Semiconductor Nanocrystal Quantum Dots

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Sept. 23, 2004

Outline

1. Quantum Devices
   - Particle in a Box
2. Quantum Dots
   - Particle in a Sphere
3. Quantum Size Effect

4. Nanocrystal Growth

5. Biological Tagging

Quantum Devices

Quantum Well Review

Thin semiconductor layer(s) with reduced bandgap result in quantum confinement

Time-independent Schrödinger eqn – $$-\frac{\hbar^2}{2m^*}\frac{d^2\psi(z)}{dz^2}+V(z)\psi(z)=E_n\psi(z)$$

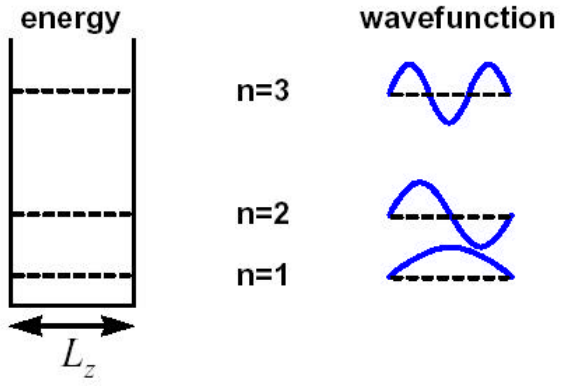
Infinite well – $$-\frac{\hbar^2}{2m^*}\frac{d^2\psi(z)}{dz^2}=E_n\psi(z)$$

Boundary conditions – $$\psi(0)=\psi(L_z)=0$$

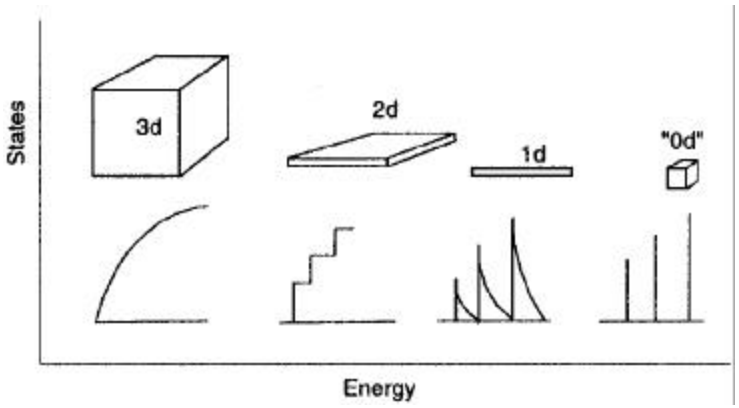
Eigenfunctions – $$\psi_n(z)=A_n\sin\left(\frac{n\pi z}{L_z}\right)$$

Energy levels (Eigenvalues) – $$E_n=\frac{\hbar^2}{2m^*}\left[\frac{n\pi}{L_z}\right]^2$$

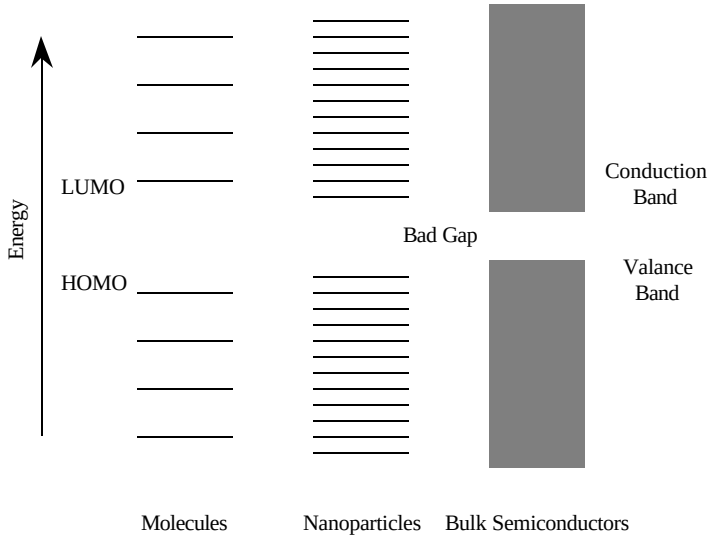
$$\left(\frac{1}{m^*}=\left[\frac{d^2E}{dk^2}\right]\frac{1}{\hbar^2}\right)$$



Size Quantization Effect



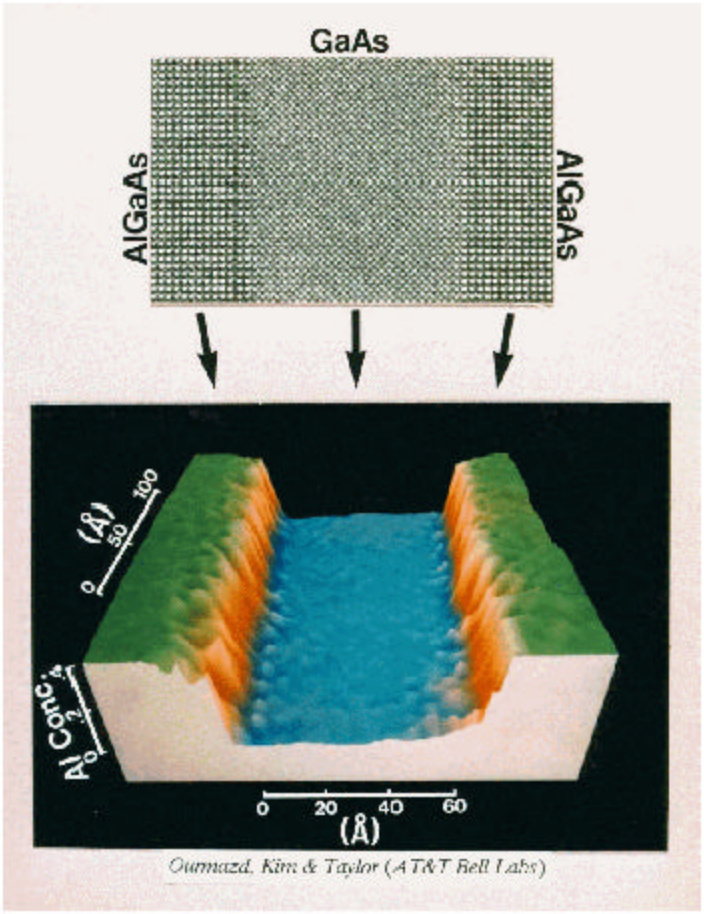
Density of states versus dimensionality



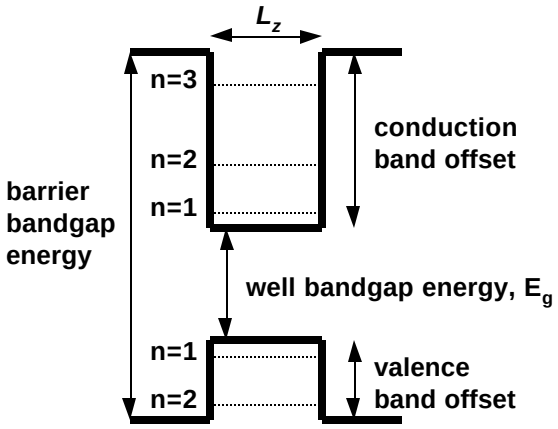
Available energy levels versus material type

Nann, T., Polymers and Adhesives in Microelectronics and Photonics, 2001. First International IEEE Conference on , 2001, 49-53

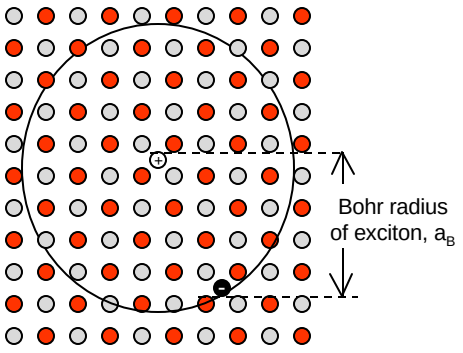
Single QW Semiconductor Structure



HRTEM of Single Quantum Well



$$E_n = \frac{\hbar^2}{2m^*}\left[\frac{n\pi}{L_z}\right]^2$$



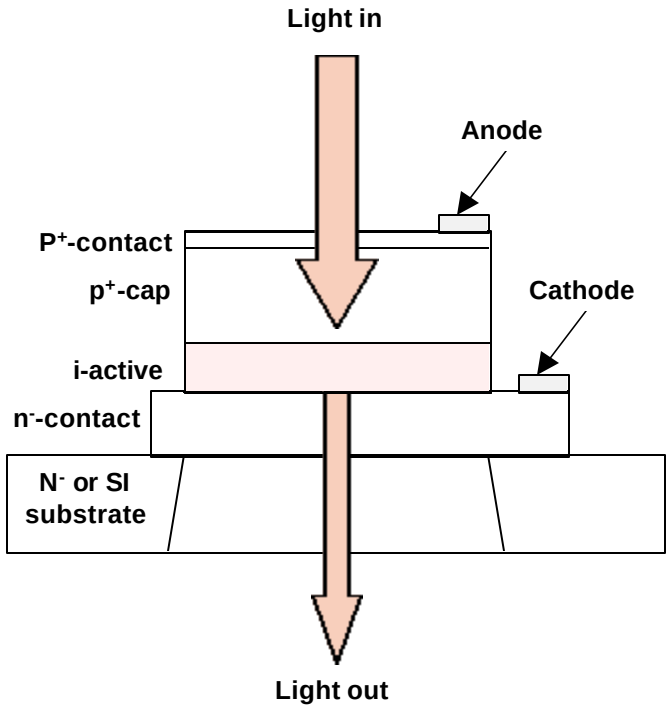
$$E_a = E_g + E_n^e + E_n^h - B_{ex}$$

Bulk Free Space EA Structure

Optical modulator based on a PIN diode structure

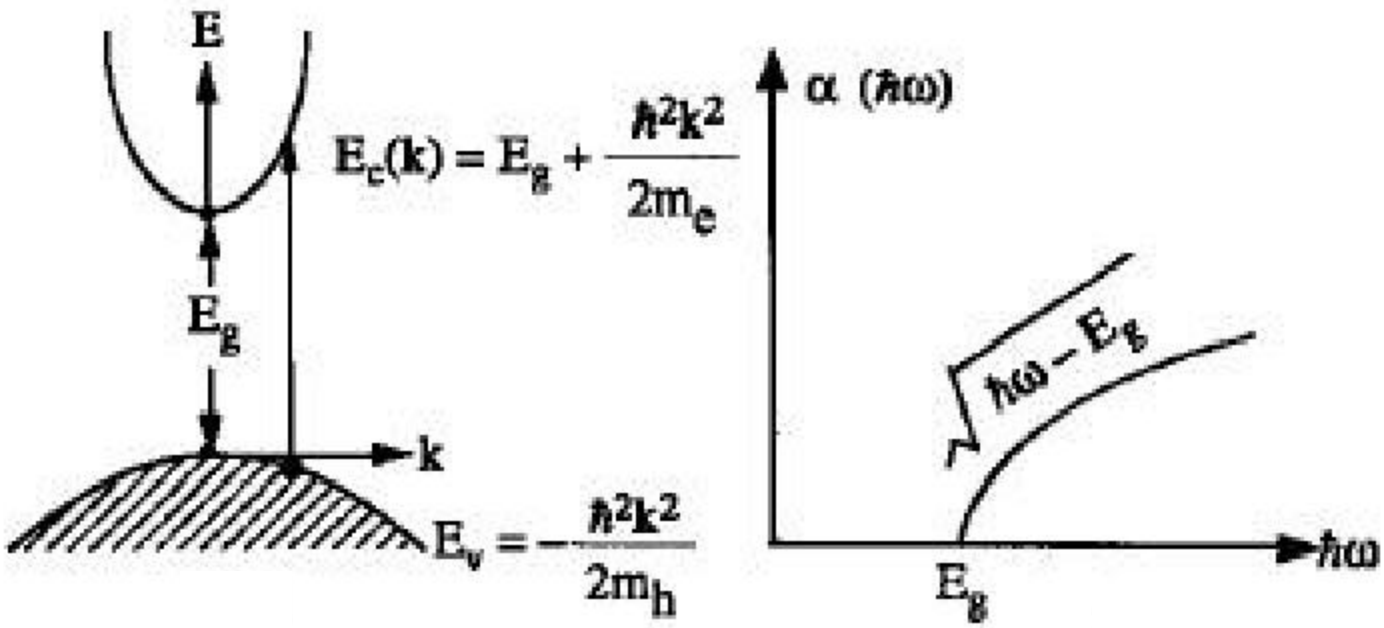
Transmission Devices

- grown doped layers are transparent at operating wavelength
- may be necessary to etch away substrate in some material systems (i.e. GaAs/AlGaAs)
- waveguide devices more common



Generic Transmission EA Device Structure

Bulk Semiconductor Absorption

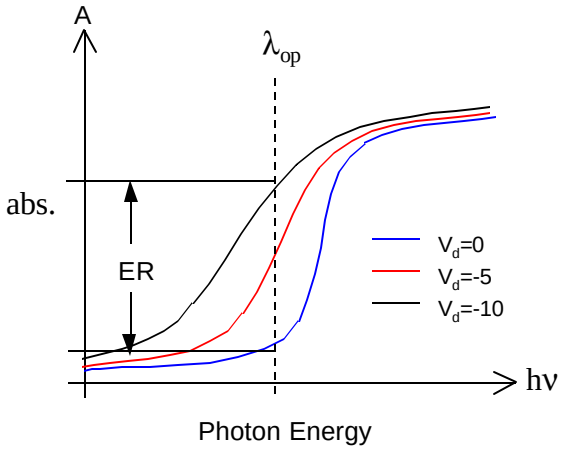


Absorption and band structure

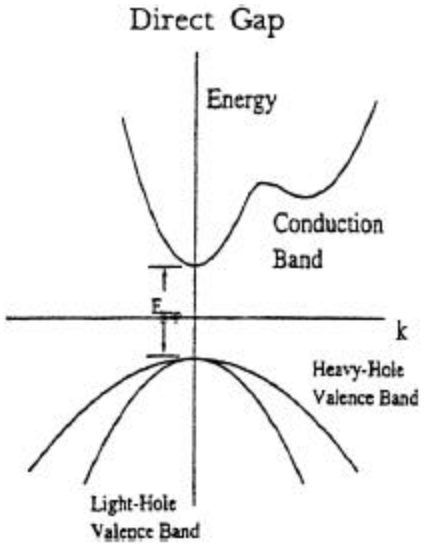
Bulk Semiconductor Absorption

Optical absorption is important for many types of semiconductor device

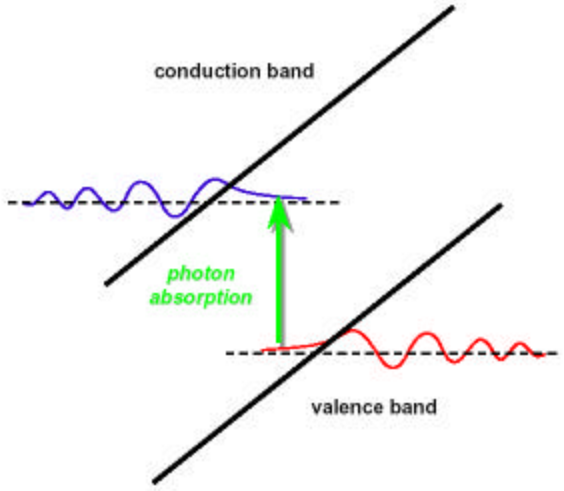
- e.g. electroabsorption (EA) modulators
- rely on change in absorption with applied reverse bias to a PIN diode structure
- early EAs used the Franz-Keldysh Effect (FKE) in bulk material
- Applied field causes band sloping ® change in absorption edge



FKE EA Modulator Characteristic



Typical band structure of a direct-gap semiconductor



Franz-Keldysh Effect

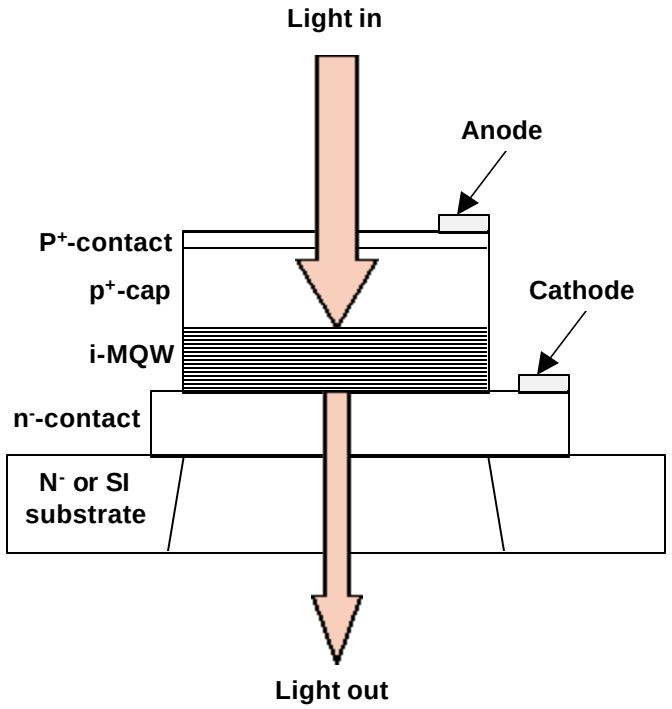
(Actually is a little more complicated - there are excitonic effects but E_b~4.2meV)

MQW- EA (or SEED) Structure

Also based on a PIN diode structure

Transmission Devices

- quantum wells grown using MBE, MOCVD or CBE
- reflection and F-P devices also possible through mirror stack growth

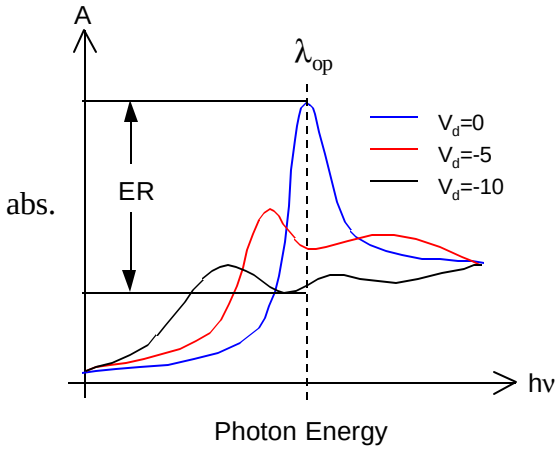


Generic Transmission MQW-EA/SEED Device Structure

Quantum Well Confinment

Modern EAs (and SEEDs) utilize the Quantum-Confined Stark Effect (QCSE)

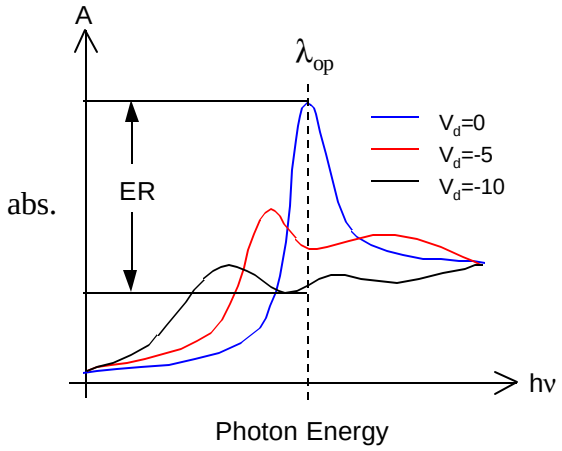
- stronger effect than FKE -> smaller interaction length required
  - » still need many wells for a vertical device
- trade-off with wavelength sensitivity



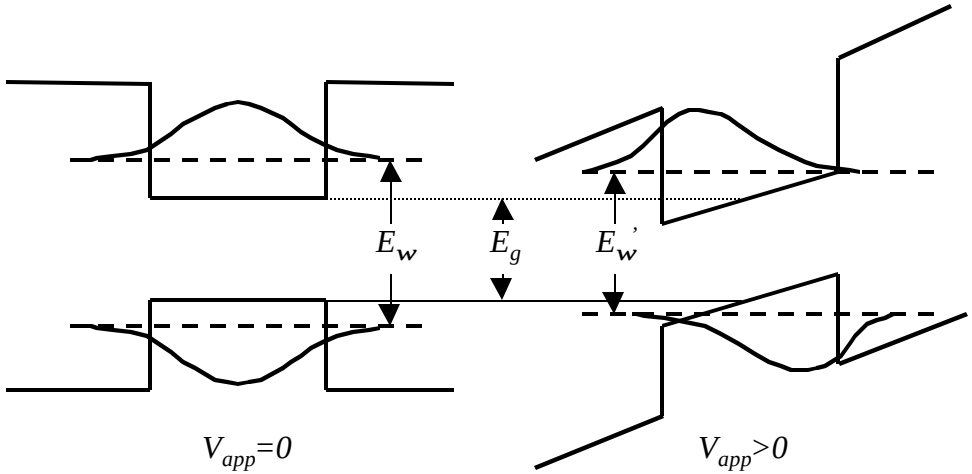
QCSE EA Modulator Characteristic

- ➥ Behaviour is a little more complex in the case due to quantum effects
- ➥ Note there are two regimes in which this can be used

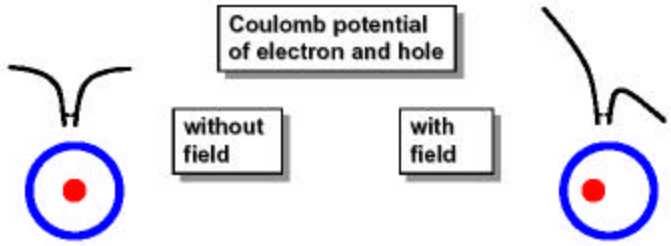
QCSE - Putting it all together



QCSE EA Modulator Characteristic



QCSE Band Tilt Shift

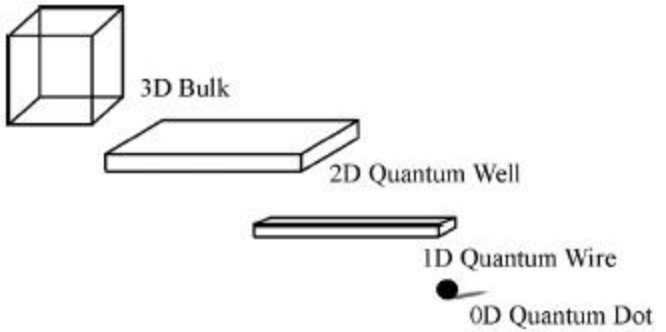


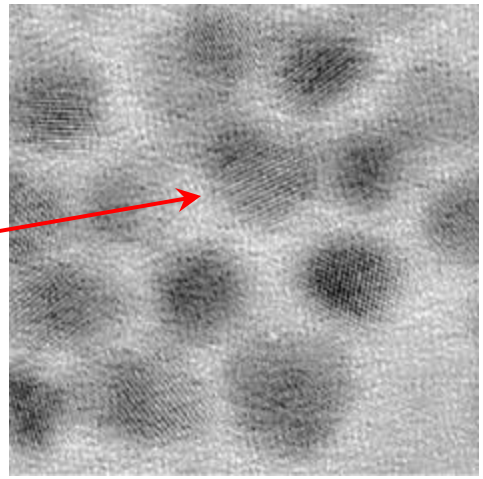
QCSE Exciton Energy Shift (also causes field ionization)

Quantum Dots

What are Quantum Dots

- **Quantum dots are nanometer-sized semiconductor crystals with size-dependent optical, physical, electronic and chemical properties**
  - **highest degree of quantum confinement available**





Properties of Semiconductor QDs

- Size-tuneable properties
- Discrete optical exciton transitions
- Large oscillator strengths & nonlinear response
- Highly luminescent
- Photochemically robust
- Compatible with a variety of hosts
  - (e.g. SiO_2, polymer, etc.)

- Act as a "molecular semiconductor"

Particle in a Sphere

Particle in a Sphere

Effects seen in a spherical nanoparticle can be modeled as quantum confinement in a sphere

T-I Schrödinger eqn separable – $\psi_{nlm}(z) = R_{nl}(r) Y_{lm}(\theta, \phi)$

Radial T-I Schrödinger eqn – $-\frac{1}{r}\frac{d^2(rR_{nl}(r))}{dr^2} + \left(\frac{l(l+1)}{r^2} - k^2\right) R_{nl}(r) = 0$

Boundary condition – $R_{nl}(a) = 0$

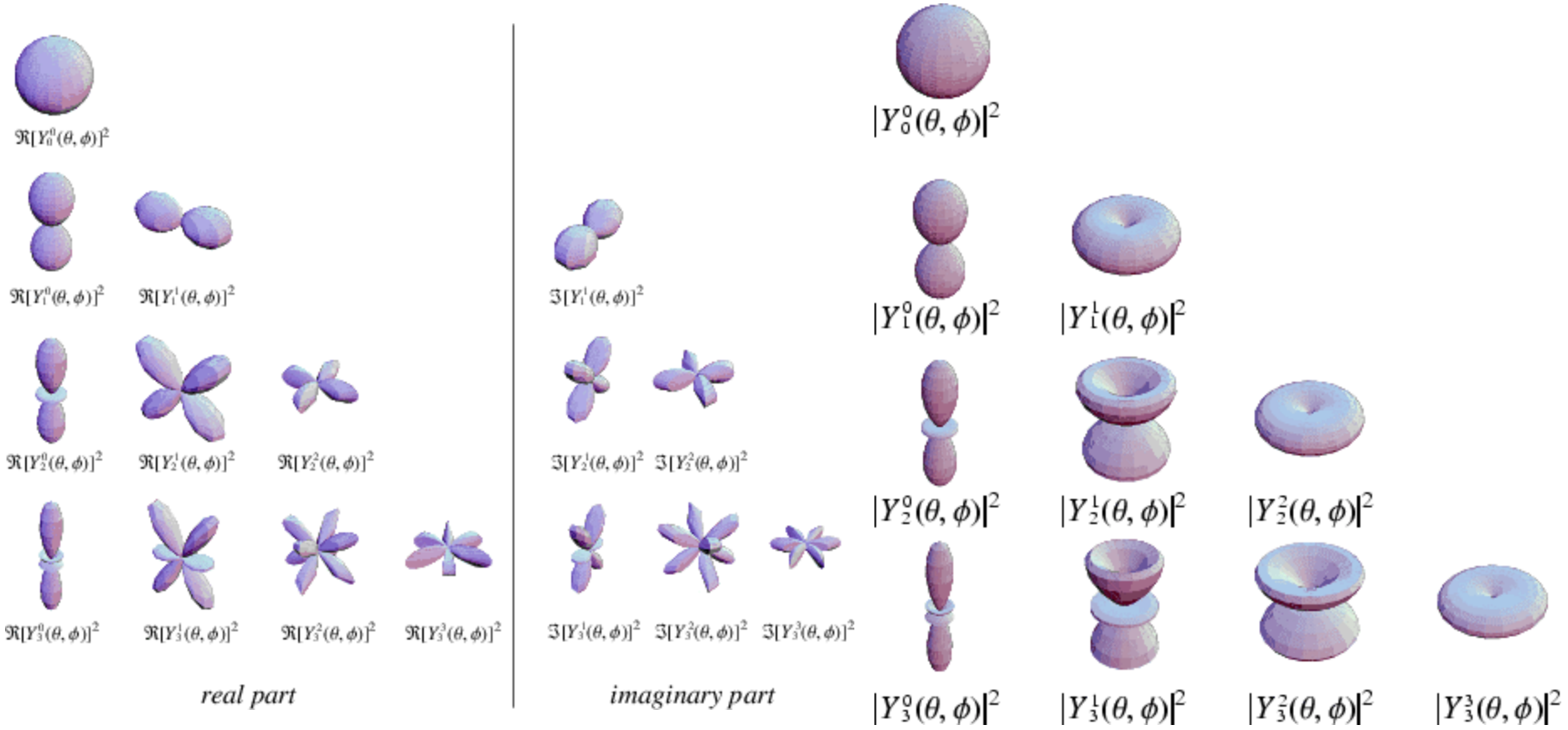
Eigenfunctions – $R_{nl}(r) = \sqrt{\frac{2}{a^3}} \frac{j_l(\kappa_{nl} r/a)}{j_{l+1}(\kappa_{nl})}$

Energy levels (Eigenvalues) – $E_{nl} = \frac{\hbar^2}{2m_r^*}\left[\frac{\kappa_{nl}}{a}\right]^2$

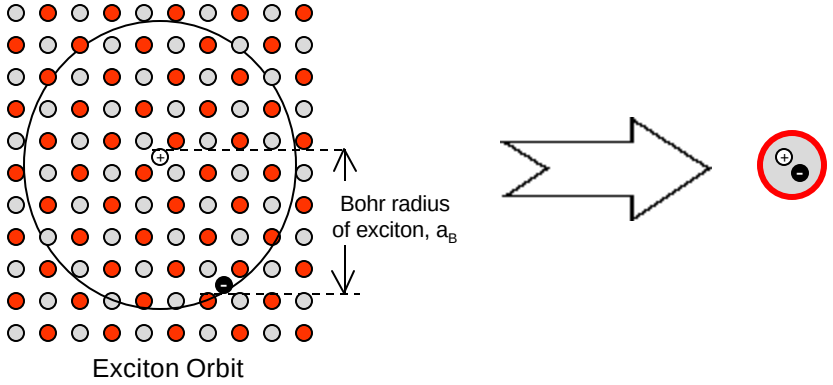
$$\left(\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

Particle in a Sphere

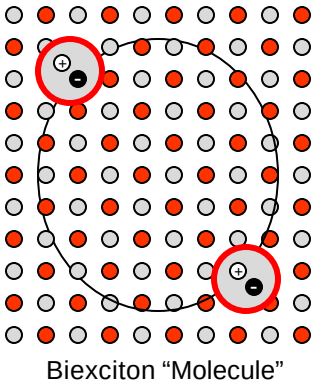
Spherical Harmonics



Excitons in a Sphere



NC exciton energy - $$\hbar\omega_{oe} = \hbar\omega_g + \frac{\hbar^2}{2m_r^*}\left[\frac{k_{nl}}{a}\right]^2 - \frac{1.786e^2}{\varepsilon a} - 0.248E_R \qquad \textit{where} \qquad E_R = \frac{\hbar^2}{2m_t a_B^{\,2}}$$



NC biexciton energy - $$\hbar\omega_{ob} = 2\hbar\omega_{oe} - \Delta E_b$$

P. K. SEN, J. T. ANDREWS, Superlattices and Microstructures, Vol. 29, No. 4, 2001

Exitons in a Sphere - other issues

- Optical phonons
  - polar coupling depends on charge distribution
- Acoustic phonons
  - deformation modes of the sphere - E~1/a
- Phonon bottleneck
  - does it really exists - none observed in II-VIs (Moire effect?)
- Auger
  - a moderate optical powers biexciton-Auger can occur
  - one high energy carrier ejected to the matrix
  - long return time for ejected carrier (up to 10 min. observed)
  - significant problem for NLO applications (including amps)

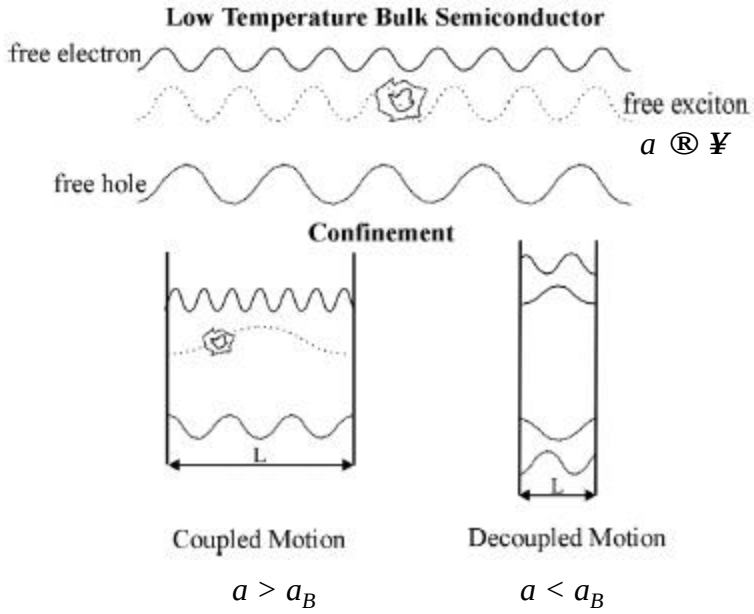
Effect of confinement on mass*

- For little or no confinement with $a > a_B$ the Coulomb force dominates and the exciton acts as a single particle so:

$$m_r^* = m_e^* + m_h^*$$

- For strong confinement with $a < a_B$ the wave functions of the electron and hole are decoupled by the dominant quantizations effect so:

$$\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$



$$E_{nl} = \frac{\hbar^2}{2m_r^*}\left[\frac{k_{nl}}{a}\right]^2$$

Quantum Size Effect

Engineering Desired Properties

- Control of NC size determines
  - Linear optical properties
  - Nonlinear optical response
  - Luminescence wavelength
  - Electrical properties
  - Etc.

Bohr diameter and mass*

Semiconductor	Exciton Bohr Diameter	Band gap Energy
CuCl	13Å	3.4 eV
ZnSe	84Å	2.58 eV
CdS	56Å	2.53 eV
CdSe	106Å	1.74 eV
CdTe	150Å	1.50 eV
GaAs	280Å	1.43 eV
Si	37Å(longitudinal) 90Å(transverse)	1.11 eV
Ge	50Å(longitudinal) 200Å(transverse)	0.67 eV
PbS	400Å	0.41 eV

Exciton Bohr diameters and band gap energies for various semiconductors.

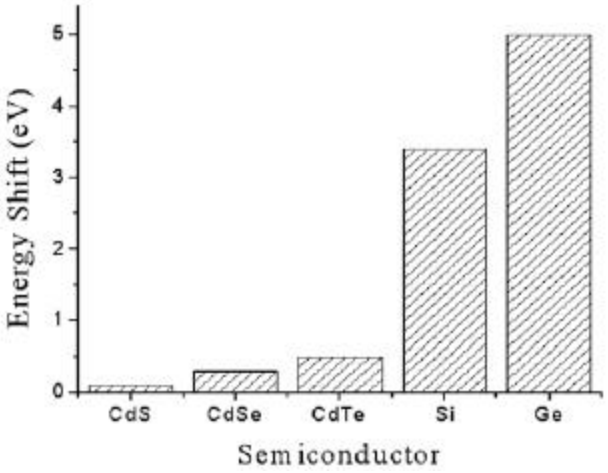
Semiconductor	m_e^*	m_h^*
GaN	0.2	0.8
CdS	0.2	0.9
CdSe	0.13	0.8
CdTe	0.11	0.35
GaAs	0.07	0.5
Si	0.98(longitudinal) 0.19(transverse)	0.52
Ge	1.58(longitudinal) 0.08(transverse)	0.3
PbS	0.1	0.1

Electron and hole masses for various semiconductors.

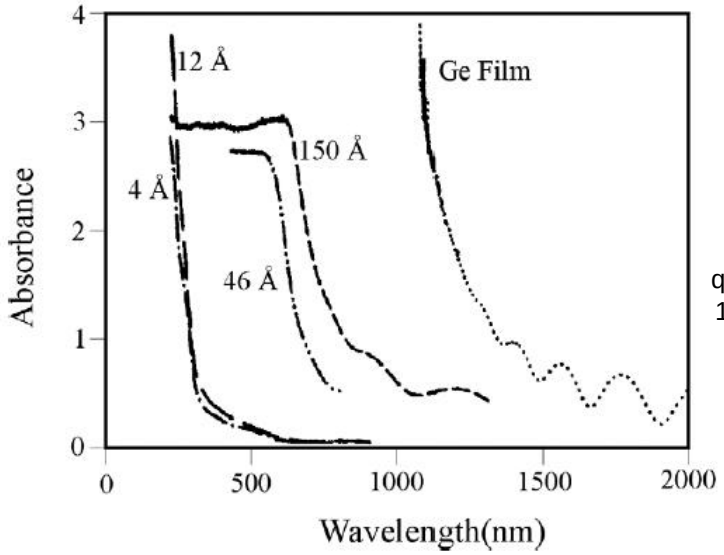
Remember - $m \propto m^{*-a}$ where $a_{phonon} = 5/2$, $a_{impurity} = 1/2$ (also ballistic)

T. J. Bukowski et al, Critical Reviews in Solid State and Materials Sciences, 27(3/4):119–142(2002)

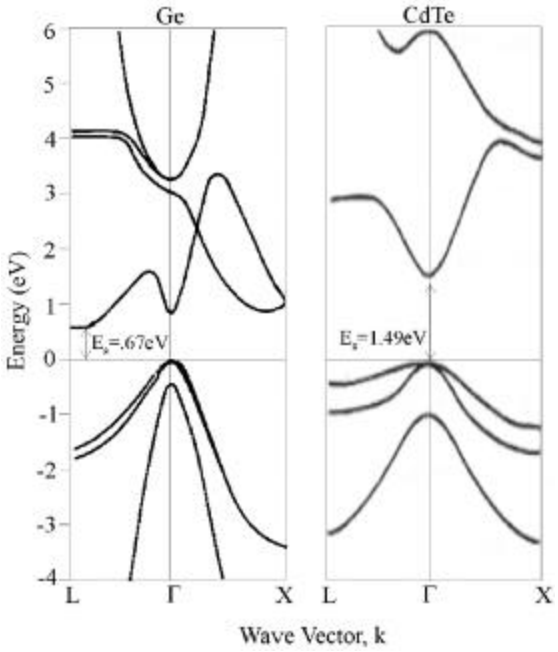
Quantum Well Review



Relative degree of band gap energy shifts due to quantum confinement for several direct and indirect semiconductors.



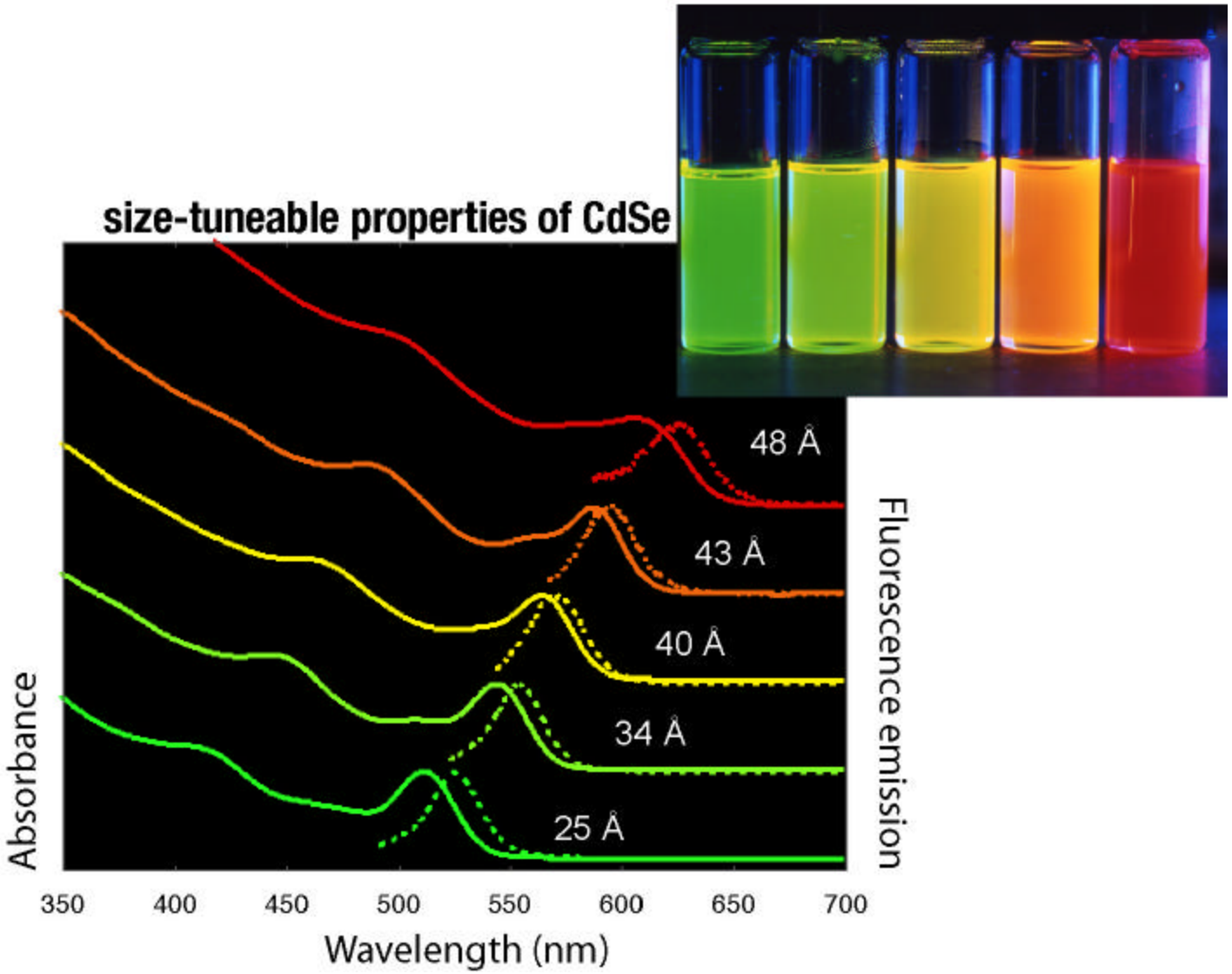
Absorbance vs. wavelength for a Ge film and for various Ge quantum dots 150 Å, 46 Å, 12 Å, and 4 Å in diameter.



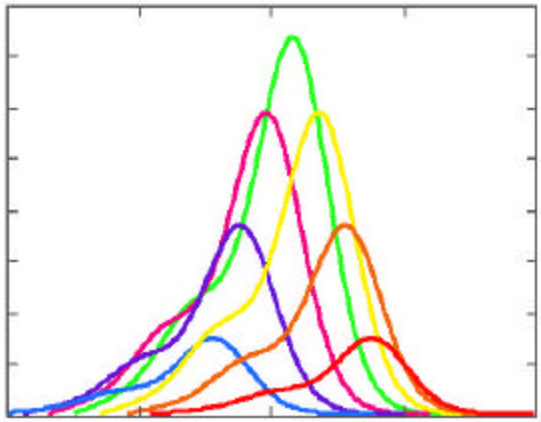
Energy band diagrams for germanium, Ge, and cadmium telluride, CdTe.

T. J. Bukowski et al, Critical Reviews in Solid State and Materials Sciences, 27(3/4):119–142(2002)

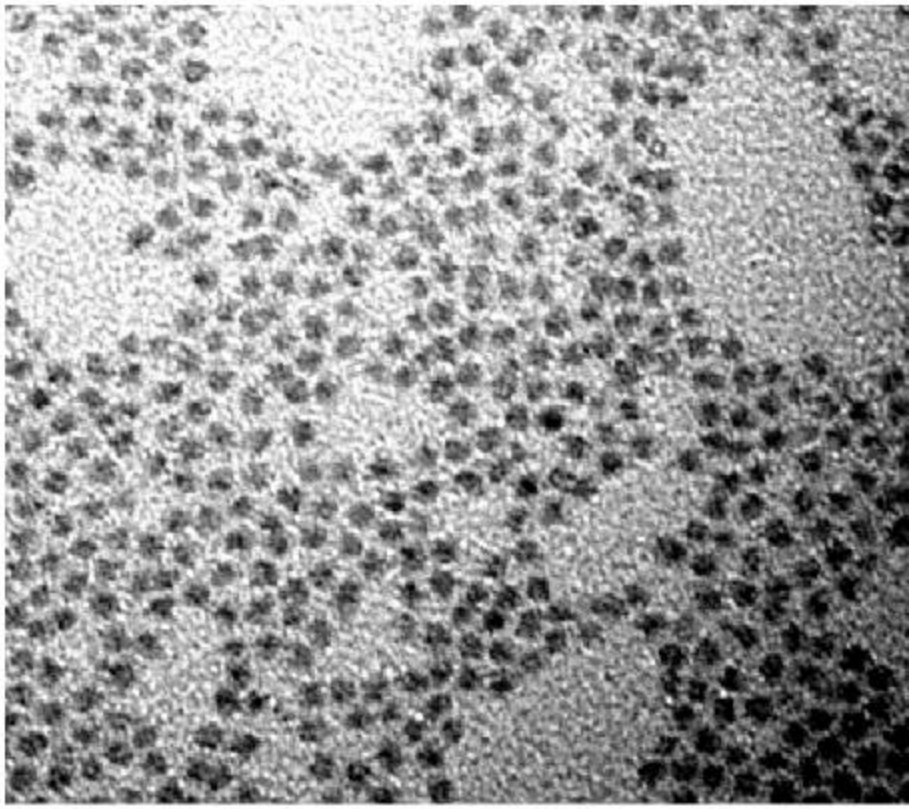
Quantum Confinement



Finite Size Distribution - Polydispersity



inhomogeneous distribution
of optical spectra

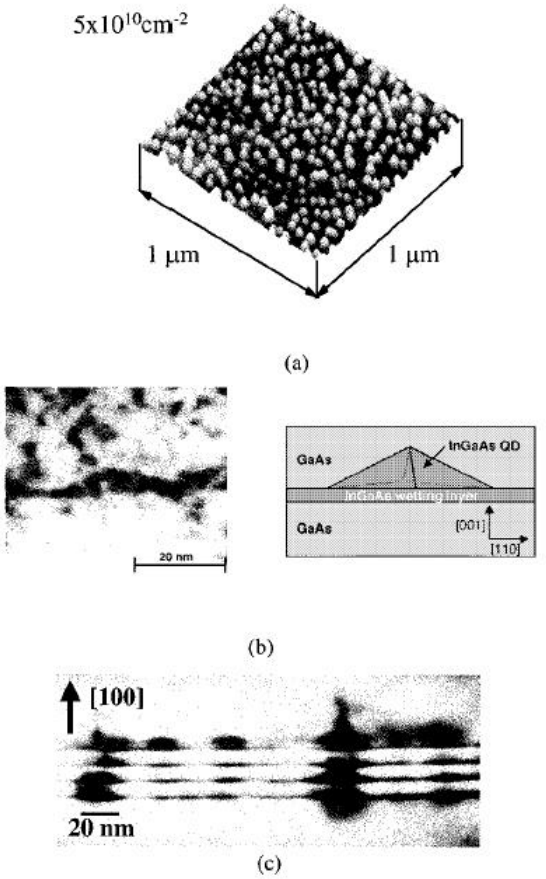


CdSe quantum dots
TEM image

20 nm

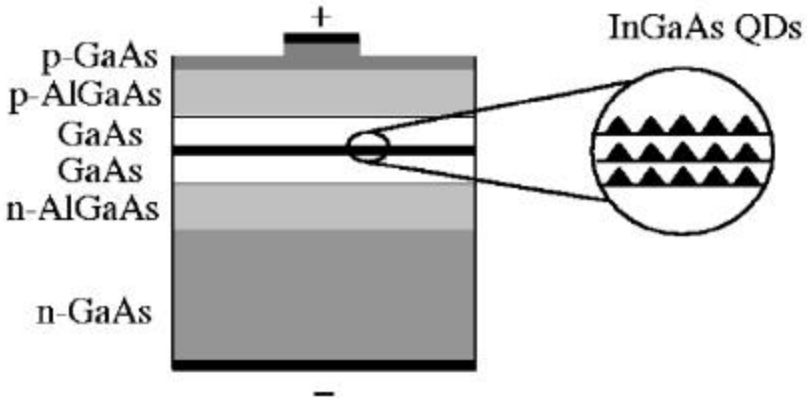
Nanocrystal Growth

Island Growth of QDs



Structural characteristics of In Ga As–GaAs self-organized QD's:
(a) AFM image,
(b) cross-sectional TEM image of single dot and its schematic, illustrating a near-pyramidal shape, and
(c) XTEM image of 4 layers of vertically coupled dots with 15 Å of GaAs barrier layers in between.

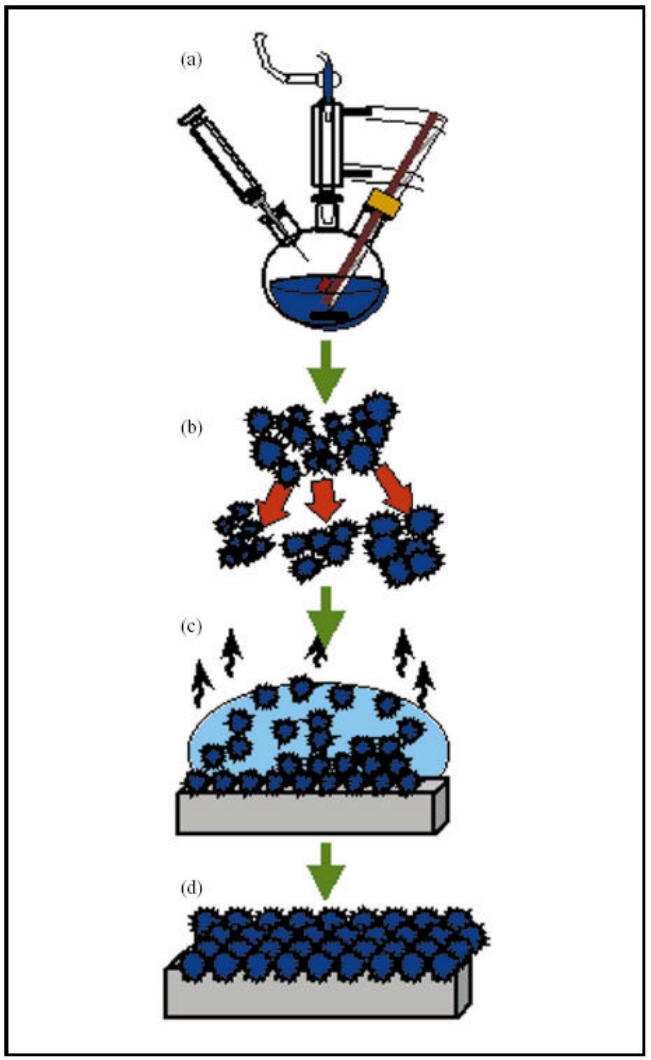
BHATTACHARYA et al., IEEE JOUR OF SEL TOP IN QUANT ELECTS, VOL. 6, NO. 3, MAY/JUNE 2000



Typical ridge-guide structure containing arrays of InGaAs QDs clad in GaAs grown by MOCVD.

BORRI et al, IEEE JOUR OF SEL TOP IN QUANT ELECTS, VOL. 8, NO. 5, Sept/Oct 2002

Chemical Synthesis of Nanocrystals



(a) synthesize NC samples by high-temperature solution-phase routes
- usually using hot surfactant, n-trctylphosphine oxide (TOPO)

(b) narrow the NC sample size distribution by size-selective precipitation

(c) deposit NC dispersions that self-assemble

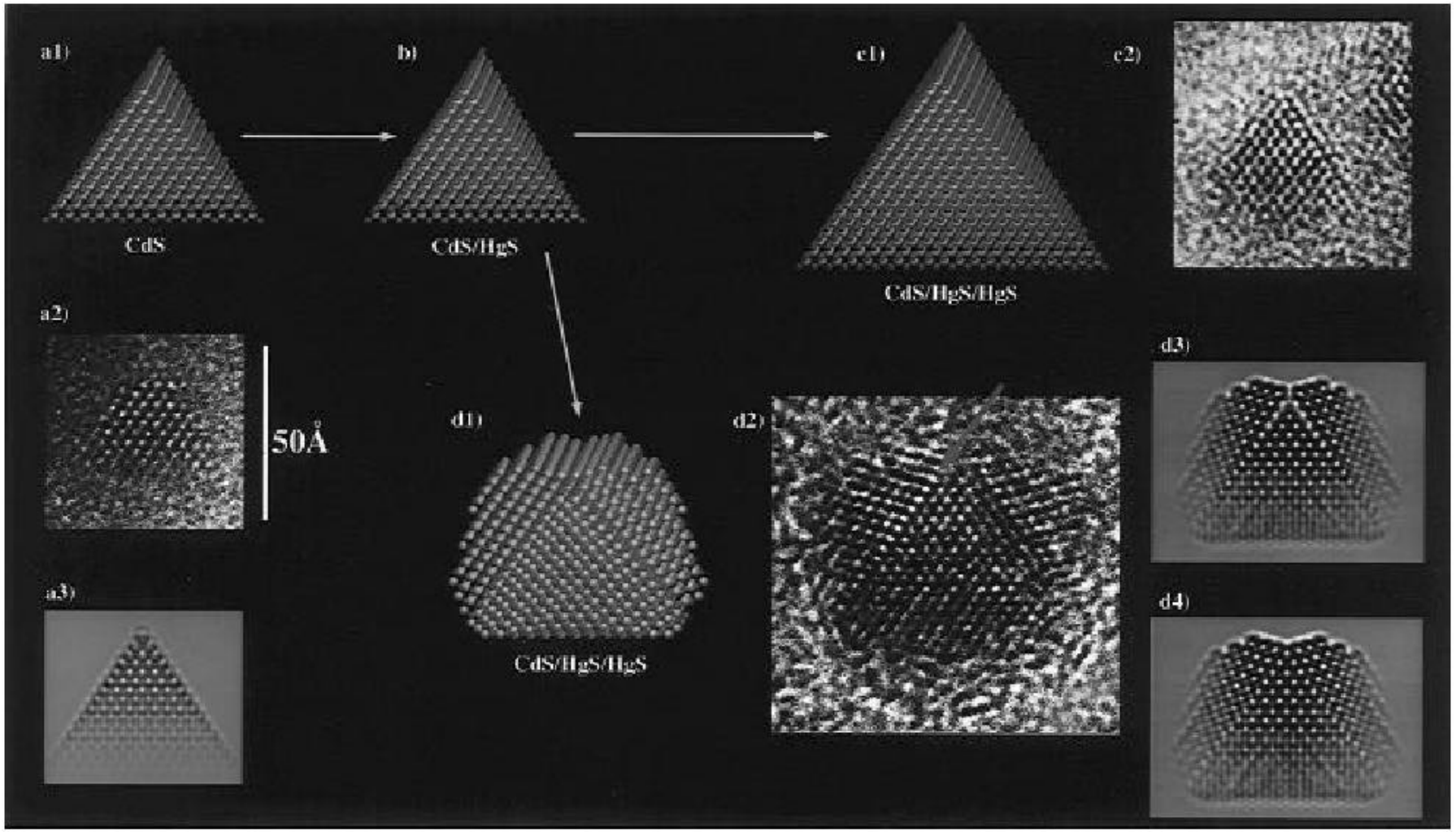
(d) form ordered NC assemblies (superlattices) or disperse

C. B. MURRAY ET AL. IBM J. RES. & DEV. VOL. 45 NO. 1 JANUARY 2001

Colloidal Materials

- Colloidal NCs are mostly II-VI materials
  - CdSe, CdTe, CdS
  - HgSe, HgTe, HgS
  - PbSe, PbS
  - ZnS
  - Etc.
- Most common - CdSe & CdTe

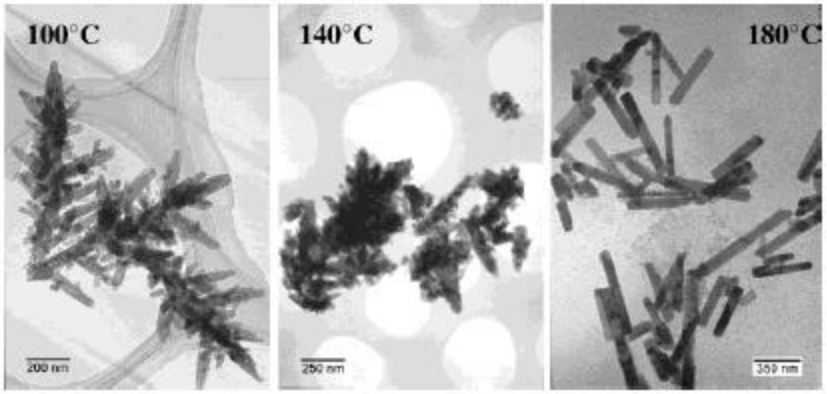
Chemical Synthesis of Nanocrystals



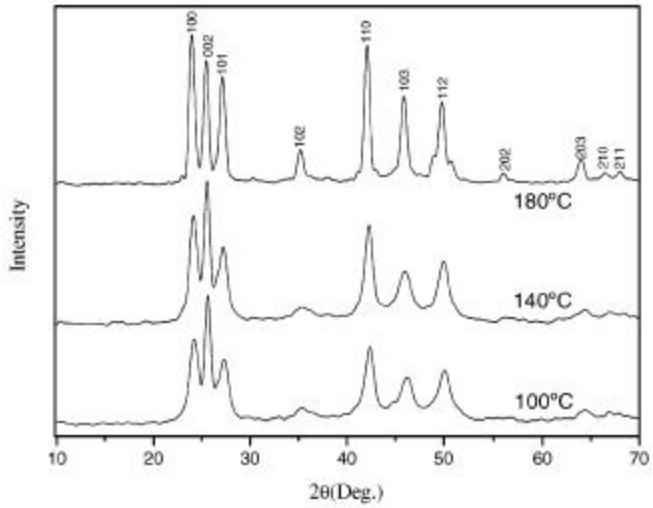
Transmission electron microscopy study of the growth of a CdS/HgS/CdS quantum dot quantum well. The micrograph of a CdS core cluster (a2) exhibits tetrahedral morphology which is in agreement with TEM simulation (a3). The corresponding molecular model (a1) shows that all surfaces are Cd terminated (111). Picture (b) shows a model of the CdS particle after surface modification with Hg. A typical micrograph of a tetrahedral CdS/HgS/CdS nanocrystals is shown in (c2) along with a corresponding model (c1). Model (d1) and micrograph (d2) represent a CdS/HgS/CdS nanocrystal after winned epitaxial growth. The arrow marks the interfacial layer exhibiting increases contrast due to the presence of HgS, in agreement with the simulation (d3). No contrast is seen in a simulation of a model with all Hg replaced by Cd (d4).

Alivisatos, J. Phys. Chem., Vol. 100, No. 31, 1996

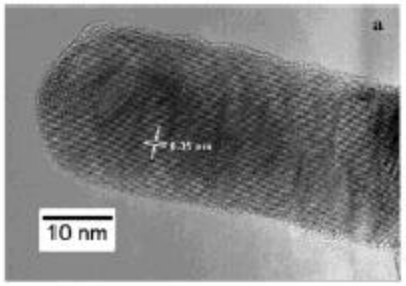
CdSe Nanorods and Fractal Nanocrystals

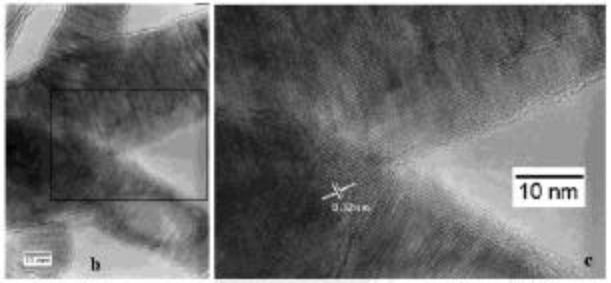


Evolution from CdSe fractals to nanorods based on reaction temperature



XRD patterns of CdSe nanocrystals





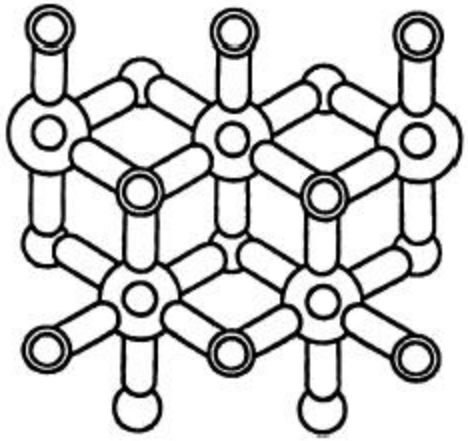
HRTEM images of CdSe fractals:

(a) a typical fractal tip

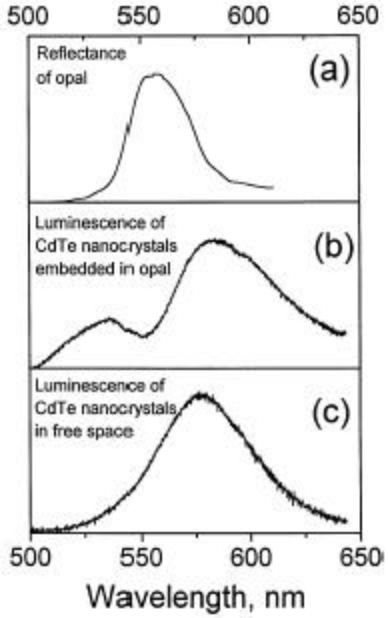
(b) crossed branches

(c) partial enlarged detail of two crossed branches in the black frame of b.

Dispersal of NCs in Opal Matrix



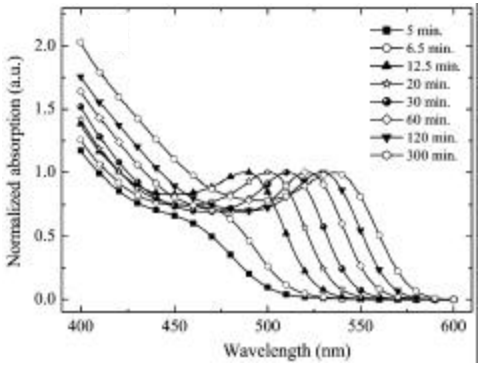
Opal structure - spheres represent voids connected by channels



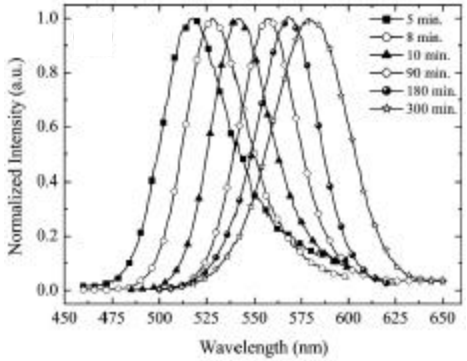
Modification of the spontaneous emission of CdTe nanocrystals embedded in opal. Nanocrystal mean diameter is 2.4 nm.
(a) Optical reflection spectrum of opal sample
(b) modified spontaneous emission spectrum of CdTe nanocrystals in opal
(c) reference emission spectrum of CdTe nanocrystals in free space.

S.V. Gaponenko et al., Journal of Luminescence 87-89 (2000) 152-156

Growth of CdTe Nanocrystals

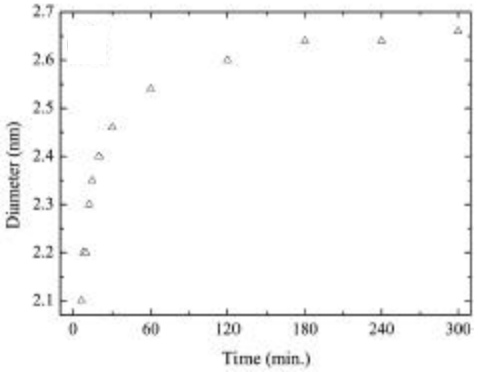


Absorption spectra (normalized to the first absorption maximum, except for 5 and 6.5 min)



Emission spectra (normalized to the emission maximum, λ_{ex} = 400 nm)

All spectra recorded at room temperature.



Average size of CdTe QDs (diluted in toluene) taken for a synthesis at 165 C at different time intervals.

- synthesized in a mixture of TOP and DDA
- fast initial growth is observed in the first 30 min followed by a slower growth to the final particle size
- luminescence lifetimes of up to approximately 10 ns

S. F. Wuister et al, Phys. Chem. Chem. Phys., 2003, 5, 1253–1258

Biological Tagging

An Array of QD Luminescent Tags

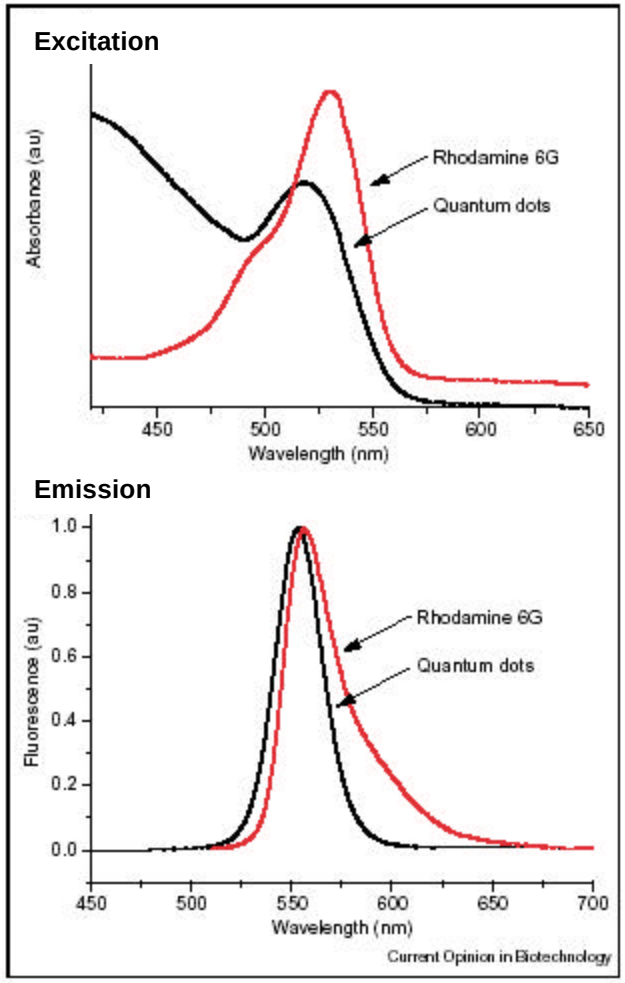
Luminescent quantum dots for multiplexed biological detection and imaging Chan *et al.*

Ten distinguishable emission colors of ZnS capped CdSe QDs excited with a near-UV lamp. From left to right (blue to red), the emission maxima are located at:

443, 473, 481,500, 518, 543, 565, 587, 610, and 655 nm.

QDs vs Dye Molecule Tags

- Protein coated QDs very stable (>2yrs)
- Narrow spectral width (FWHM~25nm)
- Broad excitation spectrum
- High quantum yields (40-50%)
- High cross-section
- Low photobleaching
- Compared to rhodamine 6G
  - 20x brighter
  - 100-200x more stable



ZnS-capped CdSe QDs grown in TOPO

Attaching the Tag

Tagging can be accomplished in a number of ways:

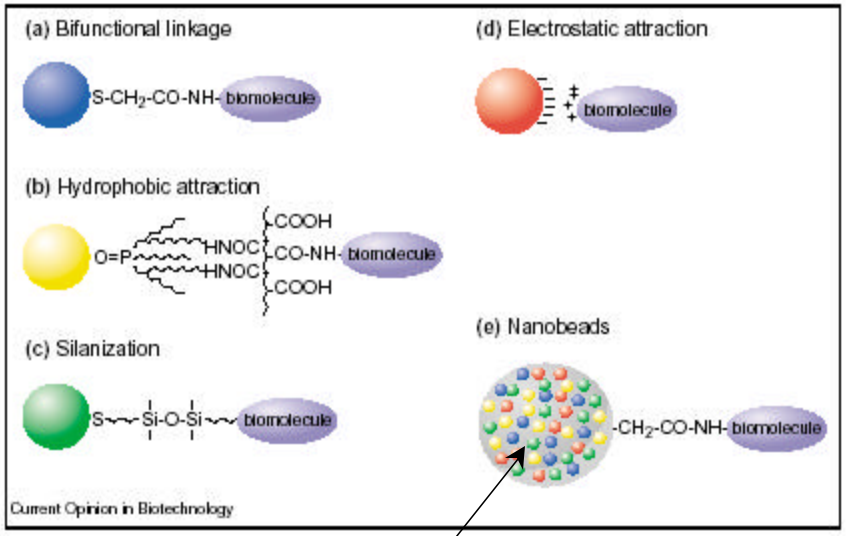
(a) Use of a bifunctional ligand linking QDs to biomolecules

(b) TOPO-capped QDs bound to a modified acrylic acid polymer by hydrophobic forces.

(c) QD solubilization and bioconjugation using a mercaptosilane compound

(d) Positively charged biomolecules are linked to negatively charged QDs by electrostatic attraction

(e) Incorporation of QDs in microbeads and nanobeads



Micro/nanobeads can individually carry a "code" to expand tag range

QD Flourescent Tags in Action

Carleton UNIVERSITY

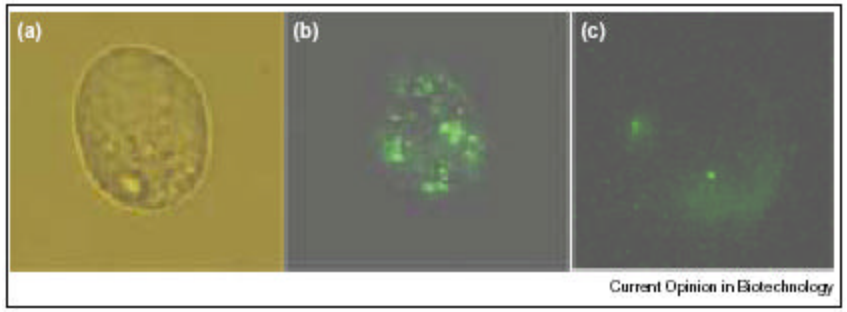
Fluorescence imaging of folate-conjugated QDs inside human cancer cells.

(a) Brightfield image of control KB cell (without QDs).

(b) KB cell incubated with folate-conjugated QDs.

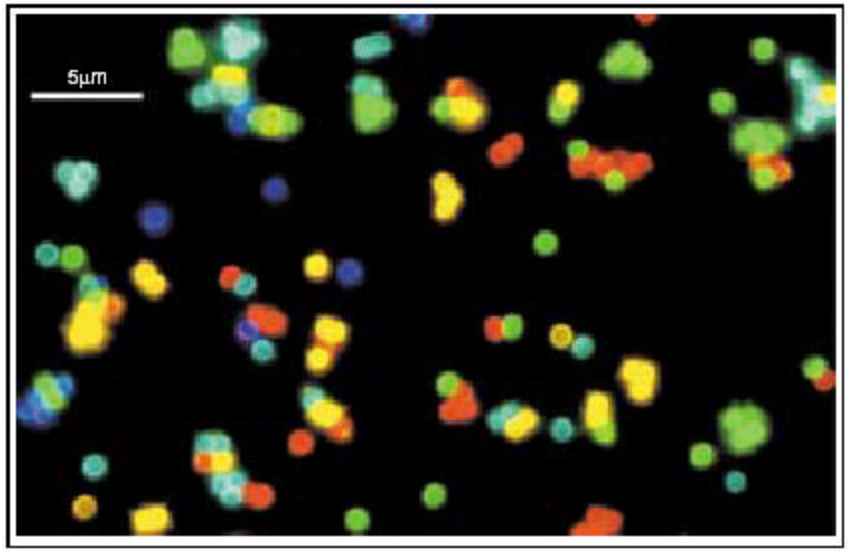
(c) KB cell incubated with bovine serumalbumin-conjugated QDs.

Receptor-mediated endocytosis occurs only when the QDs are conjugated to folic acid, which is recognized by folate receptors overexpressed on the surface of cancer cells.

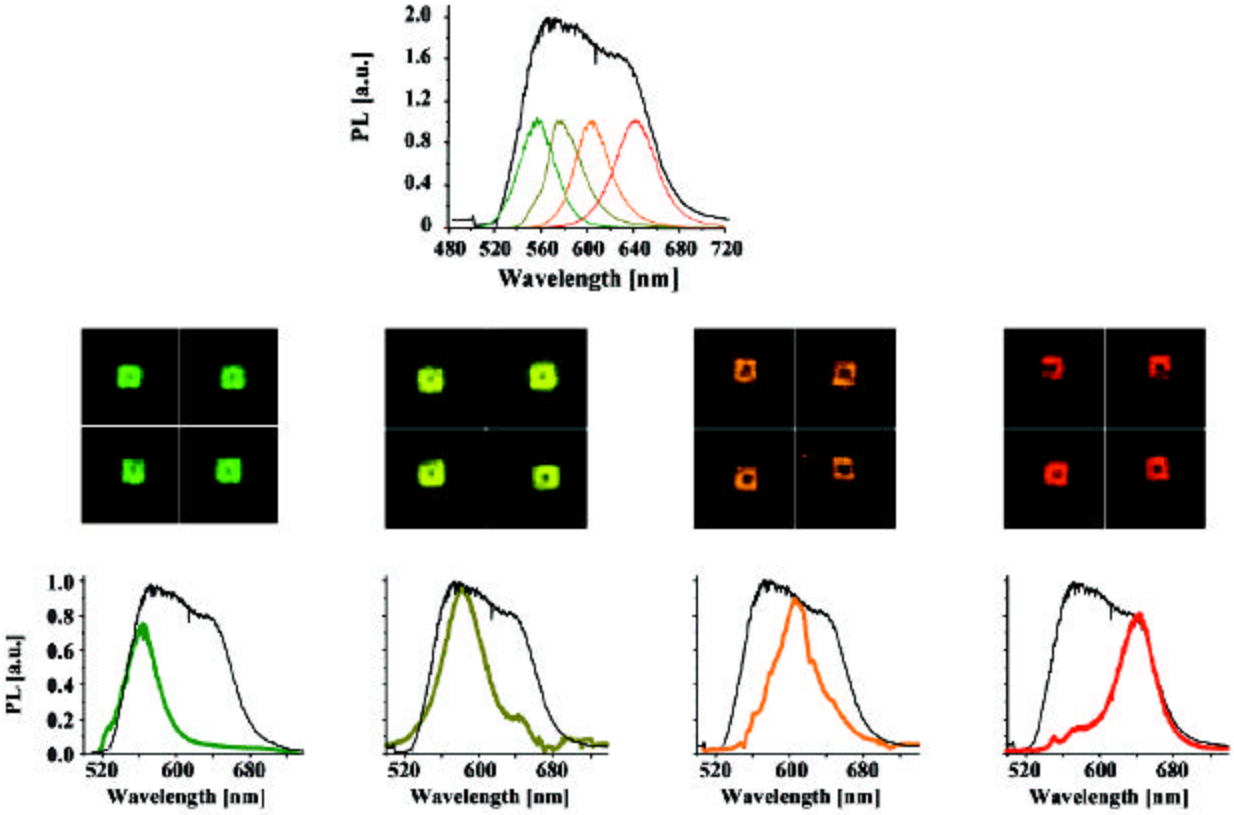


Fluorescence micrograph of a mixture of CdSe/ZnS QD-tagged beads emitting single color signals at:

484, 508, 547, 575, and 611 nm



Sorting with DNA



The fluorescence of the solution (in black) is the superposition of the fluorescence of four different DNA-nanocrystal samples. All spectra are normalized.

The same solution is exposed to four substrates, each being activated with a different oligonucleotide. The gold patterns exhibit a strong fluorescence with a minimal background signal. The capture time is 5 s.

The fluorescence spectrum of the squares (color) shows significant narrowing compared to that of the solution (black), and each set of squares has a characteristically different spectrum.

Conclusions

- **A very cross-disciplinary field requiring a variety of scientific and engineering expertise**
- **Many exciting applications emerging in a number of disparate fields**
  - **enhanced optoelectronic devices**
  - **NLO “all-optical” elements**
  - **Biological cross-over applications**
  - **etc.**
- **Semiconductor nanocrystals/QDs now “ready for prime-time” in some applications**