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1938-2

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

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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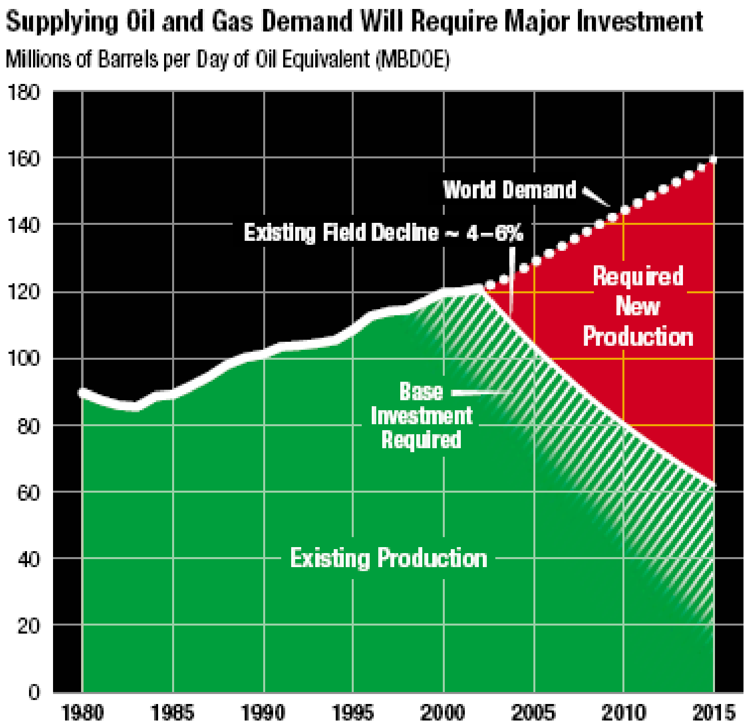
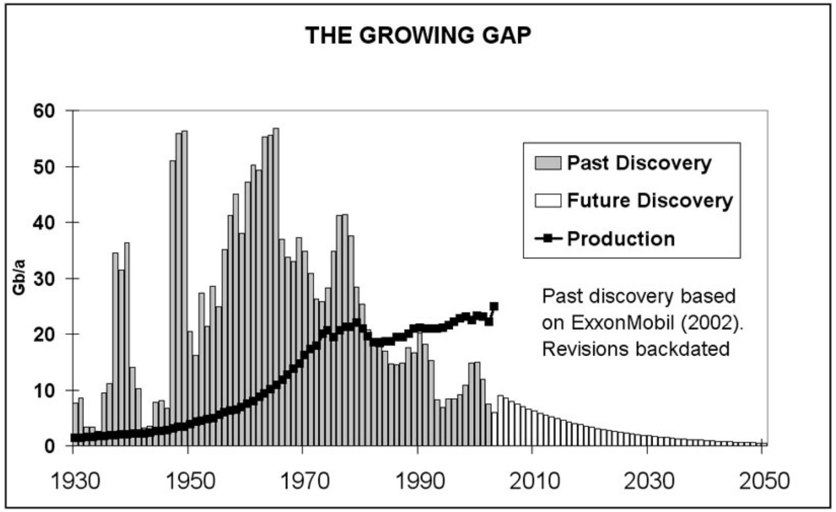
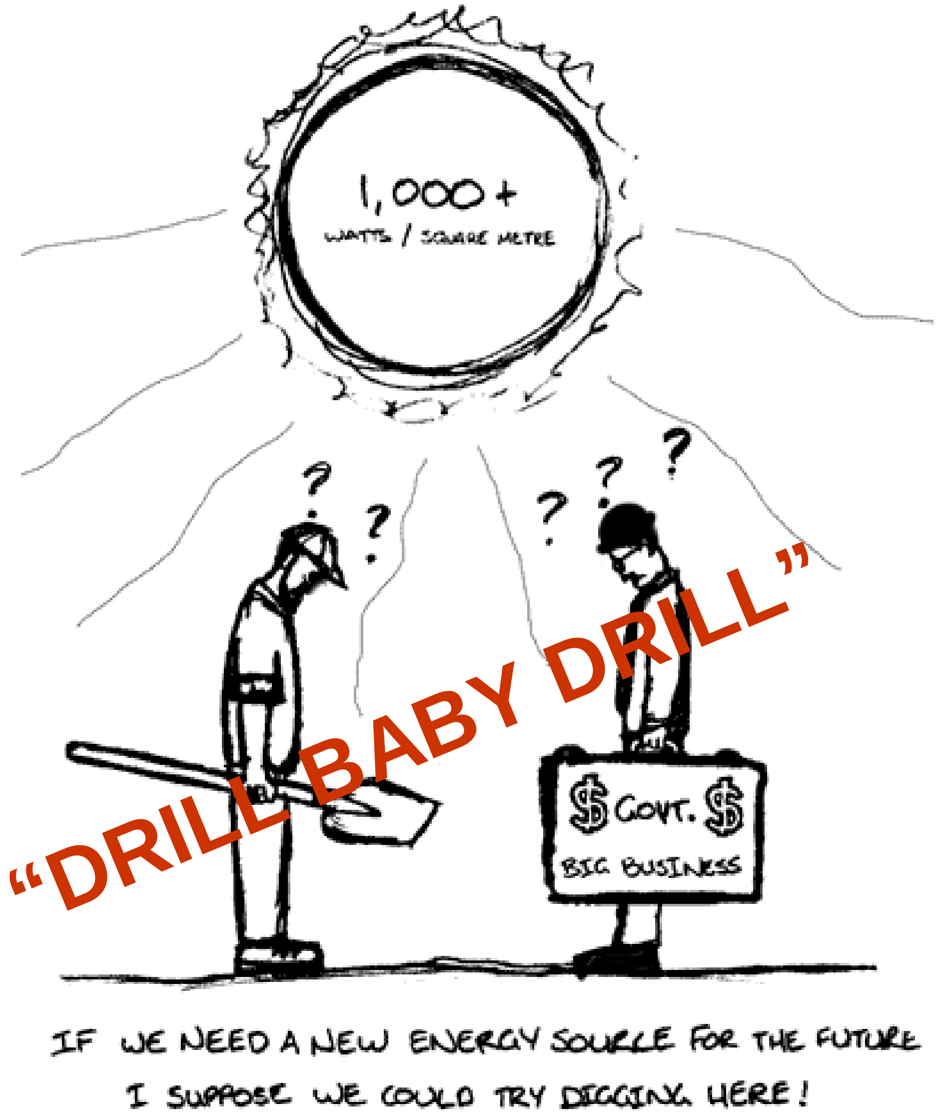
Support: US DOE (BES)

http://www.nd.edu/~pkamat

Meeting the Energy Demand



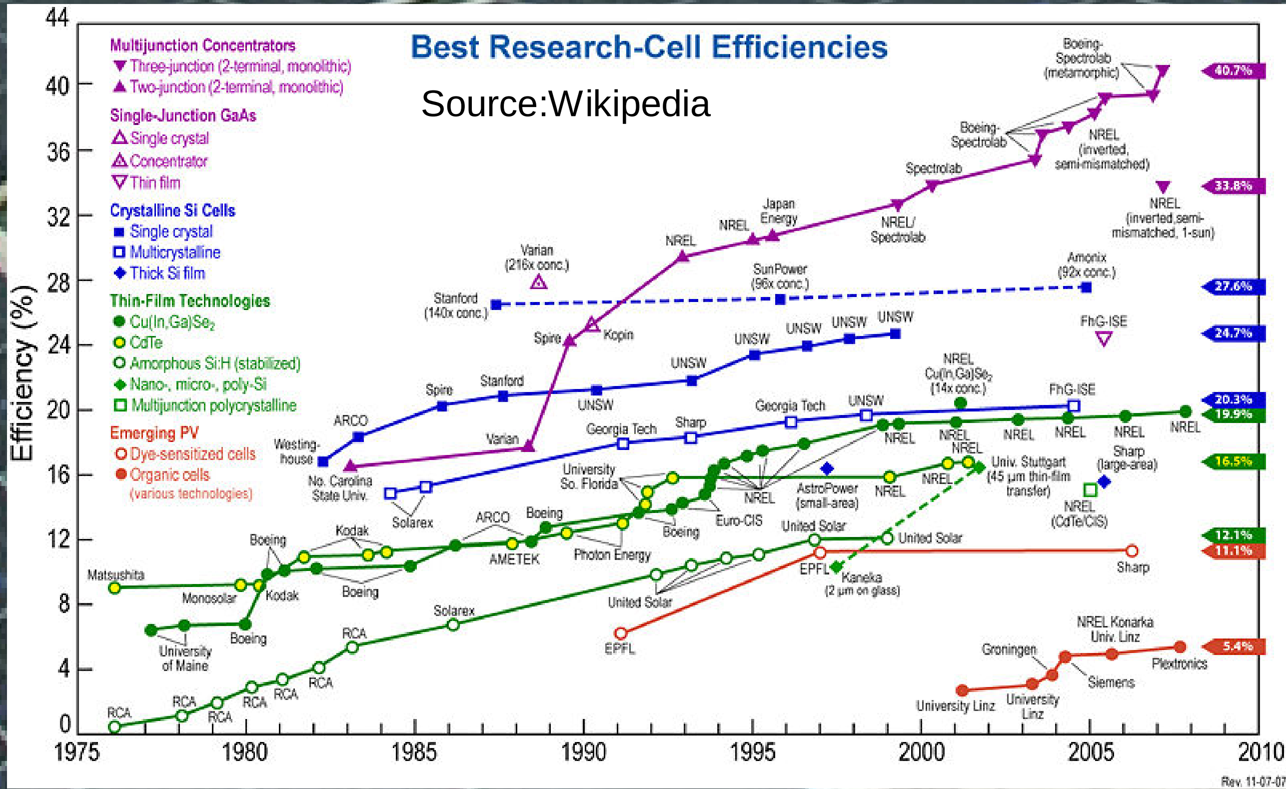




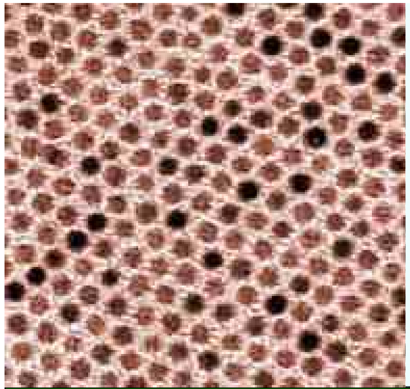
www.solarsales.com.au

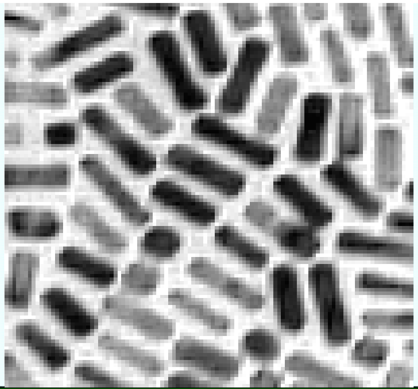
World Oil Production vs. Discovery
Source: Dr. C.J. Campbell

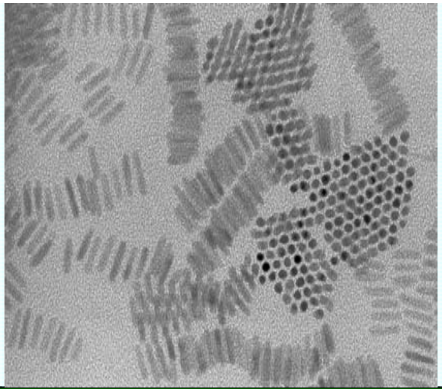
Solar Revolution

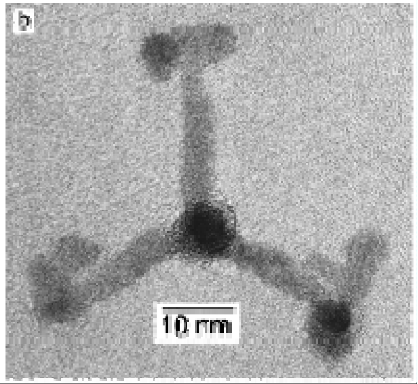


What if all you needed to capture energy was a new coat of paint?

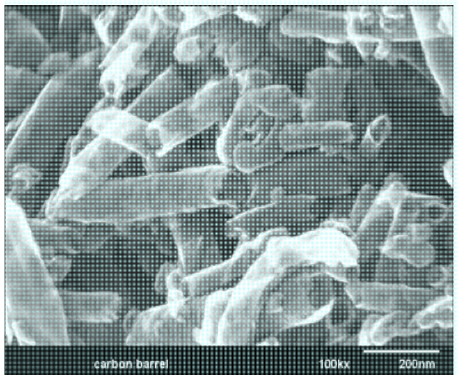


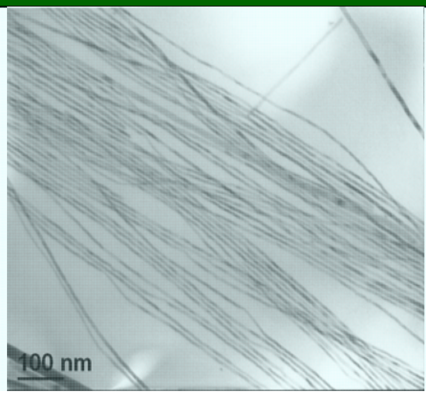


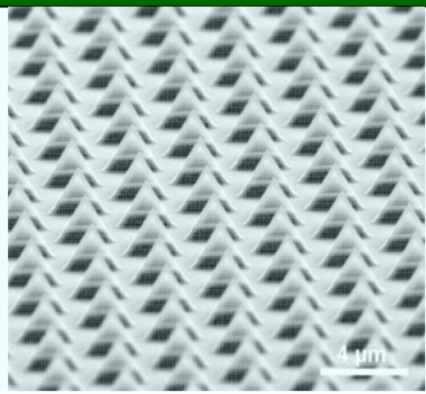


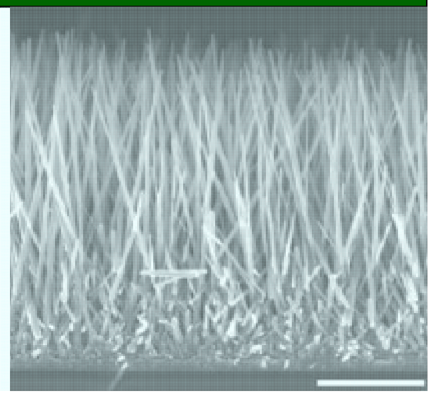


Can we address the clean energy challenge with Nanotechnology?





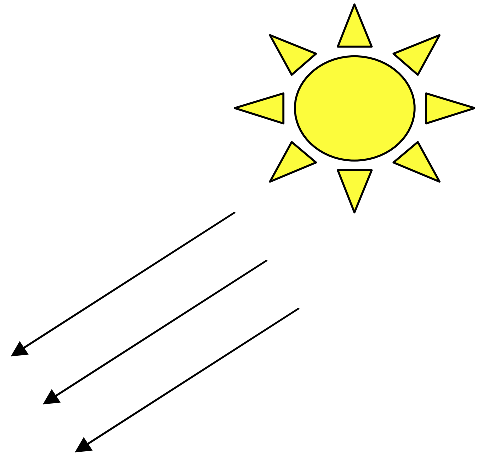


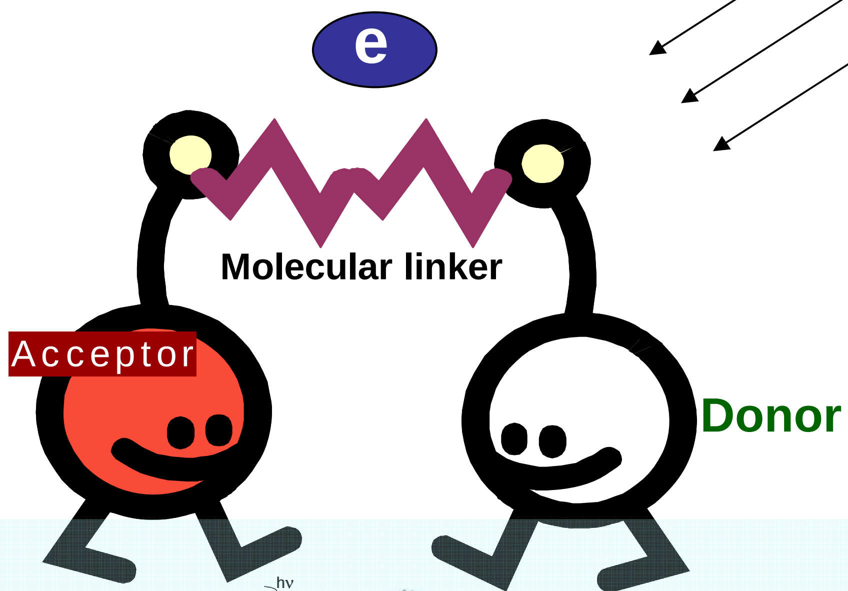


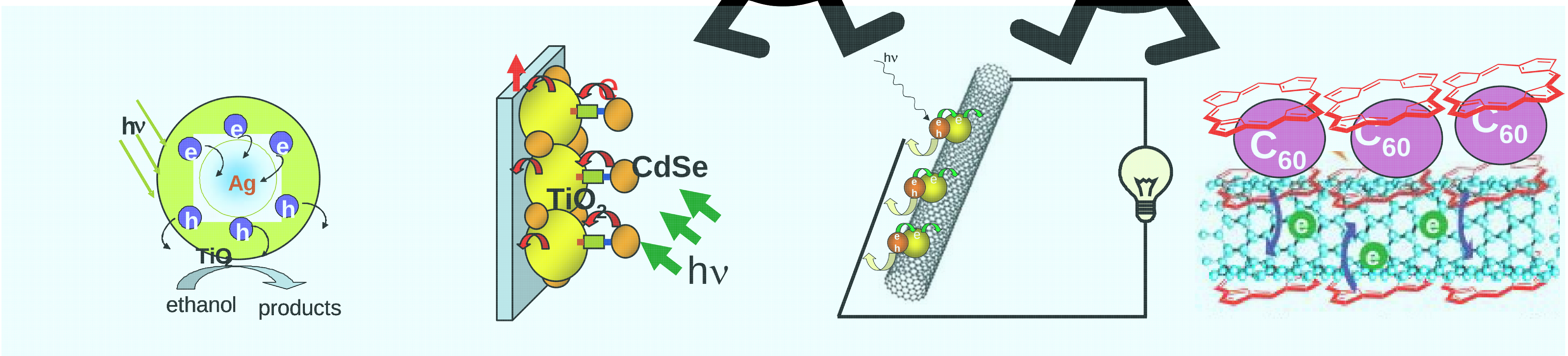
Our Research Focus

Photoinduced electron transfer in light harvesting systems

- **Donor- Acceptor**
- **Semiconductor-Sensitizer**
- **Semiconductor-Semiconductor**
- **Semiconductor-Metal**



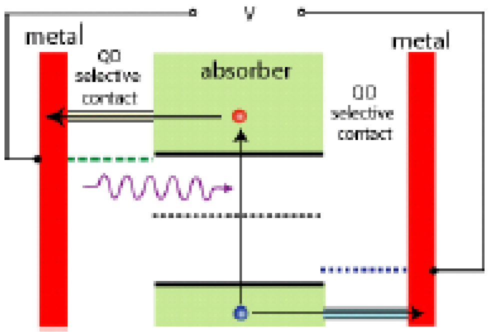




Quantum Dot Solar Cells

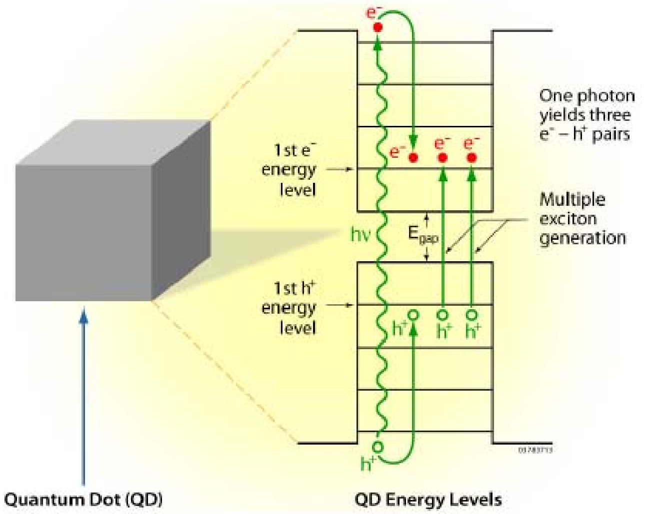
Tunable band edge

Offers the possibility to harvest light energy over a wide range of visible-ir light with selectivity



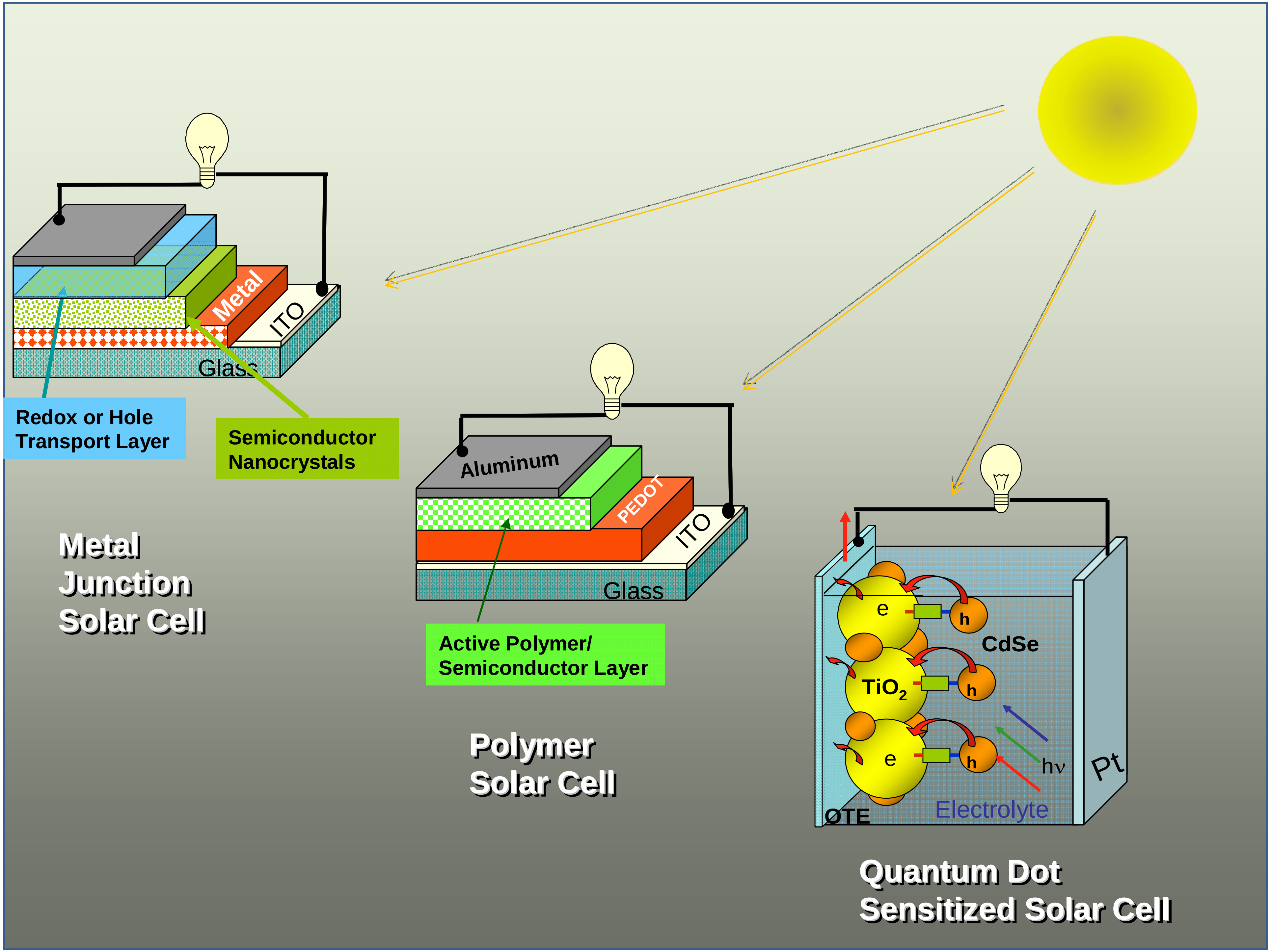
Hot carrier injection from higher excited state

(minimizing energy loss during thermalization of excited state)



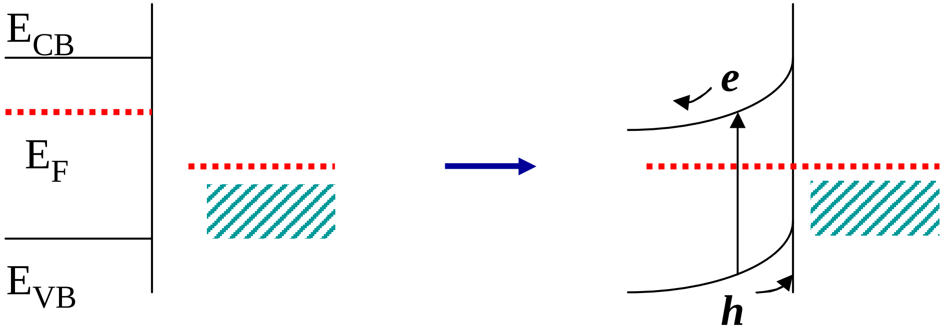
Multiple carrier generation solar cells.

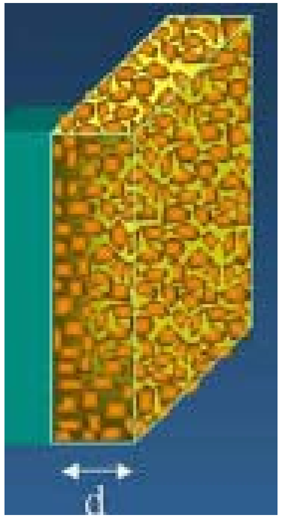
Utilization of high energy photon to multiple electron-hole pairs

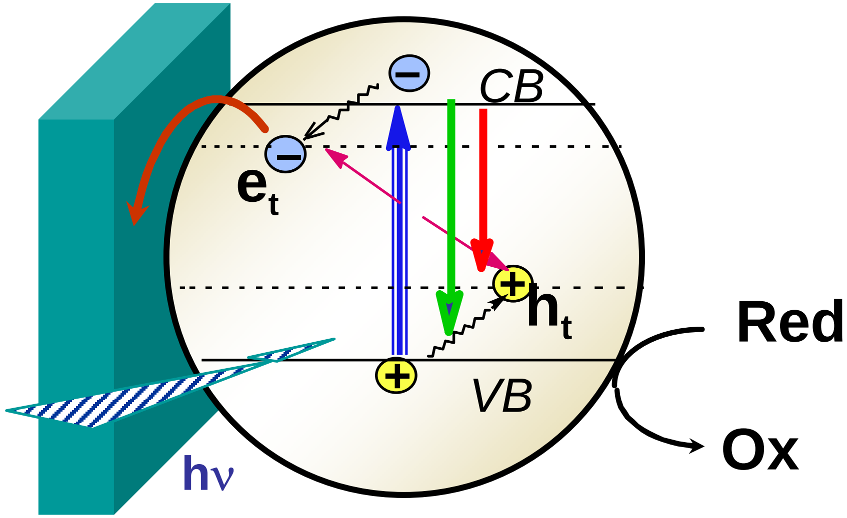


Metal
ITO
Glass
Redox or Hole Transport Layer
Semiconductor Nanocrystals
Metal Junction Solar Cell
Aluminum
PEDOT
ITO
Glass
Active Polymer/ Semiconductor Layer
Polymer Solar Cell
e
h
CdSe
TiO_2
h
e
h
hν
Pt
OTE
Electrolyte
Quantum Dot Sensitized Solar Cell

1. Semiconductor/metal Interface







Because of smaller dimensions charge separation and transport issues in nanostructure films need to be tackled

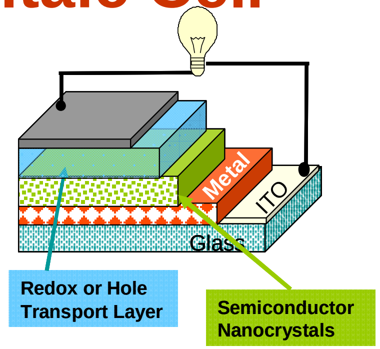
Metal/PbSeNC/Metal Sandwich Photovoltaic Cell

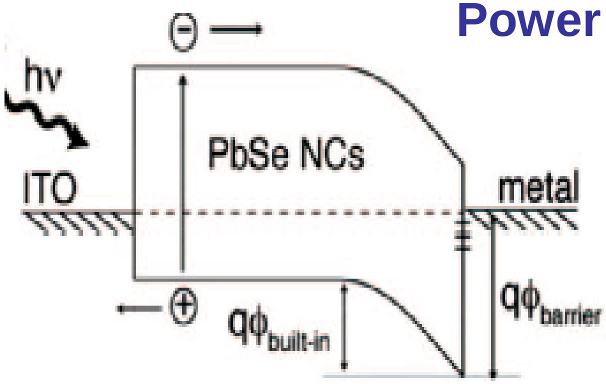
PbSe NC film, deposited *via* layer-by-layer dip coating

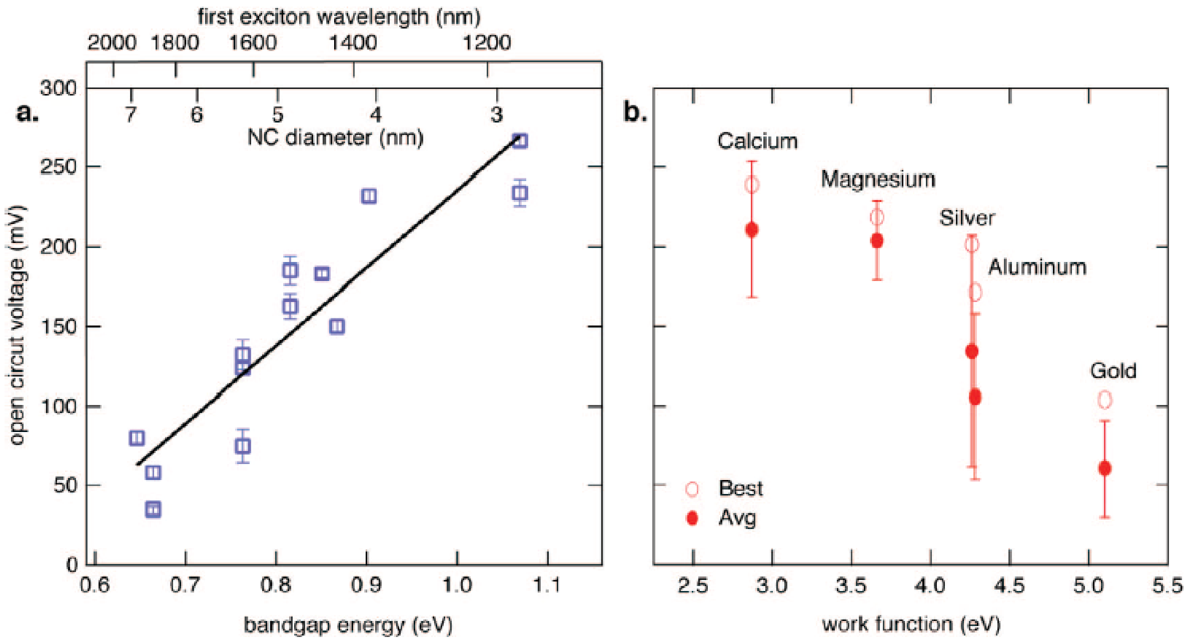
Short-circuit photocurrent (>21 mA cm^{-2}) by way of a Schottky junction

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

Power conversion efficiency of 2.1%.

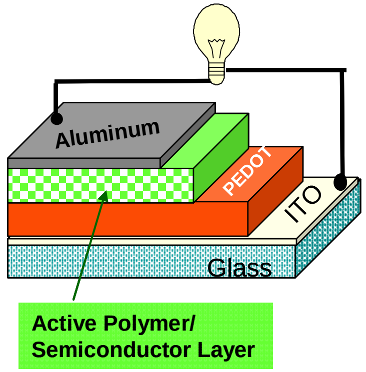


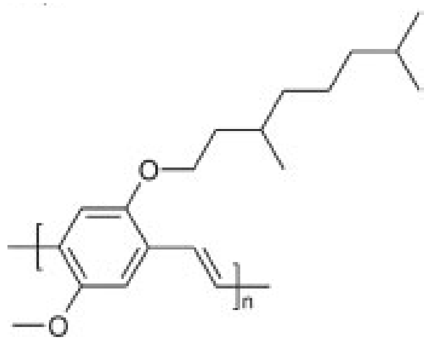


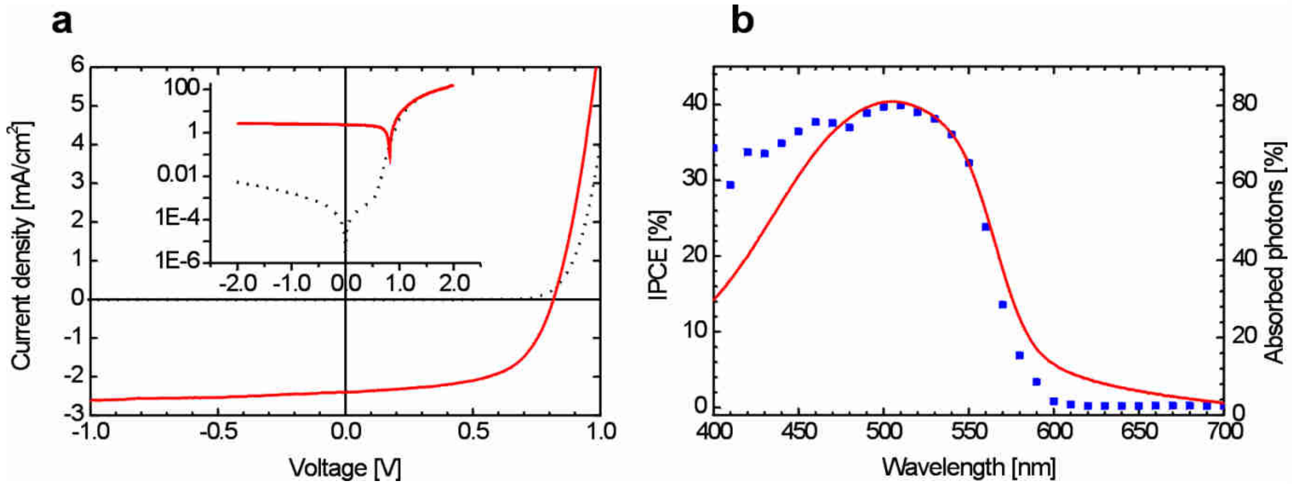


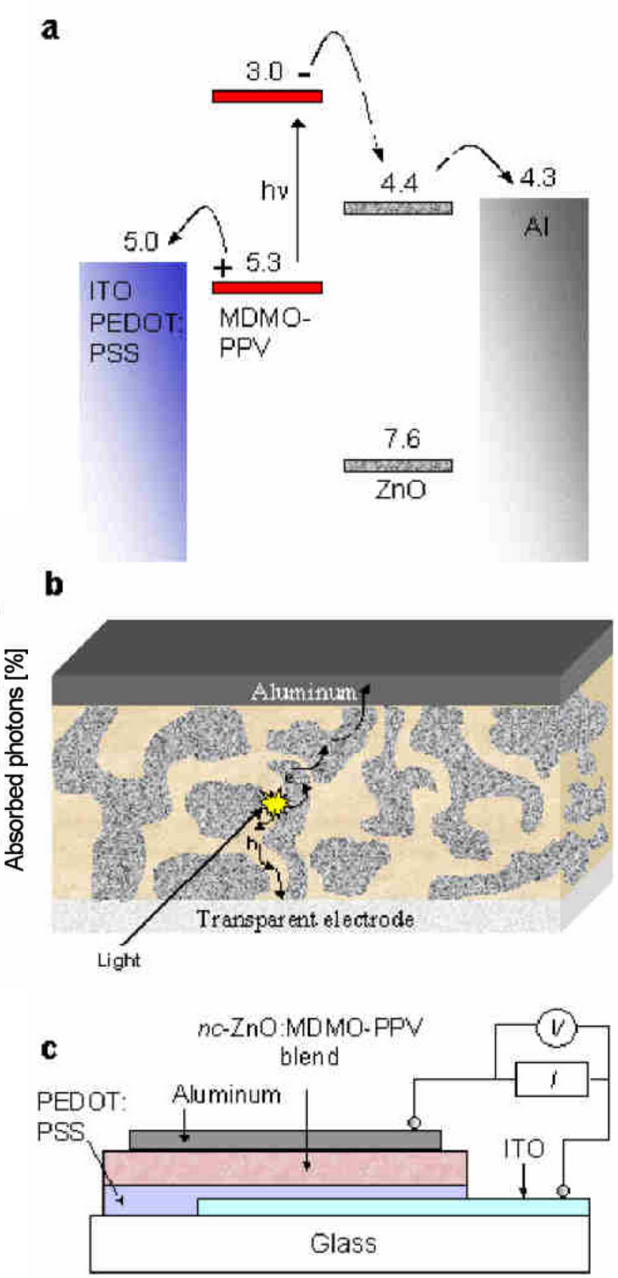
Luther et al *Nano Lett., Vol* 8, 2008, 3488

2. Polymer –Semiconductor Nanocrystal Hybrids

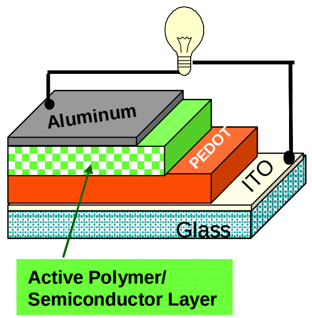




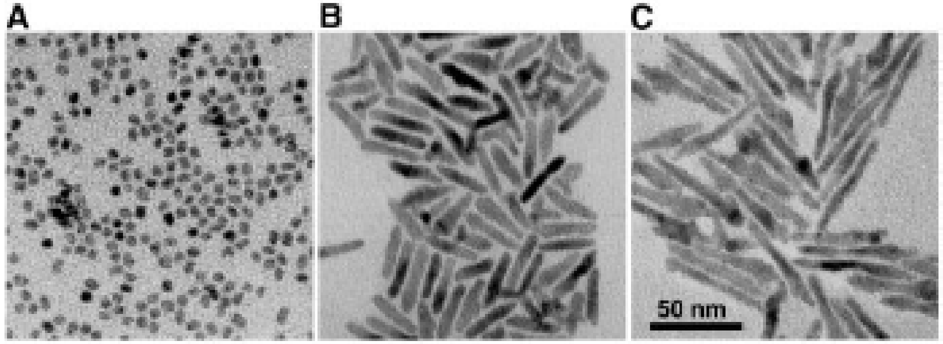


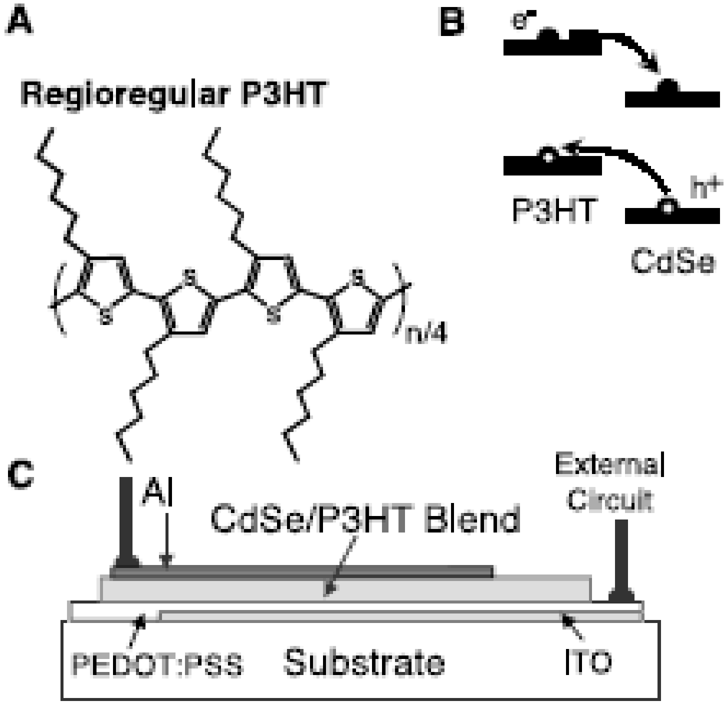


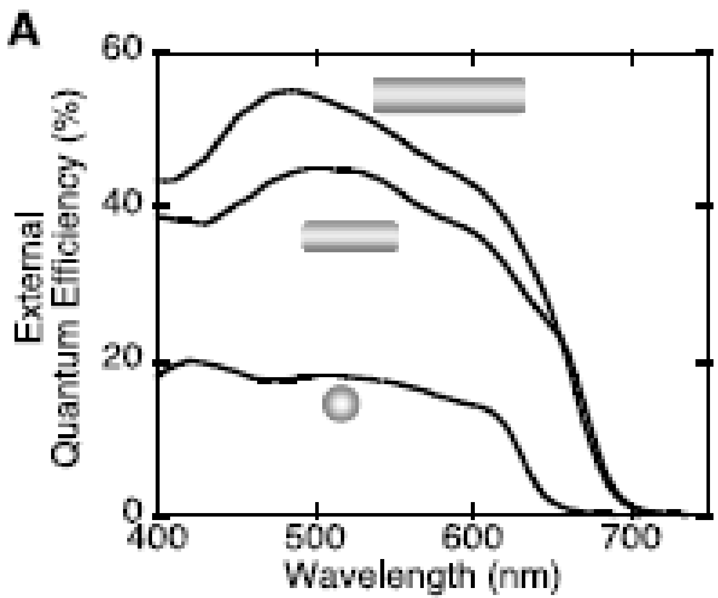
Adv. Mater, 2004, 16, 1009-1013



Hybrid Nanorod-Polymer Solar Cells

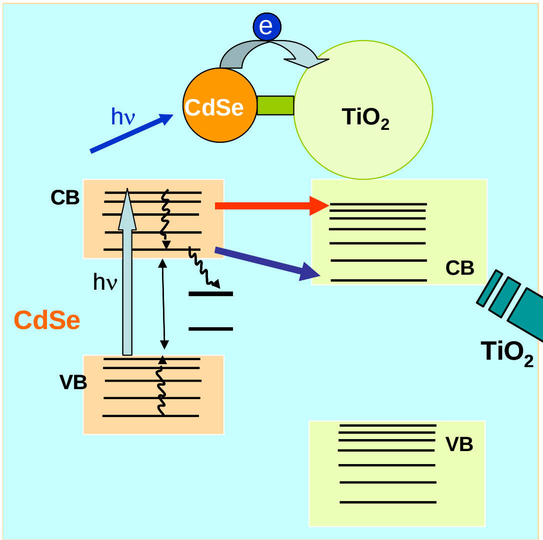


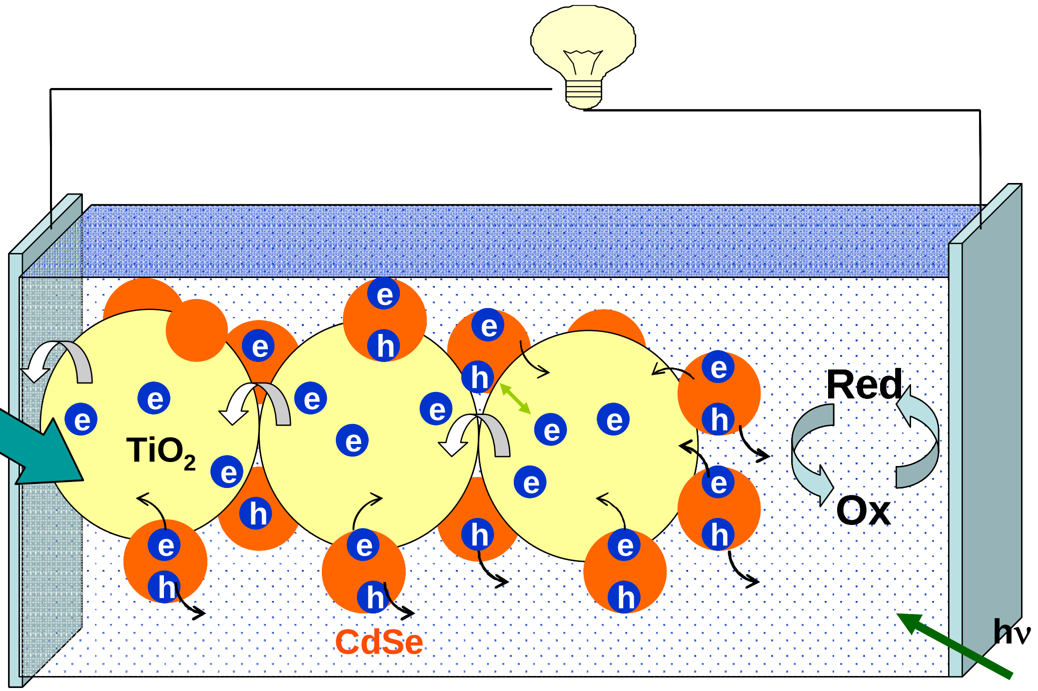


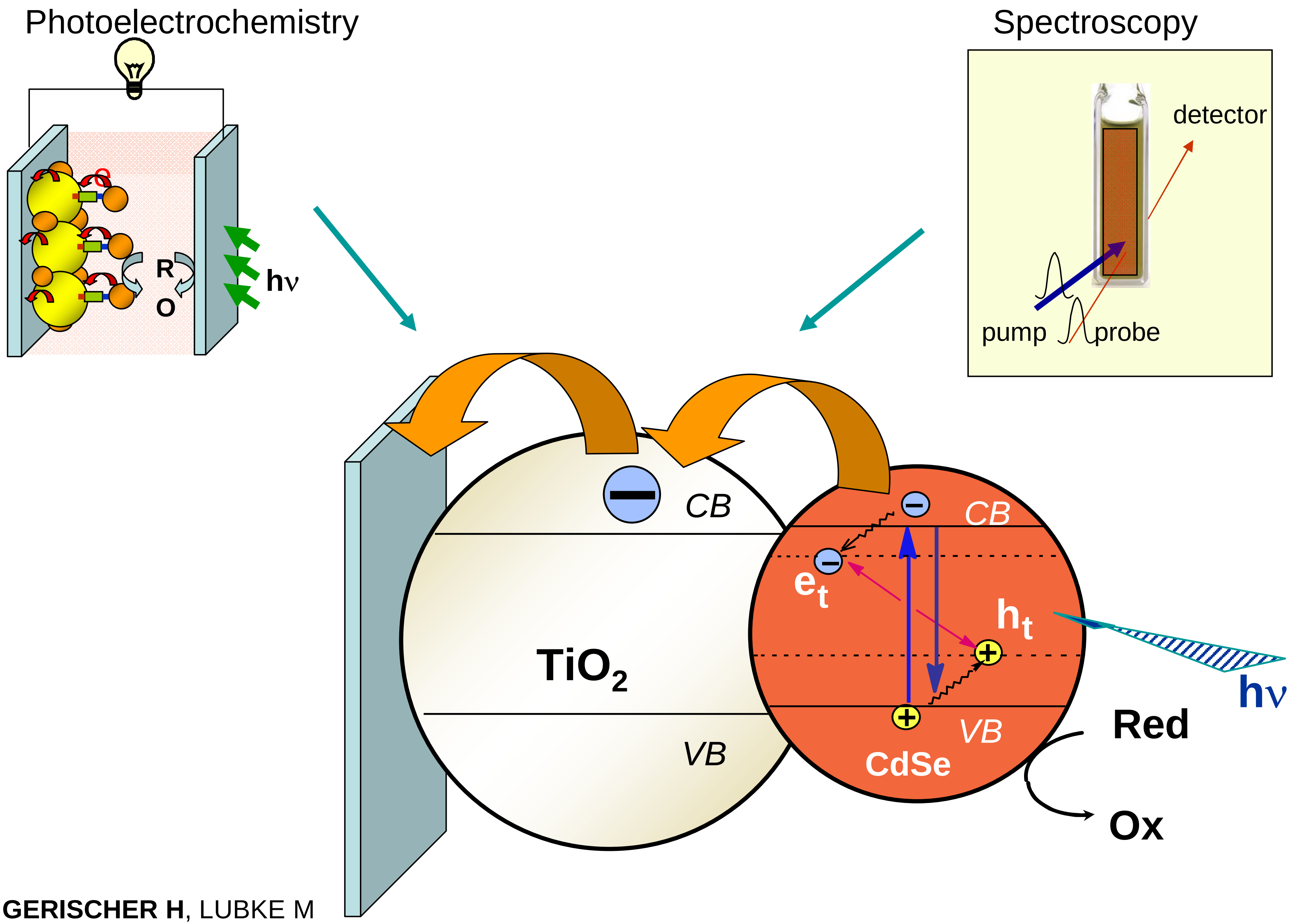


SCIENCE VOL 295, 2002 2425

3. Quantum Dot Sensitized Solar Cell (QDSSC)

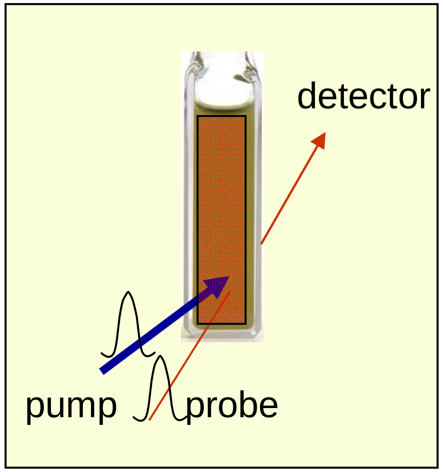


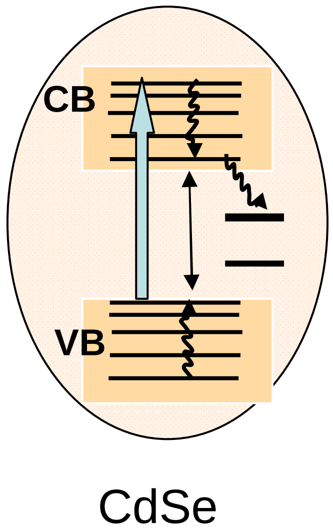


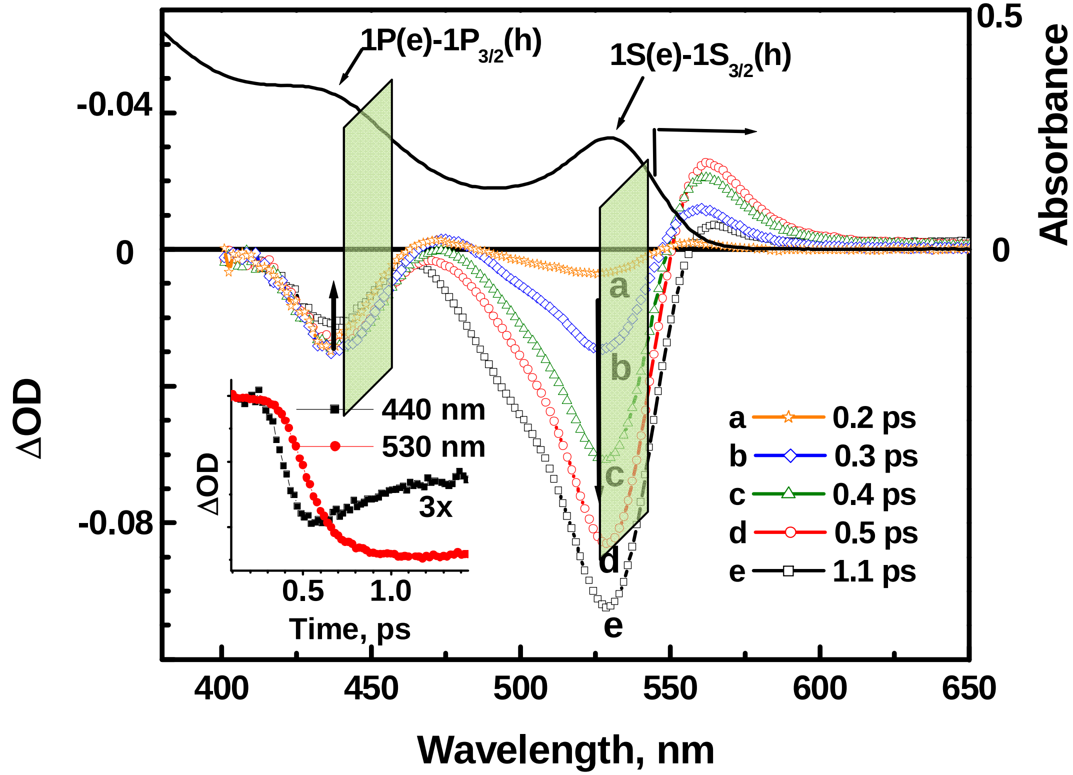


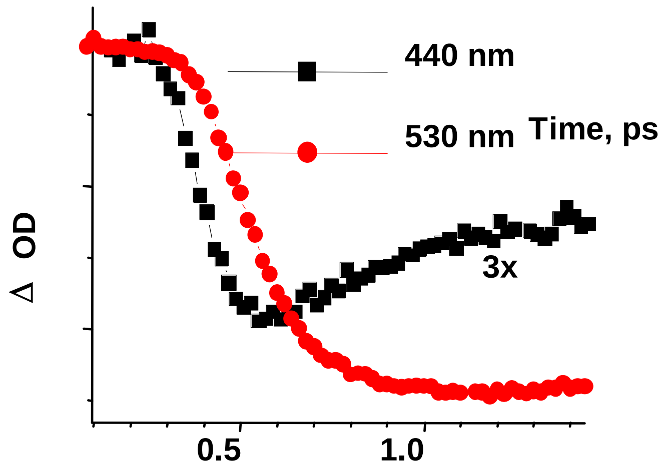
GERISCHER H, LUBKE M
A PARTICLE-SIZE EFFECT IN THE SENSITIZATION OF TIO2 ELECTRODES BY A **CDS** DEPOSIT
JOURNAL OF ELECTROANALYTICAL CHEMISTRY 204 (1-2): 225-227 1986

Photoexcitation of CdSe Quantum Dots





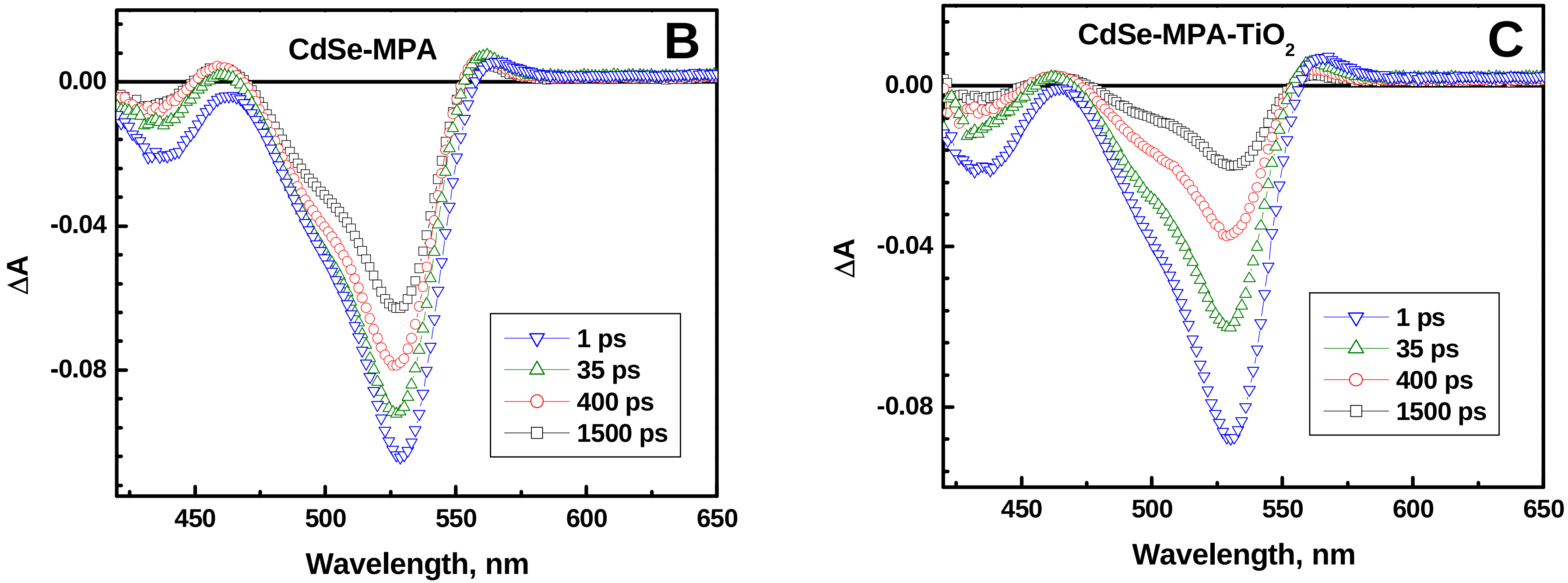




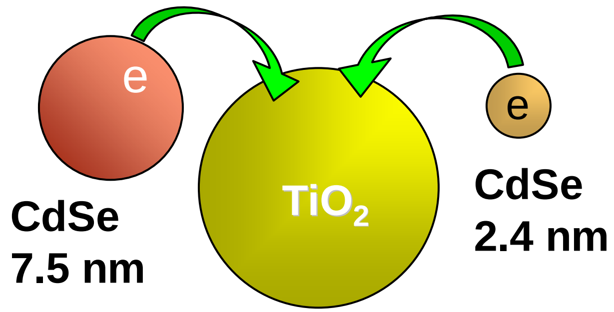
Charge Separation in TiO_2/CdSe

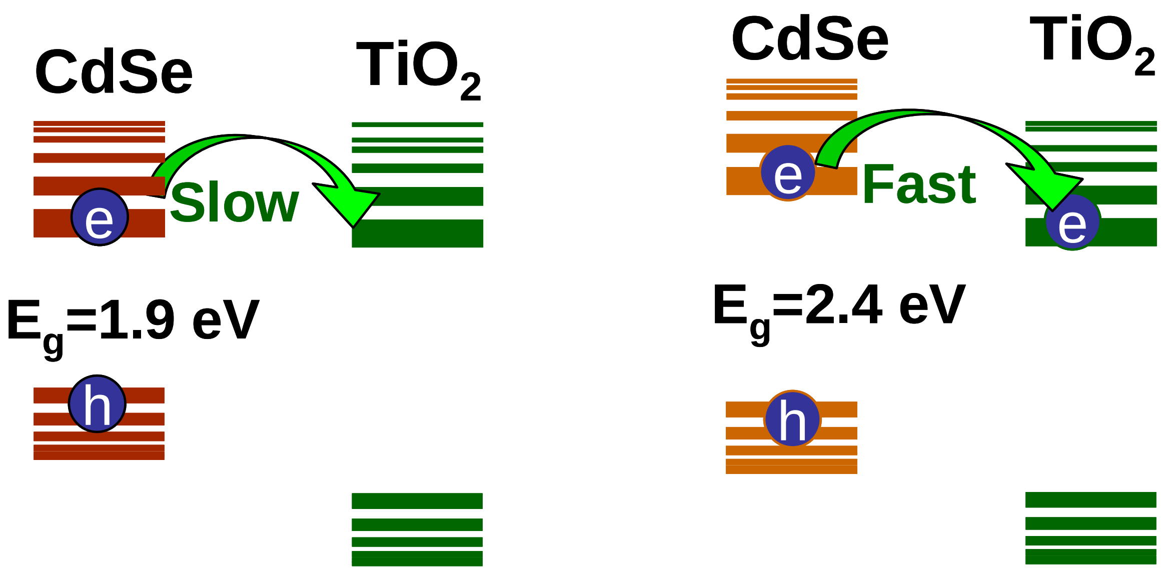
Transient Bleaching Recovery of 3 nm CdSe Quantum Dots

Ex. 387 nm



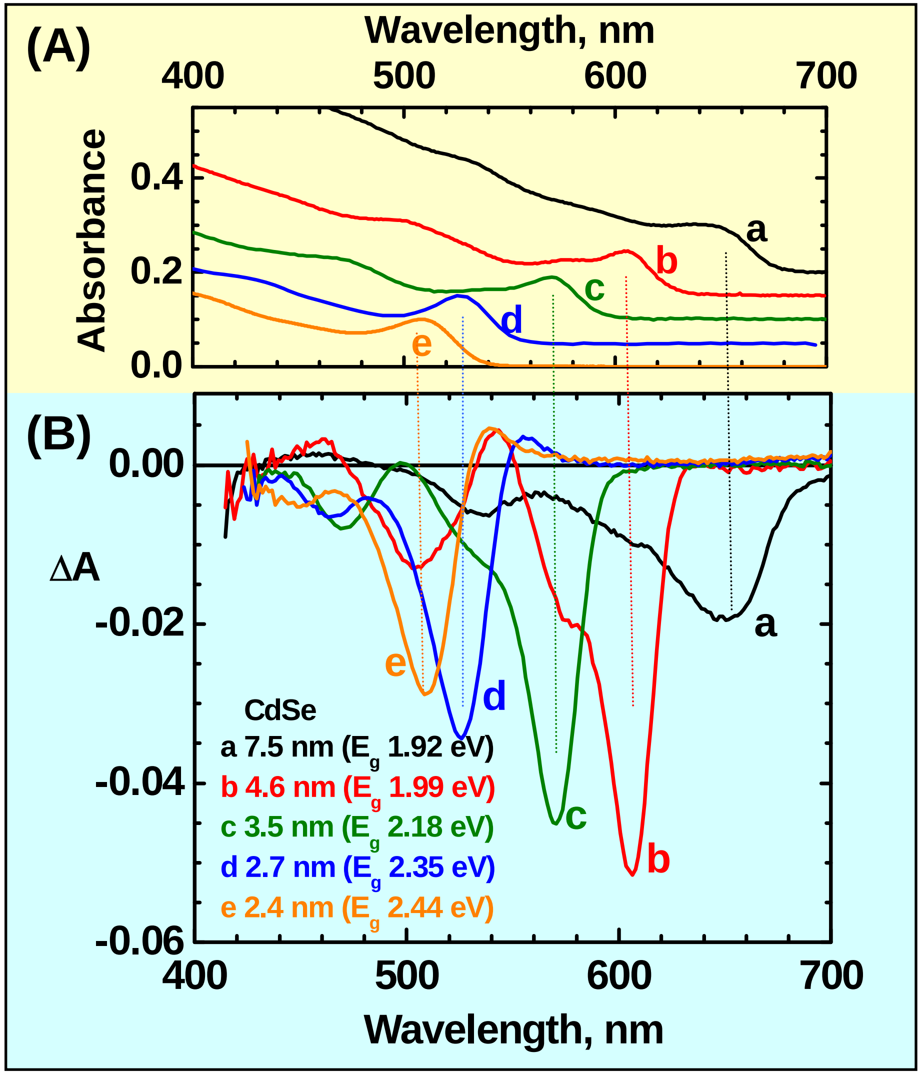
Modulation of the charge injection process by controlling the particle size?





Photoexcitation of CdSe Quantum Dots

$$CdSe + h\nu \rightarrow CdSe\,(e_p + h_p) \rightarrow CdSe\,(e_s + h_s)$$



CdSe quantum dots of size 2.4 nm to 7,5 nm were excited with 387 nm laser pulse (130 fs)

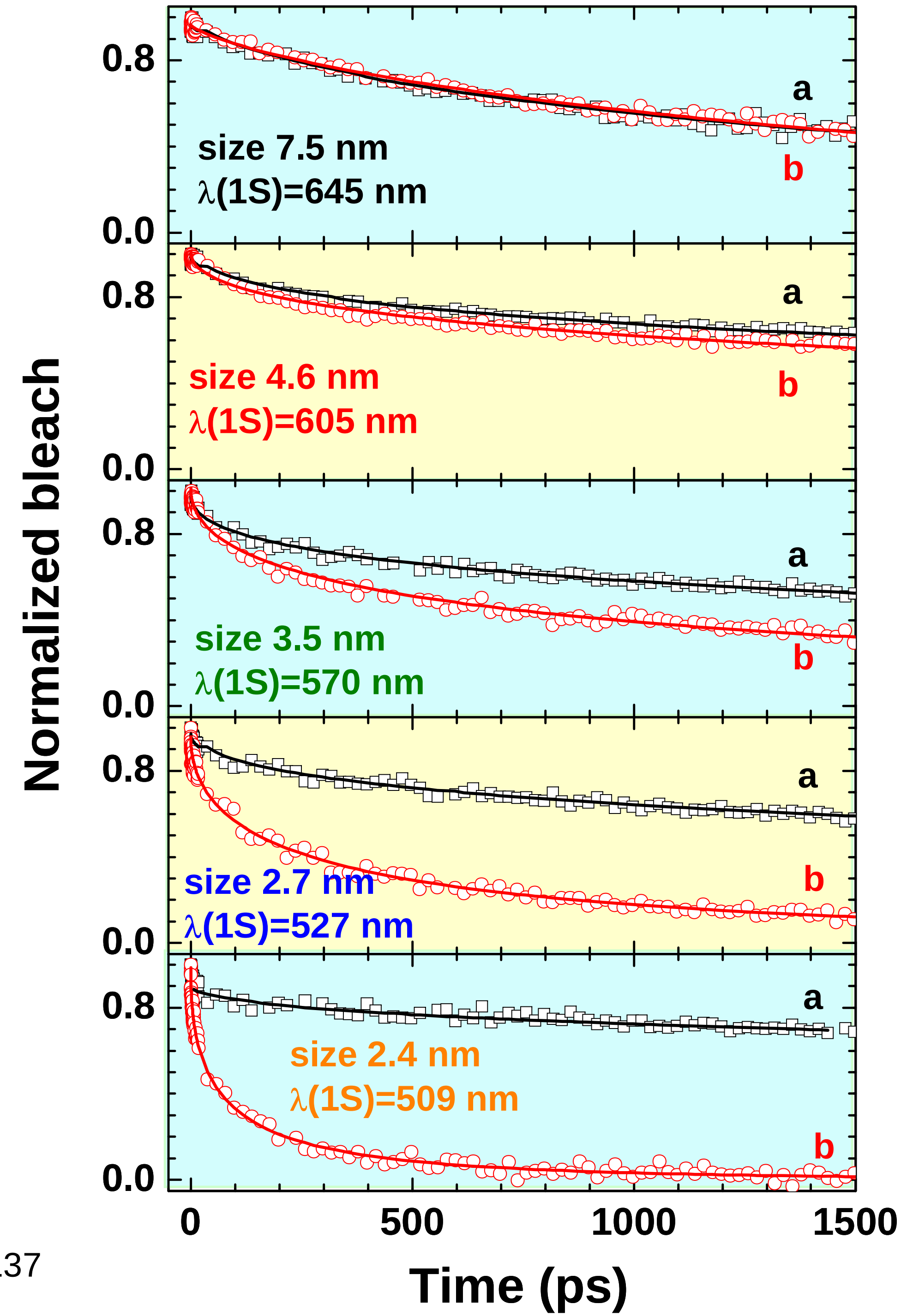
As the particle size decreases from 7.5 nm to 2.4 nm, the first ($^1S_{3/2}{}^1S_e$) excitonic peak shifts from 645 nm (1.92 eV) to 509 nm (2.44 eV).

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

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

- where τ is the peak value of the characteristic lifetime

Robel, Kuno, Kamat, JACS **2007;** *129*(14) pp 4136 - 4137

Size Dependent Quenching Phenomenon

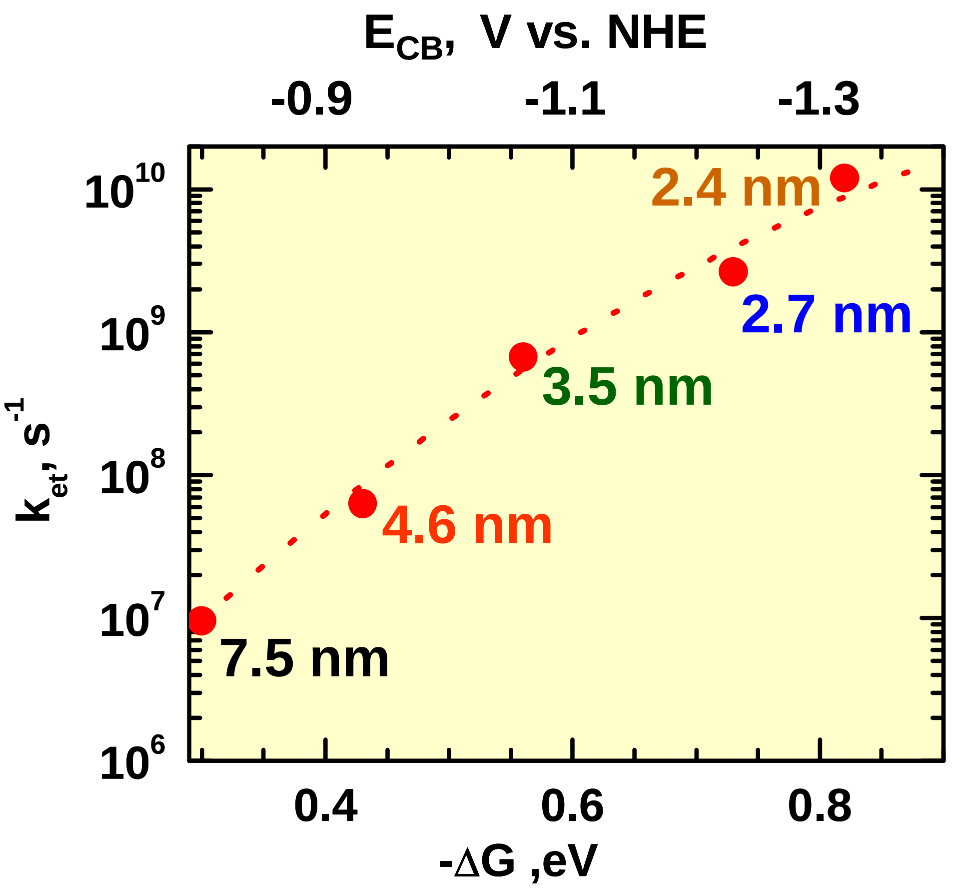
Diameter [nm]	E_g [eV]	τ_{CdSe} [ps]	β_{CdSe}	$\tau_{CdSe-TiO2}$ [ps]	$\beta_{CdSe-TiO2}$	k_{et} [s^{-1}]
7.5	1.92	2332	0.697	2281	0.755	9.58×10^{6}
4.6	1.99	7224	0.474	4961	0.446	6.3×10^{7}
3.5	2.18	4420	0.417	1117	0.475	6.7×10^{8}
2.7	2.35	6739	0.457	357	0.505	2.65×10^{9}
2.3	2.44	23119	0.51	83	0.493	1.2×10^{10}

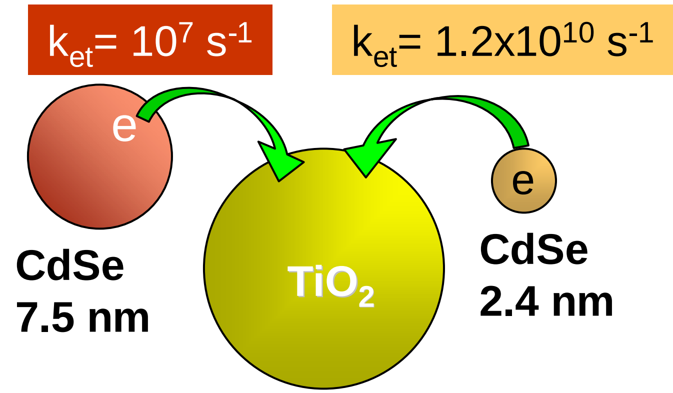
$$\Delta A(t)=\Delta A(0)\times\exp[-(t/\tau)\beta]$$

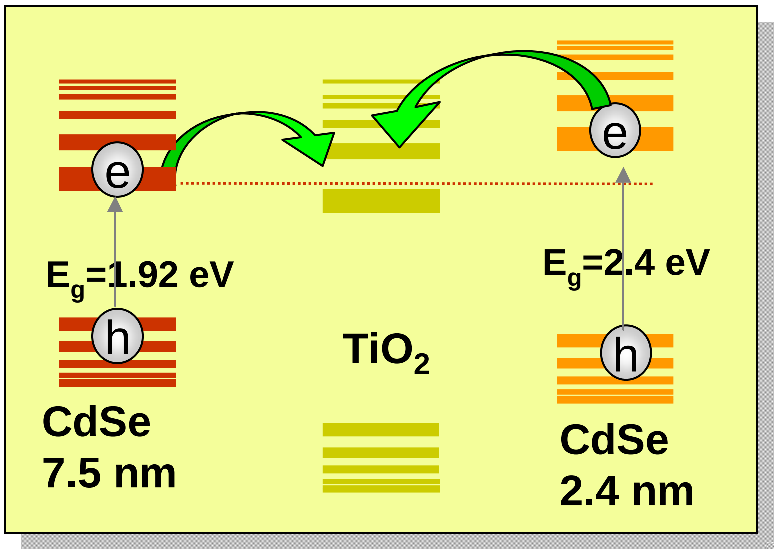
- where τ is the peak value of the characteristic lifetime

$$1/\tau' - 1/\tau = k_{et}$$

Size Dependent Electron transfer between CdSe and TiO_2

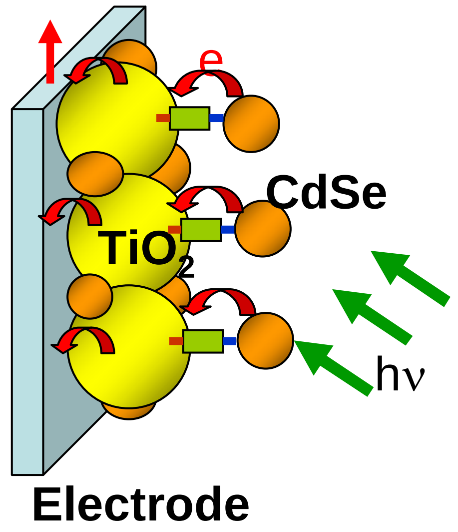


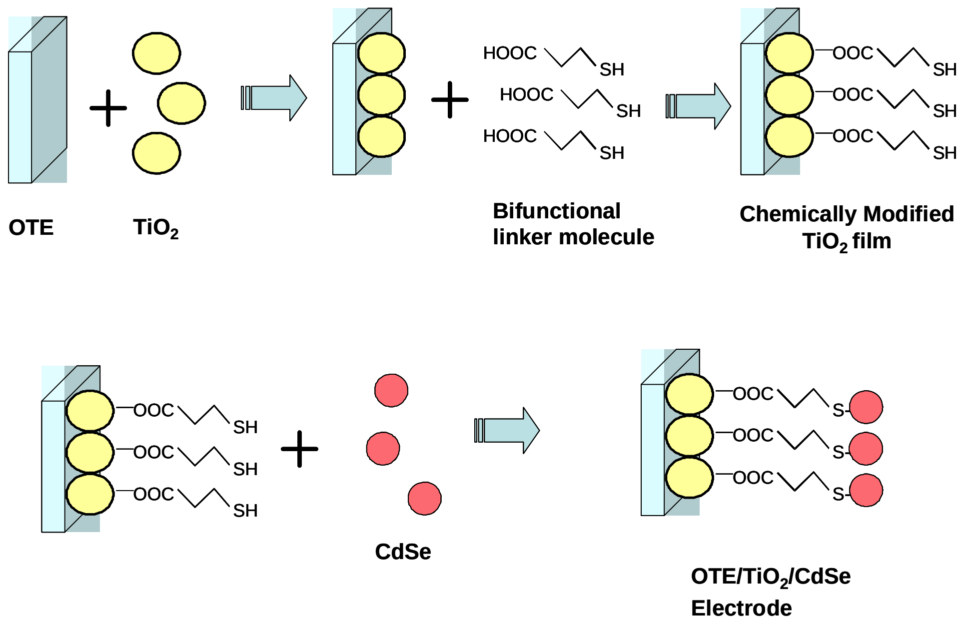


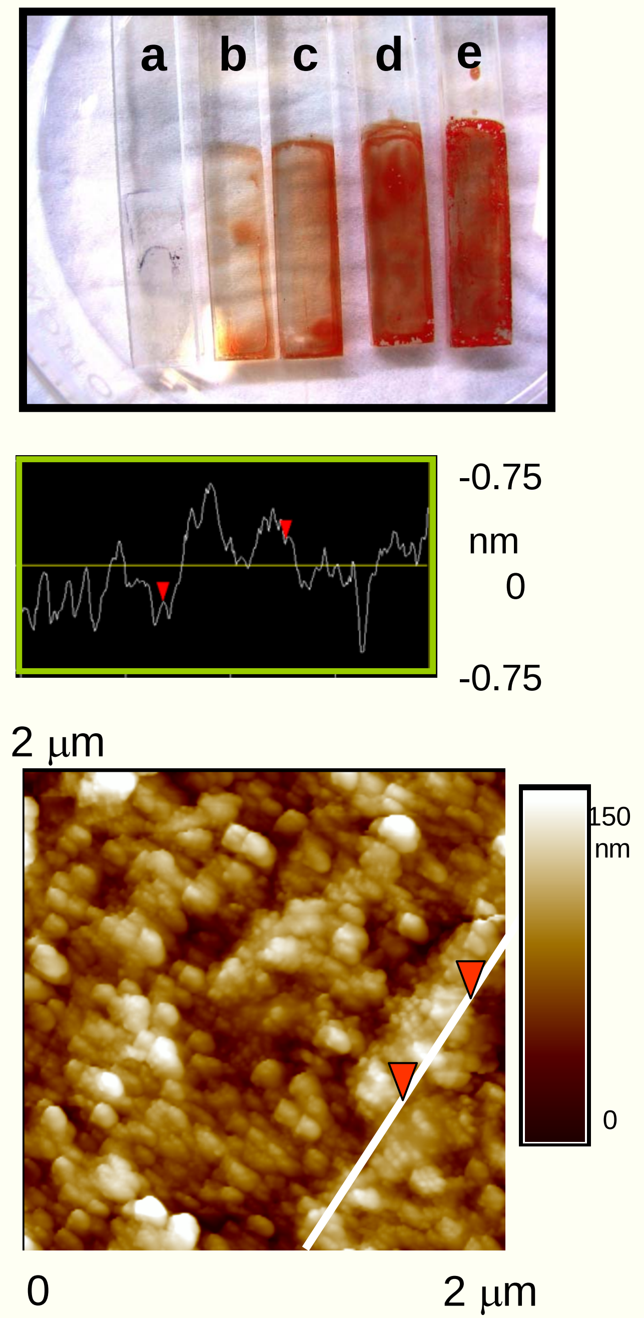


Robel, Kuno, Kamat, JACS **2007;** *129* pp 4136 - 4137

Linking Q-CdSe to TiO_2 particles

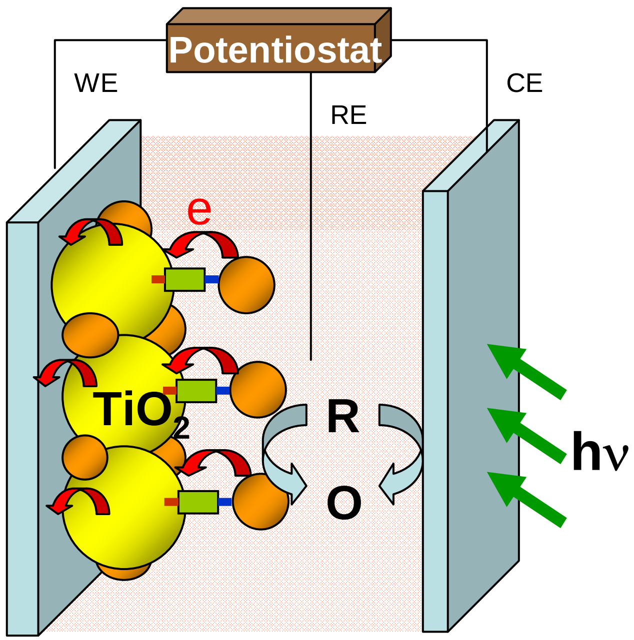


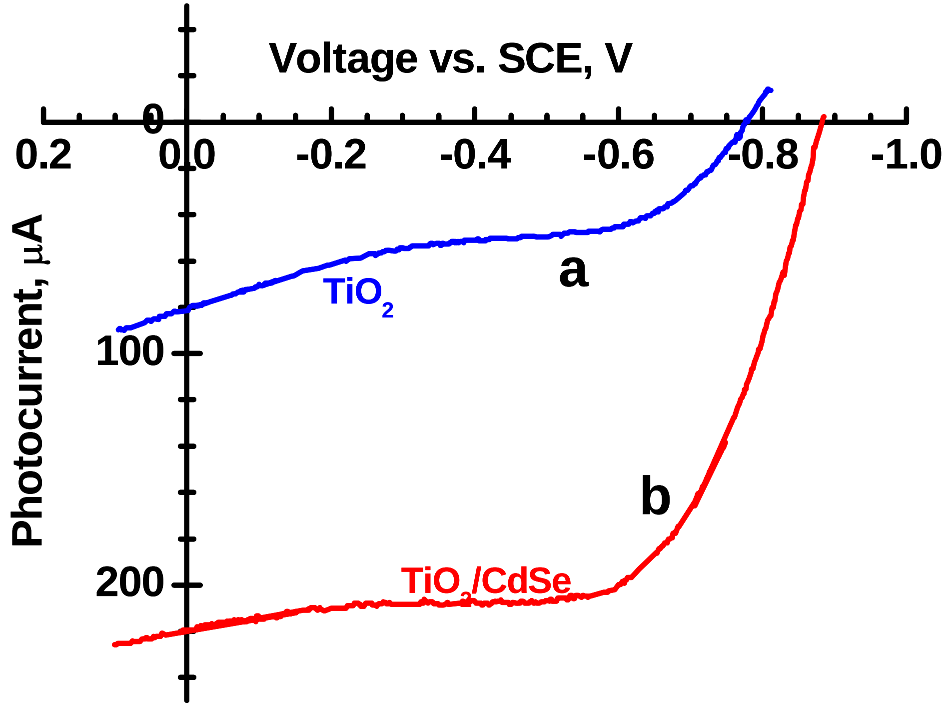




J. Am. Chem. Soc. 2006,128, 2385-2393

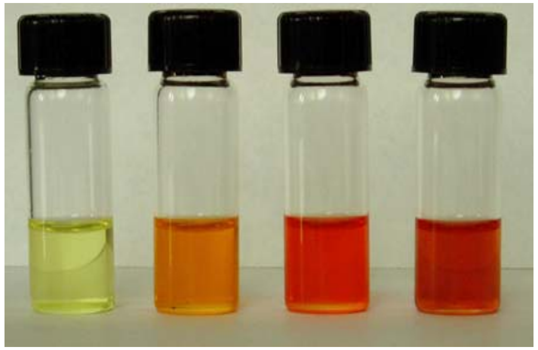
Photoelectrochemical behavior of Q-CdSe-TiO_2 films





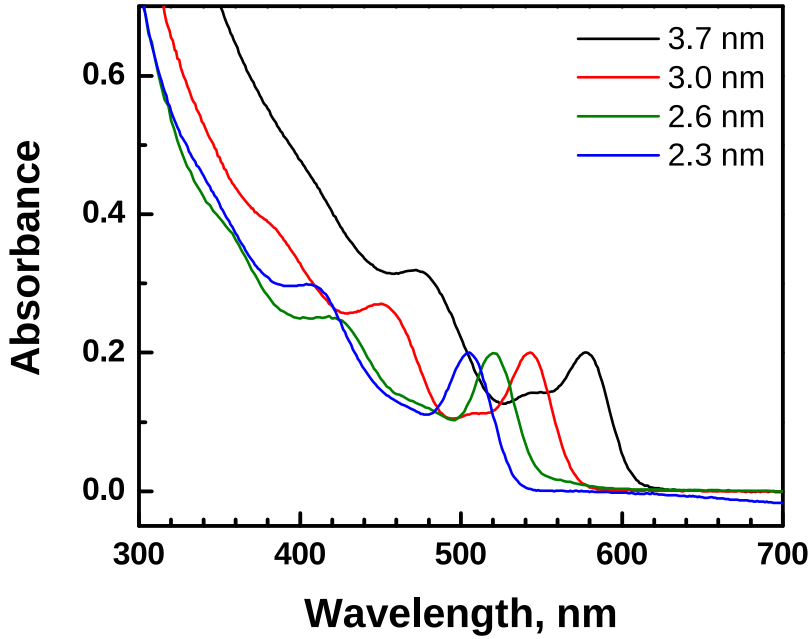
I-V characteristics of (a) OTE/TiO_2 and (b) OTE/TiO_2/MPA/CdSe films. Electrolyte 0.1 M Na_2S. The filtered lights allowed excitation of TiO_2 and CdSe films at wavelengths **greater than 300 and 400 nm** respectively

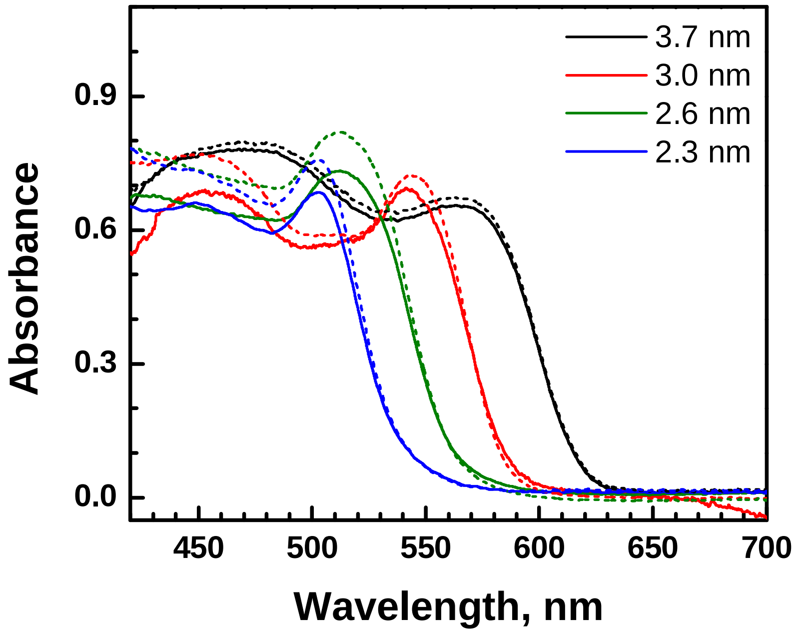
Modification of TiO_2 Films with Different Size CdSe Particles

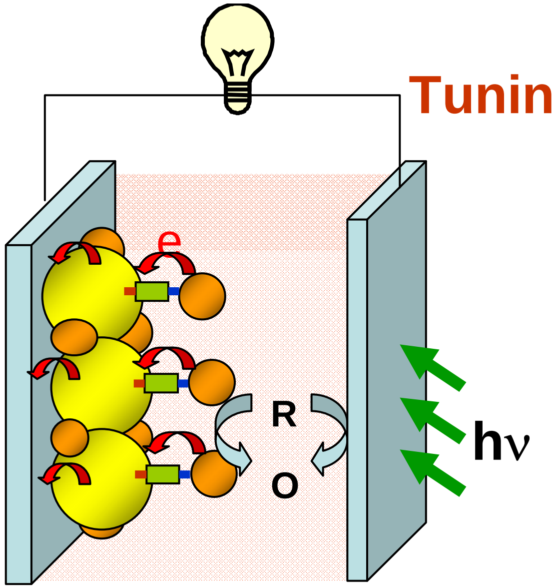


2.3nm 2.6nm 3.0nm 3.7nm

2.3nm 2.6nm 3.0nm 3.7nm



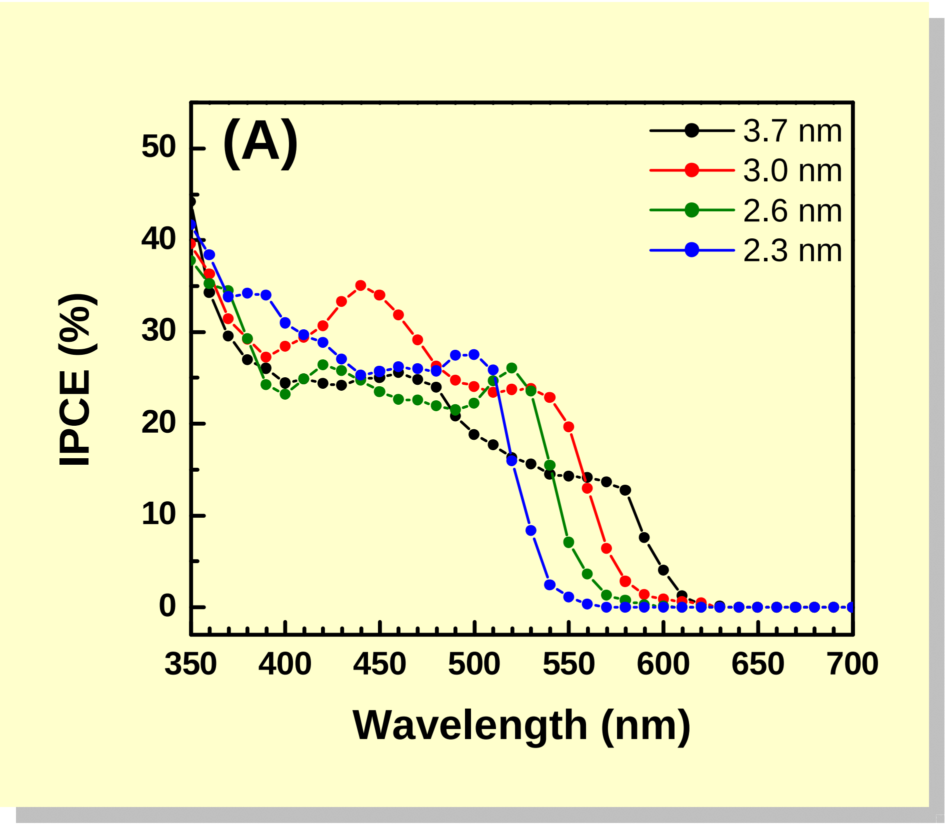


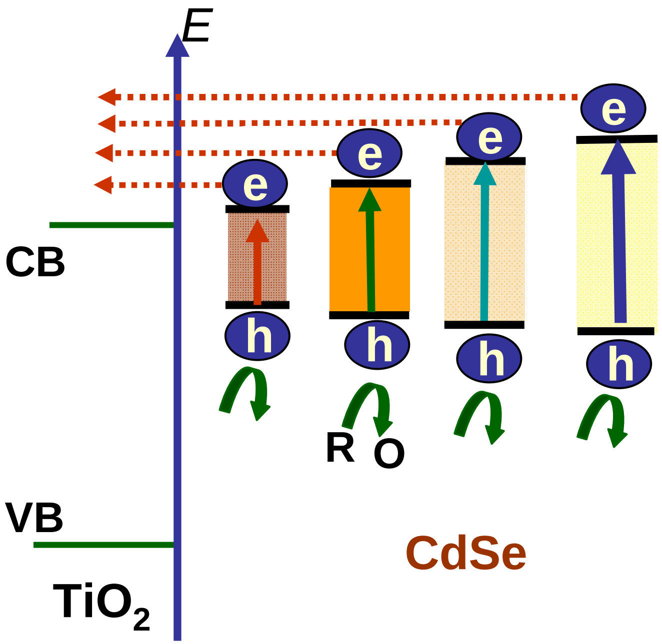


Tuning the Photoresponse of Quantum Dot Solar Cells

IPCE or Ext. Quantum Eff.

$= (1240/\lambda) \times (I_{sc}/I_{inc}) \times 100$

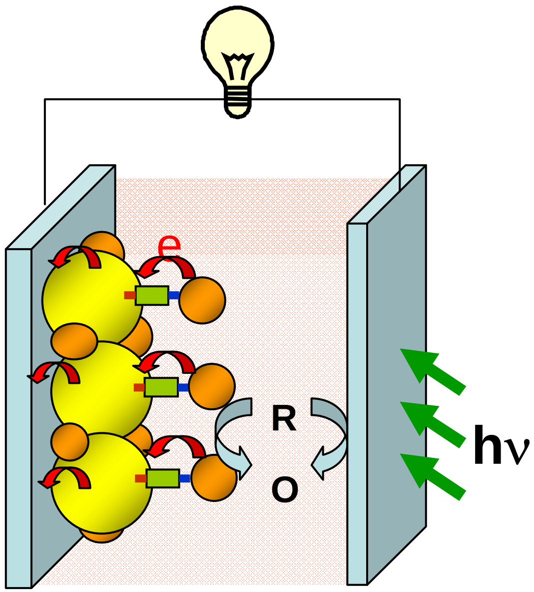


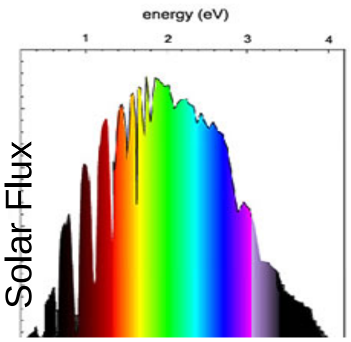


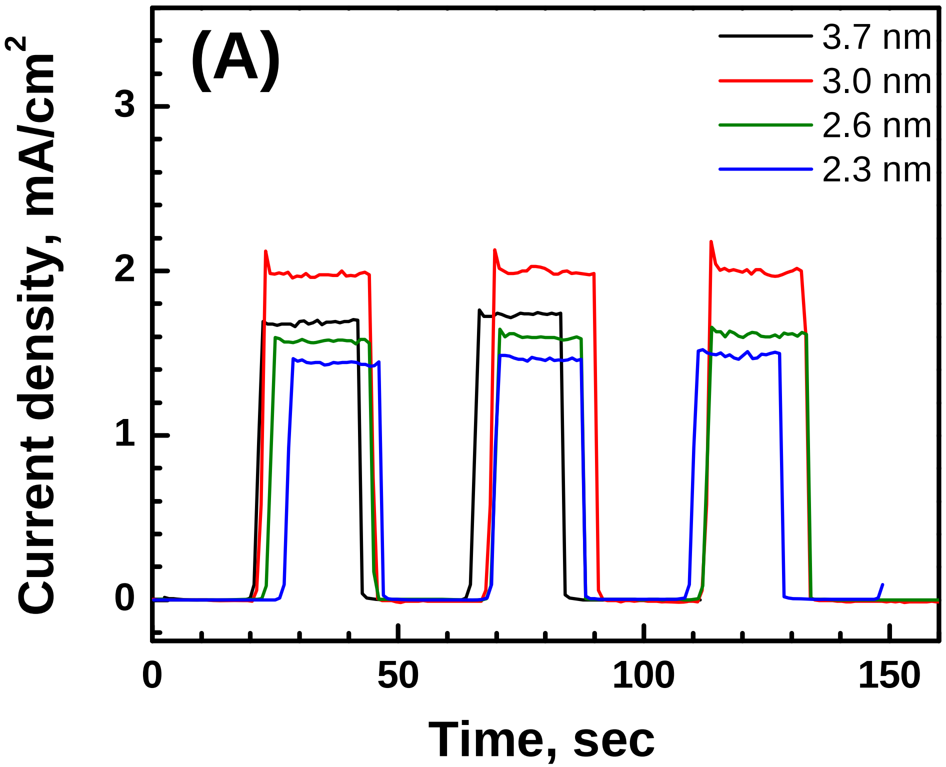
J. Am. Chem. Soc., **130** (12), 4007 -4015, 2008

Photocurrent Response

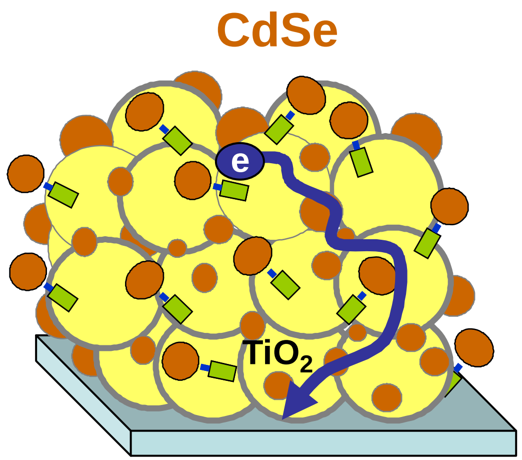
Efficiency of Charge Injection vs. Light absorption





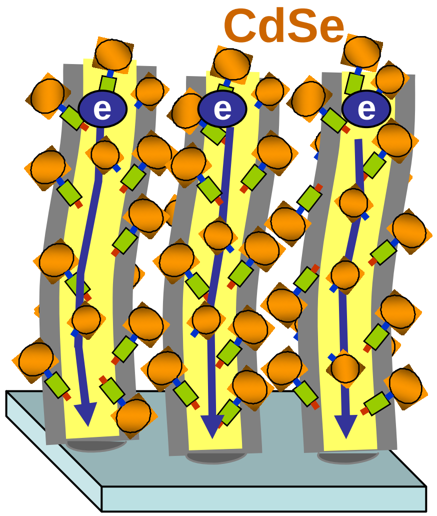


Can we employ the nanowire/nanorod architecture to improve the performance of quantum dot solar cells?



OTE/TiO_2 nanoparticles

(a)

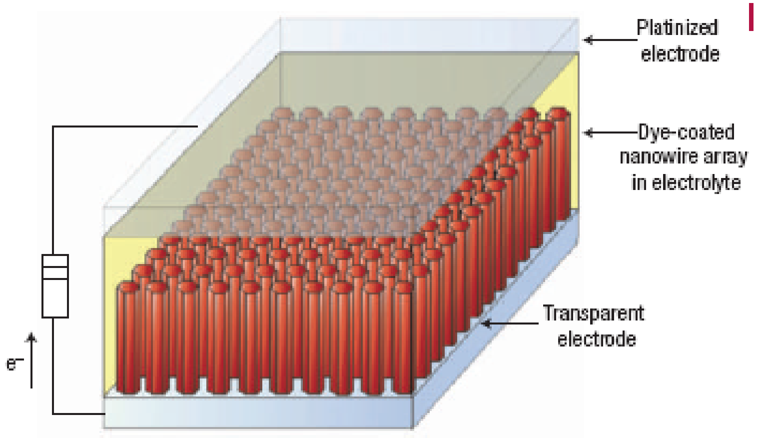


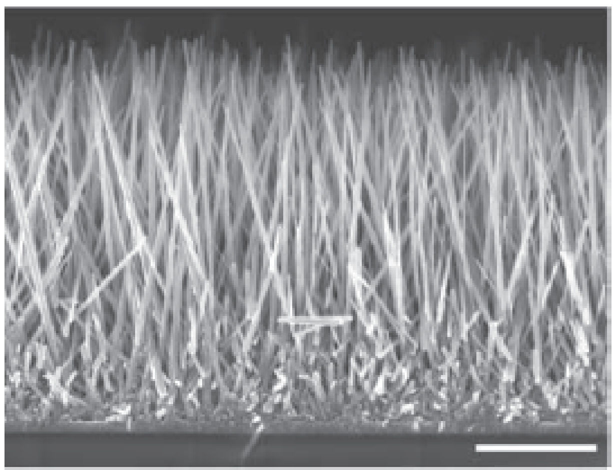
Ti/TiO_2 nanotubes

(b)

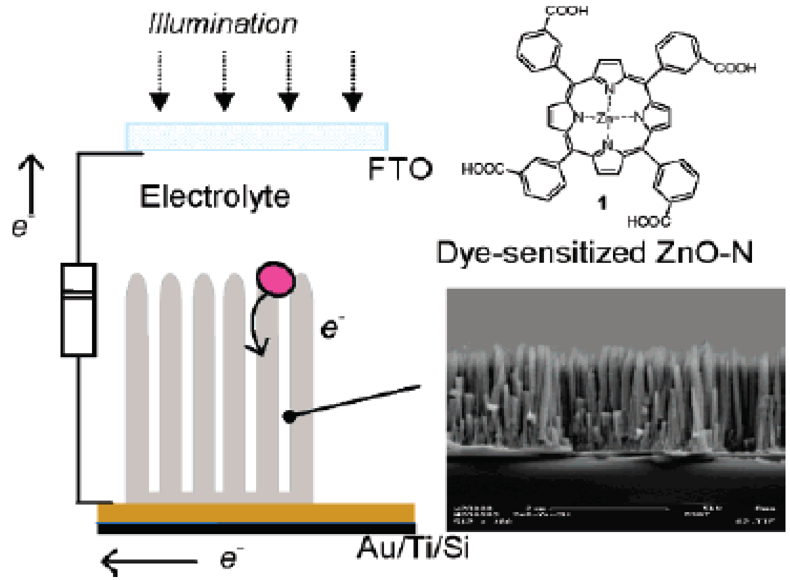
Recent advances

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





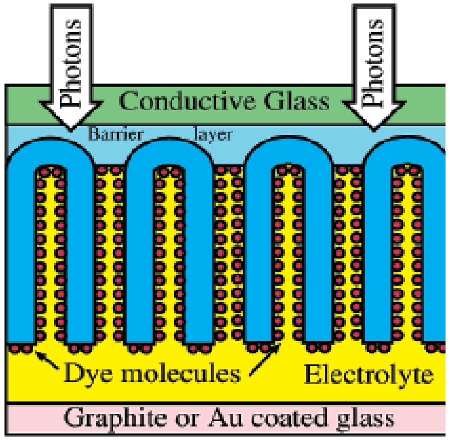
Fast Electron Transport in Metal Organic Vapor Deposition Grown Dye-sensitized ZnO Nanorod Solar Cells
Galoppini, Rochford, Chen, Saraf, Lu, Hagfeldt, and Boschloo J. Phys. Chem. B; **2006;** *110* 16159

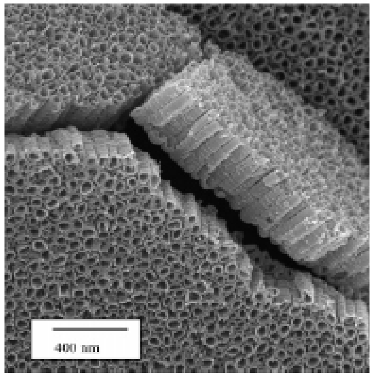


Electron transport in solar cells with ZnO-nanorod electrodes was about 2 orders of magnitude faster (30μs) than ZnO-colloid electrodes

Mor, G. K. et al *Use of highly-ordered TiO_2 nanotube arrays in dye-sensitized solar cells.*

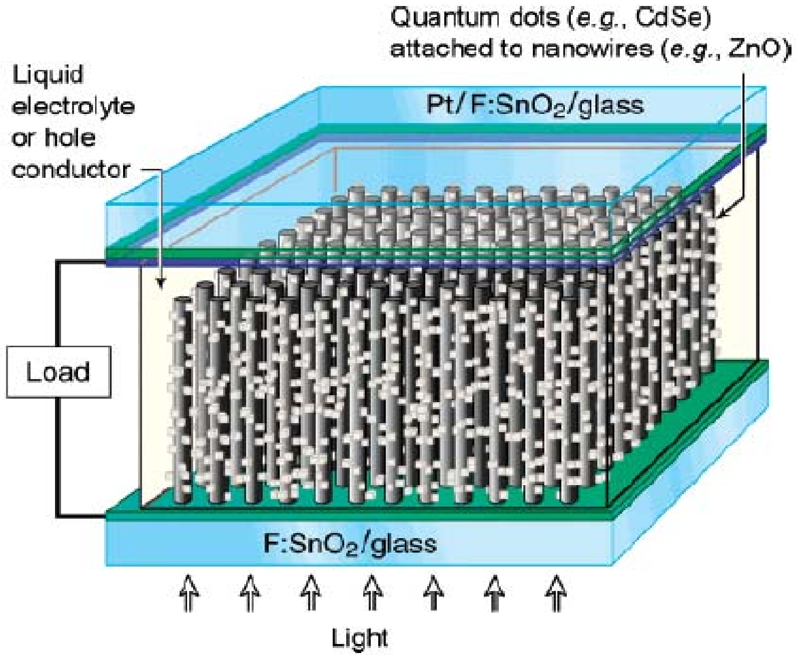
Nano Lett., **2006**. *6*, 215-218.

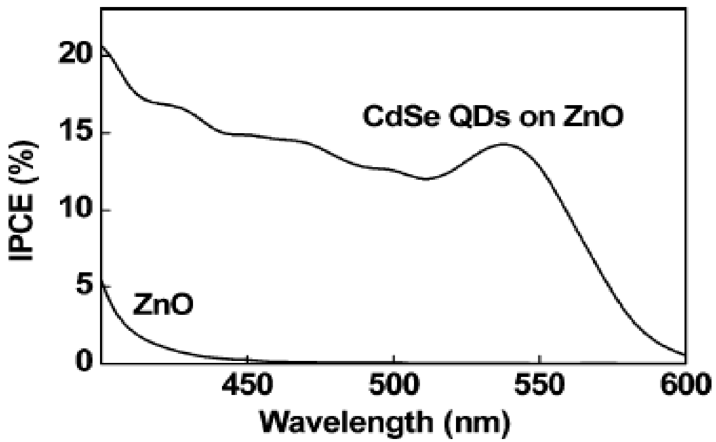




Leschkies, K. S et al *Photosensitization of ZnO nanowires with CdSe quantum dots for photovoltaic devices.*

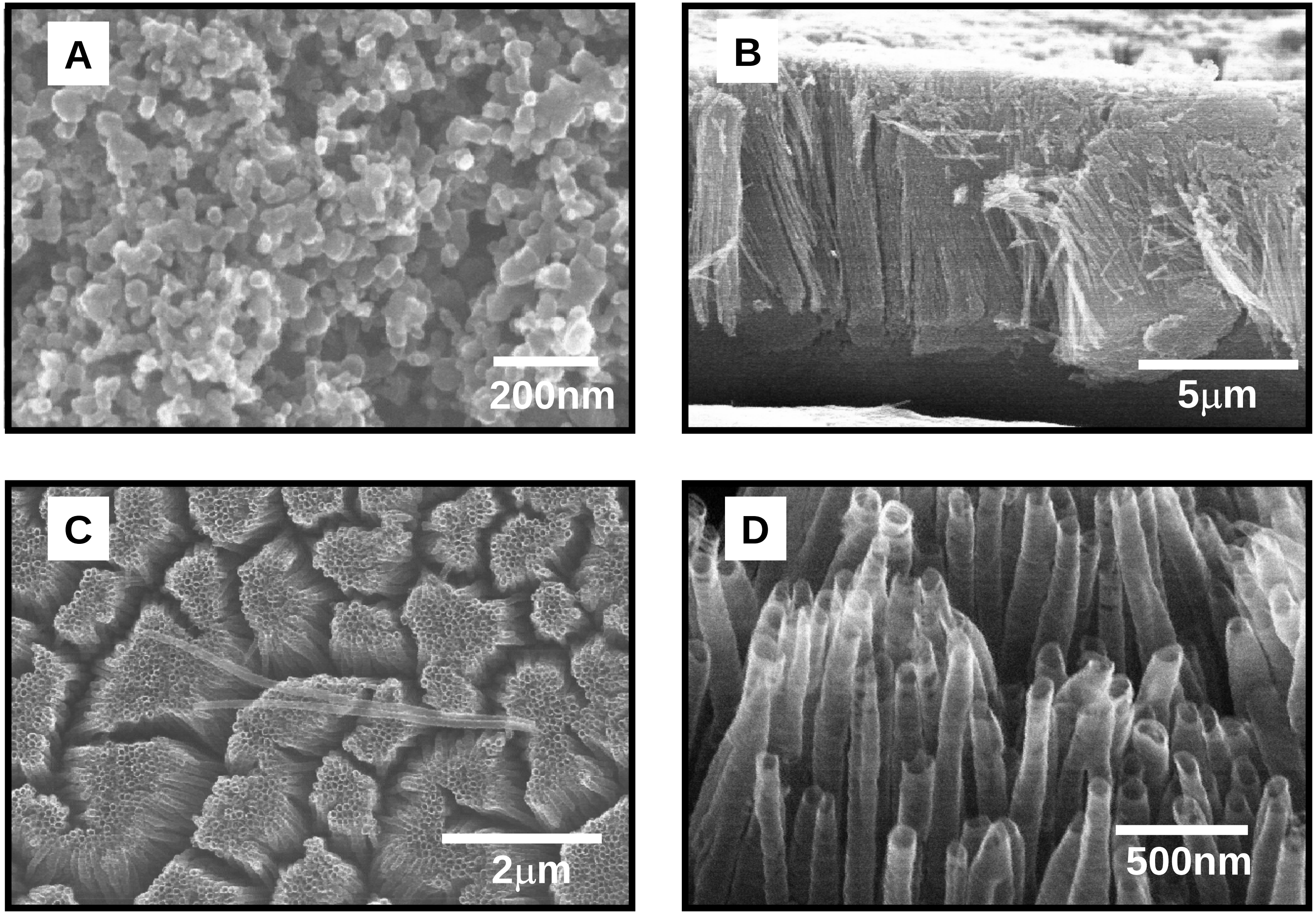
Nano Lett., **2007**. *7*, 1793-1798.

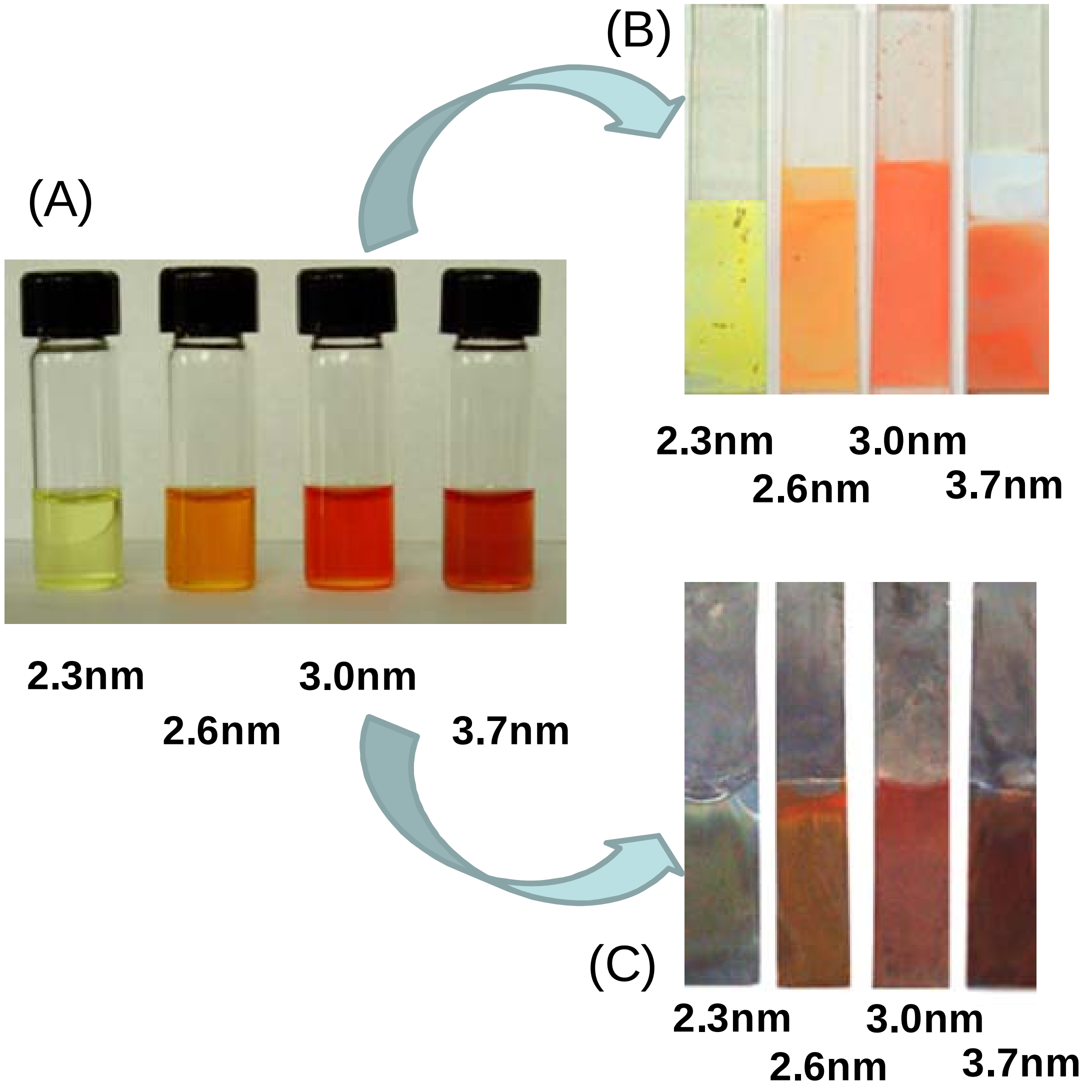




Martinson, A. B. F. et al., *ZnO nanotube based dye-sensitized solar cells ZnO nanotube based dye-sensitized solar cells.*

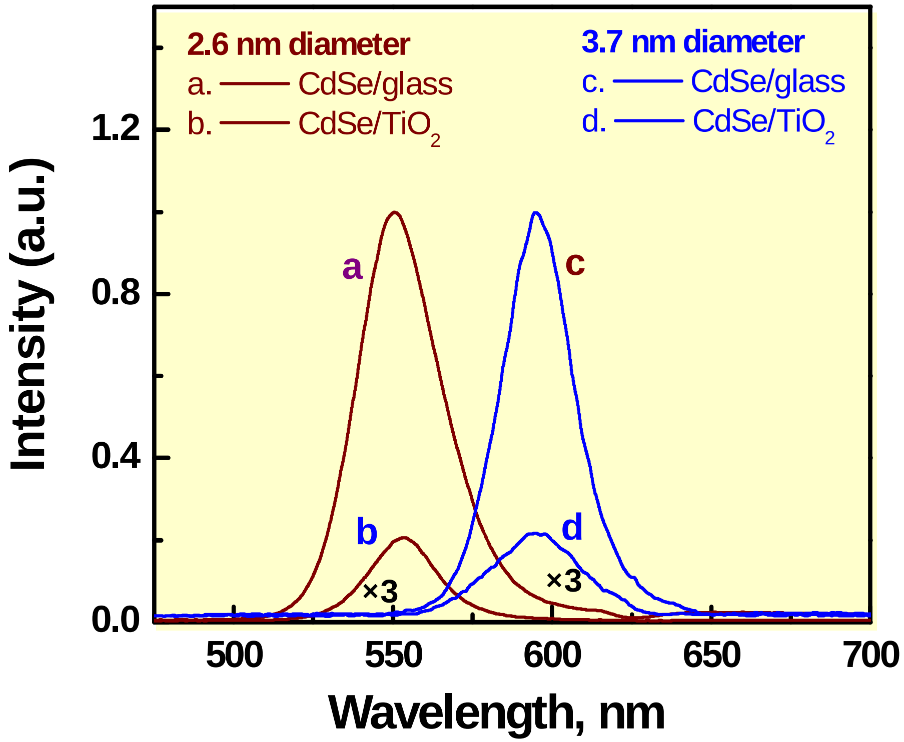
Nano Lett., **2007**. *7*, 2183-2187.


A
200nm
B
5μm
C
2μm
D
500nm

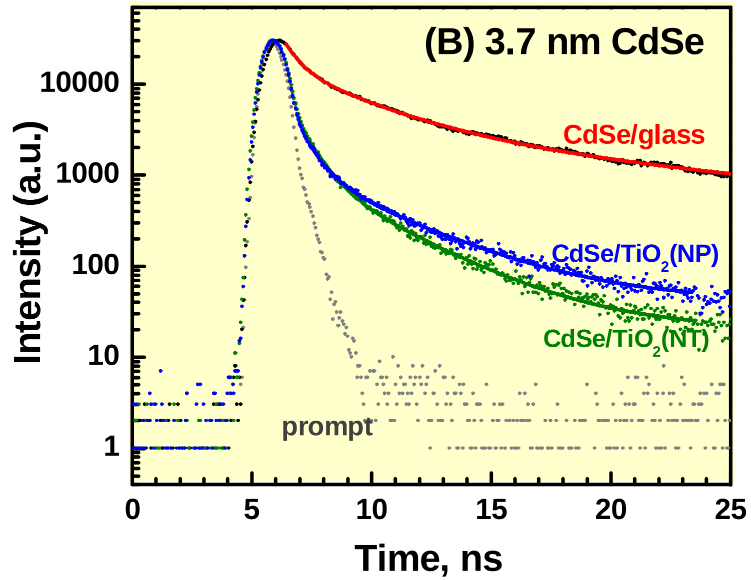


(A)
2.3nm
2.6nm
3.0nm
3.7nm
(B)
2.3nm
2.6nm
3.0nm
3.7nm
(C)
2.3nm
2.6nm
3.0nm
3.7nm

Photoemission of CdSe/glass and CdSe/TNP

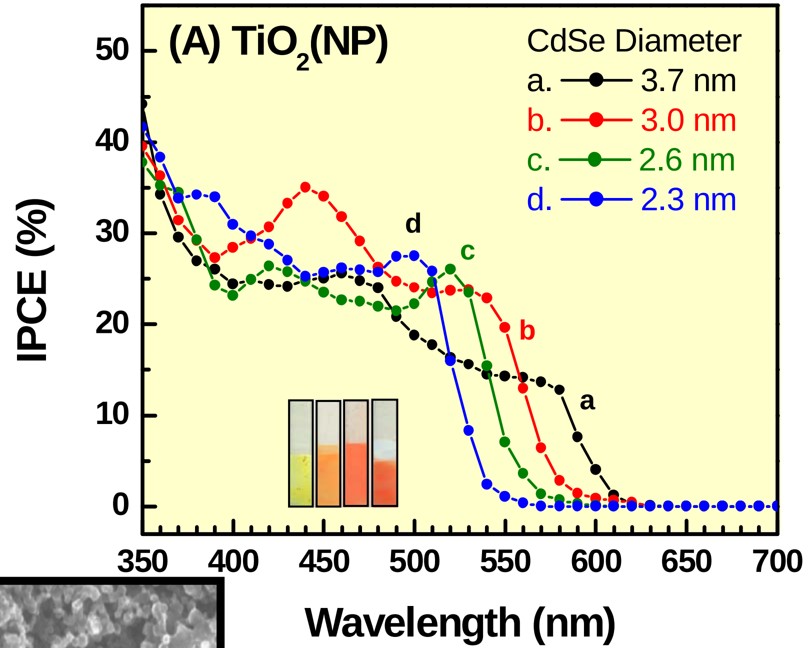


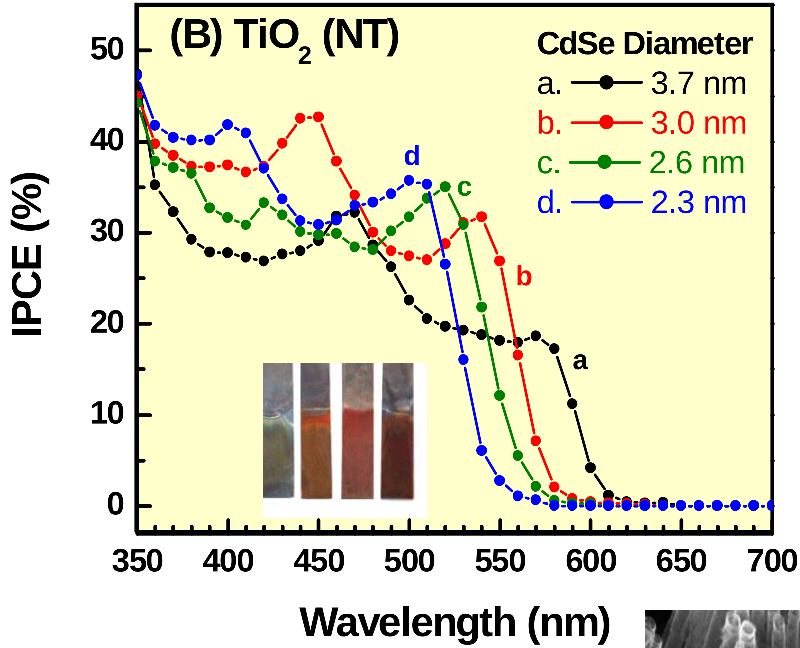
Emission spectra of CdSe QDs (a, c) on glass and (b, d) chemically bound to TiO_2 nanoparticle films at 2 different sizes of QDs (2.7 and 3.7 nm). Excitation was at 480 nm.

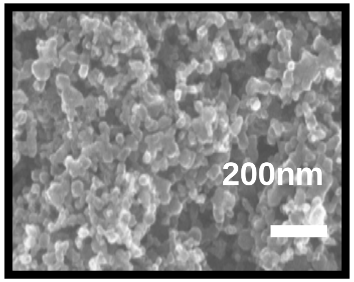


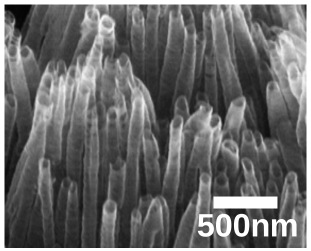
		<t>, ns	k_{et}, sec^{-1}
CdSe/ glass	2.6nm	4.1	
	3.7nm	7.9	
CdSe/ tnp	2.6nm	0.4	2.5E+09
	3.7nm	1.3	6.3E+08
CdSe/ tnt	2.6nm	0.4	2.2E+09
	3.7nm	1.5	5.5E+08

Quantum Dot Solar Cells – Particle versus Tube Architecture







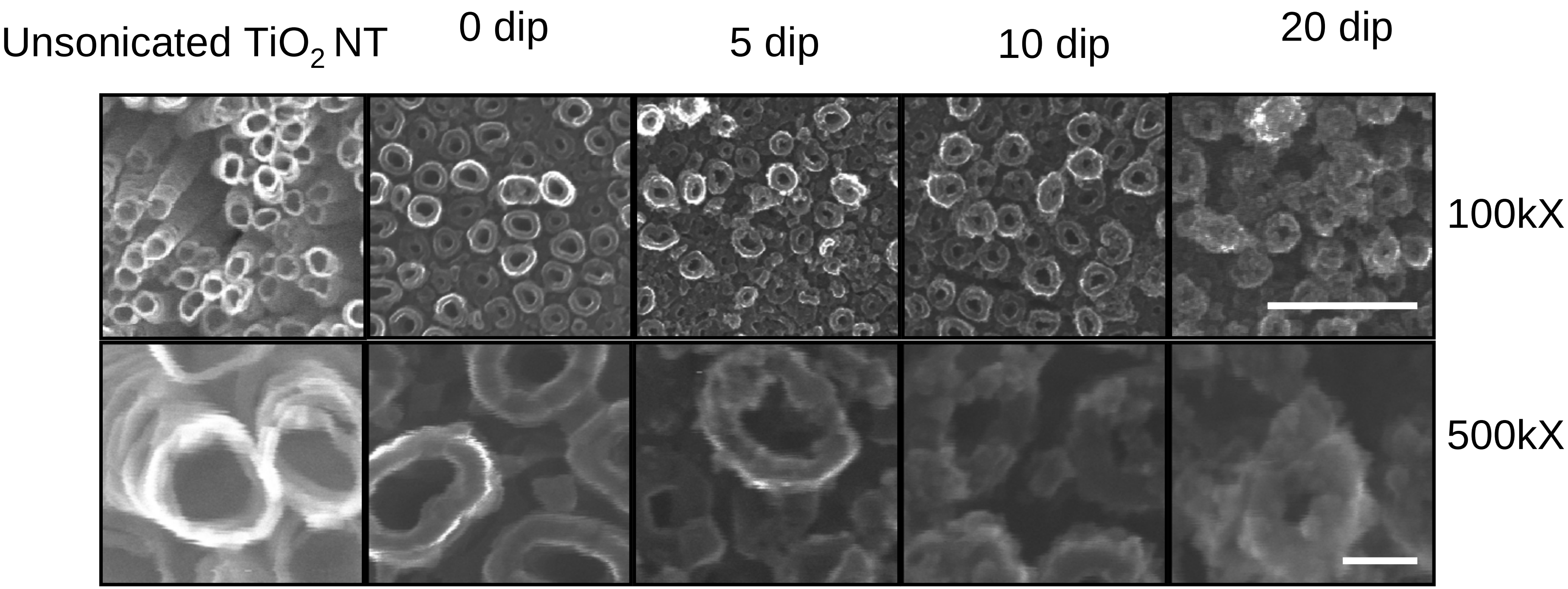


	I_{SC} mA/cm²	V_{OC} V	P_{max} mW/cm²	FF
CdSe-TNP	1.64	0.591	0.25	0.26
CdSe-TNT	1.95	0.582	0.29	0.26

Power conversion efficiency ~1%

J. Am. Chem. Soc., **130** (12), 4007 -4015, 2008

Depositing CdS quantum dots on TiO_2 nanotubes

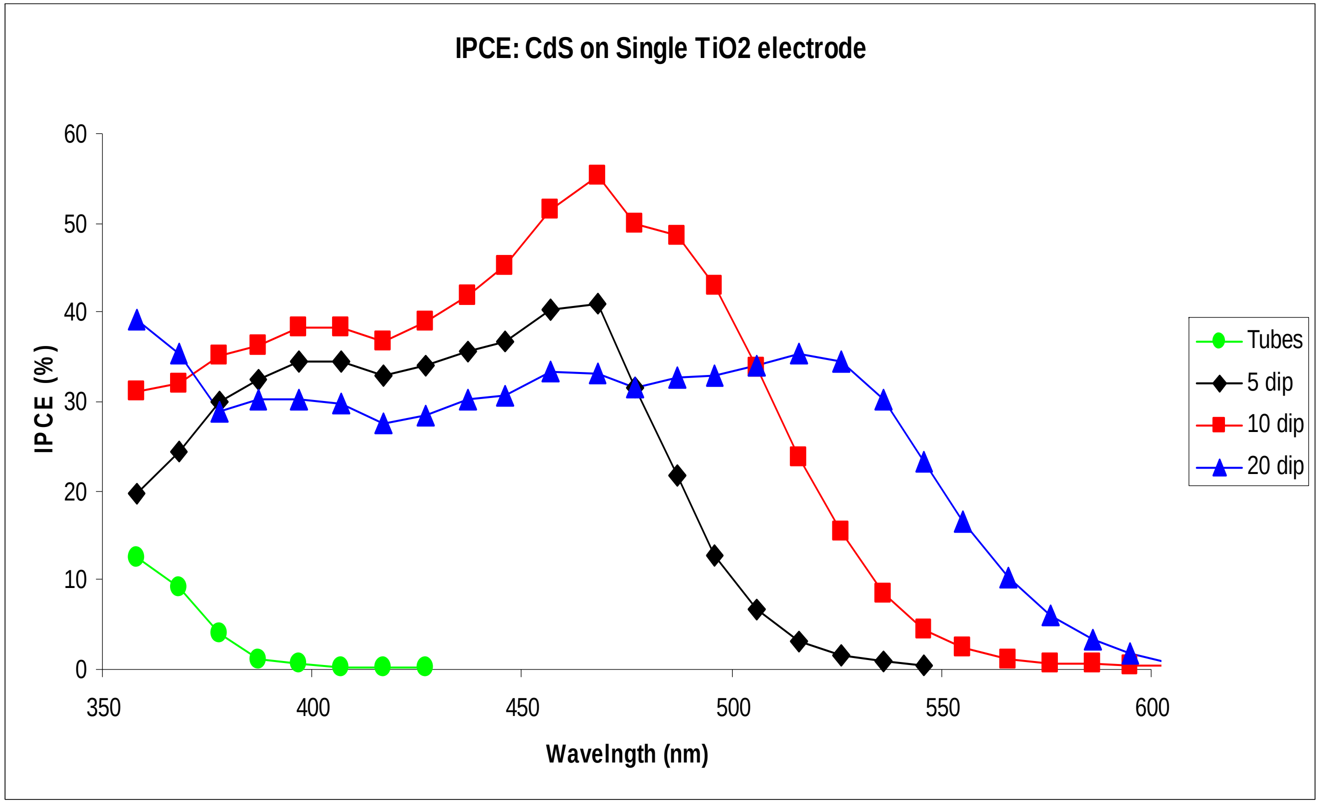


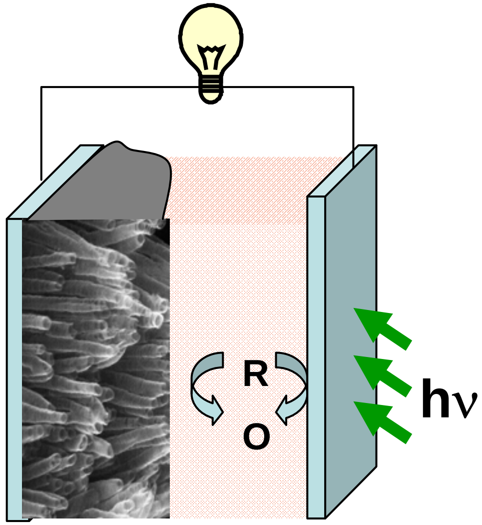
Scale bars: Top 500nm, bottom 50nm

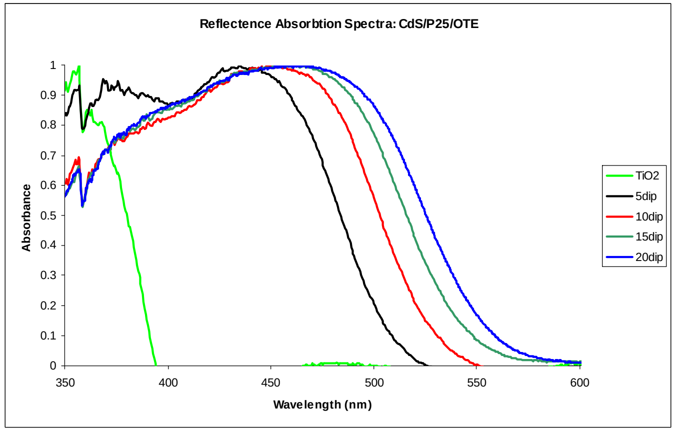
$(TiO_2) \xrightarrow{Cd^{2+}} (TiO_2)Cd^{2+} \longrightarrow \text{Wash} \xrightarrow{S^{2-}} (TiO_2)CdS \longrightarrow \text{Wash}$

1 dip cycle

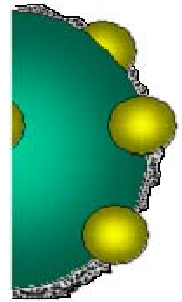
Photocurrent Response of TiO_2 (nanotube)CdS Films





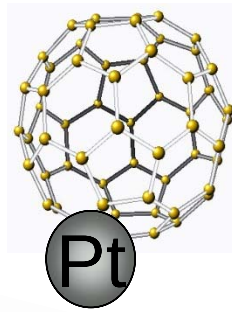


Carbon nanostructures as conduits to transport charge carriers



Advantages

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

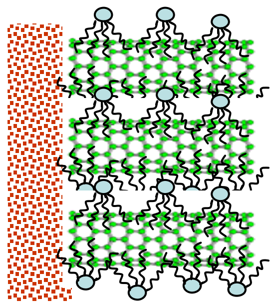


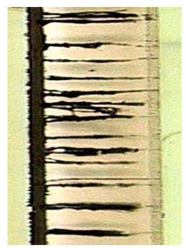
Goal

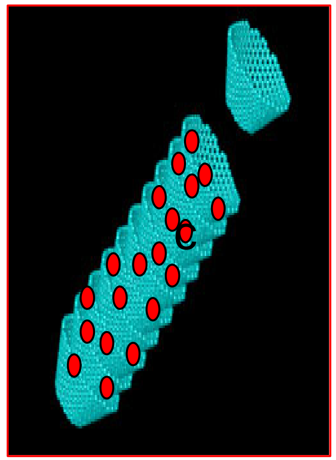
Effective utilization of carbon nanostructures for improving the performance of energy conversion devices

- 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

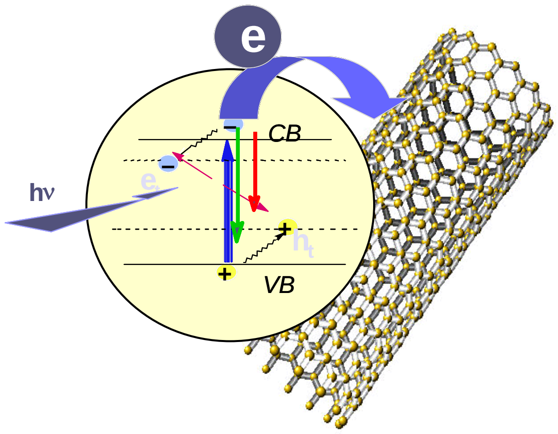






SWCNT- TiO_2 composite films

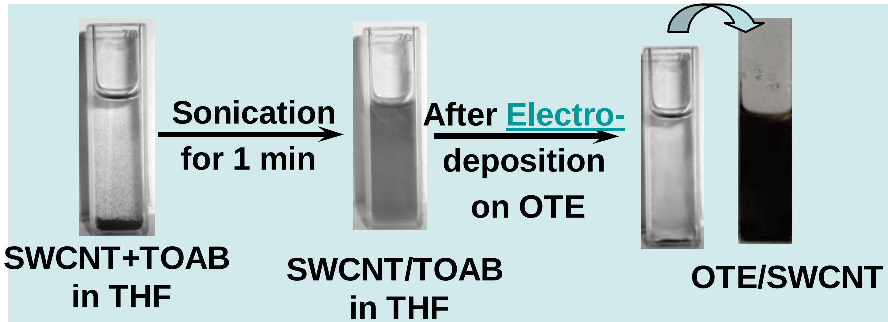
- **Mesoscopic TiO_2 films are extensively used in Dye-Sensitized Solar Cells**
- **A carbon nanotube support architecture can disperse the TiO_2 particles and facilitate charge collection and charge transport within the film.**
- **The first step is to design the SWCNT-TiO_2 network and test the feasibility of the composite system in solar cells**

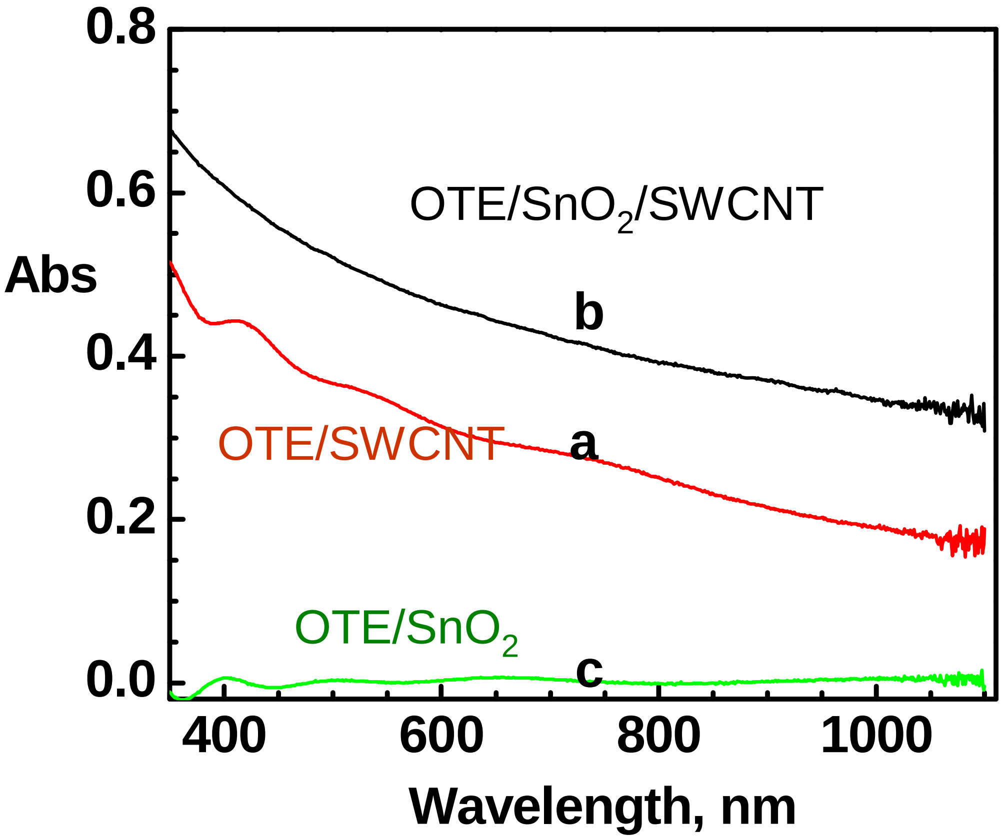


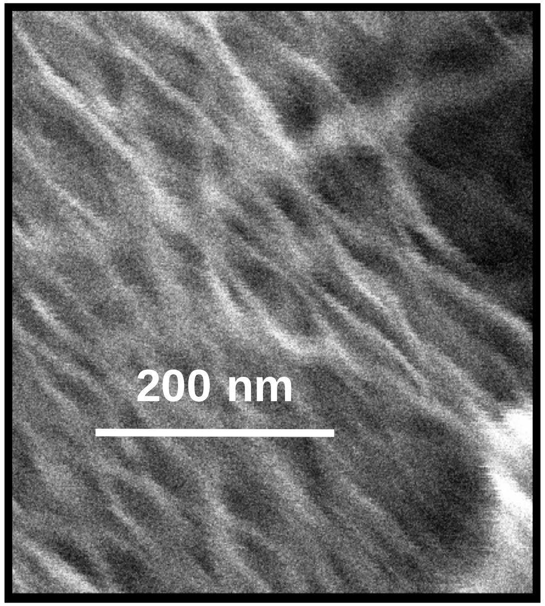
Kongkanand, A.; Domínguez, R.M.; Kamat, P.V., *Single Wall Carbon Nanotube Scaffolds for Photoelectrochemical Solar Cells. Capture and Transport of Photogenerated Electrons.* **Nano Lett., 2007**. *7*, 676-680.

Vietmeyer, F.; Seger, B.; Kamat, P.V., *Anchoring ZnO Particles on Functionalized Single Wall Carbon Nanotubes. Excited State Interactions and Charge Collection.* **Adv. Mater., 2007,** *19: 2935-2940*

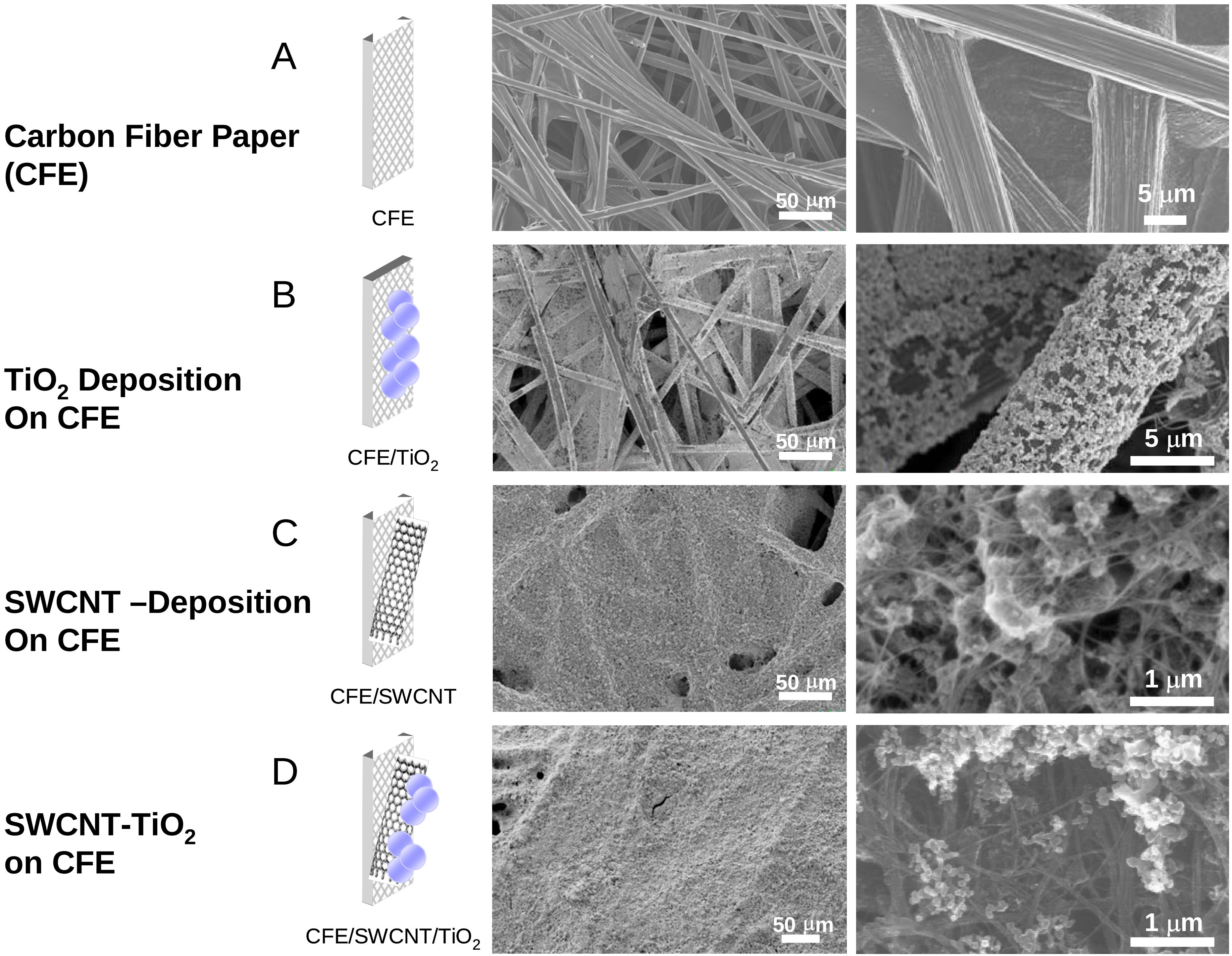
Electrophoretic Deposition of SWCNT on Electrode Surfaces







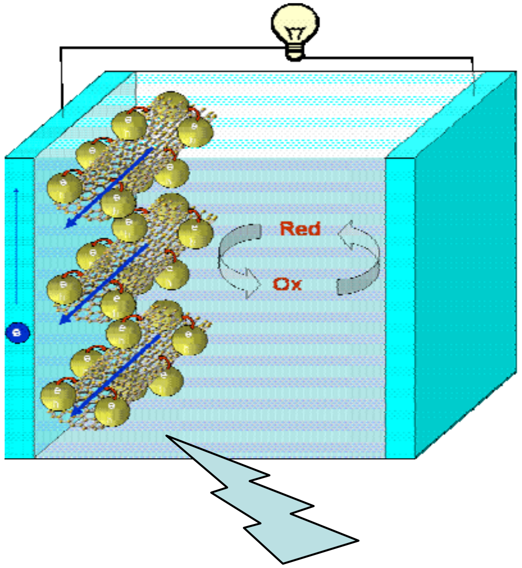
J. Am. Chem. Soc., 2004. **126** 10757-10762.



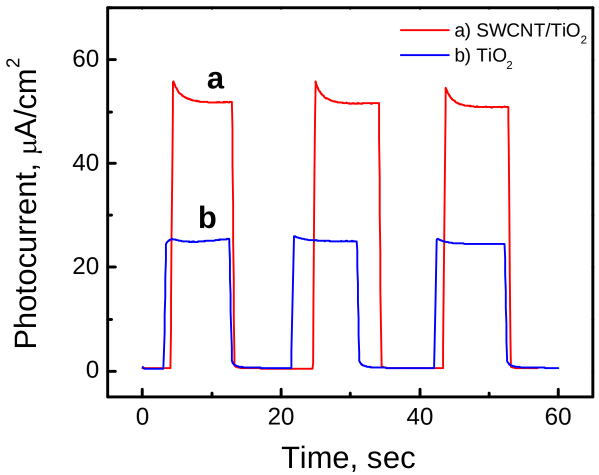
A
Carbon Fiber Paper (CFE)
CFE
50 μm
5 μm
B
TiO_2 Deposition On CFE
CFE/TiO_2
50 μm
5 μm
C
SWCNT –Deposition On CFE
CFE/SWCNT
50 μm
1 μm
D
SWCNT-TiO_2 on CFE
CFE/SWCNT/TiO_2
50 μm
1 μm

Photocurrent Generation

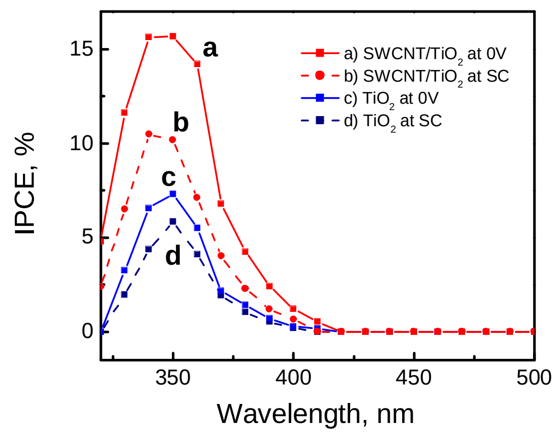
CFE/TiO_2 versus CFE/SWCNT –TiO_2



UV light



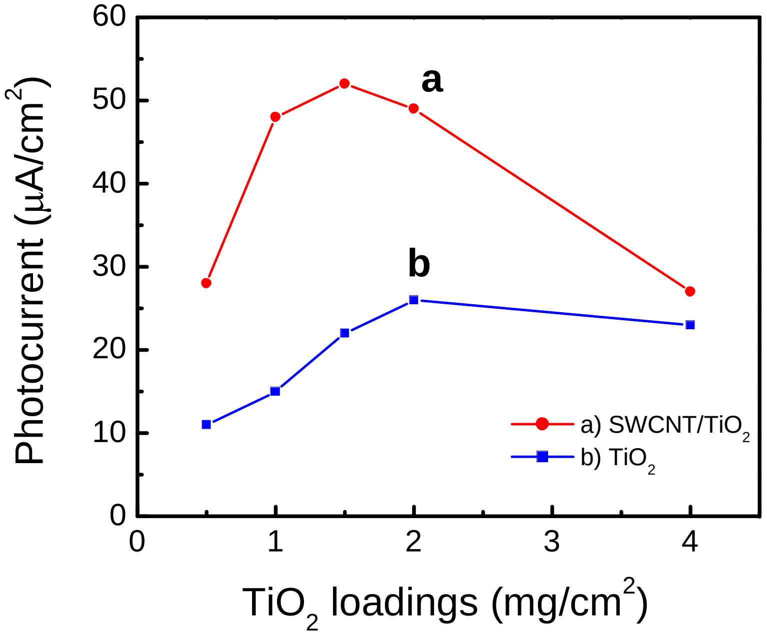
Higher IPCE (increase of factor ~2) was observed for mesoscopic CFE/SWCNT-TiO_2 films

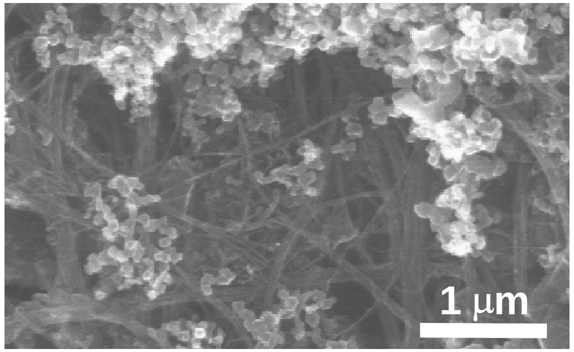


The results are indicative of better charge collection and transport provided by the SWCNT -Network

Nano Lett., **2007**. *7*, 676-680

Dependence of TiO_2/SWCNT Ratio on the Photocurrent Generation



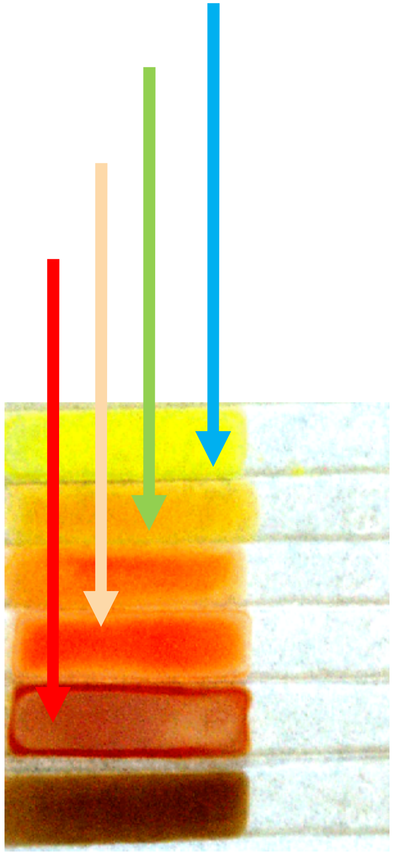


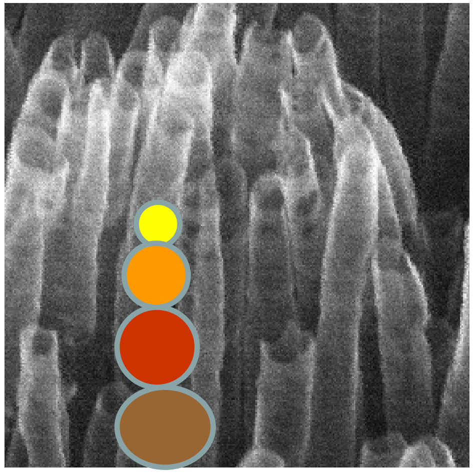
Increasing the TiO_2 concentration results in enhanced photocurrent as they are dispersed on SWCNT network.

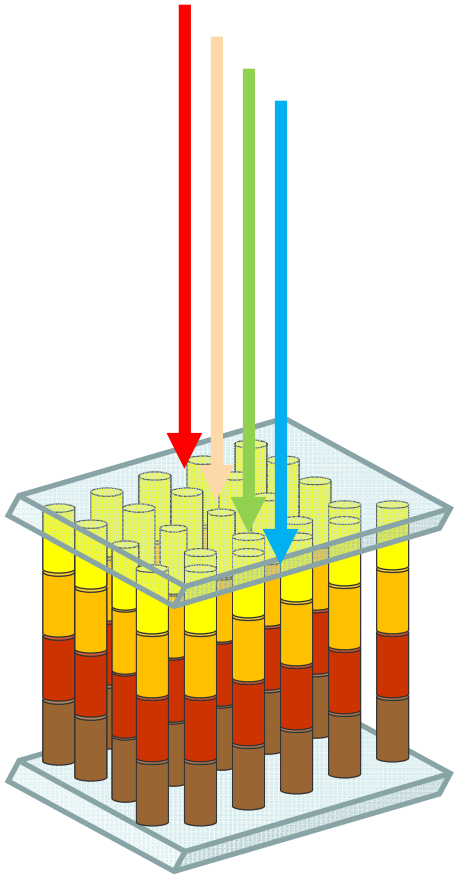
At concentrations greater than 2 mg/cm^2 the beneficial effect of SWCNT disappears. Under these conditions. TiO_2 particles aggregate and the charge recombination dominates

Nano Lett., **2007**. *7*, 676-680

Where do we go from here?

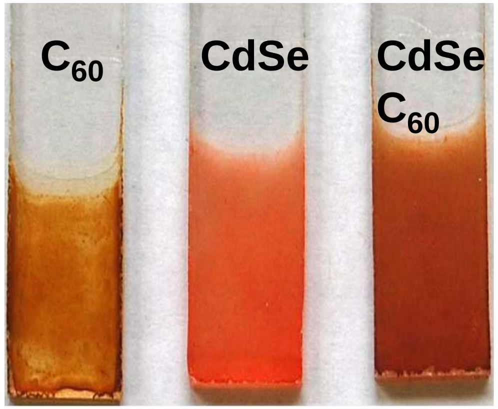


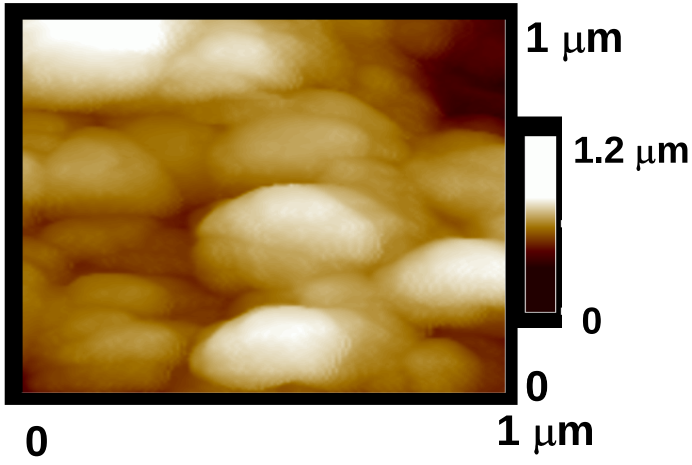


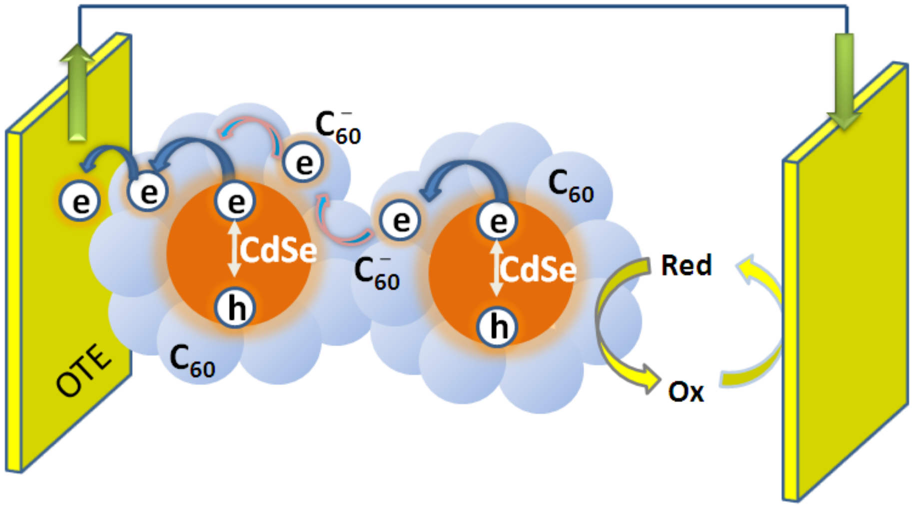


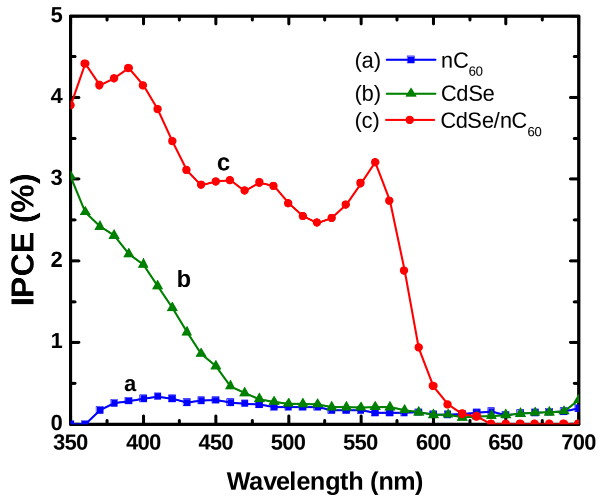
Capping CdSe with an Electron Acceptor Shell

Electrophoretic deposition of Cluster films



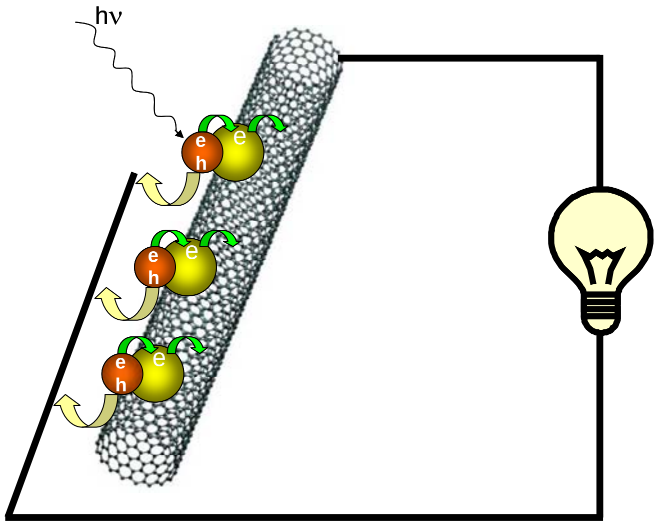


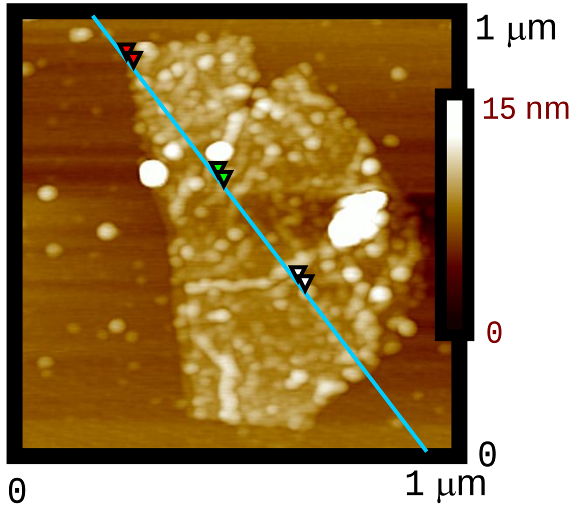




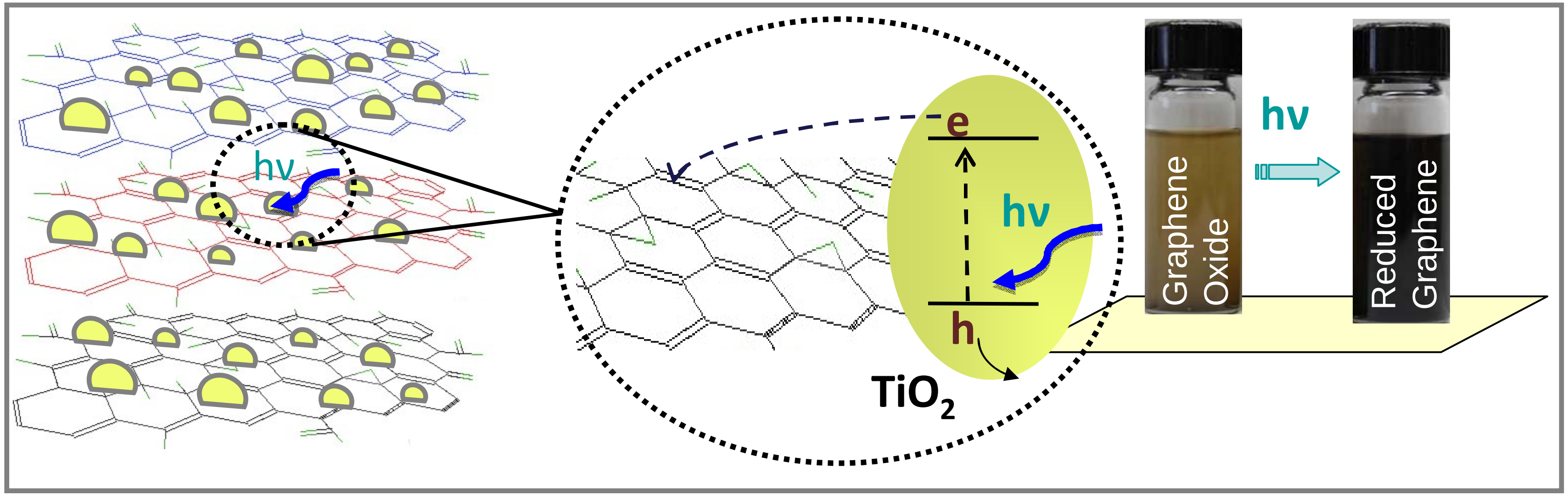
J. Am. Chem. Soc., 2008, *130*, 8890–8891

Organized light harvesting assembly using carbon nanostructures



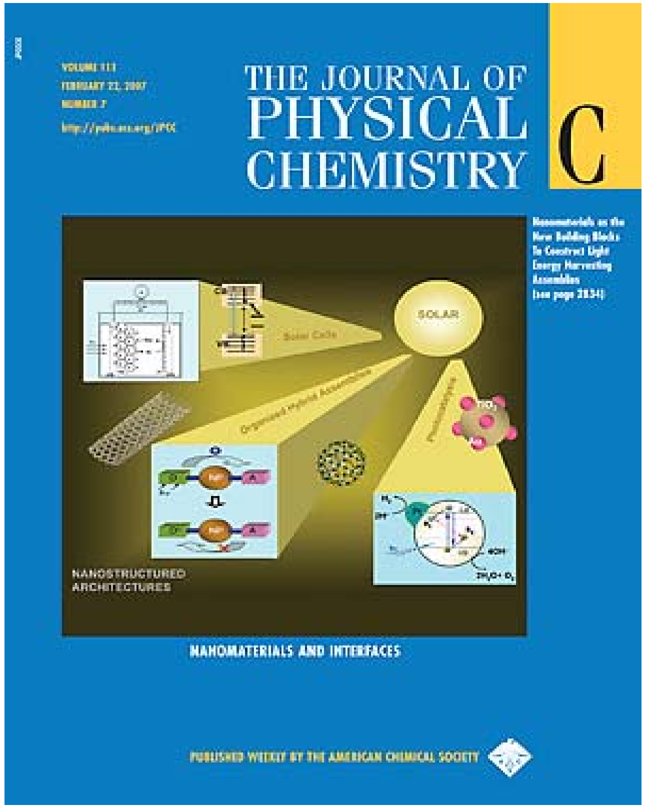


Graphene-Semiconductor Nanocomposites ***ACS Nano, 2008****, 2,* 1487-1491



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.



Kamat, P. V. *Meeting the Clean Energy Demand: Nanostructure Architectures for Solar Energy Conversion (Review)*
J. Phys. Chem. C, 2007. **111** 2834 - 2860.

Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters (Centennial Feature) J. Phys. Chem. C 2008, 112, in press

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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)

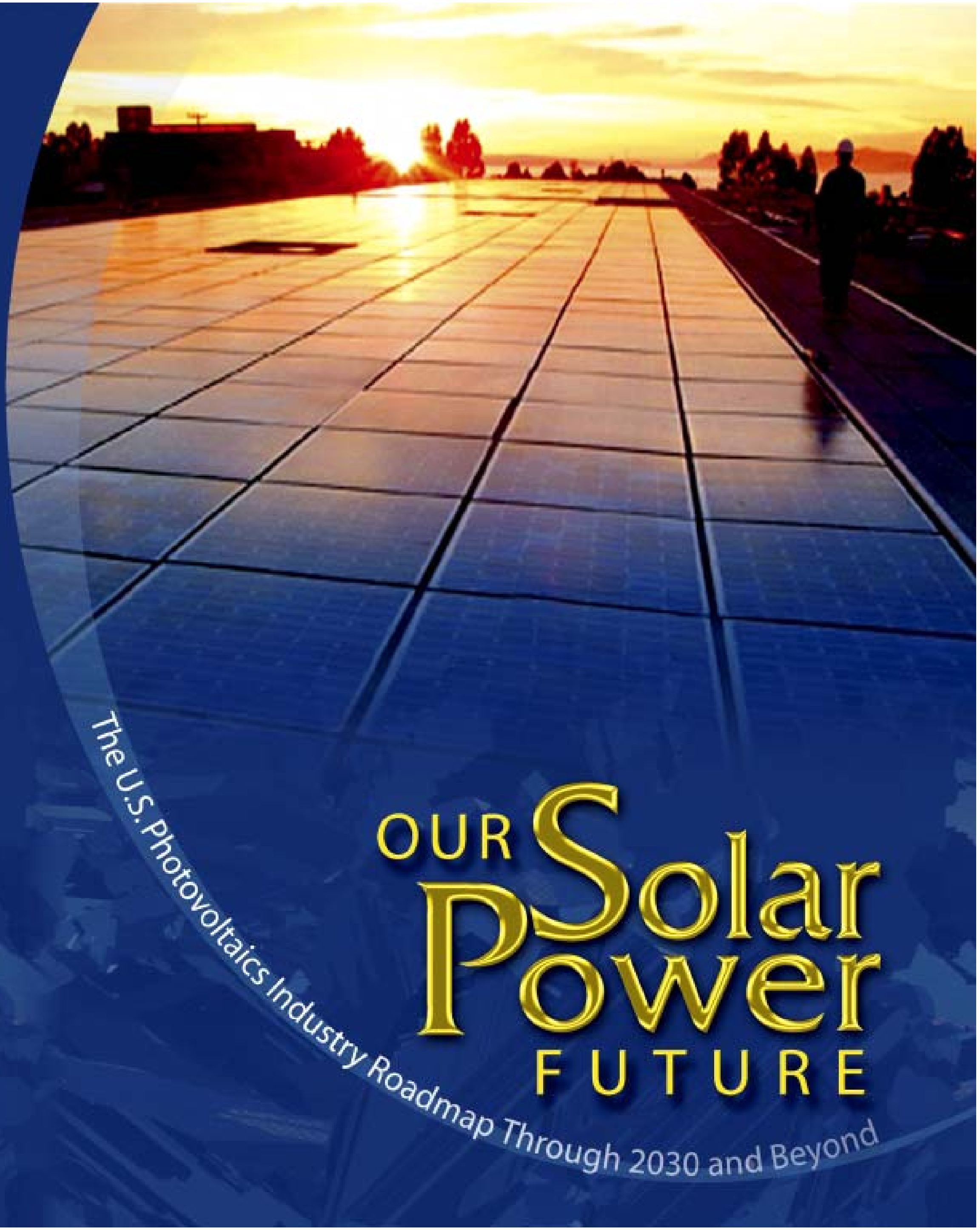
Post-Docs/Visiting Scientists
Jin Ho Bang

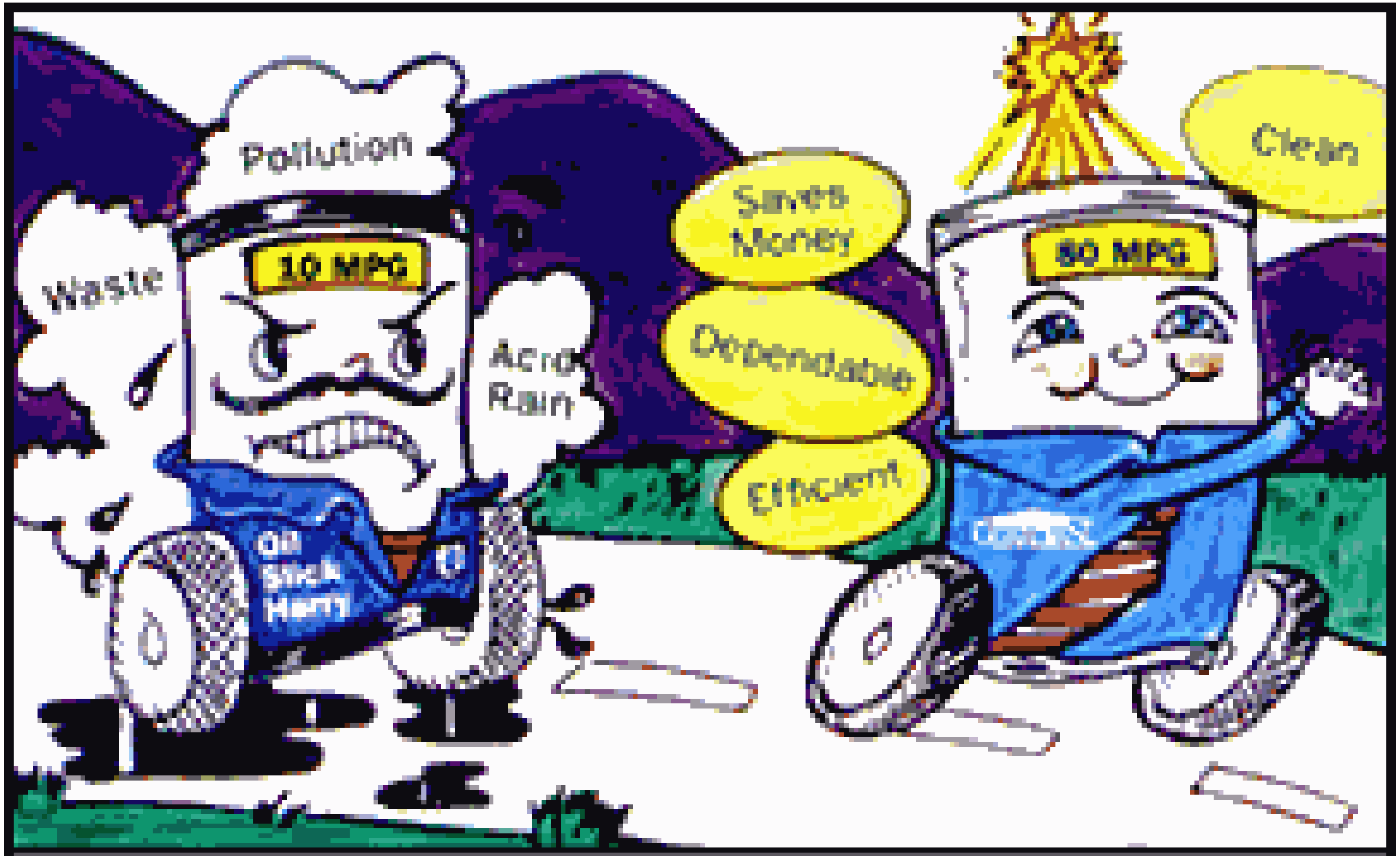
Undergraduate students
Pat Brown
Chris Rodriguez
David Riehm
Rachel Staran

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