Fabrication of Core/Shell

structured Nanoparticles



Representative heterogeneous nucleation

Peter Reiss,* Myriam Protie`re, and Liang Li, "Core/Shell Semiconductor Nanocrystals," Small 2009, 5, 154.

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

Margaret A. Hines and Philippe Guyot-Sionnest, *J Phys. Chem. B* **1996**, 100, 468. 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 \pm 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.

PL spectra of CdSe and CdSe/ZnS core/shell NCs



- 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

M. G. Bawendi, J Phys. Chem. B 1997, 101, 9463.

Published: NOV 13 1997 Times Cited: 2,322

Strongly Luminescing ZnS-Capped CdSe Nanocrystals

Margaret A. Hines and Philippe Guyot-Sionnest, *J Phys. Chem. B* **1996**, 100, 468. 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.

2-step Synthesis of ZnS-Capped CdSe QDs







The Nobel Prize in Physics 2000

"for basic work on information and communication technology"

"for developing semiconductor heterostructures used in highspeed- and opto-electronics" "for his part in the invention of the integrated circuit"



Zr	nore	s	I. AI	terov	
Φ	1/4	of	the	prize	

Russia

A.F. Ioffe Physico-Technical Institute St. Petersburg, Russia

h.	1930
- · ·	2200

Herbert Kroemer
9 1/4 of the prize
Federal Republic of Germany
University of
California
Santa Barbara, CA, USA
b. 1928



b. 1923 d. 2005



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





Peter Reiss,* Myriam Protie`re, and Liang Li, "Core/Shell Semiconductor Nanocrystals," Small 2009, 5, 154.

Novel properties of core-shell QD's:

 Overcoating with higher band-gap materials improved the PL-QY by passivating surface nonradiative recombination sites.

2) More robust that 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 $42 \pm 10\%$ Å diameter CdSe cores. The spectra are for (a) 0, (b) 0.65, (c) 1.3. (d) 2.6. and (e) 5.3 monolavers 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.



Figure 8. 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 \sim 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



Published in: J. Jack Li; Y. Andrew Wang; Wenzhuo Guo; Joel C. Keay; Tetsuya D. Mishima; Matthew B. Johnson; Xiaogang Peng; *J. Am. Chem. Soc.* **2003**, 125, 12567-12575. DOI: 10.1021/ja0363563 Copyright © 2003 American Chemical Society 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.

Atomic-Layer-Deposition (ALD) Monolayer growth condition depends on both chamber temperature and pulsing timings. тма VIA: AI(CH.). Press tydroxyl: OH H.C Aethane: CH, Vater: H.O TMA Time Step1: Chemical sorption of TMA

tep2: Removal of TMA and CH₄ Step3: Reaction with H₂O and Al

Step4: Removal of H₂O and CH₄

http://www.brl.ntt.co.jp/people/yharada/res_pro/projects/ald.html

- 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.

Xiaogang Peng; J. Am. Chem. Soc. 2003, 125, 12567-12575.

Type-II Core/Shell CdS/ZnSe Nanocrystals:

Victor I. Klimov (Los Alamos National Laboratory), J. Am. Chem. Soc. 2007, 129, 11708.





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Zhores I. Alferov						
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Russia

A.F. Ioffe Physico-Technical Institute St. Petersburg, Russia

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Santa Barbara, CA,
USA
h 1928



b. 1923

d. 2005

P-n junction Homojunction vs. Heterojunction



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

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 Moungi 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.



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)). otentials (eV) ⇔ ⇔ ♭ ∾ Potentials (eV) 2 CdSe CdTe Organic Organic _igands Ligands -16 b) -18 10 20 Distance from Center (Å) 30 10 20 Distance from Center (Å) 6 6 Absorptivity PL intensity intensity 3 3 400 40010001000Wavelength(nm) Wavelength(nm)

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

Modified after Nozik, A. J. and coworkers, J. Phys. Chem. 1995, 99, 7754.





Figure 2. Transmission electron micrograph of InP nanocrystals.



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.

Core/shell nanocrystals with InAs cores

JACS 2000, 122, 9692 by Uri Banin at Hebrew U.

- 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 quanched in InAs/InP,
- but increases up to 20% for InAs/CdSe and InAs/ZnSe.



Evolution of Absorption spectra during growth of shell



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. Small lattice mismatch

InAs/CdSe InAs/CdSe InAs/ZnSe InAs/ZnSe InAs/ZnS InAs/ZnS 1.2 nm core 2.5 nm core 1.2 nm core 2.8 nm core 1.2 nm core 1.7 nm core



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 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), InA nd InAs/CdSe core/shell (frame C, core radius 1.7 nm, shell thickness 1.5 nm). The scale bar is 2 nm. The n

Epitaxial growth of Shell

2θ

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 [In(MA)x], zinc stearate,

tris(trimethylsilyl)phosphine [P(TMS)3], and dodecanethiol

were mixed in 1-octadecene (ODE) under inert atmosphere

at RT & subsequently heated to 300 °C within 3 min.

- -(3) Kwon, S. G.; Piao, Y.; Park, J.; Angappane, S.; Jo, Y.; Hwang, N. M.; Park, J. G.; Hyeon, T. J. Am. Chem. Soc. **2007**, 129, 12571–12584.
- (4) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Angew. Chem., Int. Ed. **2007**, *46*, 4630–4660.

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)

 $4nKSi + nSiCl_4 \rightarrow Si$ nanoparticles + 4nKCl

HSiO1.5 Sol-Gel Polymer for Synthesis of Silicon Nanocrystals Chem. Mater. 2009, 21, 5426 by Veinot (U. Alberta).

- ncSi were synthesized by thermal processing of trichlorosilane-derived sol-gel glasses followed by HF etching and surface passivation with alkyl chains
- 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 (HSiO_{1.5})_n Polymers from H-SiCl₃

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% H₂/95% 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 Using Density Gradient Ultracentrifugation JACS 2011, 133, 11928 by Ozin (U. Tronto).

- 1) Monodisperse silicon nanocrystals (ncSi) by size-separation of polydisperse alkyl-capped Si NCs using organic density gradient ultracentrifugation (used for separation of SWCNTs)
- ncSi were synthesized by thermal processing of trichlorosilane-derived sol-gel glasses followed by HF etching and surface passivation with alkyl chains
 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

Size-Dependent Absolute Quantum Yields for Size-Separated Colloidally-Stable Silicon NCs

Nano Lett. 2012, 12, 337. by Ozin

