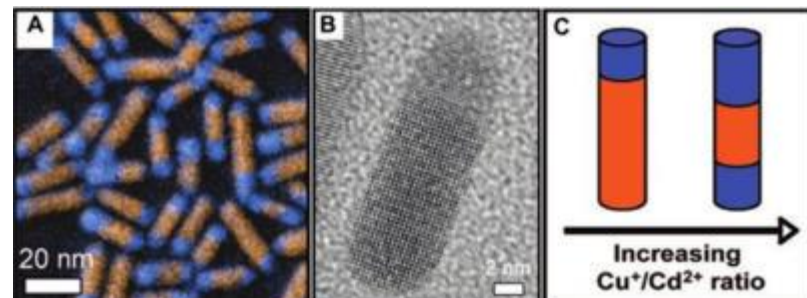
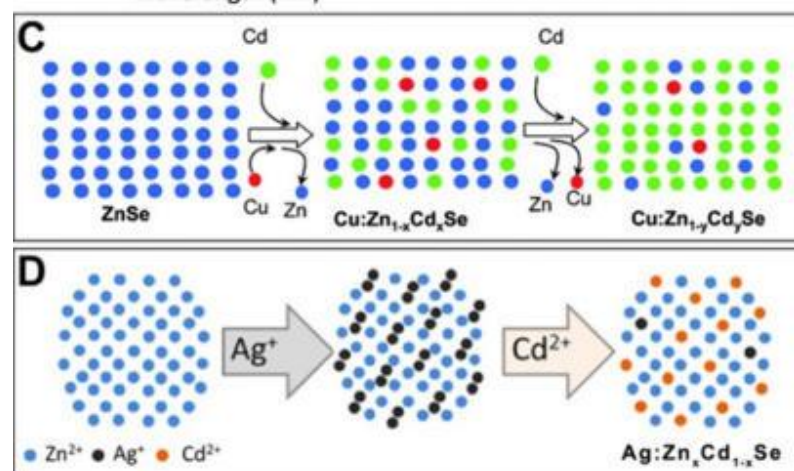
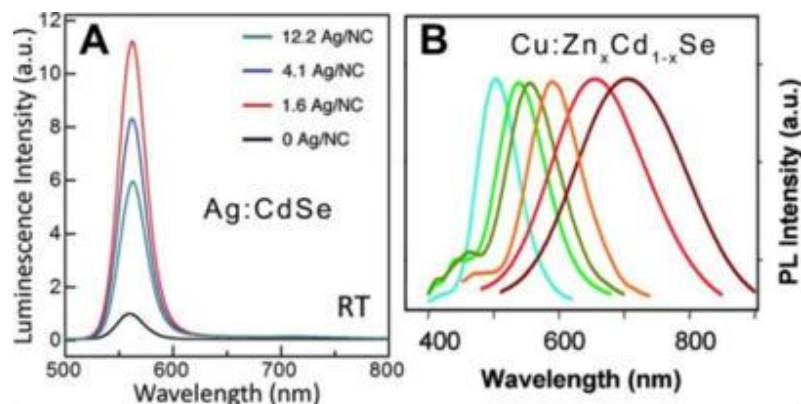


Table 4. List of Reactant and Product Materials of Known CE Reactions in NCs

class	reactant	shape	product
oxides	CuO	sphere	NiO, CoO, Fe ₂ O ₃ , Mn ₃ O ₄ ¹⁵³
selenides	CdSe	rod, sphere, wire, sheet	Cu ₂ Se, ^{75,92,154} Ag ₂ Se, ^{28,76,78,155} PdSe, PtSe, ⁶⁶ PbSe ^{118,121,156}
	PbSe	rods, cubes	CdSe ^{41,145}
	Cu _{2-x} Se	rod, sphere, cube	ZnSe, ⁹² Ag ₂ Se, ¹⁵⁷ SnSe ¹⁴⁹
	SnSe	sphere	PbSe ¹⁵⁸
	ZnSe	sphere	Ag ₂ Se, ¹⁵⁹ PbSe, ^{89,130} CdSe ¹⁴⁵
	Ag ₂ Se	wire, sphere, rod	CdSe, ^{28,29,99} Cd _{1-x} Zn _x Se ¹¹¹
	CdS	sphere, rod, wire, platelet	CuS, ⁷⁷ Cu ₂ S, ^{88,117,160-163} PdS, PtS, ⁶⁶ PbS ^{118,164}
sulfides	CuS	sphere	Ag ₂ S ⁸⁷
	ZnS	rod, sphere	Cu ₂ S, ⁴⁹ PbS ¹¹⁸
	Ag ₂ S	sphere	CdS ¹¹⁴
	Cu ₂ S	Sphere, rod, platelet, wire	ZnS ^{107,160} CdS, PbS, ^{88,117,160} Au ₂ S, ¹⁶⁵ Ag ₂ S ¹⁶²
	PbS	sphere	CdS ⁴⁰
	Cu _{2-x} (S _y Se _{1-y})	sphere, platelet	Cd(S _y Se _{1-y}) ^{105,166} Zn(S _y Se _{1-y}) ¹⁶⁶
	CdSe/CdS	core/shell	Cu ₂ Se Cu ₂ S ^{73,79,80,93,160,167,168}
selenide-sulfide	Cu ₂ Se/Cu ₂ S	core/shell	PbSe/PbS, ^{79,160} ZnSe/ ZnS, ^{93,160} CdSe/CdS, ⁸⁰
	CdTe	wire, sphere, tetrapod	PbTe, ¹¹⁸ Ag ₂ Te, ²⁸ PtTe, ³¹ PdTe, PtTe, ⁶⁶ Cu ₂ Te ⁹⁷
	Cu ₂ Te	platelet	CdTe ¹⁰⁹
pnictides	Cd ₃ As ₂	sphere	InAs, GaAs ¹⁴⁴
	Cd ₃ P ₂	sphere	InP, GaP ¹⁴⁴
	Cu ₃ P	platelet	InP ¹⁰⁴
lanthanide fluorides	GdF ₃ , EuF ₃	sphere	LaF ₃ ¹⁶⁹
	NaYF ₄	sphere	LaF ₃ ¹⁶⁹
	Ln:CaF ₂ (Ln = Yb, Ho, Er, Tm)	cube, sphere	Ln:NaGdF ₄ ¹⁷⁰
hybrid metal-chalcogenide	SelAg ₂ Se	core/shell sphere	SelZnSe, SelCdSe, Sel PbSe ^{30,98}
	AuAg ₂ S	core/shell rod, sphere	Au/CdS ^{112,171}
	AuAg ₂ X (X = S, Se, Te)	core/shell sphere	Au/CdSe, Au/CdTe, Au/PbS, Au/ZnS, Au/Cd(S _x Se _{1-x}) ¹⁰⁶

