Nanoscience and nanotechnology as seen through quantum dots

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What is “nano”?
Size scales
Categories

A preliminary look at the buzz

• What happens when the transistors are the size of electrons?
• What happens when the wires are molecules?
• How will computers work when they are no longer classical?

Nano in the news

[Graphs and charts showing trends in nanotechnology publications, patents, and news articles over time.]
Nano in the news: controversy

- Toxicity (asbestos revisited?)
- ‘Grey goo’? (self-assembly run amok) – Eric Drexler
- Playing God? – Ray Kurzweil, Bill Joy

- A reality check:
  courtesy of Rick Smalley (Rice) and George Whitesides (Harvard)

What is different about “nano”

Macrosopic device performing macrosopic tasks:
fire → steam engines → computers

Microscopic objects serving macrosopic tasks:
most of chemistry (“One word… plastics”)

A new paradigm:
microscopic functionality

NanoScience → NanoTechnology

- Computers
- Lasers
- Solar energy
- Medicine
- Materials

The path from science to technology

- MRI – a good thing!

- But where did it come from?
  - Quantum Mechanics (1920’s)
  - I.I. Rabi and atomic physics (Nobel 1944)

- NMR: fundamental and applied science (1950 – present)
- MRI: 1977
Nano and computers: Moore’s law

Hitting the brick wall

Problem
All the incremental progress will stop in a couple of decades!

Can we use nanoscience to make a ‘quantum leap’?

- Analog circuits
- Digital circuits
- Quantum circuits???
  Incremental → Transformative?
Quantum computers?

- $101$ - voltage or light (on/off/on)

$$|\psi\rangle = a|000\rangle + b|001\rangle + c|010\rangle + d|011\rangle + e|100\rangle + f|101\rangle + g|110\rangle + h|111\rangle$$

- Let's turn on quantum mechanics.

- What does this $|\psi\rangle$ mean?

Lasers: another good thing

- Telecommunications
- Surgery
- Medical imaging
- Machining
- Defense
- Fundamental Science

Lasers & Nano: smaller, cheaper, better

Making the Internet on the cheap – quantum wells
Making the Internet really cheap! quantum dots

Energy:

Statement of the problem

- Increasing population + increasing energy needs/person = global energy problem
- Finding energy sources and ultimately finding clean energy sources
- Current consumption at 13 TW-year
- Projected need: 30 TW-year by 2050
- 600 TW of solar energy reaches earth at practical sites (10,000 TW total)
Solar cells: finding the Holy Grail

- The problem: global energy needs
- A solution: renewable energy (solar)
- The reality:
  - efficient & expensive
  - inefficient & cheap

Nano and solar cells

- Harvesting, collecting, and storing energy
- Can we perform these operations cheaply and efficiently?
- Solutions:
  - Light harvesting
  - Quantum dots
  - Conducting polymers

A few other areas of NanoScience research

- Materials – learning from Nature
- Medicine
  - “monitoring, control, construction, repair, defense, and improvement of human biological systems, working from the molecular level, using engineered nanodevices and nanostructures.” (R. Freitas)

Our activities in nanoscience

- How do quantum dots actually work?
- Dynamics: lasers & photovoltaics
- Artificial atoms: cryptography & basic physics
- Optical gain: lasers and light sources

A box for electrons (Zunger Nano Lett 2003)
A brief history of a quantum dot:

**Timescales**

It's routine to generate pulses < 1 nanosecond (10⁻⁹ s). Researchers can generate pulses a few femtoseconds (10⁻¹⁵ s) long.

<table>
<thead>
<tr>
<th>Computer clock cycle</th>
<th>Camera flash</th>
<th>Age of pyramids</th>
<th>Human existence</th>
<th>Age of universe</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻¹²</td>
<td>10⁻¹⁰</td>
<td>10⁻⁹</td>
<td>10⁻⁶</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>

1 femtosecond

Such a pulse is to one minute as one minute is to the age of the universe.

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Ultrafast Laser Spectroscopy: i.e. building a better camera

- New materials
  - Imaging, paints, coatings, structures

- Simple applications
  - Drug delivery, lasers

- “Disruptive” applications
  - Quantum computing
  - Solar energy

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One way of looking at things with a fast camera

The “Galloping Horse” Controversy
Palo Alto, CA 1872

Leland Stanford Eadweard Muybridge

Time Resolution: 1/60th of a second

(Trebino’s notes)
Outlook

- Popular buzz has upside and downside
- There probably will be a Nanotech bubble – brace yourselves and invest wisely!
- After the bubble bursts, then the real fun will start!
- Consider the startup vs. the large company
- Get ready for some cool things in the coming decades!!!

A brief introduction to quantum dots

- What is a quantum dot
- How to make a quantum dot
- How to characterize it
- How to think of it physically
- Some key publications
What is a quantum dot

- How do you make a nanometer sized object?
- How do you make many (identical) nanometer sized objects?
- How do the optical and electrical properties of this nanoscale object change with size?
- How does its optical and electrical properties change with its "dimensionality"?
- How do changes behave in nanoscale objects?
- How does charge transport occur in these materials?
- Do these nanoscale materials possess new and previously undiscovered properties?
- Are they useful?
How to make a quantum dot

Reaction solution (1:9:1 Cd:Se:Te):
169 µL Cd(CH₃)₂, 0.996 g Se⁹ and
12 mg TBP are injected into 12 g TOPG

1. Imaging – TEM, STM
2. Absorption, PL, PLE
3. TCSPC – lifetime
4. Dynamics – femtosecond spectroscopy

Figure 1. Procedure for synthesizing high-quality, monodisperse CdSe nanocrystals by the pyrolysis of organometallic precursors. This one-pot synthesis is designed to be used in a glove box. The reaction can be performed outside a glove box under argon.

How to characterize a quantum dot

1. Imaging – TEM, STM
2. Absorption, PL, PLE
3. TCSPC – lifetime
4. Dynamics – femtosecond spectroscopy
How to characterize a quantum dot

How to think of a quantum dot

Chapter 3

Length scales

Bilogic wavelength and etr ease esl

How to think of a quantum dot

How to think of a quantum dot
Density of states

The dot in the middle of the new quantum state is a quantum dot. It is an area with an energy level (i.e., the energy of the dot itself) that can only have a finite number of discrete states. Each energy level is associated with a specific set of allowed quantum states, which can be thought of as 'quantum states' in which the dot can exist.

3 Dimensions (in bulk)

Consider the volume of a cube with edge length $a$:

$$V = a^3$$

The number of states in this volume is:

$$N = a^3$$

The density of states is then:

$$\rho(E) = \frac{N}{V} = \frac{a^3}{a^3} = 1$$

For a rectangular parallelepiped:

$$V = abh$$

The number of states in this volume is:

$$N = abh$$

The density of states is then:

$$\rho(E) = \frac{N}{V} = \frac{abh}{abh} = 1$$

For a sphere with radius $R$:

$$V = \frac{4}{3} \pi R^3$$

The number of states in this volume is:

$$N = \frac{4}{3} \pi R^3$$

The density of states is then:

$$\rho(E) = \frac{N}{V} = \frac{\frac{4}{3} \pi R^3}{\frac{4}{3} \pi R^3} = 1$$

These results are independent of the shape of the volume.

8 Dimensions (or)

The density of states for a quantum dot is given by:

$$\rho(E) = \frac{N}{V} = \frac{a^3}{a^3} = 1$$

This is known as the quantum dot density of states, which is a constant for a quantum dot.
How to think of a quantum dot

Kronig-Penney Model

The solution to the Schrödinger equation for a periodic potential is given by the Bloch wave functions:

\[ \psi(x) = e^{ikx} \phi(x) \]

where \( \phi(x) \) is a function of the periodic potential.

The solution to the Kronig-Penney model is:

\[ \psi(x) = A \sin \left( \frac{2\pi x}{a} \right) \]

The Bloch wave vector is given by:

\[ k = \frac{2\pi n}{a} \]

The energy band structure is given by the eigenvalues of the Schrödinger equation.

For a given \( n \), the energy levels are given by:

\[ E_n = \frac{\hbar^2 \pi^2}{2m a^2} n^2 \]

Band Structure – Chemists View

Bands, Energy and Free Electrons
How to think of a quantum dot

Quantum Confinement

Effective Mass Approximation (on the context of nanostructures, in particular nanowires):

\[ m^* \approx \frac{m_e + m_h}{2} \]

\[ E = \frac{p^2}{2m^*} + \frac{U}{r} \]

Jain's order solution:

\[ \psi(r) = \frac{1}{r} \left( \frac{\rho}{\rho_0} \right)^{1/4} \exp \left( -\frac{r}{\rho_0} \right) \]

\[ \psi_0(r) = \left( \frac{\rho}{\rho_0} \right)^{1/4} \exp \left( -\frac{r}{\rho_0} \right) \]

where \( \rho_0 \) is a characteristic length scale.

Artificial Atoms

Atoms to bulk

Quantum dot

The nanocrystal states are labeled by the quantum number \( n_s \). For example, \( n_s \) is similar to the notation used for atoms.

The First Exciton Energy

The first exciton:

\[ E_{1s1s} = E_1 + \frac{1}{2} \left( \frac{1}{n_1^2} - \frac{1}{n_s^2} \right) \frac{h^2}{m^*} \]

In reduced units:

\[ \Delta E_{1s1s} = E_1 \left( \frac{1}{n_1^2} - \frac{1}{n_s^2} \right) \frac{\hbar^2}{m^*} \]

where \( E_1 = \frac{\hbar^2}{2m^*} \) and \( \sigma_s = \frac{n_s^2}{n_1^2} \).

Confinement Regimes

Strong confinement:

\[ V \gg \frac{\hbar^2}{2m^*} \]

Intermediate confinement:

\[ \frac{\hbar^2}{2m^*} \ll V \ll \frac{\hbar^2}{n_s^2} \]

Weak confinement:

\[ \frac{\hbar^2}{2m^*} \ll V \ll \frac{\hbar^2}{n_s^2} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>( \sigma_s )</th>
<th>( E_{1s1s} ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.13</td>
<td>1.94</td>
</tr>
<tr>
<td>GaP</td>
<td>0.18</td>
<td>1.17</td>
</tr>
<tr>
<td>InP</td>
<td>0.21</td>
<td>0.98</td>
</tr>
<tr>
<td>Si</td>
<td>0.22</td>
<td>2.12</td>
</tr>
<tr>
<td>Ge</td>
<td>0.27</td>
<td>3.03</td>
</tr>
<tr>
<td>Sn</td>
<td>0.35</td>
<td>4.68</td>
</tr>
</tbody>
</table>
How to think of a quantum dot

Exciton Fine Structure

The band structure of semiconductors is often more complicated than the parabolic effective mass approximation. While at high energies the conduction band is well described by a parabolic energy dispersion, the valence band is not. Nonparabolicity, material- and size-dependent band mixing, and the band structure give rise to a many-body breakdown of the band structure.

Due to spin-orbit coupling, the valence band is split into two bands, split-off-band (\(\nu=1\)) and light and heavy-hole bands (\(\nu=0\)). The spin-orbit splitting is given by

\[ h = \frac{\hbar}{2m_e} \alpha. \]

In some cases due to a local field, the light-hole and heavy-hole bands further split.

K dot P Method

Due to the complexity of the real band structure more accurate quantum dot calculations require one to go beyond the simple effective mass approximation. One such approximation is based on the \(k\)-expansion method. In this approximation the solution is expanded locally around a particular point in \(k\)-space. The single-particle Schrödinger equation reads

\[ H_k = \frac{\hbar^2 k^2}{2m} + V_k. \]

We can separate the Hamiltonian into a \(k\)-independent term and a correction

\[ H_k = \frac{\hbar^2 k^2}{2m} + H_{\text{corr}}(k). \]

Using second order perturbation theory we find

\[ E_d = E_0 + \frac{1}{2} \sum_{\nu \neq \nu'} \frac{|\langle \nu | H_{\text{corr}} | \nu' \rangle|^2}{E_{\nu} - E_{\nu'}}. \]

The band structure of the quantum dot shows multiple subbands due to the quantum confinement effects. The subbands are separated by an energy gap, \(\Delta\), which is due to the quantum confinement of the electrons.
How to think of a quantum dot
Some key results: synthesis

Synthesis and Characterization of Nearly Monodisperse CdSe

C. N. Macaluso, M. J. Thorsen, and J. C. Bernal

Chemistry Department, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Recently, March 30, 1993

Some key results: characterization

Characterization of Nearly Monodisperse CdSe Nanocrystals

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Recently, March 30, 1993

How to think of a quantum dot

Some key results: synthesis

How to think of a quantum dot

Some key results: characterization

How to think of a quantum dot
Some key results: single dot
Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots
Y. I. Alivov, G. A. Samartsev, S. A. Leonichenkov

Some key results: electrical
m-Type Conducting Colloids
Non-mirroring semiconductor nanocrystals
John Whitelam, Gurdeep S. Grewal, Alexander M. Davis, Ted R. L. Dryfe

Some key results: dynamics
Fluorescence intermittency in single and double colloid nanocrystals
D. J. Thompson, A. J. Maguire, S. C. Key, T. C. To, G. H. 3

Some key results: solar
High-efficiency carrier multiplication through direct photogeneration of hot electron-multiplication states, via simultaneous electron- and hole-excitation states
Research in the Kambhampati group

Semiconductor quantum dots: the early picture

- Size must be on the order of the exciton Bohr radius
  \[ r_{\text{Bohr}} = \frac{4\pi\varepsilon_0 e^2}{\epsilon_1} \]
  (1 - 10 nm, 10^2 – 10^5 atoms)

- Size tunable properties

Excitons in Semiconductor Quantum Dots: Design principles for QD lasers and photovoltaics

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McGill University
Montreal, Canada

Size dependent electronic structure

Size dependent properties
The excitonics of semiconductor quantum dots

- Objective: understand the inner workings of the quantum dot
- Excitons in QD revealed by State-Resolved Femtosecond Pump/probe spectroscopy
- Excitons establish design principles for QD devices
  - photovoltaics
  - lasers and lighting
  - piezoelectrics
  - photon sources

Excitonics: Dynamics connects structure and function

Physical Structure:
  - size, shape, composition, doping

Electronic Structure:
  - particle in a sphere
  - effective mass
  - atomistic

Dynamics:
  - relaxation
  - recombination
  - electron-phonon coupling
  - multiexcitons

Function:
  - optical gain
  - multiple exciton generation
  - blinking

Applications:
  - solar cells
  - lasers
  - photon sources
  - LEDs

Outline

1. Excitonics of Quantum Dots
2. Optical gain and lasing
3. Multiexcitons: Unraveling optical gain and multiple exciton generation
4. Getting back to the surface

Excitons (X) in quantum dots

Coarse structure

Fine structure

(Efros, Bawendi)

(Efros, Bawendi, Klimov)

(Efros, Bawendi, Efros, Efros)
Exciton vs. electron-hole representation

Illustration of hot exciton dynamics

Chronology of events

Optical gain in quantum dots

Excitonic State-Resolved pump/probe spectroscopy (focus on CdSe)

• Threshold
• Temperature stability, Room temperature operation
• Wavelength range
• Single photon sources
• Integration, packaging, processability

(Krauss Nature 2007)
Probing optical gain in QDs

1. Linear absorption: $0 \rightarrow X$
   $X \rightarrow \chi^{(1)} \rightarrow \text{OD}_0$

2. Nonlinear absorption: $X \rightarrow XX$

3. Spontaneous emission: $XX \rightarrow \chi^{(2)} \rightarrow \text{OD}_{NL}$

4. Stimulated emission: $XX \rightarrow X$

The prevailing view of gain in QD

1. Gain is inefficient
2. Gain is strongly size dependent
3. Gain depends strongly upon matrix conditions
4. Phenomenology arises from structureless

State resolved studies of optical gain

(PRL 2009, JCP 2009)

Exploring the control parameter $\Delta \langle \Omega | \hat{H}_{\text{int}} | \Omega \rangle + \text{OD}(\lambda) \neq 0$

Result

Excitonic state controls optical gain

First observation of intrinsic gain performance of CdSe QD

Result

The 'worst' materials can yield the best performance ever measured.
Controlling gain bandwidth
(PRL 2009, JCP 2009)

Result
Optical gain bandwidth can be tailored
An effect not seen in bulk or molecules!
A new platform for ultrafast optical switching?

CdSe/ZnS/CdSe:
Tailoring optical gain via material design

CdSe/ZnS/CdSe: Massive gain bandwidth in a coupled heterostructure

Nonlinear Spectra
SE Spectra

Multiexcitons in QD:
dynamics connects structure & function

New explicit THz optical switching
MX & Multiple Exciton Generation

Observing multiexcitons using pump / probe spectroscopy

First observation of structure of biexciton

\[ X \rightarrow \chi^{(1)} \rightarrow O\Delta_0 \]
\[ XX \rightarrow \chi^{(5)} \rightarrow O\Delta_{NL} \]

(w/ A Zunger)
Biexciton Stokes shift controlling gain threshold

On Stokes shift ($\delta_X$) controls spontaneous emission

On Stokes shift ($\delta_{XX}$) controls stimulated emission

Higher multiexcitons controlling gain bandwidth

• Gain bandwidth arises from MX
• Preparation of specific MX enables shaping of gain bandwidth
• Pulse sequences enables ultrafast optical switching

Structural dynamics of multiexcitons: hot exciton relaxation

Hot exciton relaxation dynamics: illustrating the processes
Radiationless transitions on the nanoscale: A unified picture of state-resolved exciton dynamics

Structural dynamics of multiexcitons: Controlling gain dynamics

The prevailing view of QD surface

1. Broad emission at low energy is due to surface states
2. Breadth arises from wide

Thermally relating the surface to the core

1) The surface strongly brightens at low temp.
2) Surface spectrum
An electron transfer approach to describing the nature of the surface

1) Classical bath polarizability gives rise to thermal equilibrium between surface and core

2) Strong phonon coupling gives rise to large energy shift and large

Hot exciton surface trapping

Hot exciton surface trapping in time resolved & CW spectroscopy

Summary and outlook

- Overturning prevailing view of gain in NC QD
  - Gain is extremely efficient and size universal in QD
  - First observation of gain bandwidth control

- First observation of electronic structure of multiexcitons in QD using pump/probe spectroscopy
  - Gain determined by XX Stokes shift
  - Gain dynamics controlled by structural dynamics of XX
  - Hot exciton surface trapping and gain / MEG / blinking

- Development of complete amplitude / phase / polarization shaping of femtosecond pulses for Coherent Multidimensional Spectroscopy of multiexcitons in nanostructures

- Development of lasers and LEDs using QDs and nanowires
Acknowledgements

The Group (in order of appearance)

Sam Sewall
Kevin Anderson
Ryan Cooney
Eva Dias
Dr. D.M. Sagar

Pooja Tyagi
Jon Saari
Jonathan Mooney
Michael Krause
Brenna Walsh

Funding:

Publications

1. “State-to-state exciton dynamics in semiconductor quantum dots”
2. “Light harvesting and carrier transport in core/barrier/shell semiconductor nanocrystals”
3. “Breaking the phonon bottleneck for holes in semiconductor quantum dots”
4. “Unified picture of electron and hole relaxation pathways in semiconductor quantum dots”
5. “Size-resolved exciton-phonon couplings in CdSe semiconductor quantum dots”
6. “Size dependent, state-resolved studies of exciton-phonon couplings in strongly confined semiconductor quantum dots”
7. “Size-resolved processes in semiconductor quantum dots: biexciton interactions and surface trapping dynamics”
8. “Single dot spectroscopy of two-color quantum dot/quantum shell nanostuctures”
9. “Gain tailoring in semiconductor quantum dots via state-resolved optical pumping”
10. “Experimental tests of effective mass vs. atomic pictures of quantum-dot electronic structure”
11. “Direct observation of the structure of band-edge biexcitons in quantum dots”

CdSe/ZnS/CdSe:
Optical gain in a coupled heterostructure
Excitons in quantum dots

- Quantum dots have a resolvable eigenstate spectrum like atoms or molecules.
- Consequently there should be state-specific dynamics which may be measurable.
- All work on CdSe QD to explore principles.

State-resolved exciton dynamics

- These state-specific processes include relaxation dynamics, many-body interactions, optical gain, etc.
- Or... what really happens inside a quantum dot?

Real time observation of excited state (hot exciton) surface trapping

Hot exciton relaxation dynamics:
Electron and hole transition rates
Hot exciton relaxation dynamics

- How to climb down the ladder?
- Is there a phonon bottleneck?

\[ \Delta E = 10h\omega_{d} \]

Auger

~4 \[ \Delta E = 4h\omega_{d} \]

(Efros & Nozik, Nano Lett 2006)

Precision measurements of relaxation:
Radiationless transitions on the nanoscale (PRB 2006, PRL 2007, PRB 2007)

Hot exciton relaxation dynamics:
Exciton-phonon coupling

- What is the strength of exciton-phonon coupling?
- Unanimous disagreement about nearly every aspect of exciton-phonon coupling!

- Key result:
  First simultaneous observation of coherent optical and acoustic phonons

- Intrinsic couplings for each state (Femto)
- Extrinsic coupling for trapped state (CW – Raman, PL)

Excitonics:
Fundamental dynamics connects structure & function
Hot exciton relaxation dynamics:
Exciton-phonon coupling

Hot exciton relaxation dynamics:
Weak coupling to phonons

How to observe biexcitons
(PRB 2006, JCP 2008, PRB 2009)

Excitonics:
Fundamental dynamics connects structure & function
Future work

- Exploring excitonics with novel probes:
  - 2D Spectroscopy, coherent control, development

- Relating excitonics to design principles for devices:
  - Photonics, piezoelectrics, optoelectronics (laser, LED, THz)

Excitonics: Fundamental dynamics connects structure & function

Excitonics: Fundamental dynamics connects structure & function