Introduction to Quantum Dot Nanocrystals and Nanocrystal Solids

Nuri Yazdani, 10.03.15
What is a QD Nanocrystal

Time: ~15m
What is a QD nanocrystal?

• Bulk Crystal
  – Periodic lattice of atoms which extends to infinity
  – Infinite crystal can be represented by finite amount of information → lattice vectors and constituent atoms
What is a QD nanocrystal?

- Bulk Crystal
  - Bloch theorem: Define eigenstates with wavevector $k$ and energy $E_k$
  - Basic form of band structure can be obtained by crystal lattice
  - Considering constituent atoms further refines band structure
What is a QD nanocrystal?

- Bulk Semiconductor
  - Fermi energy, \( E_F \), is the energy up to which all of the states below are filled with electrons at 0K
  - \( E_F \) for a semiconductor lies in a band-gap; a region in energy in which there are no available states
What is a QD nanocrystal?

- Electron-Hole creation
  - A photon with energy larger than or equal to the bandgap can be absorbed, generating an electron in the conduction band and a hole in the valence band
  - Energy and momentum are both conserved

\[
\alpha \propto (E - E_g)^{1/2}
\]
What is a QD nanocrystal?

- Free electron and holes
  - In most semiconductors at room temperature, once generated, conduction band electrons and valence band holes are free to diffuse and drift in the crystal.
What is a QD nanocrystal?

• Free electron and holes
  – In most semiconductors at room temperature, once generated, conduction band electrons and valence band holes are free to diffuse and drift in the crystal
  – At low temperatures, Coulomb attraction between the electron and hole can remain bound as an exciton

\[ E_n = -\frac{\mu R_H}{m_0 \epsilon_r n^2} \]
\[ r_n = \frac{m_0 \epsilon_r n^2 a_H}{\mu} \]

\( \epsilon_r, \mu \) Material dependent
What is a QD nanocrystal?

• Size scale:
  – For crystals of size considerably larger than the exciton radius $r_0$ can be considered as bulk
  – As the crystal size shrinks below the size of $r_0$, excitons become increasingly more confined
  – Coulomb energy of the exciton also increases
Quantum Confinement

- Simplest model: Ignore constituent material, treat NCs as infinite quantum wells

\[ V = \infty \]

\[ V = 0 \]

\[ E_{1,s} = 0.06\text{eV} \]

\[ E_{1,p} = 0.18\text{eV} \]

\[ E_{1,d} = 0.36\text{eV} \]

\[ E_{n,l} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_e r^2} \]
Quantum Confinement

- Next level of sophistication: Envelope Approximation
- Carrier maintain effective mass from bulk band structure

\[
E_k^c = \frac{\hbar^2 k^2}{2 m_{eff}^c} + E_g
\]

\[
E_k^y = \frac{-\hbar^2 k^2}{2 m_{eff}^y}
\]

\[
E_{ehp}(n_h L_h, n_e L_e) = E_g + \frac{\hbar^2}{2a^2} \left\{ \frac{\alpha_{n_h \cdot L_h}^2}{m_{eff}^y} + \frac{\alpha_{n_e \cdot L_e}^2}{m_{eff}^c} \right\}
\]

\[V = \infty\]
Quantum Confinement

• Additional Corrections
  – Coulomb interaction energy of electron and hole
  – Degeneracy of bands in constituent material
  – Interactions between degenerate bands
  – Nonparabolicities of bands
  – Finite potential outside of NCs

• Spectroscopic methods
  – Absorption and Luminescence
  – PLE spectroscopy
  – FLN spectroscopy
Case Study: PbS

\[ E_{g,\text{QD}} \sim E_{g,\text{bulk}} + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.8e^2}{\epsilon_r R} \]

\[ \epsilon_r = 169 \]
\[ E_{g,\text{bulk}} = 0.42eV \]
\[ m_c \sim 0.116m_0 \]
\[ m_v \sim 0.121m_0 \]
\[ \mu = 0.058m_0 \]

Colloidal Synthesis

Time: ~10m
## NC Syntheses

<table>
<thead>
<tr>
<th><strong>Self Assembled Quantum Dots</strong></th>
<th><strong>Colloidal Quantum Dots</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Beam Epitaxy</td>
<td>Solution processed</td>
</tr>
<tr>
<td>Grown directly on substrate</td>
<td>Dispersion of NCs in Solution</td>
</tr>
<tr>
<td>Poor size distribution and therefore optical properties</td>
<td>Monodisperse</td>
</tr>
<tr>
<td>Materials &amp; size well suited to IR</td>
<td>Tunable</td>
</tr>
</tbody>
</table>

[Image of 100 nm scale with dots]
[Image of three bottles with different colored solutions]
Hot Injection Method

When the solution is supersaturated, nucleation of NCs occur
Below supersaturation, monomers attach to nucleated NCs
With sufficient time, the larger NCs eat up the smaller ones

Monodisperse colloid growth (La Mer)

Concentration of precursors (a.u.)

Time (s)

Nucleation
Injection
Growth from solution
Ostwald ripening
Saturation

Nanocrystal Quantum Dots, Klimov V., CRC Press 2010
Critical radius and total free energy

\[ r^* = \frac{2\gamma V_m}{RT \ln S} \]

\[ \Delta G^* = \frac{16\pi \gamma^3 V_m^2}{3(RT \ln S)^2} \]

Nucleation rate

\[ \frac{dN}{dt} = A \exp \left[ \frac{-\Delta G^*}{RT} \right] \]

Kwon et al. Small 2011, 7, 2685
Growth rate
\[
\frac{dr}{dt} = \frac{DV_m([A]_{sol} - [A]_{surf})}{r - \frac{D}{k}}
\]

Most of real systems are in the mixed growth regime

\[
\frac{dr}{dt} = kV_m([A]_{sol} - [A]_{surf})
\]

Kwon et al. Small 2011, 7, 2685
Colloidal Synthesis

\[ A + B \rightarrow AB \]

**Indium salt**

**Antimony salt**

**Surfactant**

**T, °C/t, min/C, mmol**

InSb

Hydrophobic chain:
- oleic acid
- hexadecylamine
- dodecanethiol
- tri-n-octylphosphine

Polar group:
- COOH
- NH₂
- SH
- P

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Colloidal Synthesis

\[ A + B \rightarrow AB \]

Ligands can affect all stages of the reaction, from precursor reaction to growth of nanocrystals. They can be a part of monomers or intermediates, modify the surface tension on the crystal-solution interface, participate in redox processes or metathetic reactions, define solubility of monomers and nanocrystals, change the reaction rate constant, and affect the diffusion coefficient. They can also determine the shape of nanocrystals.
Colloidal Synthesis

- Synthesis Optimization
  - Hard to predict a priori
Colloidal Synthesis
Optical Applications
Optical Applications

- Colloidal QD-NCs offer:
  - Easy tunability of luminescence color
  - Very narrow spectral distributions
- Filters/downconverters
- LEDs
Generating the Visible Spectrum

- A set of three colors can be mixed to generate any color enclosed by the triangle formed between the three points.
- The sharpness of the initial colors determine the sharpness of the final mixed color.

LCD Displays and Television!
Generating the Visible Spectrum

![Diagram showing emission spectra and a television screen displaying a cityscape.](Image)
LEDs

- Solution processable
- Compatible with flexible substrates
- Good efficiencies (~20%)
- Air Stability

Field driven LEDs

- Driven with AC voltage
- Helped with fundamental research
- Very high power consumption / low efficiency

NC-Solids, Processing and Applications
NC-Solids

- Synthesis → NCs terminated with long, insulating ligands, suspended in solution
- Spin-coating, dip-coating, drop casting onto substrate
- Insulating ligands
  - poor charge transfer between NCs
  - insulating film
- Strategy: Ligand Exchange
  - Drastically enhance coupling between NCs
  - Semiconducting, and metallic films
  - FETs, Solar Cells, photo-detectors ...

Lead Chalcogenides (PbS, PbSe) dominate for applications in electronics
NC FETs


NC Solar Cells

NC Solar Cells

- Heterojunction solar cell architecture
  - Electron extraction from the TiO$_2$/FTO, hole extraction from the MoO$_x$/Au

![Image of solar cell layers](image)

![Current Density vs Bias Graph](image)

- $J_{SC} \sim 22$ mA/cm$^2$
- $V_{OC} \sim 0.54$ V
- $\eta \sim 6\%$
Transport in NC-Solids

- Nature of charge transport is densely packed NC solids is still under debate.
- Transport is considered to occur predominately through the first excited electron and hole states.
- Transport is likely via variable range hopping between neighboring NCs.
- It has been argued that in some cases coupling between the dots is large enough to form Bands that extend through the solid.
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Transport in NC-Solids

- **NCs**
  - Material and Size
    
    \[ E_g \quad \mu \]

- **NC-NC separation**
  - Coupling between NCs
    
    \[ \mu \]

- **Choice of Ligands**
  - Dielectric environment
    
    \[ E_f \quad E_C \quad E_V \quad \mu \]

- **Surface Chemistry**
  - Dielectric environment
  - Fermi-level modification
    
    \[ E_f \quad \mu \]

- **Size Distribution**
  - Disorder in band gap
    
    \[ \mu_{eff} \quad \eta \]
Transport in NC Solids

- Size plays an important role in determining the bandgap of the NC solid
- NC size also influences the carrier mobility through the **NC-NC coupling**

Carrier mobility is dependent on the extent of the wavefunction overlap (coupling) between neighboring NCs, which depends on:
- NC-NC separation
- Energetic barrier between NCs
- NC size

- Smaller NCs $\Rightarrow$ higher $E_k$ of carrier on the NC $\Rightarrow$ enhanced leakage of the wavefunction outside of the NC

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Transport in NC Solids

- Following the same line of argument on the NC-NC coupling, the NC-NC separation also strongly affects the carrier mobility.
- Shorter Ligand $\rightarrow$ increased coupling and higher mobilities.

Transport in NC Solids

- Affect of the surface terminating ligand is crucial!
- NC-NC separation
- Energetic barrier seen by charges between NCs
- Through surface dipoles: modifies the absolute position of the conduction and valence band in the NCs

Choice of Ligands
- Dielectric environment

\[ E_f \quad E_C \quad E_V \quad \mu \]

Transport in NC Solids

Surface Chemistry
• Dielectric environment
• Fermi-level modification

$E_f \quad \mu$

• The largest challenge in NC-solids!
• Huge surface area available for reactions!
• Oxidation and reduction of the surface can modify Fermi level in the NC solid

• For PbS FETs, !!NO AIR EXPOSURE!!
• For PbS Solar Cells, !!NEED AIR EXPOSURE!!

If surface chemistry can be tamed $\rightarrow$ control of the fermi-level in the NC solid
Transport in NC Solids

- Size Distribution
  - Disorder in band gap

\[ \mu_{eff} \quad \eta \]

- Topic of current research