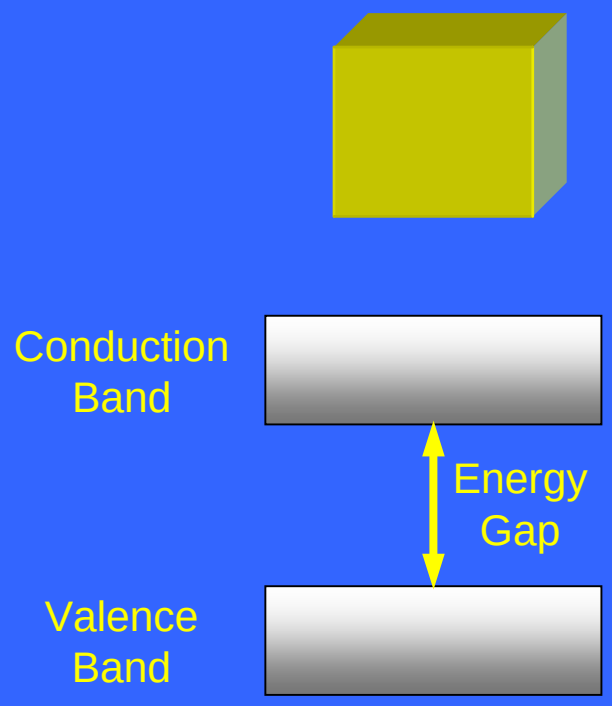
# 2004 Debye Lecture 3

C. B. Murray

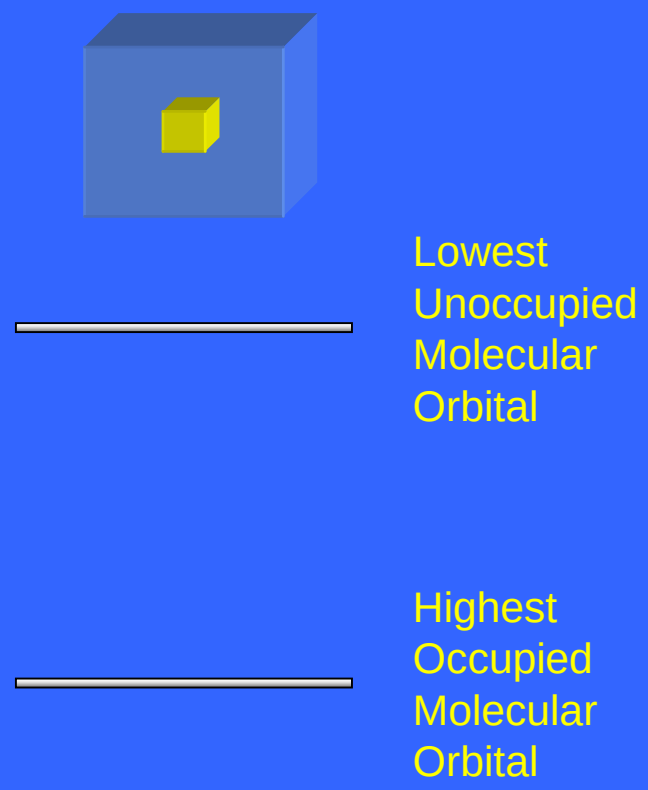
# Semiconductor Nanocrystals
# Quantum Dots Part 1

# Basic Physics of Semiconductor Quantum Dots

C. R. Kagan, IBM T. J. Watson Research Center, Yorktown Heights, NY

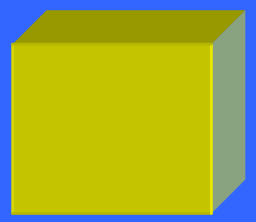


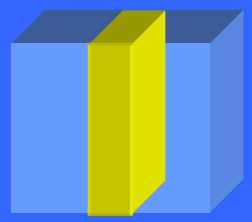

Bulk Semiconductor

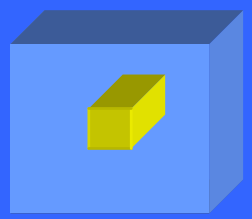


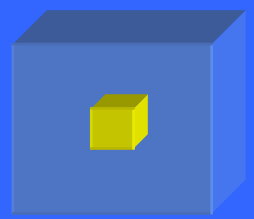

Quantum Dot Like a Molecule

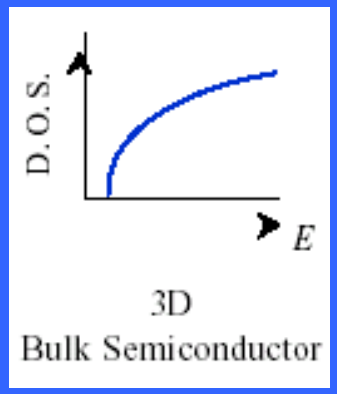
# Quantum Confinement
# Low Dimensional Structures

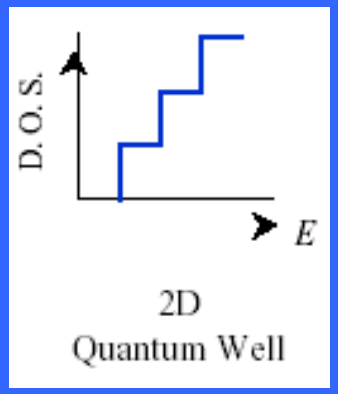


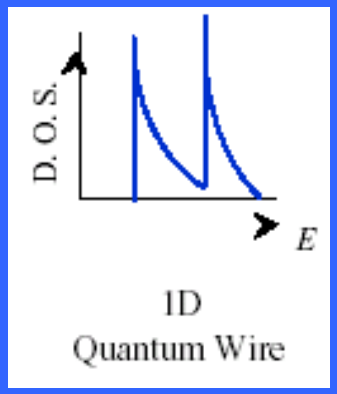


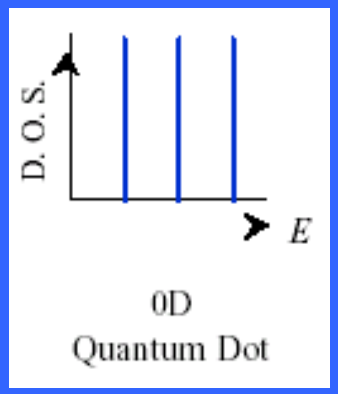






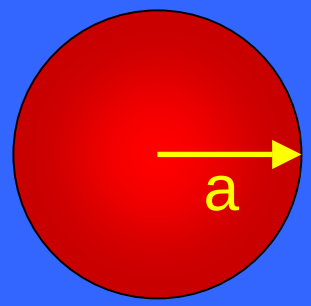

$$\rho_c(E) \propto \sqrt{(E - E_C)}$$

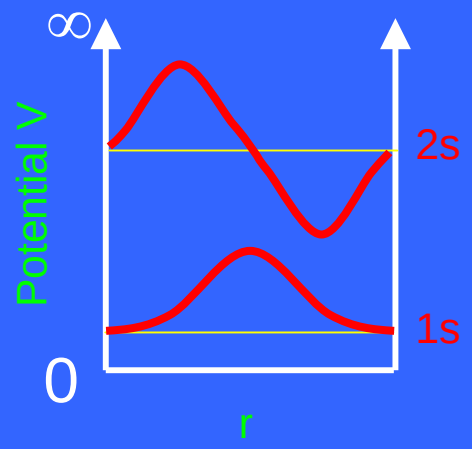
$$\rho_c(E) = constant$$

$$\rho_c(E) \propto \frac{1}{\sqrt{(E - E_n)}}$$

$$\rho_c(E) \propto \delta(E - E_n)$$

# Particle-in-a-Sphere




$$\Phi(r,\theta,\phi) = C\,\frac{j_l(k_{n,l}r)\,Y_l^m(\theta,\phi)}{r}$$

$Y_l^m(\theta,\phi)$ is a spherical harmonic

$j_l(k_{n,l}r)$ is the l[th] order spherical Bessel function

$$k_{n,l} = \frac{\alpha_{n,l}}{a}$$

$$E_{n,l} = \frac{\eta^2 k_{n,l}^2}{2m_o} = \frac{\eta^2 \alpha_{n,l}^2}{2m_o a^2}$$

**Discrete energy levels**

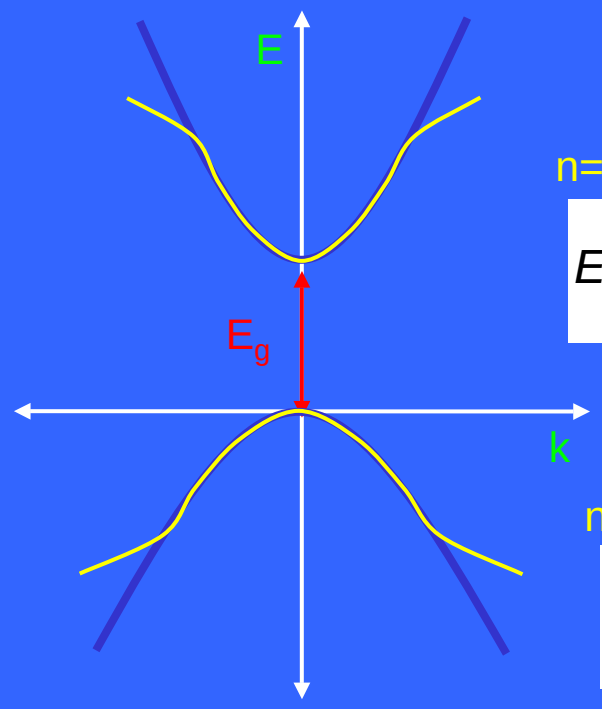
size-dependence

**solutions give hydrogen-like orbitals with quantum numbers**
**n (1, 2, 3 …)**
**l (s, p, d …)**
**m**

# The Quantum Dot is a Semiconductor

**The Effective Mass Approximation**

parabolic conduction and valence bands




n=conduction band

$$E_k^c = \frac{\eta^2 k^2}{2m_{eff}^c} + E_g$$

n=valence band

$$E_k^v = -\frac{\eta^2 k^2}{2m_{eff}^v}$$

Direct Bandgap Semiconductor

**Bloch's Theorem**

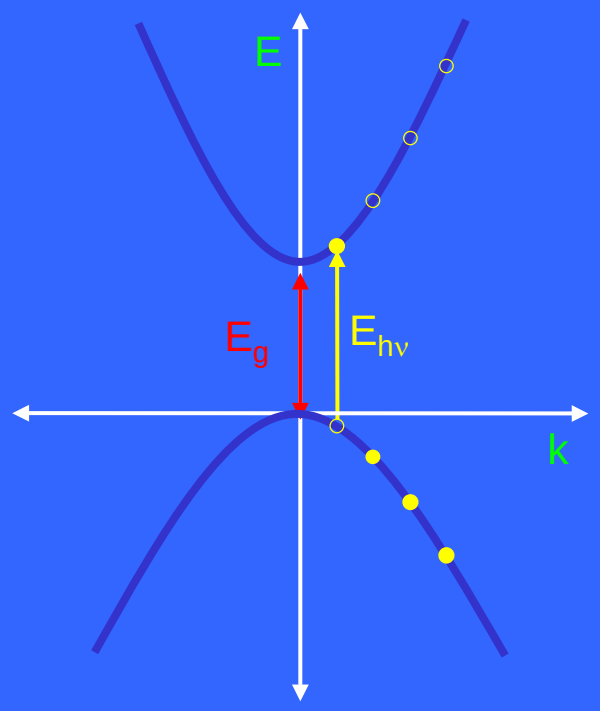
$$\Psi_{nk}(\vec{r}) = u_{nk}(\vec{r})\exp(i\vec{k}\cdot\vec{r})$$

with periodicity of crystal lattice

Free particles treated by effective mass:

- describing graphically the curvature of the bands
- representing the potential presented by the lattice

# Combining the Effective Mass Approximation with a Spherical Boundary Condition




Single Particle (sp) Wavefunction

(1) $$\Psi_{sp}(\vec{r}) = \sum_k C_{nk} u_{nk}(\vec{r}) \exp(i\vec{k}\cdot\vec{r})$$

linear combination of Bloch functions

(2) $$\Psi_{sp}(\vec{r}) = u_{n0}(\vec{r}) \sum_k C_{nk} \exp(i\vec{k}\cdot\vec{r}) = u_{n0}(\vec{r}) f_{sp}(\vec{r})$$

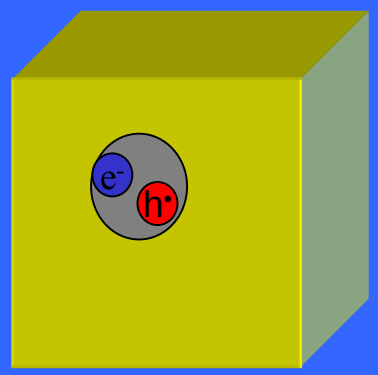
assume $u_{nk}$ has weak k-dependence

Envelope Function Approximation valid for $r_{QD}$ > lattice constant which for QDs is given by the **"Particle-in-a-Sphere"**

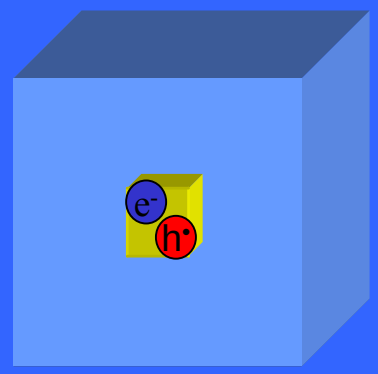
(3) $$u_{n0}(\vec{r}) = \sum_i C_{ni} \varphi_n(\vec{r} - \vec{r}_i)$$

linear combination of atomic orbitals with atomic wavefunctions $\varphi_n$ (n= CB or VB)
i=lattice sites

# Coulomb Attraction




Bulk semiconductors,
Coulomb attraction
creates bound excitons




Confinement Energy $\propto 1/a^2$
Coulomb Attraction $\propto 1/a$

For small a:

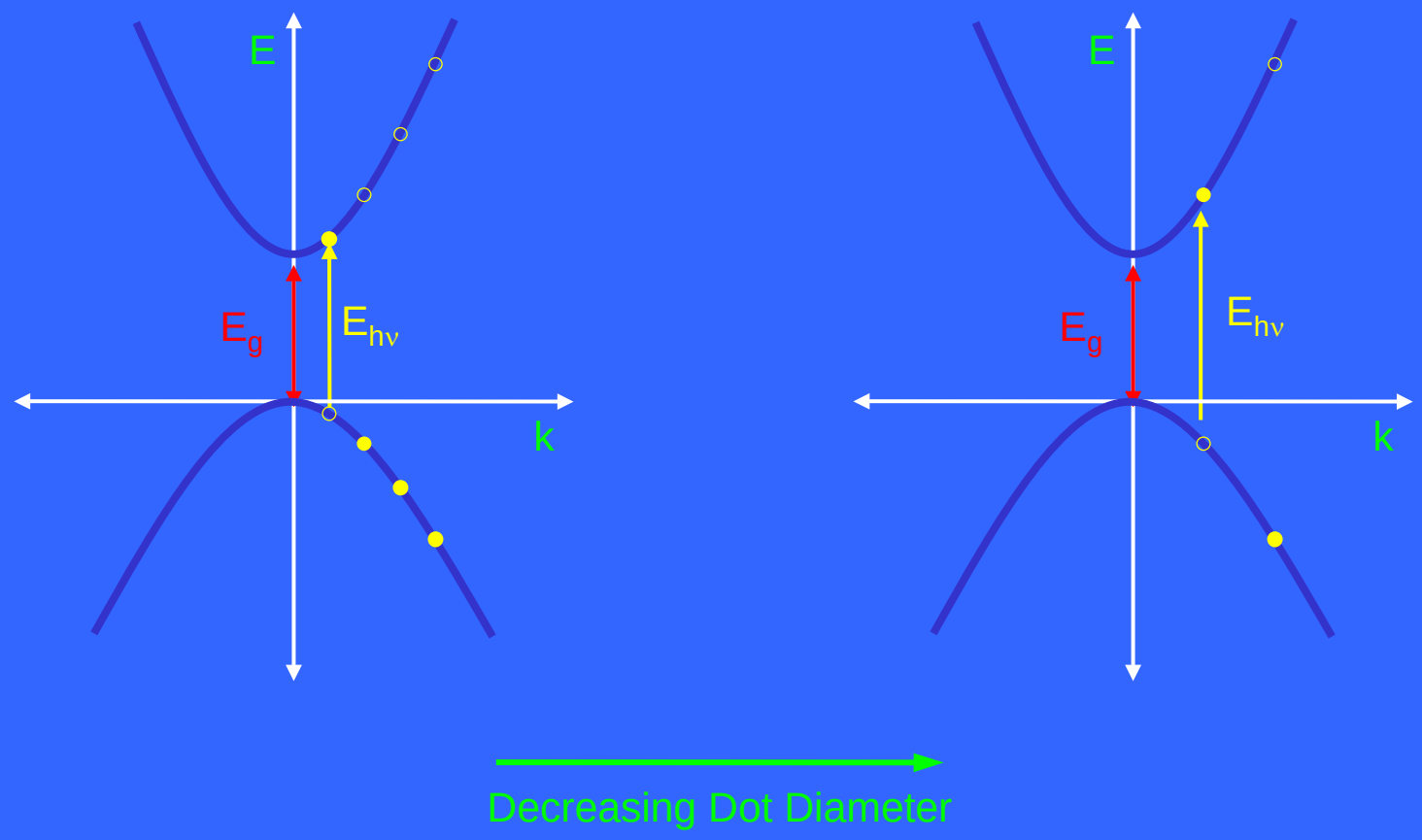
- Confinement Energy>Coulomb Attraction
  electron and hole are treated independently
- Coulomb interaction added as a correction

$$E_{ehp}(n_h L_h n_e L_e) = E_g + \frac{\eta^2}{2a^2}\left\{\frac{\varphi^2_{n_h,L_h}}{m^v_{eff}} + \frac{\varphi^2_{n_e,L_e}}{m^c_{eff}}\right\} - E_{coulomb}$$

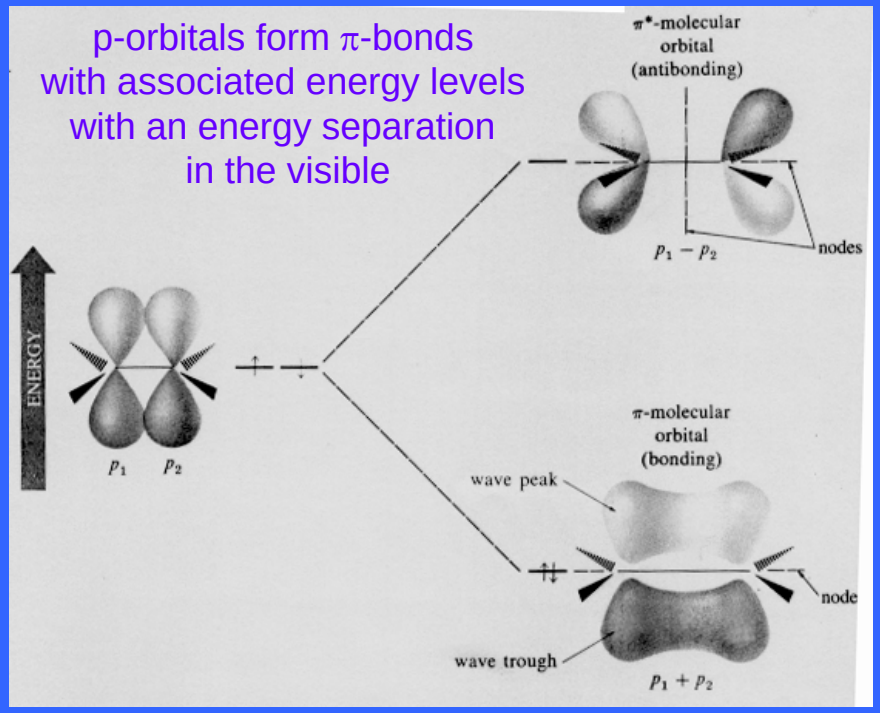
For $1S_e$ pairs of states $E_{coulomb}=1.8e^2/\varepsilon a$

Brus, J. Phys. Chem. **90**, 2555 (1986).

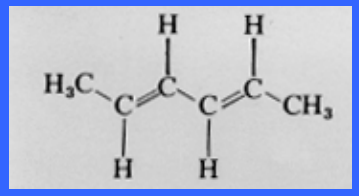
# Size Dependence of Electronic Structure

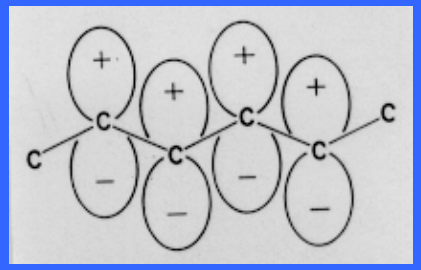


# Development of Electronic Structure Similar to Length Dependence in 1D polyenes




Example of alternating double/single bond
π-bond extends over many C atoms




Lowest
Unoccupied
Molecular
Orbital

LUMO

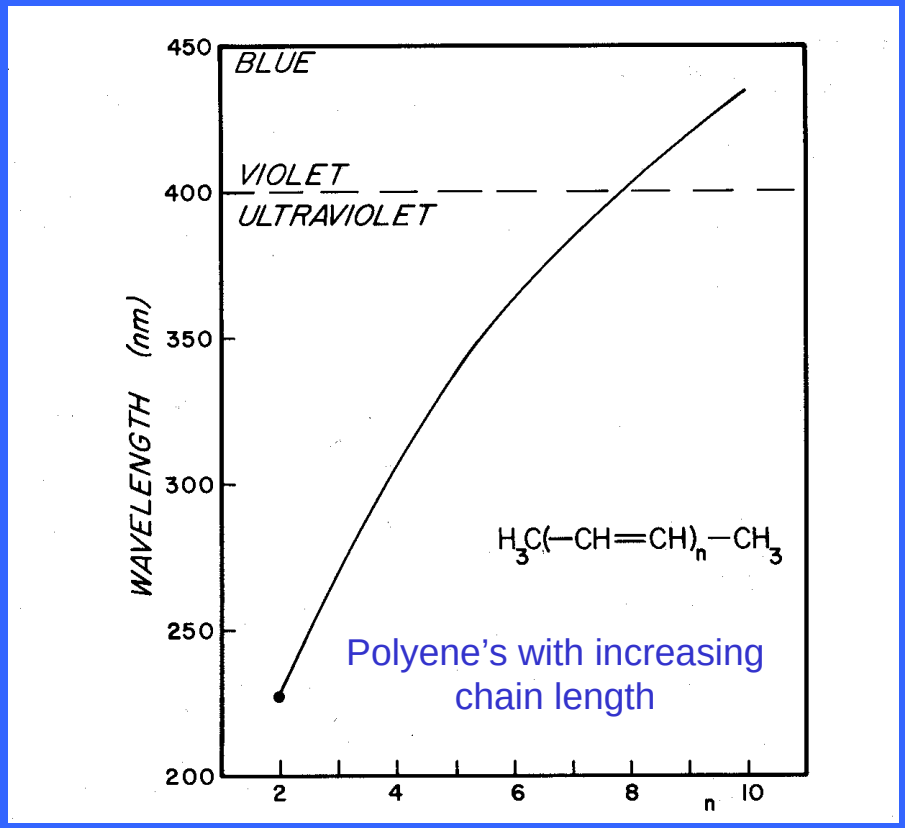
$\pi^*$

Highest
Occupied
Molecular
Orbital

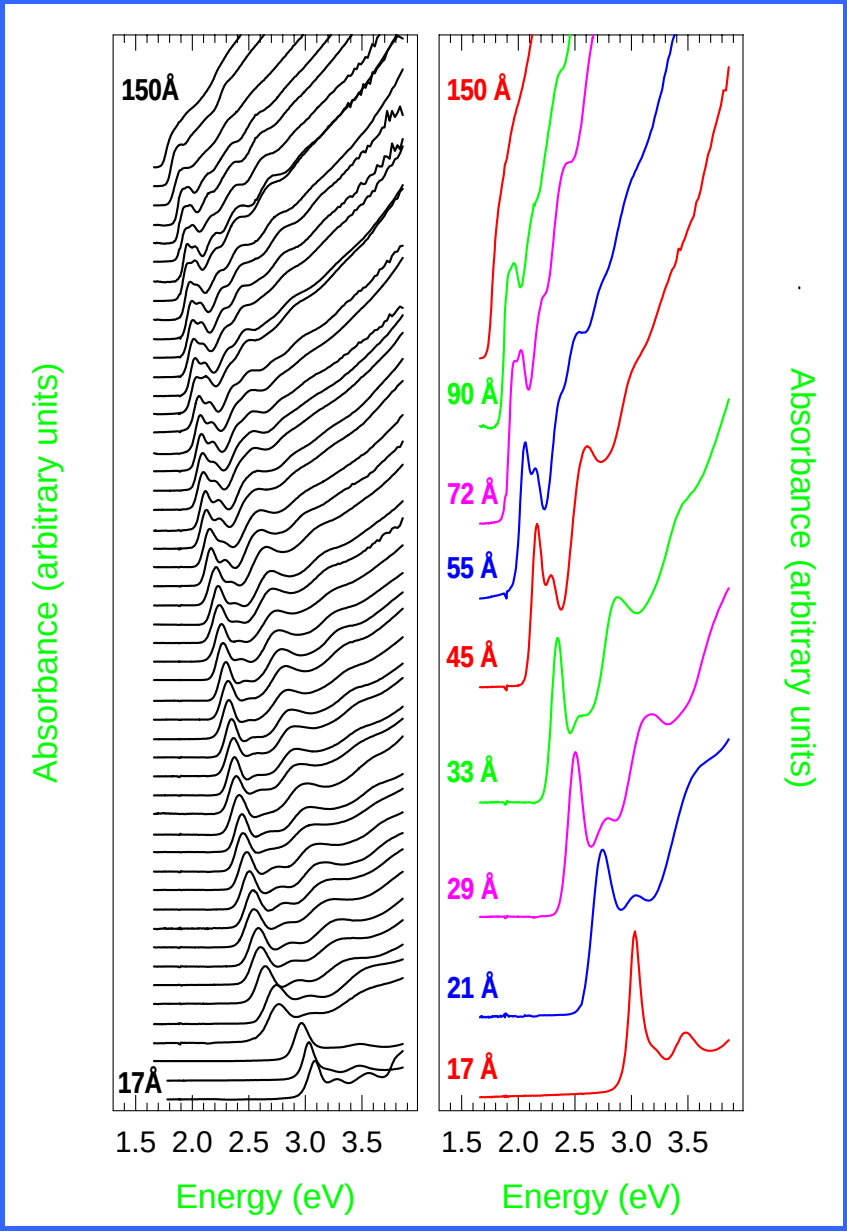
HOMO

π

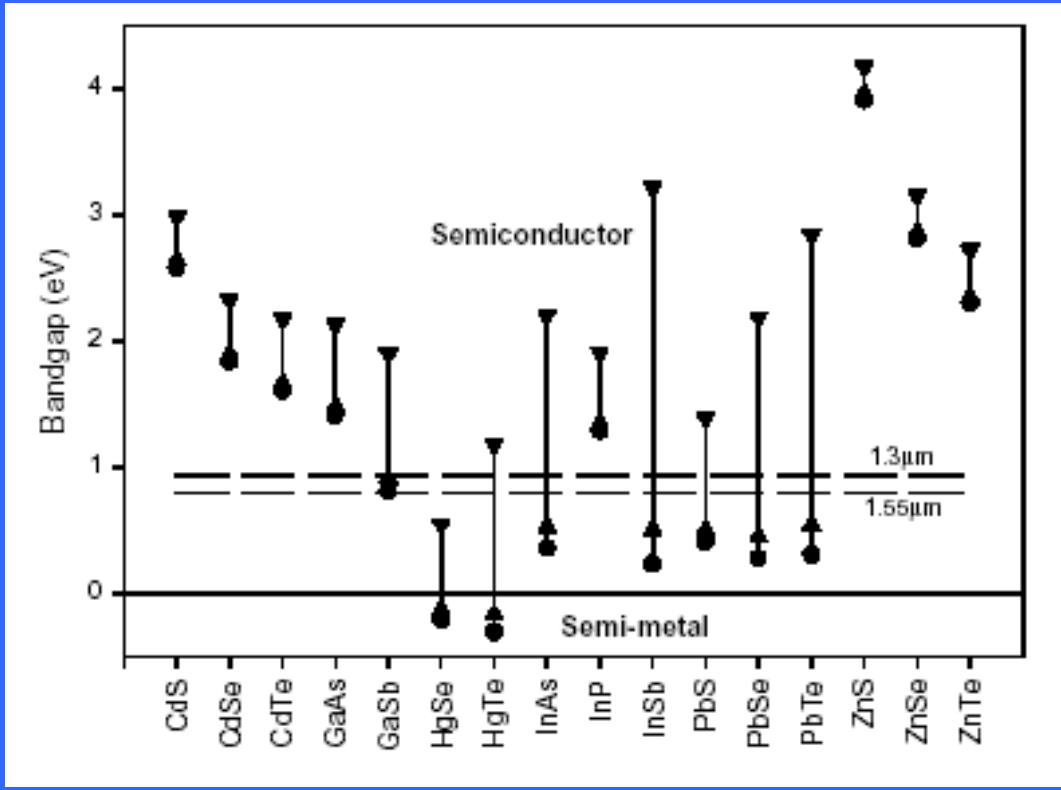
Ground



# Size Dependent Absorption
# Example: CdSe




# Semiconductor Materials

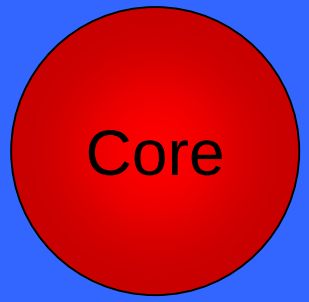



Range from 30 nm QDs to bulk crystal

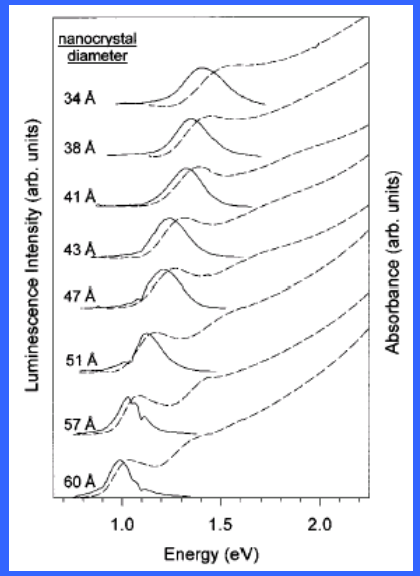
Graph from H. Weller, Pure Appl. Chem. **72**, 295 (2000).

# Absorption Spectra of Semiconductor Nanocrystals

Changing the Core

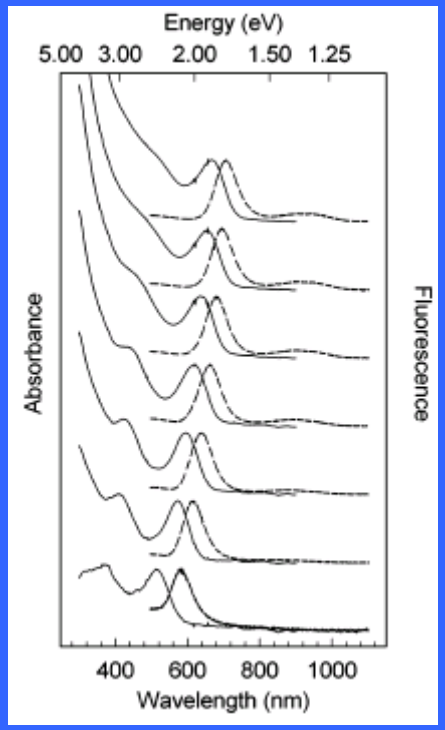



InAs




A. P. Alivisatos, UC Berkeley

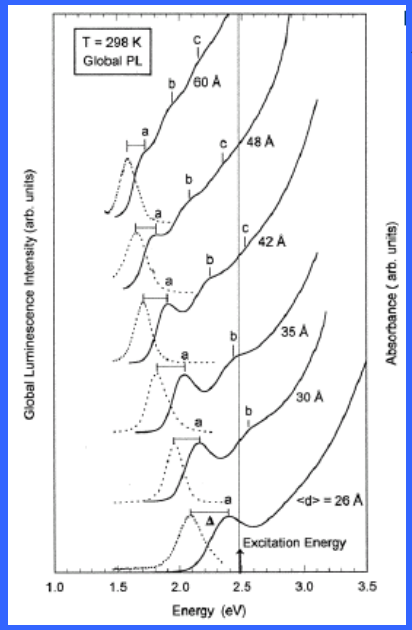
HgS



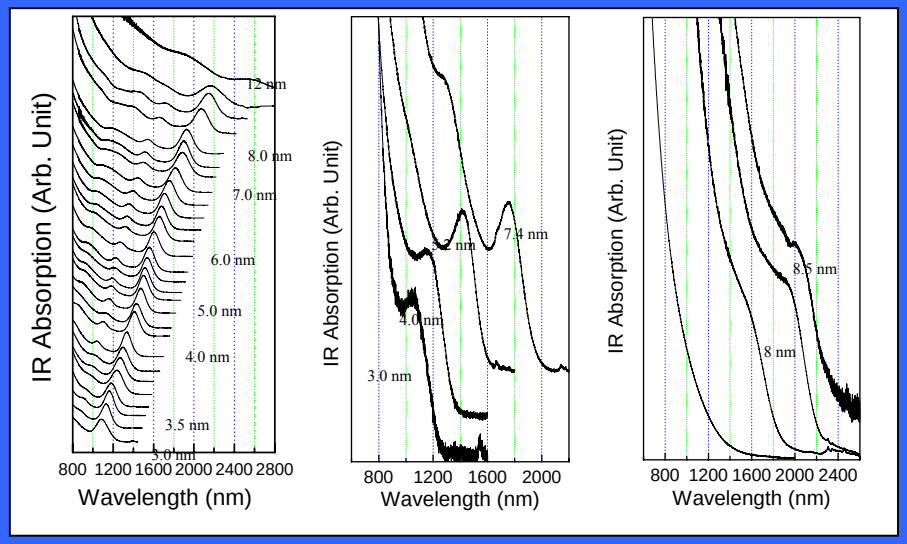

NRL group

PbSe PbS PbTe

InP




O. Micic, A. Nozik, NREL

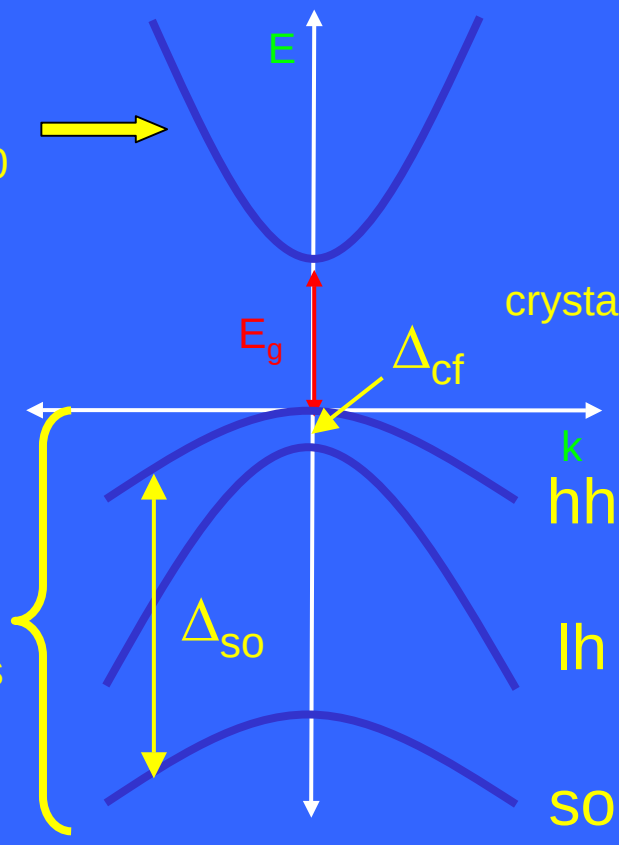



C. B. Murray, IBM

# Real Band Structure

Example: CdSe

Cd 5s orbitals
2-fold degenerate at k=0




J=1/2

crystal field splitting

Se 4p orbitals
6-fold degenerate at k=0
Introduces splitting of bands

hh heavy hole

J=3/2

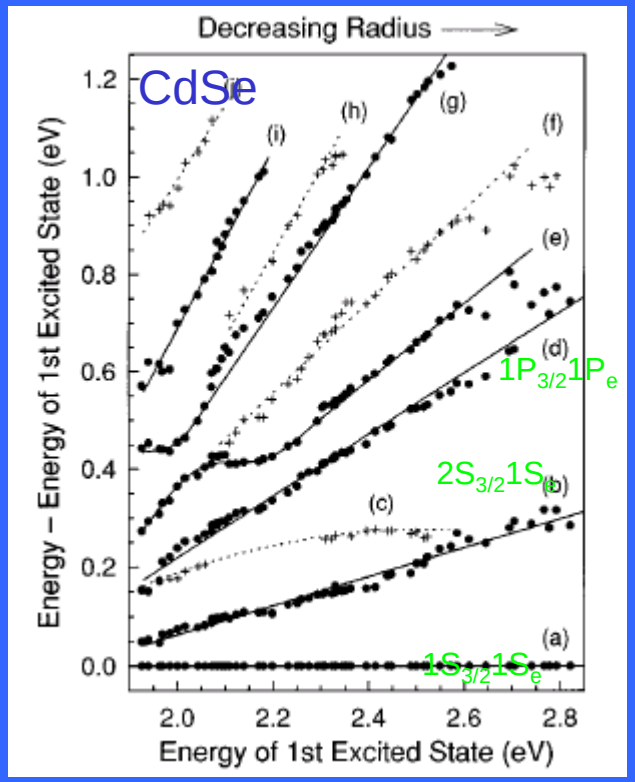
lh light hole

so spin-orbit splitoff J=1/2

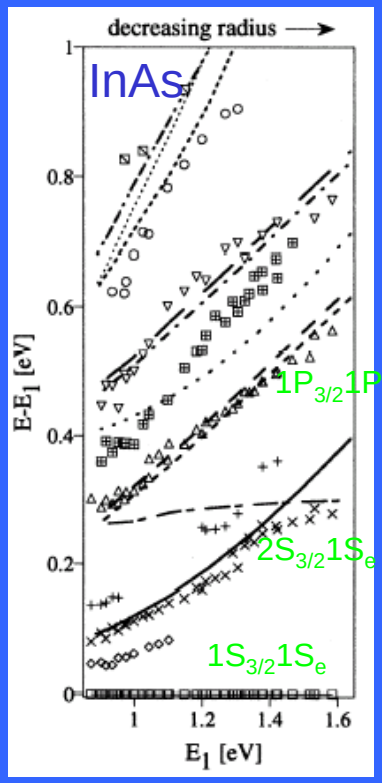
J = L + S where L=orbital angular momentum
S=spin angular momentum

J good quantum number due to strong spin-orbit coupling

# Size Evolution of Electronic States




Low Band gap InAs modeling must also account for valence-conduction band coupling




D. J. Norris, M. G. Bawendi, Phys. Rev. B **53**, 16338 (1996).

U. Banin et al., J. Chem. Phys. **109**, 2306 (1998).

F=J+L where L=envelope angular momentum
J=Bloch-band edge angular momentum

Hole states labeled by $n_h L_F$ [$L_F$=L + (L+2)]
Electron states labeled $n_e L_e$

# Selection Rules

$$P = \left| \langle \Psi_e | \vec{e} \cdot \hat{p} | \Psi_h \rangle \right|^2$$

polarization vector of light

momentum operator

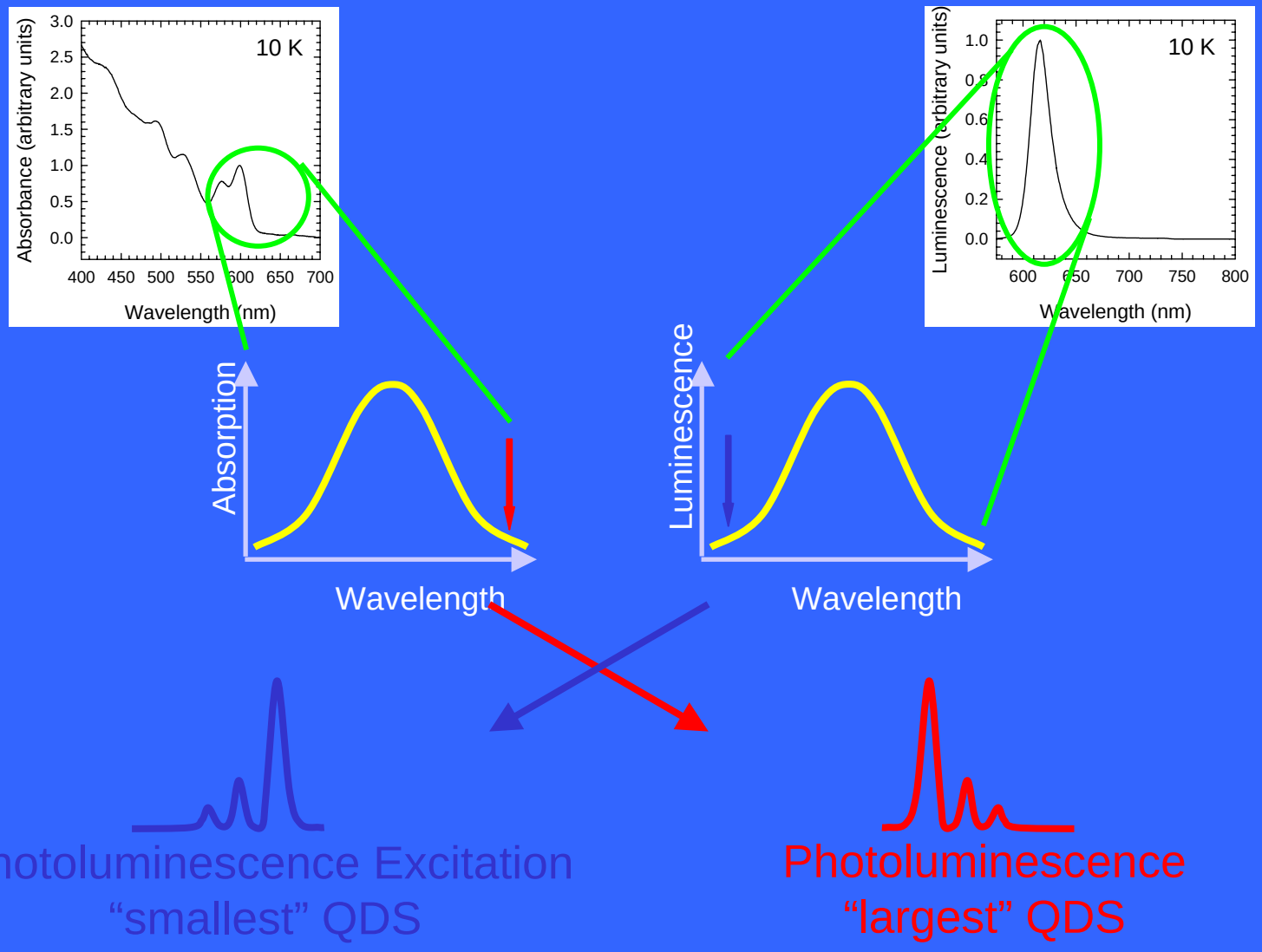
acts only on unit cell portion of wavefunction

$$P = \left| \langle u_c | \vec{e} \cdot \hat{p} | u_v \rangle \right|^2 \left| \langle f_e | f_h \rangle \right|^2$$

$$P = \left| \langle u_c | \vec{e} \cdot \hat{p} | u_v \rangle \right|^2 \delta_{n_e, n_h} \delta_{L_e, L_h}$$

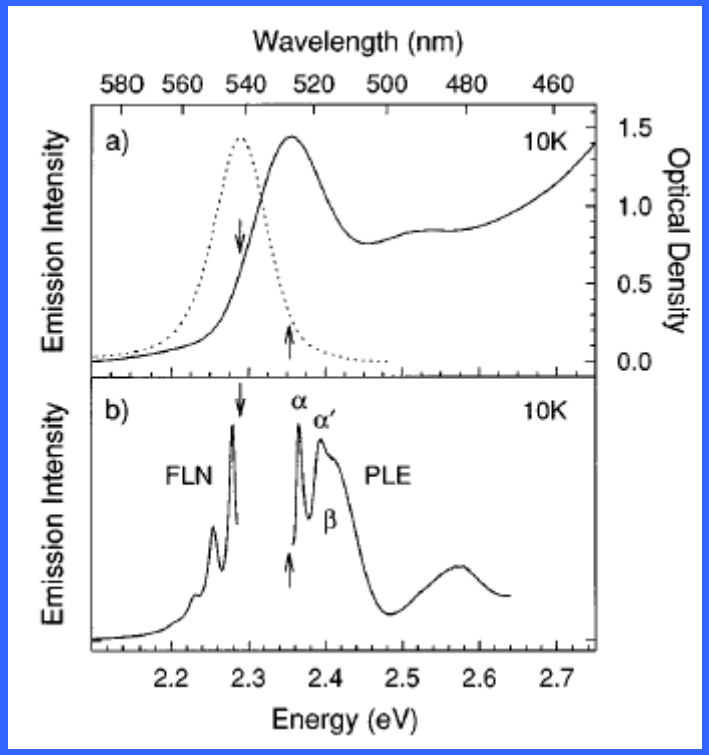
Overlap of the electron and hole wavefunctions within the QDs

# Towards the Homogeneous Distribution: Photoluminescence and Photoluminescence Excitation

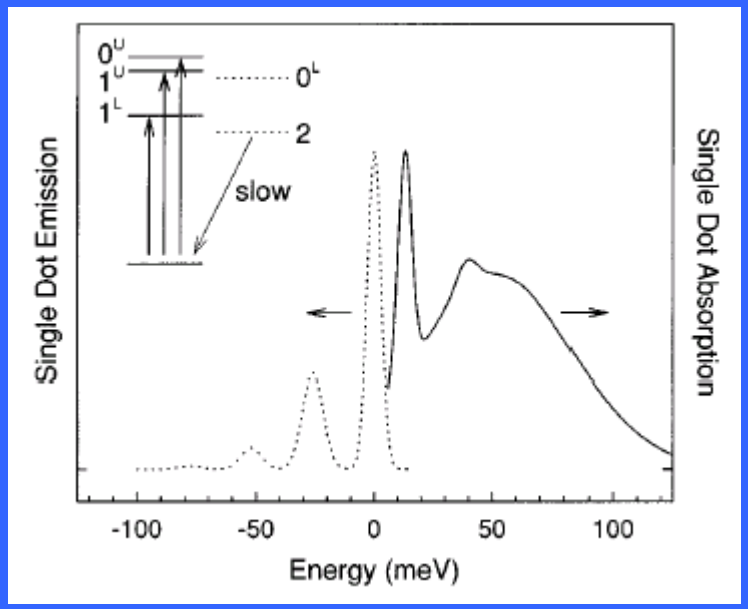



Distribution in ensemble from size, structure, and environmental inhomogeneities

# Fluorescence Line Narrowing and Photoluminescence Excitation



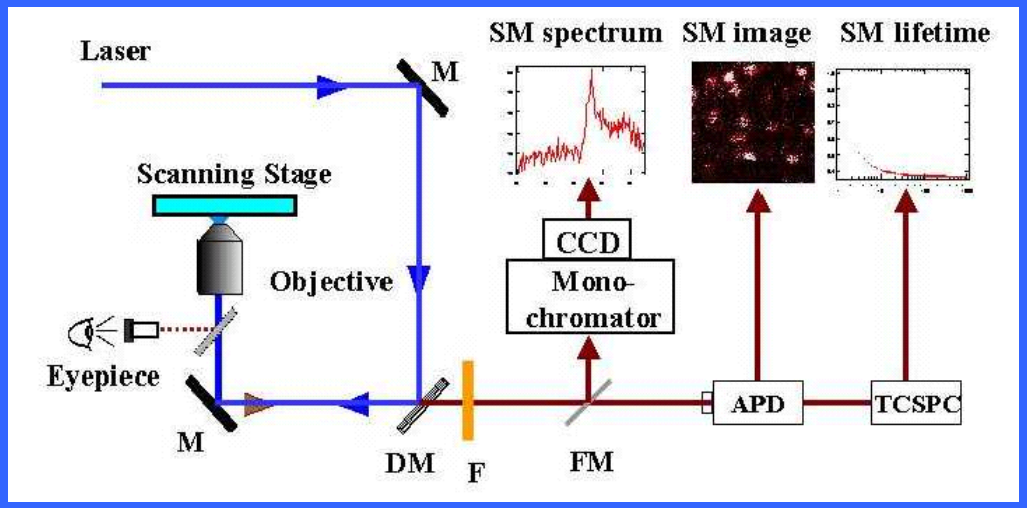

Band Edge Exciton Structure

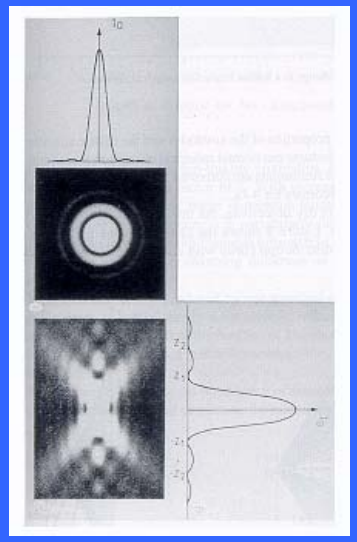



Splitting due to crystal field, non-spherical shape, and exchange interactions of quantum dots

D. J. Norris, Al. L. Efros, M. Rosen, M. G. Bawendi, Phys. Rev. B **53**, 16347 (1996)

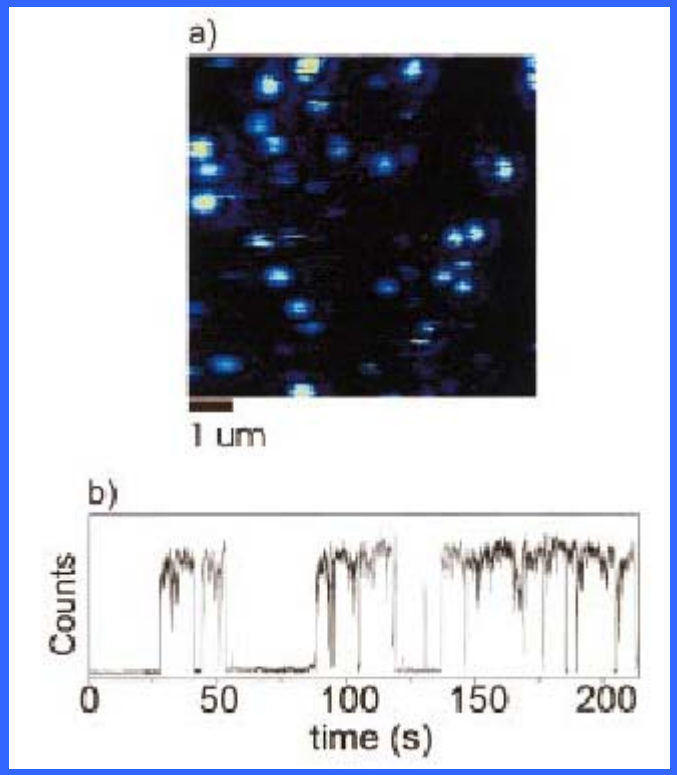
# Single Molecule Spectroscopy

Diffraction Limited Spot

# Fluorescence Intermittancy in CdSe QDs




QDs “blink” like molecules

On-period decreases with increasing illumination intensity

Off-period intensity independent

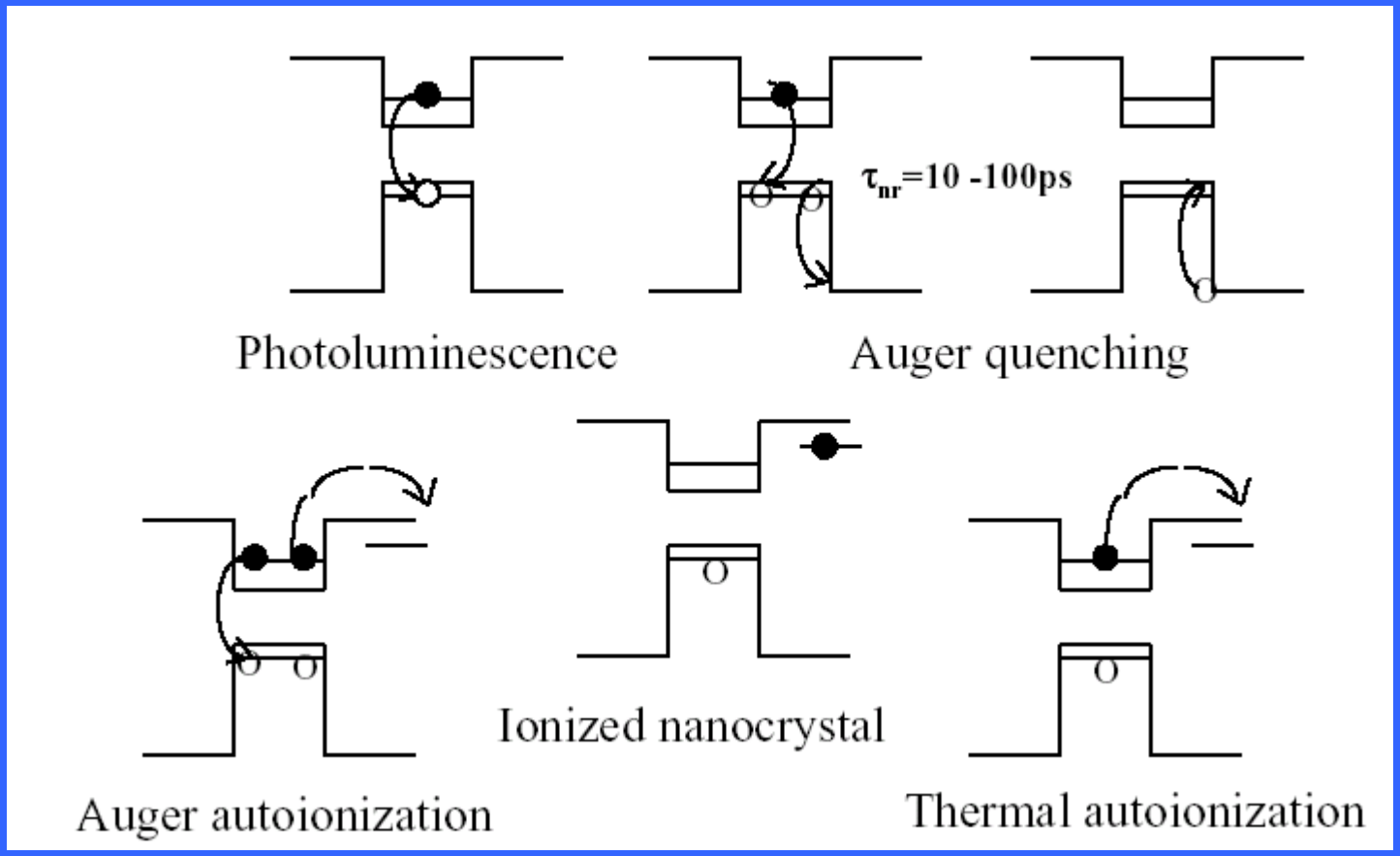
Excitation every $10^{-5}$ sec
Relaxation every $10^{-8}$ sec

But occasionally
Two electron-hole pairs may exist in a single QD

Auger ionization
Probability of photoionization/excitation $10^{-6}$
Neutralization time ~0.5 sec

M. Nirmal, L. E. Brus, Acc. Chem. Res. **32**, 407 (1999).

# Auger Ionization

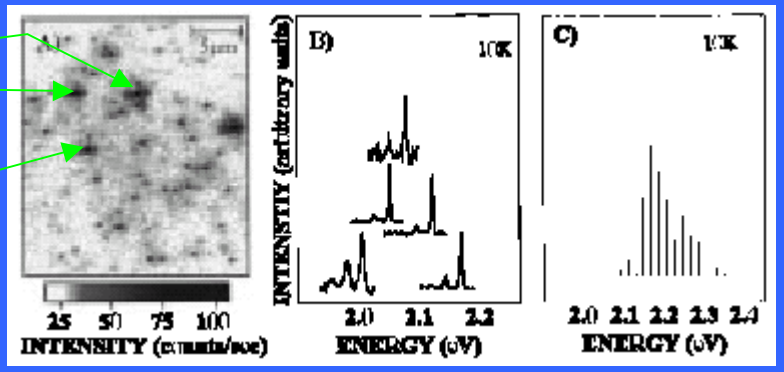



Consistent with single molecule spectroscopy and photodarkening observed in QD doped glasses

Al. L. Efros, M. Rosen, Phys. Rev. Lett., **78**, 1110 (1997).

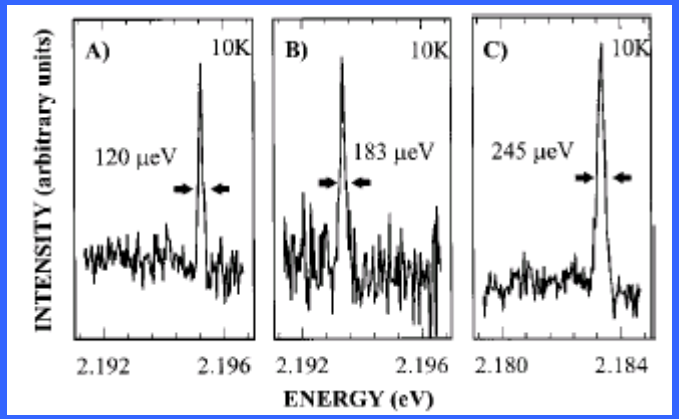
# Single Dot Spectroscopy

Individual quantum dots




Histogram of 513 43 Å QDs Including all phonon lines

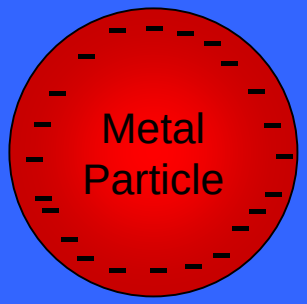
Single Quantum Dot Emission

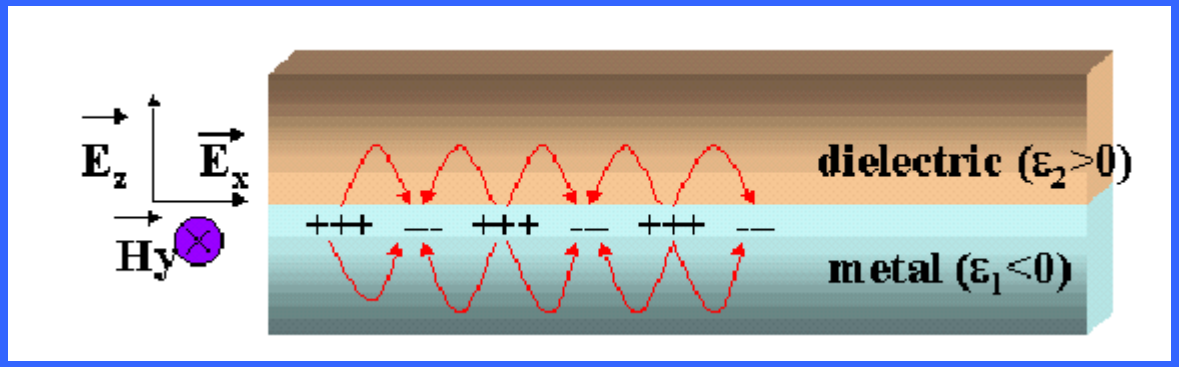


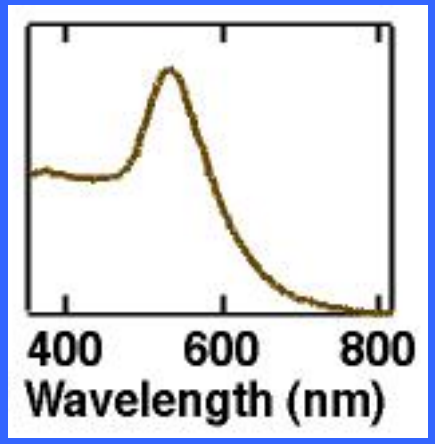

Spectral diffusion driven by environment

S. A. Empedocles, M. G. Bawendi, Acc. Chem. Res. **32**, 389 (1999).

# Metal Nanoparticles



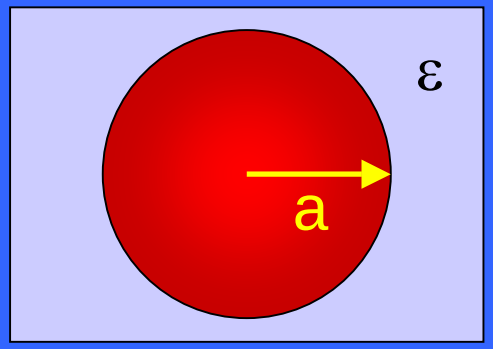




Au nanoparticle absorption

**Surface Plasmon Resonance**

- dipolar, collective excitation between negatively charge free electrons and positively charged core
- energy depends on free electron density and dielectric surroundings
- resonance sharpens with increasing particle size as scattering distance to surface increases

# Electronic Properties of Semiconductor and Metal Nanoparticles

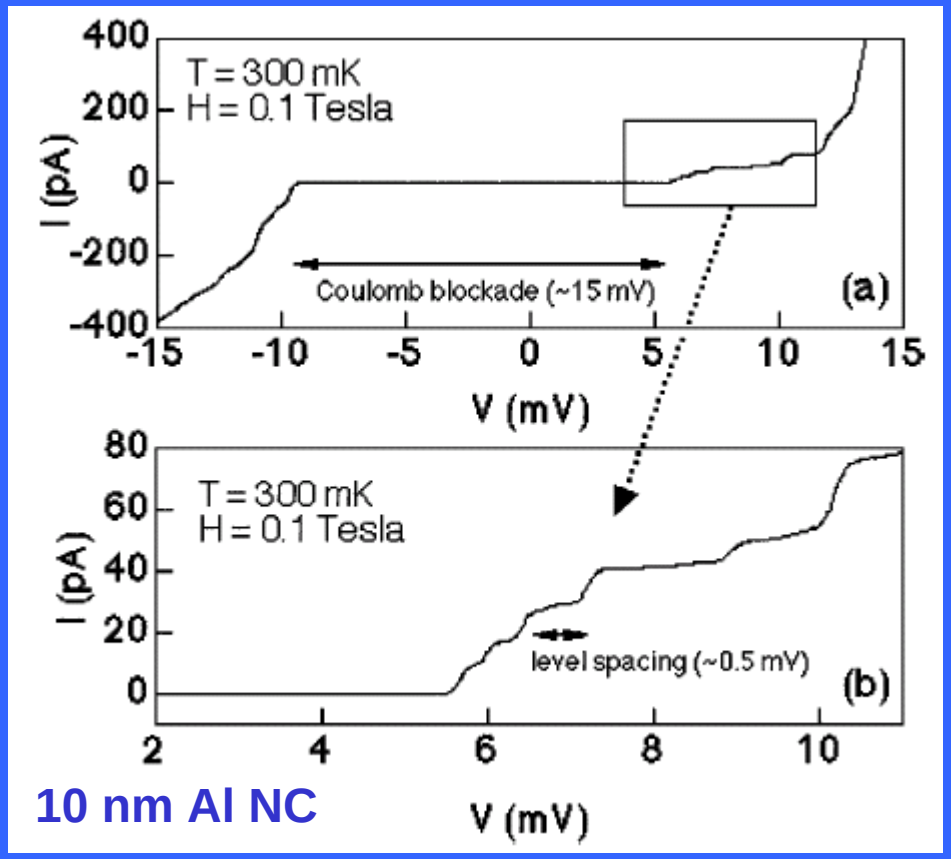



Charge not completely solvated as in infinite solid

Nanoparticle capacitance $C = 4\pi\varepsilon_o\varepsilon a$

Charging Energy $E_c = \dfrac{e^2}{2C(a)}$

Coulomb blockade at $k_B T < E_c$

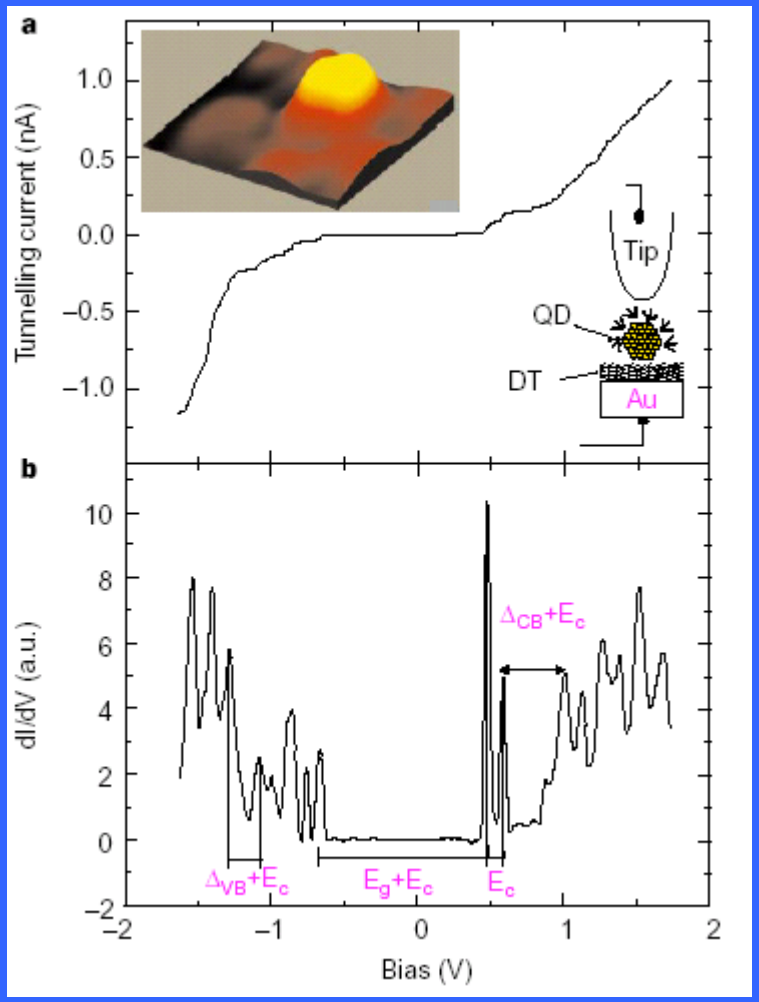



Courtesy of C. T. Black, Thesis, Harvard U.

Structure from discrete electronic states of metal NC

# STM Measurements on Single QDs

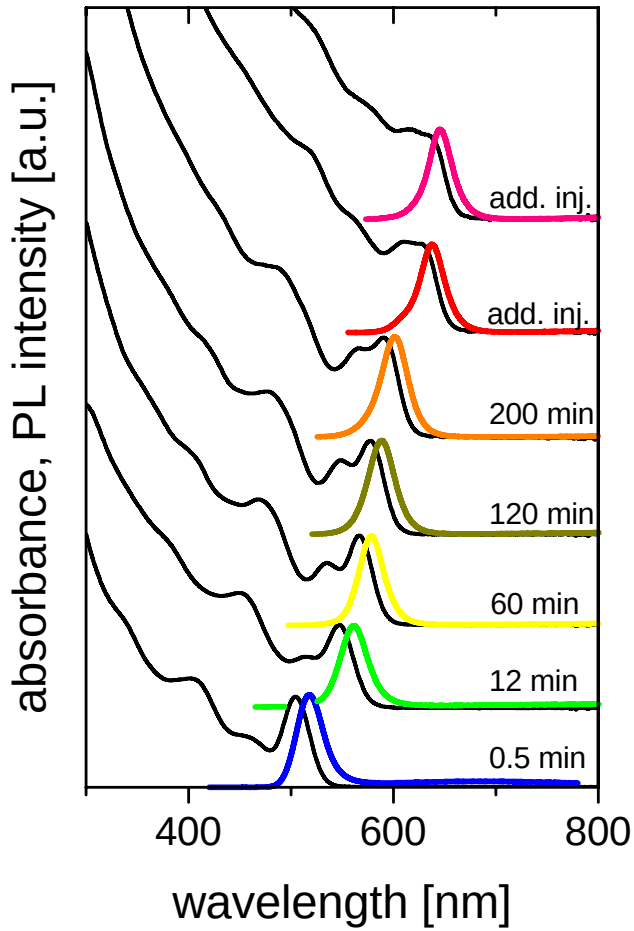
InAs QDs




U. Banin et al. Nature **400**, 542 (1999).

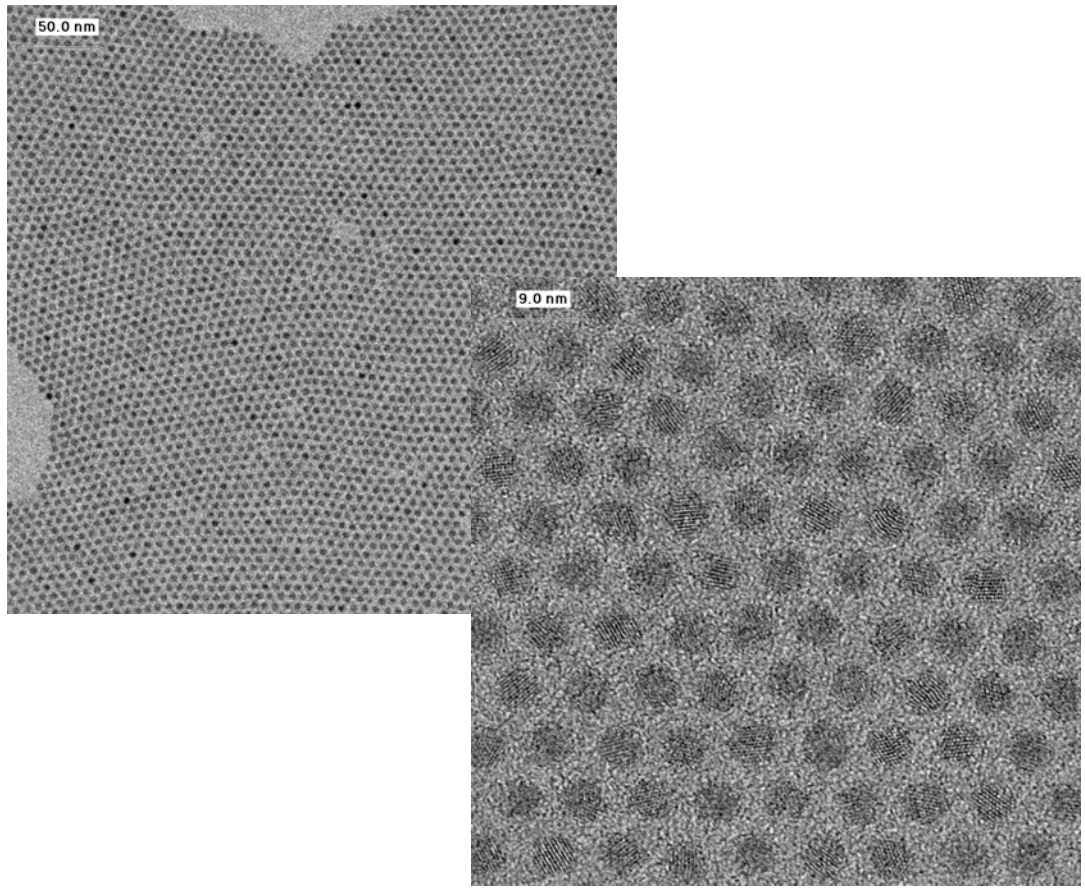
# Synthesis of monodisperse CdSe nanocrystals

$$Cd(CH_3)_2 + (oct)_3PSe \xrightarrow{HDA-TOPO-TOP,\ 300°C} CdSe + \ldots$$




*UV-Vis and PL spectra of CdSe nanocrystals in growth at 300°C*

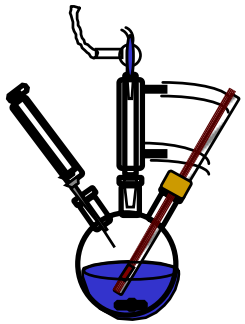
*TEM and HRTEM images of as-prepared CdSe nanocrystals.*



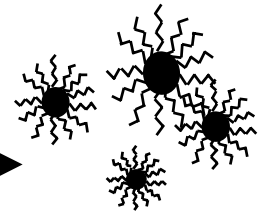

D. V. Talapin, A. L. Rogach, A. Kornowski, M. Haase, H. Weller. *Nano Lett.* **2001**, 1, 207.

# Wet Chemical Synthesis of PbSe Nanocrystals and Superlattices

**Synthesis**



$Pb(OAc)_2 + R_3PSe \xrightarrow[R_3P,\ T=150\ C]{\text{oleic acid,}}$

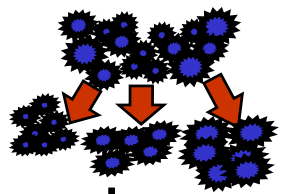


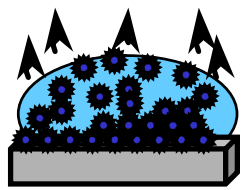
**PbSe**

R= octyl

**Size Selective Processing**

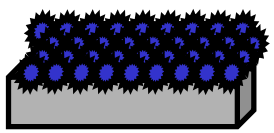
**Size selective precipitation in solvent/ non solvent pairs like hexane-methanol**





**Self Assembly**

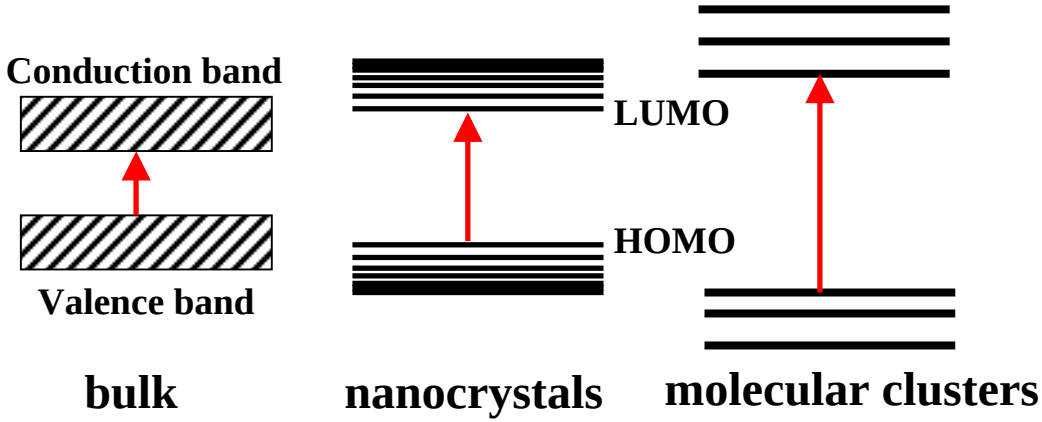
**Evaporation of the solvent**



# PbSe Nanocrystals and Nanowires

## Nanocrystals:

1.5 – 10 nm diameters
100 – 100 000 atoms



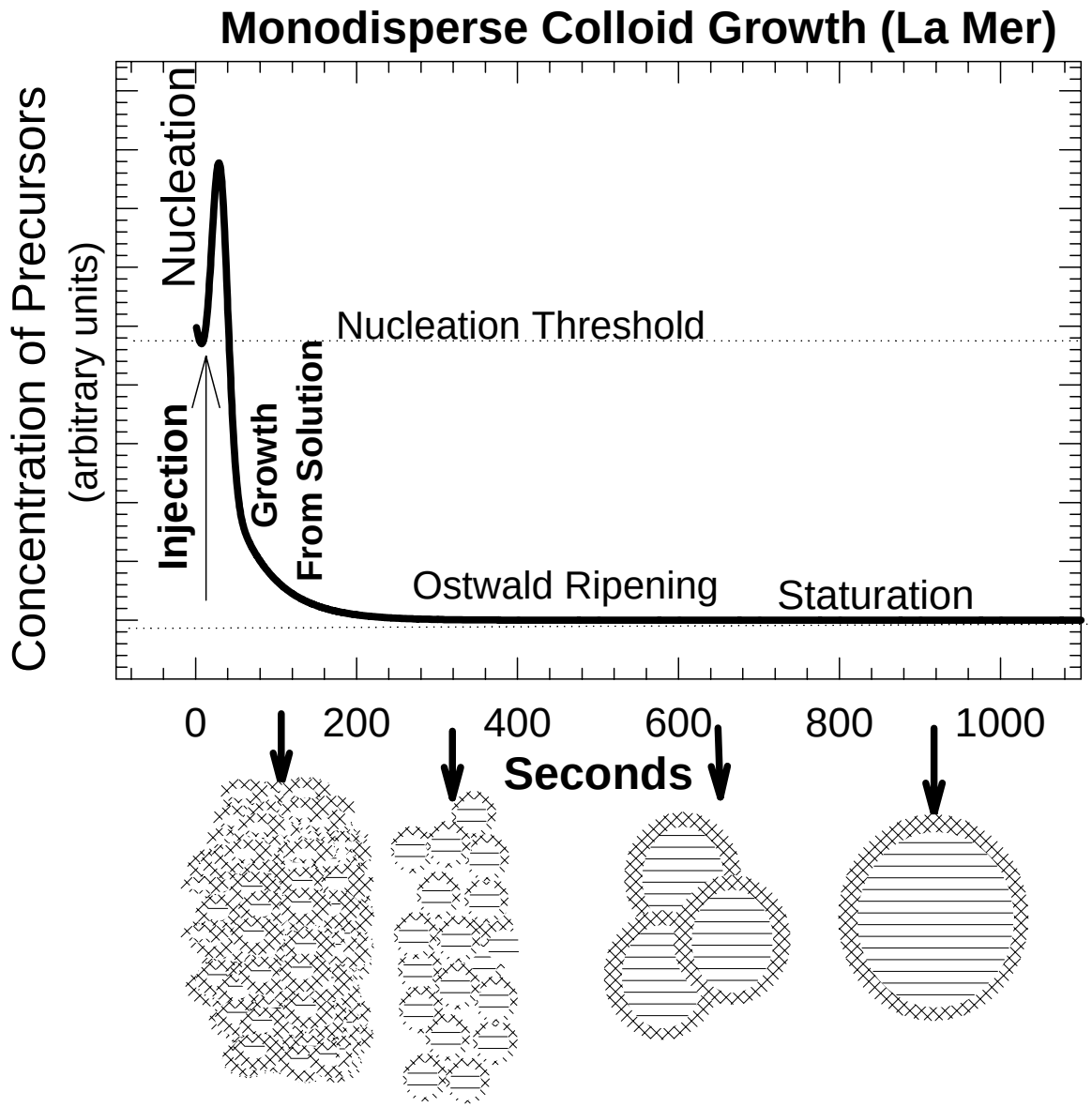

## PbSe Nanocrystal

Small Bandgap (0.28 eV, cf CdSe : 1.70 eV) ⇒ IR detector, IR diode Laser Material
Larger Bohr Radius (PbSe 46 nm, CdSe 12nm) ⇒ Strong Confinement of Electron-Hole Pair
Larger Optical Nonlinearity, Thermoelectric Cooling (ZT = 1 : PbTe)
Semiconducting, Solar Cells, Thermoelectric, Biological Application

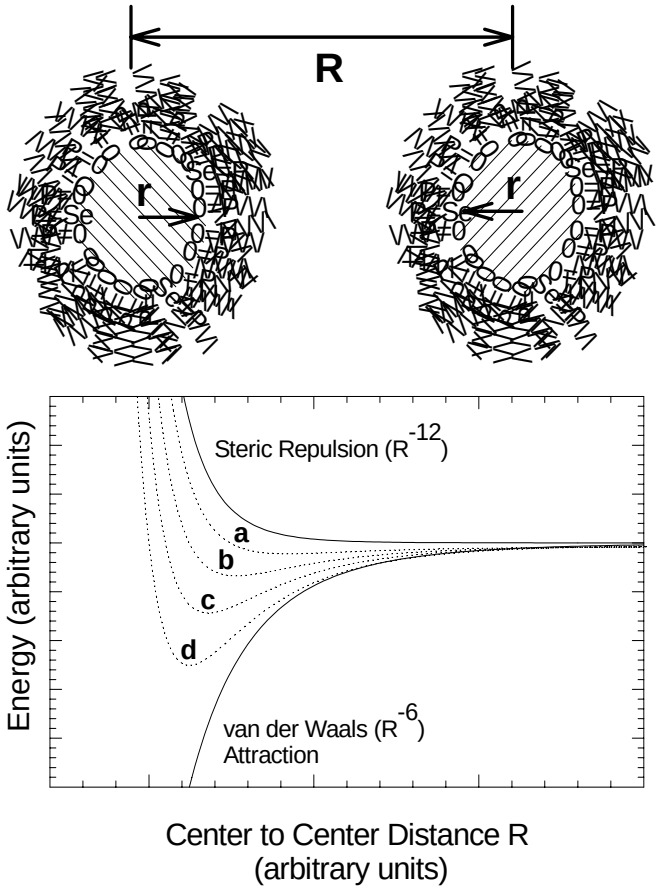
## PbSe Nanowire

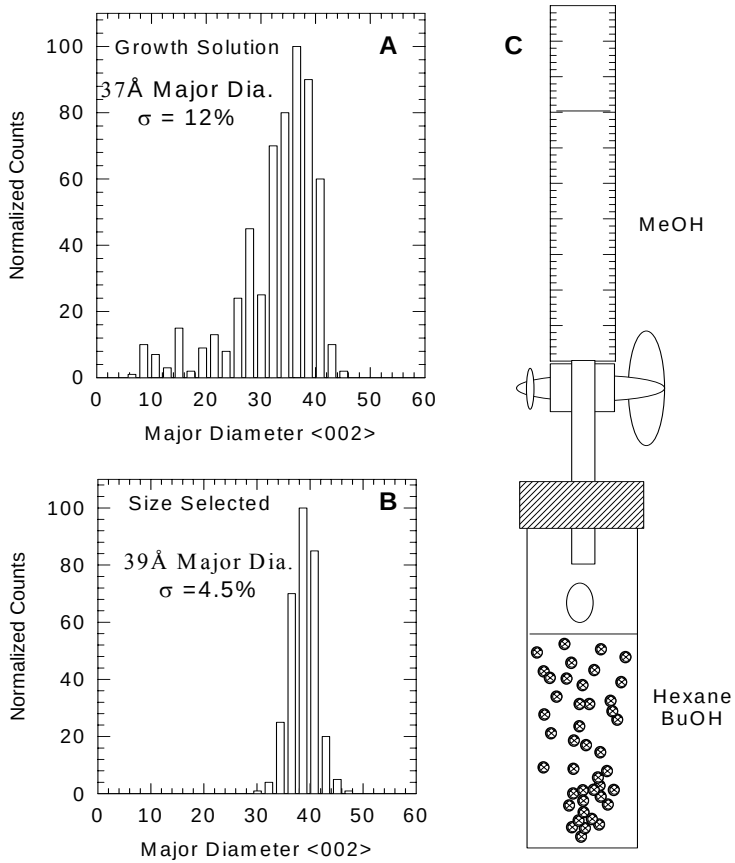
Solution Phase Synthesis using the Nanoparticles as a Building Block
Formation of the Nanowires from the Self Assembling the Particles
Controlling the wire Properties by Changing the Size and Shape of the Particles
Semiconducting device, Interconnect, Building Blocks for the Nanodevice

A

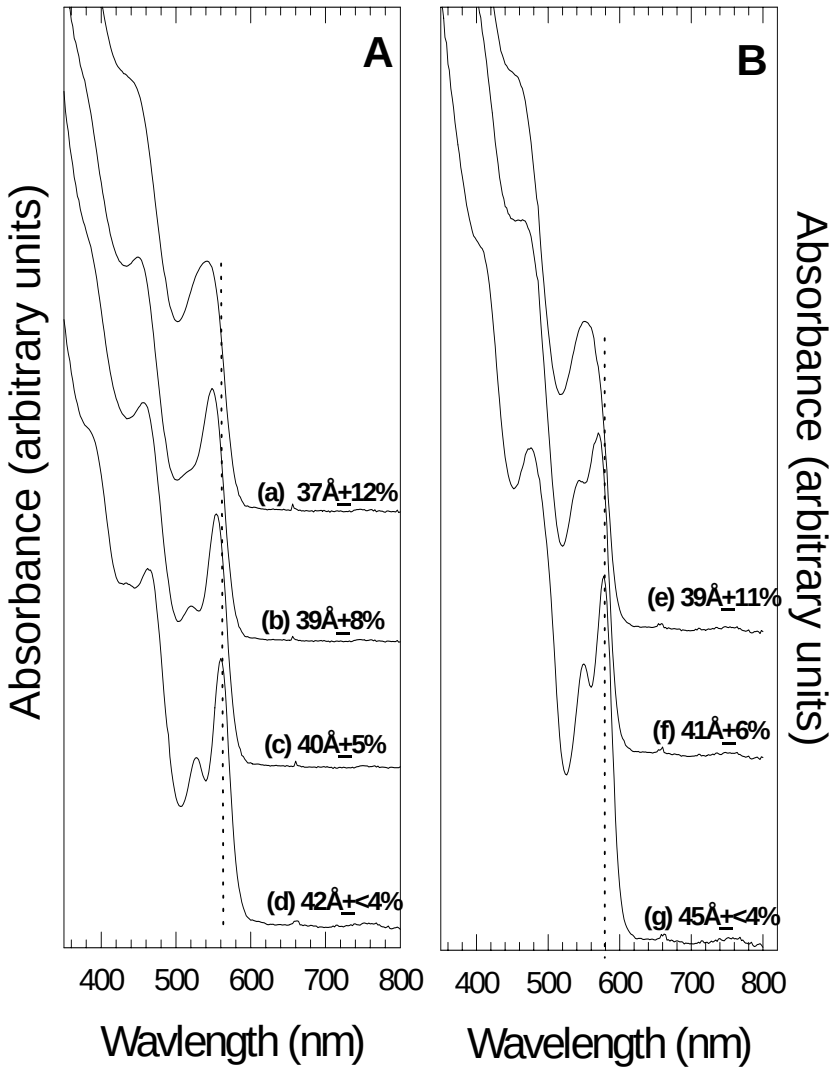

Monodisperse Colloid Growth (La Mer)
Concentration of Precursors
(arbitrary units)
Nucleation
Nucleation Threshold
Injection
Growth
From Solution
Ostwald Ripening
Staturation
0
200
400
600
800
1000
Seconds

# Size selective processing:

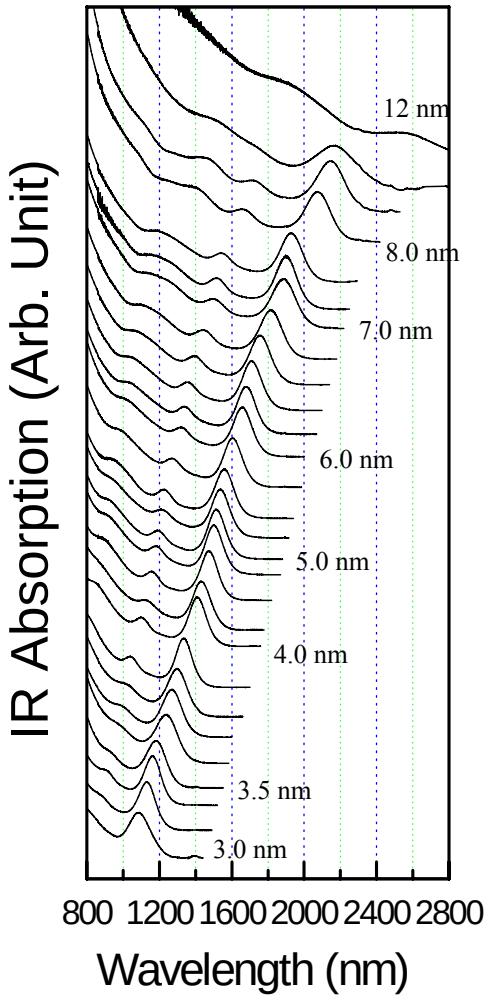


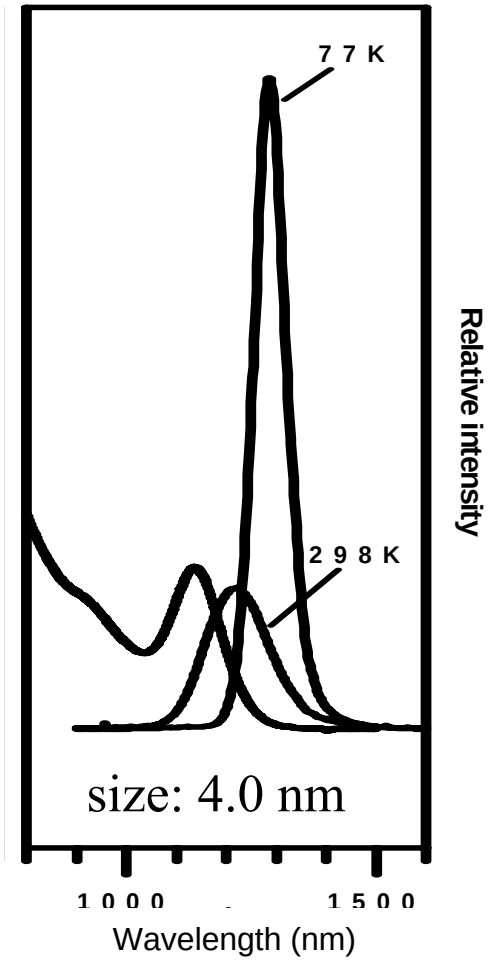



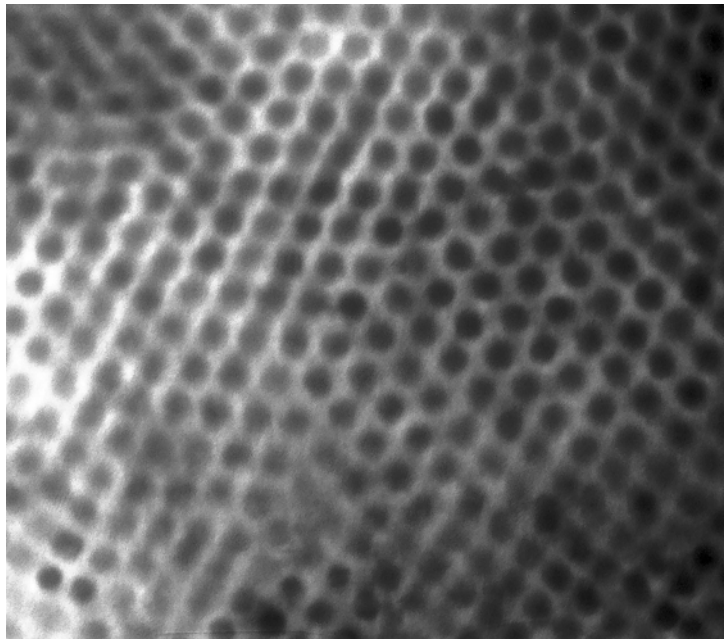
# Results of size selected Percipitation



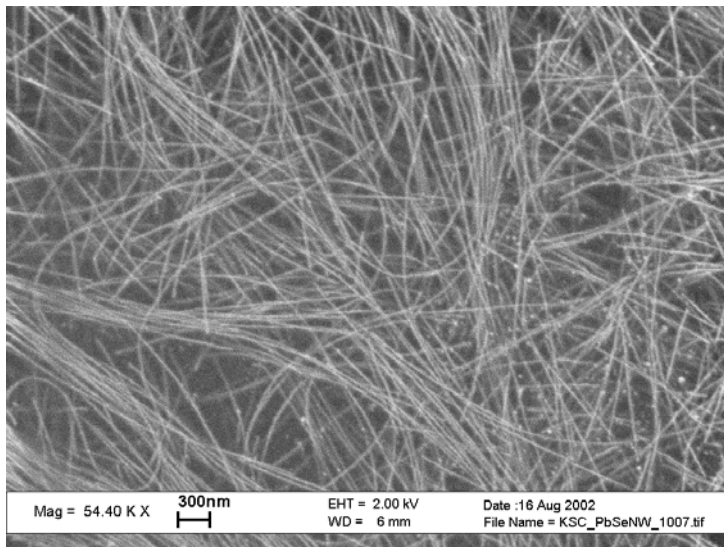
# Absorption and Photoluminescence of PbSe Nanocrystals



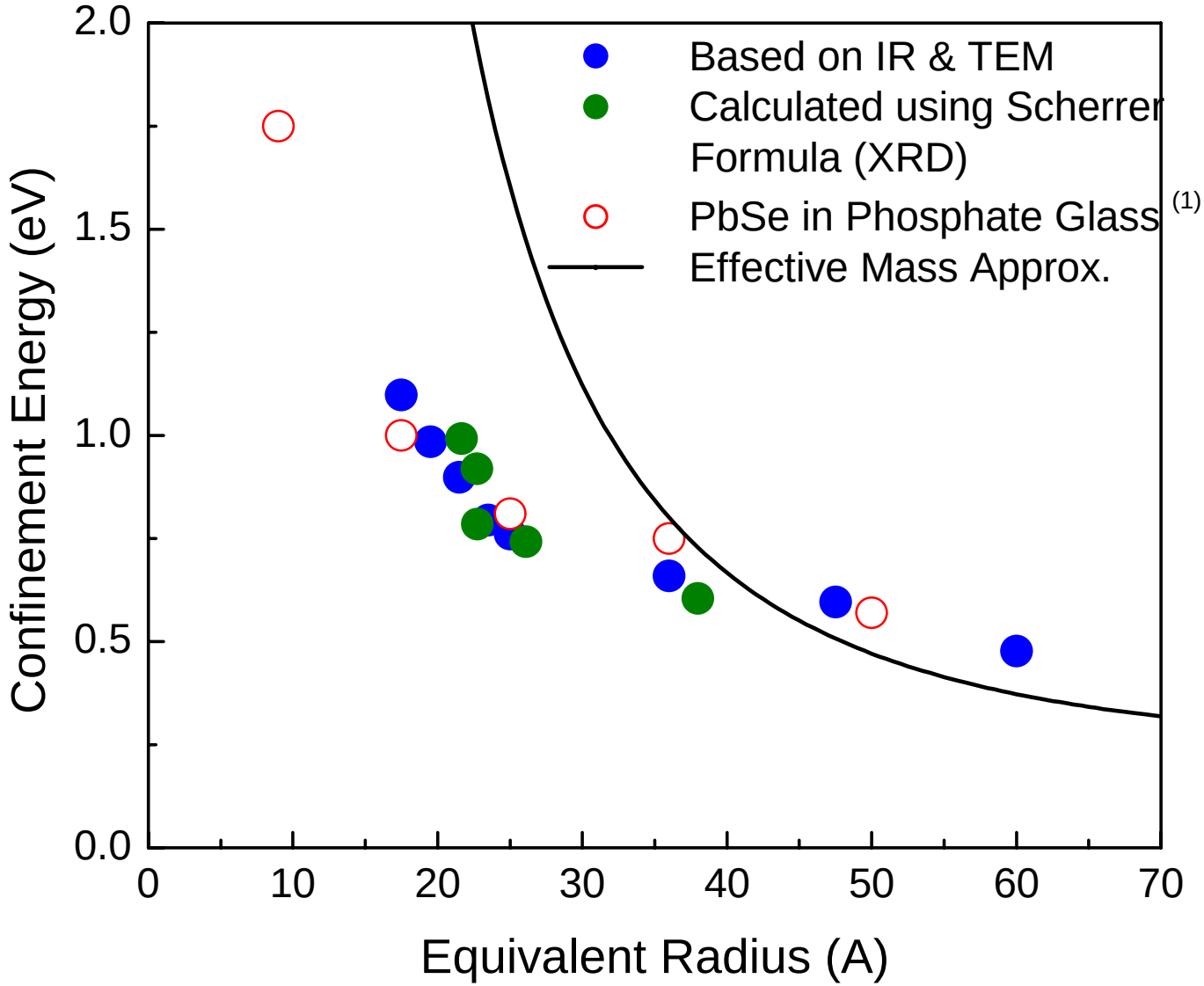



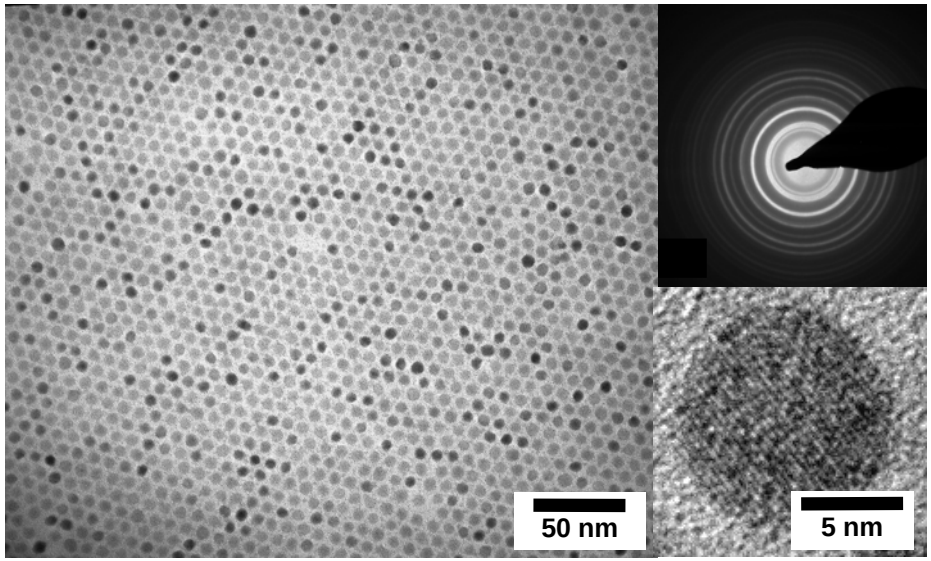
PbSe Nanocrystals

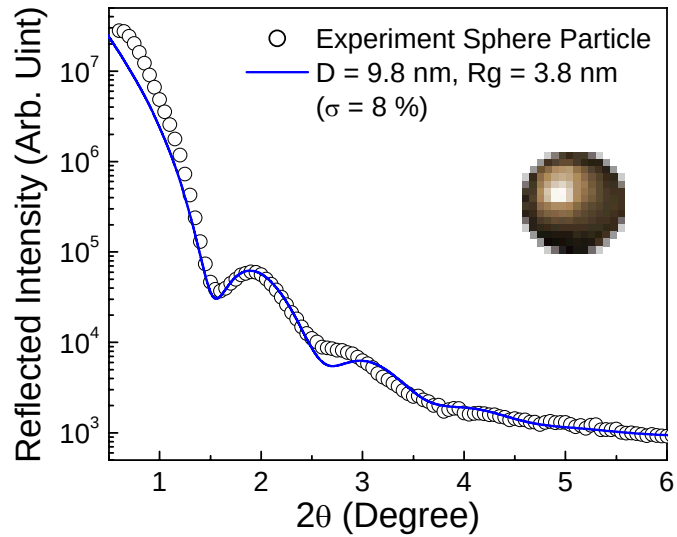


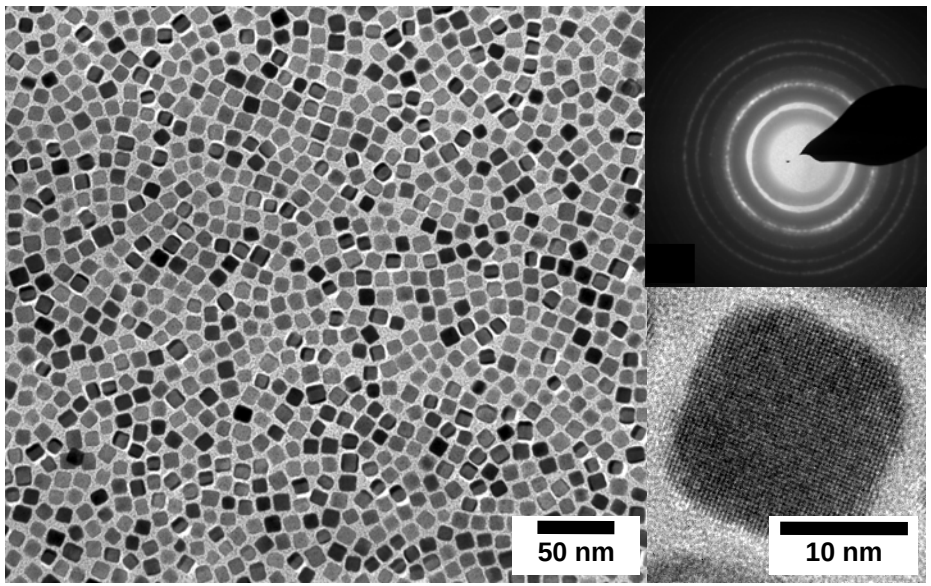

PbSe nanowires

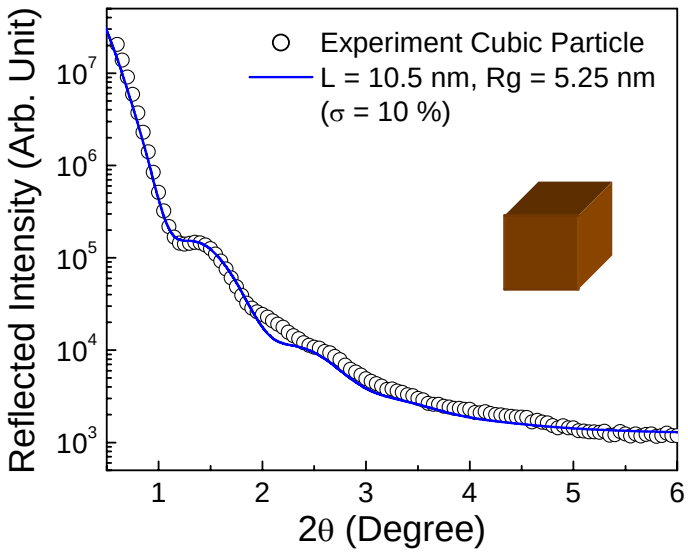

Based on IR & TEM
Calculated using Scherrer Formula (XRD)
PbSe in Phosphate Glass (1)
Effective Mass Approx.
Confinement Energy (eV)
Equivalent Radius (A)
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70

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



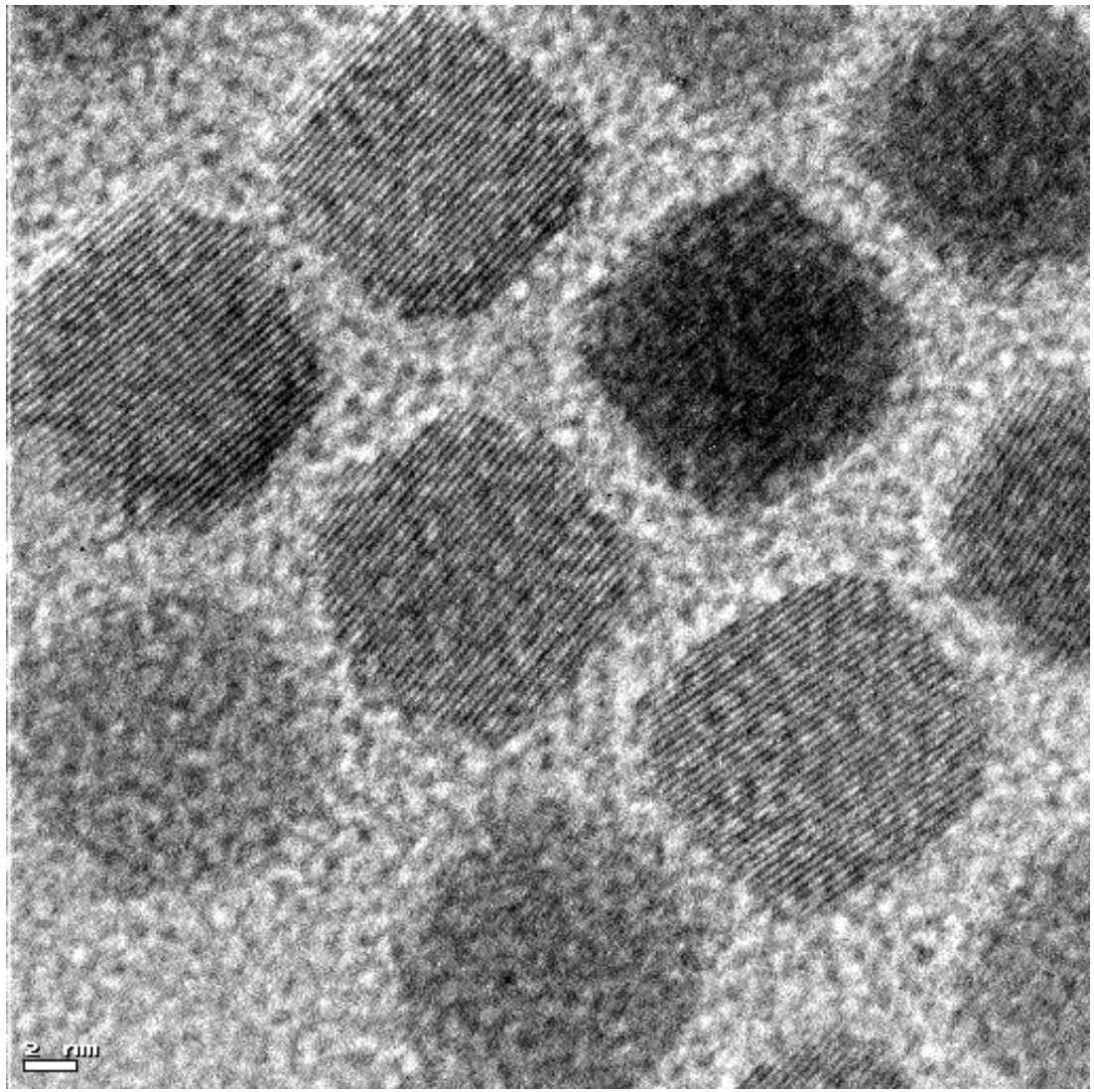



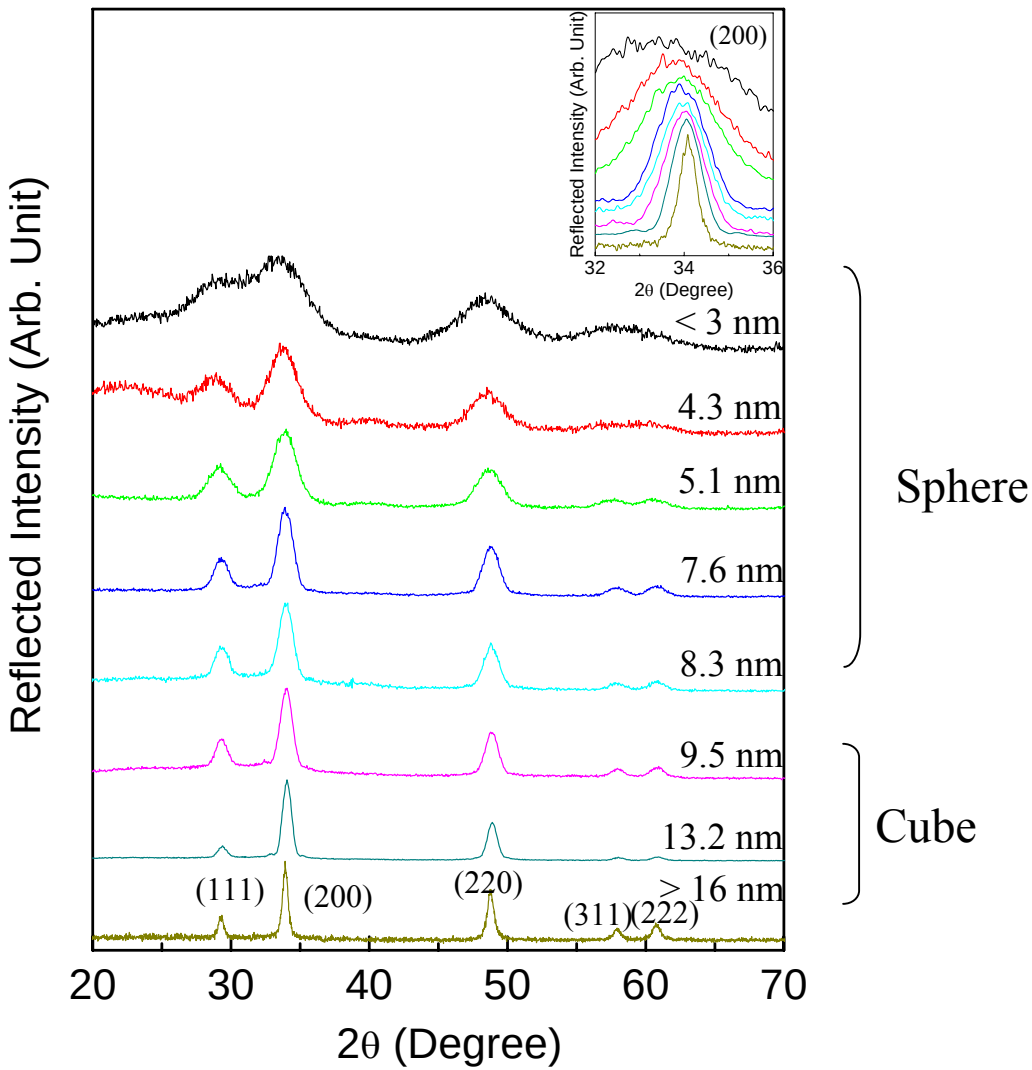



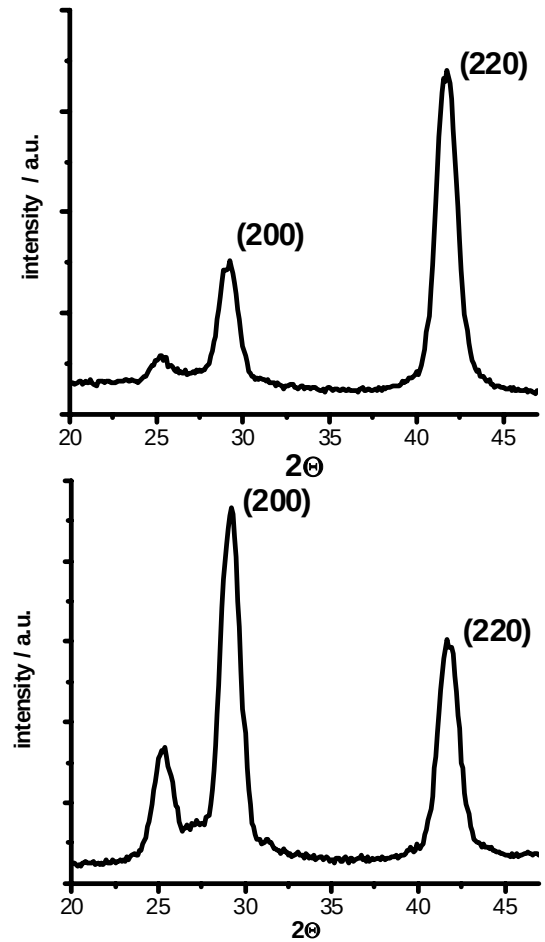




K.-S. Cho, W. Gaschler

# PbSe Quantum Cubes

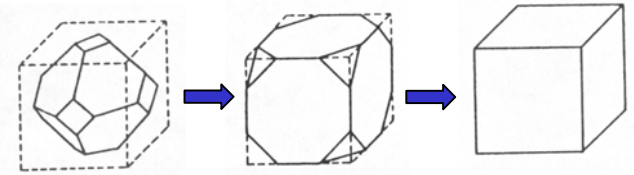




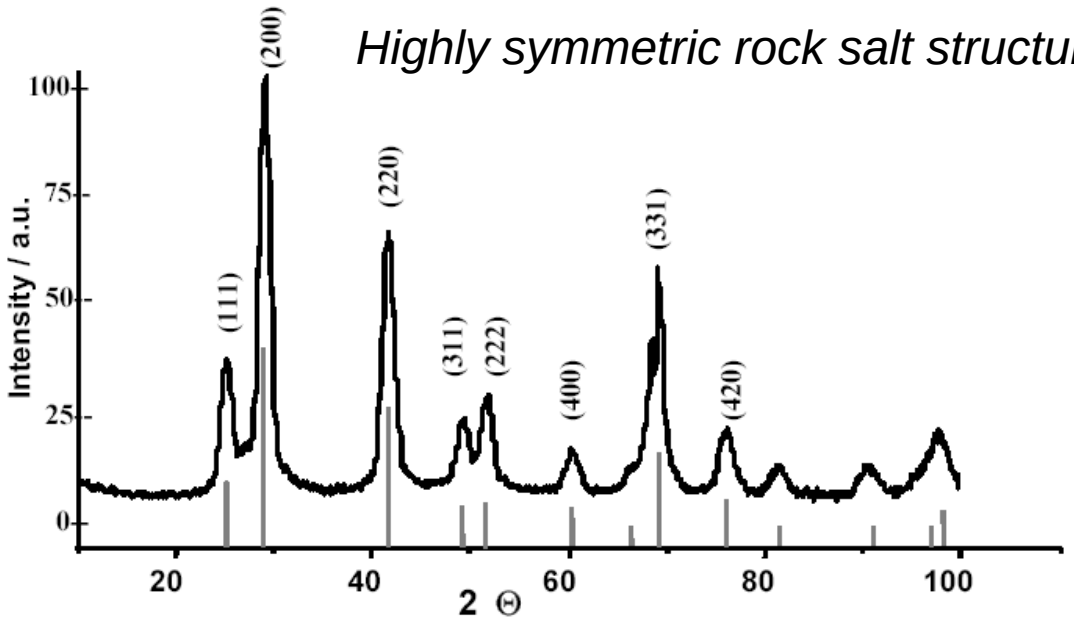



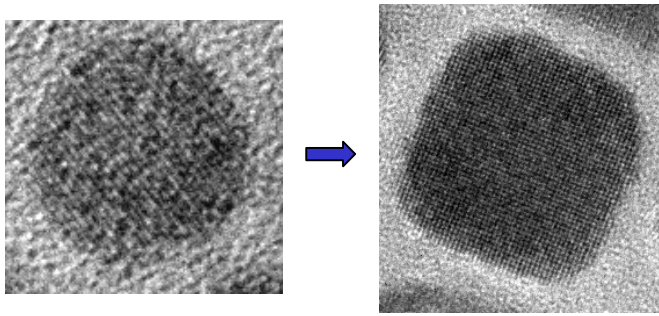

**WAXS of 10 nm PbSe quantum cubes slowly deposited from toluene (top) and rapidly precipitated from methanol (bottom)**

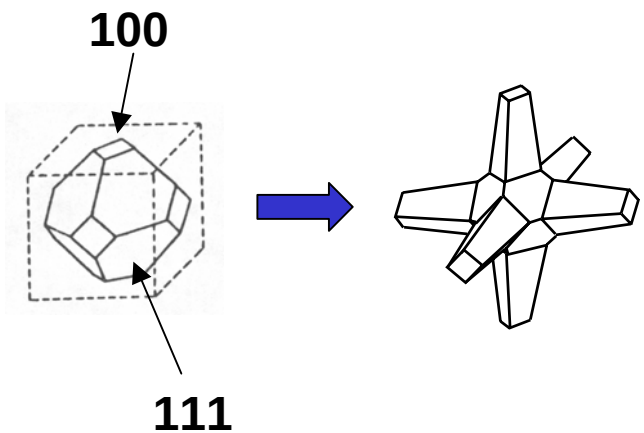
# Shape evolution of PbSe Nanocrystals

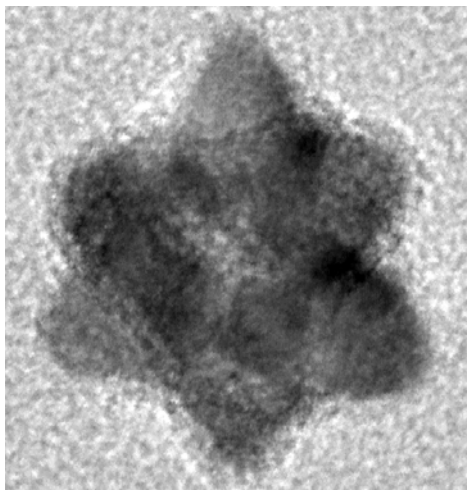


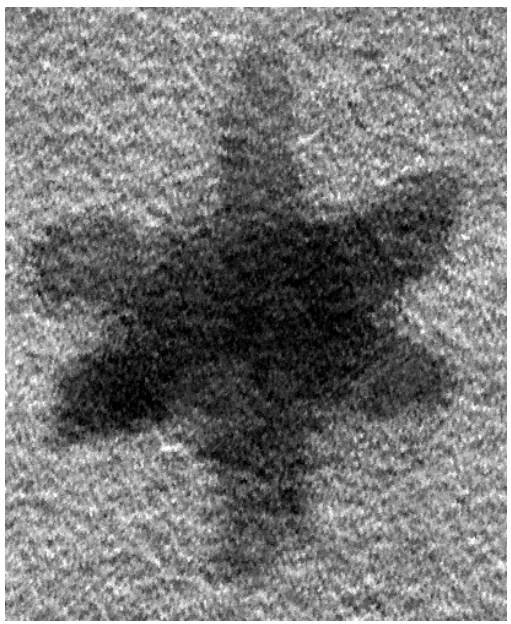
*Highly symmetric rock salt structure*







# Modeling of x-ray diffraction:

The Debye equation which is valid in the kinematical approximation is shown in equation 4.6 [8].

$$I(q) = I_0 \sum_m \sum_n F_m F_n \frac{\sin(qr_{m,n})}{qr_{m,n}}$$

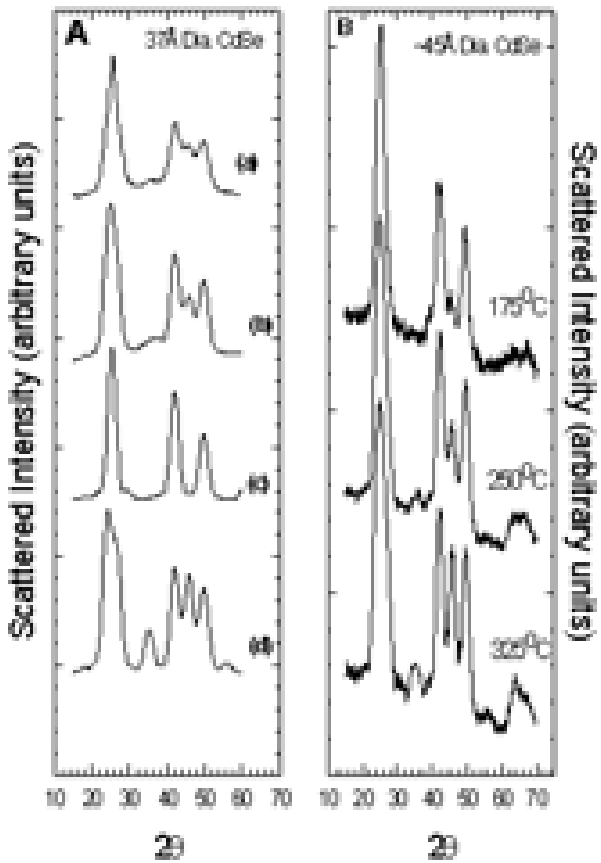
(4.6)

Where I(q) is the scattered intensity , Io is the incident intensity, q is the scattering parameter [$q = 4\pi\sin(\theta)/l$] for X-rays of wavelength l diffracted through angle θ. The distance between atoms m and n is $r_{mn}$ . A discrete form of the Debye is shown in eguation (4.7)[9].

(4.7)

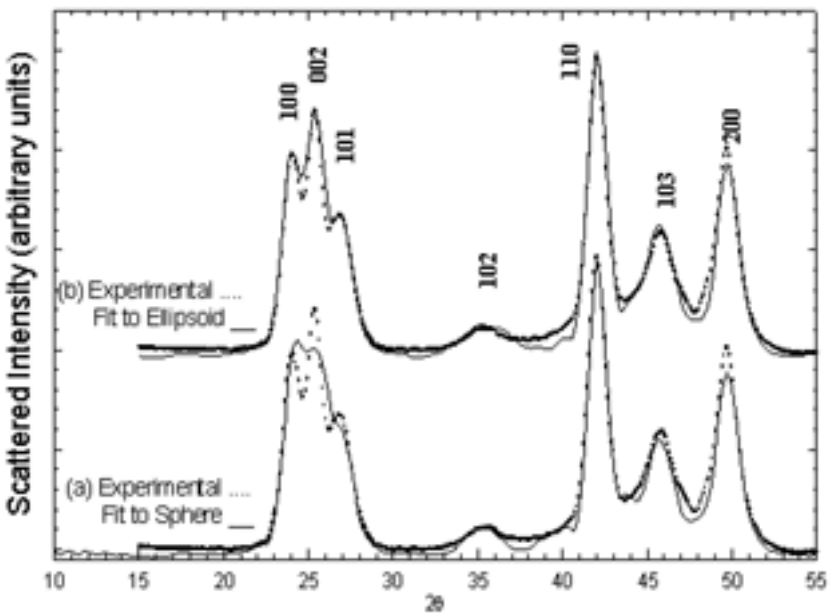
$$I(q) = I_o \frac{f^2(q)}{q} \sum_k \frac{\rho(r_k)}{r_k} \sin(qr)$$

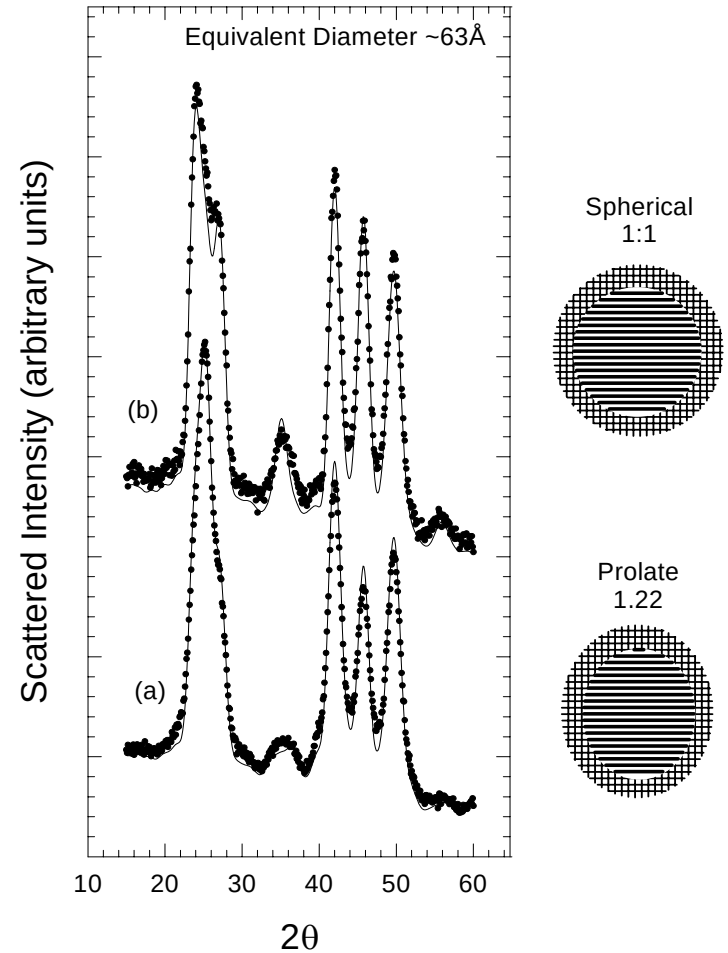
where is the incident intensity, f(q) is the angle dependent scattering factor q is the scattering parameter[$4\pi\sin(\theta)/\lambda$] for X-rays of wavelength λ diffracted through angle θ. The sum is over all inter atomic distances, and $\rho(r_k)$ is the number of times a given interatomic distance $r_k$ occurs. Since the number of discrete interatomic distances in an ordered structure grows much more slowly than the total number of distances, using the discrete form of the equation is significantly more efficient in the simulation of large crystallites[9].



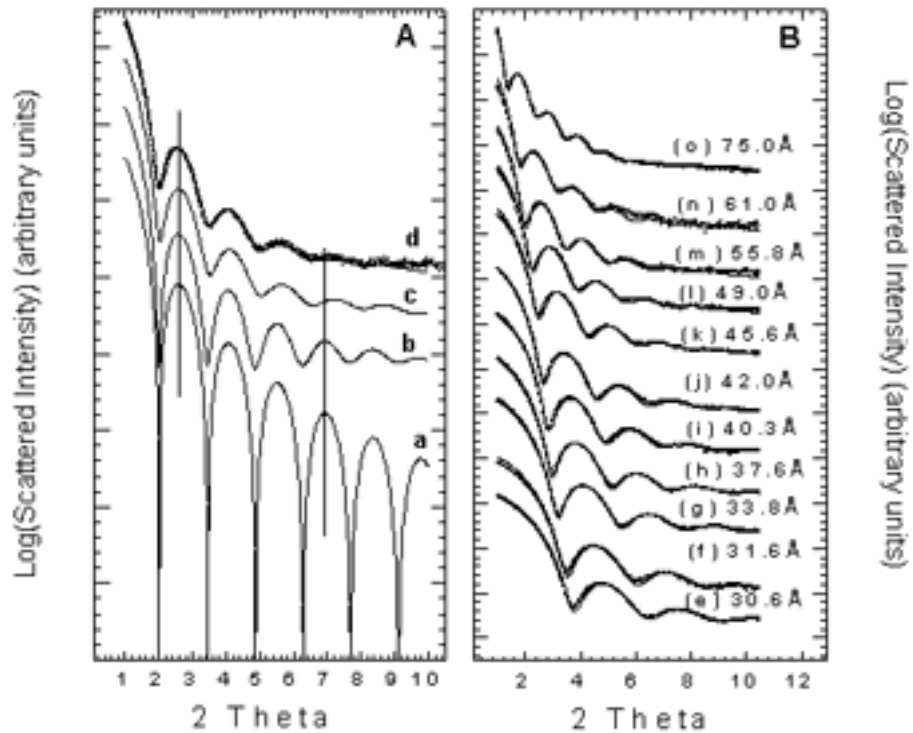
# Modeling NP Shape

# Modeling Stacking faults



# Small angle X-ray Scattering SAXS



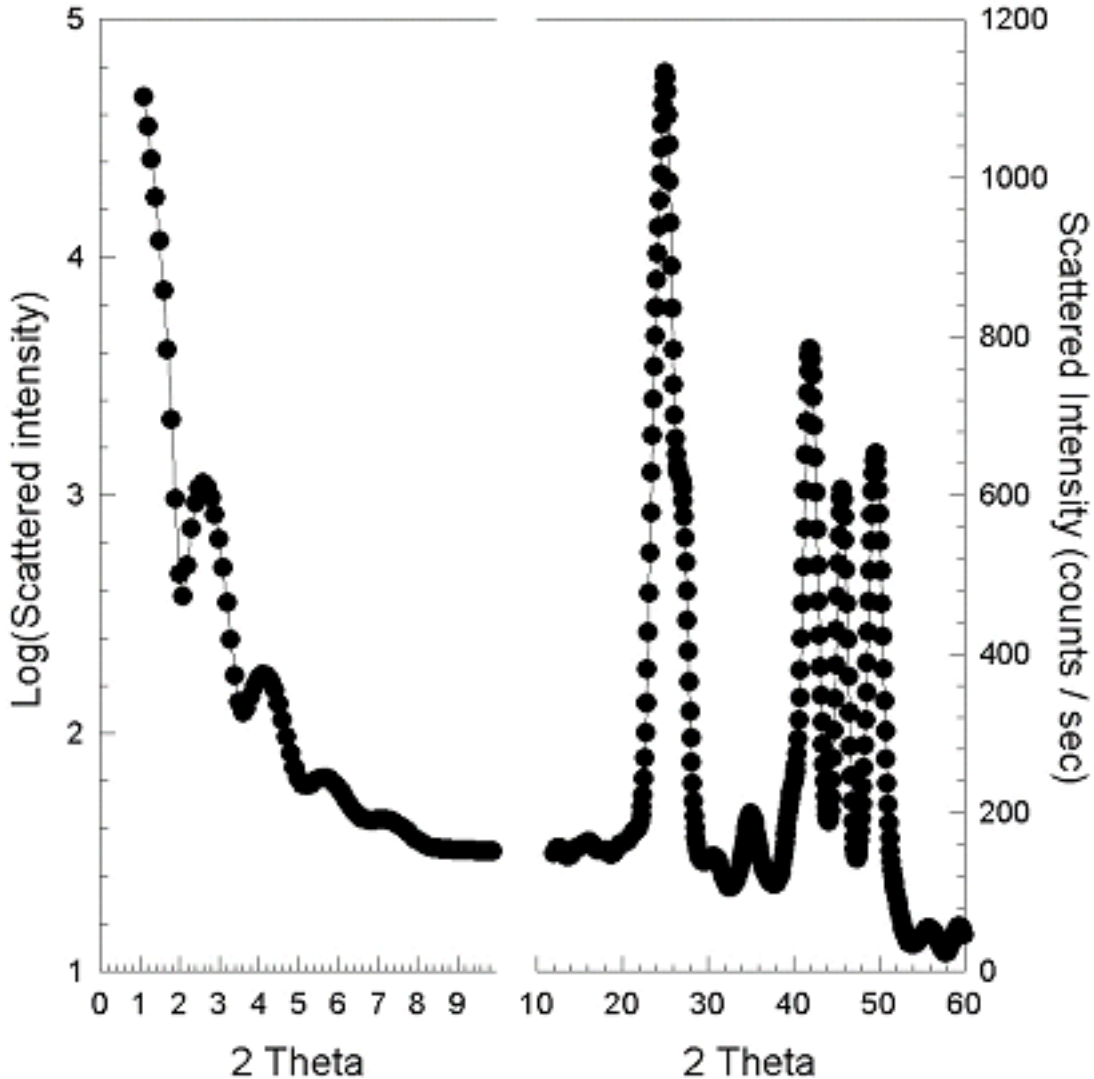

(4.8) $$I(q) = I_o N[(\rho - \rho_o)^2 \frac{4}{3}\pi R^3 [3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}]]^2$$

Where ρ and $\rho_o$ are the electron density of the particle and the dispersing medium respectively. $I_o$ is the incident intensity and N is the number of particles. F(q) is the material form factor (the fourier transform of the shape of the scattering object) and is the origin of the oscillations observed. Thus for a spherical particle of radius R

(4.9) $$I(q) = I_o N(\rho - \rho_o)^2 F^2(q)$$

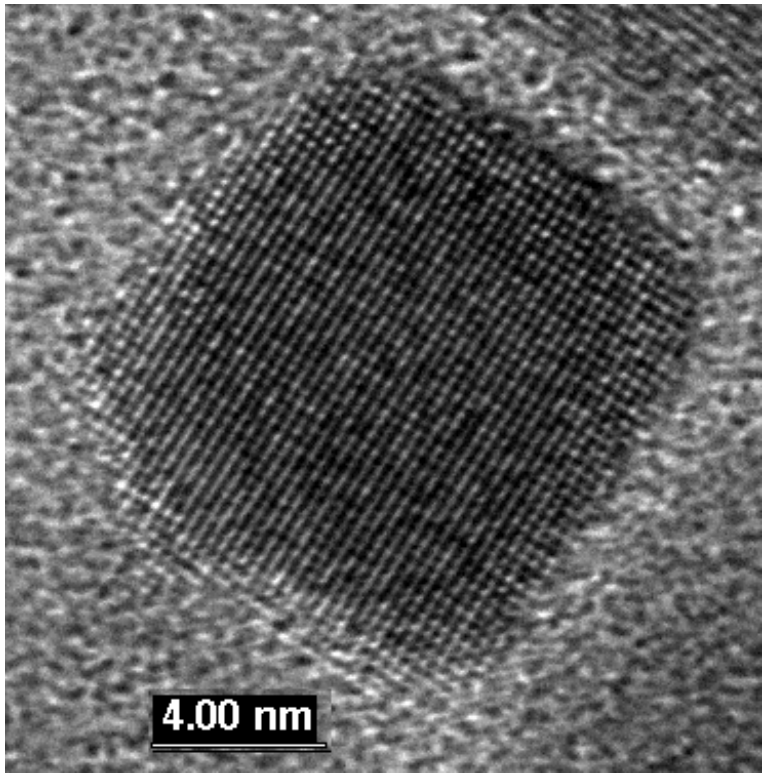
(4.10) $$F(q) = \frac{4}{3}\pi R^3 [3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}]$$

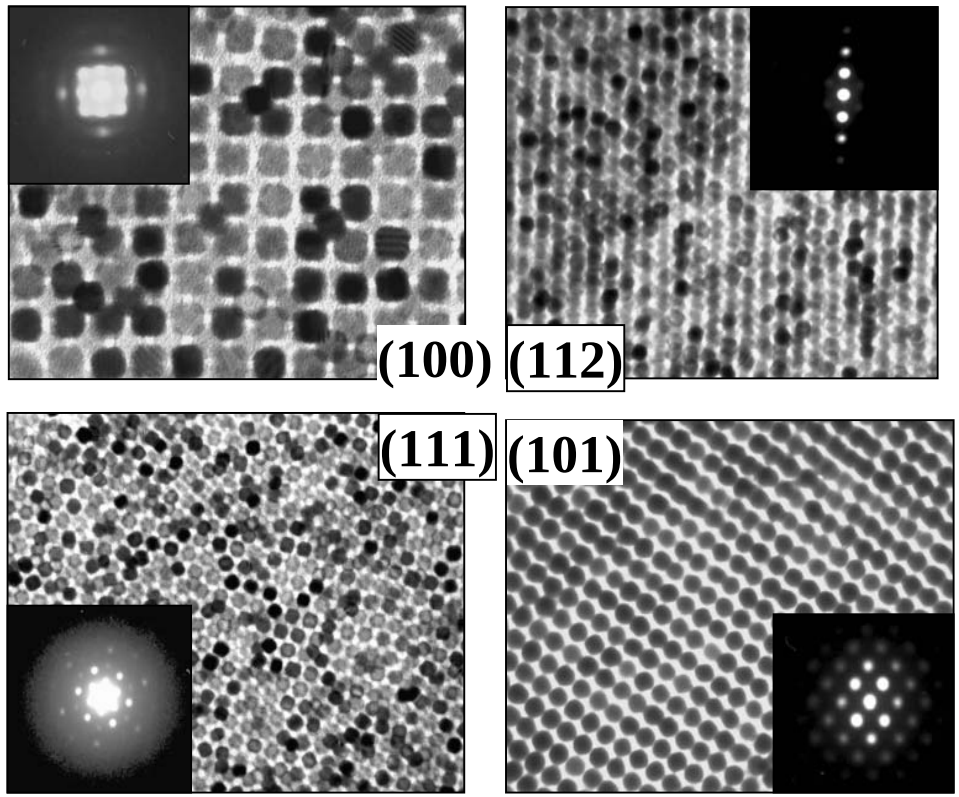
# Combined SAXS and WAXS Modeling.

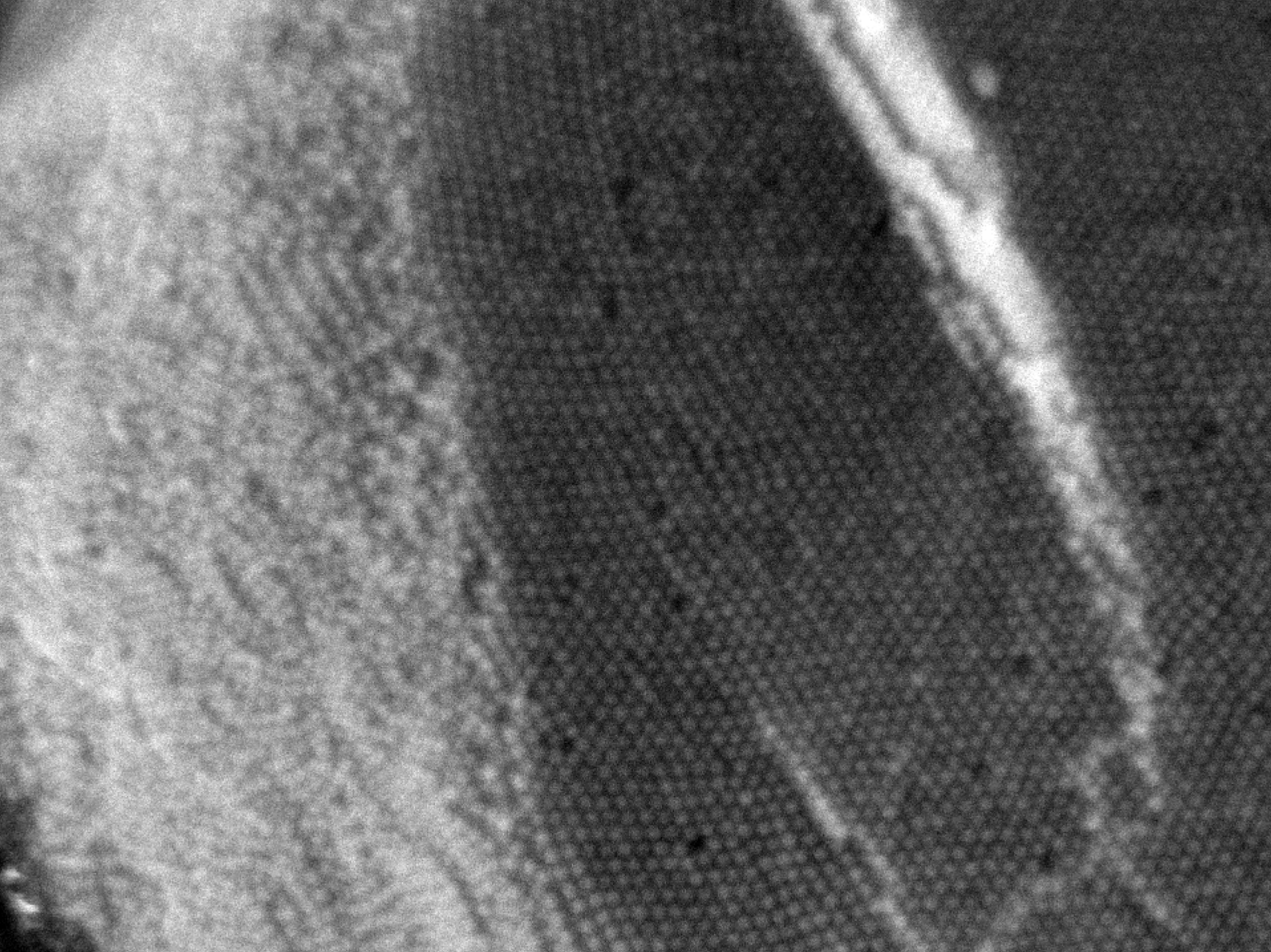


# Qunatum cubes:

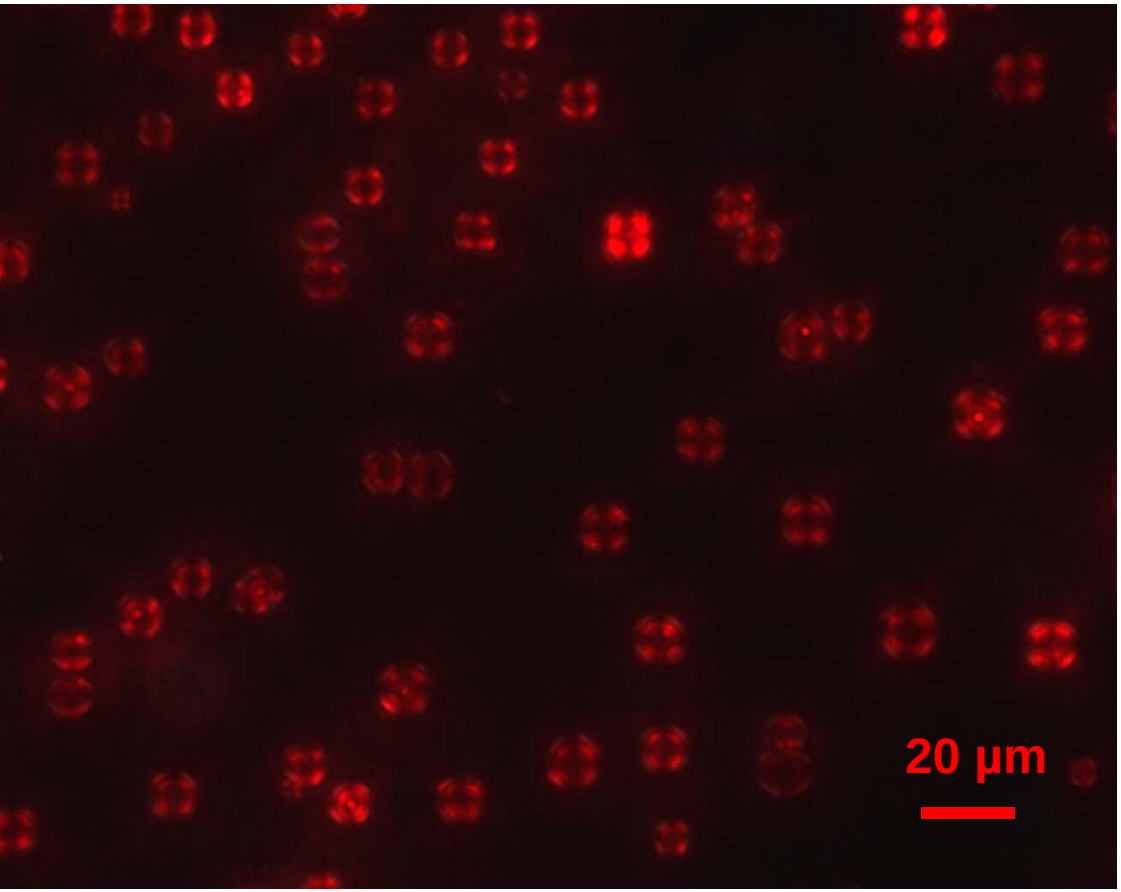
## Cubic 12 nm PbSe nanocrystals Assembling into a superlattice.





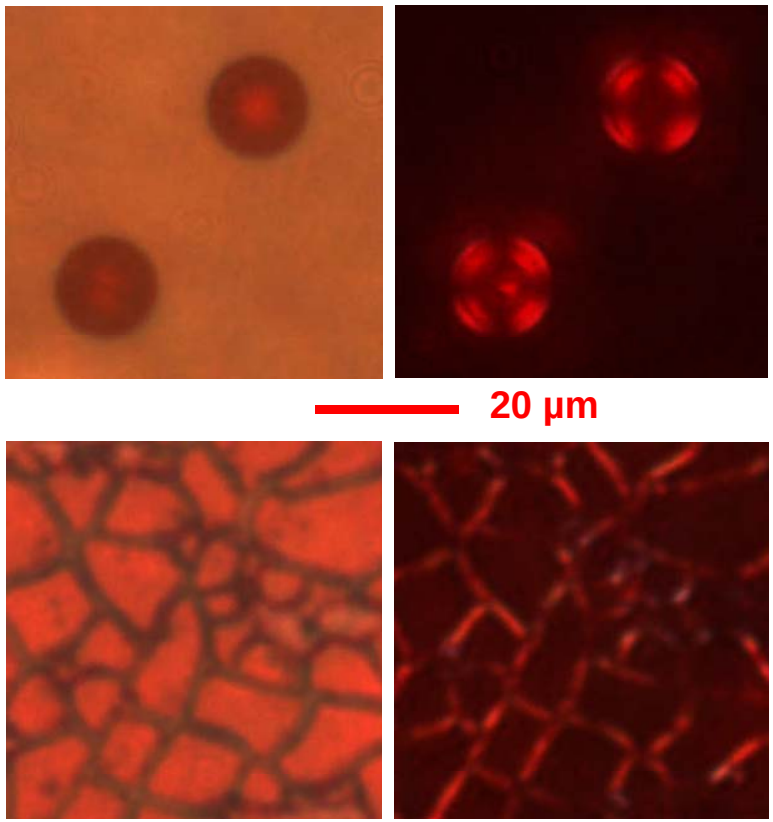
# Self-assembled CdSe nanorod solids




*Optical micrograph of self-assembled CdSe nanorods (between crossed polarizers).*

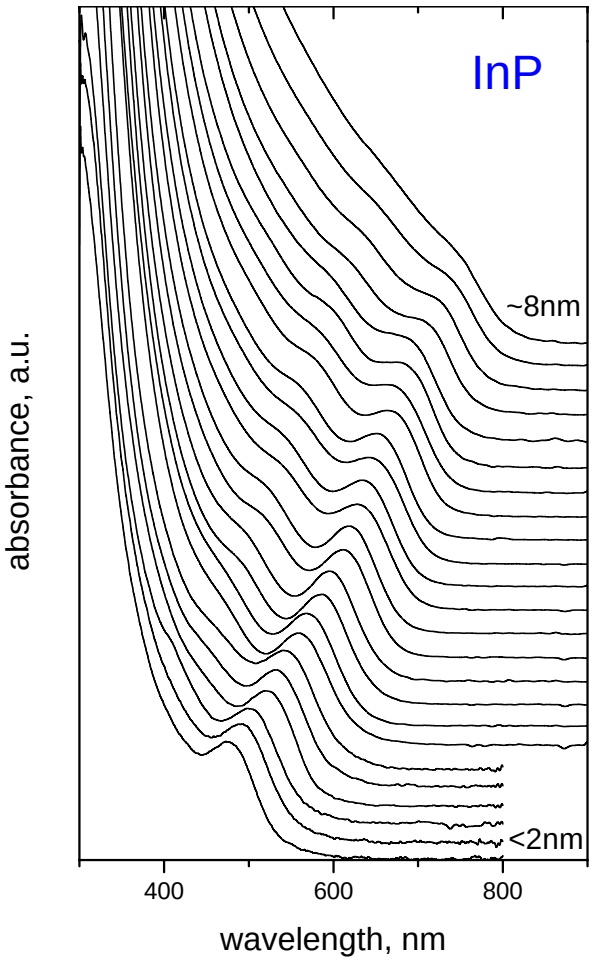
*without polarizers*

*with crossed polarizers*

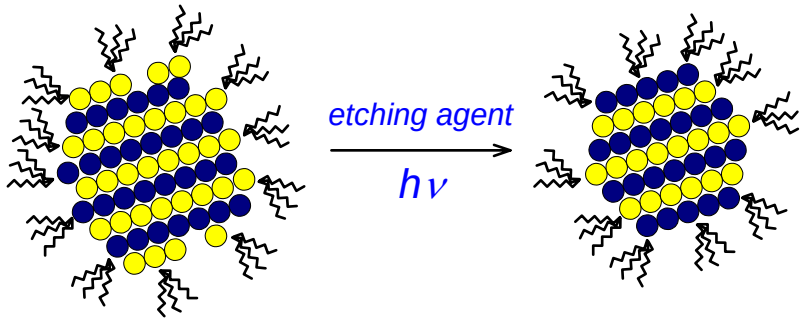


# III-V semiconductor nanocrystals : InP

$$InCl_3 \cdot (oct)_3P + [(CH)_3Si]_3P \xrightarrow{TOPO-TOP,\ 180-260°C} InP + \ldots$$




*Size-dependent evolution of absorption spectra of InP colloidal quantum dots*



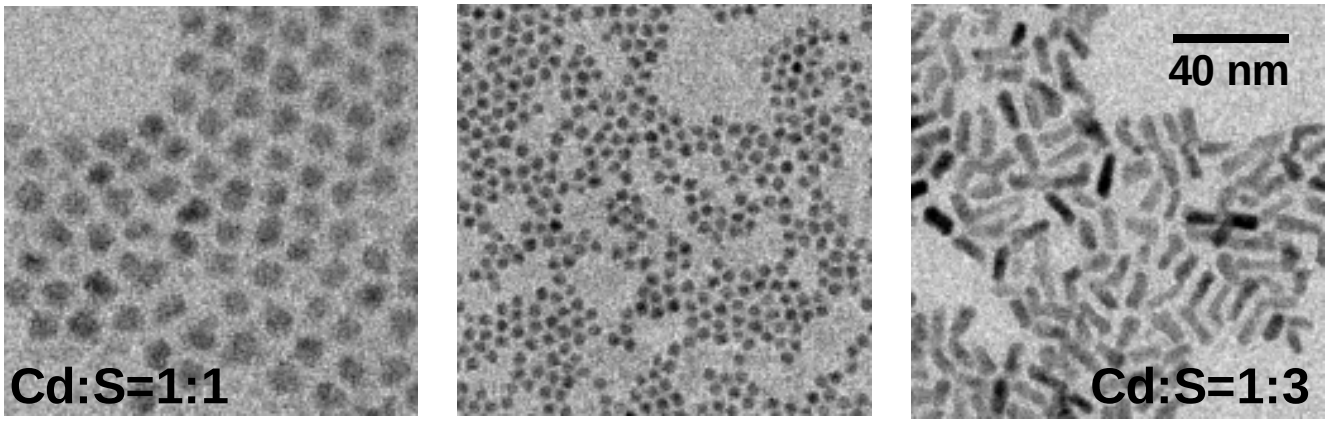

$$\text{InP (as-prepared, weak } PL) \xrightarrow{HF,\ TOPO,\ h\nu} \text{InP (strong } PL)$$

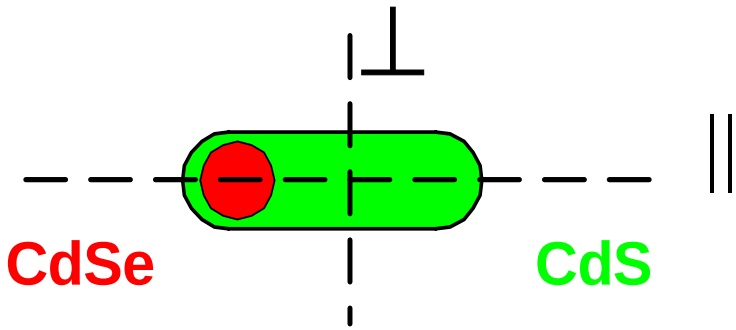
*PL quantum efficiency ~25-40%*

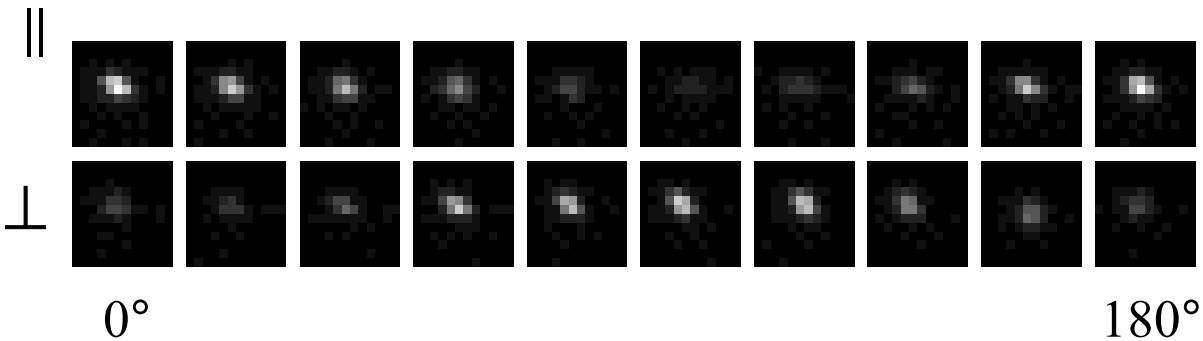
*J. Phys. Chem. B*, **2002**, *106*, 12659.

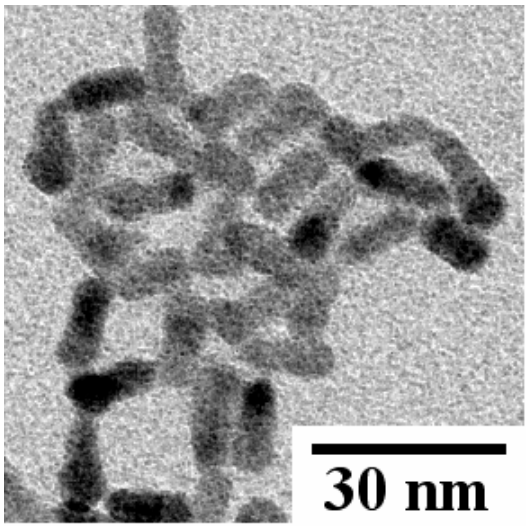
# CdSe/CdS quantum dot - quantum rods

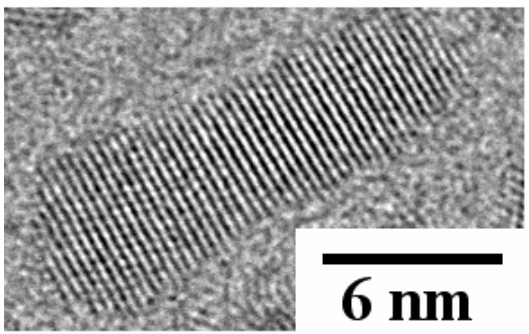
CdSe/CdS ← ***CdSe** cores* → CdSe/CdS



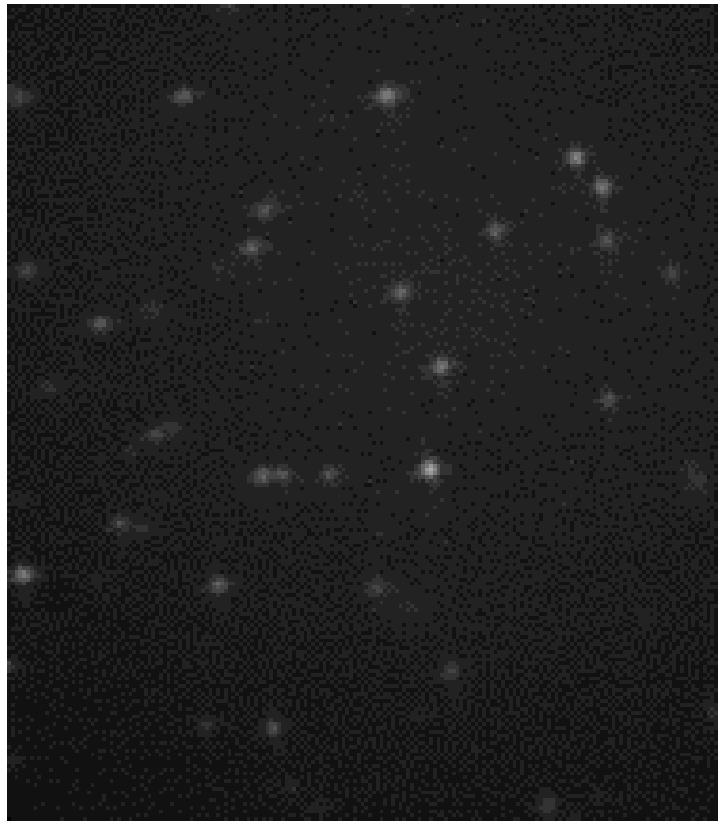



# Luminescent II-VI nanocrystals

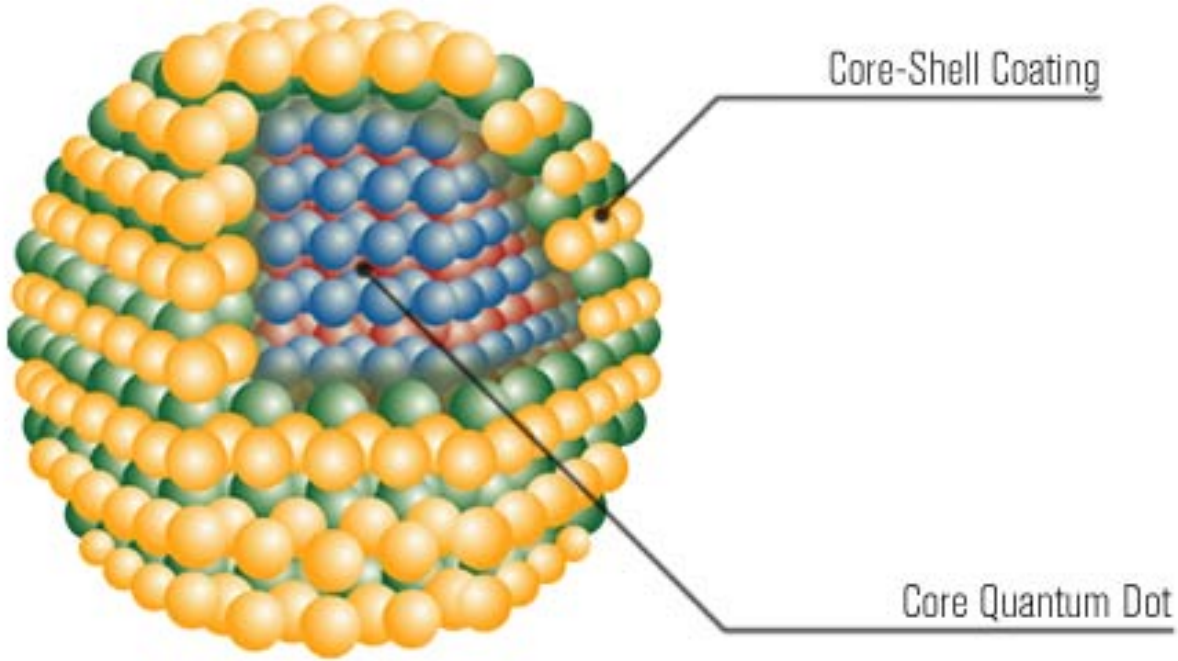
***Room temperature PL quantum efficiencies 50-70%***

*Colloidal solutions of CdSe/ZnS core-shell nanocrystals.*

*CdSe/CdS core-shell nanocrystals in a polymer matrix*



*Single particle luminescence of CdSe/ZnS nanocrystals*




CORE-SHELL EVIDOT

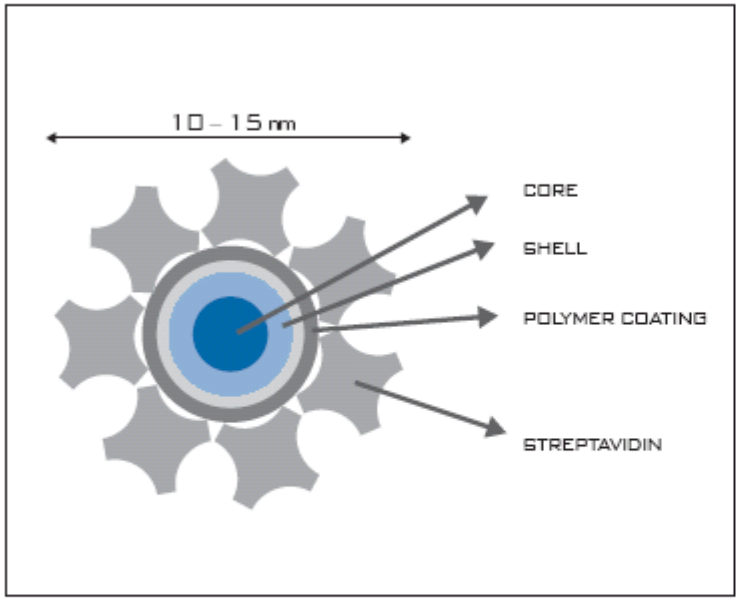



**Figure 1. Diagram of a Qdot Streptavidin Conjugate.** The layers represent the distinct structural elements of the Qdot nanocrystal and are roughly to scale. As shown Qdot quantum dots contain a semiconductor (CdSe) nanocrystal core, a semiconductor (ZnS) shell, then a polymer coat, and finally streptavidin on the outer surface.

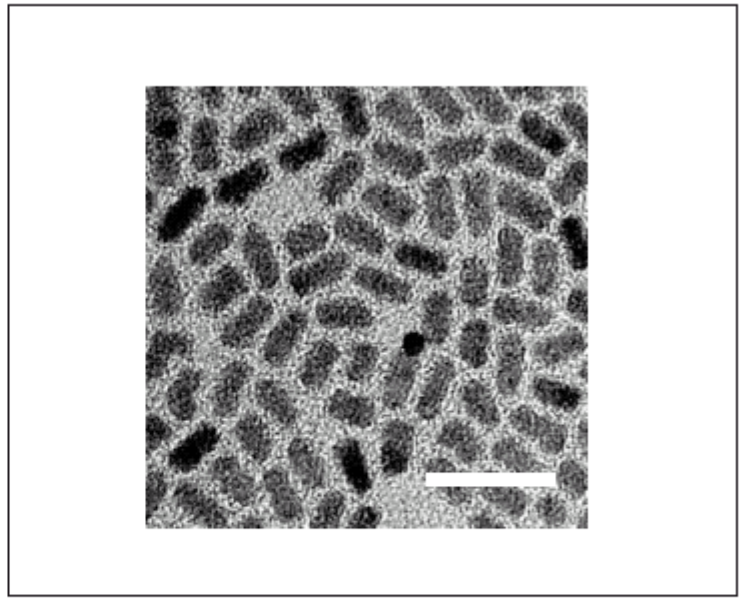


**Figure 2. Transmission electron micrograph of Qdot core-shell nanoparticles.** Shown at 200,000X magnification. Scale bar = 20 nm.

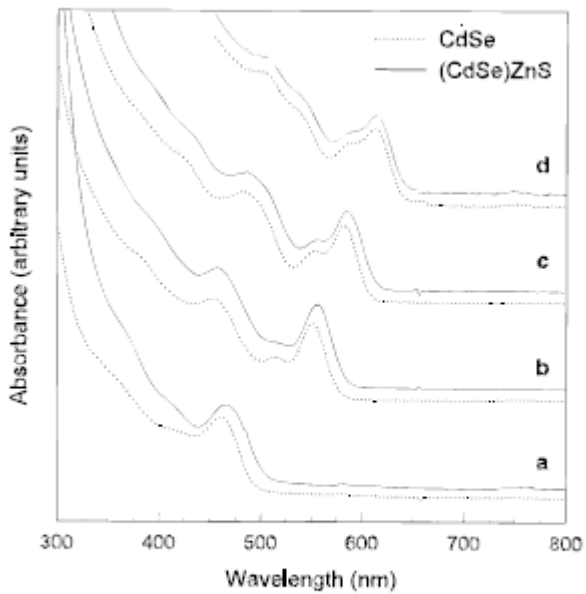



**Figure 1.** Absorption spectra for bare (dashed lines) and 1−2 monolayer ZnS overcoated (solid lines) CdSe dots with diameters measuring (a) 23, (b) 42, (c) 48, and (d) 55 Å. The absorption spectra for the (CdSe)ZnS dots are broader and slightly red-shifted from their respective bare dot spectra.

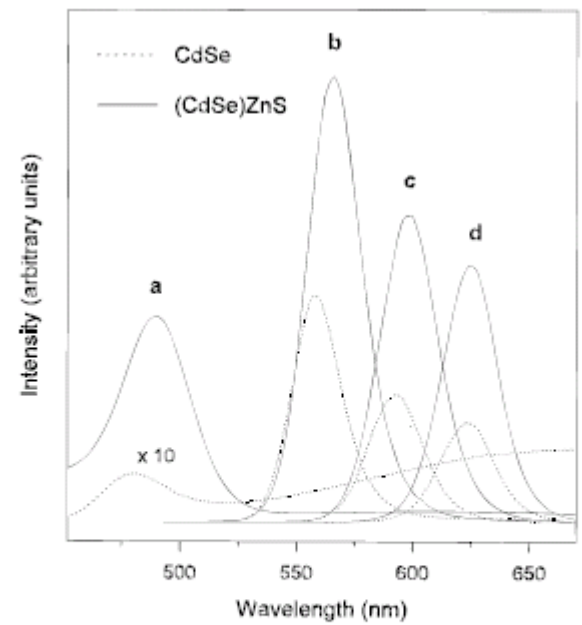



**Figure 2.** Photoluminescence (PL) spectra for bare (dashed lines) and ZnS overcoated (solid lines) dots with the following core sizes: (a) 23, (b) 42, (c) 48, and (d) 55 Å in diameter. The PL spectra for the overcoated dots are much more intense owing to their higher quantum yields: (a) 40, (b) 50, (c) 35, and (d) 30.

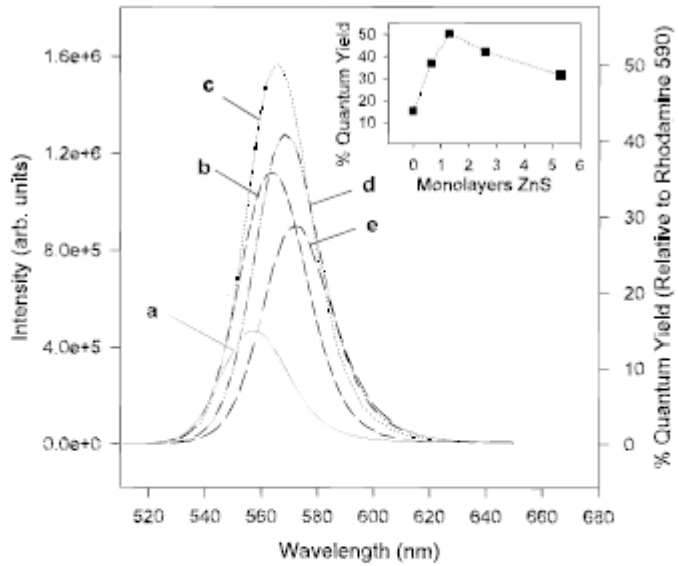



**Figure 5.** PL spectra for a series of ZnS overcoated dots with 42 ± 10% Å diameter CdSe cores. The spectra are for (a) 0, (b) 0.65, (c) 1.3, (d) 2.6, and (e) 5.3 monolayers ZnS coverage. The position of the maximum in the PL spectrum shifts to the red, and the spectrum broadens with increasing ZnS coverage. (inset) The PL quantum yield is charted as a function of ZnS coverage. The PL intensity increases with the addition of ZnS reaching, 50% at ~1.3 monolayers, and then declines steadily at higher coverage. The line is simply a guide to the eye.

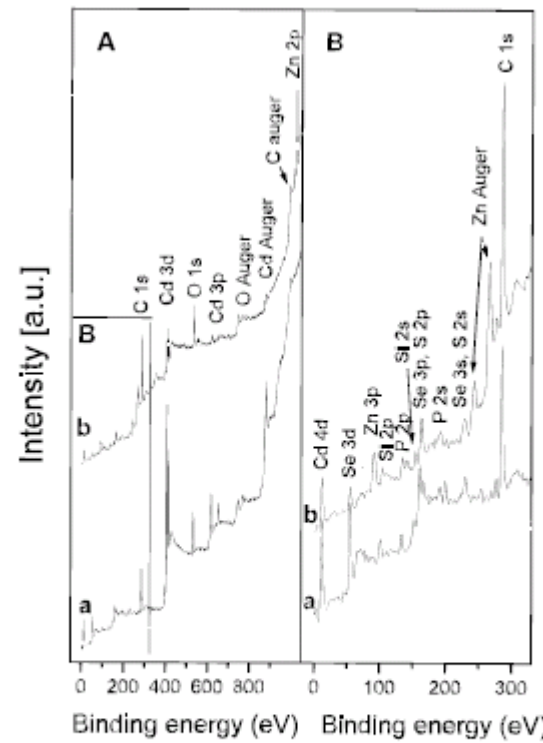



**Figure 6.** (A) Survey spectra of (a) ~40 Å diameter bare CdSe dots and (b) the same dots overcoated with ZnS showing the photoelectron and Auger transitions from the different elements present in the quantum dots. (B) Enlargement of the low-energy side of the survey spectra, emphasizing the transitions with low binding energy.

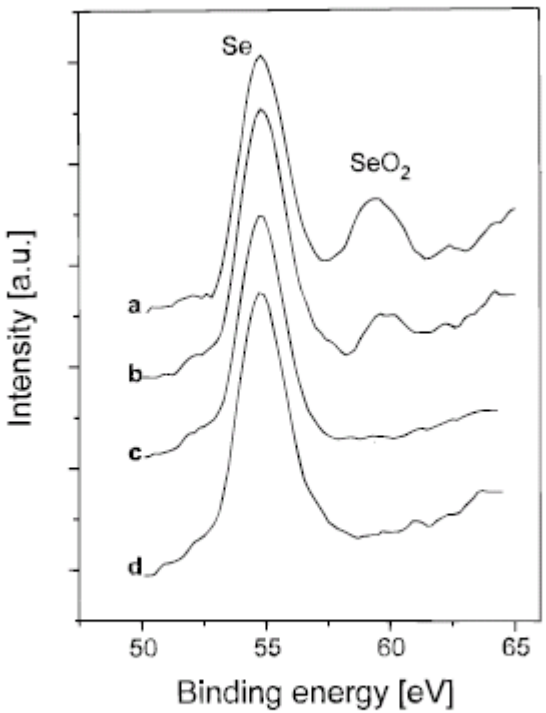



**Figure 7.** X-ray photoelectron spectra highlighting the Se 3d core transitions from ~40 Å bare and ZnS overcoated CdSe dots: (a) bare CdSe, (b) 0.65 monolayers, (c) 1.3 monolayers, and (d) 2.6 monolayers of ZnS. The peak at 59 eV indicates the formation of selenium oxide upon exposure to air when surface selenium atoms are exposed.

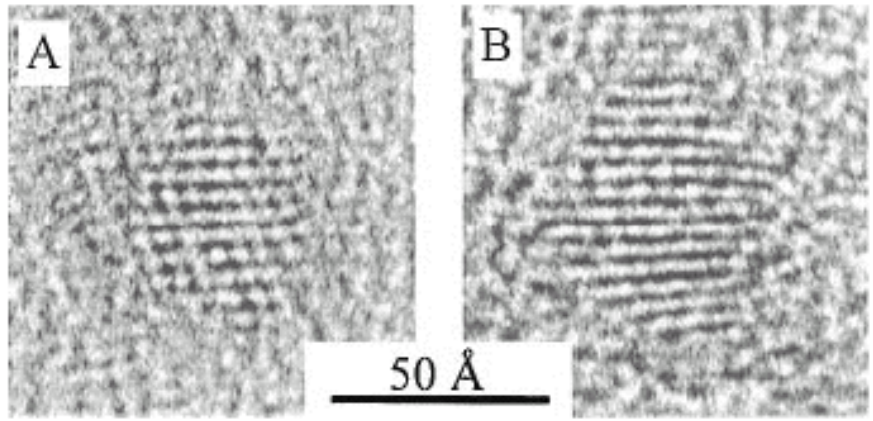



**Figure 8.** Transmission electron micrographs of (A) one "bare" CdSe nanocrystallite and (B) one CdSe nanocrystallite with a 2.6 monolayer ZnS shell.