Colloidal Q-dot Solar Cells

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Outline

- Nanomaterials
- Colloidal nanoparticles
  - Quantum dots-QDs
    - Core-Shell QDs
    - Anisotropic QDs
- QD solar cells
  - QD sensitized solar cells
  - QD–polymer NC solar cells
- Summary
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<td>Nanocrystals and clusters (quantum dots)</td>
<td>1 - 10 nm (diam.)</td>
<td>Metals, semiconductors, magnetic materials</td>
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<td>Nanoporous solids</td>
<td>0.5-10 nm (pore diam.)</td>
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<td>2D arrays (of nanoparticles)</td>
<td>Several nm² - μm²</td>
<td>Metals, semiconductors, magnetic materials</td>
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<td>1-100 nm (thickness)</td>
<td>A variety of materials</td>
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<td>3D structures (superlattices)</td>
<td>Several nm in the three dimensions</td>
<td>Metals, semiconductors, magnetic materials</td>
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Size sensitive changes in optoelectronic properties:

- Single atom
  - Ground state (Valence state)
  - Excited state (Conduction state)

Crystal lattice (Bulk)
- Conduction Band
- Band Gap
- Valence Band

Crystal lattice (Quantum Dot)
- Band Gap

A continuous density of states results in conduction and valence ‘bands’

When the number of atoms in the lattice is very few, the density of states becomes discrete, and loses the continuous ‘band’ like feature

Particles **small enough** to show **discrete density of states** are called Quantum Dots.

More generally, when a material has one or more **dimensions small enough** to affect its **electronic density of state**, then the material is said to be confined. Accordingly we can have quantum wells (thin films), quantum wires (wires), and quantum dots (particles).
Quantum Dots - QDs

- Size must be on the order of the **exciton Bohr radius**
  \[ a_0 = \frac{4\pi\varepsilon_0\varepsilon_0 h^2}{mq^2} \]
  
  \( (1 - 10 \text{ nm}; 10^2 - 10^5 \text{ atoms}) \)

- Size tunable properties – a new degree of freedom

**CdSe Quantum Dots drawn to scale**

2 - 10 nm

Bohr radius

'radius of excited state or exciton'
A colloidal dispersion is a system in which particles of colloidal size of any nature (e.g. solid, liquid or gas) are dispersed in a continuous phase of a different composition (or state).

The term colloid may be used as a short synonym for colloidal system.

QDs dispersed in a liquid or polymer → Colloidal QDs → CQDs
Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites

C. B. Murray, D. J. Norris, and M. G. Bawendi

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 22, 1993

Abstract: A simple route to synthesize and a high degree of monodispersity in organometallic reagents by selecting portions of the growth solution results in sharp absorption and emission spectra. Computed simulations indicate the pronounced quantum size effects observed in these nanocrystallites. Surface derivatization, structural and spectroscopic measurements of the nanocrystallites are discussed.

PL excitation (red) and emission (blue) spectra of 3.1 nm CdSe QDs
1. The shell can alter the charge, functionality, and reactivity of the surface

2. The shell can enhance the stability and dispersability of the colloidal core

3. Magnetic, optical, or catalytic functions may be readily imparted to the dispersed colloidal core

4. Encasing colloids in a shell of different composition may also protect the core from extraneous chemical and physical changes
General Synthesis Scheme/Protocol

Synthesis, encapsulation, purification and coupling of single quantum dots in phospholipid micelles for their use in cellular and in vivo imaging

Olivier Carion, Benoît Mahler, Thomas Pons & Benoît Dubertret

**MATERIALS**

**REAGENTS**

- 1-Octadecene (Sigma Aldrich, cat. no. 080-6)
- Cadmium nitrate tetrahydrate (Sigma Aldrich, cat. no. 229520)
- Sodium myristate salt (Fluka, cat. no. 70140)
- Selenium (100 Mesh, Aldrich, cat. no. 229865)
- Trioctylamine (TOA) (Fluka, cat. no. 92828)
- Zinc oxide (Fluka, cat. no. 96479)
- Cadmium oxide (Sigma Aldrich, cat. no. 202894)
- Oleic acid (Sigma Aldrich, cat. no. 36,452-5)
- Trioctylphosphine (TOP) (Alfa Aesar, cat. no. 089793)
- Sulfur (Sigma Aldrich, cat. no. 213292)

*Figure 2* | Schematics of the QD synthesis set up.
CdSe/ZnS Core-Shell QDs

Thermal decomposition under inert atmosphere in oil.

\[ \text{Me}_2\text{Cd} + \text{TOPSe} \rightarrow \text{CdSe} \]

\[(\text{TMS})_2/\text{Me}_2\text{Zn}/\text{TOP} \rightarrow \] 300 °C

\[ \Delta T \]

Synthetic Scheme

CdSe QDs

Cd precursor + TOPSe

Coordinating Ligands/Surface Passivation

Core Shell (CdSe)ZnS QDs

Size Select if needed, Overcoat with ZnS

ZnS

CdSe
CdSe/ZnS Core-Shell QDs

Evolution of PL excitation spectra during shell growth. CdSe core (blue), immediately (green) and 1 h (orange) after TOPS injection, and final core/shell excitation (brown) and fluorescence (red) spectra.

Figure 8 | Transmission electron microscope image of core/shell CdSe/CdZnS.
In-vivo imaging of core-shell QCDs

(a) QD bioconjugates
- CdSe
- ZnS
- PEG
- Antibodies against Cancer Markers

(b) Intravenous injection of QD bioconjugates into mouse

(c) Active targeting of tumor cells by QD bioconjugates
CQDs - In-vivo imaging

Figure 2. (A, B) Spectral images of quantum dot–prostate-specific membrane antigen conjugates in live animals with and without tumor (control). (A) Image of control animals, with no fluorescence (unmixed spectral). (B) Xenograft tumor-bearing animal showing bright red fluorescence of tumor. (C) Autofluorescent superimposed image of control and tumor-bearing animals. (D) Autofluorescent unmixed quantum dot image. From Gao et al. (2004) and reproduced with permission from the Nature Publishing Group.

Core-Shell QDs

Type-I vs. Type-II QDs

- In Type-I QDs, all charge carriers are confined in the core material in which radiative recombination occurs.
- In Type-II QDs, charge carriers are segregated in the core and shell; radiative recombination occurs across the material interface.
Core-shell CQDs

Aqueous Layer-by-Layer Epitaxy of Type-II CdTe/CdSe Quantum Dots with Near-Infrared Fluorescence for Bioimaging Applications**

Yi Zhang, Yan Li, and Xiu-Ping Yan*

Scheme 1. Layer-by-layer epitaxy of CdTe/CdSe core/shell QDs with NIR fluorescence.
CdTe/CdSe Core-shell CQDs

Figure 1. Temporal evolution of a) the fluorescence emission peak positions; b) fluorescence intensity of CdTe and CdTe/CdSe (with single layer of CdSe shell) QDs; c) the UV/Vis absorption spectra, and d) the corresponding fluorescence spectra of CdTe and CdTe/CdSe (with 1–6 layers of CdSe shell) QDs.

Yan X.P. et al., small 2008, x, No. x, 1–5
Anisotropic CQDs

Rod-Shaped Nanocrystals Elicit Neuronal Activity In Vivo**

Maria Ada Malvindi, Luigi Carbone, Alessandra Quarta, Angela Tino, Liberato Manna, Teresa Pellegrino, and Claudia Tortiglione*

Figure 1. Characterization of QDs used in this study. a) A schematic representation of the CdSe/CdS rods, highlighting the asymmetrical shape derived from the synthesis procedure. The rod samples are an average of 35 nm in length and 4 nm in diameter as confirmed by b) the TEM image of the corresponding sample and c) the "mean dilation image" obtained...
Highly Emissive Colloidal CdSe/CdS Heterostructures of Mixed Dimensionality

Dmitri V. Talapin, Robert Koepe, Stephan Götzinger, Andreas Kornowski, John M. Lupton, Andrey L. Rogach, Oliver Barson, Jochen Feldmann, and Thorl Weller

Figure 1. Overview TEM images of (a) spherical CdSe nanocrystals used as seeds for the growth of (b) CdSe/CdS nanorods. (c) CdSe/CdS nanorods aligned on a TEM grid upon evaporating the solvent. High-resolution TEM images of (d) spherical CdSe nanocrystals and (e–g) CdSe/CdS nanorods with different aspect ratios prepared by the asymmetric epitaxial growth of the CdS shell on spherical CdSe seeds. The diameter of the rods is comparable to the diameter of the spherical seeds.

Figure 2. (a) Powder X-ray (Cu Kα radiation) diffraction patterns of the spherical CdSe cores and two samples of CdSe/CdS nanorods (aspect ratios 1.5:1 and 2.8:1) showing the crystallinity of all samples as well as the evolution from the pure hexagonal phase of CdSe to a system dominated by the hexagonal phase of CdS. The higher intensity and smaller width of the (002) reflection show that the long axis of the CdSe/CdS nanorods is the c axis of a wurtzite structure. The CdS reference is given in orange, and the CdSe reference, in red. (b) TEM image of CdSe/CdS nanorods showing the contrast change toward one end of the rods, which indicates that the cores are located at an asymmetric position inside the rods. (c) High-resolution TEM image of a CdSe/CdS nanorod with an asymmetric structure comprising a CdS core uniformly covered with thin CdS shell and fused onto a CdS rod. (d) Valence-band scheme of a dot and a rod with the crossover between A and B bands induced by the crystal field along the c axis.
CdSe/CdS CQDs

Figure 3. (a) Molar extinction coefficient $\varepsilon$ for 4-nm CdSe cores (solid black line) and 17 nm × 4.5 nm CdSe/CdS nanorods (solid red line) dispersed in chloroform. The PL excitation spectrum of nanorods detected at an emission wavelength of 615 nm (solid blue line) closely traces the extinction coefficient, indicating efficient carrier capture in the core. The black and red dashed lines show PL spectra measured under excitation at 450 nm for CdSe cores and CdSe/CdS nanorods, respectively, normalized to the particle concentration. (b) Evolution of the global Stokes shift for CdSe/CdS nanorods with different aspect ratios. For comparison, we measured the global Stokes shifts of spherical core–shell CdSe/CdS nanocrystals upon increasing thickness of the CdS shell. CdSe/CdS nanorods and nanospheres can be compared by quoting the CdS/CdSe molar ratio (top axis). (c) Room-temperature PL quantum yield of CdSe cores and CdSe/CdS nanorods in chloroform vs their aspect ratio.
CdTe Tetrapods

Controlled growth of tetrapod-branched inorganic nanocrystals

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AND A. PAUL ALIVISATOS**

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High temperature nucleation: Wurtzite crystals

High temperature growth

Low temperature nucleation; Zinc blende crystals

100 nm
 CdTe Nanotetrapods

Figure 2: Electron microscopy images of CdTe nanotetrapods. TEM of the CdTe tetrapods grown at various reaction conditions. The CdTe ratio was varied from 1:1 to 5:1, and the Cd/CdTe ratio was varied from 1:2 to 1:5. The Cd/CdTe ratio (or the CdTe ratio) must be at least 1:2 or 1:1 for the CdTe to decompose completely. An increase in the Cd/CdTe leads to tetrapods with longer arms.

Figure 4: Influence of the shape of CdTe tetrapods on optical absorption spectra. Ensemble optical absorption spectra, a, for a series of tetrapods having comparable arm lengths but different diameters, and b, for a series of tetrapods having comparable arm diameters but different lengths. The confinement energy is mainly dictated by the arm diameter.

Alivisatos A. P. et al., nature materials | VOL 2 | JUNE 2003 | 382-385.
HR TEM images show a cubic structure in the core area only, and hexagonal structures in the arms only.
New Mechanism Suggested

Low-temperature synthesis of photoconducting CdTe nanotetrapods

Charge Extraction is possible.

Sugunan A. E t al., J. Mater. Chem., 2010, 20, 1208–1214
What limits the efficiency:

- Photons with lower energy than the band gap are not absorbed.
- Photons with greater energy than the band gap are absorbed but the excess energy is lost as heat.

Silicon Solar Cells

Efficiency limited: not all incident solar energy convertible to electricity

From J.J. Schermer, Radboud Univ. Nijmegen, The Netherlands

Efficiency:
Theor. (AM1.5G) 33 \%
Max. achieved 24 \%
Usual 15-20 \%

Theoretical losses:
- 47 \% thermalization
- 18 \% not absorbed IR
- 2\% radiative recombination/thermodynamic loss
Colloidal Quantum Dots - CQDs

CQD Synthesis
- Colloidal chemistry
  - Simple, cheap, fast

CQD Film Deposition
- Spin coating
  - CQDs suspended in organic solvents
  - Simple, cheap, fast
- Multiple advantages
  - No lattice matching of CQDs and substrate
  - No limitations on materials combinations
  - Near-ambient conditions
  - Large area deposition
  - Multiple exciton generation
  - Access to infrared wavelengths
The strategies to develop QD based solar cells: (a) metal-semiconductor junction, (b) polymer-semiconductor, and (c) semiconductor-semiconductor systems.
How Can Quantum Dots Improve the Efficiency?

- The quantum dot band gap is tunable and can be used to create intermediate bandgaps. The maximum theoretical efficiency of the solar cell is as high as 63.2% with this method.
The hybrid silicon/PbS NC solar cells show external quantum efficiencies of 7% at infrared energies and 50% in the visible and a power conversion efficiency of up to 0.9%. This work demonstrates the feasibility of hybrid PV devices that combine advantages of mature silicon fabrication technologies with the unique electronic properties of semiconductor NCs.

Device Architecture

Architecture

- Type-II heterojunction
- Nanoporous metal oxide / infiltrated CQD film
- ITO – superior conductivity (~0.5 Ω.cm⁻¹)
- Mg cathode – low work function

Operation

- Light absorption in PbS CQD film
- Charge separation at distributed ITO/CQD interface
- Hole transport in PbS CQD
- Electron transport in nanoporous ITO

46% EQE at 500 nm
- > 5% at 1st excitonic feature
- Absorption beyond 1700 nm
- Suitable for integration in multi-junction solar cells

Solution Processed Solar Cells

- low-cost
- large area
- substrate compatibility

Current solution-processed devices

- Solar power conversion efficiency 3% - 5%
- Most limited to visible light absorption
- Sensitive to < 50% of available solar energy,

PbS CQD photovoltaic devices

- Absorb light in visible and IR
- All cost and manufacturing benefits of organic photovoltaics
How Can CQDs Improve the Efficiency?

- Quantum dots can generate multiple exciton (electron-hole pairs) after collision with one photon.

from A.J. Nairk
High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion

R. D. Schaller and V. I. Klimov
Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
(Received 25 November 2003; published 3 May 2004)

Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots

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Received February 19, 2003; Revised Manuscript Received March 18, 2004

On the Absence of Detectable Carrier Multiplication in a Transient Absorption Study of InAs/CdSe/ZnSe Core/Shell/Shell2 Quantum Dots

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(Received January 31, 2008; Revised Manuscript Received February 20, 2008)

In Spite of Recent Doubts Carrier Multiplication Does Occur in PbSe Nanocrystals

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(Received March 11, 2008; Revised Manuscript Received May 1, 2009)

Assessment of carrier-multiplication efficiency in bulk PbSe and PbS

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(Received October 19, 2009; Revised Manuscript Received February 1, 2010)
Multiple Exciton Generation in QDs

- The onset is near 3X the bandgap
- Largest multiplication factor is 7

Quantum Dot Solar Cells. Electrophoretic Deposition of CdSe–C\textsubscript{60} Composite Films and Capture of Photogenerated Electrons with nC\textsubscript{60} Cluster Shell

Patrick Brown and Prashant V. Kamat\textsuperscript{*}

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(A) AFM image of CdSe-nC\textsubscript{60} composite clusters deposited on OTE, (B) absorption spectra, (C) emission spectra, and (D) emission decay: (a) C\textsubscript{60}, (b) CdSe, and (c) CdSe-nC\textsubscript{60} mixed clusters in toluene/acetonitrile.

KAMAT et al., J. AM. CHEM. SOC. 2008, 130, 8890–8891
The observed photocurrent generation efficiency with CdSe-$nC60$ films is 2 orders of magnitude greater than CdSe films alone.

The strategy of encapsulating CdSe quantum dots in $nC60$ clusters paves the way for developing new and effective strategies toward light energy harvesting.
3.3% efficiency. The ultimate achievable solar conversion efficiency will be dependent on the ability to optimize the nanocrystal film and the respective thicknesses and absorption spectra of the components of the tandem cell.
Under Air Mass (A.M.) 1.5 Global solar conditions, a power conversion efficiency of 1.7% was obtained.
Solar power conversion efficiencies of 1.8% were achieved under AM1.5 illumination for a device containing 86 wt % of nanoparticles.

Figure 1. Transmission electron microscopy images of (a) tetrapods and (b) nanorods as described in the text.

Figure 3. Short-circuit external quantum efficiency (EQE) action spectra of photovoltaic devices containing CdSe nanorods (---) and tetrapods (--).
Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO₂ Films

István Robel,†,Ⅱ Vaidyanathan Subramanian,†,Ⅱ Masaru Kuno,*,†,Ⅰ and Prashant V. Kamat*,†,Ⅰ,Ⅱ

Contribution from the Notre Dame Radiation Laboratory, Department of Chemistry and Biochemistry, Department of Chemical and Biomolecular Engineering, and Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556-5674

Scheme 1. (a) Linking CdSe Quantum Dots to TiO₂ Particle with Bifunctional Surface Modifier; (b) Light Harvesting Assembly Composed of TiO₂ Film Functionalized with CdSe QDs on Optically Transparent Electrode (Not to Scale)
The photocurrent generation observed upon visible light excitation of CdSe QDs highlights the feasibility of their use as light harvesting antennae. These studies point out the need for further improvement in the design of semiconductor QDs to maximize the photoconversion efficiency.

Robel et al. J. AM. CHEM. SOC. 9 VOL. 128, NO. 7, 2006 2393
Random versus Directed Electron Transport through Support Architectures, (a) TiO2 Particle and (b) TiO2 Nanotube Films Modified with CdSe Quantum Dots
CdSe-TiO₂

- Smaller-sized CdSe quantum dots show greater charge injection rates.
- Larger particles have better absorption in the visible region but cannot inject electrons into TiO₂ effectively.
- Because of the interplay of various factors, we observe maximum power-conversion efficiency (<1%) with 3 nm diameter quantum dots.

Exciton escape in CdSe core-shell quantum dots: Implications for the development of nanocrystal solar cells

Exciton tunneling times in QDs are highly dependant on QD size, shell thickness, and barrier height...

Efficient charge extraction depends on the careful selection of geometrical parameters.

Ideal QD NC Solar Cells

Analysis of Power Conversion Limits:

- Each QD is connected to electron (e) and hole (h) collecting electrodes.
- All extrinsic losses are ignored.
- Ultimate efficiency: 36%.

Rainbow Solar Cells

A rainbow solar cell, which employs an ordered assembly of CdSe QDs of different diameters. TiO2 nanotubes decorated with different-sized CdSe nanoparticles.

As white light enters the cell, smaller sized CdSe particles (larger band gap) absorb the portion of the light with smaller wavelengths (blue region). Light with longer wavelengths (red region), which is transmitted through the initial layer, is absorbed by subsequent layers, and so on. By creating an orderly gradient of quantum dots of different size, it should be possible to increase the effective capture of incident light.

Challenges

Nano-enabled Solar Products/Applications

First Level Integration

Processing

Compositions

Nano-wires

Nano-dots

Nano-rods

Purification

Harvesting

Substrate, deposition

Orientation, alignment

Surface chemistry

Ligand chemistry

QD down-conversion layers

New areas

Processing

Conversion step

Light absorption

exciton creation

exciton diffusion

charge separation

charge transport

charge collection

Loss mechanism

incident photons

Exciton Recombination

Charge Recombination

charges at electrodes

http://www.qdsoleil.com/iproperty.php
Synthesis and component Fabrication

- Design and fabrication of
  - Quantum dots core
  - Fabrication of Shells
- Integration into conducting polymeric matrix

System Integration

- Conventional structures
- Advanced solar cells design (Tandem cells)
- Nano-antennas
Summary

Advantages

- Low-cost
- Potential for integration
- Access to IR wavelengths
- Promise of high-performance CQD device applications

Challenges

- Low efficiency
- Carrier extraction
- Tailoring of CQD-polymer active layer