

# Columbia University in the City of New York



## Recent Faculty Hires:

### Condensed Matter physics

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Aron Pinczuk  
Tony Heinz  
Phillip Kim  
Andy Millis  
Igor Aleiner

### Chemistry and Materials

Jack Norton   David Reichman  
Jim Leighton   Laura Kaufman  
Colin Nuckolls  
Virginia Cornish  
David Adams  
Dalibor Sames  
Brian Gibney  
Stephen O'Brien

# Chemistry and Physics of Semiconductor Nanocrystals

Louis Brus  
Chemistry Department  
Columbia University

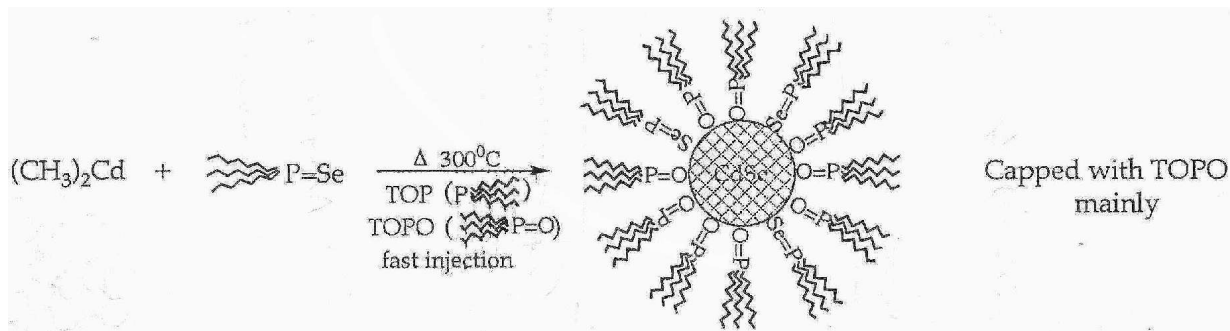
## History

Synthesis and self-assembly into solids  
Electronic Structure and Luminescence  
Optical Spectra of Single Nanocrystals  
Charge State of Single Nanocrystals.

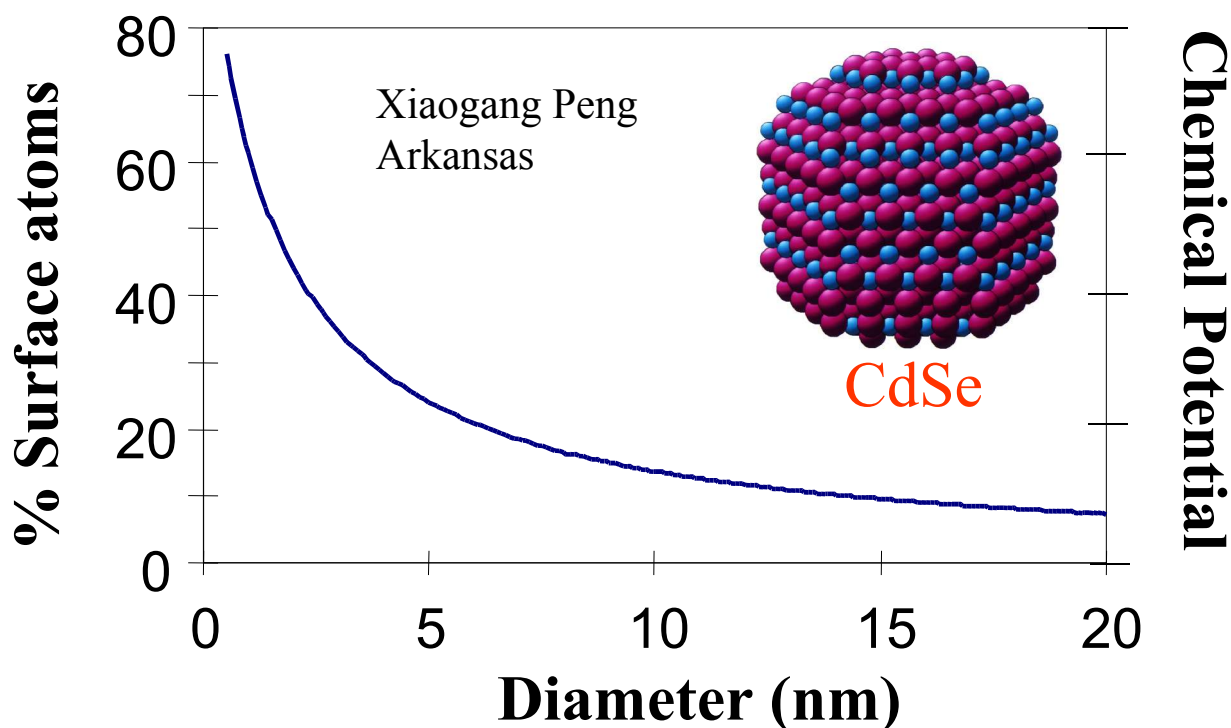


NSF Nanocenter on Electrical Conductivity of  
Single Molecules and Carbon Nanotubes

## What is a CdSe 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.





# 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  $\approx 35$  Å, which corresponds to about six unit cells. The mass weighted average diameter  $\bar{d}$  is  $\approx 45$  Å. 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  $\bar{d} \approx 125$  Å. 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.

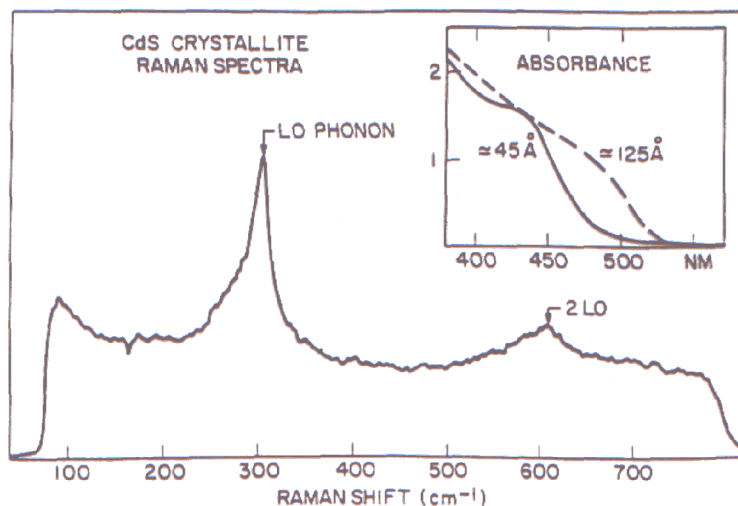
Resonance Raman (RR) spectroscopy<sup>3</sup> in principle allows an *in situ* vibrational characterization despite the low crystallite concentration  $\approx 2 \times 10^{-6}$  M in fresh colloids. The 416 nm RR spectrum in Fig. 1 shows the LO (longitudinal optical) phonon at  $305 \text{ cm}^{-1}$  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  $\approx 10^{-3}$  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>8,10</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.

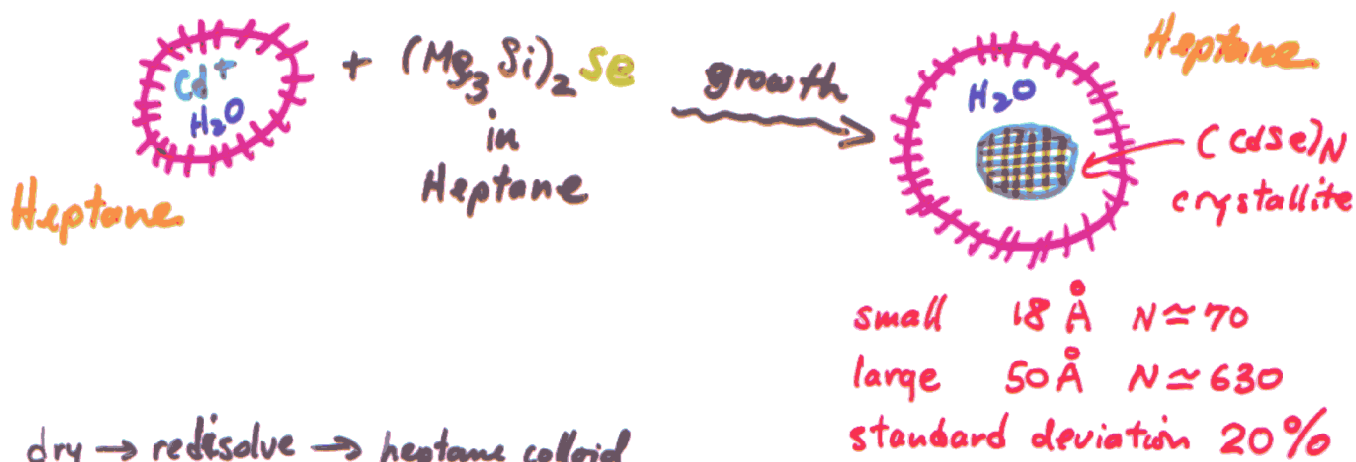
Letters to the Editor



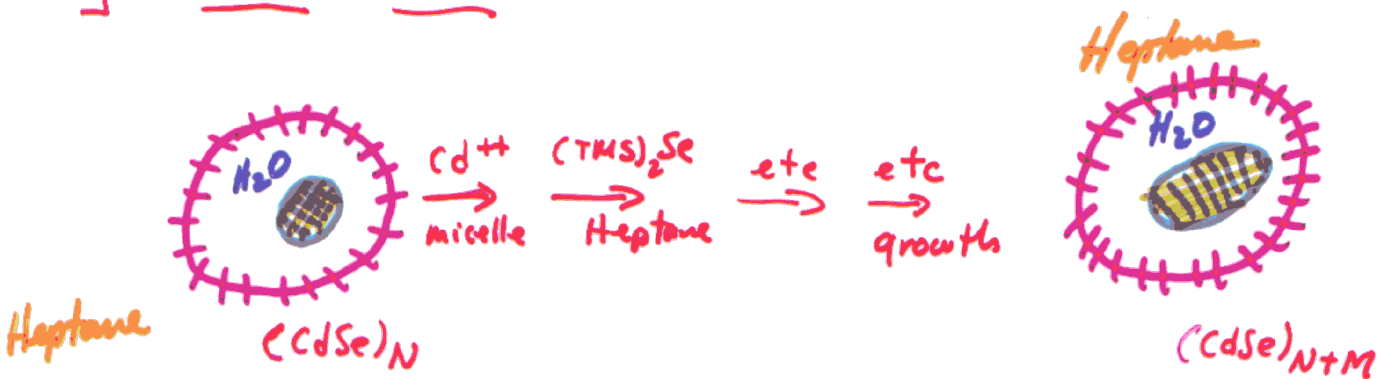
Organometallic synthesis, controlled Growth, Surface "capping"  
and isolation of stabilized clusters

A] Take advantage of hydrocarbon phase - hydrophobic reagents

\* Mike Steigerwald  
Paul Alivisatos  
Lou Brus



B] Controlled Growth



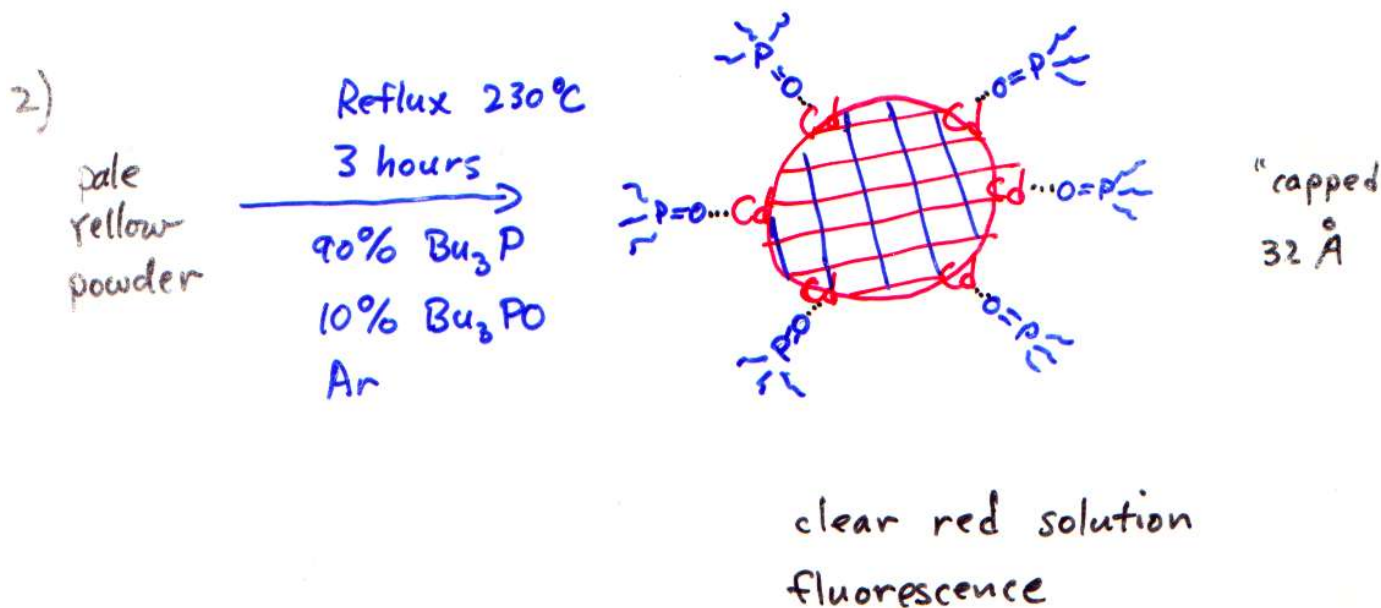
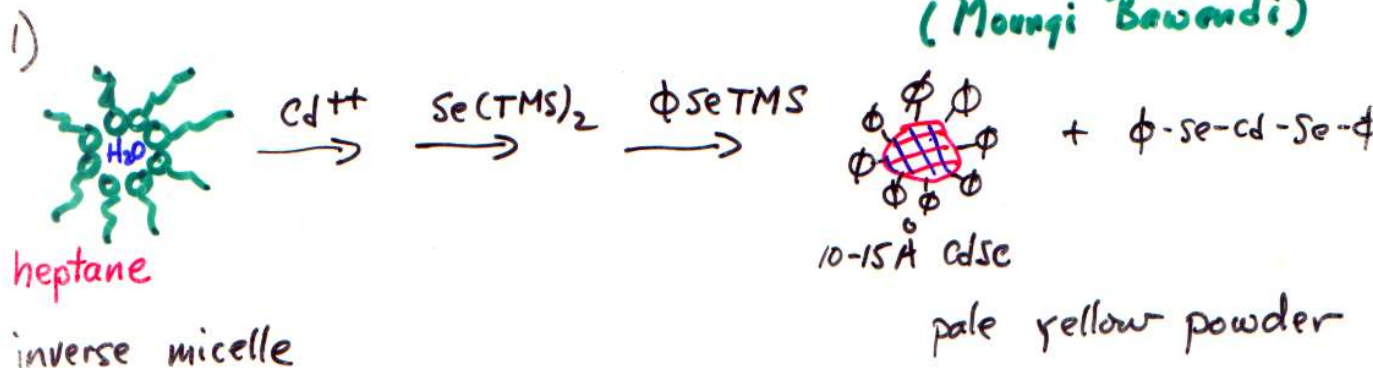
Crystallite in micelle, with water present,  
is stable yet can grow further

$\Rightarrow$  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

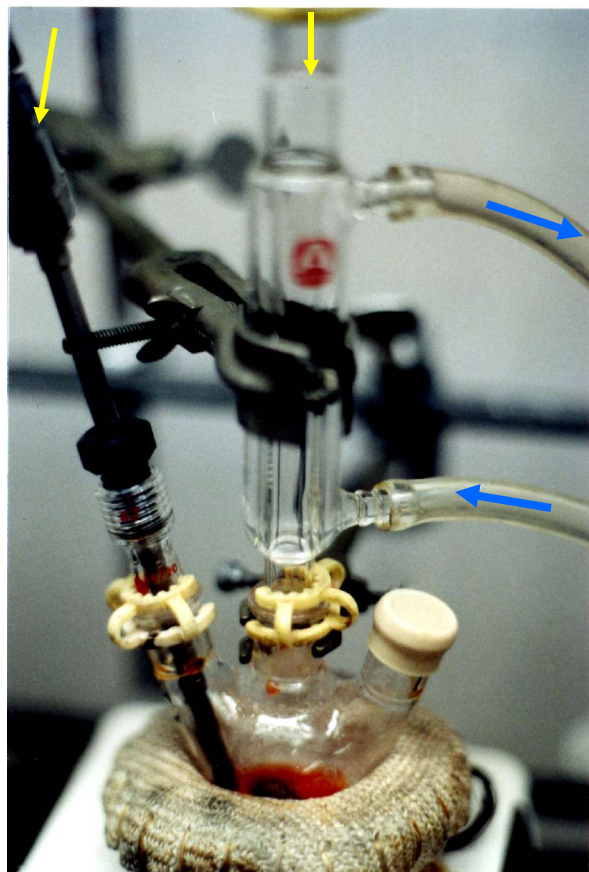
# Chemical synthesis of CdSe nanocrystals

Thermocouple

Argon gas at little above ambient pressure

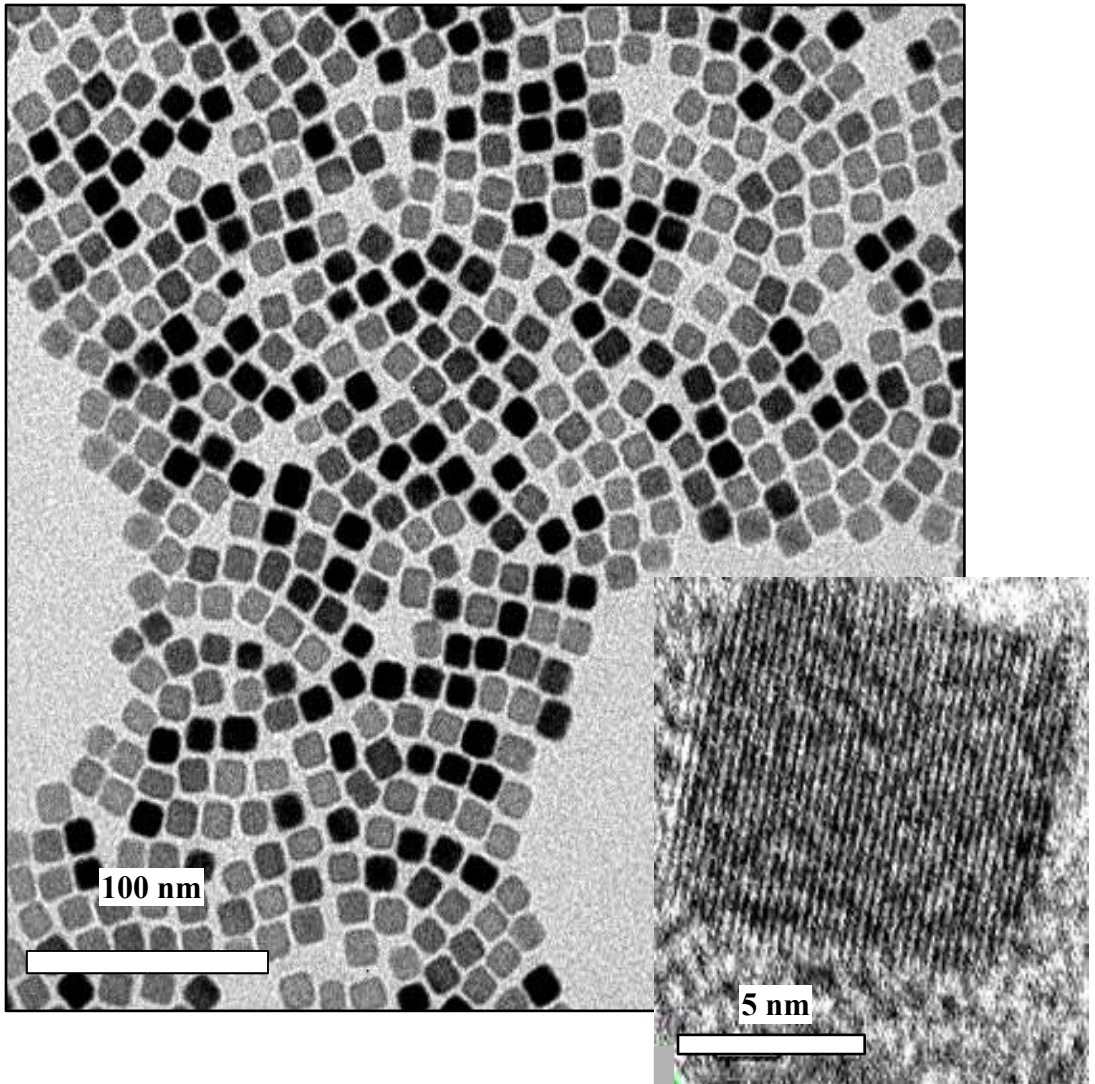
- Narrow size distribution ( $\sim 5\%$ ) is obtained by the fast injection of the chemical reagents into the flask at high temperature ( $\sim 350$  C).
- The precursors are prepared in the glove box to avoid oxygen and water.

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





# TEM of cubic PbSe nanocrystals



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

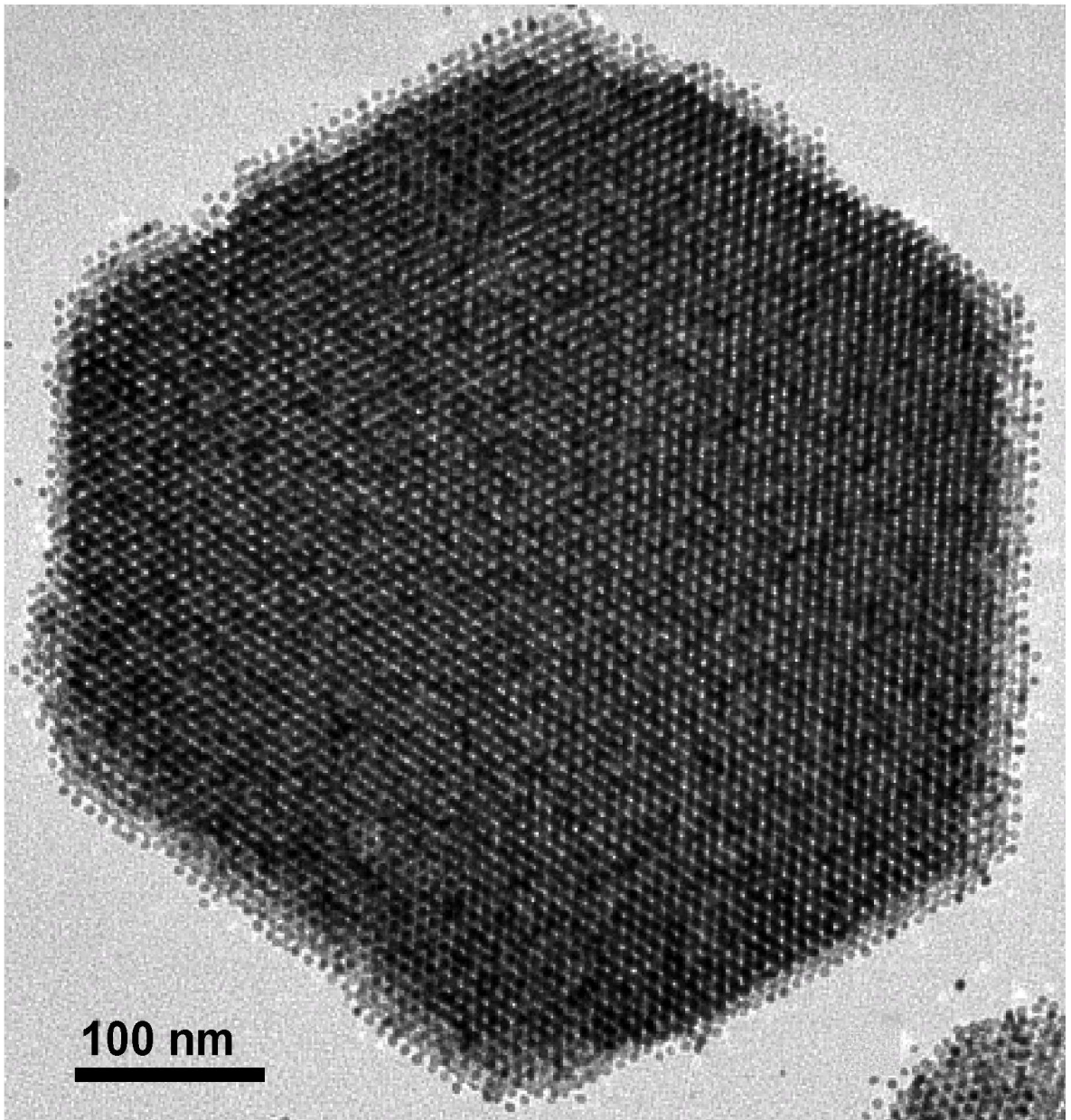
**Change of shape from spheric to cubic in the size regime of  
8 to 11 nm**

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



# 3D solid structures

Elena Shevchenko  
O'Brien – Murray  
Columbia-IBM

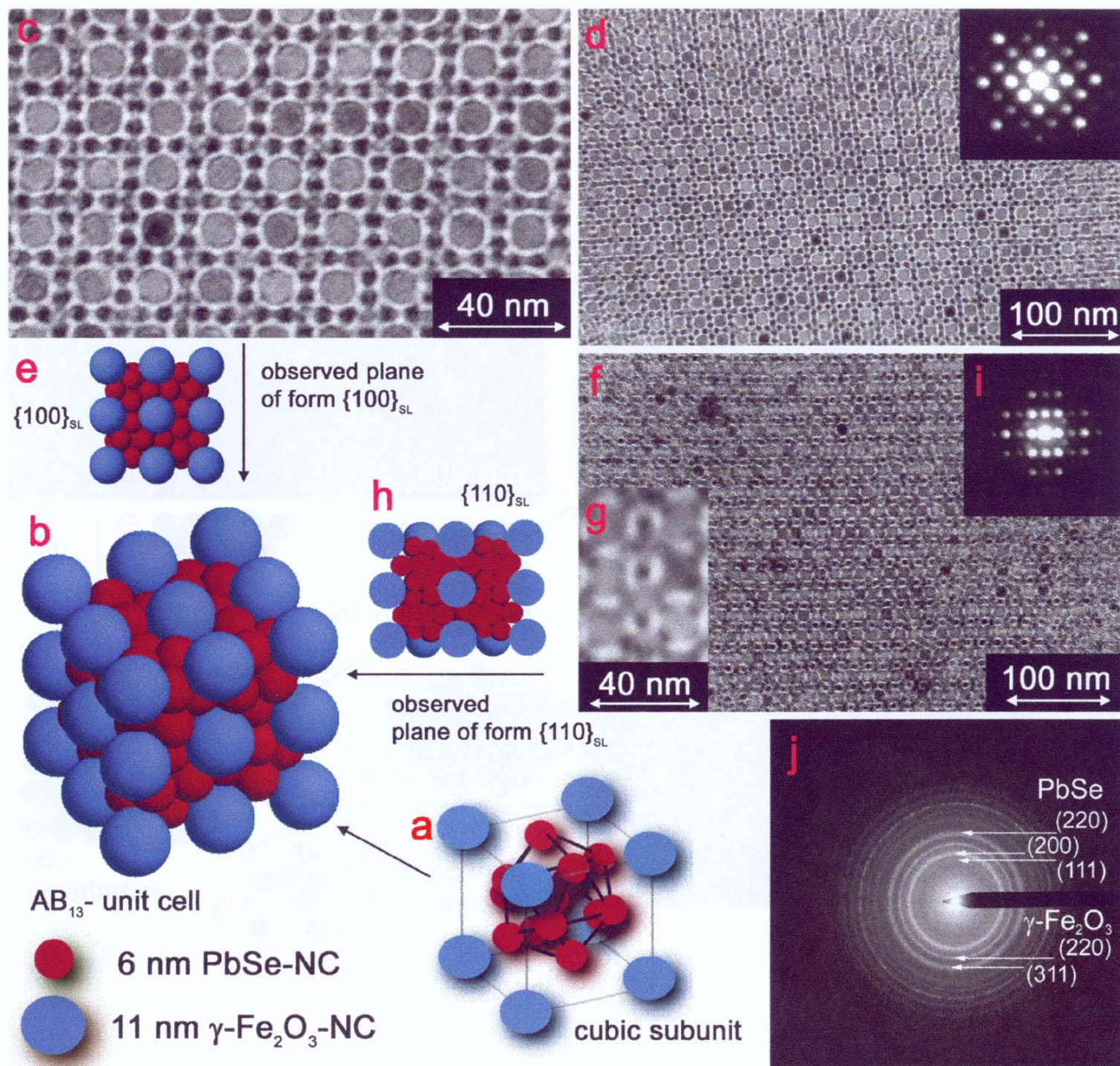


**CoPt<sub>3</sub> nanoparticles**



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

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



NATIONAL SCIENCE FOUNDATION

Materials Research  
Science and Engineering Center

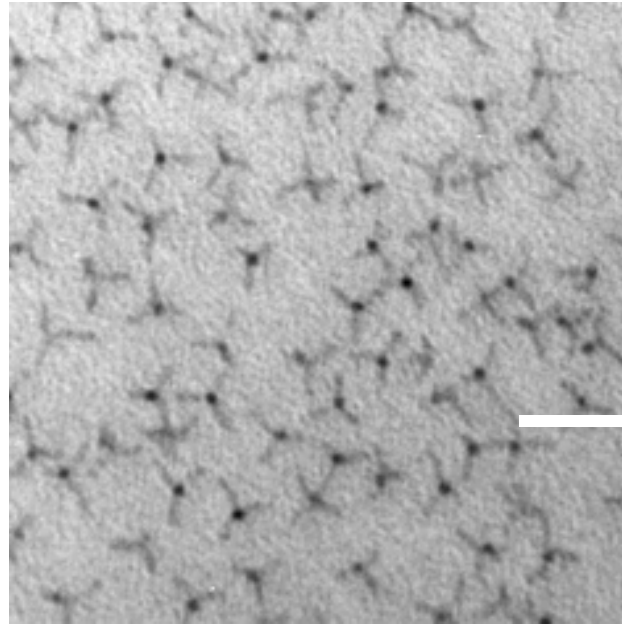
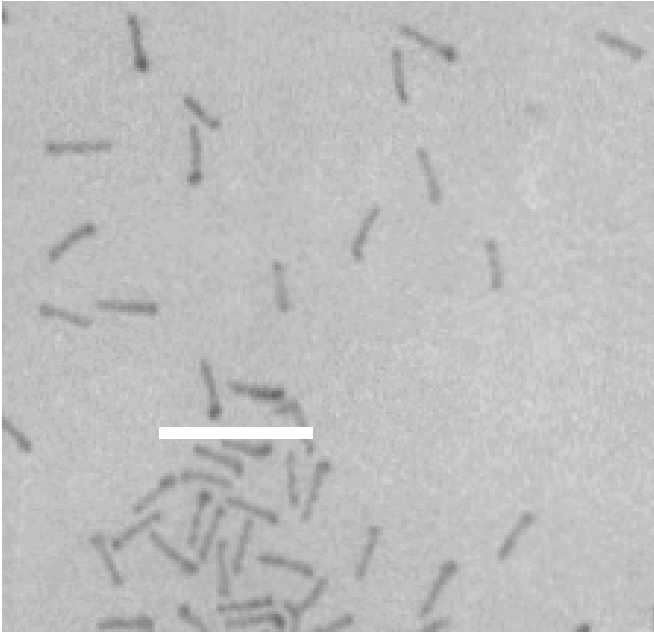
Columbia University



Xiaogang Peng *Arkansas*

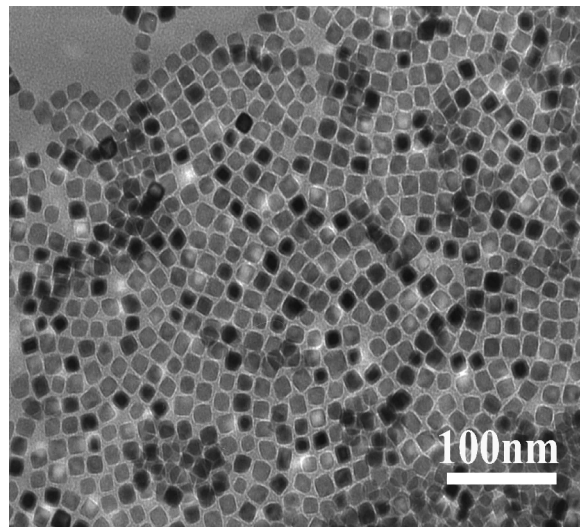
## Shape Control via Kinetics and Thermodynamics

### Key Concept: Tuning Monomer Activity



CdSe rods and tetrapods

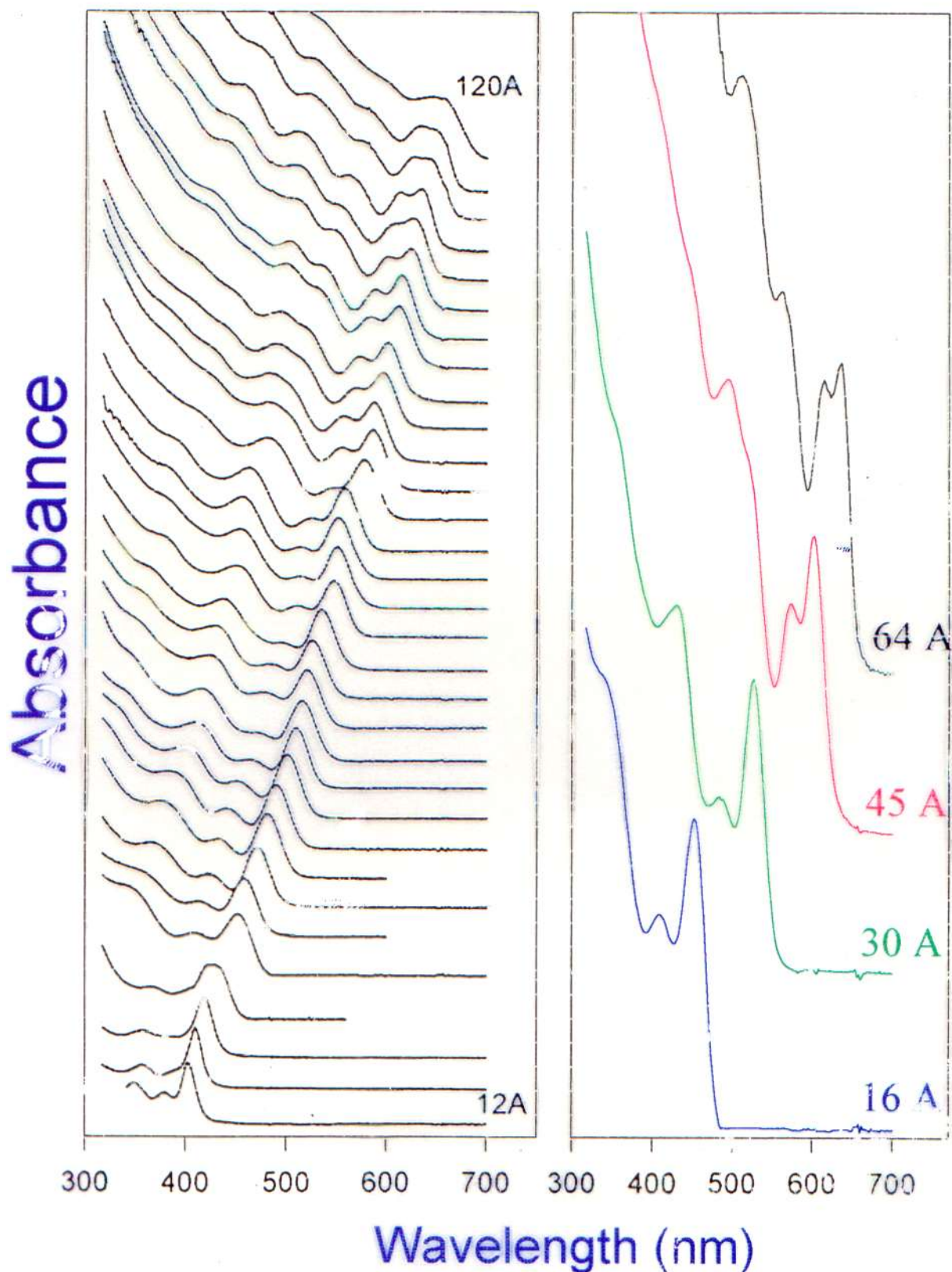
Cubic FeO  
Wuestite



Stephen O'Brien, Applied Physics, Columbia



# CdSe Size Dependent Absorbance



C. Murray and M. Bawendi

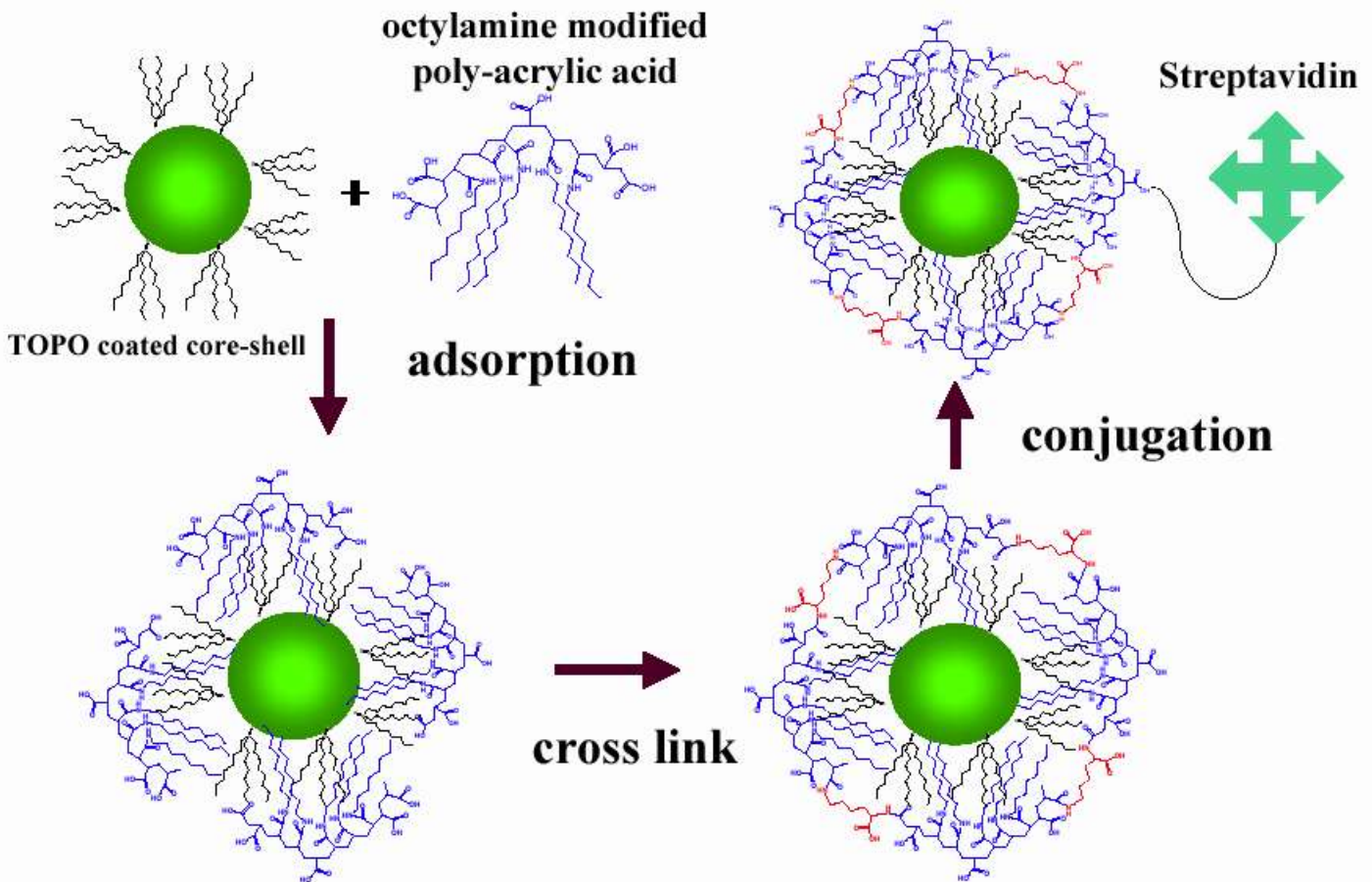
Chris Murray & Moungi Bawendi (MIT)

Size tunable luminescence  
Narrow emission band

High Quantum Yield Luminescence  
More stable than dye molecules  
Possible use in biological imaging



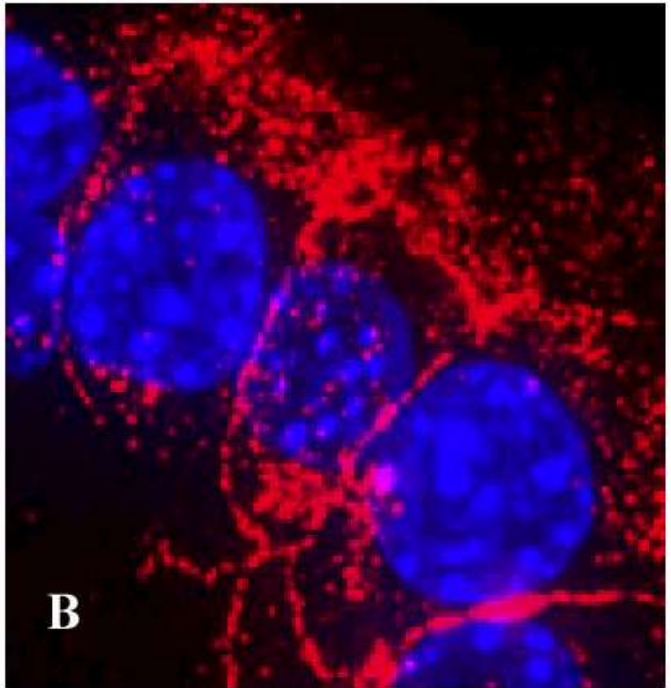
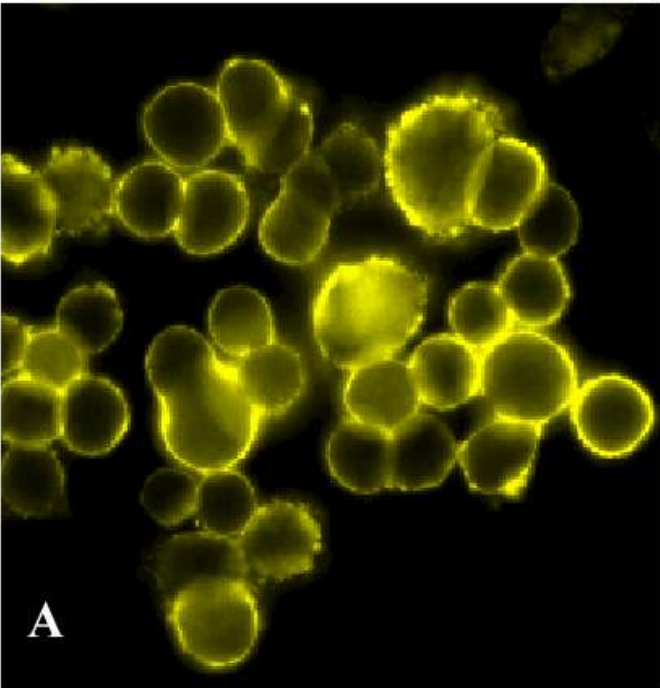
## Surface Stabilization & Biomolecule Conjugation



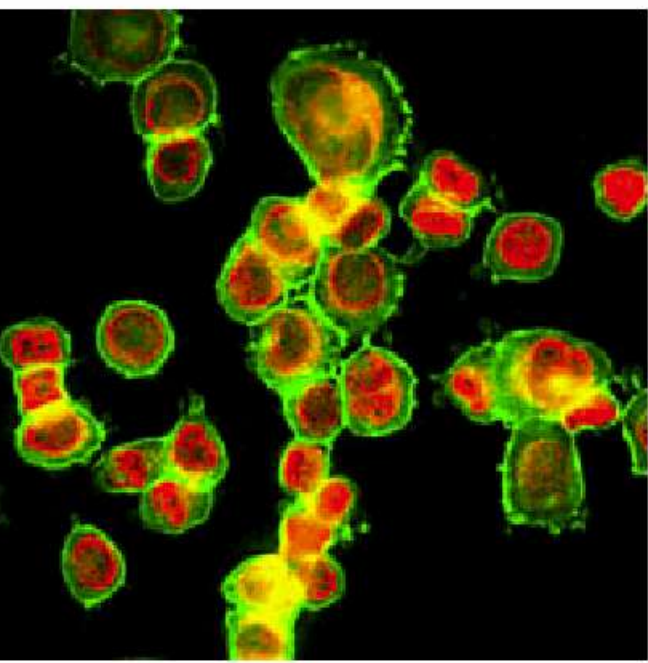
Q Dot Corporation  
[www.qdots.com](http://www.qdots.com)

Published in Nature Biotechnology Online



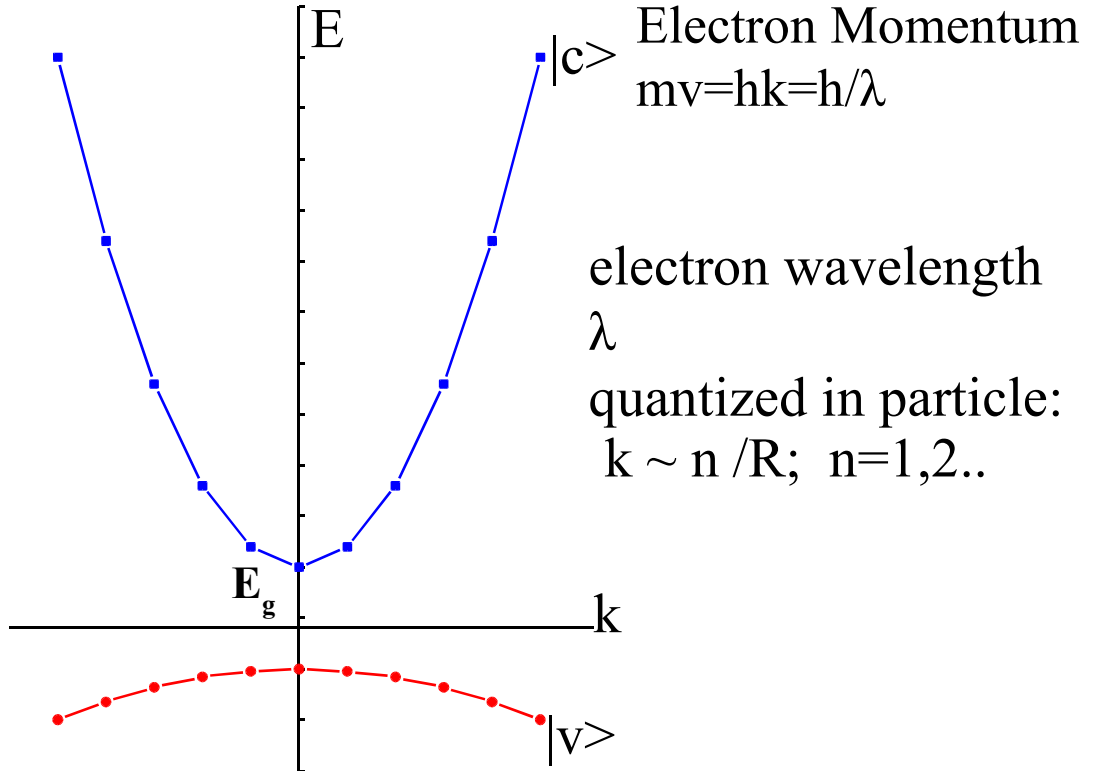


SK-BR3 breast cancer cells (A) and mouse mammary tumor tissue section (B) were stained with humanized anti-Her2, biotinylated anti-human IgG and **QD 560-streptavidin** and **QD 630-streptavidin**.



Cancer marker Her2 on the surface of SK-BR3 cells were stained with mouse anti-**QD 535-IgG**. Nuclear antigens were labeled with human anti-nuclear antigens antibodies, biotinylated goat anti-human IgG and **QD 630-streptavidin**. When the sample was observed under a fluorescence microscope the nuclei were red and the cell membrane appeared green simultaneously. All colors of QDs can be excited by a common light source, which makes QDs ideal labels for multiplexed detection.

# Simple Model for Electronic Structure: Quantum Size Effect



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

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

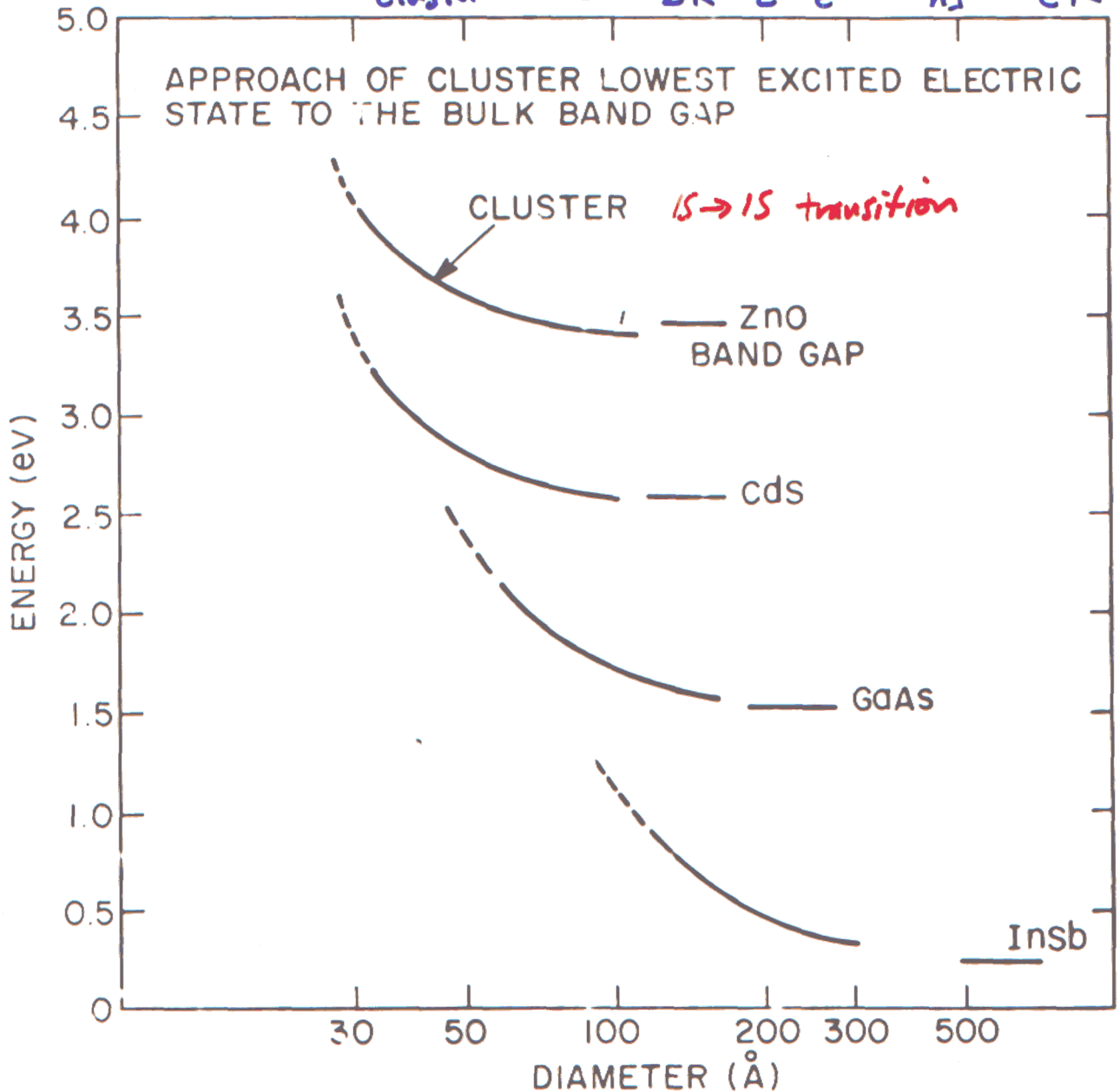
- Optical Spectra are Discrete and Size Dependent
- Model uses known bulk band structure, and ignores bonding reconstruction on surfaces

# 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!*



# Failure of Quantum Model in Silicon Nanocrystals:

Why does an H passivated 1.3 nm silicon nanocrystal emit in the blue, but an 1.3 nm oxide shell passivated nanocrystal emit in the red?

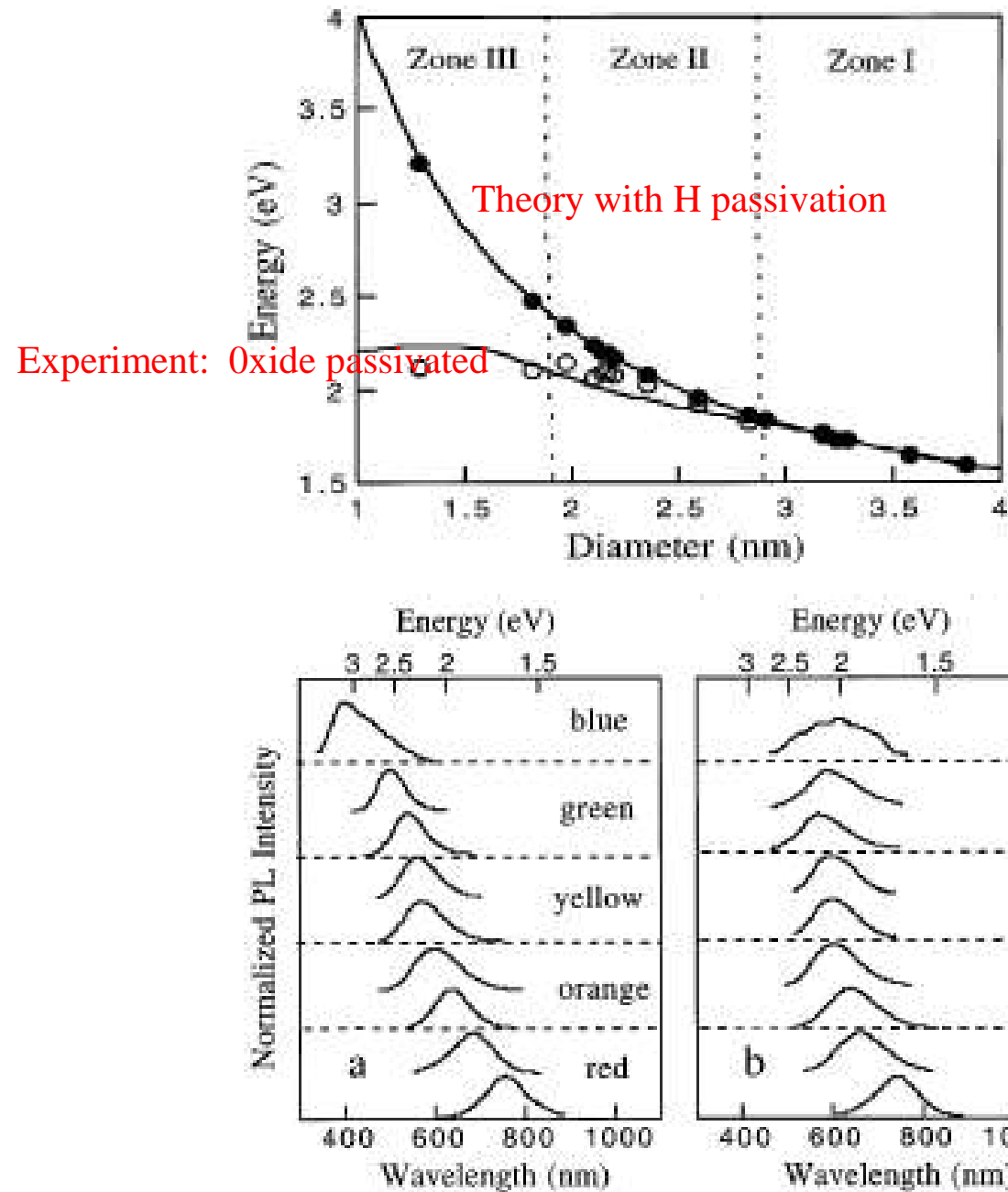


FIG. 1. Room temperature photoluminescence spectra from PSi samples with different porosities kept under Ar atmosphere (a) and after exposure to air (b).

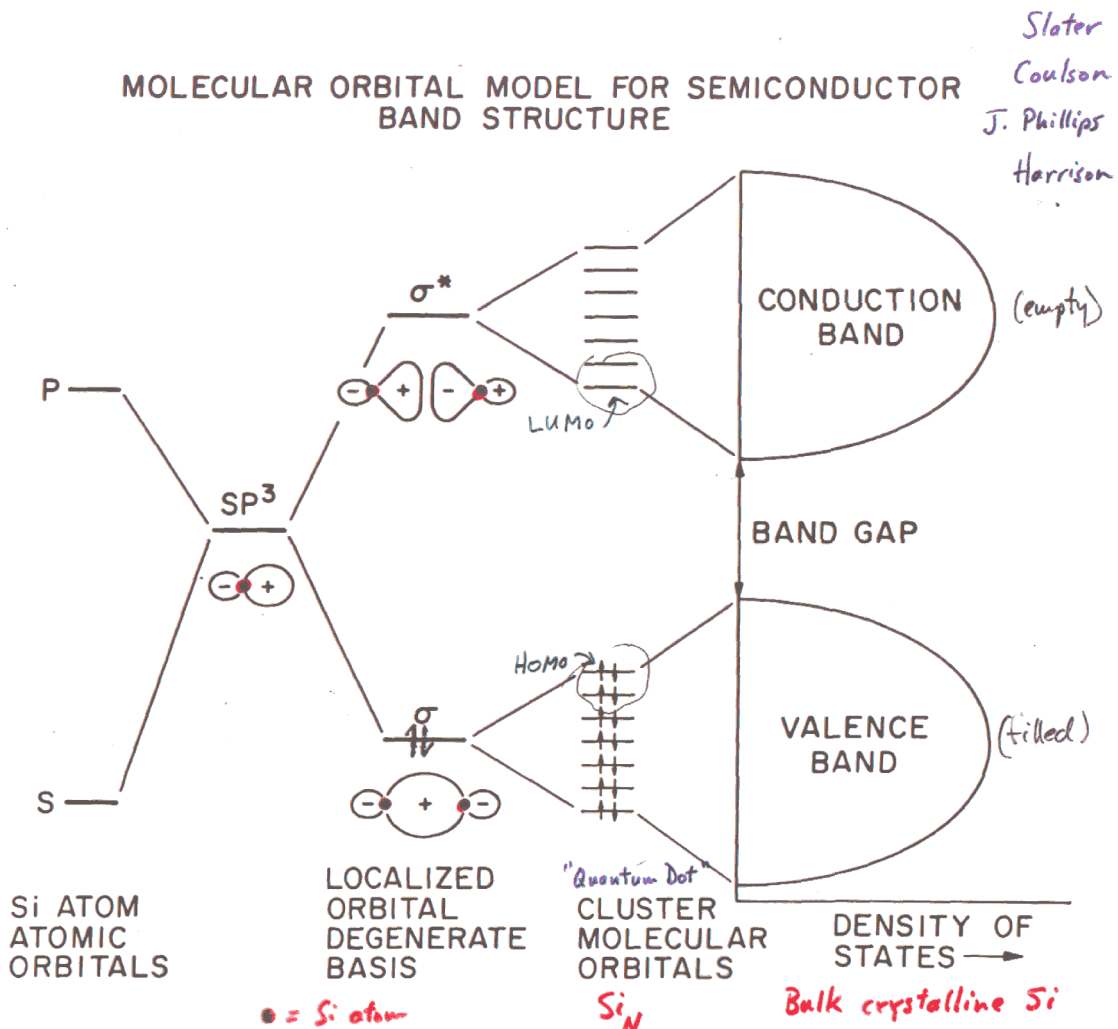
# Ab Initio Electronic Structure Calculation

## Surface Bonding and Geometrical Optimization

## Independent of bulk band structure

## Molecular Orbitals extend over entire nanocrystal

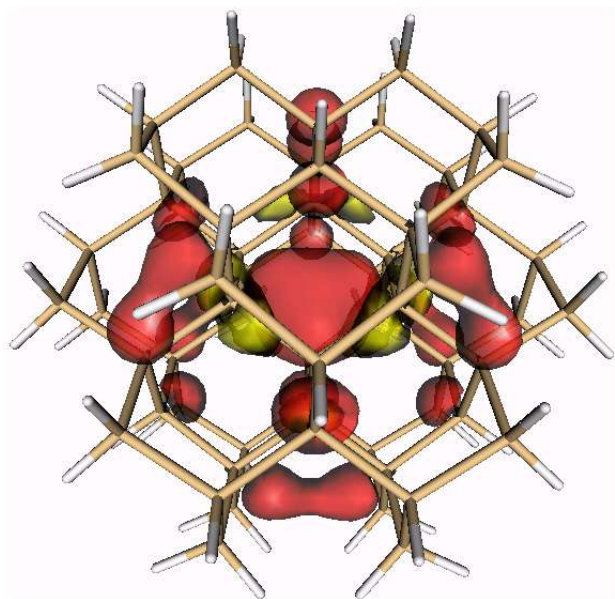
## Problem: too many atoms



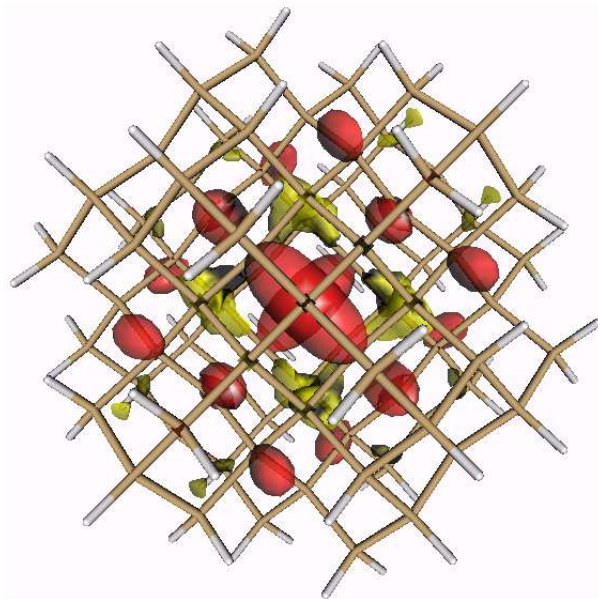
All electron Density Functional Theory  
Becke B3YLP Hybrid Functional  
Structure completely optimized

Zhou, Friesner, Brus Nanoletters **3**, 163 (2003)  
JACS **125**, 15599 (2003)

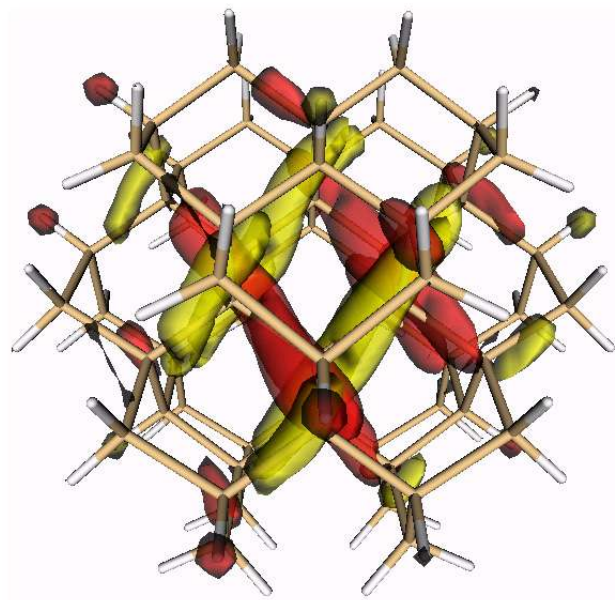
Si66H64 LUMO



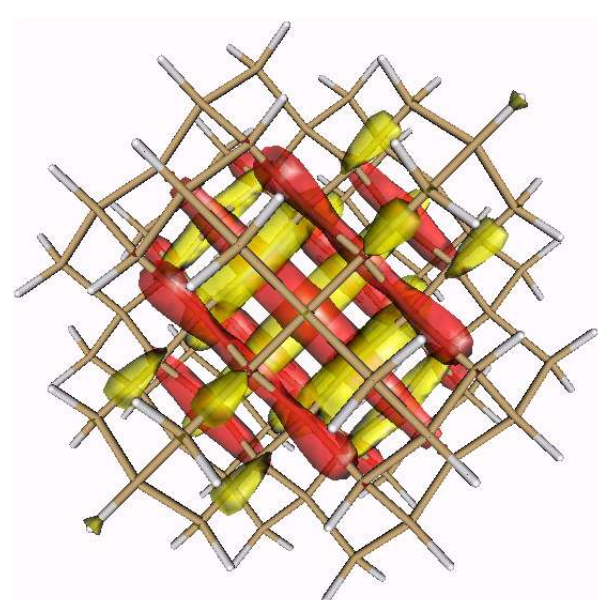
Si87H76 LUMO



Si66H64 HOMO

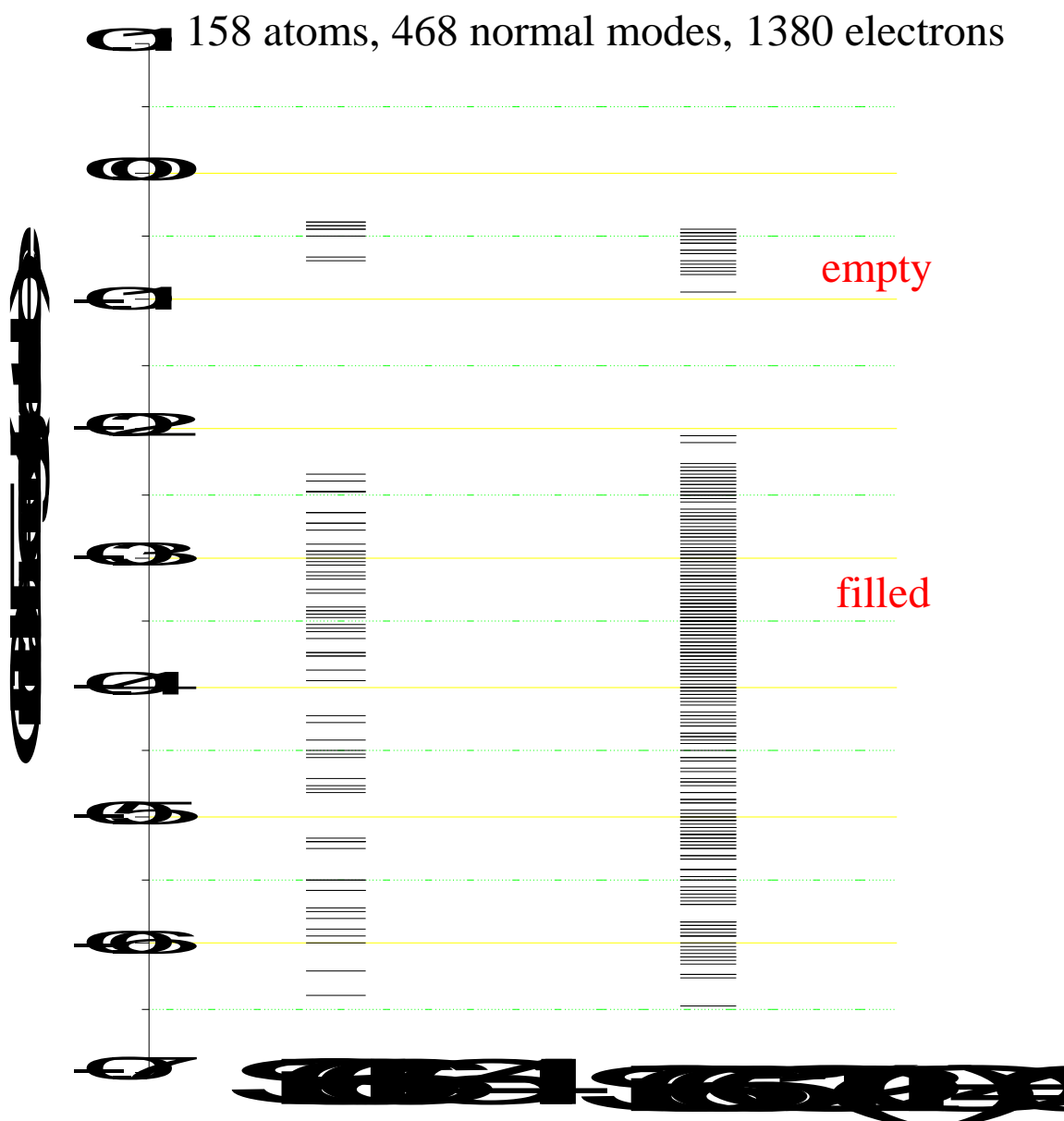


Si87H76 HOMO





# Molecular Orbitals of Si66 Species

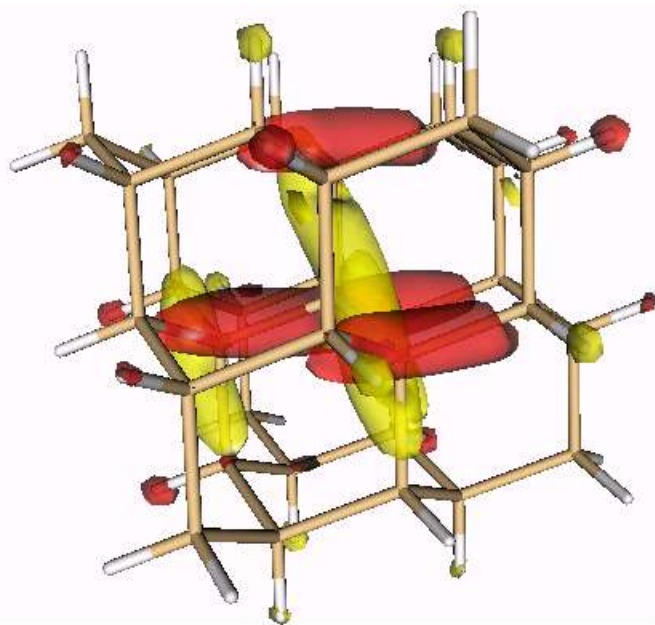


Oxide passivation lowers band gap by 1.5 eV  
LUMO moves down  
HOMO moves up

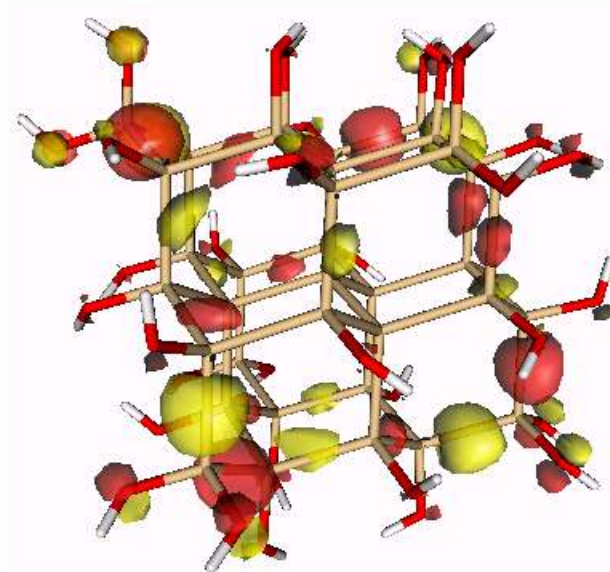
Fermi level unchanged; hardness decreases

# Frontier orbitals of Si35

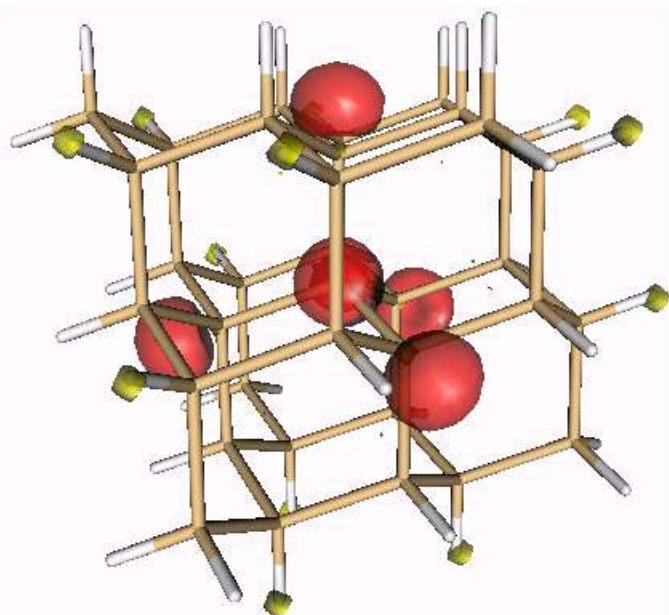
Si35H36 HOMO



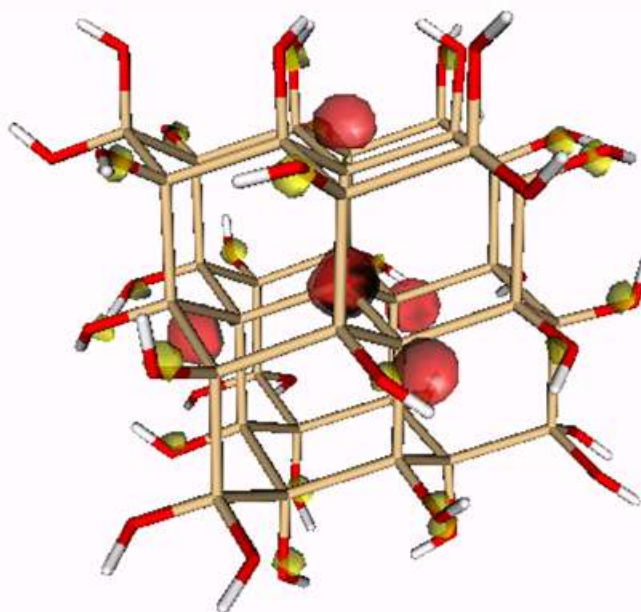
Si35(OH)36 HOMO



Si35H36 LUMO

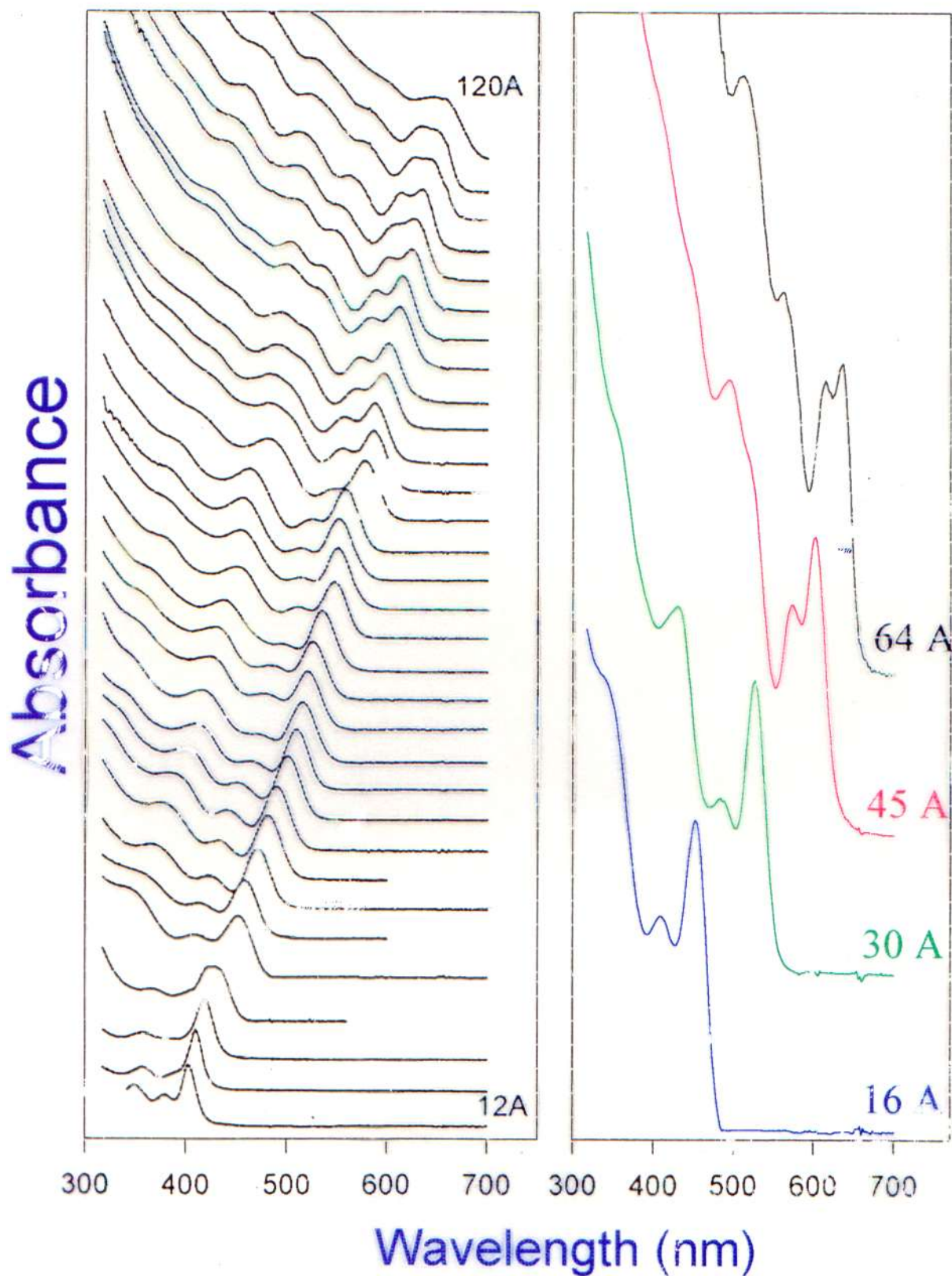


Si35(OH)36 LUMO



HOMO pulled to surface by electronegative O atoms  
HOMO resides on weakened Si-Si back bonds

# CdSe Size Dependent Absorbance



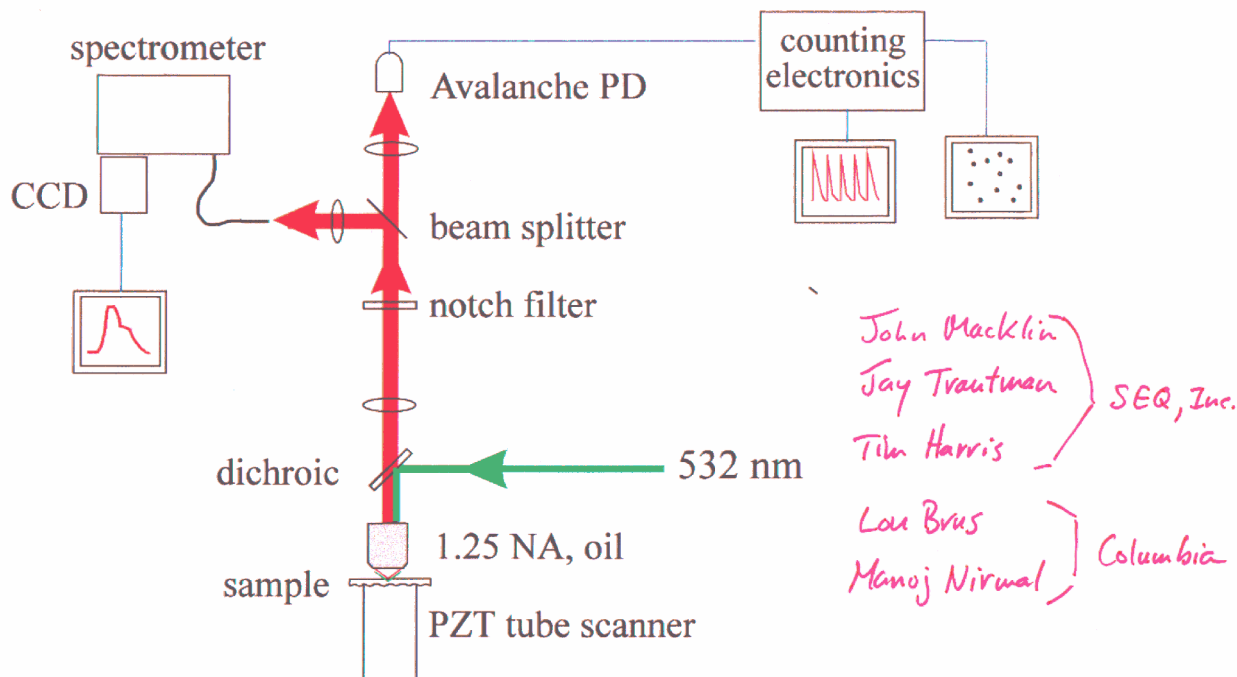
Bawendi group

Chris Murray & Moungi Bawendi (MIT)

## 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



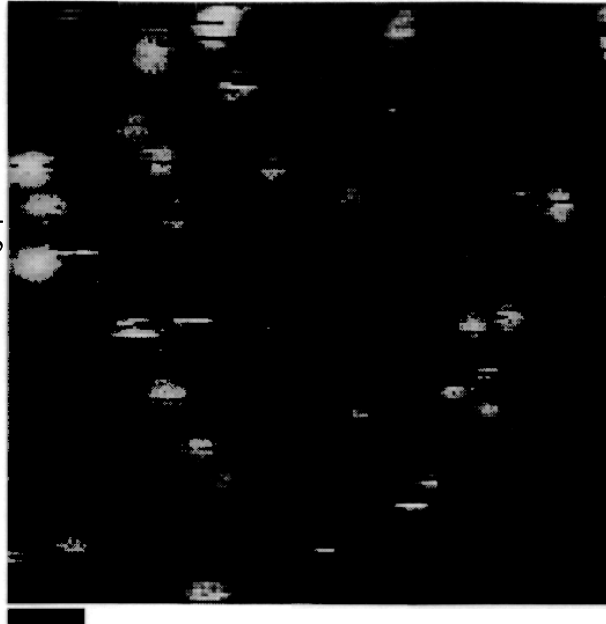
Betzig, Trautman (Bell Labs):  
Confocal Scanned Stage Luminescence Spectrometer

Macklin et al, Science 272, 255 (1996)



Random Field of Single CdSe Nanocrystals  
 cw optical excitation

a)

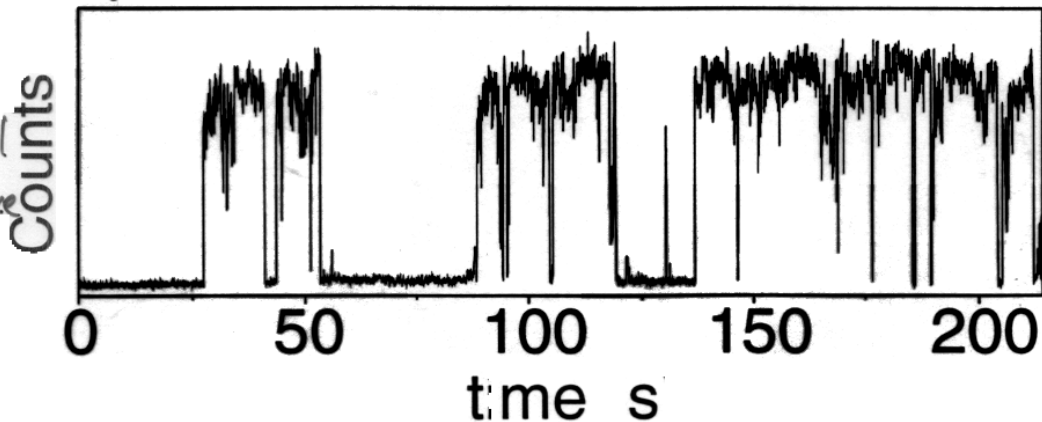


Lin. c. c.  
 Image

1  $\mu$ m

Individual nanocrystals "blink" on and off

b)



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

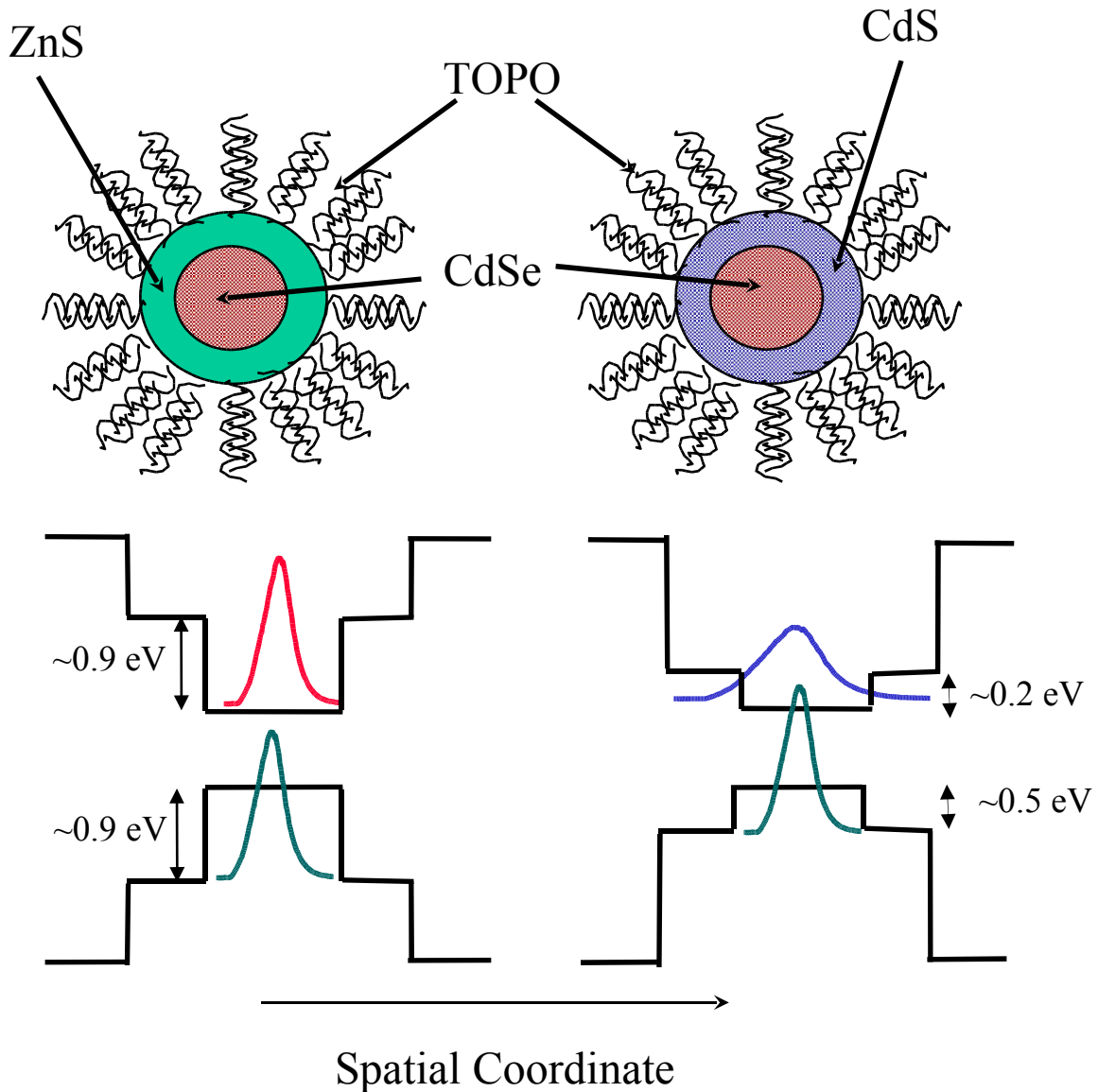
Nov 1996 Nature 383 2(66)

ig.

Nirmal et al, Nature 383, 802 (1996)

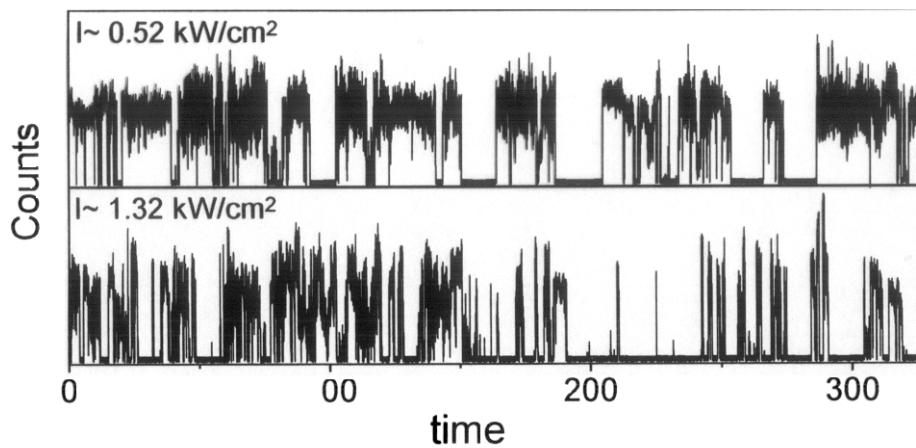
# Semiconductor Capped QDs

- EFM of CdS capped CdSe



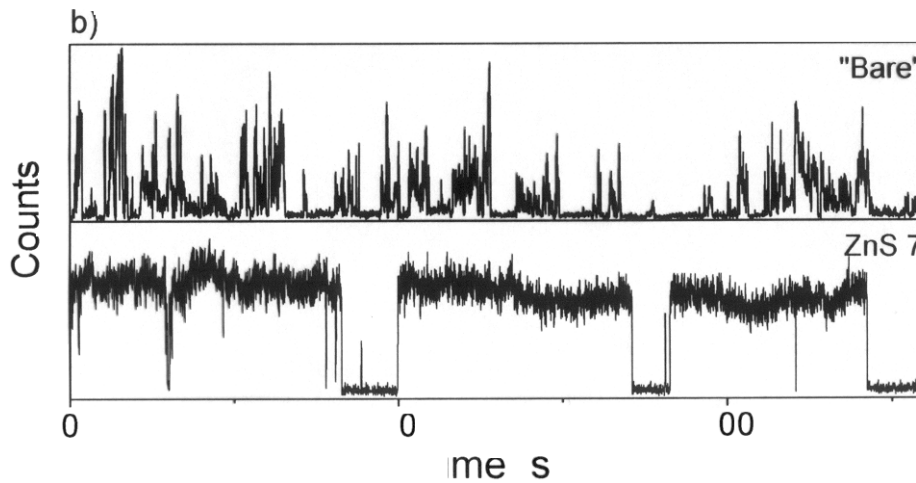
B. O. Dabbousi, *et al.* (1997)

Power dependence on  $I_L$



"on time  $\propto I_L$

off time independent of  $I_L$

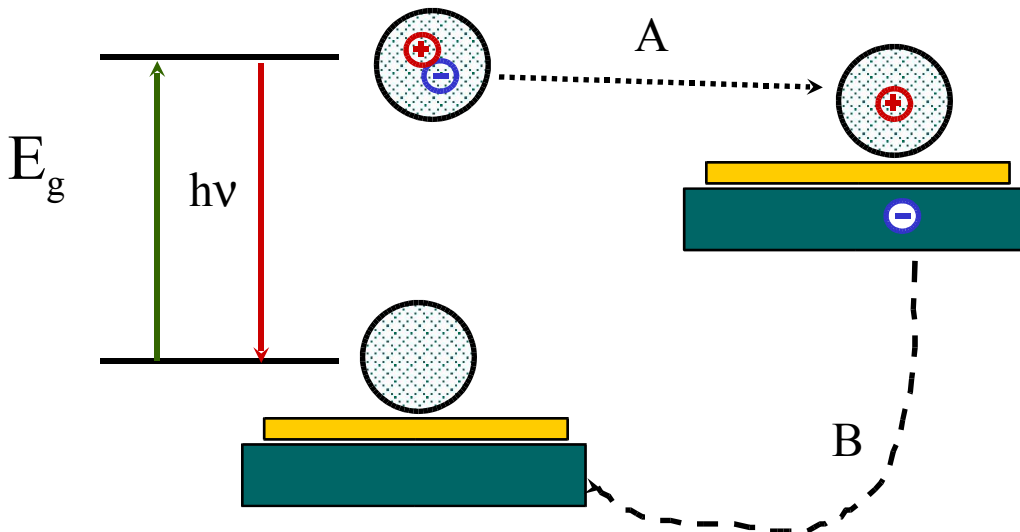
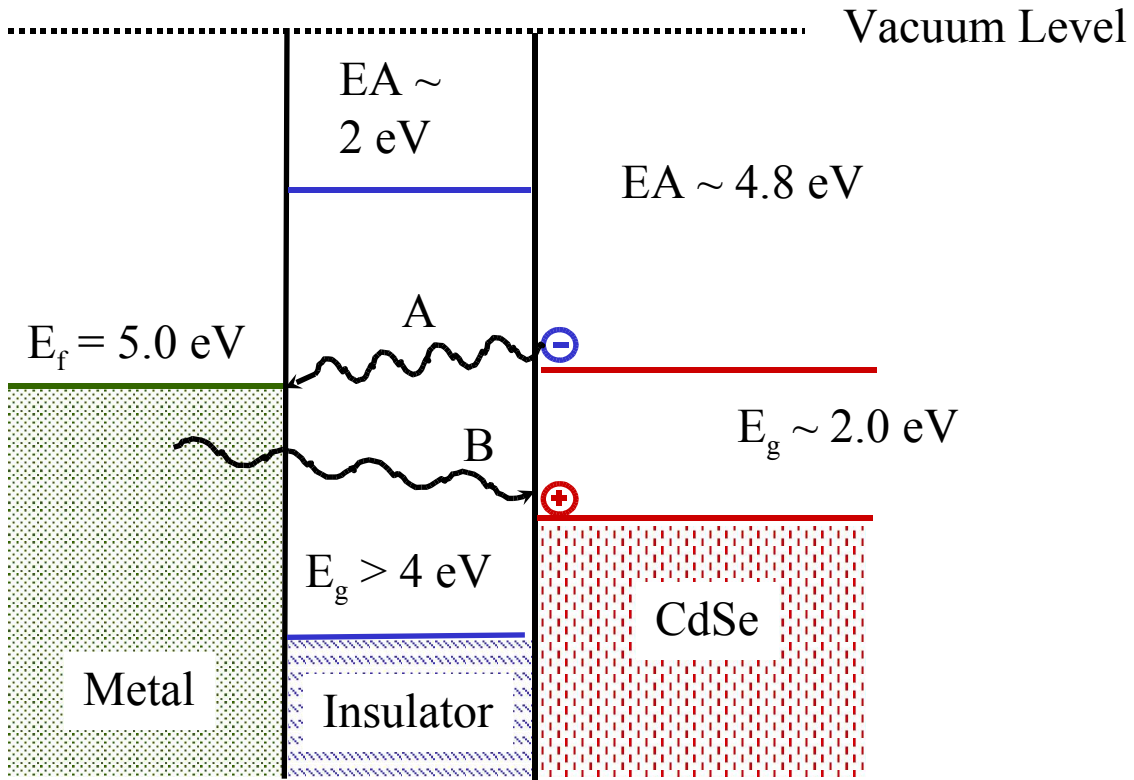


ZnS coated

Blinking rate increases at higher laser power

ZnS layer on surface slows down blinking rate

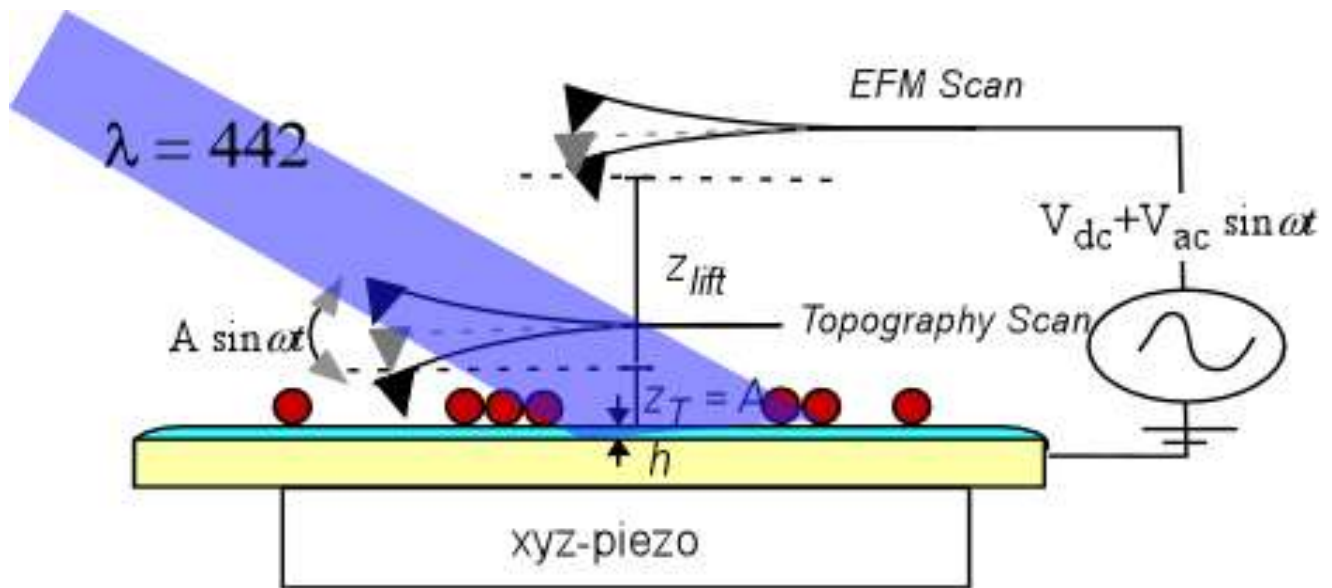
# Schematic Blinking Mechanism: Photoionization and Re-neutralization



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



# Direct Measurement of Electric Field Due to One Ionized Nanocrystal



Electric Force Microscopy Invention:

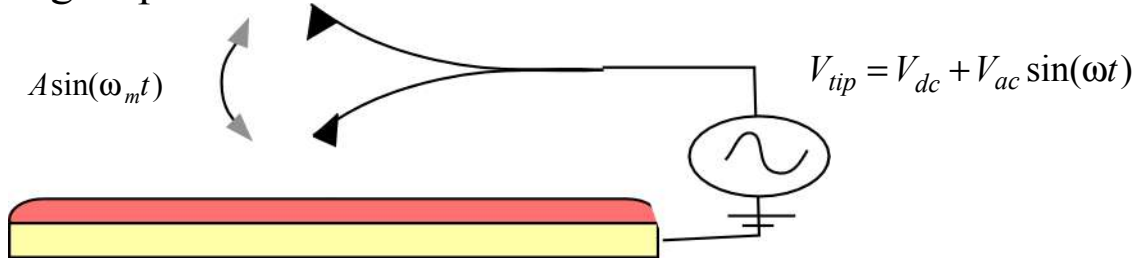
Wickramasinghe IBM

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

# Can we measure a single charge on a single nanocrystal?

## Electric Force Microscopy EFM

Oscillating Capacitor



Electrostatic Force

$$F_{coul} = \frac{Q_1 Q_2}{4\pi\epsilon z^2}$$

Energy Stored in a Capacitor

$$U = \frac{1}{2} C V^2 = \frac{1}{2} \frac{Q^2}{C}$$

Capacitive Force

$$F = -\frac{dU}{dz} = -\frac{d}{dz} \left( \frac{1}{2} \frac{Q^2}{C} \right) = \frac{1}{2} \frac{Q^2}{C^2} \frac{dC}{dz} = \frac{1}{2} \frac{dC}{dz} V^2$$

When a voltage is applied to the tip it feels a sum of electrostatic and capacitive forces. If there are static charges on the surface, image charges are induced in the metal tip.

$$F_e = F_{cap} + F_{coulomb} = \frac{1}{2} \frac{dC}{dz} V^2 + \frac{Q_1 Q_2}{4\pi\epsilon z^2} \quad V_{CPD} = (W_{substrate} - W_{tip}) / (-e)$$

$$= \frac{1}{2} \frac{dC}{dz} \left( (V_{dc} + V_{CPD}) + V_{ac} \sin(\omega t) \right)^2 - \frac{Q_s}{4\pi\epsilon z} \left( Q_s + C V_{dc} + C V_{ac} \sin(\omega t) \right)$$

$$= \frac{1}{2} \frac{dC}{dz} \left( (V_{dc} + V_{CPD})^2 + \frac{1}{2} V_{ac}^2 \right) - \frac{Q_s}{4\pi\epsilon z^2} \left( Q_s + C(V_{dc} + V_{CPD}) \right)$$

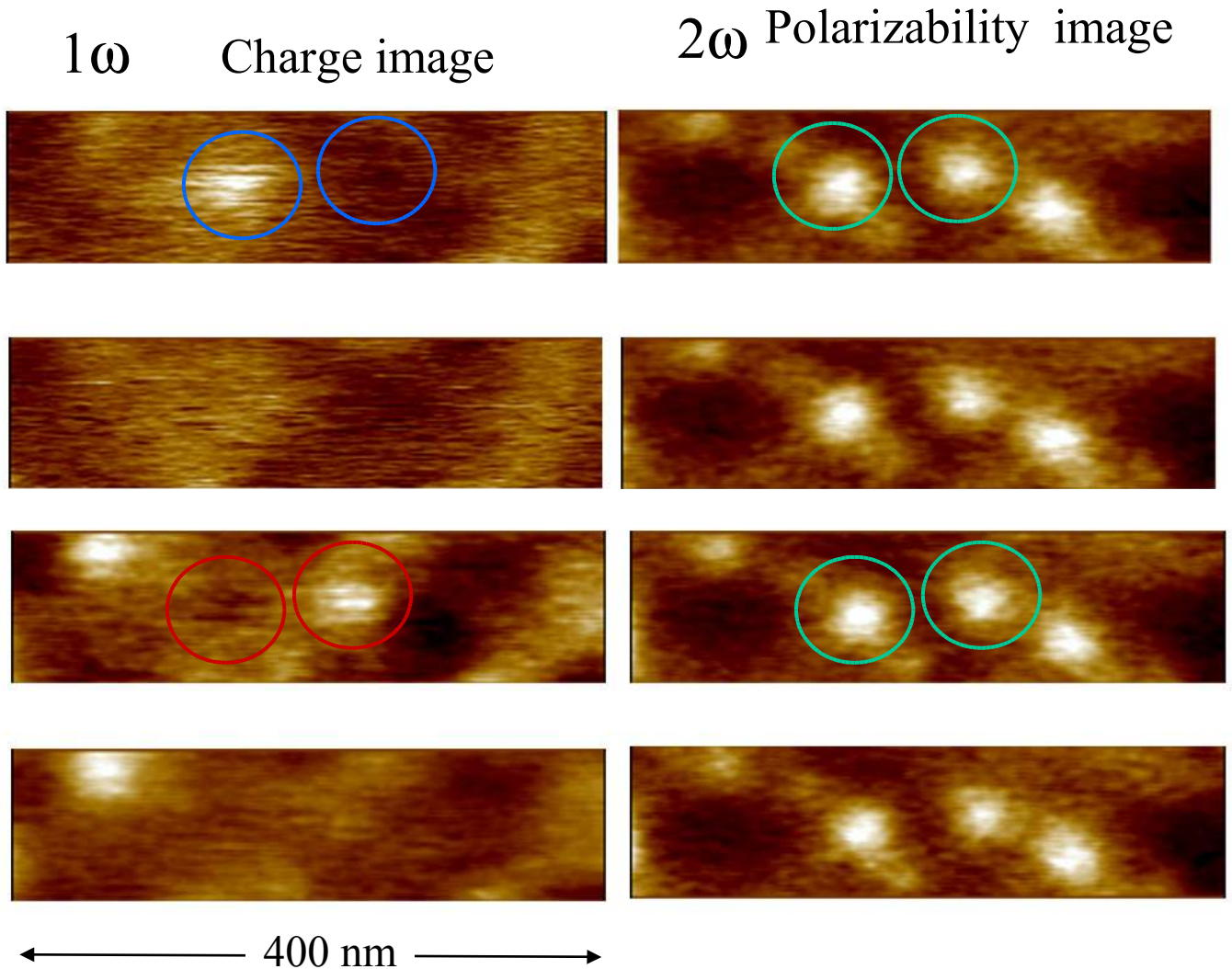
$$+ \underbrace{\left( 2(V_{dc} + V_{CPD}) \frac{dC}{dz} - \frac{Q_s C}{4\pi\epsilon z^2} \right) V_{ac} \sin(\omega t)}_{F(\omega)} + \underbrace{\frac{1}{4} \frac{dC}{dz} V_{ac}^2 \cos(2\omega t)}_{F(2\omega)}$$

$$F(\omega)$$

$$F(2\omega)$$

# CdSe/ZnS Charge Blinking on Graphite

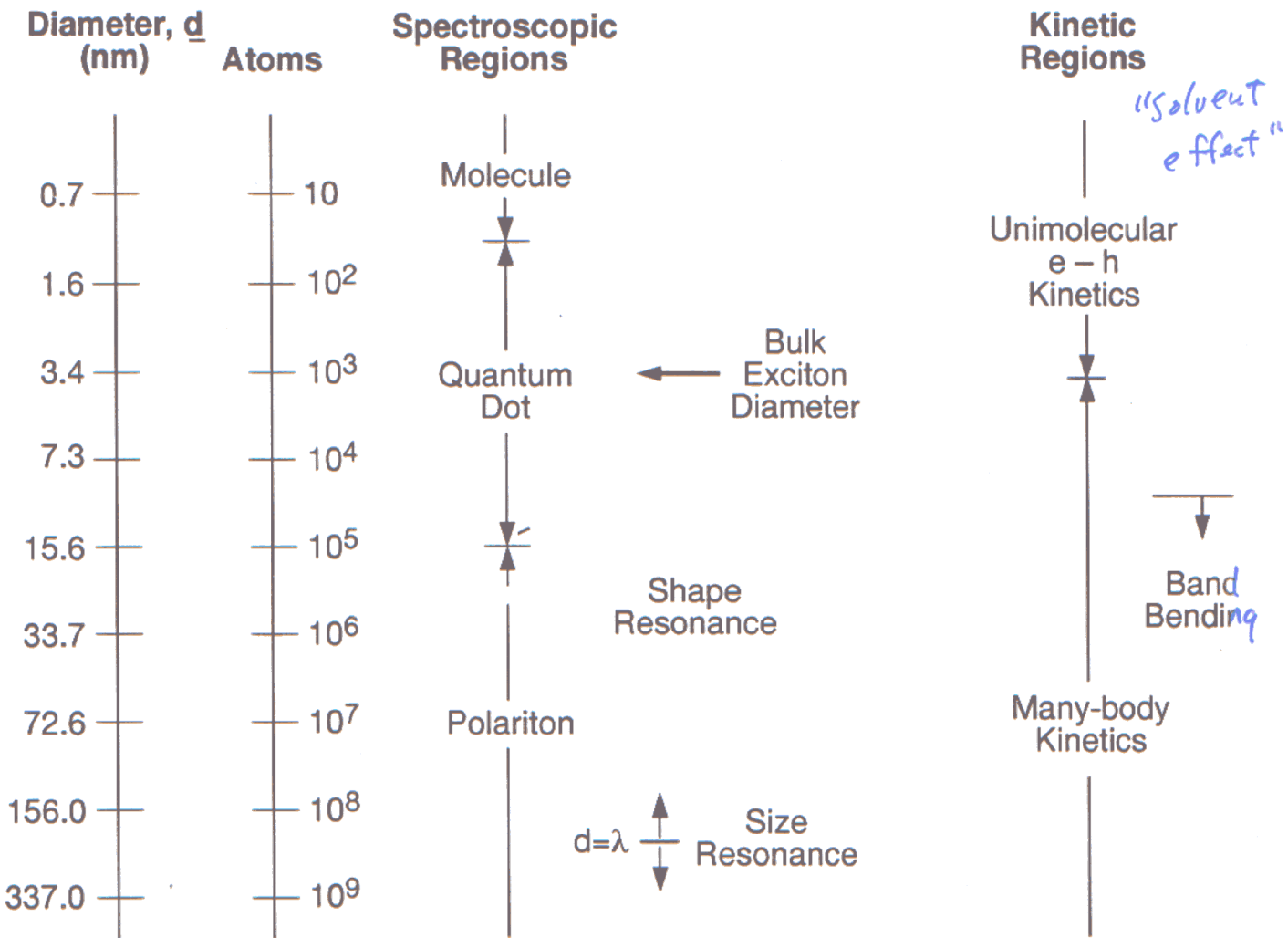
Krauss et al J. Phys. Chem. 2001, B105, 1725



- Illuminated with 20 W/cm<sup>2</sup> at 442 nm
- Direct observation of Charge Blinking provides evidence for photoionization mechanism of Luminescence Blinking



# Physical Size Regimes for Semiconductor Nanocrystals



Evolution from molecules to solid state as size increases