Debye Lecture 9

Multi-Component Nanocrystal Assemblies

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Most of the work in this tutorial can be found in:
Absorption and Fluorescence of CdSe Quantum Dot Solids

Wavelength (nm)

Absorbance (arbitrary units)

Fluorescence

Intensity (arbitrary units)

Absorption

Wavelength (nm)

400 500 600 700 800

60 Å

49 Å

38 Å

28 Å

49 Å

38 Å

28 Å
Quantum Dot Solids

Particle Size and Nearest Neighbor Distance from Small Angle X-ray Scattering

Small-Angle X-ray Scattering

Radial Distribution Functions

CdSe QD in PVB

Form Factor of Sphere

CdSe QD Glass

Distance (Å)

Amplitude

Log(Intensity)

θ

0 2 4 6 8 10

Log(Intensity)

θ

0 2 4 6 8 10

Distance (Å)

Amplitude

-2

-1

0

1

2

62 Å CdSe QD Glass

38.5 Å CdSe QD Glass

62 Å CdSe QD Glass

38.5 Å CdSe QD Glass
Mixed QD Solids

Didn’t satisfy radius ratio rules to form ordered intermetallic phases

Ordered

Glassy

18% 38.5 Å/82% 62Å CdSe QDs
Photoconductivity in Quantum Dot Solids

Spectral Response of Photoconductivity

- Photocurrent at -500V
- Absorbance (arb. units)
- Photocurrent at +500V
- Absorption Spectrum

Energy (eV)

Photocurrent (arb. units)

Voltage (V)
Size and Interparticle Distance Dependence of Photoconductivity

- Spectral response maps the size-dependent, discrete electronic states of QDs
- Photocarriers thermalize to lowest excited state before being separated

Increased energy required to overcome binding energy with decreasing QD size
**Temperature Dependence of the Photoconductivity**

Scale I-V curves to nearly universal curve

Temperature dependence of the Quantum Yield

Decrease in photocurrent and the decrease in lifetime and Quantum Yield have the same temperature dependence
Fluorescence Quenching

Well passivated QDs
Deep trap emission quenched at lower fields than band edge emission
Quenching not observed in PL of isolated QDs in applied field
Quenching not directly proportional to charge separation efficiency as free charges in film may quench PL by Auger process
Measureable quenching possible sign of free charges in film

Poorly passivated QDs

Charge Separation versus Geminate Recombination

Efficiency of Charge Separation

\[ \eta(E,T) = \frac{k(E,T)}{k(E,T) + k_{nr}(T) + k_r(T)} \]

assume weakly field-dependent

For \( k(E,T) \ll k_r(T) + k_{nr}(T) \)

\[ \eta(E,T) = \tau(T)k(E,T) \]

Overcome:
- Coulomb attraction between e\(^-\) and h
- Charging Energy
Dipole-Dipole Interaction

Excited Donor

Unexcited Acceptor

Field Created by Transition Dipole of Donor

Transfer Energy

Interaction Energy

Induce Transition Field Created by Transition Dipole of Acceptor

Coulombic Interaction

Couple via Mutual Radiation Fields Created by Transition Dipoles
Electronic Energy Transfer

Excitation as an Entity

Transfer of Charge Neutral

Excited Donor

Ground State Acceptor

D* + A → D + A*

Radiationless Energy Transfer

Near Field
d < 100 Å

Requires Coupling between the Excited Donor and Ground State Acceptor

Radiative Transfer

Far Field

D* → D + hν
A + hν → A*

No Direct Donor-Acceptor Interaction

One Step Process

Two Step Process

“Real” Photon Mediates Energy Transfer

Ground State Donor

Excited Acceptor

D + A*
Long Range Resonance Transfer of Excitations

|D> \arrow{u} \rightarrow \arrow{d} |g>

|A>\subscript{1} \arrow{u} \rightarrow \arrow{d} \arrow{left} \rightarrow \arrow{right} |A>\subscript{2} \arrow{u} \rightarrow \arrow{d} \arrow{left} \rightarrow \arrow{right} |g>

Very fast

Couple via Radiation Fields
Created by Transition Dipoles

Donor

38.5 Å CdSe QD

Quenching of Donor
Luminescence
Quantum Yield and Lifetime

Enhancement of Acceptor
Luminescence
Quantum Yield and Lifetime

Acceptor

62 Å CdSe QD

\(e^-\) \arrow{left} \rightarrow \arrow{right} \(h^+\)

Quantum Yield and Lifetime
Spectral Overlap of Donor Emission and Acceptor Absorption

Transition Dipole of Excited Donor

Normalized Spectrum for Donor Emission

Transition Dipole of Ground State Acceptor

Molar Extinction Coefficient for Acceptor Absorption

Room Temperature

62 Å QD Acceptor Absorption
38.5 Å QD Donor Emission

10 K

62 Å QD Acceptor Absorption
38.5 Å QD Donor Emission

Intensity (arbitrary units)

Energy (eV)

2.1 2.2 2.3 2.4

Spectral Overlap varies with Temperature as:
Spectral Features Shift Blue as T decreases
Narrow
Mixed CdSe Quantum Dot Solid

**Room Temperature**

- Absorbance
- PL

**10 K**

- Absorbance
- PL

**Energy (eV)**: 1.5, 2.0, 2.5, 3.0

**Intensity (arbitrary units)**

**Absorbance**

- 0.0
- 0.0
- 0.2
- 0.3
- 0.4

**Energy (eV)**

- 1.5, 2.0, 2.5, 3.0
Efficiency of Long Range Resonance Transfer

\[ R_o \rightarrow \text{“critical radius” -- distance of donor and acceptor separation at which} \]

\[ k_{D^* + A \rightarrow D + A^*} = \frac{1}{\tau_D} \]

Energy Transfer Rate

Donor Lifetime = Sum of Rates of De-excitation by other competing processes

Spectral Overlap of Donor Emission and Acceptor Absorption

Quantum Yield of Donor

Index of Refraction

Spectral Overlap

\[ R_o \propto \left( \frac{\phi_D}{n^4} \int_0^\infty F_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \right)^{1/6} \]

\[ \Rightarrow 47 \text{ Å at Room Temperature} \]
\[ \Rightarrow 67 \text{ Å at 10 K} \]

\[ \Rightarrow R_{DA} = 61.25 \text{ Å} \]

compared to

Nearest Neighbor Interaction

Room Temperature \( k_{DA} = 1 \times 10^8 \text{ sec}^{-1} \)
Photoluminescence of a Mixed QD Solid and Solution Containing 82% 38.5 Å and 18% 62 Å CdSe Quantum Dots

Quenching of the Luminescence QY of the small 38.5 Å QDs accompanied by Enhancement of the Luminescence QY of the large 62 Å QDs in the Mixed CdSe QD Solid

Photoluminescence Excitation: The Origin of Emission

Mixed Film
- 38.5 Å CdSe QDs
- $1S_{3/2}1S_{e}$
- $1P_{3/2}1P_{e}$
- $2S_{3/2}1S_{e}$

Mixed Solution
- $1S_{3/2}1S_{e}$
- $2S_{3/2}1S_{e}$
- $2S_{1/2}1S_{e}$
- $3S_{1/2}1S_{e}$

Solution of 62 Å QD
- $2S_{3/2}1S_{e}$
- $2S_{1/2}1S_{e}$
- $3S_{1/2}1S_{e}$
- $3S_{1/2}1P_{e}$
Time Dependence of Energy Transfer in Mixed QD Solids

- Donors—38.5 Å CdSe QD
  - Pure Film
  - Mixed Film

Quenching of Donor Lifetime

- Acceptors—62 Å CdSe QD
  - Mixed Film
  - Excitation Red of 38.5 Å QDs
  - Mixed Film
  - Excitation Blue of 38.5 Å QDs

Energy Transferred to Acceptor Calculated from Quenching of Donor

$R_0 = 48$ Å
Energy Transfer within the Inhomogeneous Distribution of Electronic States

Inhomogeneous Distribution of Emission Energies in a QD Sample

Dispersed System

No Interaction between QDs

Close Packed System

Energy Transfer between Proximal QDs

QDs Dispersed in Solution $\rightarrow$ Close Packed in QD Solid

$\rightarrow$ Red Shift

$\rightarrow$ Narrowing of the Emission Lineshape

$\rightarrow$ Asymmetric

Energy Transfer within the Sample Inhomogeneous Distribution

Experimental Solution Luminescence

Sample Distribution

Single Dot Lineshape

Fit Solution Luminescence

Sample Distribution

Energy Transfer within Sample Distribution

Efficiency Calculated From Spectral Overlap

Calculated Film Luminescence reproduces Experimental Film Luminescence
Probability of Energy Transfer

$$P_{DA} = \frac{R_o^6}{R_o^6 + R_{DA}^6}$$

Nearest Neighbor Distance in QD Solid
Spectral Overlap from the Absorption Spectrum for the QD Solid, Emission Spectrum for the QDs in Solution, Quantum Yield of the QD Solid

<table>
<thead>
<tr>
<th>D</th>
<th>$R_o$</th>
<th>$R_{DA}$</th>
<th>$P_{DA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 Å</td>
<td>37.9 Å</td>
<td>41.3 Å</td>
<td>0.38</td>
</tr>
<tr>
<td>39.5 Å</td>
<td>35.4 Å</td>
<td>50.4 Å</td>
<td>0.11</td>
</tr>
<tr>
<td>48 Å</td>
<td>47.3 Å</td>
<td>59.1 Å</td>
<td>0.21</td>
</tr>
<tr>
<td>62 Å</td>
<td>53.9 Å</td>
<td>73.1 Å</td>
<td>0.14</td>
</tr>
</tbody>
</table>

$R_o$ and $P_{DA}$ vary with the Quantum Yield for the QD Solid
$R_o$ increases, Spectral Overlap increases, Stokes shift between Absorption and Emission Spectra decreases
$P_{DA}$ decreases, $R_{DA}$ increases faster than $R_o$
Broad versus Narrow Size Distribution

**Peak in Emission Shifts Red**

- Narrow Distribution $\Delta E = 14.6$ meV
- Broad Distribution $\Delta E = 29.6$ meV

**Emission Lineshape Narrows**

- Narrow Distribution $\Delta$FWHM = 11 meV
- Broad Distribution $\Delta$FWHM = 23 meV

Red Shift Increases with Increasing Sample Inhomogeneous Distribution

Emission Lineshape Narrows from Solution $\rightarrow$ Film

Narrowing Increases with Increasing Sample Inhomogeneous Distribution
Concentration Dependence of Luminescence Lineshape

Decreasing Concentration of 62 Å QDs in Matrix of 38.5 Å QDs

- Increases Average Separation between 62 Å QDs
- Reduces Probability of Energy Transfer between 62 Å QDs

Luminescence Lineshape

\[ \text{Shift Blue} \to \text{Solution} \]
\[ \text{Asymmetric} \to \text{“Gaussian-like”} \]

Mixed QD Solids:
- 18% 62 Å QDs
- 6.2% 62 Å QDs
- 4.4% 62 Å QDs
- 3.2% 62 Å QDs
- 2.2% 62 Å QDs
AFC media magnetization response to magnetic field

CoPtCrB  
Ru  
Cr  
underlayers  
Glass substrate

M_{rt_{top}} = 0.31
M_{rt_{bottom}} = 0.09

A super strong magnet will enable exchange-spring magnets

material requirements:
High $M_s$, high $H_c$, high $(BH)_{\text{max}}$

nature limits: $M_s$ vs. $H_c$

solution: exchange-spring magnets

exchange-spring magnets

concept

t$_S$ ≤ 2$\delta_w$ (10-20 nm)

nanoparticle self-assembly-bottom-up approach
Nanoscale Engineering for Optimum Exchange-Coupling


TEM images of the binary composite assemblies of
(A) $\text{Fe}_3\text{O}_4(4 \text{ nm}):\text{Fe}_{58}\text{Pt}_{42}(4 \text{ nm})$;
(B) $\text{Fe}_3\text{O}_4(8 \text{ nm}):\text{Fe}_{58}\text{Pt}_{42}(4 \text{ nm})$;
(C) $\text{Fe}_3\text{O}_4(12 \text{ nm}):\text{Fe}_{58}\text{Pt}_{42}(4 \text{ nm})$;
(D) $\text{FePt}\text{Fe}_3\text{O}_4$ core-shell

Hysteresis loops of $\text{FePt}-\text{Fe}_3\text{Pt}$ nanocomposite derived from $\text{Fe}_3\text{O}_4:\text{FePt}$ binary assembly (A) $4 \text{ nm}:4 \text{ nm}$; and (C) $12 \text{ nm}:4 \text{ nm}$

36% energy product enhancement compared to single-phase FePt!
TEM images of two different binary assemblies prepared directly from particle dispersions of 4 nm FePt as well as 4 nm Fe$_3$O$_4$ and 8 nm Fe$_3$O$_4$.

HRTEM image of an exchange-coupled nanocomposite (FePt-Fe$_3$Pt) made from 4nm FePt and 4nm Fe$_3$O$_4$ nanoparticles under reductive annealing. Shown here is a modulated structure with FePt and Fe$_3$Pt in intimate contact, resulting in exchange-coupling.

Nanocomposite magnetics

Hysteresis loops at room temperature with the composites from 4nm:4nm and 4nm:8nm nanoparticles respectively.

(BH)\text{max}, energy product, reflects the ability for a composite to store the magnetic energy, the larger the better.
Binary Nanocrystal Array’s a New Class of Nanostructured Materials
Franz Redl, Kyung-Sang Cho and C. B. Murray

Composites of: Ferromagnets, Noble Metals, Semiconductor QDs, Ferroelectrics, Superconductors, may all be possible.

New Near IR Magneto-Optic Composite ~13nm Fe2O3 and 5nm PbSe QDots
Binary nanocomposites via self-assembly of two kinds of NPs

A nanoparticle dispersion in an organic solvent. The particles are stabilized by a layer of organic surfactant to prevent them from aggregation.

Binary nanocomposite: Magnetic-magnetic composite or magnetic-semiconductor composite.
PbSe – Au binary mixture
Fe$_2$O$_3$ – Au binary mixture
PbSe (large) – Ag (small) binary nanoparticle mixture
PbSe (large) – Ag (small) binary nanoparticle mixture
PbSe – Ag binary nanoparticle mixture
$\varepsilon_{\text{particle}} / (\text{l mol}_{\text{particle}}^{-1})$

wavelength / nm

a) 
b) 
c) 
d)
Simultaneous Reaction
A & B Compounds & Alloys

Ferromagnets,
Noble Metals,
Semiconductor QDots,
Ferroelectrics,
Superconductors

Binary Assembly
AB$_2$ & AB$_{13}$

Anneal to remove Organic

Customize organic linkers (molecular wires)

Dicyanobenzene linked Cobalt Nanocrystals

150 nm
50 nm