Semiconductor Quantum Rods; From Science to Applications

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Sampling of our research infrastructure
Semiconductor clusters, nanocrystals, and nanorods

- Size & shape dependent properties
- Applications in nanotech

Transforming from ‘0’ D to 1 D

InAs quantum dots

CdSe

InAs nanorods

50 nm

100 nm

10 nm
Outline

- Nanocrystal basics; quantum dots as artificial atom

Shape Control – Quantum Rods;

- Synthesis of semiconductor quantum rods: CdSe, InAs
- Size dependent level structure; CdSe & InAs QRs.
- Lasing from quantum rods in cylindrical microcavities
Synthesis of II-VI and III-V semiconductor nanocrystals

InCl₃ + As(SiMe₃)₃ → InAs + 3Me₃SiCl

room T precursors
In/GaCl₃ and
P/As(SiMe₃)₃

liquid surfactant,
stirring and at
“high T,” 250-300 °C
Artificial solids of InAs nanocrystals

TEM images of different orientations of superlattices with a fcc structure

(111)_{SL} (110)_{SL} (100)_{SL}

60°

70.52°

90°
Quantum confinement in InAs nanocrystals

Optical spectra
Single InAs nanocrystal (d ~ 6.5 nm)

STM Topography

Tunneling Spectroscopy

Prof. O. Millo, D. Katz, Racah Institute of Physics

III-V semiconductor Core/Shell nanocrystals

Nanocrystals Outshine Laser Dyes

JERUSALEM — Semiconductor nanocrystals fabricated at Hebrew University produce a bright fluorescence radiation that can be size-tuned to the near-infrared. Chemists Uri Banin and Yun-Wie Cao’s method for making the nanocrystals with an indium arsenide core and a shell of either indium phosphide or cadmium selenide was reported in Angewandte Chemie, International Edition (Vol. 38, 1999).

Small crystals, like those in the current study, are termed nanocrystals. They have properties from both the bulk material and the quantum dots. They have been used for a wide range of applications, including light emission.

Core/Shell Nanocrystals with High Emission Yield at 1.3 μm

- Two ways to achieve PL at 1.3 μm
Shape Control
Synthesis of Semiconductor Quantum Rods

Why Rods?

• Science: Fundamental issues in crystal-growth
  Evolution from zero to one-D

• Technology: Polarized emission
  Improved charge transport (photocells)
  Easier contact to nano-electrode architecture
CdSe quantum rod samples

Liquid surfactant stirring and at “high T”

TDPA, HPA

CdSe quantum rod samples – Surfactant controlled growth mechanism

Schematic structure of CdSe quantum rods in growth. The most stable form of a rod is shown, its (001) facet terminated by Se atoms does not have any ligand on it.

NIR light emitting diode with semiconductor (InAs/ZnSe) n’xtal-polymer composites (with Prof. Nir Tessler, Technion)

Semiconductor pillars grown by VLS

18 mm

Semiconductor nanowires grown by VLS (Lieber, Yang)

Setup for laser assisted catalytic growth (LCG) of semiconductor nanowires

Vapor-Liquid-Solid growth Mechanism (Si with Fe)

GaAs nanowires

Pseudobinary phase diagram

Synthesis of InAs nanorods

Room T precursors InCl$_3$, As(SiMe$_3$)$_3$ & gold particles

Solution-Liquid-Solid growth mechanism

InCl$_3$ + As(SiMe$_3$)$_3$ $\rightarrow$ InAs + 3Me$_3$SiCl

Synthesis of InAs QRs using \( \text{Au}_{101}(\text{PPh}_3)_{21}\text{Cl}_5 \) cluster (1.4 nm) as catalyst

\[ \text{Au}_{101} \text{ cluster} \]  \hspace{1cm} \[ \text{InAs QRs} \]

Growth

\[ (\text{TMS})_3\text{As-InCl}_3 \]
TEM of InAs nanorods

• Separation via centrifugation. 1st precipitate contains ‘nanowires’

Structural characterization of the rods: HRTEM & XRD

A

B

Intensity (a.u.)

Intensity (a.u.)

rods

bulk InAs

wires

2θ (deg.)
InAs nanorods – Chemical Analysis (EDS)

- Au content increases in longer rods.
- Growth terminated due to Au depletion

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>3.7x3.7</th>
<th>7.4x3.7</th>
<th>14x3.7</th>
<th>20x4</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>52.29</td>
<td>51.2</td>
<td>54.67</td>
<td>53.49</td>
</tr>
<tr>
<td>As</td>
<td>46.16</td>
<td>47.29</td>
<td>41.14</td>
<td>41.63</td>
</tr>
<tr>
<td>Au</td>
<td>0</td>
<td>0.05</td>
<td>2.53</td>
<td>3.85</td>
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</table>
Size-dependent melting of gold nanocrystals

\[
\frac{T_m(r)}{T_m(\infty)} = 1 - \frac{4}{\rho_s L} \left[ \gamma_s - \gamma_l \left( \frac{\rho_s}{\rho_l} \right)^{2/3} \right] \frac{1}{d}
\]

\( \rho_s = 19 \text{ g cm}^{-3}, \rho_l = 17.3 \text{ g cm}^{-3}, \)

\( \gamma_s = 0.9 \times 10^3 \text{ erg cm}^{-2}, \gamma_l = 0.74 \times 10^3 \text{ erg cm}^{-2}, \)

\( L = 5.38 \times 10^8 \text{ erg g}^{-1} \)

InAs nanorods via the SLS mechanism with Au particles; The importance of melting point depression

Optical and electronic properties of quantum rods

Transforming from ‘0’ D to 1 D

CdSe/ZnS rod/shell luminescence

Increase diameter
Quantum confinement in semiconductor nanocrystals and quantum rods

Combining optical & tunneling spectroscopies;

VB to CB Transitions
selection rules
no charging

VB and CB levels individually
very weak selection rules
single electron charging effects

Symmetry of atomic-like QD levels can be directly identified

Size selected PLE spectroscopy of CdSe quantum rods

T=10K

20x4 nm Rods

Emission

Absorption

PLE

Intensity (a.u.)

Energy (eV)

1.6 2.0 2.4 2.8 3.2 3.6
Length and diameter dependence of PLE spectra on nanorods

- Spectra depend mainly on diameter, not on length.

*PRL 89*, paper 086801 (2002).
Tunneling spectroscopy of single nanocrystals and quantum rods

- Tunneling into discrete QR energy levels.
- Double barrier tunnel junction (DBTJ) configuration.
- $\Gamma_2 \gg \Gamma_1 \Rightarrow$ negligible charging effects.

Prof. Oded Millo, D. Katz, T. Wizansky, Racah Institute of Physics
STM measurement of single CdSe nanorod

• Positive bias: resonant tunneling peaks through conduction-band levels.
Energy levels depend mainly on diameter, not on length. (spectra alligned horizontally for clarity)
Summary – level structure of CdSe rods

- Band gap and excited states mainly depend on diameter not length, for rods longer than ~10 nm.

- Can control color by diameter, and tune length at will.

*PRL* 89, paper 086801 (2002).
**Shape effect on Artificial Atoms**

**Qdot**  
Particle in a sphere

- **Spherical Harmonics:** $n,l,m$  
  - eg. $1s_e$, $1p_e$

**Qrod**  
Particle in a cylinder

- **Cylindrical coordinates:**  
  - **Radial:** $n,l_z$  
  - **Length:** $m$
  - **Ground state:** $1,0,1$ ($l_z=0$, degeneracy 2)
  - **Higher $l_z$**, degeneracy 4.

**CdSe** $a_0 \sim 5$ nm  
**Strong Quantum Confinement:** $L < a_0$

**Weak Quantum Confinement:** $L \gg a_0$

**InAs** $a_0 \sim 35$ nm
InAs nanorods – Length dependent optical properties

• Band gap red-shifts with increasing length. Modeld with infinite barrier cylindrical box model
InAs nanorods – Polarized PL

- Dots & rods in stretched polymer film. Rods show polarized PL.
Lasing of CdSe quantum rods in cylindrical microcavities
**Colloidal nanostructures as laser materials**

**Potential:**
- Extremely broad spectral coverage

ZnS  CdSe  CdTe  InAs

- Low threshold lasing predicted for QDs
  lasing threshold may be independent of temperature, at an excitation level of only one e-h pair per dot.

- Nanorods have linearly polarized emission

**Difficulties:**
- Surface trapping of carriers – partially solved in core/shell nanocrystals.

- Competing fast non-radiative Auger process

- Bawendi, Klimov, and co-workers reported the observation of stimulated emission in CdSe nanocrystals in close packed films using fsec pumping. *[Science 290, 314 (2000)].*
Cylindrical microcavities

- Microcavities suitable for colloidal nanocrystals due to ultrahigh $Q$ factors and fast roundtrip times

CdSe/ZnS Nanorod samples

- Rod/shell configuration reduces surface trapping, leading to increased PL QY

<table>
<thead>
<tr>
<th></th>
<th>Rods size (length x diameter) (nm)</th>
<th>Shell Thickness (ML)</th>
<th>PL wavelength in maximum QY (nm)</th>
<th>Maximum Q.Y(%)</th>
<th>Q.Y after separation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11 x 3</td>
<td>2.3</td>
<td>580</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>B</td>
<td>15 x 3.8</td>
<td>2</td>
<td>614</td>
<td>28</td>
<td>19</td>
</tr>
<tr>
<td>C</td>
<td>22 x 4</td>
<td>1.7</td>
<td>614</td>
<td>28</td>
<td>18</td>
</tr>
<tr>
<td>D</td>
<td>29 x 3.7</td>
<td>1.9</td>
<td>613</td>
<td>27</td>
<td>16</td>
</tr>
<tr>
<td>E</td>
<td>20 x 5.5</td>
<td>1</td>
<td>630</td>
<td>18</td>
<td>11</td>
</tr>
</tbody>
</table>
Lasing of nanorods (25x4 nm) in the cylindrical microcavity

- Lasing appears at a threshold of 0.075 mJ

Miri Kazas
David Lewis
• Demonstrate color tunability with size, shape
• Lasing for nanocrystals in solution in spite of measurements showing induced absorption
• Lasing with nsec pumping in spite of the fast Auger processes
Lasing of core/shell nanocrystals, sequential shots at high resolution

- High pump power; observe WGMs with fluctuating intensities until burning
Polarization of lasing: Nanocrystals vs. Nanorods

- Nanocrystals – no polarization
- Nanorods – linearly polarized lasing

WGM Spacing agrees with theory:

\[ \Delta \lambda \propto \frac{\lambda_n^2}{2\pi mr} \]
Stability of lasing
Nanocrystals vs. Nanorods as laser materials

• Absorption cross-section is larger in rods vs. dots of same diameter due to larger volume

• Nanorods have larger Stokes shift between absorption and PL and therefore losses due to reabsorption should be smaller (for present samples, 80 meV vs. 45 meV).

• Auger rates in nanorods may be slower than nanocrystals due to larger size. Color tunability still available primarily through control of diameter.

• Nanorods have a linearly polarized emission and can provide polarized lasing.

Shape-control – Quantum rods; Summary

• Synthetic, materials & crystal growth challenges

• Diameter and length dependent levels

• Rods as materials for light amplification - rods better then dots
THANKS!!!!

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