Workshop on Nanoscience for Solar Energy Conversion

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Quantum Dot Solar Cells: Semiconductor Nanocrystals As Light Harvesters

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Meeting the Energy Demand

14 TW Challenge
Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters

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Support: US DOE (BES)

http://www.nd.edu/~pkamat
Meeting the Energy Demand

Supplying Oil and Gas Demand Will Require Major Investment

Millions of Barrels per Day of Oil Equivalent (MBDOE)

World Oil Production vs. Discovery

Source: Dr. C.J. Campbell

"DRILL BABY DRILL"

World Oil Production vs. Discovery

Source: Dr. C.J. Campbell

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What if all you needed to capture energy was a new coat of paint?
Can we address the clean energy challenge with Nanotechnology?
Our Research Focus

Photoinduced electron transfer in light harvesting systems
- Donor-Acceptor
- Semiconductor-Sensitizer
- Semiconductor-Semiconductor
- Semiconductor-Metal
Quantum Dot Solar Cells

Tunable band edge
Offers the possibility to harvest light energy over a wide range of visible-IR light with selectivity

Hot carrier injection from higher excited state
(minimizing energy loss during thermalization of excited state)

Multiple carrier generation solar cells.
Utilization of high energy photon to multiple electron-hole pairs
1. Semiconductor/metal Interface

Because of smaller dimensions charge separation and transport issues in nanostructure films need to be tackled.
PbSe NC film, deposited via layer-by-layer dip coating

Short-circuit photocurrent (>21 mA cm\(^{-2}\)) by way of a Schottky junction

EQE of 55-65% in the visible and up to 25% in the infrared region

Power conversion efficiency of 2.1%.

Luther et al Nano Lett., Vol 8, 2008, 3488
2. Polymer –Semiconductordor Nanocrystal Hybrids

Hybrid Nanorod-Polymer Solar Cells

![Diagram of Hybrid Nanorod-Polymer Solar Cells]

Regioregular P3HT

CdSe/P3HT Blend

PEDOT:PSS Substrate ITO

A

B

C

A

B

C

50 nm

External Efficiency (%)

External Quantum Efficiency (%)
3. Quantum Dot Sensitized Solar Cell (QDSSC)
GERISCHER H, LUBKE M
A PARTICLE-SIZE EFFECT IN THE SENSITIZATION OF TiO2 ELECTRODES BY A CdS DEPOSIT
JOURNAL OF ELECTROANALYTICAL CHEMISTRY 204 (1-2): 225-227 1986
Photoexcitation of CdSe Quantum Dots

Pump probe detector

CdSe

Time, ps

Absorbance

ΔOD

Wavelength, nm

Δ OD

440 nm

530 nm

0.2 ps

0.3 ps

0.4 ps

0.5 ps

1.1 ps

1P(e)-1P_{3/2}(h)

1S(e)-1S_{3/2}(h)

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1S(e)-1S_{3/2}(h)
Charge Separation in TiO$_2$/CdSe

Transient Bleaching Recovery of 3 nm CdSe Quantum Dots

Ex. 387 nm

CdSe-MPA

CdSe-MPA-TiO$_2$
Modulation of the charge injection process by controlling the particle size?

E_g = 1.9 eV

CdSe

TiO_2

E_g = 2.4 eV

CdSe

TiO_2

CdSe

7.5 nm

CdSe

2.4 nm
CdSe quantum dots of size 2.4 nm to 7.5 nm were excited with 387 nm laser pulse (130 fs).

As the particle size decreases from 7.5 nm to 2.4 nm, the first \(^{1}\text{S}_{3/2}^{1}\text{S}_{e}\) excitonic peak shifts from 645 nm (1.92 eV) to 509 nm (2.44 eV).

Transient bleach corresponds to the first excitonic bleach.

Robel, Kuno, Kamat, JACS 2007; 129, 4136
Electron transfer between CdSe and TiO$_2$

CdSe (es) + TiO$_2$ $\rightarrow$ CdSe + TiO$_2$(e)

Analysis of Bleaching Recovery

$\Delta A(t) = \Delta A(0) \times \exp\left[-(t/\tau)\beta\right]$

- where $\tau$ is the peak value of the characteristic lifetime

Robel, Kuno, Kamat, JACS 2007; 129(14) pp 4136 - 4137
## Size Dependent Quenching Phenomenon

\[
\Delta A(t) = \Delta A(0) \times \exp\left[-\frac{(t/\tau)^\beta}{\beta}\right]
\]

- where \( \tau \) is the peak value of the characteristic lifetime

\[
\frac{1}{\tau'} - \frac{1}{\tau} = k_{et}
\]

<table>
<thead>
<tr>
<th>Diameter [nm]</th>
<th>( E_g ) [eV]</th>
<th>( \tau_{CdSe} ) [ps]</th>
<th>( \beta_{CdSe} )</th>
<th>( \tau_{CdSe-TiO2} ) [ps]</th>
<th>( \beta_{CdSe-TiO2} )</th>
<th>( k_{et} ) [s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>1.92</td>
<td>2332</td>
<td>0.697</td>
<td>2281</td>
<td>0.755</td>
<td>( 9.58 \times 10^6 )</td>
</tr>
<tr>
<td>4.6</td>
<td>1.99</td>
<td>7224</td>
<td>0.474</td>
<td>4961</td>
<td>0.446</td>
<td>( 6.3 \times 10^7 )</td>
</tr>
<tr>
<td>3.5</td>
<td>2.18</td>
<td>4420</td>
<td>0.417</td>
<td>1117</td>
<td>0.475</td>
<td>( 6.7 \times 10^8 )</td>
</tr>
<tr>
<td>2.7</td>
<td>2.35</td>
<td>6739</td>
<td>0.457</td>
<td>357</td>
<td>0.505</td>
<td>( 2.65 \times 10^9 )</td>
</tr>
<tr>
<td>2.3</td>
<td>2.44</td>
<td>23119</td>
<td>0.51</td>
<td>83</td>
<td>0.493</td>
<td>( 1.2 \times 10^{10} )</td>
</tr>
</tbody>
</table>
Size Dependent Electron transfer between CdSe and TiO₂

Robel, Kuno, Kamat, JACS 2007; 129 pp 4136 - 4137
Linking Q-CdSe to TiO$_2$ particles

Photoelectrochemical behavior of Q-CdSe-TiO₂ films

I-V characteristics of (a) OTE/TiO₂ and (b) OTE/TiO₂/MPA/CdSe films. Electrolyte 0.1 M Na₂S. The filtered lights allowed excitation of TiO₂ and CdSe films at wavelengths greater than 300 and 400 nm respectively.
Modification of TiO$_2$ Films with Different Size CdSe Particles
Tuning the Photoresponse of Quantum Dot Solar Cells

IPCE or Ext. Quantum Eff.

\[ = \left(\frac{1240}{\lambda}\right) \times \left(\frac{I_{sc}}{I_{inc}}\right) \times 100 \]

\[ J. \text{Am. Chem. Soc.}, \textbf{130} (12), 4007 -4015, 2008 \]
Photocurrent Response

Efficiency of Charge Injection vs. Light absorption

Solar Flux

Energy (eV)

Current density, mA/cm²

Time, sec

(A)

- 3.7 nm
- 3.0 nm
- 2.6 nm
- 2.3 nm
Can we employ the nanowire/nanorod architecture to improve the performance of quantum dot solar cells?

(a) OTE/TiO₂ nanoparticles

(b) Ti/TiO₂ nanotubes
Recent advances

Nanowire dye-sensitized solar cells
LAW, GREENE, JOHNSON, SAYKALLY, YANG Nature Materials 4, 455, 2005

Fast Electron Transport in Metal Organic Vapor Deposition Grown Dye-sensitized ZnO Nanorod Solar Cells

Electron transport in solar cells with ZnO-nanorod electrodes was about 2 orders of magnitude faster (30μs) than ZnO-colloid electrodes
Mor, G. K. et al. *Use of highly-ordered TiO\textsubscript{2} nanotube arrays in dye-sensitized solar cells.*


Leschkies, K. S et al *Photosensitization of ZnO nanowires with CdSe quantum dots for photovoltaic devices.*


Martinson, A. B. F. et al., *ZnO nanotube based dye-sensitized solar cells ZnO nanotube based dye-sensitized solar cells.*

Photoemission of CdSe/glass and CdSe/TNP

Emission spectra of CdSe QDs (a, c) on glass and (b, d) chemically bound to TiO₂ nanoparticle films at 2 different sizes of QDs (2.7 and 3.7 nm). Excitation was at 480 nm.

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter</th>
<th>&lt;t&gt;, ns</th>
<th>kₑᵗ, sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/glass</td>
<td>2.6 nm</td>
<td>4.1</td>
<td>2.5E+09</td>
</tr>
<tr>
<td></td>
<td>3.7 nm</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>CdSe/TNP</td>
<td>2.6 nm</td>
<td>0.4</td>
<td>2.2E+09</td>
</tr>
<tr>
<td></td>
<td>3.7 nm</td>
<td>1.5</td>
<td>5.5E+08</td>
</tr>
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</table>
Quantum Dot Solar Cells – Particle versus Tube Architecture

**Table:**

<table>
<thead>
<tr>
<th></th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$P_{max}$ (mW/cm$^2$)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe-TNP</td>
<td>1.64</td>
<td>0.591</td>
<td>0.25</td>
<td>0.26</td>
</tr>
<tr>
<td>CdSe-TNT</td>
<td>1.95</td>
<td>0.582</td>
<td>0.29</td>
<td>0.26</td>
</tr>
</tbody>
</table>


Power conversion efficiency ~1%
Depositing CdS quantum dots on TiO$_2$ nanotubes

Depositing CdS quantum dots on TiO$_2$ nanotubes involves the following steps:

1. (TiO$_2$) + Cd$^{2+}$ → (TiO$_2$)Cd$^{2+}$
2. (TiO$_2$)Cd$^{2+}$ + S$^{2-}$ → (TiO$_2$)CdS
3. Wash

This process is repeated for each dip cycle.

Scale bars: Top 500nm, bottom 50nm
Photocurrent Response of TiO$_2$ (nanotube)CdS Films

**IPCE: CdS on Single TiO2 electrode**

![Graph showing IPCE for different dip counts](image)

- Tubes
- 5 dip
- 10 dip
- 15 dip
- 20 dip

**Reflectance Absorption Spectra: CdS/P25/OTE**

![Graph showing reflectance absorption spectra](image)
Carbon nanostructures as conduits to transport charge carriers

Advantages
- High surface area
- Good electronic conductivity, excellent chemical and electrochemical stability
- Good mechanical strength

Goal
Effective utilization of carbon nanostructures for improving the performance of energy conversion devices
- To develop electrode assembly with CNT supports
- Improve the performance of light harvesting assemblies
- Facilitate charge collection and transport in nanostructured assemblies

.....towards achieving ordered assemblies on electrode surface
SWCNT- TiO$_2$ composite films

• Mesoscopic TiO$_2$ films are extensively used in Dye-Sensitized Solar Cells

• A carbon nanotube support architecture can disperse the TiO$_2$ particles and facilitate charge collection and charge transport within the film.

• The first step is to design the SWCNT-TiO$_2$ network and test the feasibility of the composite system in solar cells


Electrophoretic Deposition of SWCNT on Electrode Surfaces

OTE/SnO$_2$/SWCNT

OTE/SnO$_2$

OTE/SWCNT

Carbon Fiber Paper (CFE)

TiO$_2$ Deposition On CFE

SWCNT – Deposition On CFE

SWCNT-TiO$_2$ on CFE
Photocurrent Generation
CFE/TiO$_2$ versus CFE/SWCNT –TiO$_2$

Higher IPCE (increase of factor ~2) was observed for mesoscopic CFE/SWCNT-TiO$_2$ films

The results are indicative of better charge collection and transport provided by the SWCNT -Network

Increasing the TiO$_2$ concentration results in enhanced photocurrent as they are dispersed on SWCNT network.

At concentrations greater than 2 mg/cm$^2$ the beneficial effect of SWCNT disappears. Under these conditions, TiO$_2$ particles aggregate and the charge recombination dominates.

Where do we go from here?
Capping CdSe with an Electron Acceptor Shell

Electrophoretic deposition of Cluster films

Organized light harvesting assembly using carbon nanostructures

Graphene-Semiconductor Nanocomposites  
ACS Nano, 2008, 2, 1487-1491
Summary

- Unique properties of quantum dots offer new opportunities to develop low-cost and high efficiency solar cells.
- 1-D architectures are useful for designing next generation solar cells.
- Opportunities exist for carbon nanostructures to facilitate capture and transport of electrons in nanostructure semiconductor based solar cells.


Researchers/Collaborators

Graduate students
Brian Seger (Chem. Eng.)
David Baker (Chem. Eng.)
Kevin Tvrdy (Chemistry)
Clifton Harris (Chemistry)
Matt Baker (Physics)
Ian Lightcap (Chemistry)
Philix Vietmeyer (Chemistry)
Yanghai Yu (Chem. Eng.)
Istvan Robel (Physics)

Post-Docs/Visiting Scientists
Jin Ho Bang

Undergraduate students
Pat Brown
Chris Rodriguez
David Riehm
Rachel Staran

Collaborators
Dr. K. G. Thomas (India)
Prof. Fukuzumi (Osaka U.)
Prof Ken Kuno (UND)
Prof. K. Vinodgopal (IUN)
What will the future hold?

Over the last twenty years, the per-kWh price of photovoltaics has dropped from about $500 to nearly $5; think of what the next twenty years will bring.
"Move over Oil Slick Harry. Your energy guzzling days are over. It's time for a cleaner more efficient heater like me"!

http://www.theleveredge.com/images/isw_cartoon.gif