

# Kavli Prize Lecture Semiconductor Nanocrystals

Lou Brus  
Chemistry Department  
Columbia University  
New York

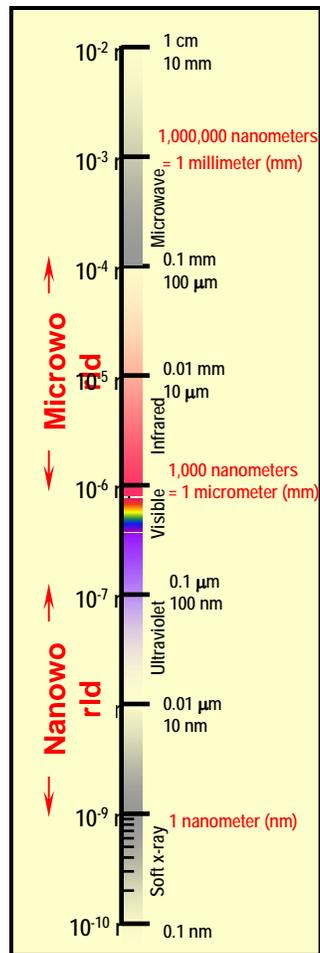
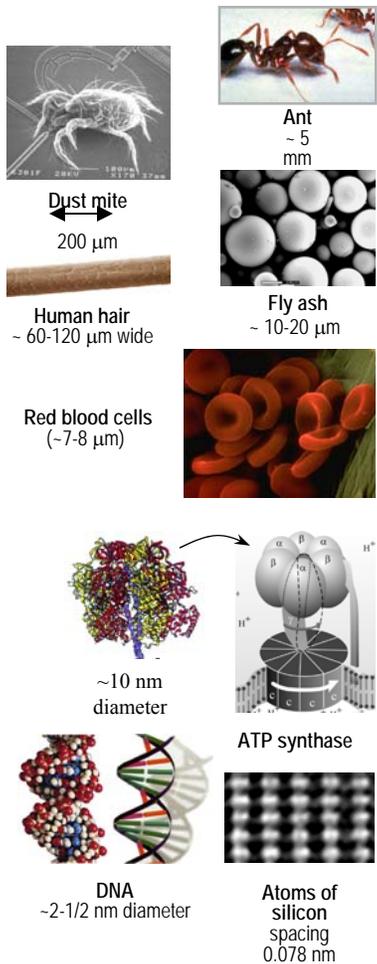
Trondheim, Norway – Sept 11, 2008



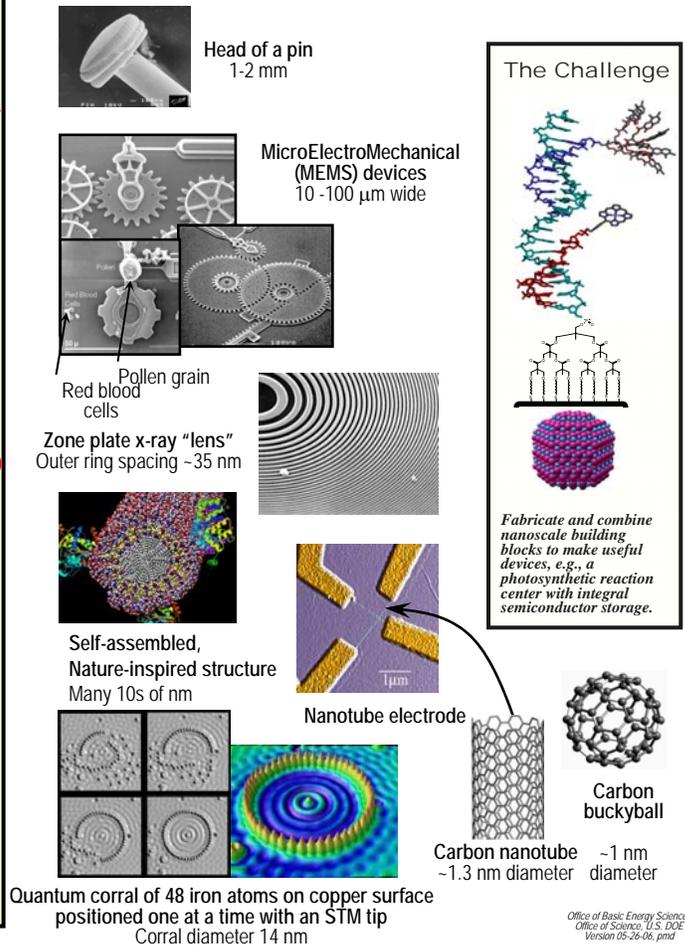
Columbia University in the City of New York

# The Scale of Things – Nanometers and More

## Things Natural



## Things Manmade



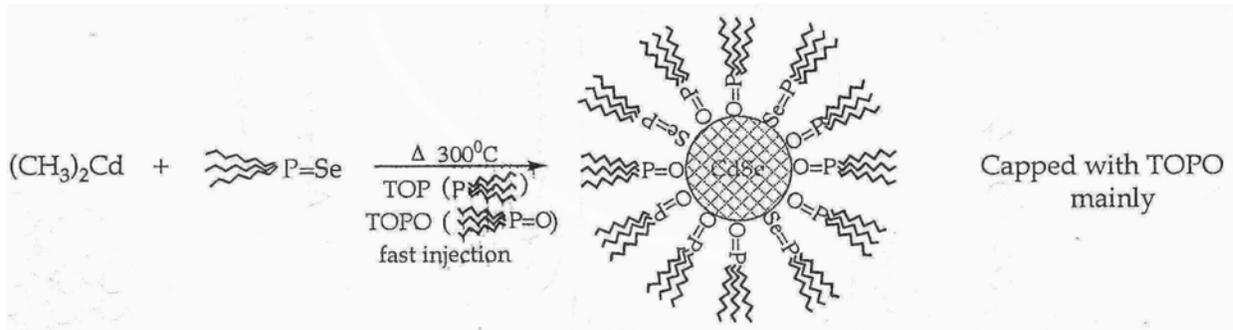
Office of Basic Energy Sciences  
Office of Science, U.S. DOE  
Version 05-26-06, pmd

NSF

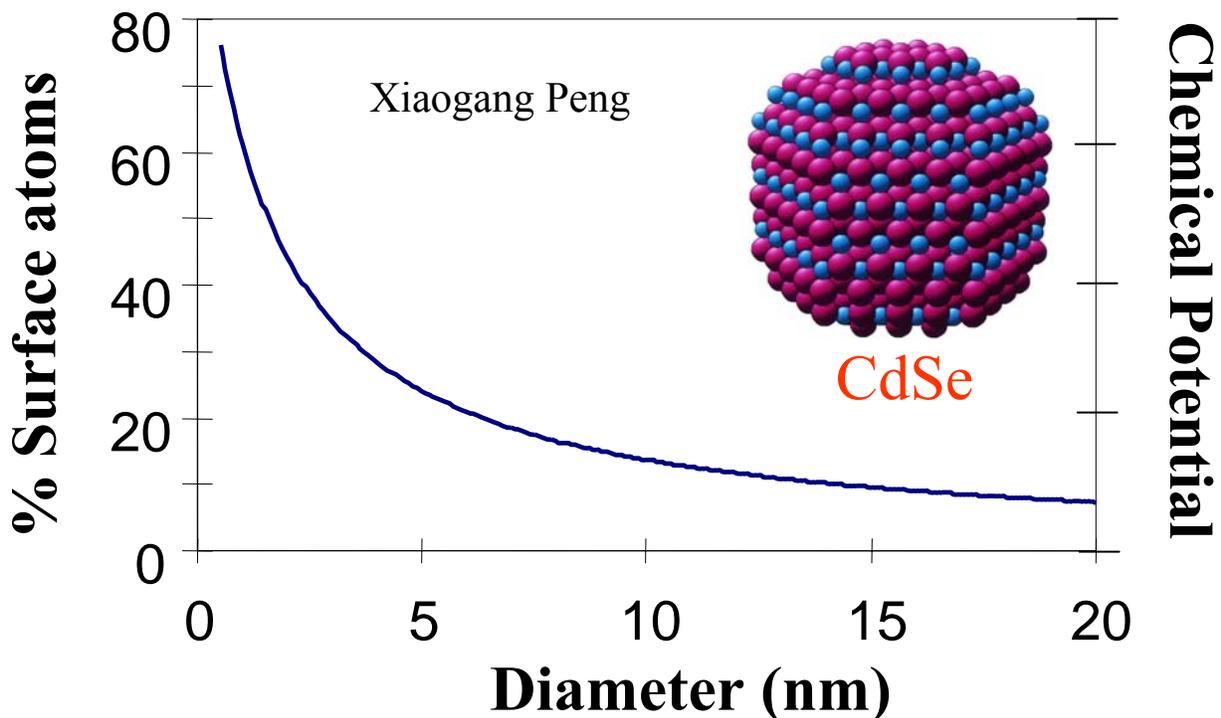
## Kavli Prize in Nanoscience 2008

carbon nanotubes  
semiconductor nanocrystals

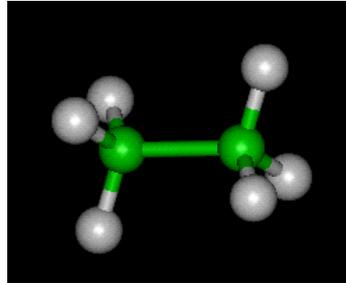
# What is a Semiconductor nanocrystal?



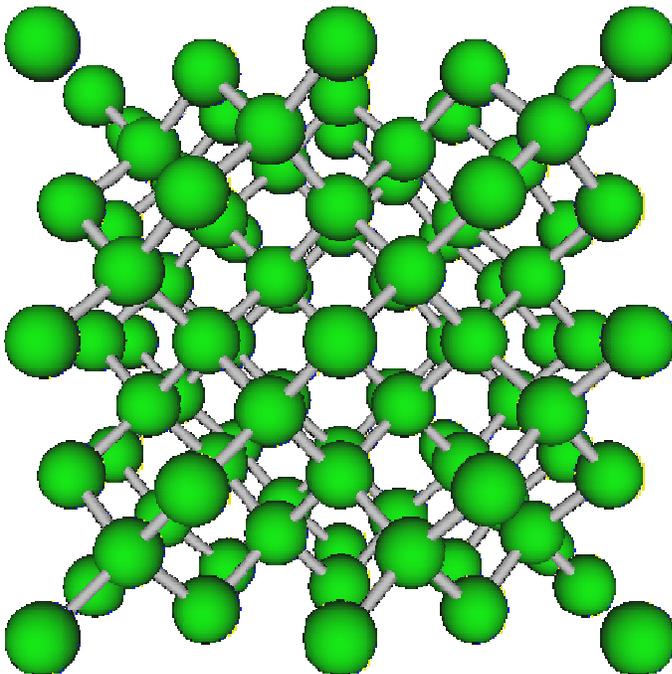
- Organic molecules ‘cap’ the outer surface of core semiconductor. They prevent aggregation, oxidation, and stabilize nanoparticles in the solution. Most important, they electronically isolate the particles and passivate the surface states.



# The evolution from molecules to bulk crystals



$\text{Si}_2\text{H}_6$  disilane molecule



Very large silicon  
Crystal –  
surface H  
capped

Local chemical bonding around each Si atom is the same in the molecule and crystal – tetrahedral covalent  $\text{sp}^3$  hybridization

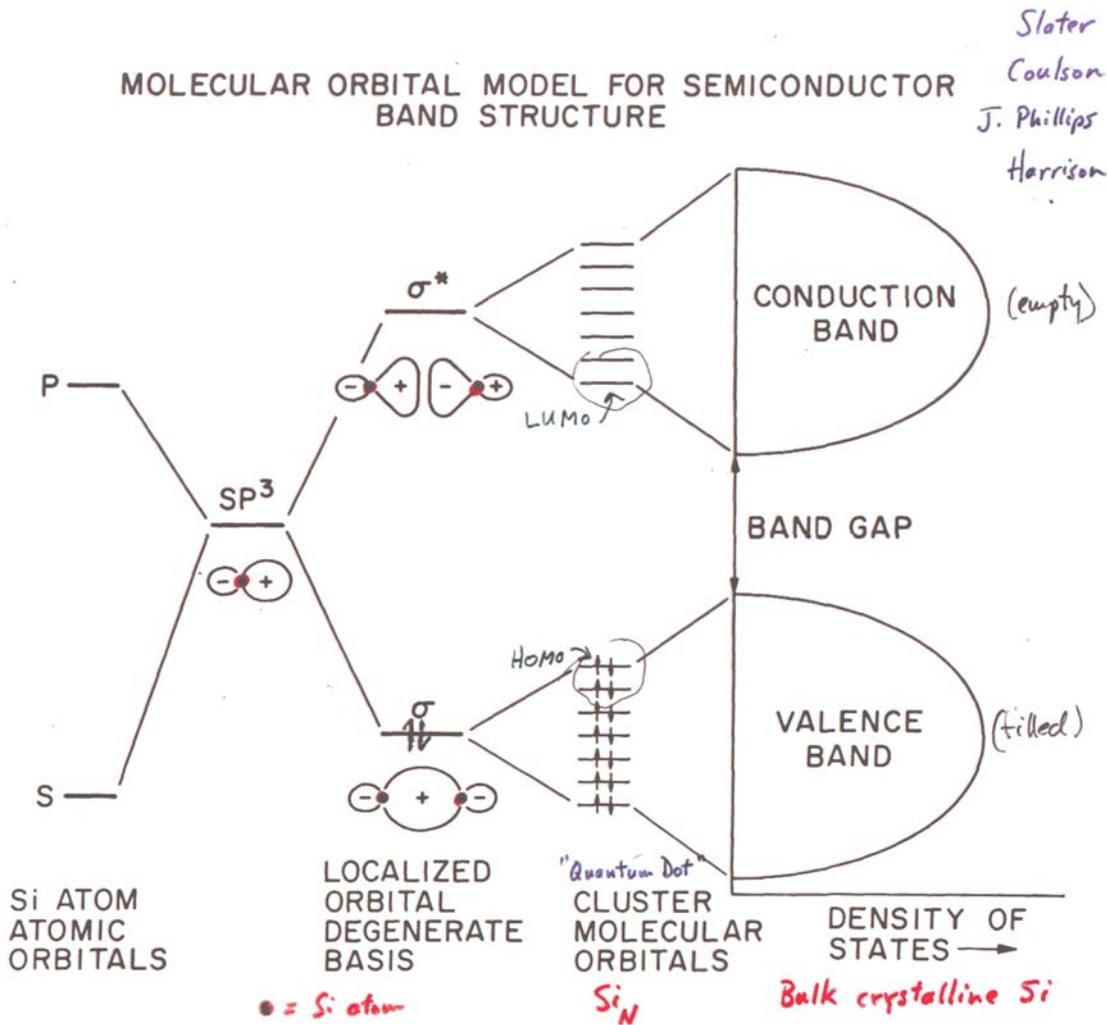
# What does theory predict?

## Chemistry perspective:

### Bonding and Antibonding local Si-Si Molecular Orbitals

Nanometer crystallite should have discrete molecular orbitals rather than continuous bands

Nanometer crystallite should have larger bandgap than bulk crystal -- **band gap increases with decreasing size**



# The evolution from molecules to bulk crystals

## Challenges for Nanoscience

**Intellectual challenge:** how to quantitatively describe electronic properties as a function of size? Physics concepts? Chemistry concepts?

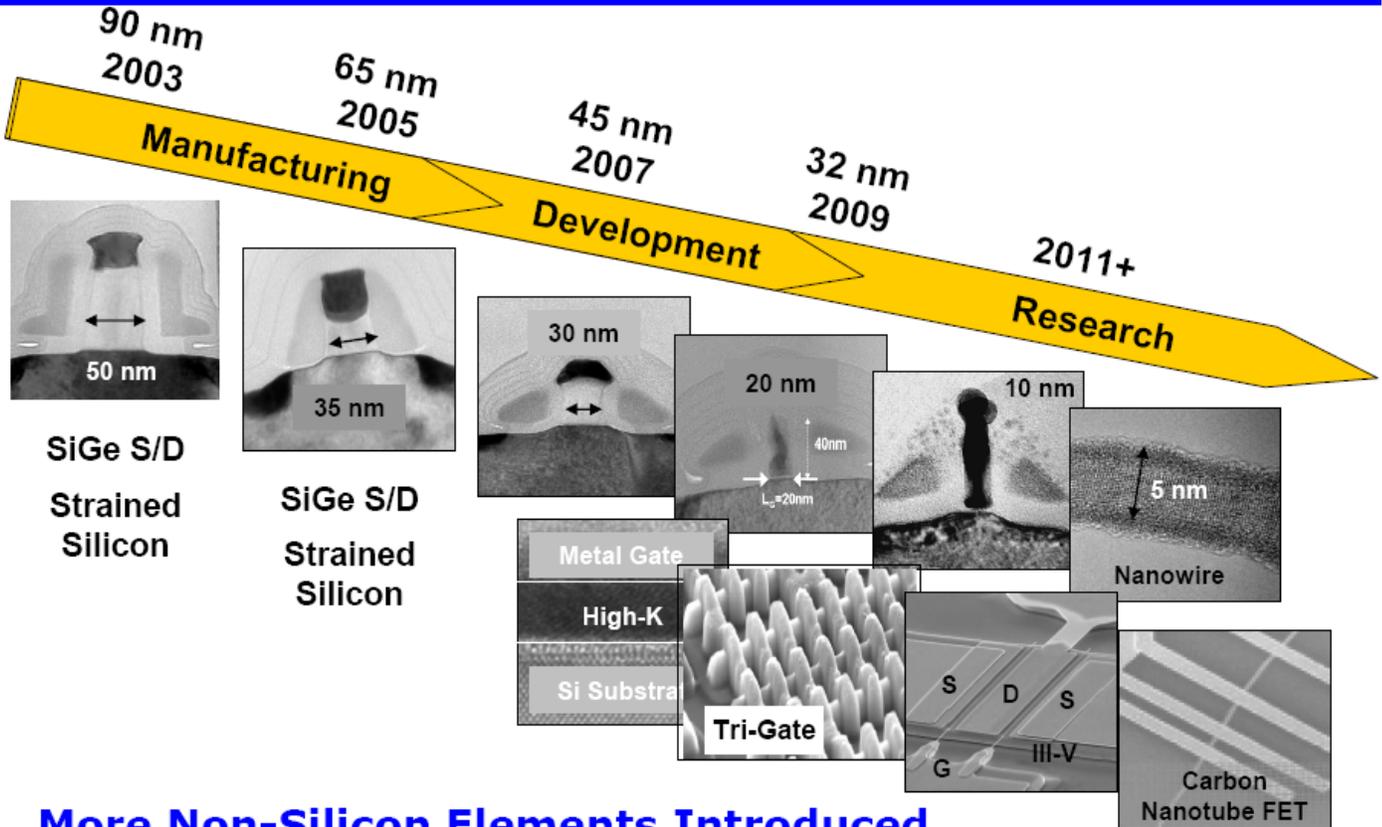
**Synthetic challenge:** can we actually make well defined nanometer crystallites? Can we vary the surface chemistry?

**Characterization challenge:** can we measure physical properties one nanocrystal a a time?

**Technology Challenge:** Nanocrystals are new families of large molecules. Can we use them in technology?

Technological motivation in the early 1980s

## Transistor Nanotechnology



**More Non-Silicon Elements Introduced**

Intel Corp.

*Future options subject to change*

Can we understand the electronic properties of crystalline silicon when it reaches molecular scale?

Transistor Design must change on the nanometer scale

*Journal of Chemical Physics* 79, 1086 (1983)

## Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution

R. Rossetti, S. Nakahara, and L. E. Brus

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 31 March 1983; accepted 5 May 1983)

We report observation of size effects in the excited electronic properties of small, crystalline CdS particles. We also theoretically model the leading small size correction terms applicable to the photochemical redox potentials and lowest exciton energy. Our experiment involves controlled formation of CdS crystallites in aqueous solution; the photophysics and surface redox chemistry of electrons  $e^-$  and holes  $h^+$  in these colloidal crystallites has been of recent interest.<sup>1-6</sup>

Transmission electron microscope examination of particles from a freshly prepared colloid shows a narrow size distribution.<sup>7</sup> A typical particle diameter is  $\approx 35 \text{ \AA}$ , which corresponds to about six unit cells. The mass weighted average diameter  $\bar{d}$  is  $\approx 45 \text{ \AA}$ . The particles are crystalline (cubic CdS), with moderate diffraction ring broadening due to small crystallite size. In colloidal solution, thermodynamics favors growth of larger crystallites at the expense of smaller ones. We observe that, if these colloids "age" for  $\approx 1$  day at pH 3, the size distribution becomes broader with  $\bar{d} \approx 125 \text{ \AA}$ . On the average, 21 small crystallites dissolve and recrystallize onto one larger "seed" crystallite. The colloid remains transparent without CdS precipitation as it ages. The crystal structure is mixed cubic and hexagonal after aging; the hexagonal phase is thermodynamically more stable.

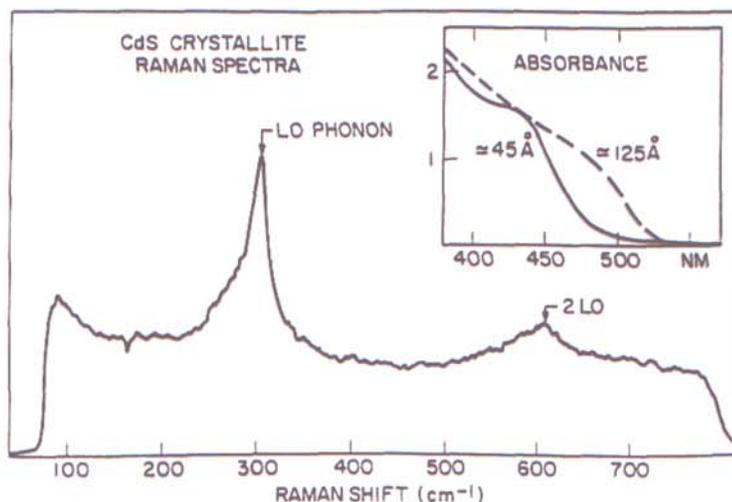
Resonance Raman (RR) spectroscopy<sup>8</sup> in principle allows an *in situ* vibrational characterization despite the low crystallite concentration  $\approx 2 \times 10^{-6} \text{ M}$  in fresh colloids. The 416 nm RR spectrum in Fig. 1 shows the LO (longitudinal optical) phonon at  $305 \text{ cm}^{-1}$  and a weaker overtone near  $605 \text{ cm}^{-1}$ . These CdS peaks are superimposed on nearly continuous water Raman scattering.  $e^- - h^+$  recombination luminescence has been largely quenched by addition of  $\approx 10^{-3} \text{ M}$  benzoquinone.<sup>3</sup> At 395, 448, and 460 nm similar spectra are observed. To the red (480, 503, and 532 nm) and to the blue (355 and 266 nm), the CdS RR spectra are far weaker and not detected.

To our knowledge these are the smallest isolated crystallites that have been examined by Raman spec-

troscopy.<sup>9,10</sup> The LO peak occurs within a couple of  $\text{cm}^{-1}$  of the bulk CdS frequency. In Fig. 1 the low frequency wing, in the region of expected surface mode maxima,<sup>11</sup> is slightly stronger than the high frequency wing. In other fresh colloids, the LO peak is more symmetrical. Shifts and surface mode maxima have been reported for small crystalline grains in Si films.<sup>12,13</sup>

In aged colloids the CdS RR excitation spectrum changes markedly. RR scattering at 395, 416, and 448 nm is not detectable, with the cross section per unit mass decreasing by at least a factor of 10. Recall that there is no loss of CdS mass during aging; mass shifts from smaller to larger crystallites. CdS RR scattering is detected in the red shifted and narrower spectral range 463–480 nm. The spectra are similar to those in Fig. 1, with an LO peak decrease of  $\approx 3 \text{ cm}^{-1}$  and a slight narrowing.

Letters to the Editor



## **An Accidental Observation**

### **Why is band gap a function of size?**

Size effect in spectroscopy, that is, in Maxwell's equations??

Size effect in the basic wavefunctions, that is, in Schrodinger's equation??

Conclusion: stiochiometric 50 Å diameter CdS nanocrystal with ca. 5000 atoms is not yet a bulk crystal!

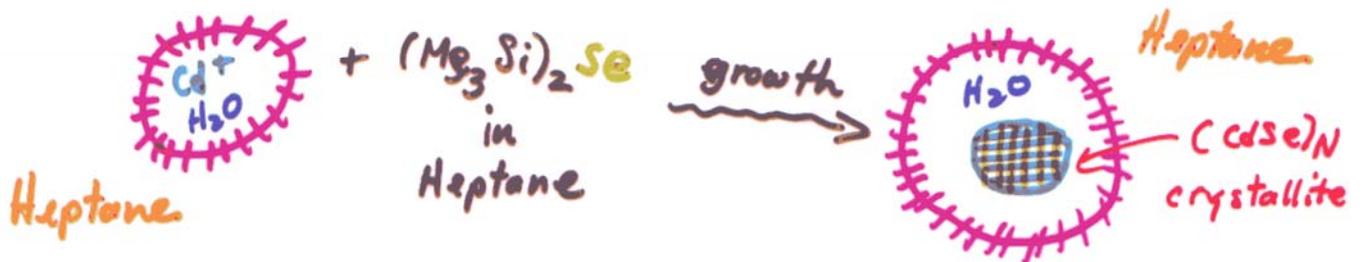
### **Resulting Plan:**

1. Simple theoretical modeling of quantum mechanics and electrostatics.
2. **Begin research in synthesis of smaller sizes.**

Organometallic synthesis, controlled Growth, Surface "capping"  
and isolation of stabilized clusters

A] Take advantage of hydrocarbon phase - hydrophobic reagents

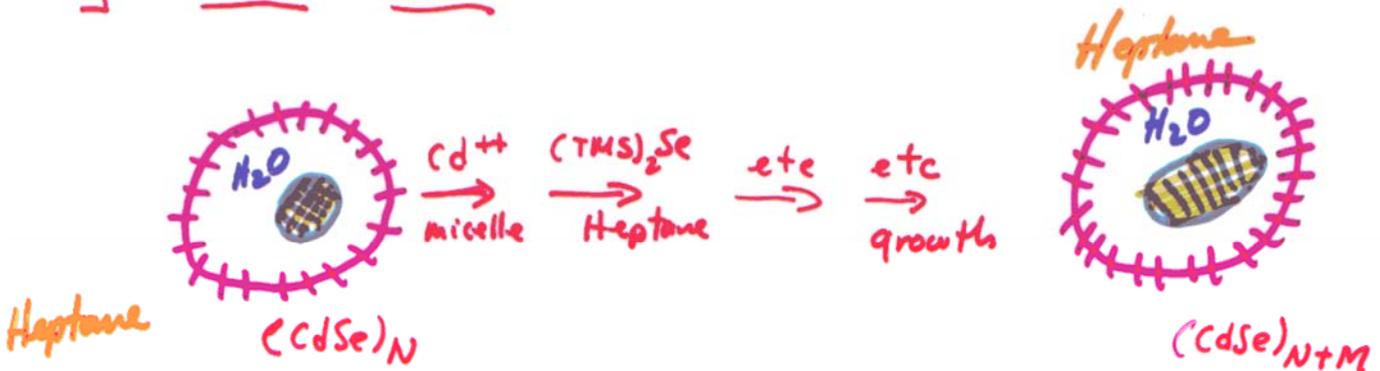
\* Mike Steigerwald  
Paul Alivisatos  
Lou Brus



small 18 Å  $N \approx 70$   
large 50 Å  $N \approx 630$   
standard deviation 20%

dry  $\rightarrow$  redissolve  $\rightarrow$  heptane colloid

B] Controlled Growth

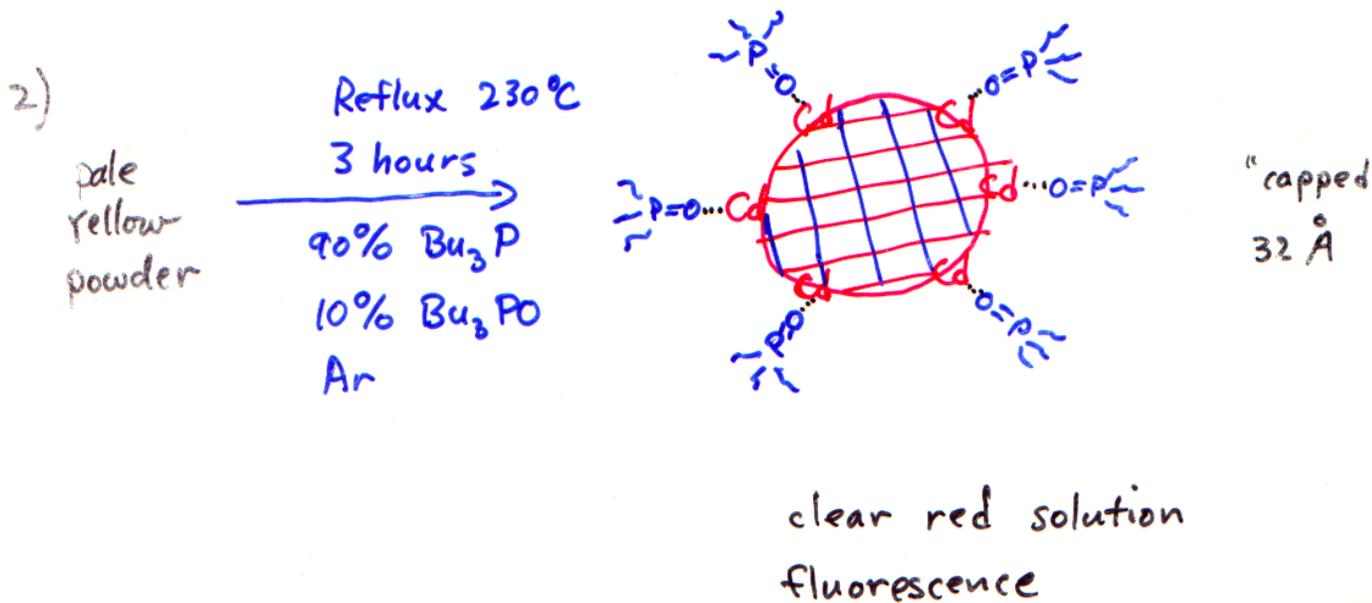
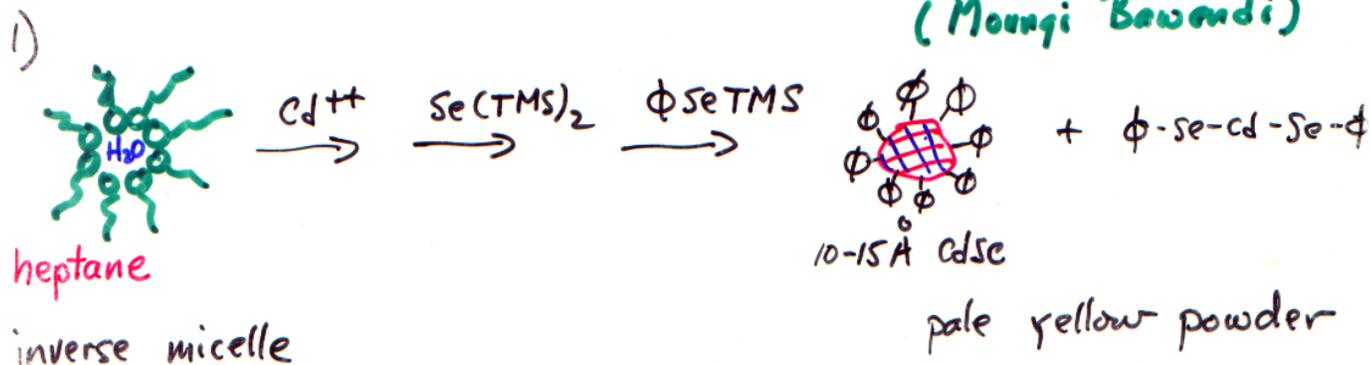


Crystallite in micelle, with water present,  
is stable yet can grow further

$\Rightarrow$  exotic chemistry on surface

$\Rightarrow$  concentric growth of one material on another

Two Step Organometallic Synthesis of CdSe Single Crystallites  
 (Mike Steigerwald)  
 (Moungi Bawendi)



Characterization

TEM	Pat Carroll
Powder x-ray	Refik Kortan
$^{77}\text{Se}$ NMR	Peter Reynders
Se, Cd EXAFS	Matt Marcus

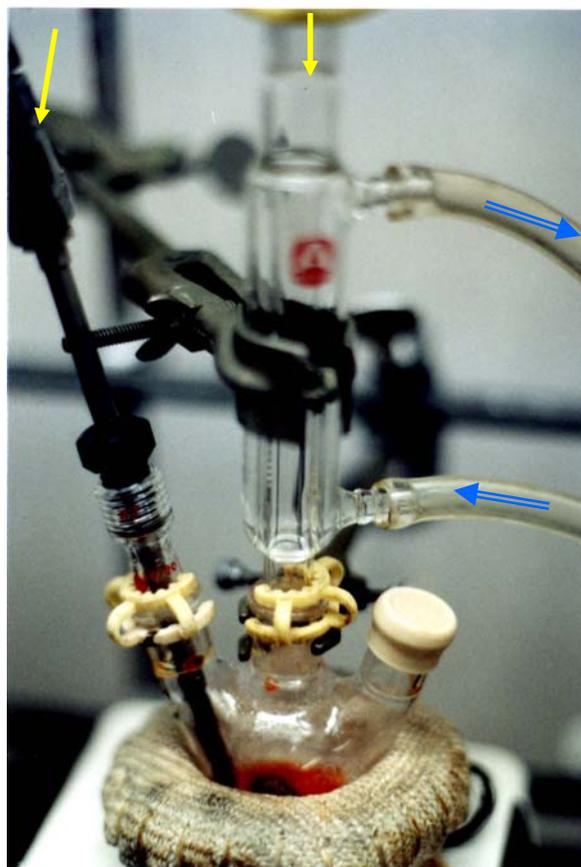
# Organometallic chemical synthesis of nanocrystals

- Narrow size distribution ( $\sim 5\%$ ) is obtained by the fast injection of the chemical reagents into the flask at high temperature ( $\sim 350^\circ\text{C}$ ).
- The precursors are prepared in the glove box to avoid oxygen and water.

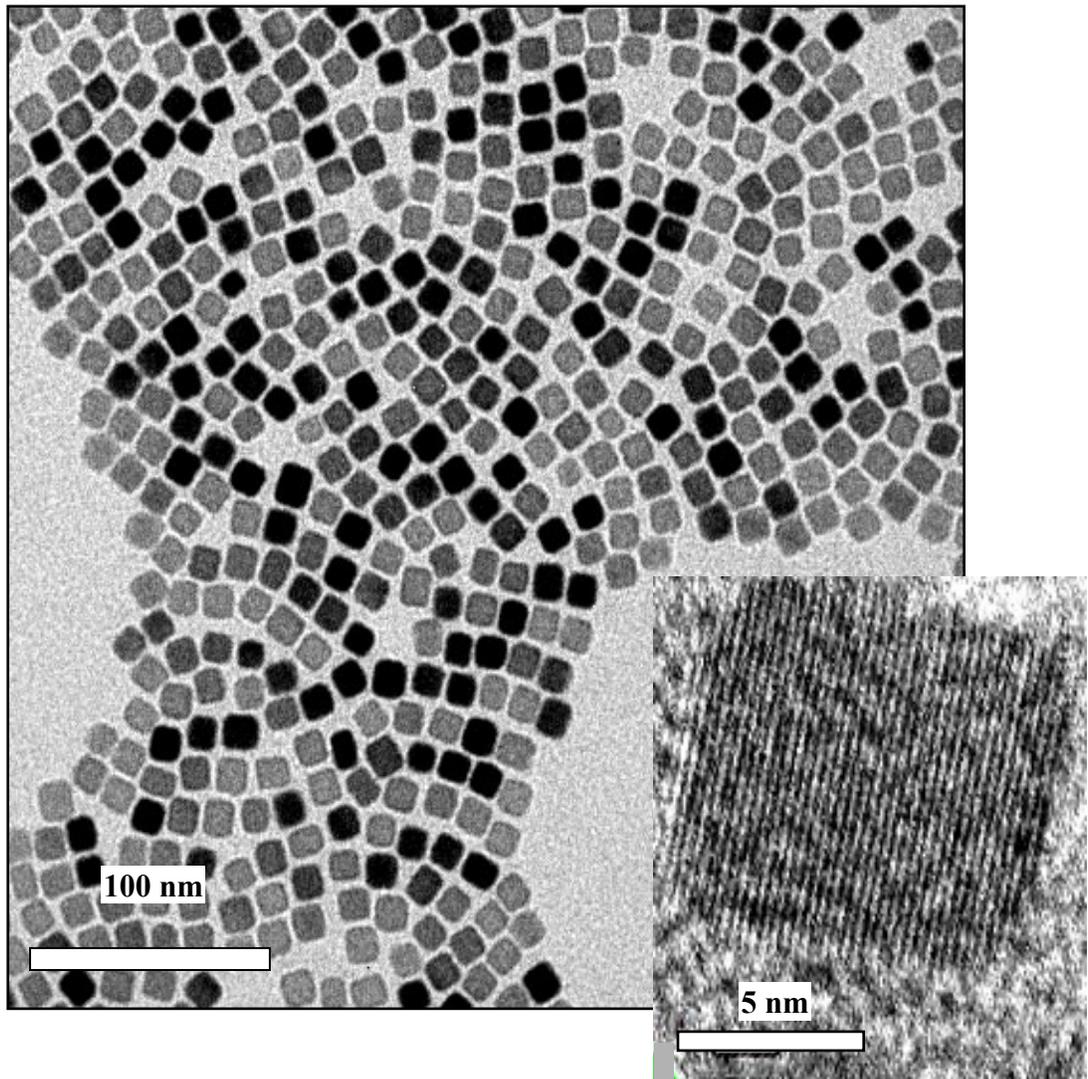
Semiconductor: CdSe, CdTe, PbSe, etc.  
Metal: PtFe

Thermocouple

Argon gas at little above ambient pressure



# PbSe nanocrystals: chemical synthesis and size separation



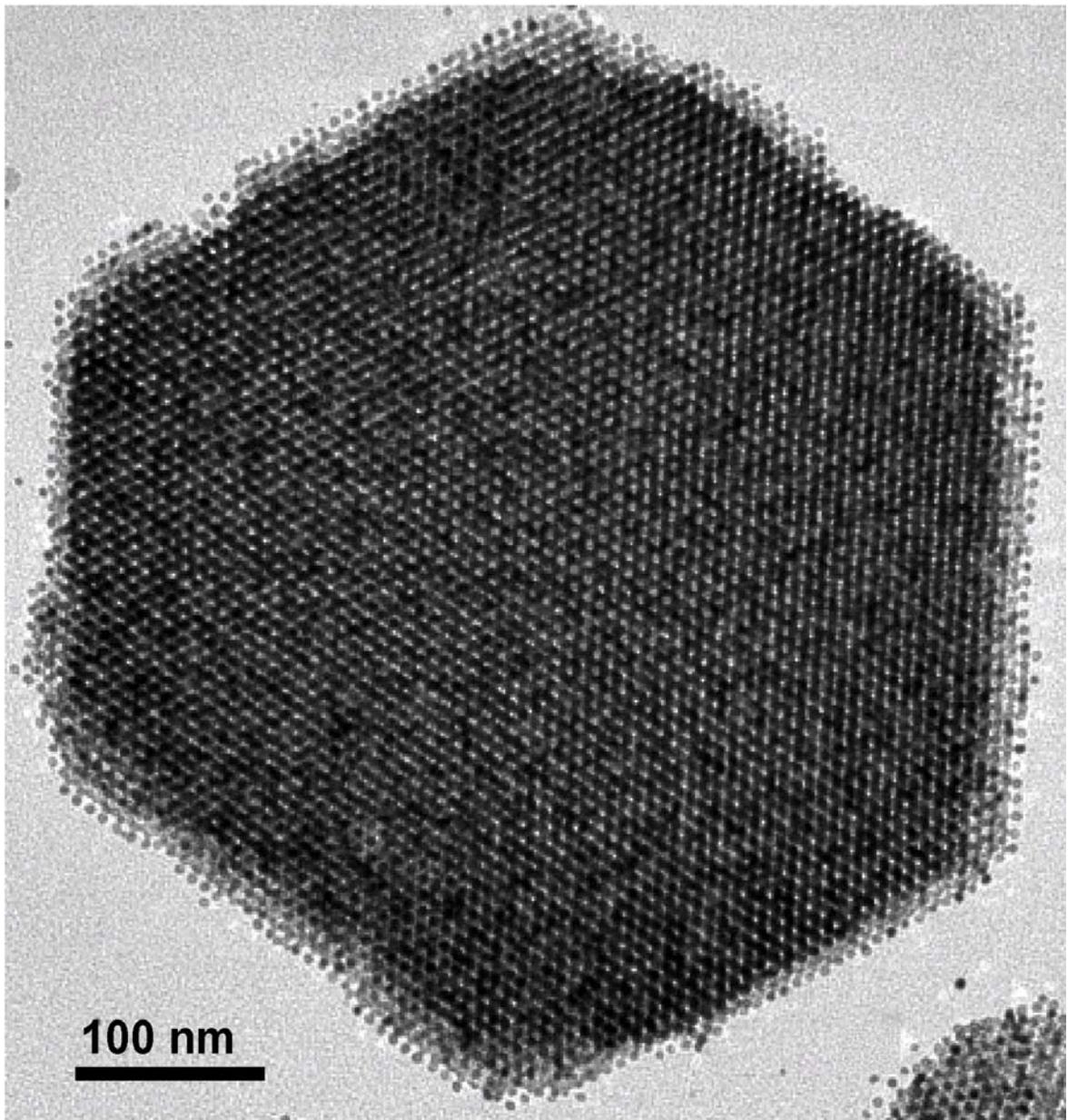
**TEM images of PbSe quantum cubes after size selection (reaction temperature 215°C), size ~12 nm**

**Change of shape from spherical to cubic in the size regime of 8 to 11 nm**

Chris Murray, Wolfgang Gaschler, Franz Redl, IBM-Columbia

## Self Organization of Nanocrystals

van der Waals crystal of nanocrystals  
Hexagonal close packing of spheres

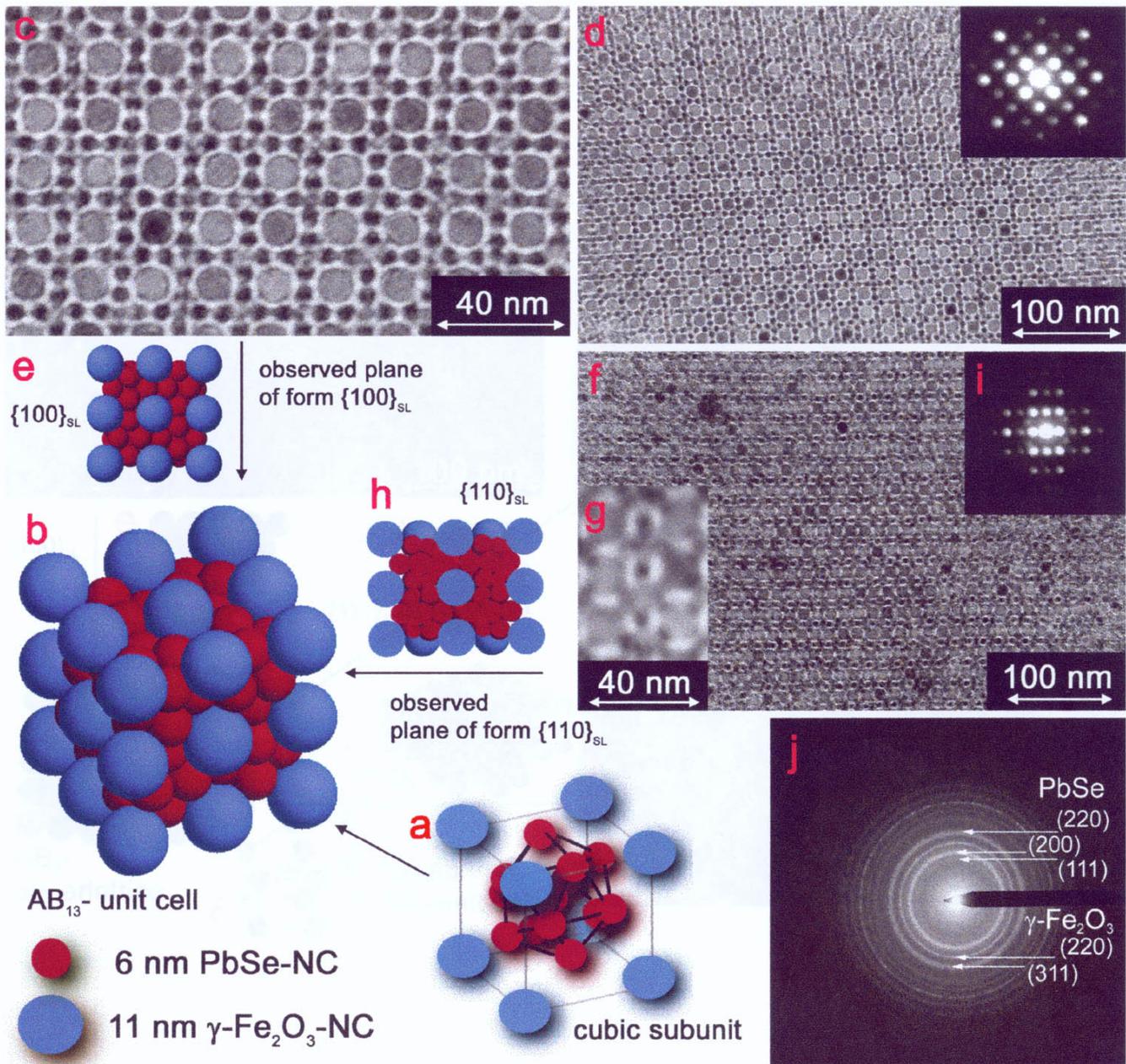


**CoPt<sub>3</sub> nanoparticles**

Columbia-IBM collaboration

# Bimodal superlattice crystal of 11 nm magnetic $\text{Fe}_2\text{O}_3$ nanocrystals and semiconducting 5 nm PbSe nanocrystals

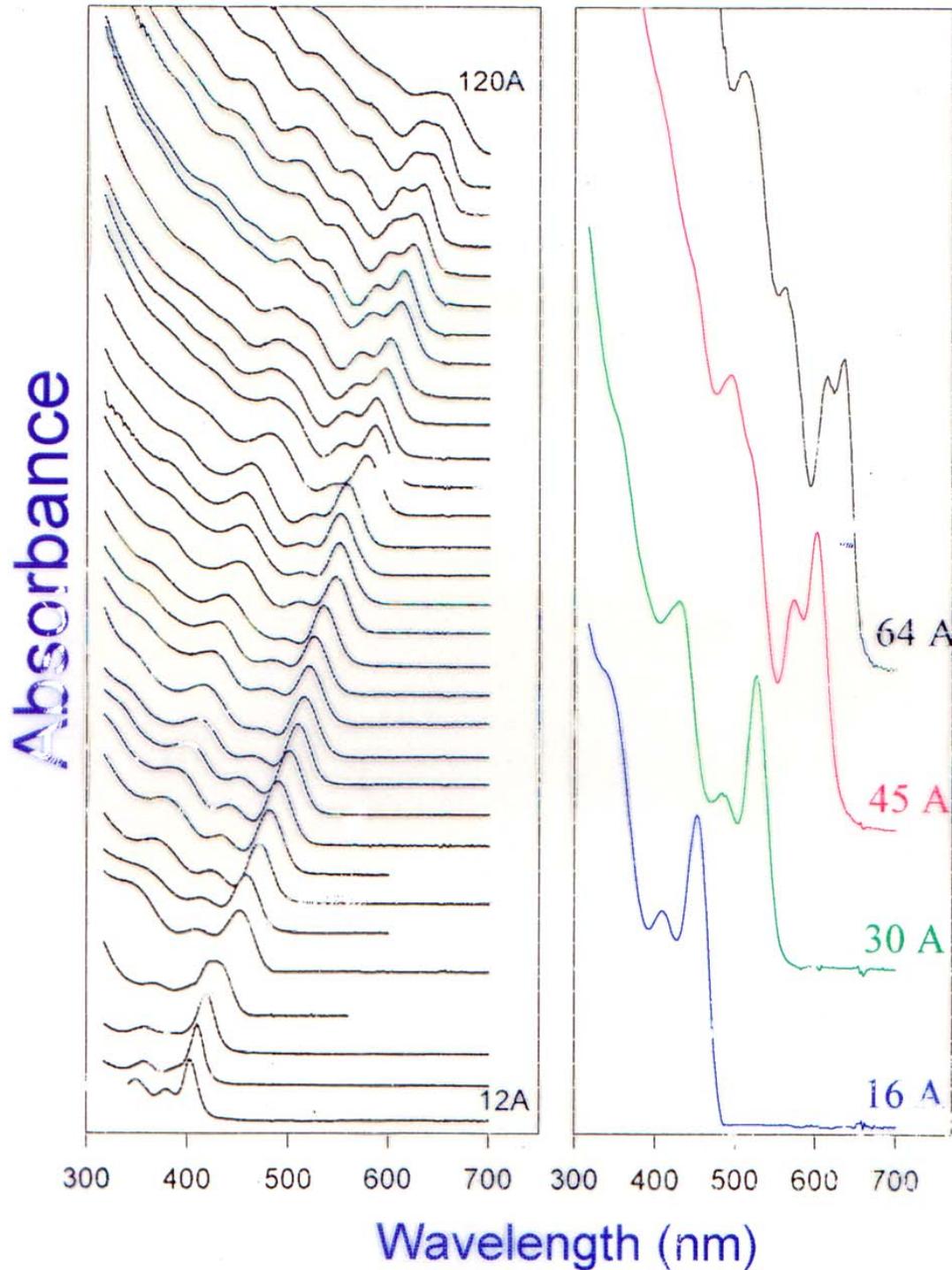
Redl, Cho, Murray, O'Brien Nature 423, 968 (2003)



Columbia – IBM collaboration

# Optical Spectra of CdSe Semiconductor Nanocrystals solubilized in hexane at 23 C

## CdSe Size Dependent Absorbance



Chris Murray & Moungi Bawendi (MIT)

## Semiconductors are excellent light emitters

### Nanocrystals – Size Dependent Luminescence Color

High Quantum Yield Luminescence if surface passivated

More stable and brighter than dye molecules

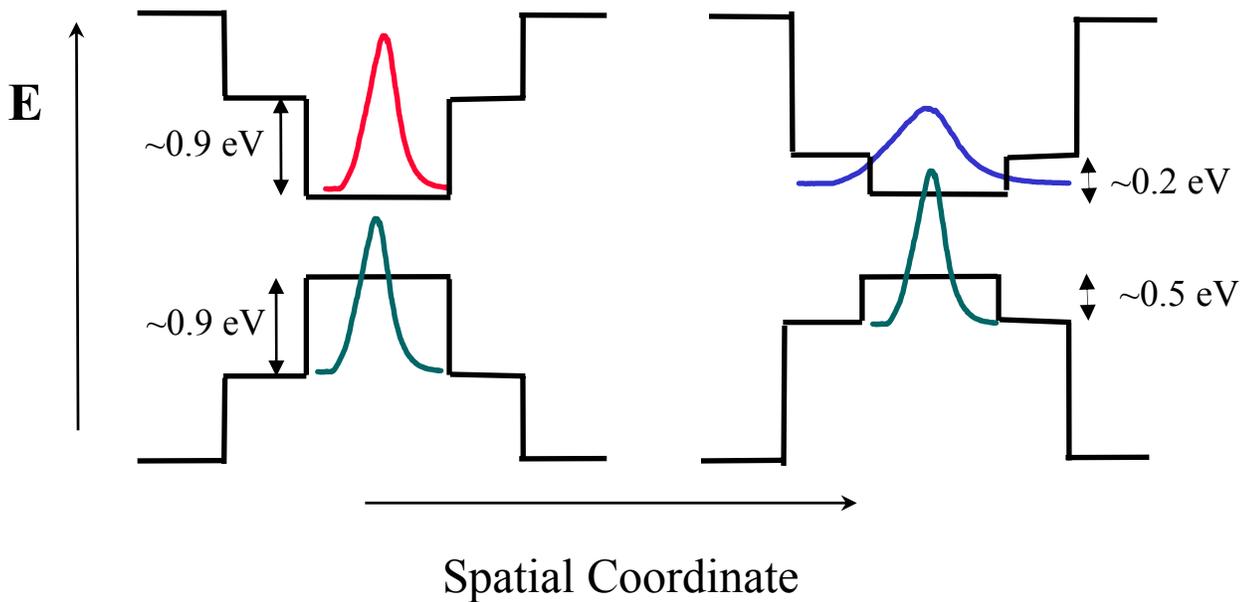
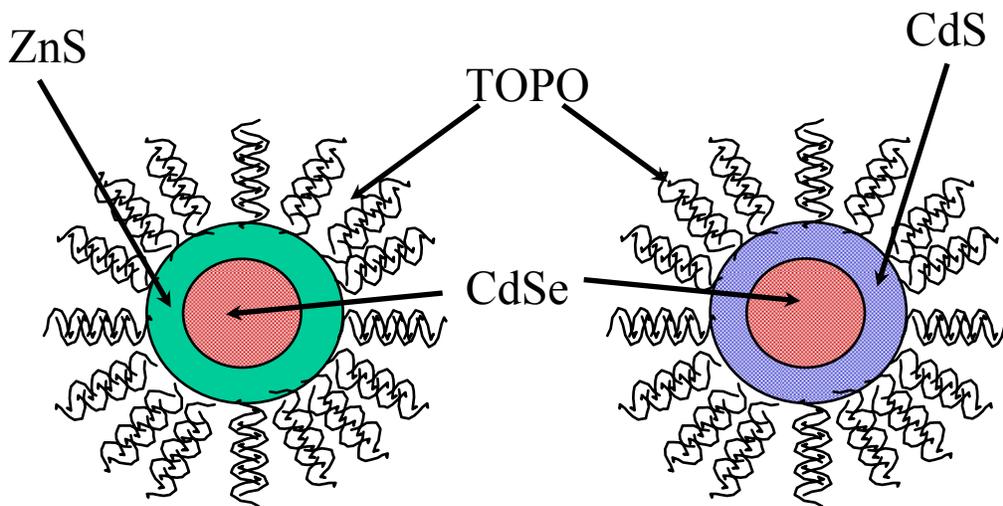
Possible use in biological imaging if surface is biologically compatible



# Core/Shell Nanocrystals:

ZnS surface shell layer “insulates” the luminescent CdSe core

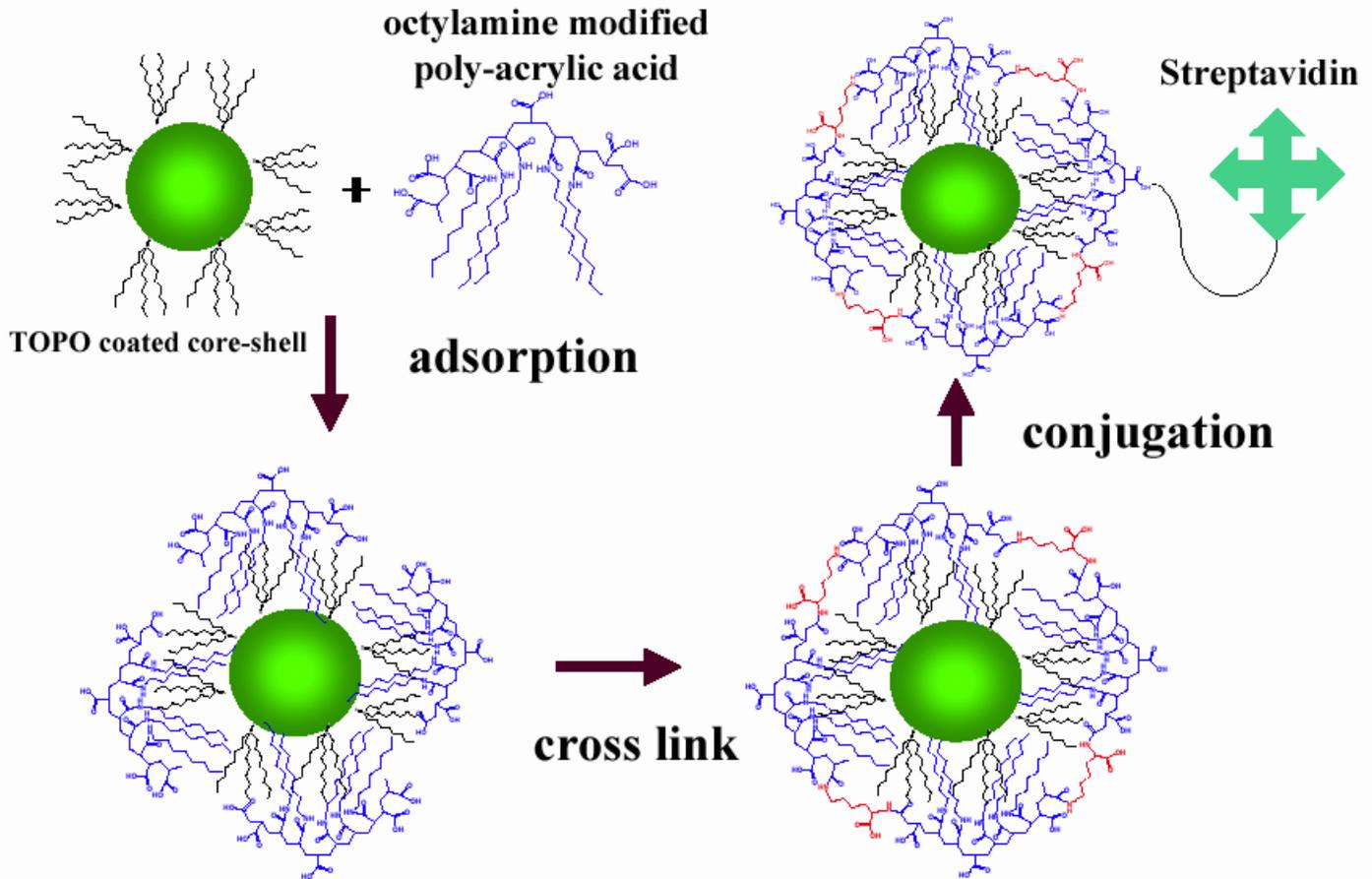
high quantum yield and photostability



B. O. Dabbousi, *et al.* (1997)

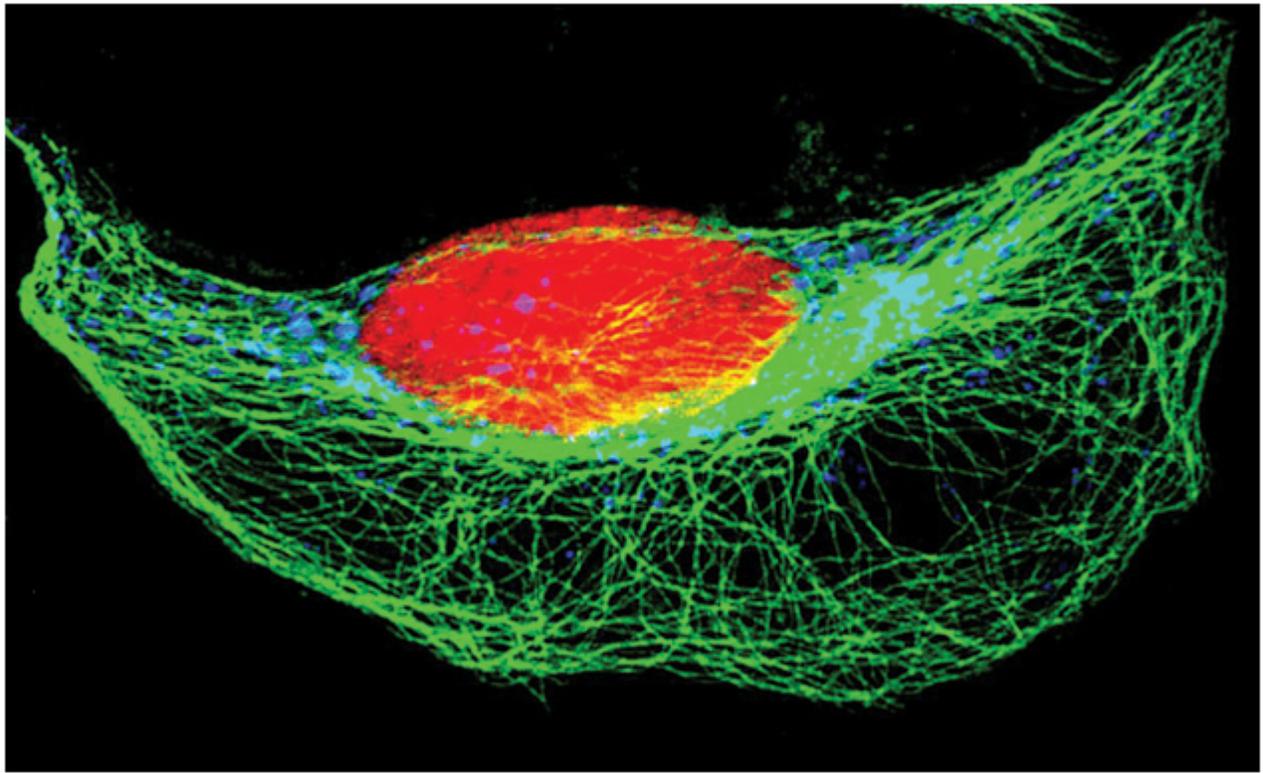
# Biological Imaging Applications

## Surface Stabilization & Biomolecule Conjugation



Qdots, Inc. – Invitrogen

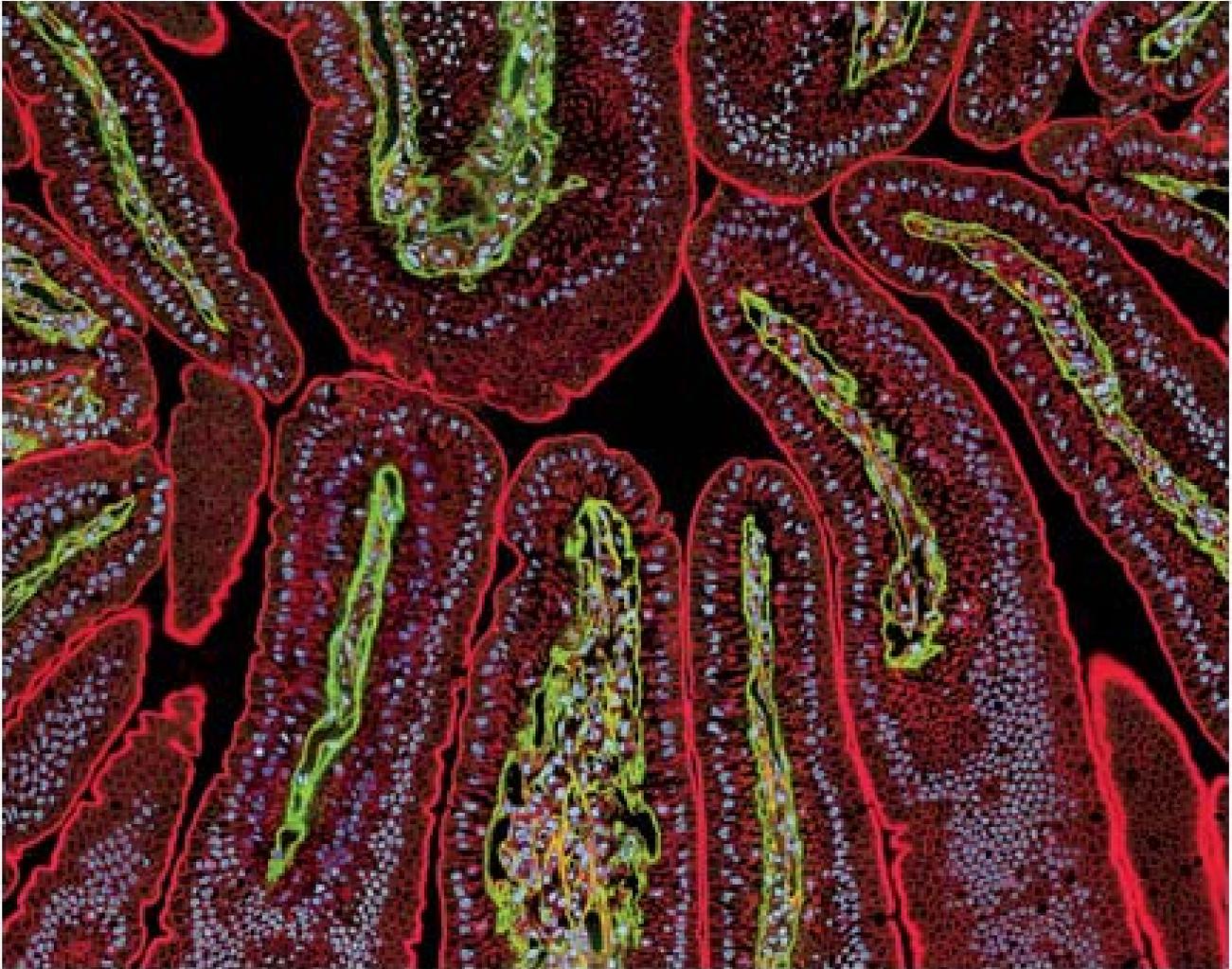
Nature Biotechnology Online



Three-color staining of HeLa cells using fluorescent Qdot® nanocrystal conjugates. The intracellular structures in fixed HeLa cells were visualized using a red-fluorescent Qdot® 655 F(ab')<sub>2</sub> goat anti-mouse IgG (Q11021MP, Q11022MP)(nuclei), a yellow-fluorescent Qdot® 585 F(ab')<sub>2</sub> goat anti-rabbit IgG (Q11411MP)(Golgi), and a green-fluorescent Qdot® 525 streptavidin conjugate (Q10141MP)(microtubules).

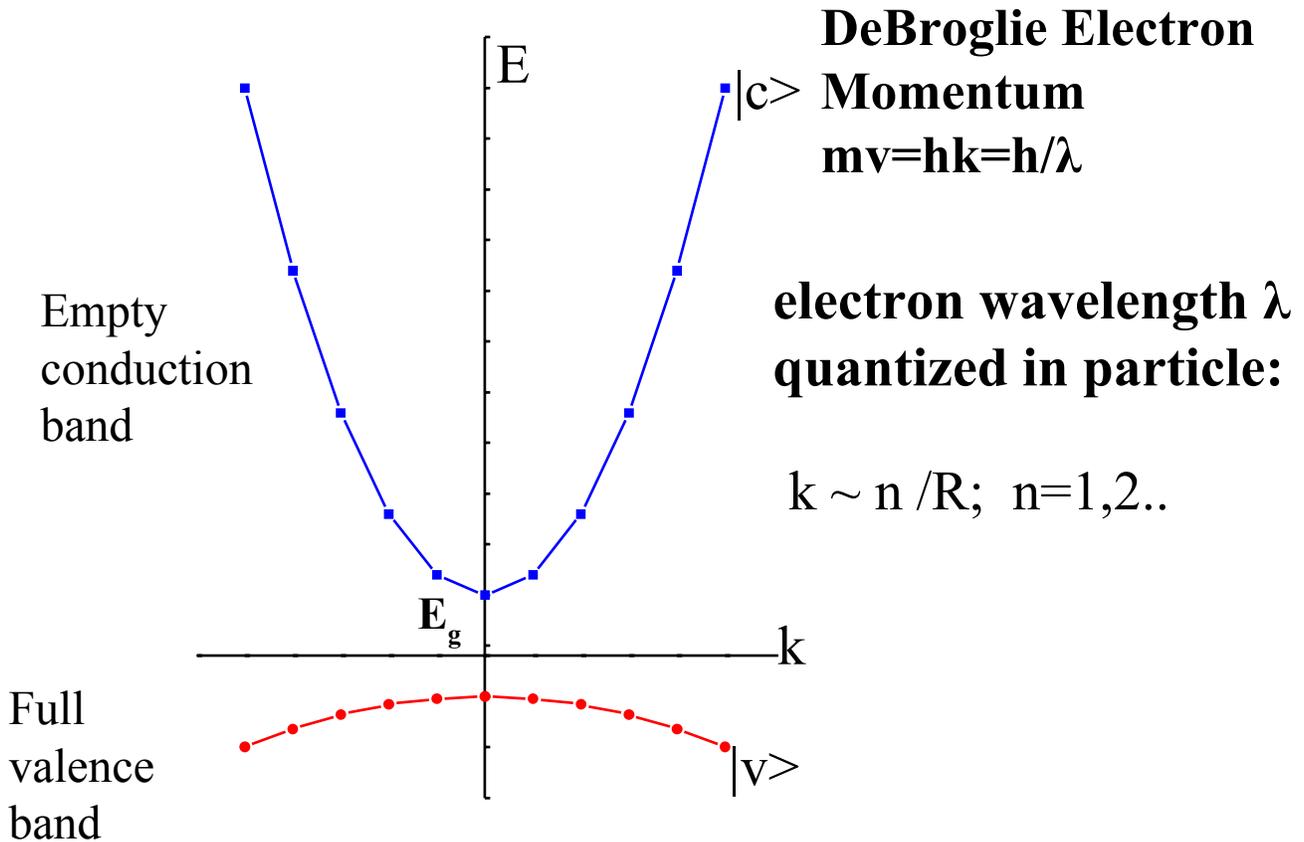
**Invitrogen Website**

## Imaging Mouse Intestine



A mouse intestinal section visualized using fluorescent Qdot nanocrystal conjugates. Actin was labeled with a mouse anti-actin monoclonal antibody and visualized using red-fluorescent Qdot 655 goat F(ab')<sub>2</sub> anti-mouse IgG ([Q11022MP](#), [Q11221MP](#)). Laminin was labeled with a rabbit anti-laminin polyclonal antibody and visualized using green-fluorescent Qdot 525 goat F(ab')<sub>2</sub> anti-rabbit IgG ([Q11441MP](#)). Nuclei were stained with blue-fluorescent Hoechst 33342 ([H1399](#), [H3570](#), [H21492](#)). Image contributed by Thomas Deerinck and Mark Ellisman, The National Center for Microscopy and Imaging Research, San Diego,

# Simple Quantitative Model for Electronic Structure: Quantum Size Effect



- Energy of HOMO-LUMO Blue Shifted from bulk band gap

$$E(k) \sim E_g + n^2 \hbar^2 / (8m_e R^2) + n^2 \hbar^2 / (8m_h R^2)$$

Optical Spectra are Discrete and Size Dependent

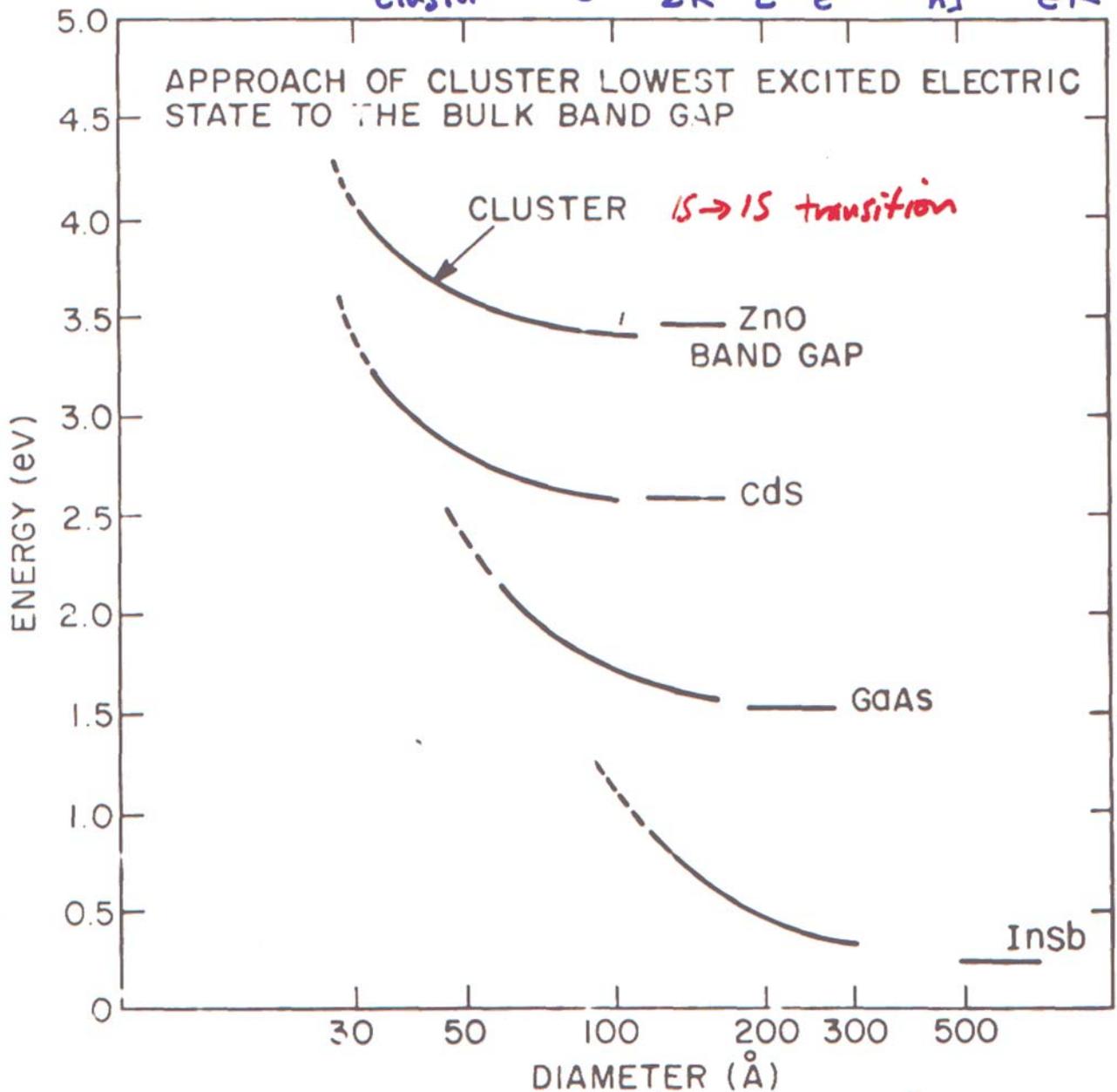
Model uses known bulk band structure, and ignores bonding reconstruction on surfaces

# Quantum Size Effect including Electrostatics

Electron Correlation — Coulomb attraction between  $e^-$  and  $h^+$

$$\Psi \approx \phi_{1s}(r_e) \phi_{1s}(r_h) \quad \text{zero order}$$

$$E_{\text{cluster}}^* = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R} +$$



*No adjustable parameters!*

Even the best chemical synthesis is not Perfect

Nanocrystal samples have distributions of size, shape  
and surface chemical structure

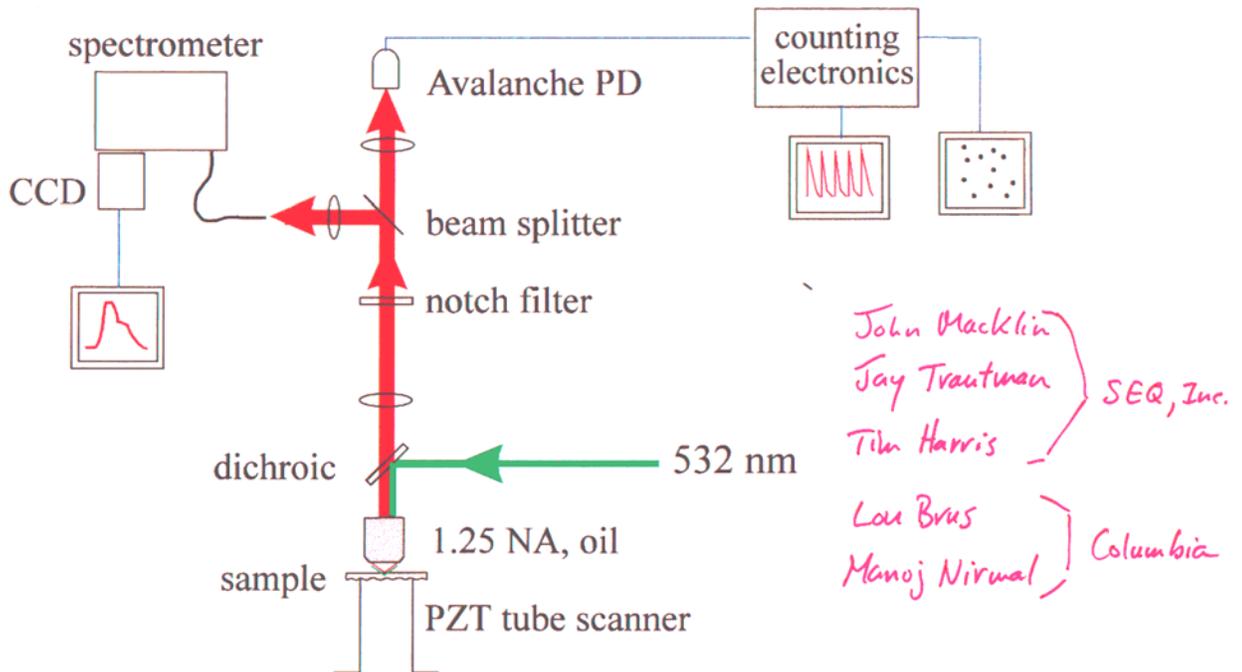
Properties depend strongly on size

Thus, we need to characterize physical properties  
of **individual** nanocrystals

## How can we observe the band gap luminescence of single nanocrystals?

Nanocrystals have several thousand atoms  
Size distribution ca. 5% in diameter  
Each nanocrystal is unique  
Spectra average over distributions

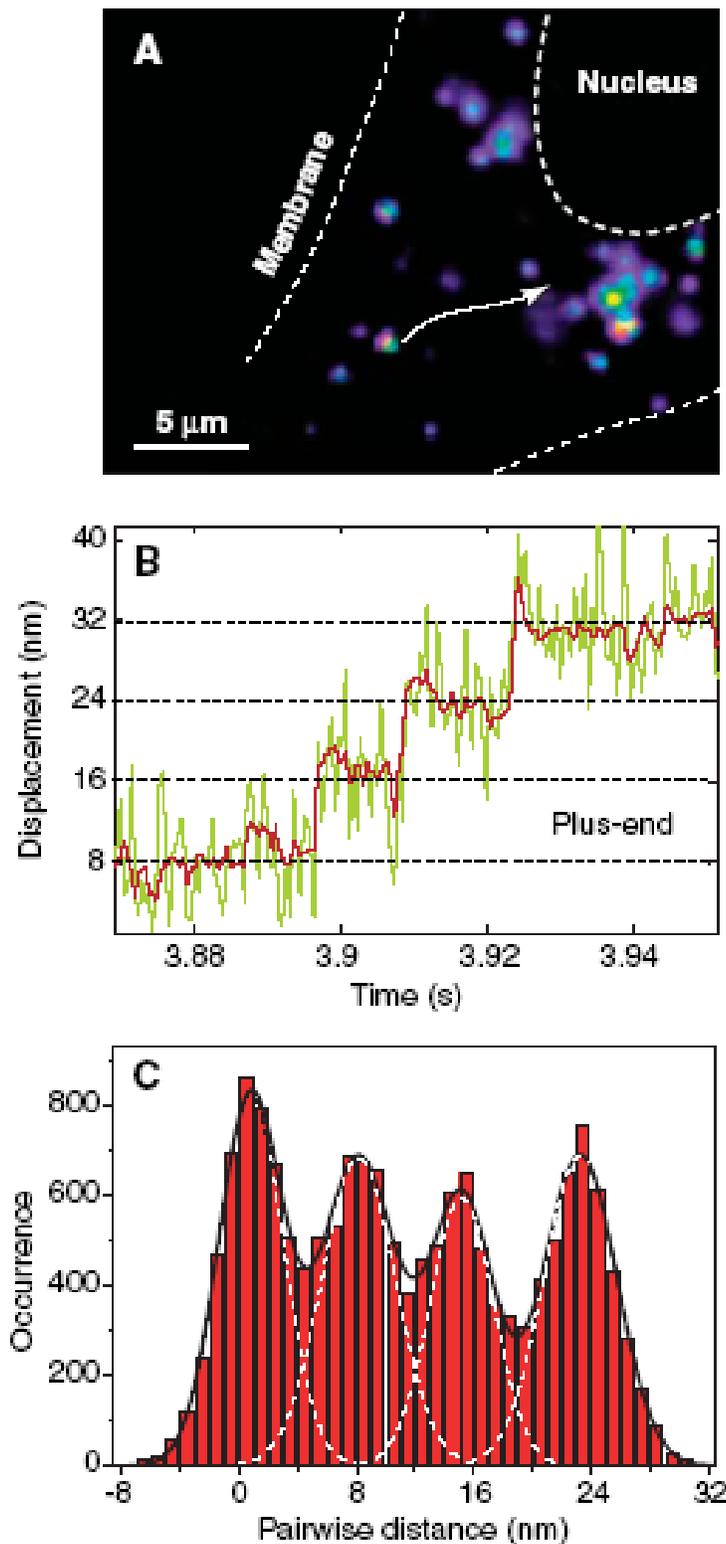
### Experimental Setup: Far-Field Illumination



Betzig, Trautman (Bell Labs):  
Confocal Scanned Stage Luminescence Spectrometer

Macklin et al, Science 272, 255 (1996)

# Single Nanocrystal Luminescence: Kinetics of Microtubule Motor Steps



**Fig. 2.** Observation of individual microtubule motor steps in a live cell with endocytosed quantum dots. **(A)** Live A549 cell with QD-containing endosomes (bright dots), many of which undergo active transport by kinesin (outward movements) or dynein (inward movements, white arrow). **(B)** Displacement trajectory of a outward-going (microtubule plus-end) endosome, exhibiting stepwise movements of the underlying motor (likely kinesin). Green, raw data; red, filtered data. **(C)** Pairwise distance histogram of the filtered displacement trace in **(B)**, with an 8-nm spacing between adjacent peaks.

Sunney Xie et al, Science 312, 228 (2006)

# Luminescence "blinking" of single nanocrystals

Random Field of Single CdSe Nanocrystals  
cw optical excitation

Raster scan image  
field of luminescing  
nanocrystals

a)



Luminescence  
Image

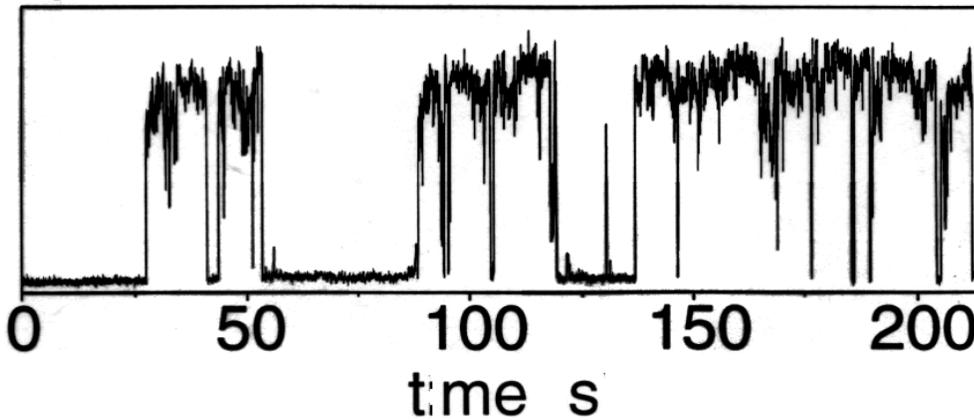
1  $\mu\text{m}$

Individual nanocrystals "blink" on and off

b)

single  
Nanocrystal  
Luminescence

Counts



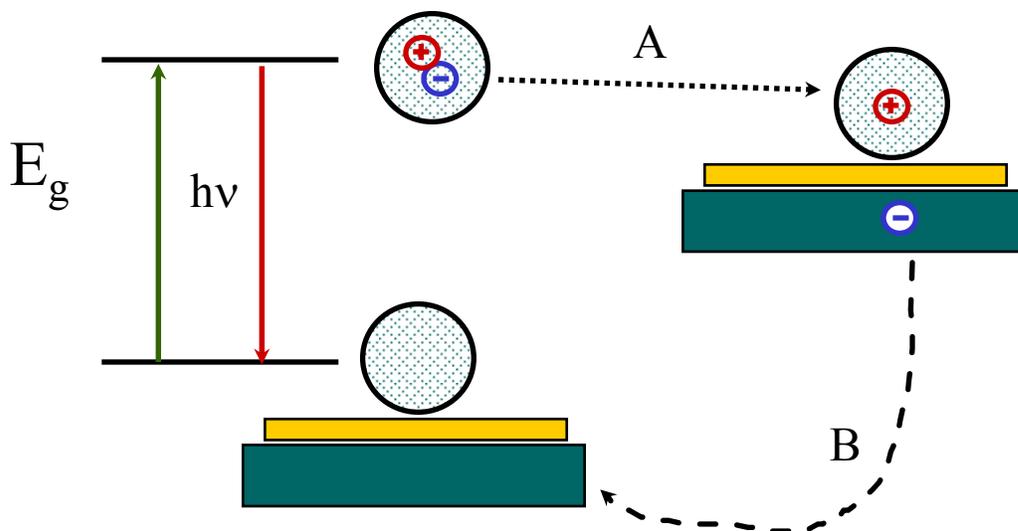
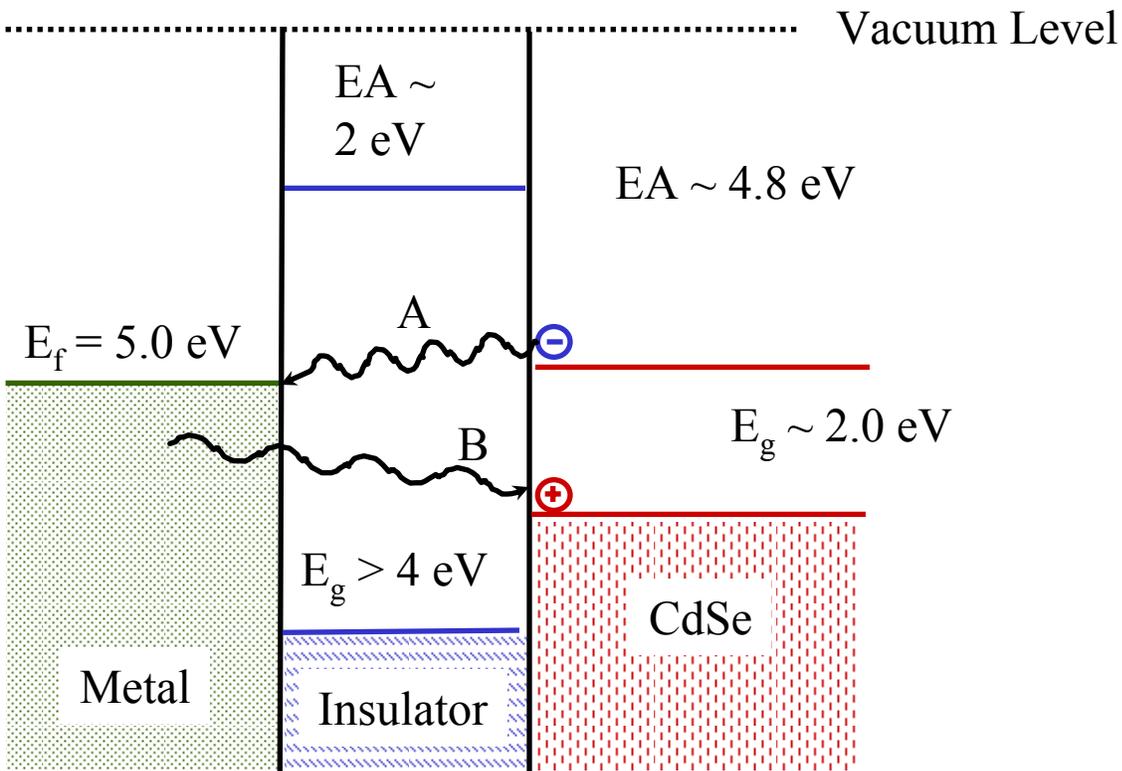
M. Nirmal et al. Nature (accepted for publication)

Nov 1996 Nature 383 2(66)

fig.

Nirmal et al, Nature 383, 802 (1996)

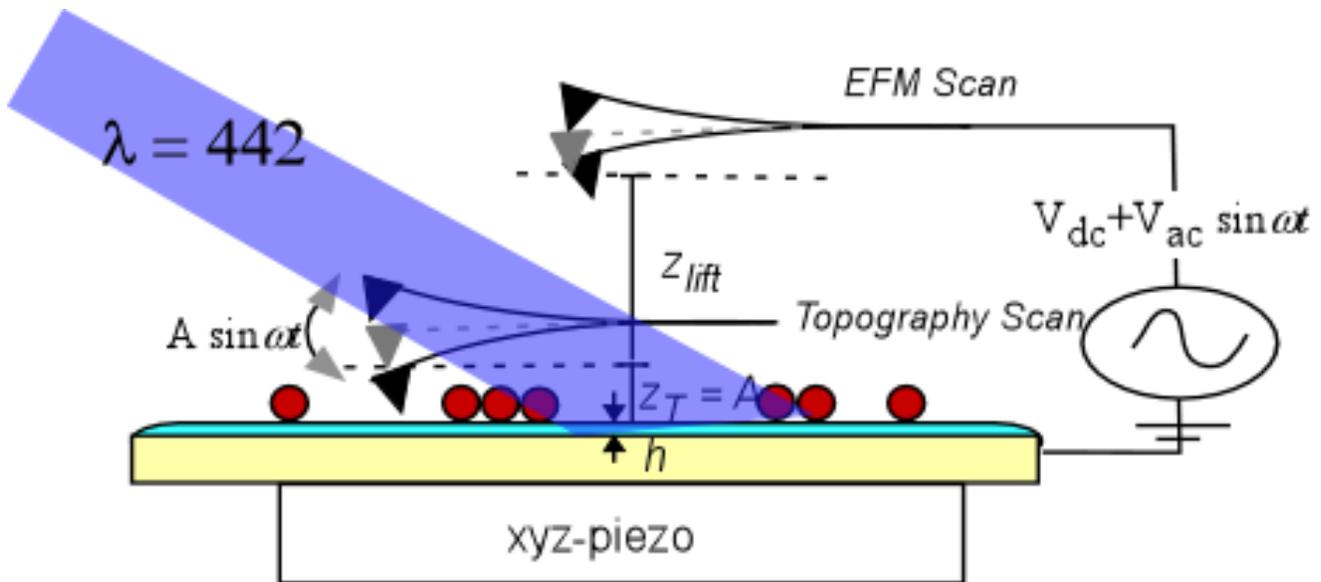
# Schematic Blinking Mechanism: Photoionization and Re-neutralization



Dark State: Ionized Nanocrystal with hole inside  
 Bright State: Neutral Nanocrystal

# Electric Force Microscopy

## Direct Measurement of Electric Field Due to One Ionized Nanocrystal

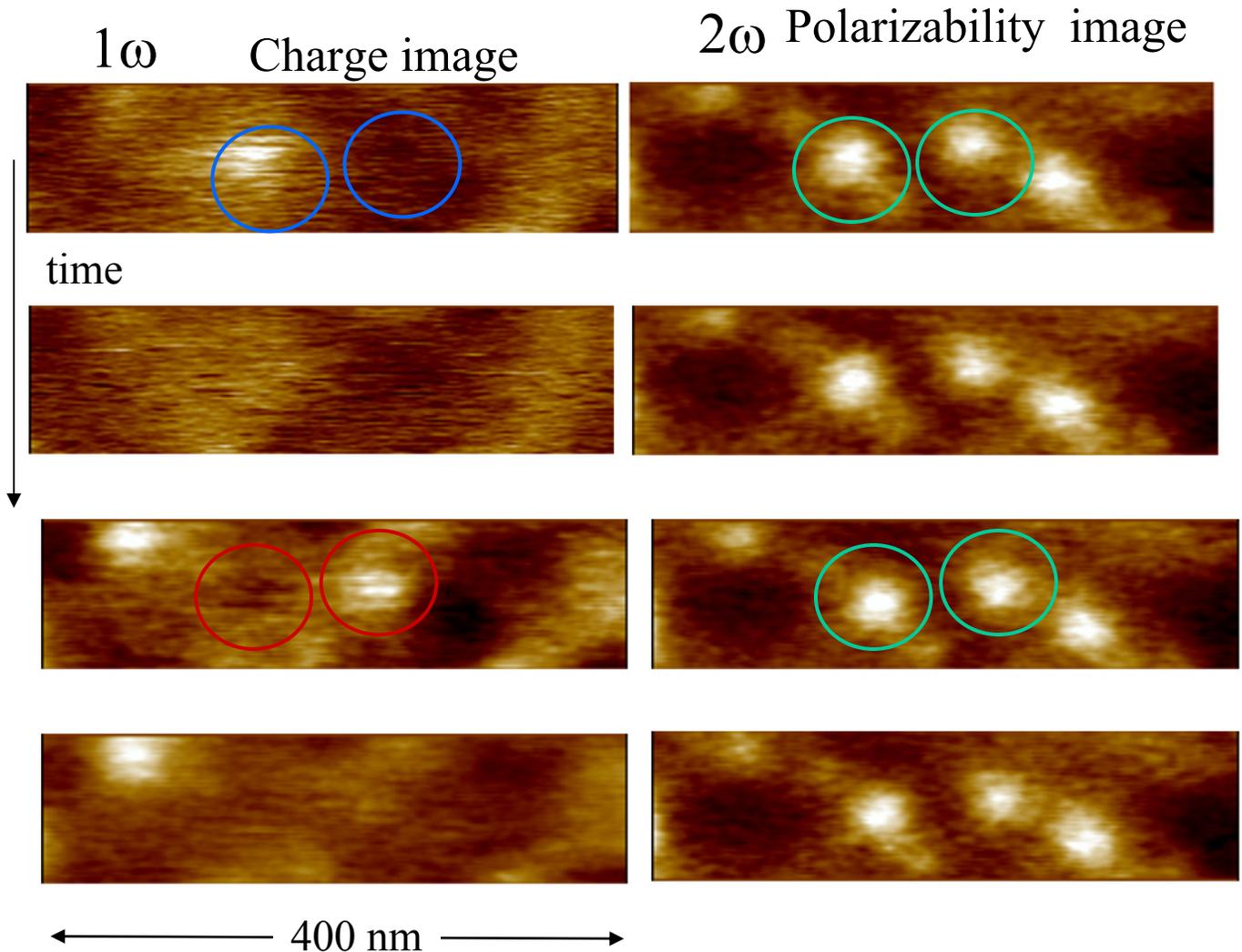


IBM invention

Martin et al, Appl. Phys. Lett. 52, 1103 (1988)E

# CdSe/ZnS Charge Blinking on Graphite

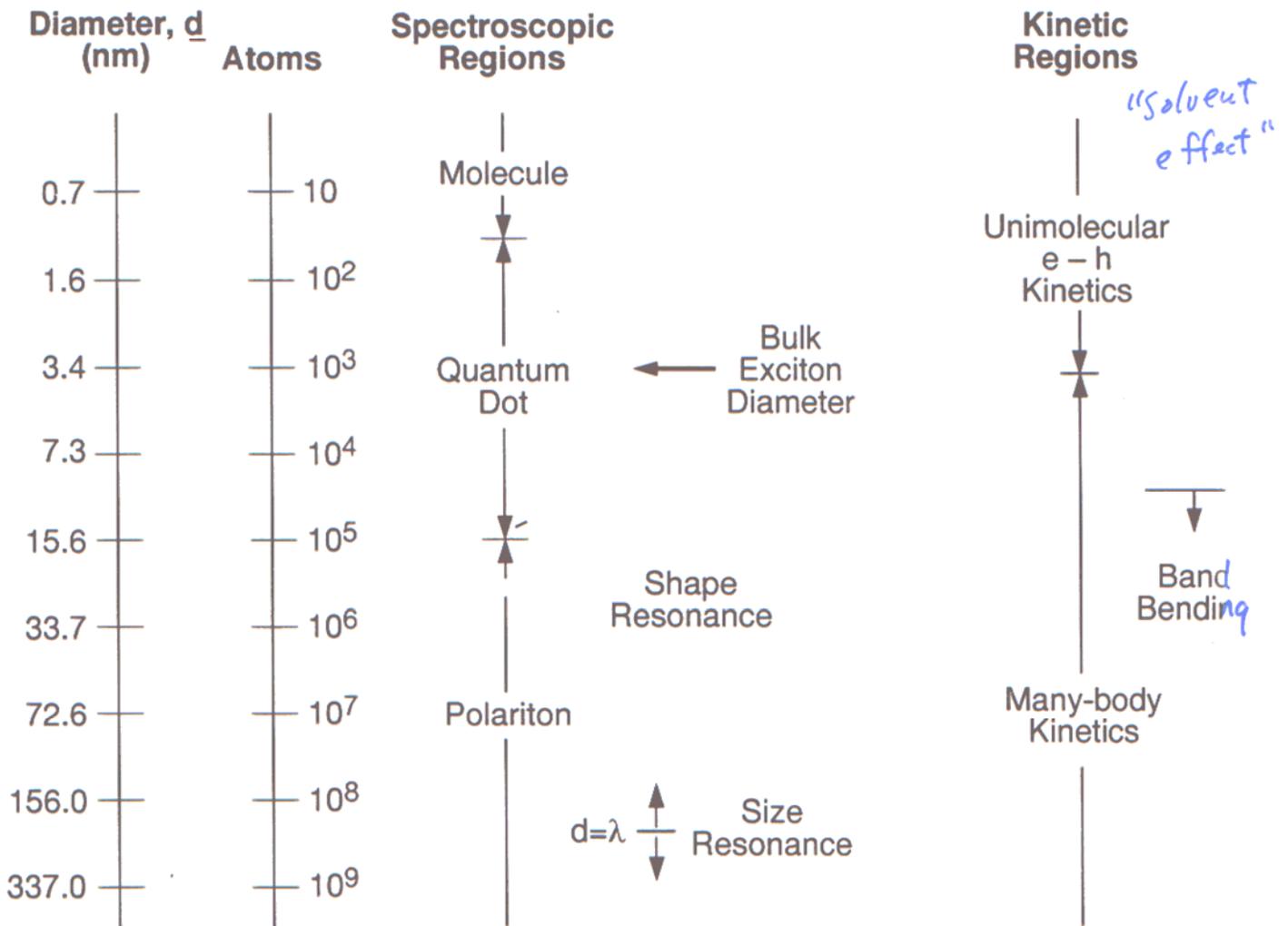
Krauss et al J. Phys. Chem. 2001, B105, 1725



- Illuminated with  $20 \text{ W/cm}^2$  at 442 nm
- Direct observation of Charge Blinking provides evidence for photoionization mechanism of Luminescence Blinking

# Evolution from molecules to bulk crystals as size increases

## Physical Size Regimes for Semiconductor Nanocrystals



## Thoughts for Students:

We are all trapped by our educational backgrounds.

Learn something new every day; this is the greatest skill we have.

What are your colleagues working on, why is it important?

Search continuously for a better problem than the one you are working on at present. **The choice of problem is the most important scientific decision you will ever make.**

Problems difficult in one field are easy in other fields

Intelligence, dedication and discipline required, but not genius.

.