Fabrication of Core/Shell structured Nanoparticles

Representative heterogeneous nucleation

Core/shell versus Core only Semiconductor Nanocrystals

- Shell provides a physical barrier between the optically active core and the surrounding medium, thus making the nanocrystals less sensitive to environmental changes, surface chemistry, and photo-oxidation.

- The shell provides an efficient passivation of the surface trap states, giving rise to a strongly enhanced fluorescence quantum yield.

- Band gap tuning by type I and II heterojunctions
  *epitaxial-type shell growth*: 1) appropriate band alignment, 2) crystallize in the same structure & exhibit a small lattice mismatch

- Defects, trap sites
- Oxides are most stable.
Strongly Luminescing ZnS-Capped CdSe Nanocrystals


Published: JAN 11 1996  Times Cited: 1,721

- ZnS-capped CdSe semiconductor nanocrystals using organometallic reagents by a two-step single-flask method

- Core of nearly monodisperse CdSe of 27-30 Å diameter with a ZnS capping 6 ± 3 Å thick.

- ZnS capping with a higher bandgap than CdSe passivates the core crystallite removing the surface traps. The nanocrystals exhibit strong and stable band-edge luminescence with a 50% quantum yield at RT.
TEM picture of (CdSe)ZnS nanocrystals

- Core of nearly monodisperse CdSe of 27-30 Å diameter with a ZnS capping 6 ± 3 Å thick.
- Fluorescence spectrum of (CdSe)-TOPO has a broad tail due to surface traps (700-800 nm).
- (CdSe)-ZnS retains the sharp peak with a small red shift (5 nm) but has a flat baseline and high QY of 50%
(CdSe)ZnS Core-Shell Quantum Dots: Highly luminescent Nanocrystallites


Published: NOV 13 1997   Times Cited: 2,322

Strongly Luminescing ZnS-Capped CdSe Nanocrystals


Published: JAN 11 1996   Times Cited: 1,721
• Synthesis of highly luminescent (CdSe)ZnS composite quantum dots with CdSe cores ranging in diameter from 23 to 55 Å.
• The narrow photoluminescence spans most of the visible spectrum from blue through red with quantum yields of 30-50% at room temperature.
• Overcoating nanocrystals with higher band gap inorganic materials has been shown to improve the photoluminescence quantum yields by passivating surface nonradiative recombination sites.
• Particles passivated with inorganic shell structures are more robust than organically passivated dots and have greater tolerance to processing conditions necessary for incorporation into solid state structures.
To prevent nucleation of the shell material and uncontrolled ripening of the core NCs, T2 for the shell growth is generally lower than T1 used for the core NC synthesis.
CdSe core $\rightarrow$ Me$_2$Zn + TMS$_2$S $\rightarrow$ CdSe core

ZnS Shell
The Nobel Prize in Physics 2000

"for basic work on information and communication technology"

"for developing semiconductor heterostructures used in high-speed- and opto-electronics"

"for his part in the invention of the integrated circuit"

Zhores I. Alferov
Russia
A.F. Ioffe Physico-Technical Institute
St. Petersburg, Russia
b. 1930

Herbert Kroemer
Federal Republic of Germany
University of California
Santa Barbara, CA, USA
b. 1928

Jack S. Kilby
USA
Texas Instruments
Dallas, TX, USA
b. 1923
d. 2005

http://en.wikipedia.org/wiki/Heterojunction
Novel properties of core-shell QD’s:

1) Overcoating with higher band-gap materials improved the PL-QY by passivating surface nonradiative recombination sites.
2) More robust than organically passivated dots
CdSe cores ranging from 23 to 55 Å; Visible photoluminescence from red through blue with quantum yield of 30 – 50 %

Figure 5. PL spectra for a series of ZnS overcoated dots with 42 ± 10% Å diameter CdSe cores. The spectra are for (a) 0, (b) 0.65, (c) 1.3, (d) 2.6, and (e) 5.3 monolayers ZnS coverage. The position of the
• Absorption spectra and photoluminescence (PL) spectra for bare (dashed lines) and 1-2 monolayer ZnS overcoated (solid lines) CdSe dots with diameters of (a) 23, (b) 42, (c) 48, and (d) 55 Å.

• The absorption spectra for the (CdSe)ZnS dots are broader and slightly red-shifted from their respective bare dot spectra.

• The PL spectra for the overcoated dots are much more intense owing to their higher quantum yields: (a) 40, (b) 50, (c) 35, and (d) 30.
Transmission electron micrographs of (A) one “bare” CdSe nanocrystallite and (B) one CdSe nanocrystallite with a 2.6 monolayer ZnS shell.
Stability against oxidation

Figure 7. X-ray photoelectron spectra highlighting the Se 3d core transitions from ~40 Å bare and ZnS overcoated CdSe dots: (a) bare CdSe, (b) 0.65 monolayers, (c) 1.3 monolayers, and (d) 2.6 monolayers of ZnS. The peak at 59 eV indicates the formation of selenium oxide upon exposure to air when surface selenium atoms are exposed.
Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/Shell Nanocrystals Using Air-Stable Reagents via Successive Ion Layer Adsorption and Reaction

CdSe Core

CdO + S

Via SILAR at 240°C

CdSe/CdS Core/shell
Successive ion layer adsorption and reaction (SILAR) originally developed for the deposition of thin films on solid substrates (Atomic-Layer-Deposition (ALD)) from solution baths for the growth of high-quality core/shell QDs.
• Successive ion layer adsorption and reaction (SILAR) originally developed for the deposition of thin films on solid substrates (Atomic-Layer-Deposition (ALD)) from solution baths for the growth of high-quality core/shell QDs.
• CdO and elemental S as the precursors.
• The shell growth via one monolayer at a time by alternating injections of air-stable and inexpensive cationic and anionic precursors into the reaction mixture with core nanocrystals.
• PL QY of the as-prepared CdSe/CdS core/shell: 20% ~ 40%
• fwhm was maintained between 23 and 26 nm.

Type-II Core/Shell CdS/ZnSe Nanocrystals:
Victor I. Klimov (Los Alamos National Laboratory),
The Nobel Prize in Physics 2000

“for basic work on information and communication technology”
“for developing semiconductor heterostructures used in high-speed- and opto-electronics”

P-n junction
Homojunction vs. Heterojunction

Conduction Band (CB)
Valence Band (VB)
Straddling Gap (type I)
Staggered Gap (type II)

http://en.wikipedia.org/wiki/Heterojunction

Zhores I. Alferov
1/4 of the prize
Russia
A.F. Ioffe Physico-Technical Institute
St. Petersburg, Russia
b. 1930

Herbert Kroemer
1/4 of the prize
Federal Republic of Germany
University of California
Santa Barbara, CA, USA
b. 1928

t. 2021

Jack S. Kilby
1/2 of the prize
USA
Texas Instruments
Dallas, TX, USA
b. 1923
d. 2005
Type I versus Type II Semiconductors

- In the type-I structures, both the conduction and the valence band edges of one semiconductor are located within the energy gap of the other semiconductor.
- An electron-hole (e-h) pair excited near the interface tends to localize in semiconductor 1, which provides the lowest energy states for both electrons and holes.
Characteristics of Type II core/shell Quantum Dots

• In the type-II case, the lowest energy states for electrons and holes are in different semiconductors; therefore, the energy gradient existing at the interfaces tends to spatially separate electrons and holes on different sides of the heterojunction.

• Spatial separation between hole and electron can simplify applications of NCs in photovoltaic technologies.
Advantages of Type II core/shell Quantum Dots

• Band-edge transition energy in the type-II structure is smaller than the energy gap of either material comprising it → Can obtain infrared emission wavelengths

• Control of both single and multiexciton lifetimes: In contrast to type-I systems, PL decay times are strongly prolonged in type-II NCs due to the lower overlap of electron & hole wavefunctions.
Type-II Quantum Dots: CdTe/CdSe(Core/Shell) and CdSe/ZnTe(Core/Shell) Heterostructures

Sungjee Kim, Brent Fisher, Hans-Jurgen Eisler, and Mounqi Bawendi*  
Now at POSTECH  
*J. Am. Chem. Soc. 2003, 125, 11466. Cited 374

For CdTe/CdSe QDs, the hole is mostly confined to the CdTe core, while the electron is mostly in the CdSe shell. In CdSe/ZnTe QDs, the band offsets are reversed, so that the electron resides mostly in the CdSe core, while the hole is mostly in the ZnTe shell.

[Diagram showing potential energy levels for CdTe/CdSe and CdSe/ZnTe QDs]
Absorptivity and normalized photoluminescence spectra of 32 Å radius CdTe QD (gray lines on (a)), CdTe/CdSe (32 Å radius core/thickness of 11 Å shell) QD (black lines on (a)), 22 Å radius CdSe QD (gray lines on (b)), and CdSe/ZnTe (22 Å radius core/thickness of 18 Å shell) OD (black lines on (b)).

Photoemission from CdTe/CdSe and CdSe/ZnTe QDs is observed at longer wavelengths than that from the corresponding cores.
32 Å radius CdTe QD (upper left), CdTe/CdSe (32 Å radius core/thickness of 11 Å shell) QD (lower left), 22 Å radius CdSe QD (upper right), and CdSe/ZnTe (22 Å radius core/thickness of 18 Å shell) QD (lower right).
• By changing the two variables of shell thickness and core size, the emission of type-II QDs can be easily and widely tuned.
• PL spectra from CdTe/CdSe QDs that range from 700 nm to over 1000 nm simply by changing the core size and shell thickness.
Synthesis of Size-selected, surface-passivated InP Nanocrystals

Alivisatos (UC-Berkeley) and Heath (UCLA)  
JPC 1996, 100, 7212.

- Compared to II-VI semiconductors, much less research
- Compared to II-VI semiconductor nanocrystal, it is known to be more difficult to synthesize III-V semiconductor nanocrystals because of stronger covalent bonding of the precursors for III-V semiconductor nanocrystals, which requires high synthesis temperature and long reaction time. This high reaction temperature and long synthesis time inevitably cause Ostwald ripening process, which broadens the particle size distribution.
Characteristics of III-V QDs

• Group III-V materials, with their relatively covalent bonding and direct gap band structure (except GaP), are the most promising candidates for large quantum confinement effects. The bulk exciton diameter gives some sense of this; for InP it is 150 Å while for CdSe it is only 70 Å.

• Without a temporally discrete nucleation step, the production of monodisperse nanocrystals with a narrow size distribution is difficult.

• In the case of I-VII or II-VI nanocrystals, bare atoms or ions can be used as precursors, allowing for the direct reaction of the relevant elements. In contrast, the corresponding III-V atoms or ions, if used as precursors, may directly react with the solvent.
Very slow reaction and nucleation and growth occur simultaneously over long time scales, resulting in broad size distributions. Size selection process via the reprecipitation.

Dodecylamine: effective stabilizer
Becomes soluble in toluene and insoluble in methanol

1.7 ev for the largest
And 2.4 eV for the smallest
Bulk: 1.35 eV

**Figure 1.** UV/vis absorption spectra for a series of nanocrystal
The bulk InP band gap is at 1.35 eV.
Figure 2. Transmission electron micrograph of InP nanocrystals.
Debye-Scherrer Formula

\[ t = \frac{0.9 \lambda}{B \cos \theta} \]

\[ B = \text{FWHM} \]

**Figure 3.** Excitonic peak position from UV/vis vs nanocrystal diameter as determined by powder TEM (circles) or XRD (squares).
Absorbance and PL spectra for several sizes of InP nanocrystals

- PL spectra are composed of a high-energy band edge emission band and a low-energy trapped emission band from surface defects.
- Scaled PL spectra for a sequence of sample sizes exhibiting a smooth blue shift of the band edge emission with decreasing nanocrystal size.
1) II-VI and III-V semiconductor shells were overgrown onto InAs nanocrystal shells.

2) The band gap shift to the red upon growth of InP or CdSe. While for ZnSe and ZnS shells that have larger band offsets wrt InAs, the band gap energy is maintained.

3) PL-QY quenched in InAs/InP, but increases up to 20% for InAs/CdSe and InAs/ZnSe.
Figure 2. Evolution of the absorption spectra during the growth of InP shells on InAs cores with an initial radius of 1.3 nm (a). The InP shell thickness in number of monolayers (ML) is: (b) 0.5, (c) 1.1, (d) 1.7, (e) 2.5.
Evolution of absorption (dotted lines), and photoluminescence (solid lines) for growth of core/shells. The PL spectra are
InAs/InP core/shell
1.7 nm/2.5 nm

InAs core: 1.7 nm

InAs/CdSe core/shell
1.7 nm/1.5 nm

Figure 6. HRTEM images of InAs/InP core/shell (frame A, core radius 1.7 nm, shell thickness 2.5 nm), InAs/CdSe core/shell (frame B, core radius 1.7 nm, shell thickness 1.5 nm). The scale bar is 2 nm. The na...
Epitaxial growth of Shell

![Graph showing intensity vs. 2θ for different materials such as InAs and InP with peaks at specific 2θ values.](image)
Stability against oxidation and Photostability of InAs/CdSe and InAs/ZnSe increased a lot. Good fluorophores for Near IR range.
One-pot Synthesis of Highly Luminescent InP/ZnS Nanocrystals without Precursor Injection

JACS 2008, 130, 11588 by Peter Reiss.

1) Use “heating-up method”\(^3,4\): mixing all components at low temperature and subsequent heating to reflux. → strongly improves reproducibility and possibility of large-scale nanoparticle production.

2) Indium myristate \([\text{In(MA)}_x]\), zinc stearate, tris(trimethylsilyl)phosphine \([\text{P(TMS)}_3]\), and dodecanethiol were mixed in 1-octadecene (ODE) under inert atmosphere at RT & subsequently heated to 300 °C within 3 min.


High quality InP/ZnS core/shell NCs. QY of 50-70%; 40-60 nm fwhm; excellent photostability.
Low-Temperature Solution Phase Route for the Synthesis of Silicon Nanoclusters

JACS 1996, 118, 12461 by Susan M. Kauzlarich (UC Davis)

\[ 4nKSi + nSiCl_4 \rightarrow \text{Si nanoparticles} + 4nKCl \]
HSiO1.5 Sol-Gel Polymer for Synthesis of Silicon Nanocrystals

1) ncSi were synthesized by thermal processing of trichlorosilane-derived sol-gel glasses followed by HF etching and surface passivation with alkyl chains.

2) SiO2-embedded silicon nanocrystals (Si-NCs) from thermal processing of sol-gel polymers derived from trichlorosilane (HSiCl3).
Scheme 1. Hydrolysis and Condensation Reactions That Form \((\text{HSiO}_{1.5})_n\) Polymers from H-SiCl₃

\[
\begin{align*}
\text{≡Si─Cl} + \text{H}_2\text{O} & \xrightarrow{\text{Hydrolysis}} \text{≡Si─OH} + \text{HCl} \\
\text{≡Si─OH} + \text{HO─Si≡} & \xrightarrow{\text{Condensation}\;\text{H}^+} \text{≡Si─O─Si≡} + \text{H}_2\text{O} \\
\text{≡Si─O─Si≡} & \xrightarrow{\text{Polycondensation}} \hspace{1cm} (\text{HSiO}_{1.5})_n
\end{align*}
\]
Figure 7. Normalized photoluminescence (PL) spectra of size-controlled freestanding Si-NCs produced from \((\text{HSiO}_{1.5})_n\) processed at 1100 °C for 1 h in 5% \(\text{H}_2/95\%\ \text{Ar}\) as a function of HF etching time (35, 50, and 65 min). The blue-shift with decreasing Si-NC diameter is in accordance
Monodisperse silicon nanocrystals (ncSi) by size-separation of polydisperse alkyl-capped Si NCs using organic density gradient ultracentrifugation (used for separation of SWCNTs)

2) ncSi were synthesized by thermal processing of trichlorosilane-derived sol-gel glasses followed by HF etching and surface passivation with alkyl chains.

3) Monodisperse ncSi will allow for the quantification of the size-dependent structural, optical, electrical, and biological properties of silicon NCs.
Figure 3. PL spectra of ncSi fractions extracted from fluorescence maps (inset: ensemble average).

Intensity (a.u.) vs. Wavelength (nm) for various fractions labeled P16 to P38.
Size-Dependent Absolute Quantum Yields for Size-Separated Colloidally-Stable Silicon NCs

Nano Lett. 2012, 12, 337. by Ozin