CdSe Quantum Dots Anchored on TiO_2 and Carbon Nanotubes. 1D Architectures as Scaffolds to Improve the Efficiency of Solar Cells.

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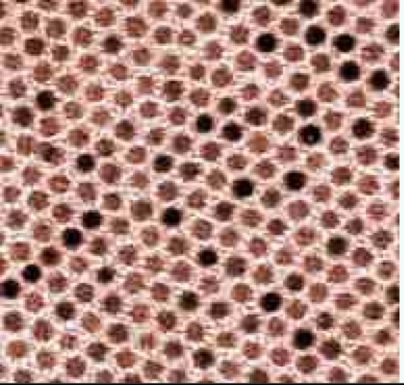
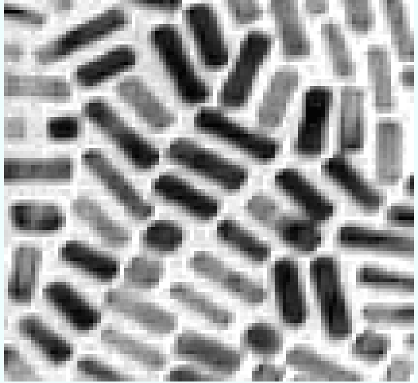
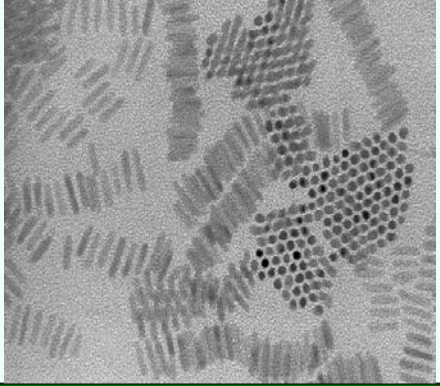
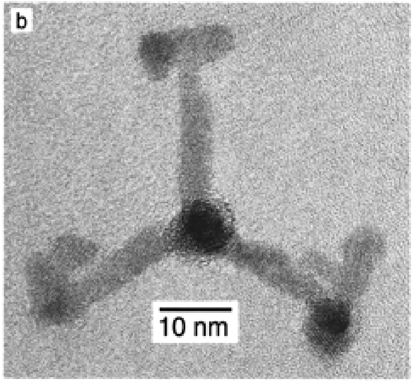
Support: US DOE (BES)

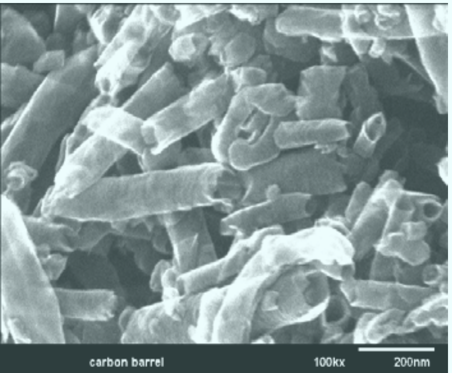


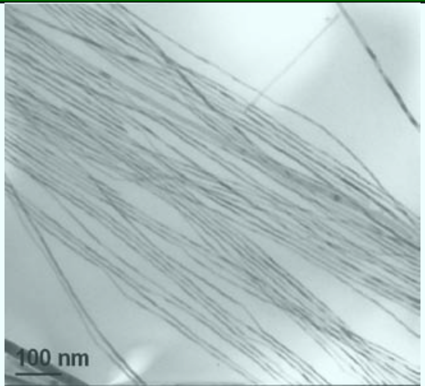


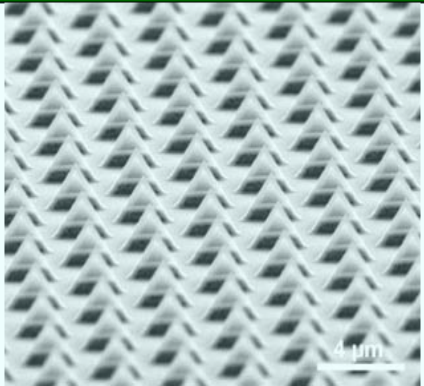


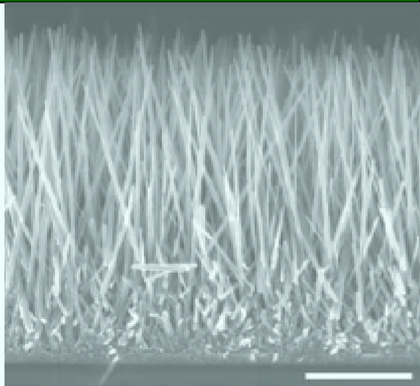


Addressing clean energy challenge with Nanostructure Interfaces





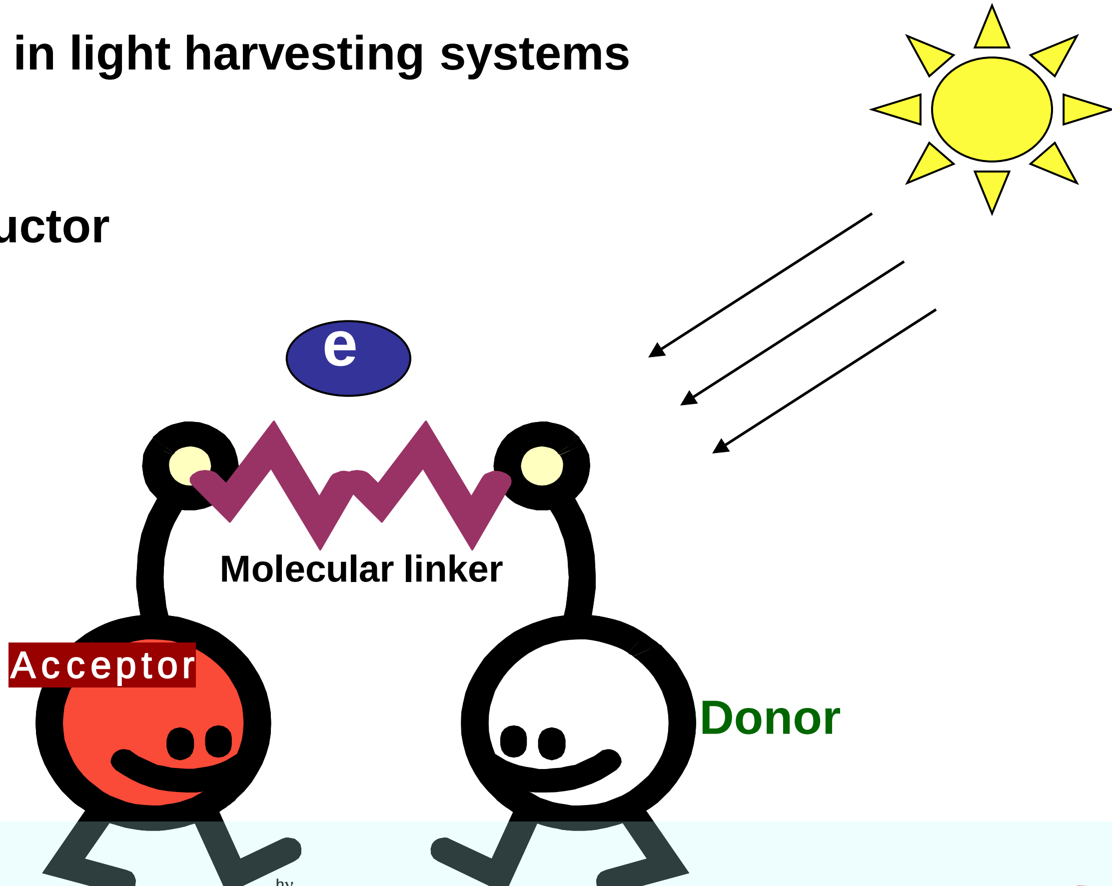


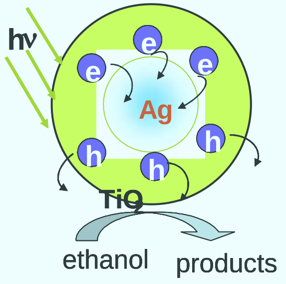


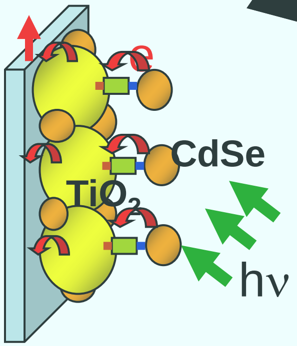
Research Focus

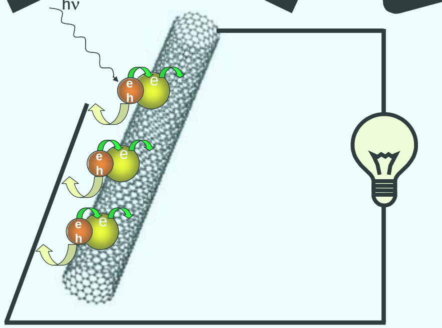
Photoinduced electron transfer in light harvesting systems

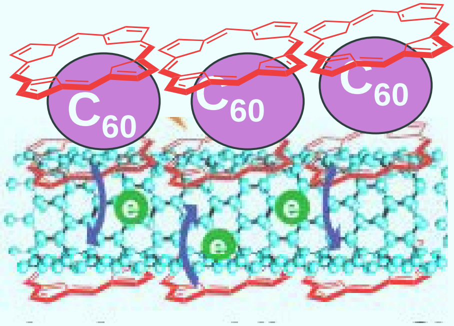
- Donor- Acceptor
- Semiconductor-Sensitizer
- Semiconductor-Semiconductor
- Semiconductor-Metal











Outline

1. **CdSe Quantum Dot Solar Cells**
   - Anchoring CdSe quantum dots on TiO_2 surface
   - Modulation of Photocurrent response with different size QDs

2. **Nanotube/Nanowire Architecture Based QDSC**
   - TiO_2-CdS systems
   - Particle versus tubular architecture

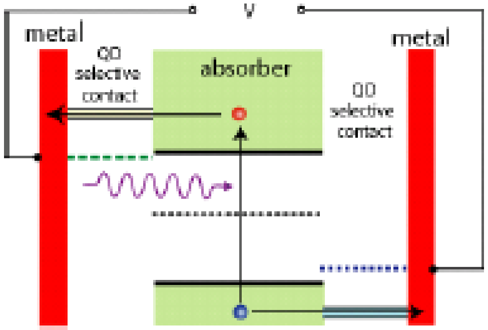
3. **Carbon Nanostructures as Conducting Scaffolds**
   - CNT-TiO_2 hybrids
   - Charge injection from excited CdSe into SCCNT

4. **Future Issues and Challenges**

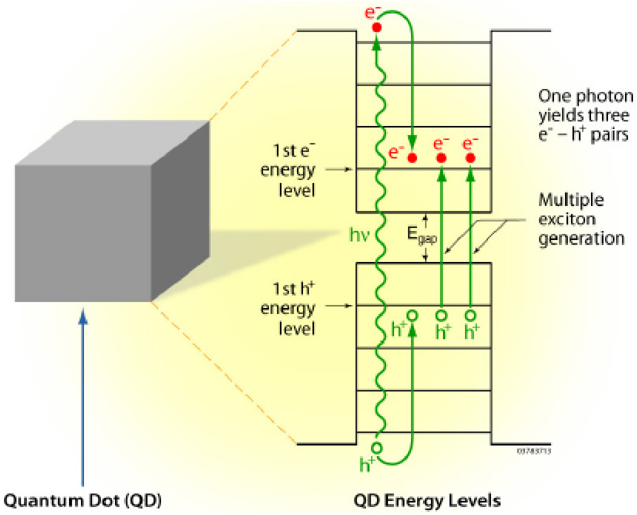
Quantum Dot Solar Cells

Tunable band edge

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



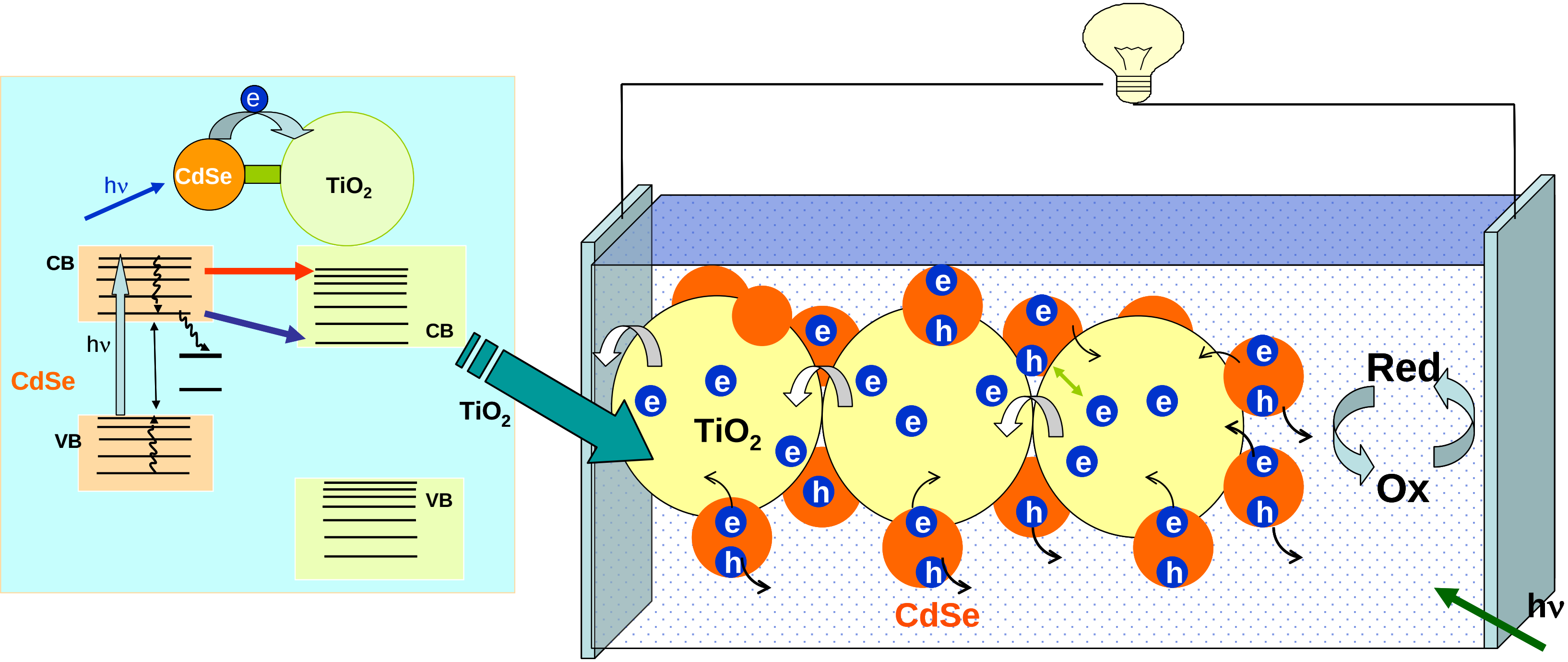
Hot carrier injection from higher excited state (minimizing energy loss during thermalization of excited state)

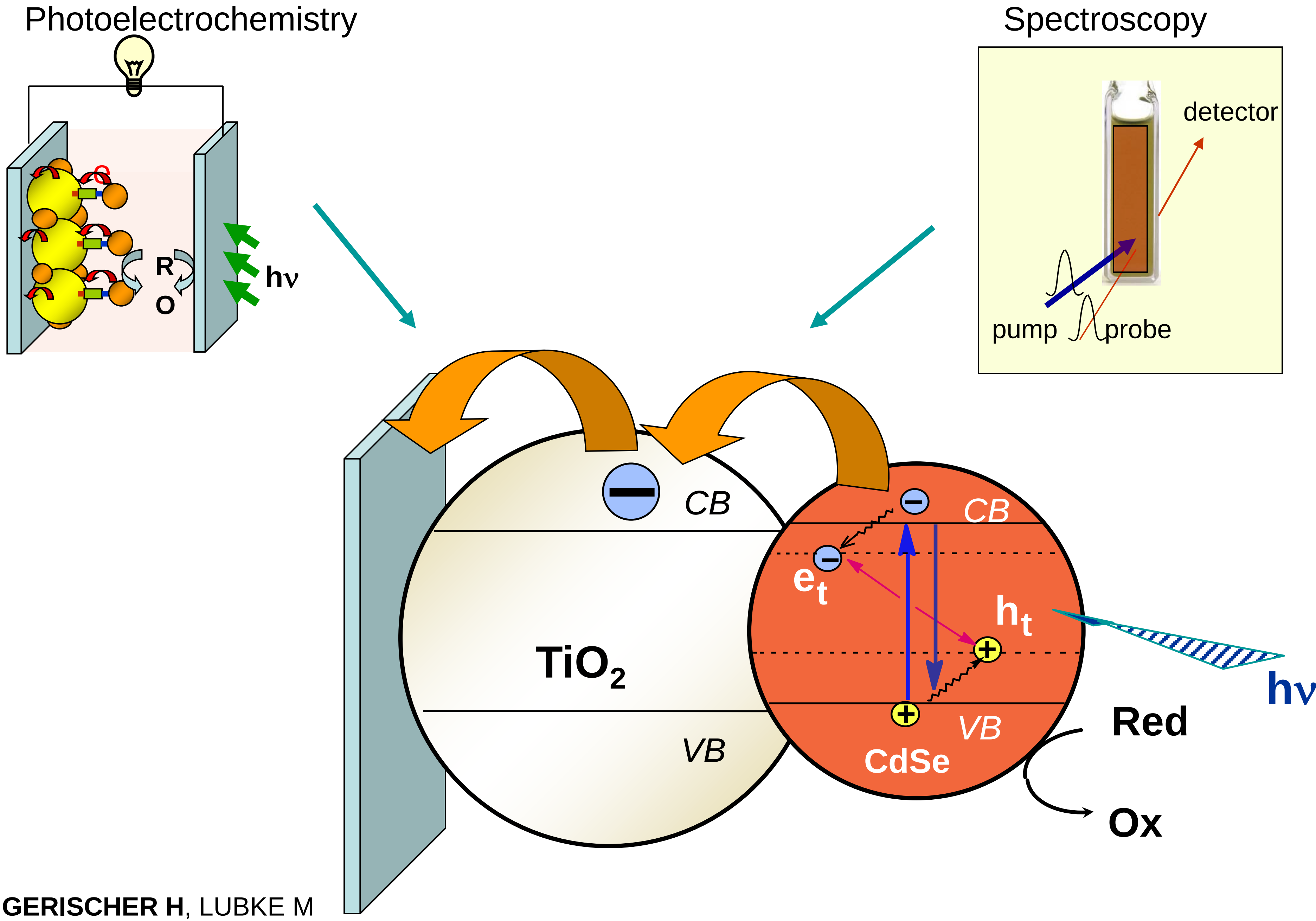


Multiple carrier generation solar cells.

Utilization of high energy photon to multiple electron-hole pairs

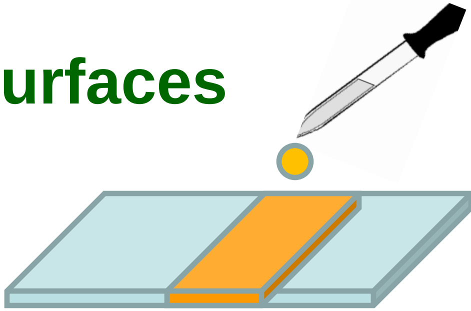
Quantum Dot Sensitized Solar Cell (QDSSC)





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

Assembling Quantum Dots on Electrode Surfaces



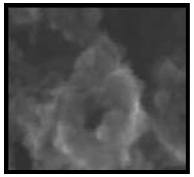
1. **Drop casting or Spin casting**

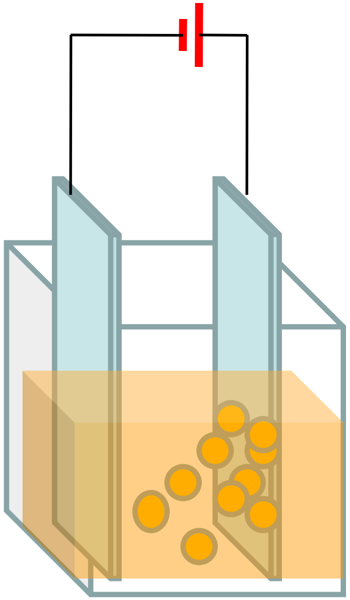
2. **Chemical Bath Deposition**

   Hodes, Chem. Mater., 2004,*16*, 2740–2744

3. **SILAR (Successive Ionic Layer Adsorption and Reaction)**

   Baker and Kamat Adv Funct Mater. 2009 *19, 805.*





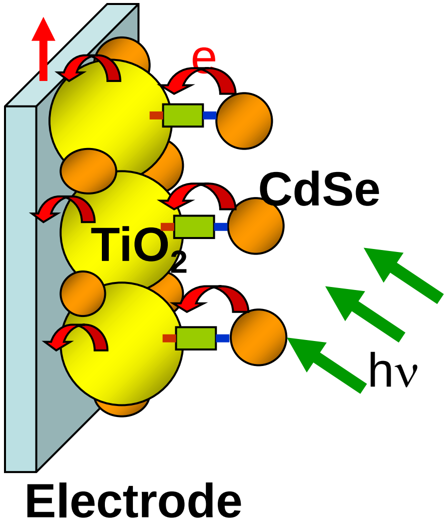
4. **Electrophoretic Deposition**

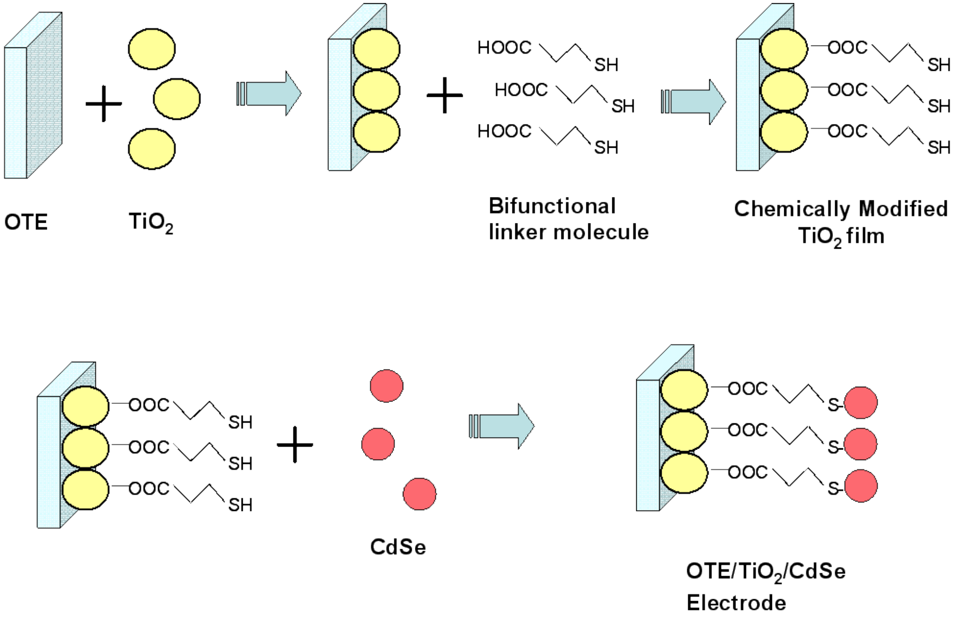
   Brown & Kamat
   J. Am. Chem. Soc., 2008, *130,* 8890–8891

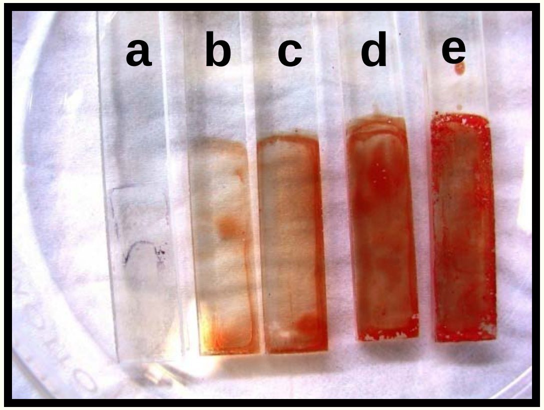
5. **Using a bifunctional Linker**

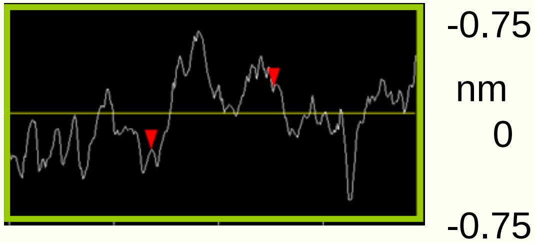
   Subramanian et al J. Am. Chem. Soc. 2006,128, 2385-2393

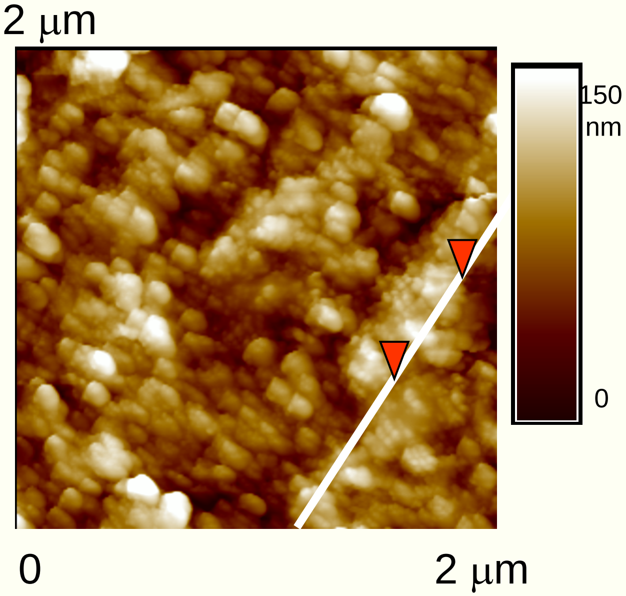
Linking Q-CdSe to TiO_2 particles





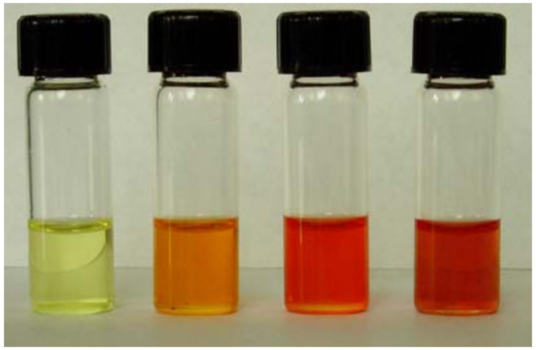






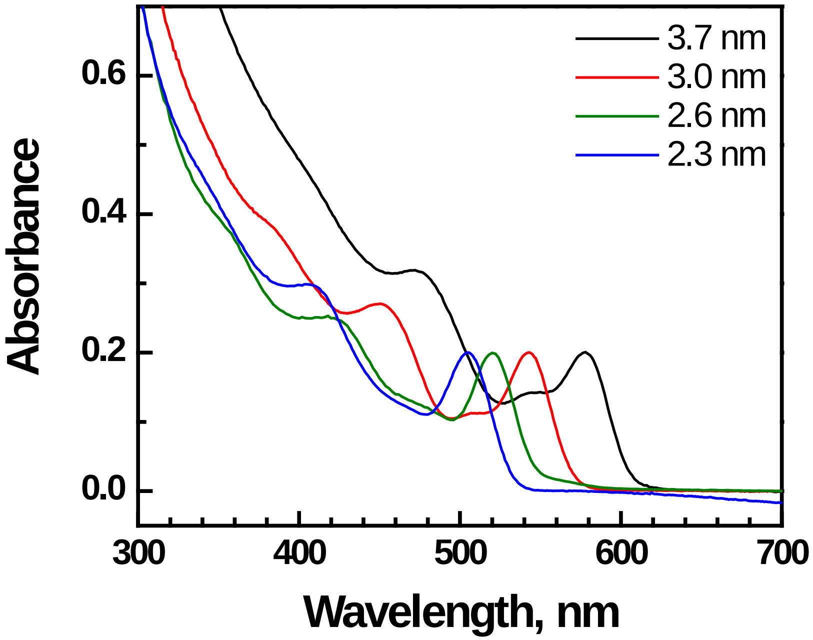
J. Am. Chem. Soc. 2006,128, 2385-2393

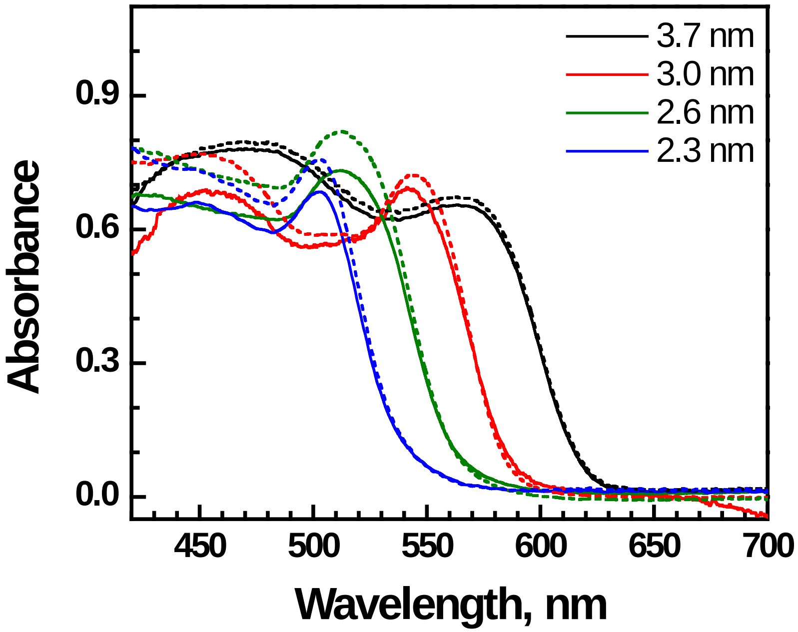
Modification of TiO_2 Films with Different Size CdSe Particles



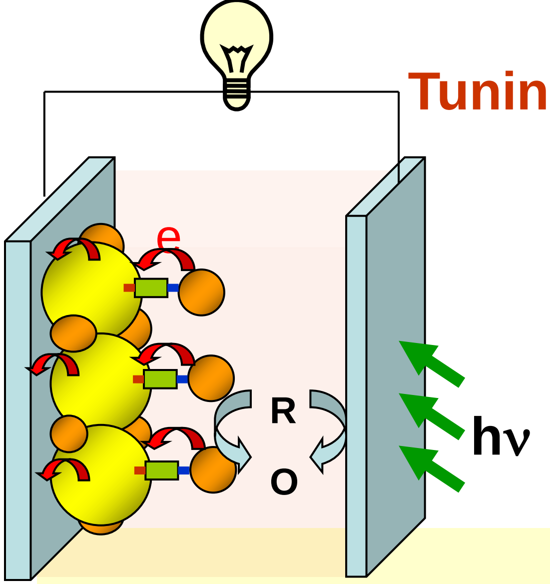
2.3nm 3.0nm
2.6nm 3.7nm

2.3nm 3.0nm
2.6nm 3.7nm



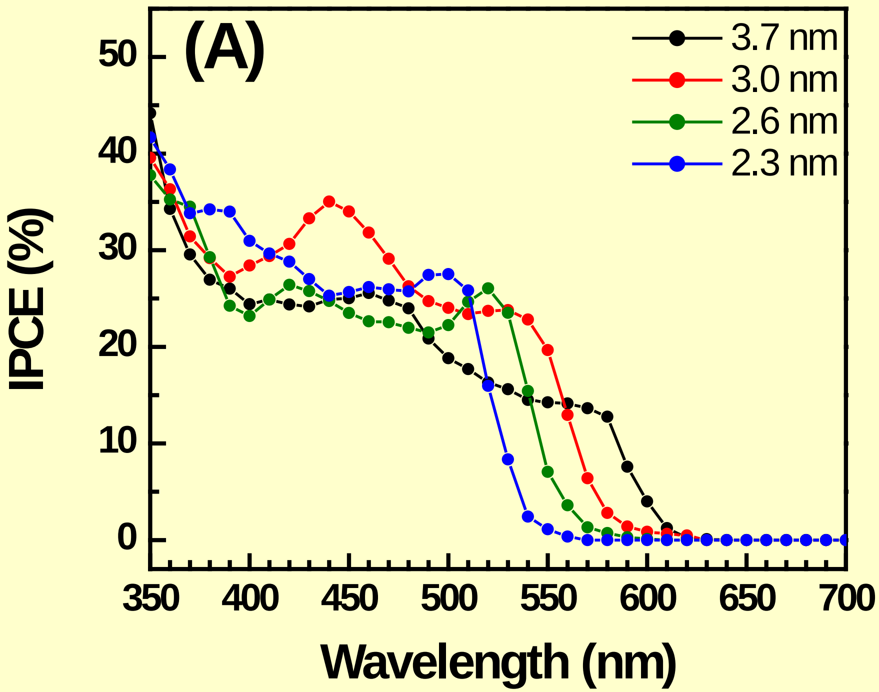


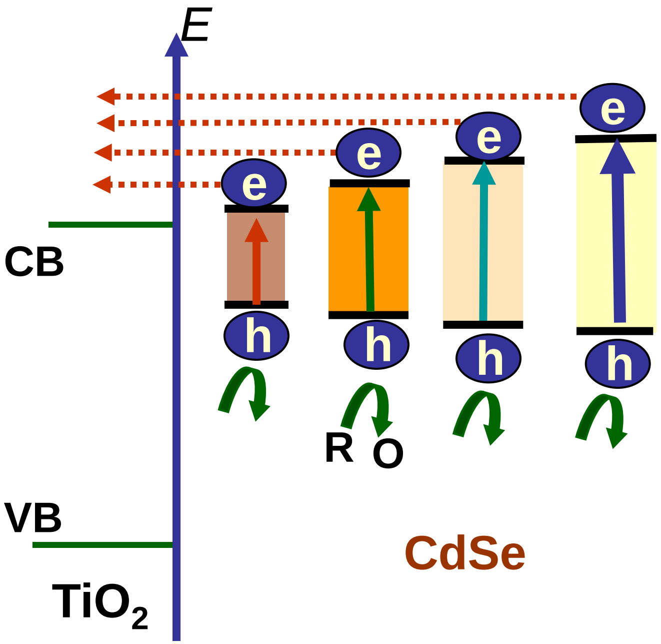
Tuning the Photoresponse of Quantum Dot Solar Cells



IPCE or Ext. Quantum Eff.

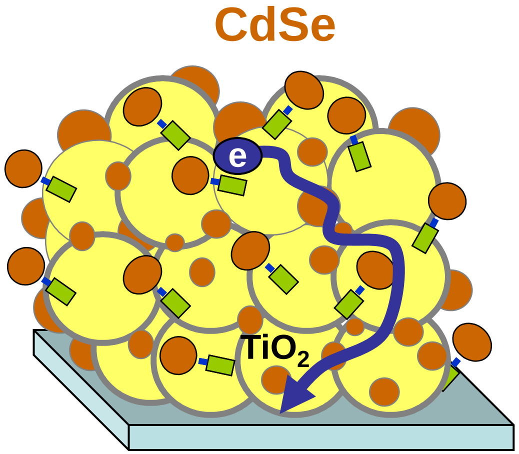
$= (1240/\lambda) \times (Isc/Iinc) \times 100$





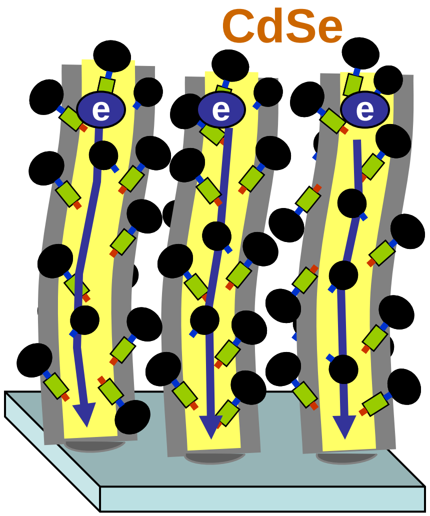
J. Am. Chem. Soc., **130** (12), 4007 -4015, 2008

Nanowire/nanotube architecture to improve the performance QDSC



OTE/TiO_2 nanoparticles

(a)



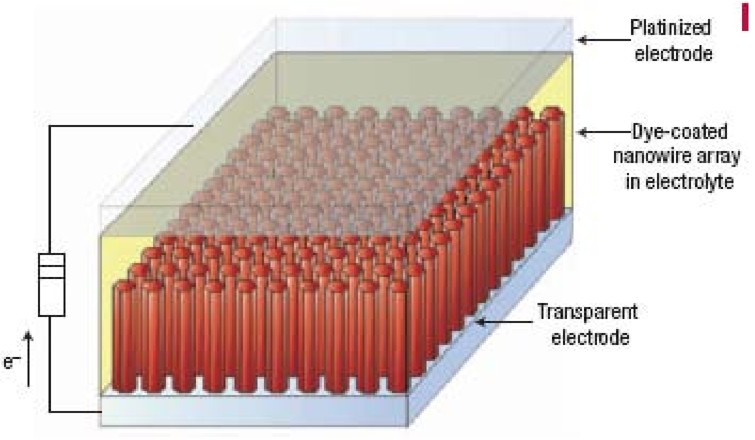
Ti/TiO_2 nanotubes

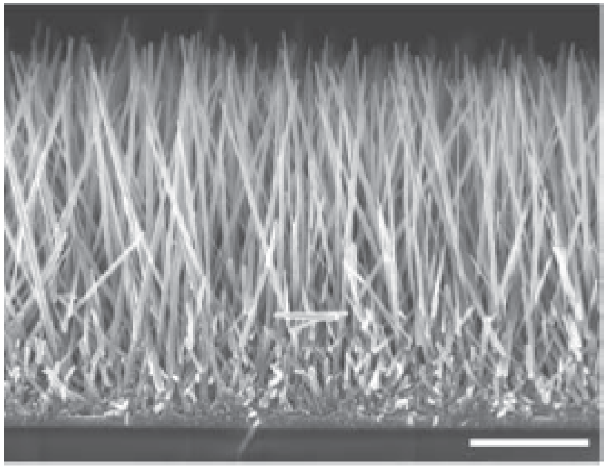
(b)

Recent advances

Nanowire dye-sensitized solar cells

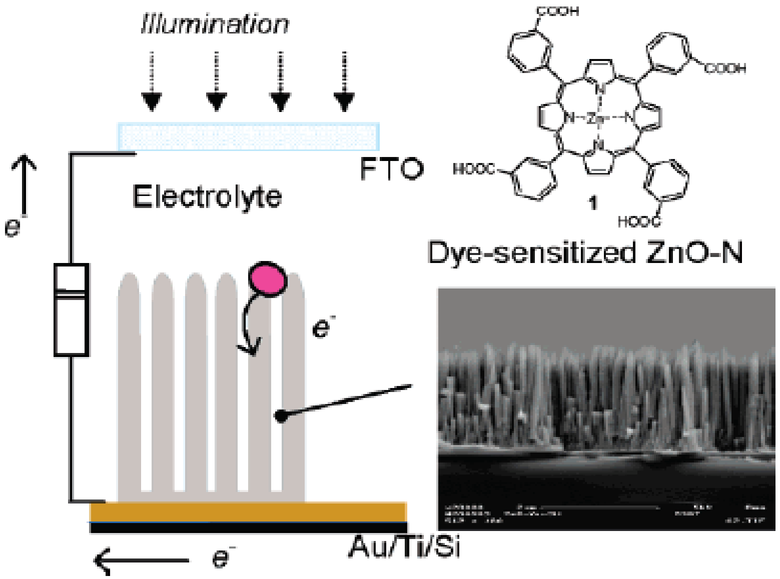
LAW, GREENE, JOHNSON, SAYKALLY, YANG Nature Materials 4 , 455, 2005





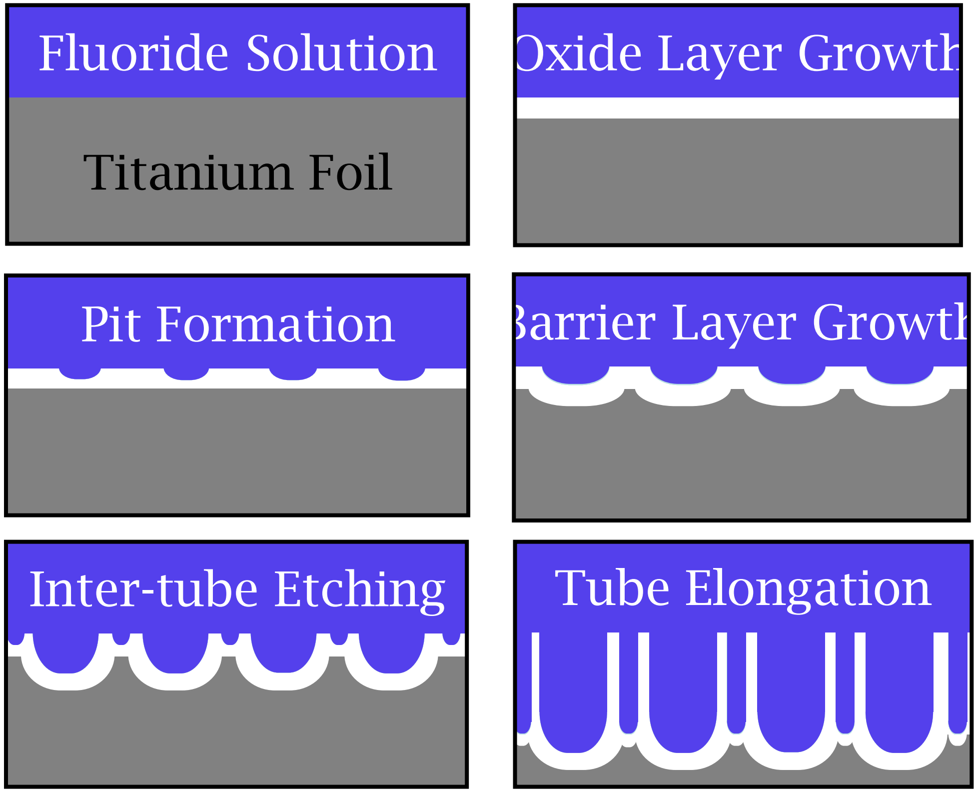
Fast Electron Transport in Metal Organic Vapor Deposition Grown Dye-sensitized ZnO Nanorod Solar Cells

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

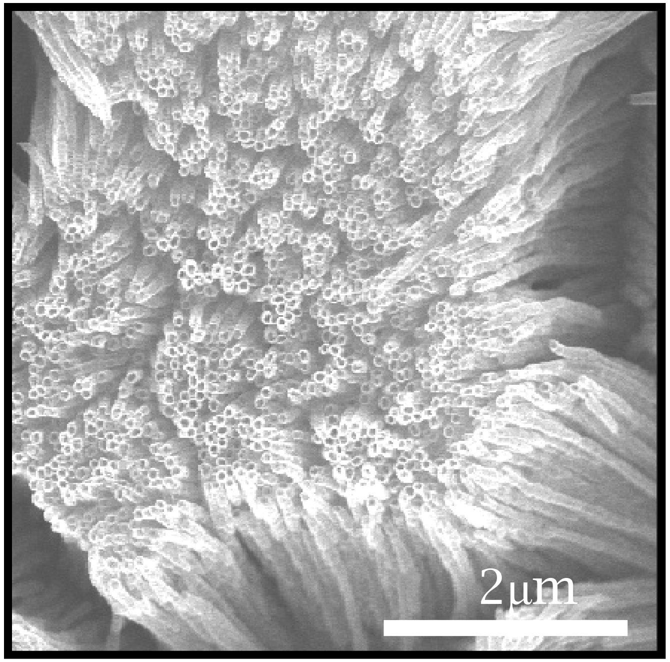
Anodic Etching of Ti Film



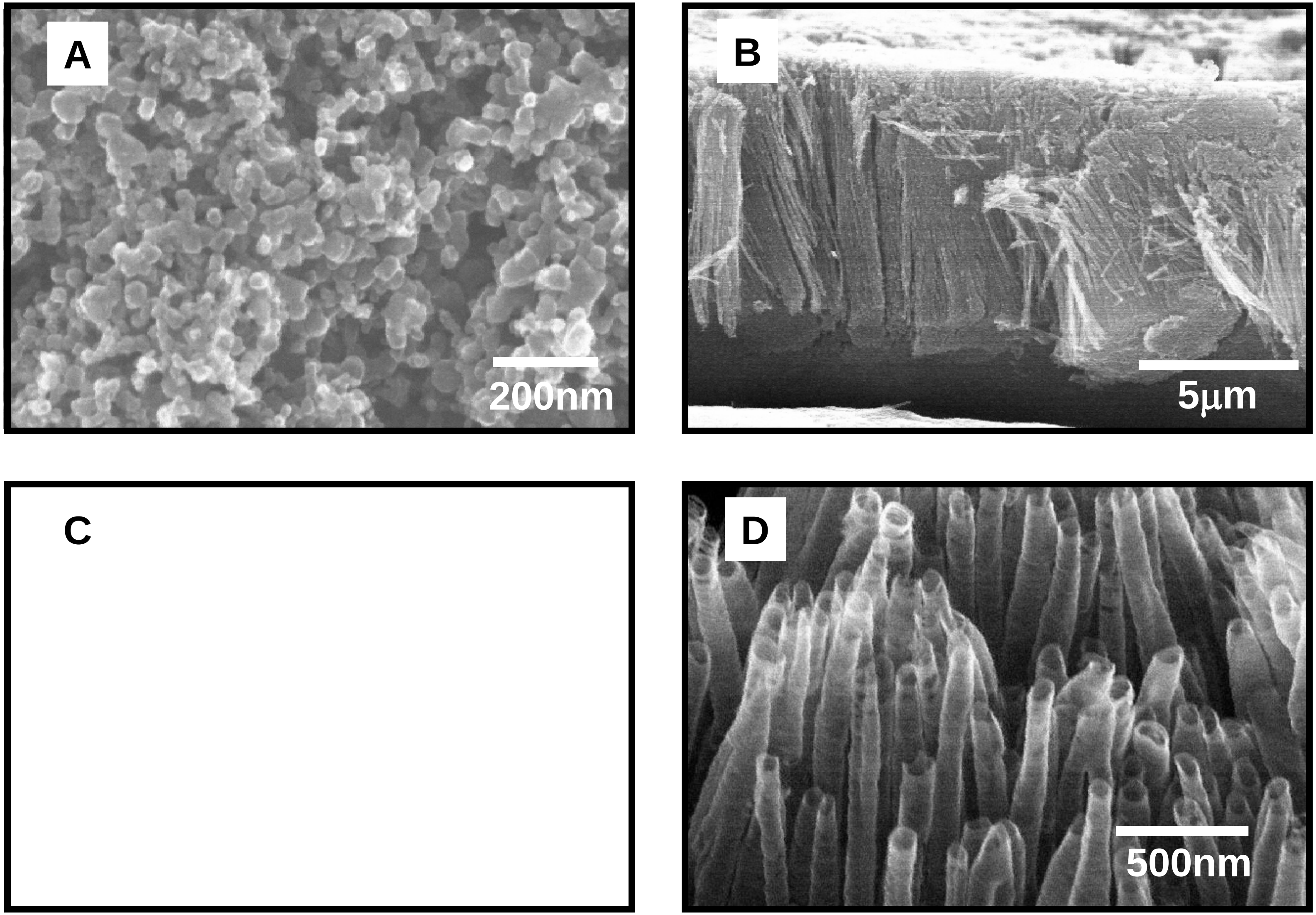
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

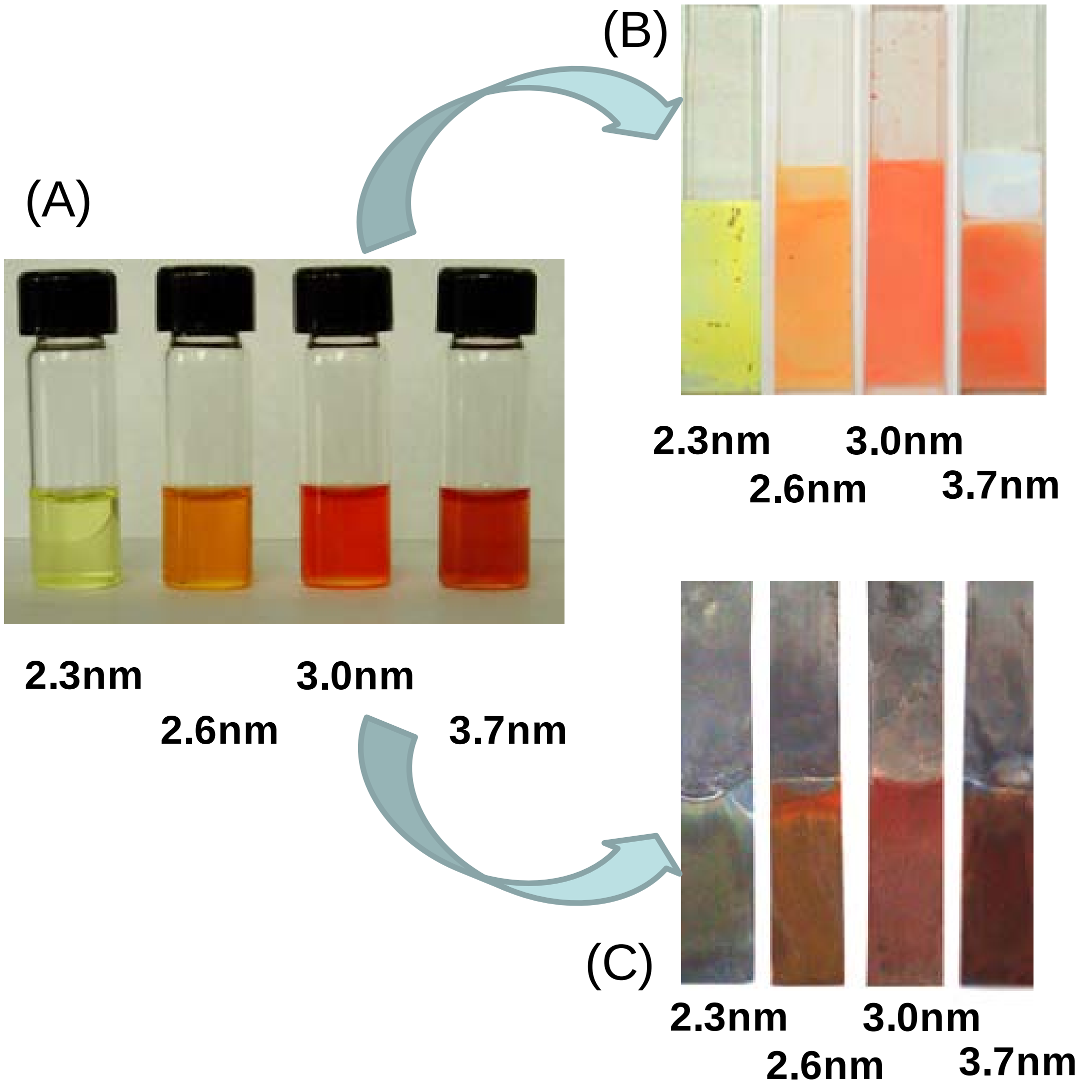
$$Ti + O_2 \rightarrow TiO_2$$

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O$$

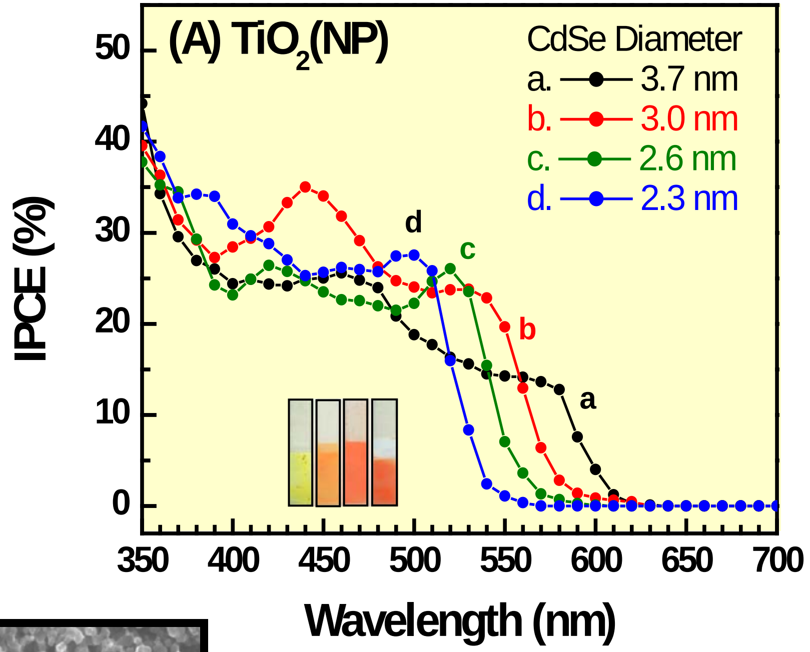


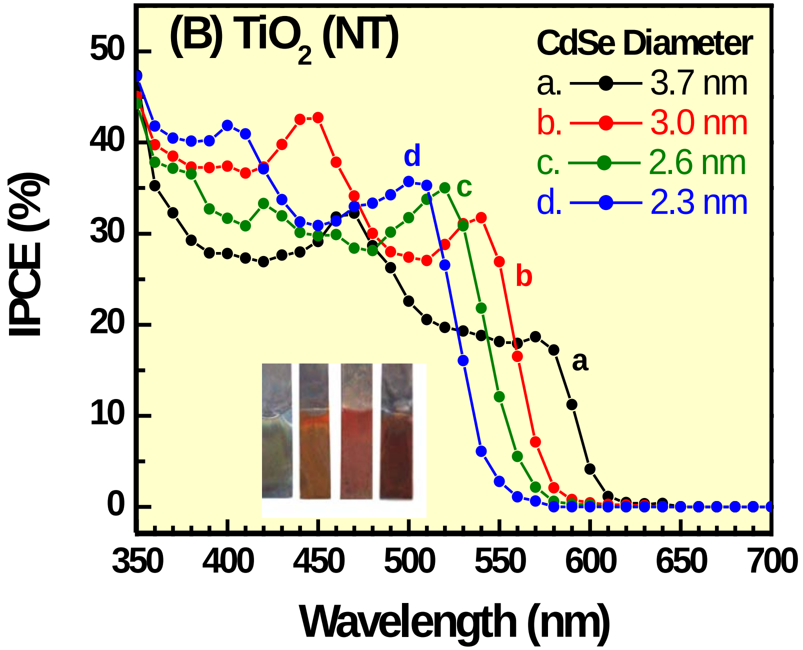
- 95% formamide
- 5% H_2O, 0.27M NH_4F
- 20V, 12h
- Anneal 450°C 3h in air
- 100nm wide, 20nm wall, 6 μm long

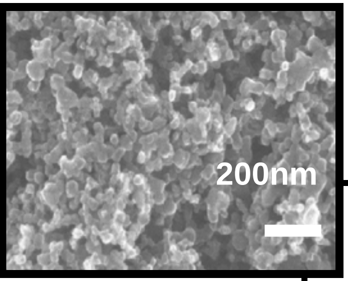

A
200nm
B
5μm
C
D
500nm

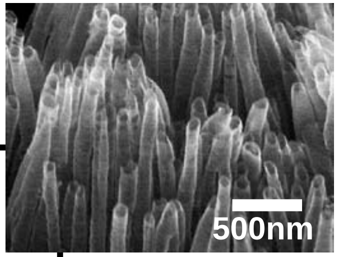

(A)
2.3nm
2.6nm
3.0nm
3.7nm
(B)
2.3nm
2.6nm
3.0nm
3.7nm
(C)
2.3nm
2.6nm
3.0nm
3.7nm

Quantum Dot Solar Cells – Particle versus Tube Architecture







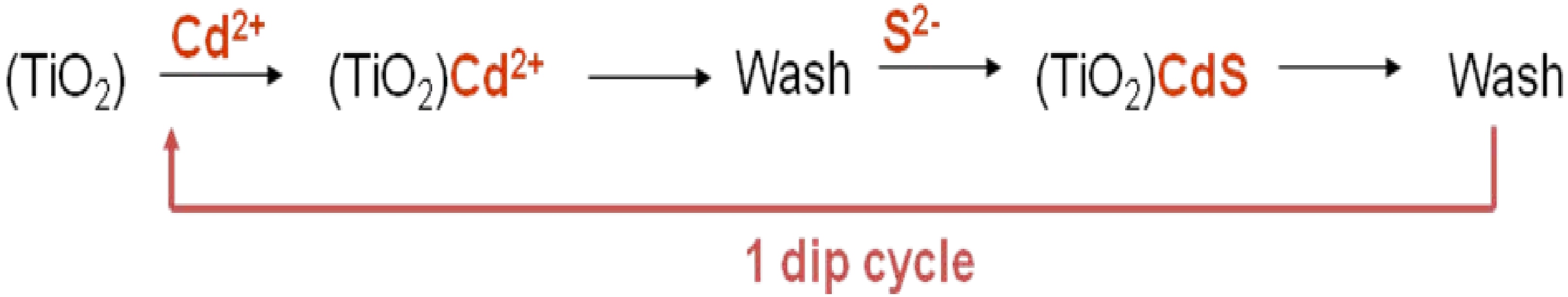


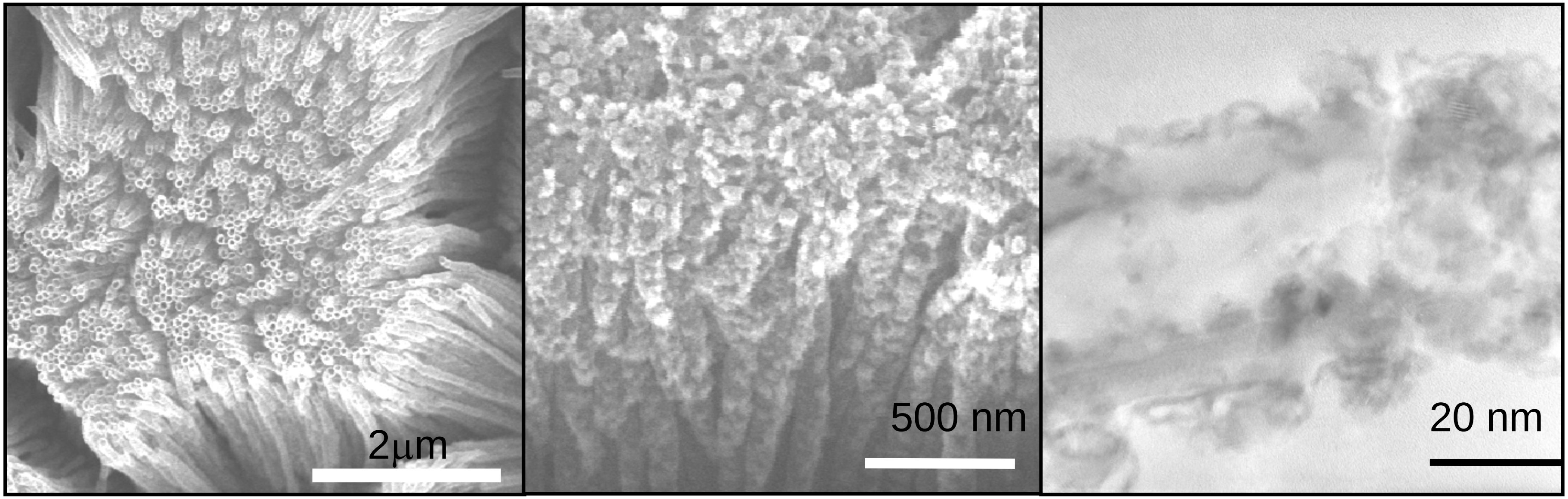
Power conversion efficiency ~1%

	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

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

Successive Ionic Layer Adsorption and Reaction (SILAR) Method to Deposit Semiconductor Quantum Dots





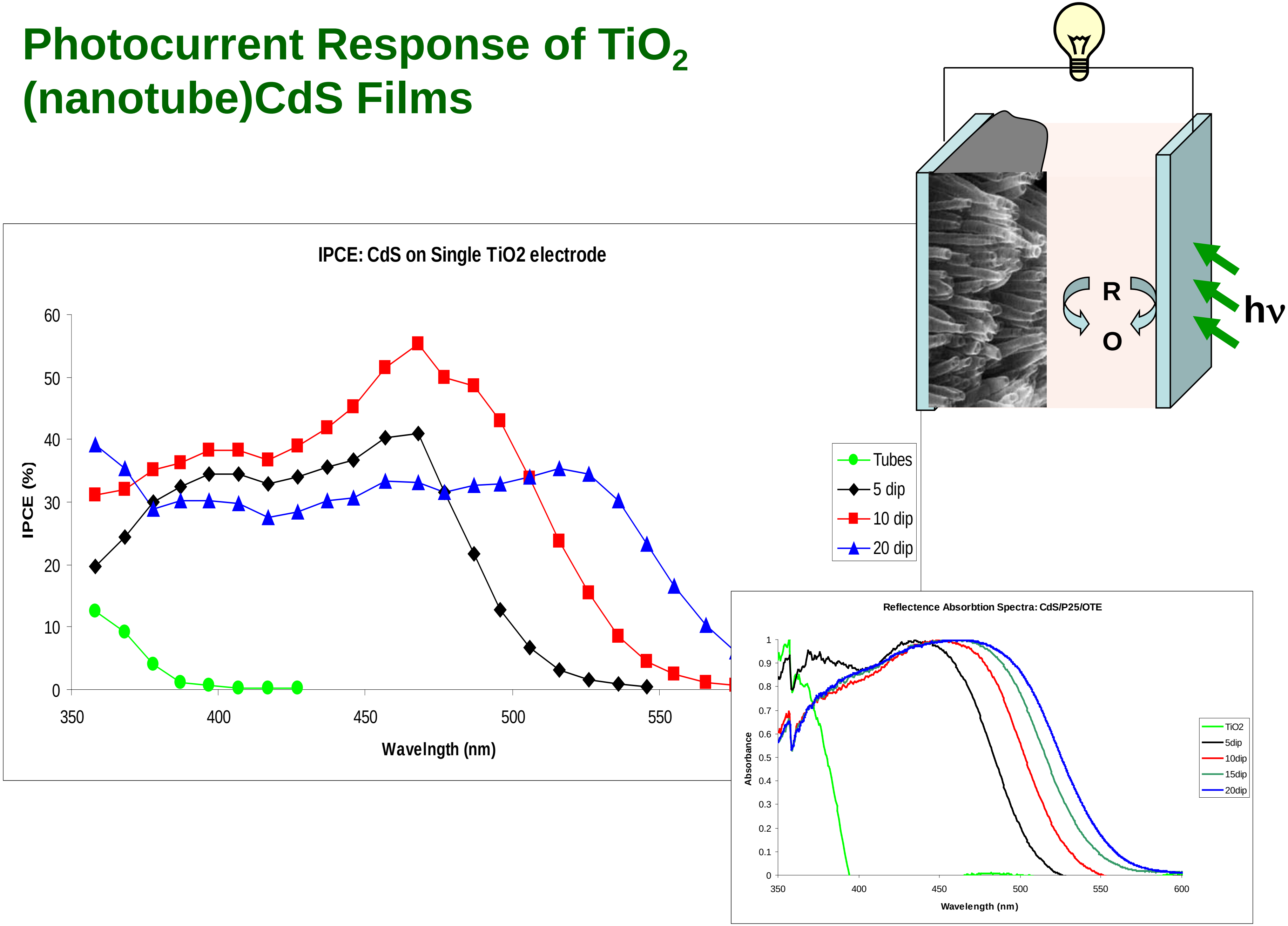
Before

SEM and TEM images after 15 cycles

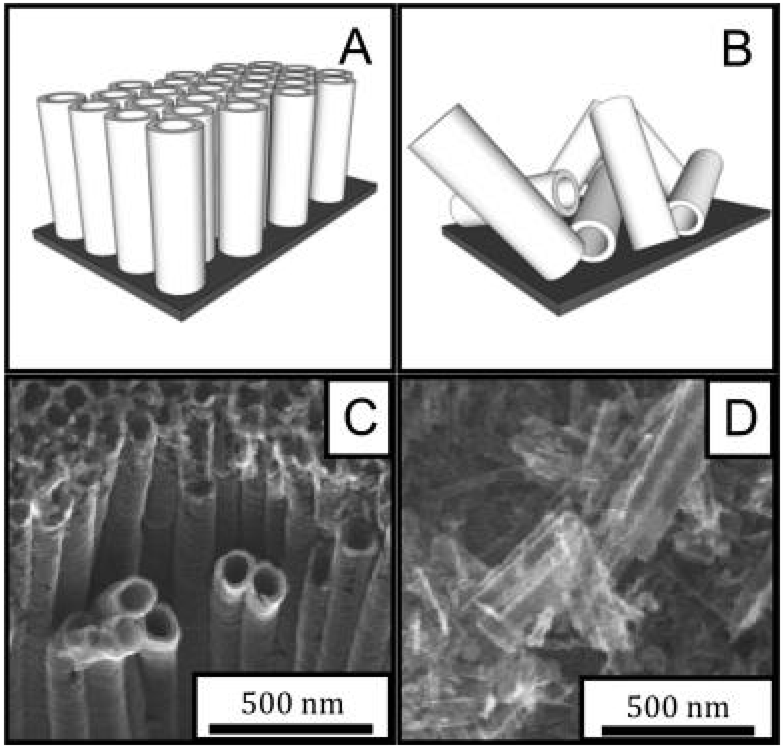
Baker and Kamat Adv. Funct. Mater. 2009

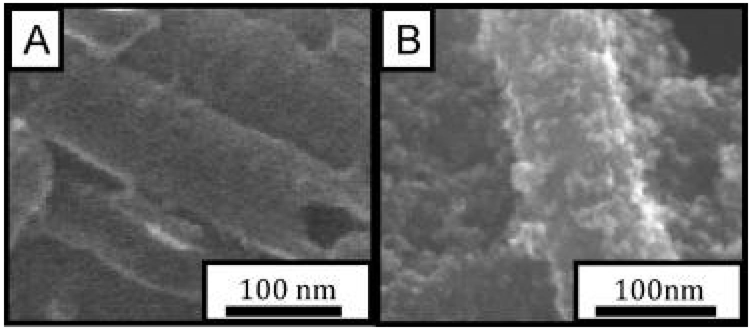
Hodes, J. Phys Chem. C 2008

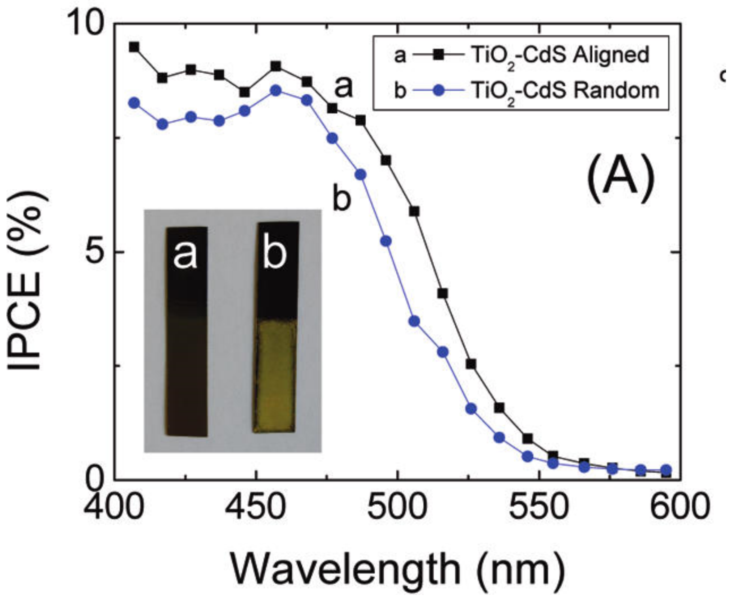
Photocurrent Response of TiO_2 (nanotube)CdS Films



Disassembly, Reassembly, and Photoelectrochemistry of Etched TiO_2 Nanotubes



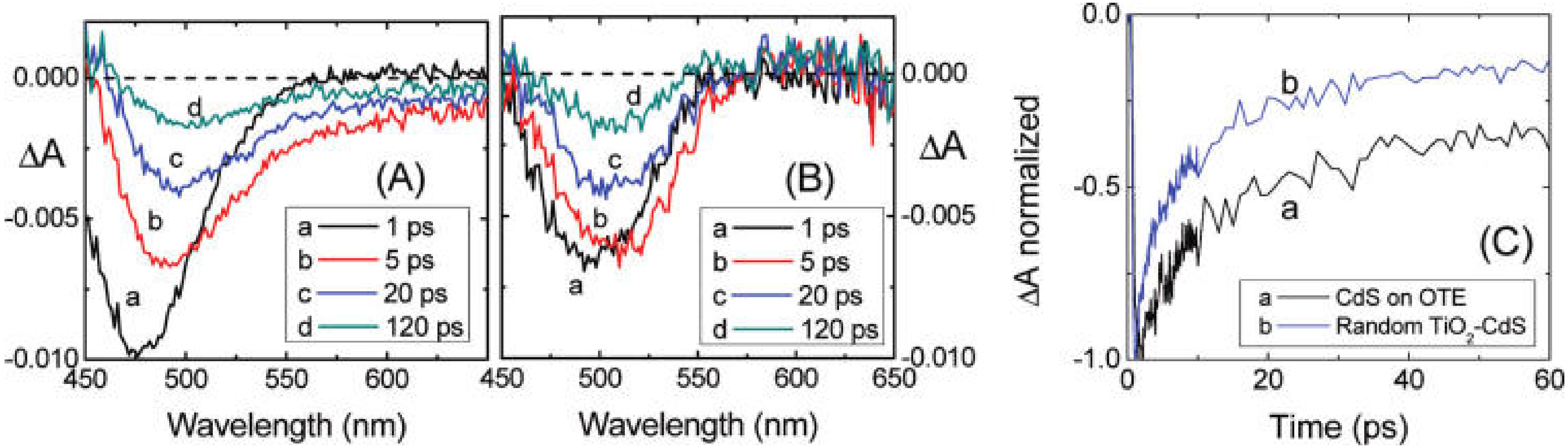




BET surface area 77 m^2/g

Baker & Kamat J. Phys. Chem. C
2009, 113, 17967–17972

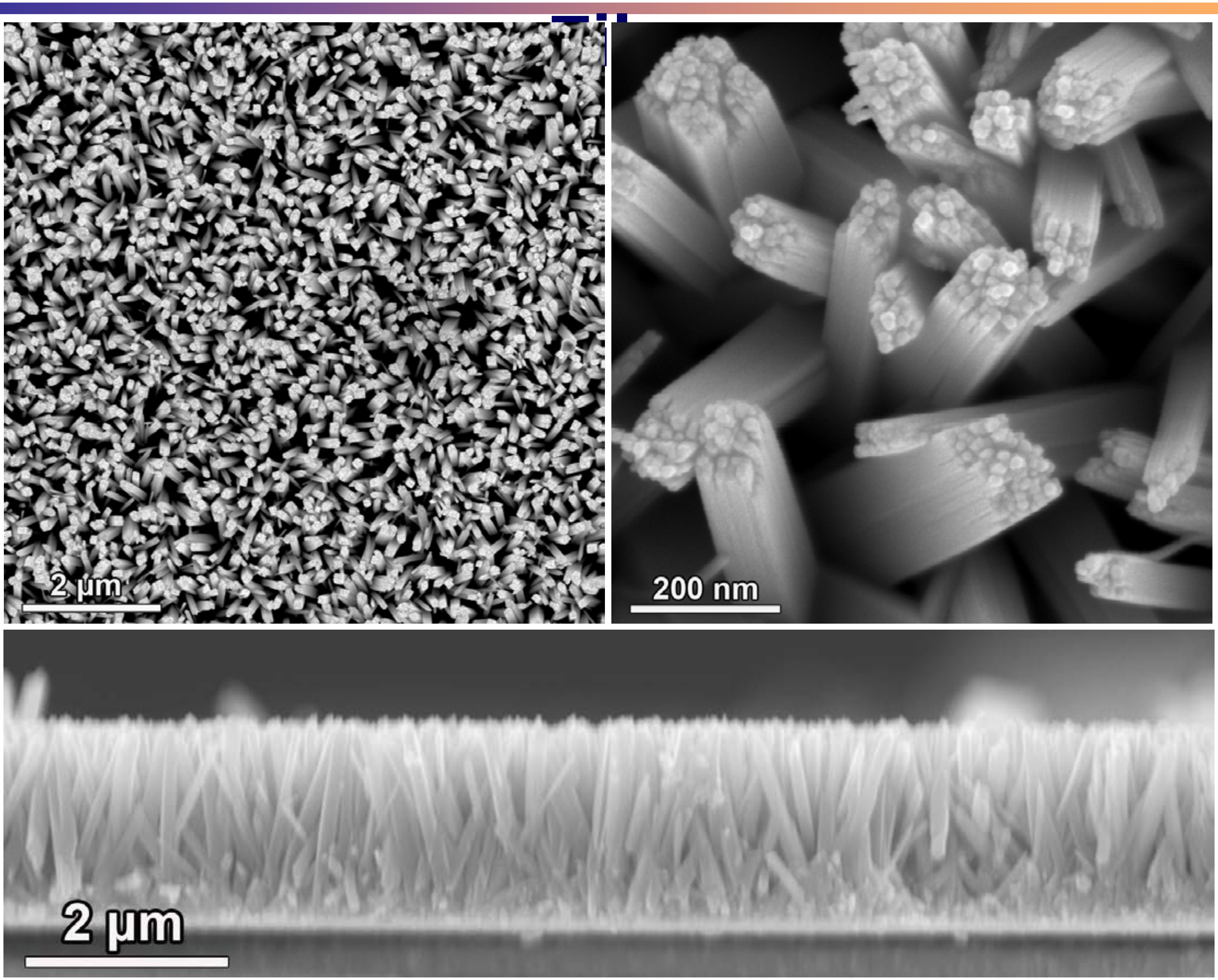
Time-resolved transient absorption spectra of (A) randomly oriented TiO_2 nanotube film on OTE coated with CdS, and (B) a film of colloidal CdS dropcast onto OTE. (C) The bleaching recovery normalized to peak response.



Electron transfer from excited CdS nanocrystallites into TiO_2 nanotubes occurs at a rate of 2.0×10^{10} s^{-1}.

*Baker & Kamat J. Phys. Chem. C **2009, 113, 17967–17972***

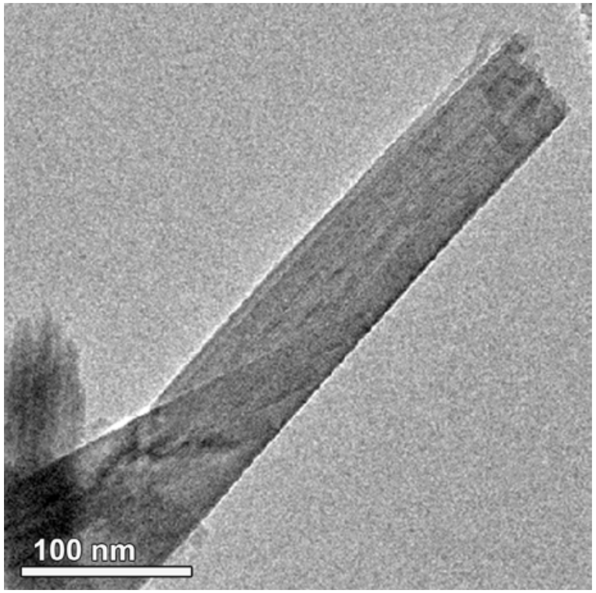
Hydrothermal Synthesis of TiO_2 Nanorod

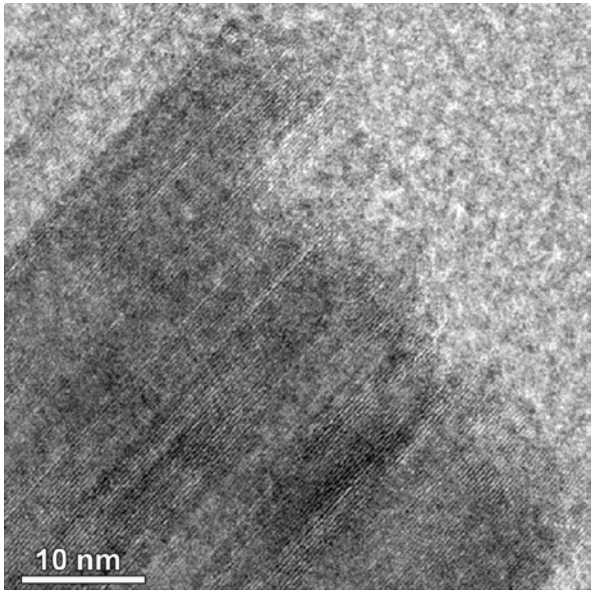


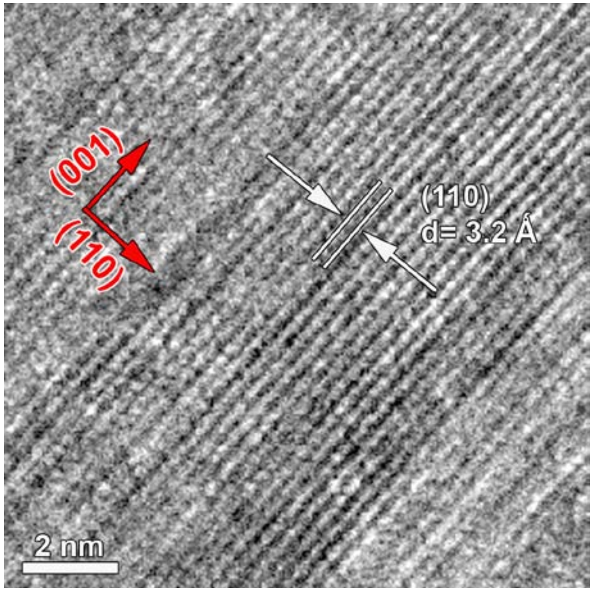
Vertically aligned TiO_2 nanorods formed on FTO glass!

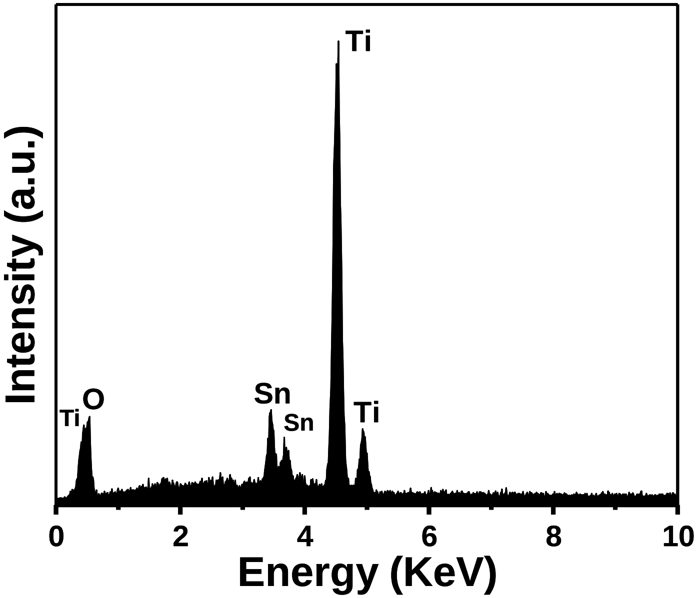
Bang and Kamat 2009, Submitted

TEM Images of TiO_2 Nanorods



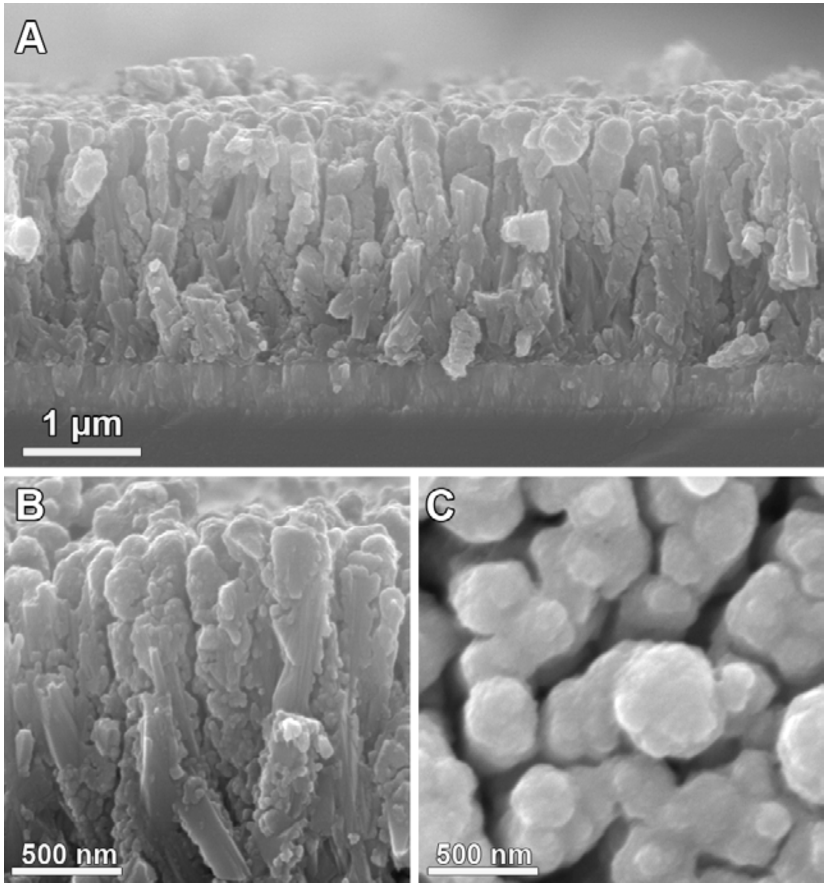


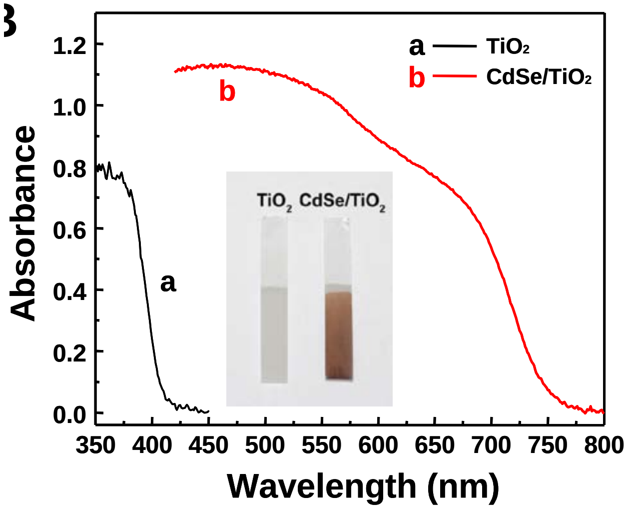


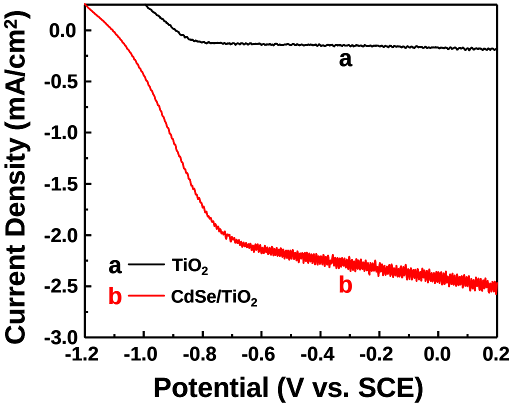


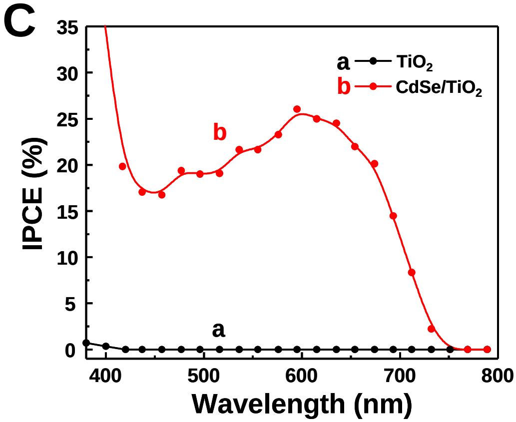
Capping TiO_2 Nanorod Array with CdSe

Electrophoretic Deposition









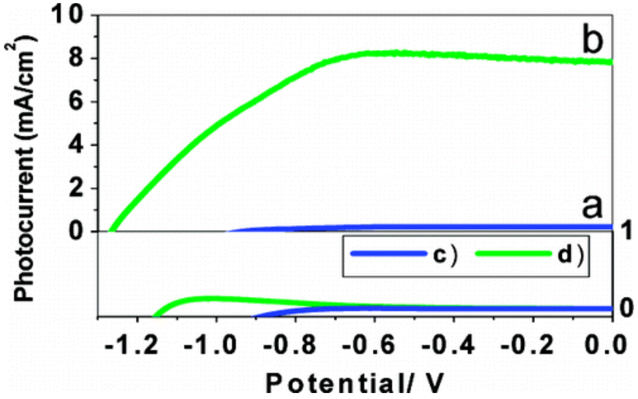
Bang and Kamat 2009, Submitted

A word of caution ……..

Exercise caution while comparing the efficiency claims in the literature

CdS Quantum Dots Sensitized TiO_2 Nanotube-Array Photoelectrodes

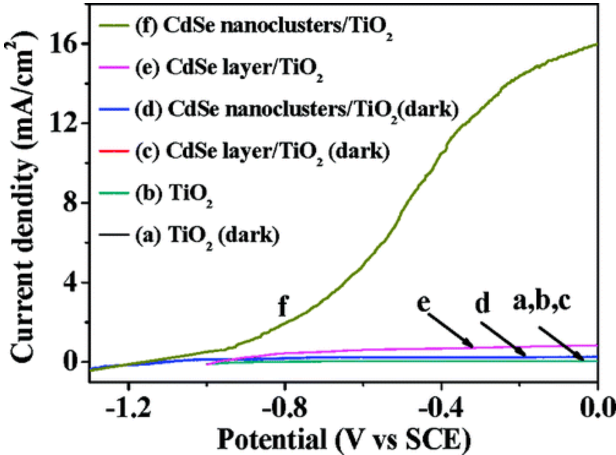
W-T Sun, Y Yu, H-Y Pan, X-F Gao, Q Chen, and L-M Peng
J. Am. Chem. Soc., **2008**, *130* (4), pp 1124–1125



…..resulted in a significant PEC cell efficiency of 4.15% under AM 1.5 G illuminations, a large open-circuit photovoltage of 1.27 V vs. Ag/AgCl, a generated photocurrent of 7.82 mA/cm^2, and a fill factor of 0.578. (Iinc = 134 mW/cm^2)

"Mulberry-like" CdSe Nanoclusters Anchored on TiO_2 Nanotube Arrays: A Novel Architecture for Remarkable Photo-Energy Conversion Efficiency

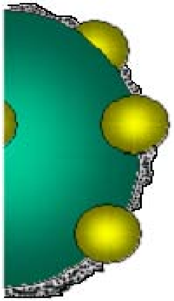
H. Zhang, X. Quan, S. Chen, H. Yu and N. Ma
Chem. Mater., Articles ASAP **DOI:** 10.1021/cm900100k

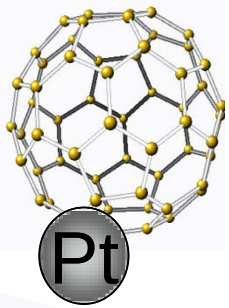


Now Corrected

Under a 100 mW/cm^2 visib [illegible] umination, the novel electrode shows an ope [illegible] voltage (V_{oc}) of 1.16 V and a short circuit curre [illegible] y (J_{sc}) of 16 mA cm^{-2}, corresponding t [illegible] er conversion efficiency (η) of 4.20% with [illegible] or (FF) of 0.23

Carbon nanostructures as conduits to transport charge carriers





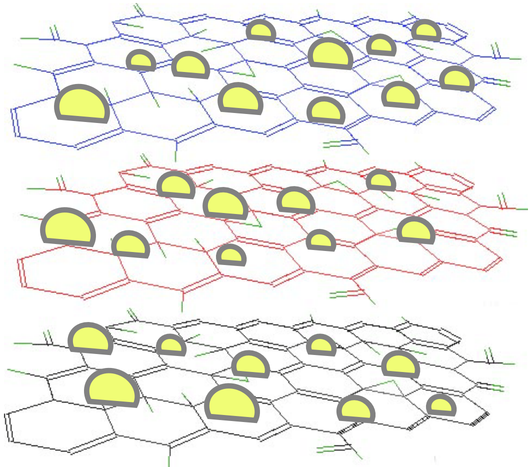
Advantages

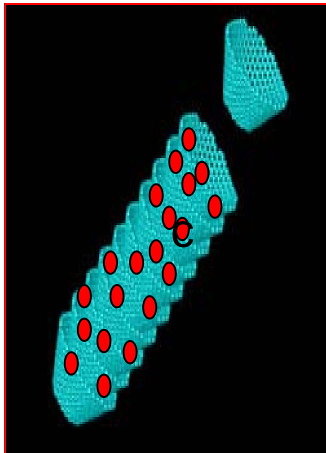
- High surface area
- Good electronic conductivity, excellent chemical and electrochemical stability
- Good mechanical strength

Goal

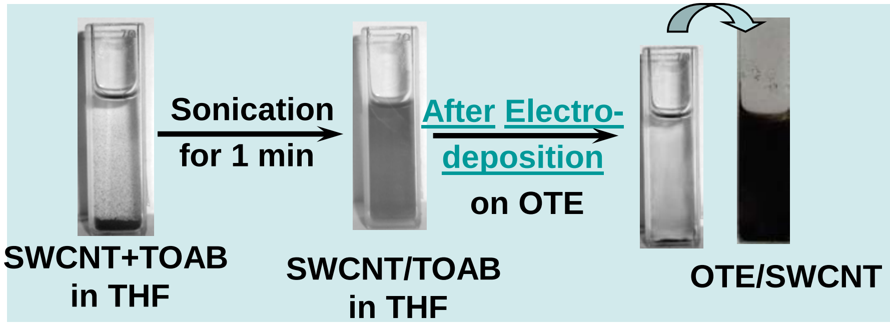
Effective utilization of carbon nanostructures for improving the performance of energy conversion devices

- To develop electrode assembly with CNT supports
- Improve the performance of light harvesting assemblies
- Facilitate charge collection and transport in nanostructured assemblies





Electrophoretic Deposition of SWCNT on Electrode Surfaces



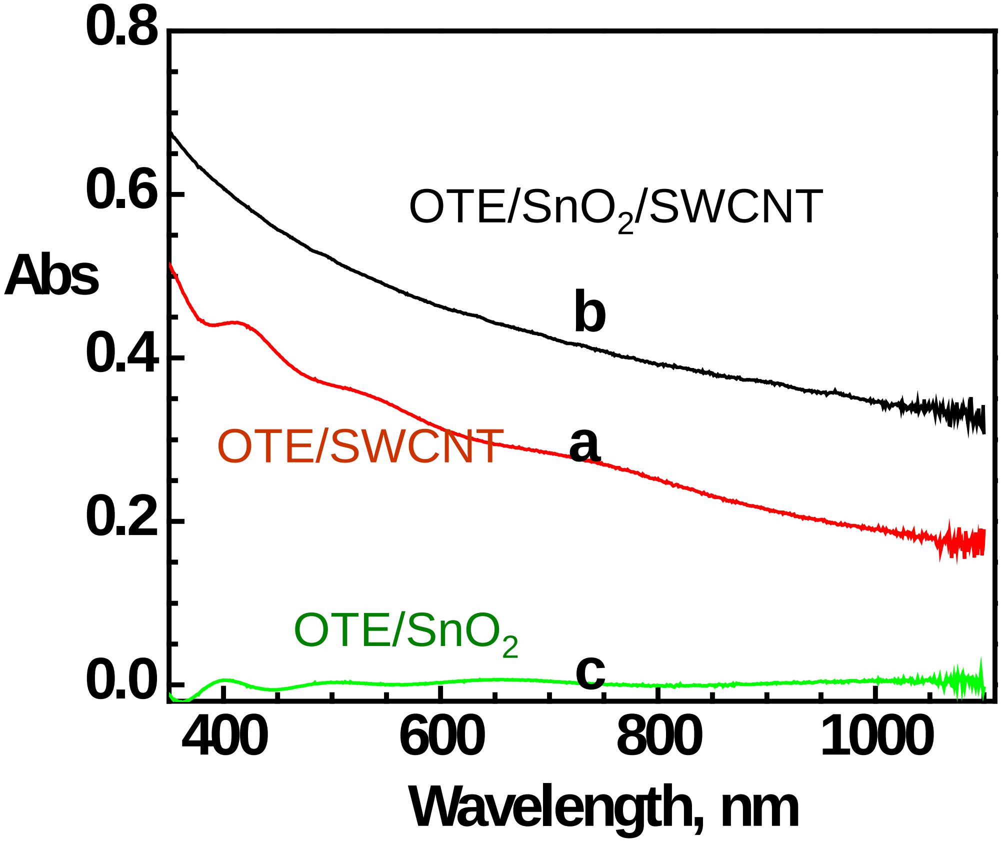
SWCNT+TOAB in THF

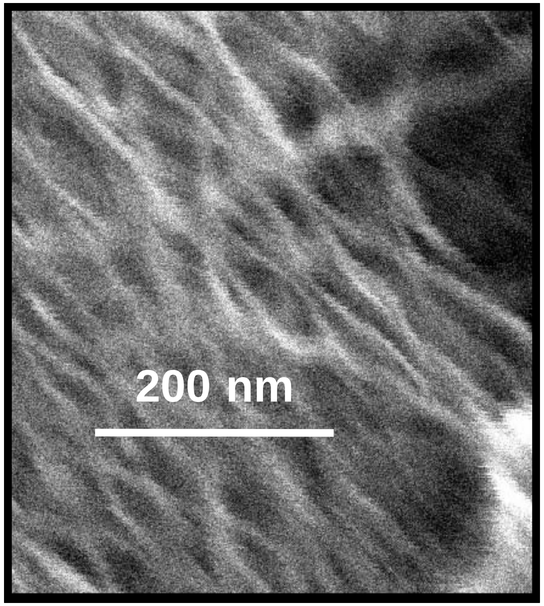
Sonication for 1 min

SWCNT/TOAB in THF

After Electro-deposition on OTE

OTE/SWCNT

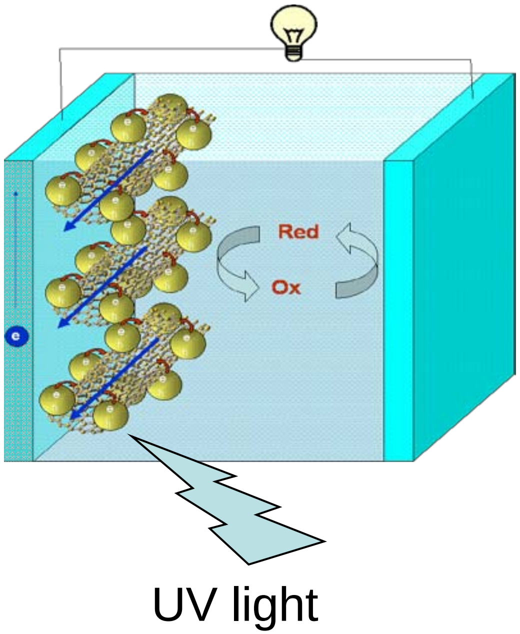


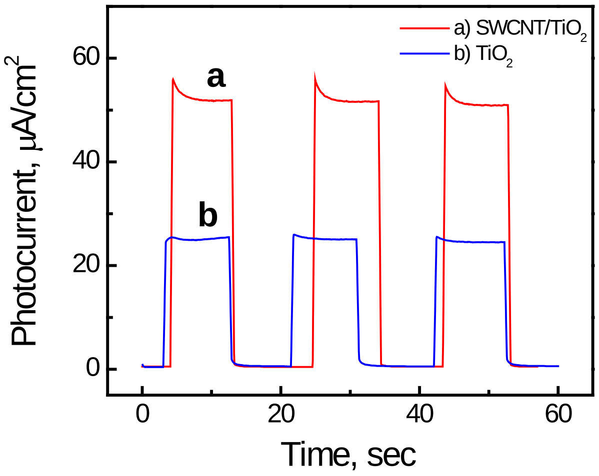


J. Am. Chem. Soc., 2004. **126** 10757-10762.

Photocurrent Generation

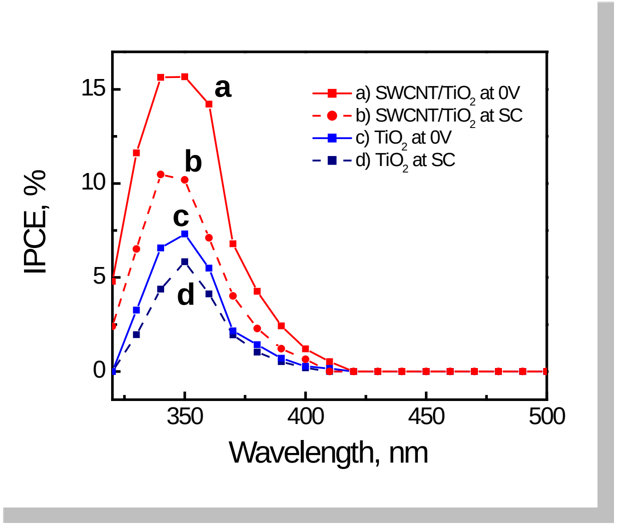
CFE/TiO_2 versus CFE/SWCNT –TiO_2





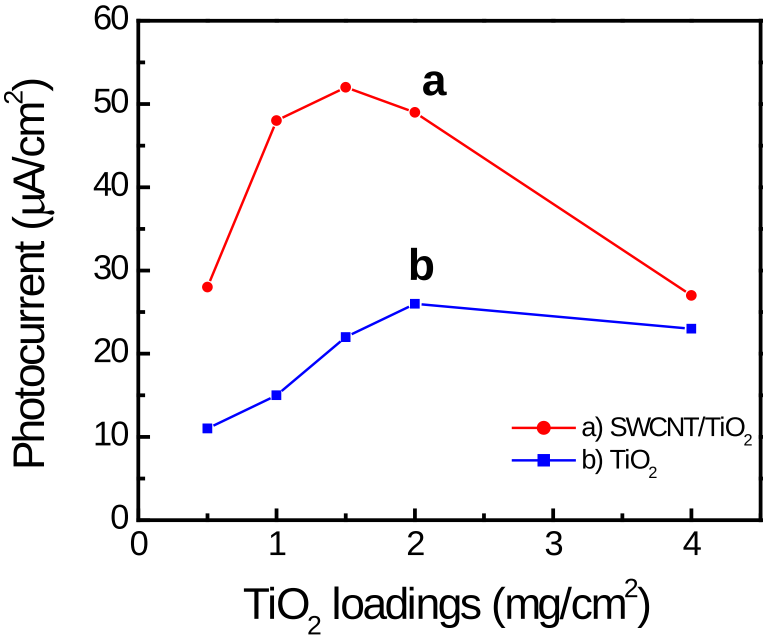
Higher IPCE (increase of factor ~2) was observed for mesoscopic CFE/SWCNT-TiO_2 films

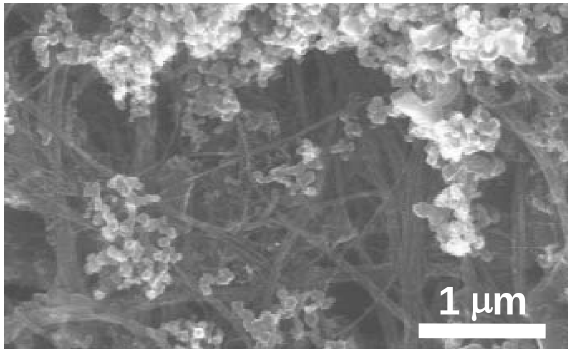
The results are indicative of better charge collection and transport provided by the SWCNT -Network



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

Dependence of TiO_2/SWCNT Ratio on the Photocurrent Generation



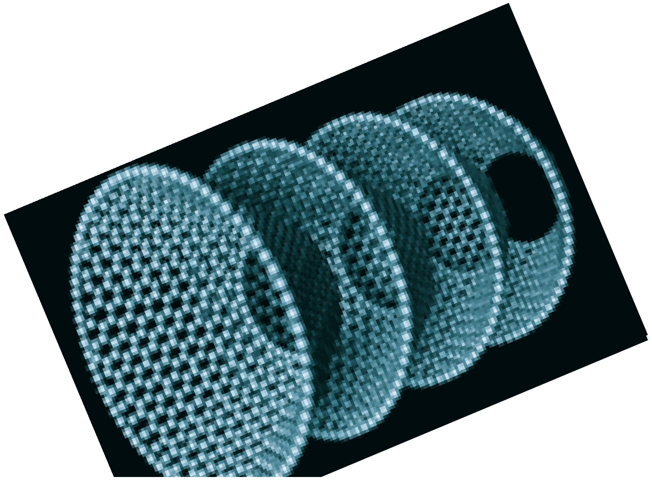


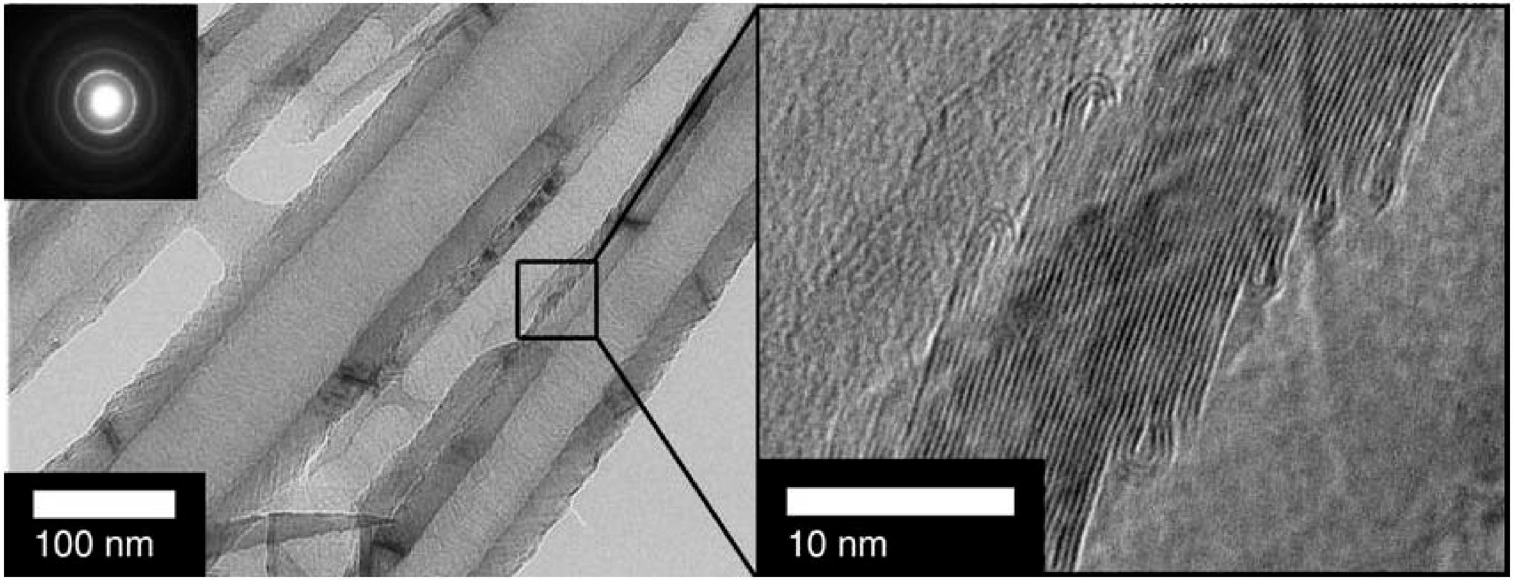
Increasing the TiO_2 concentration results in enhanced photocurrent as they are dispersed on SWCNT network.

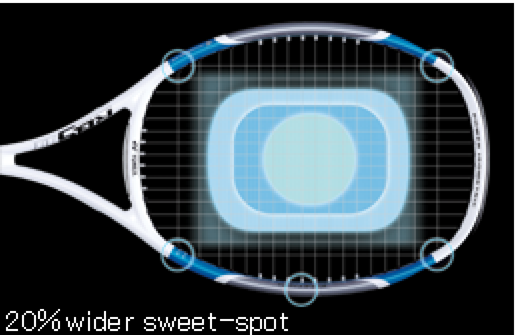
At concentrations greater than 2 mg/cm^2 the beneficial effect of SWCNT disappears. Under these conditions. TiO_2 particles aggregate and the charge recombination dominates

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

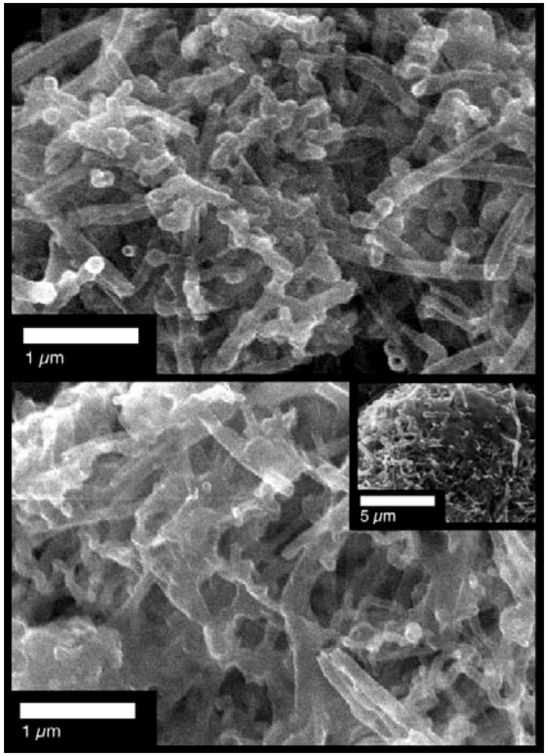
Stacked Cup Carbon Nanotubes

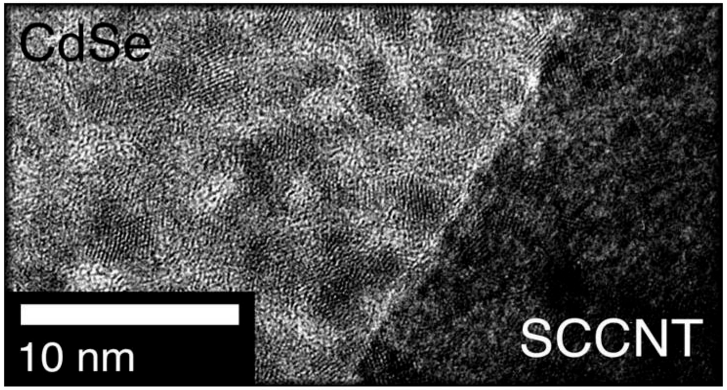


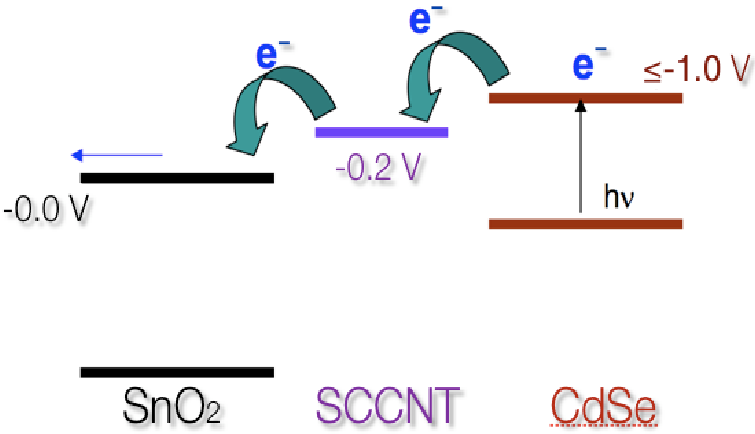


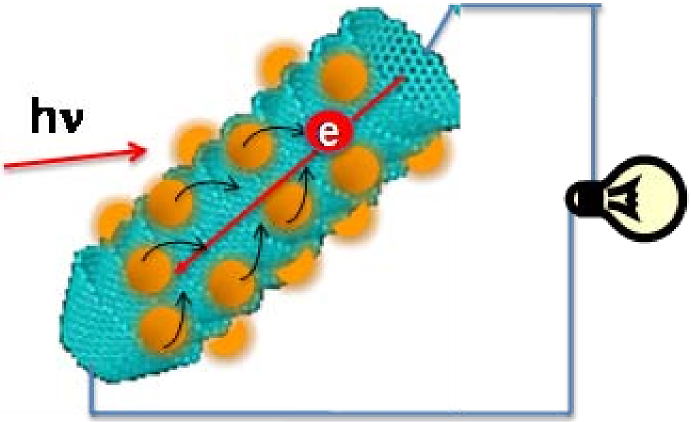


Quantum Dots Linked to Stacked Nanocups

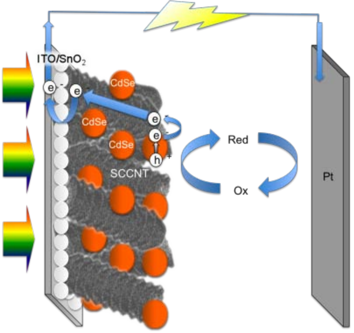


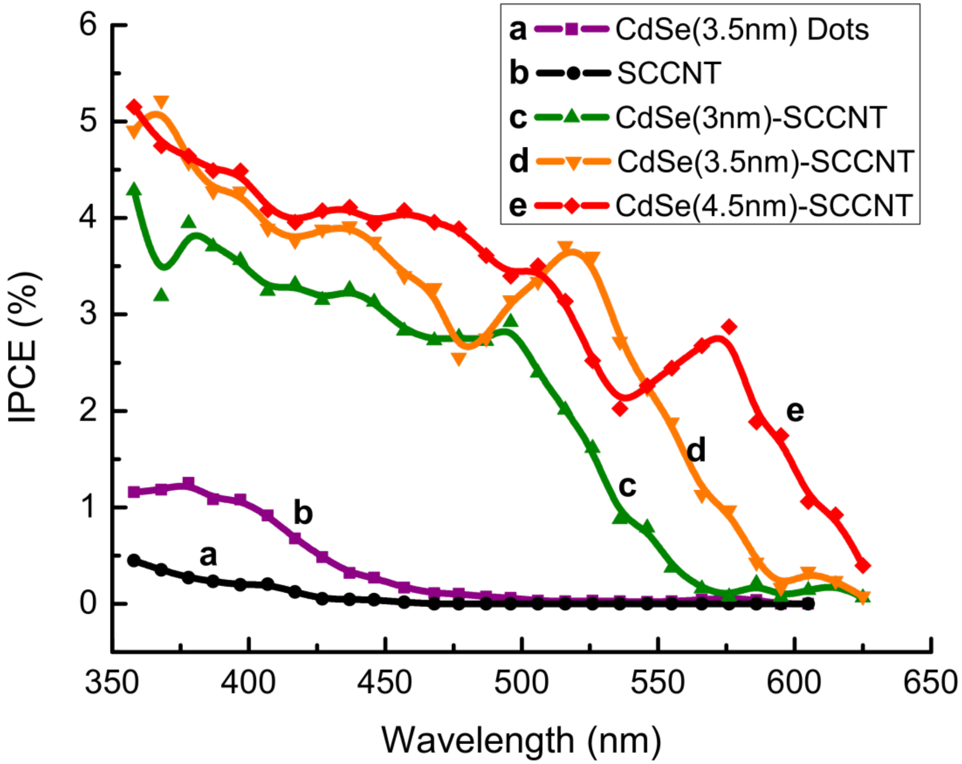


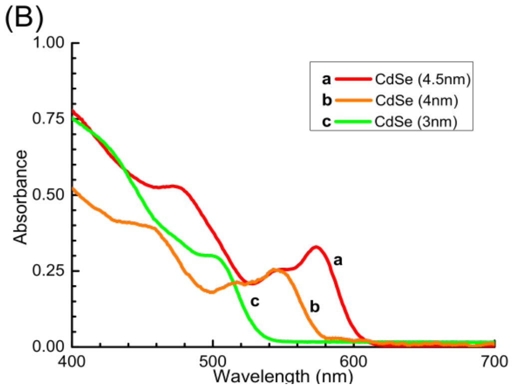




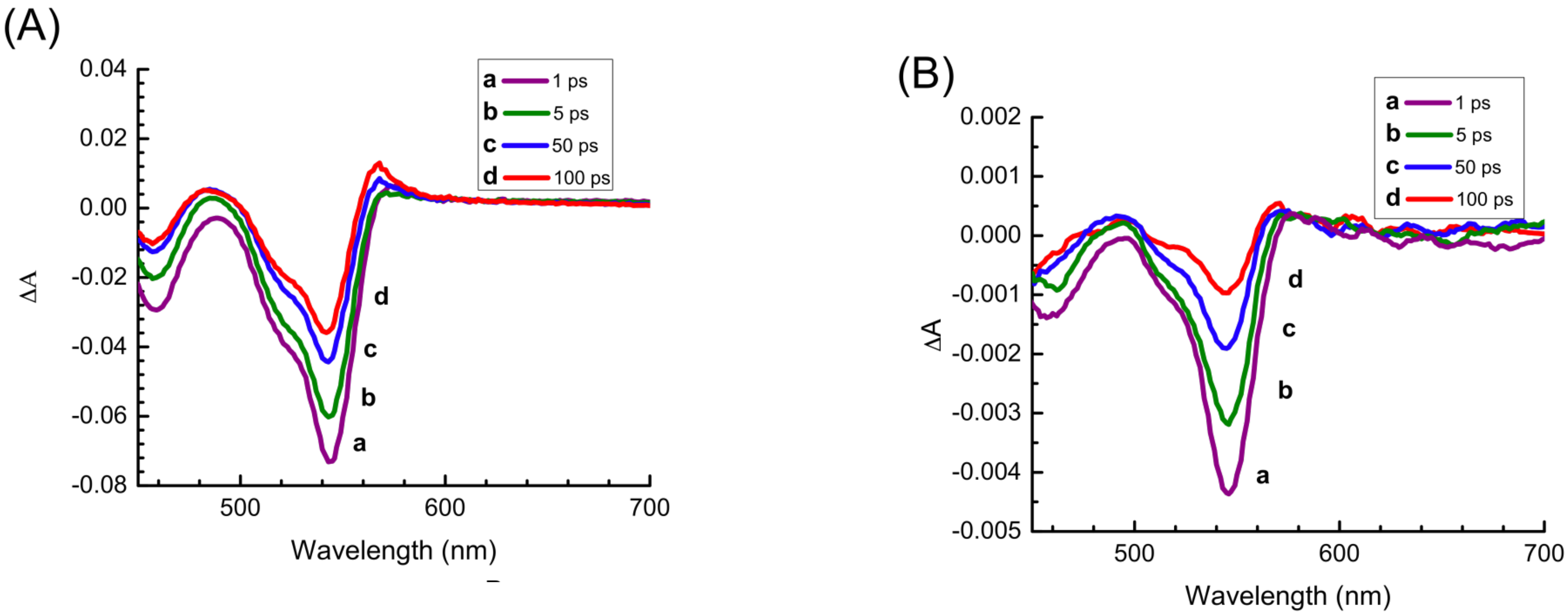
Quantum Dot Sensitized Solar Cell





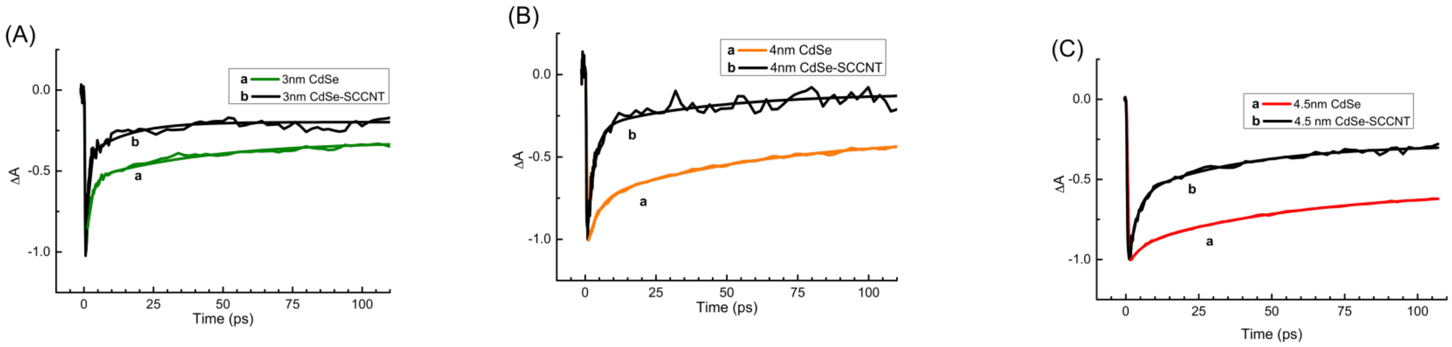


Farrow & Kamat J. Am. Chem. Soc. 2009



Time-resolved transient absorption spectra recorded following 387 nm laser pulse excitation of 4 nm diameter CdSe nanocrystals in THF:toluene:acetonitrile (1:1:4 v/v) suspension without (A) and with (B) the presence of SCCNT.

Transient absorption–time profiles of (A) 3.5 nm; (B) 4.0 nm; and (C) 4.5 nm CdSe nanocrystals.

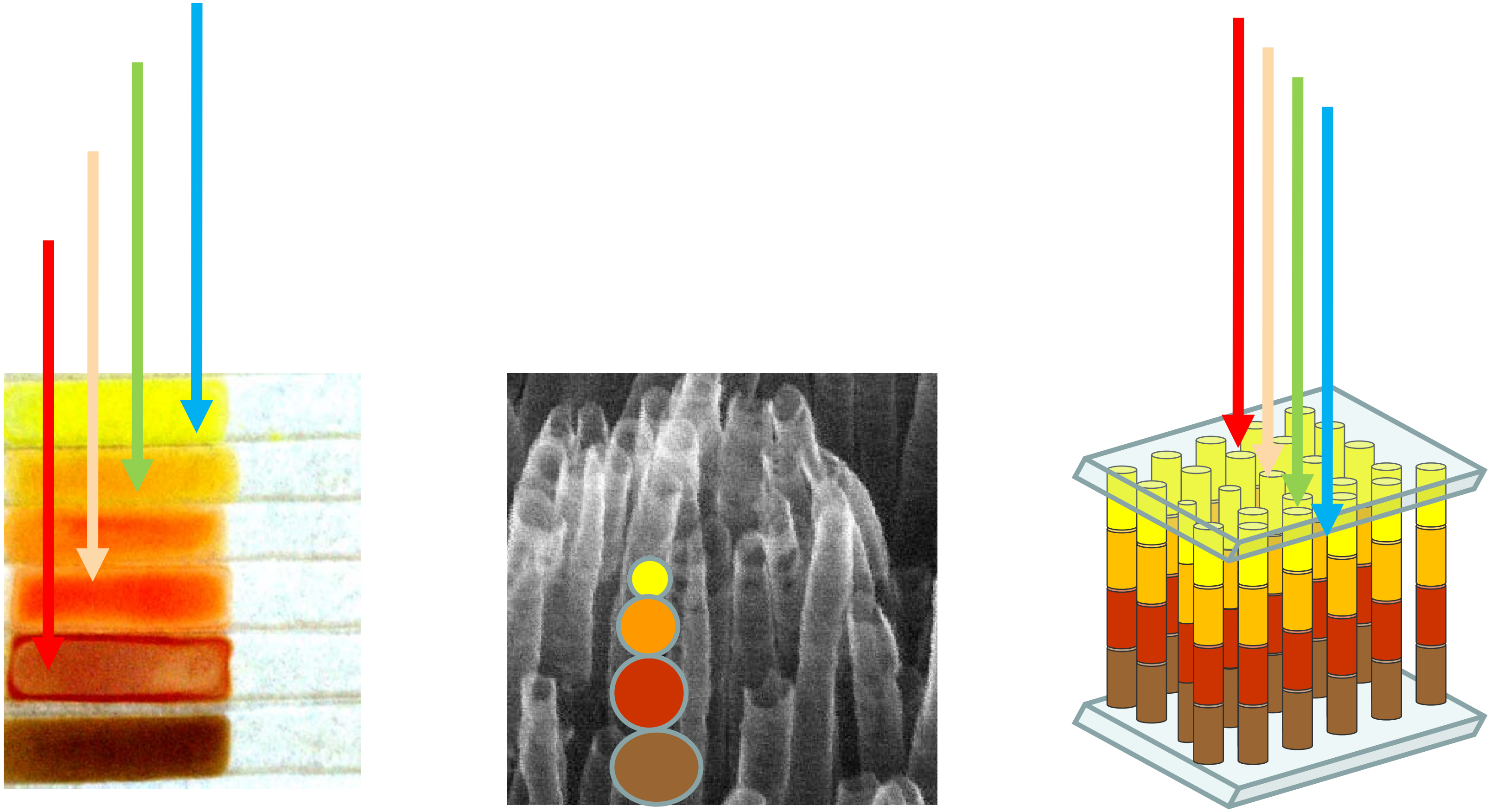


	CdSe (4.5nm) at 570nm	CdSe(4.5nm)-SCCNT at 570nm	CdSe (4nm) at 547nm	CdSe(4nm)-SCCNT at 547nm	CdSe (3nm) at 498nm	CdSe(3nm)-SCCNT at 498nm
a_1	-0.3554	-0.3256	-0.3946	-0.2163	-0.239	-0.22748
τ_1 (ps) Slow Decay	64.1251	43.7564	62.245	42.3116	43.738	14.12531
a_2	-0.1355	-0.5854	-0.338	-0.8853	-0.581	-1.67749
τ_2 (ps) Fast Decay	4.67948	2.99118	3.8606	2.45199	1.8387	0.72715
$< \tau >$ (ps)	62.5138	39.292	59.3053	34.67	39.8531	10.451
R^2	0.9996	0.99566	0.9980	0.97747	0.9943	0.9587

we observe an increase in electron transfer rate constant from 9.51×10^9 s^{-1} to 7.04×10^{10} s^{-1} as we decrease the particle diameter of CdSe from 4.5 nm to 3 nm.

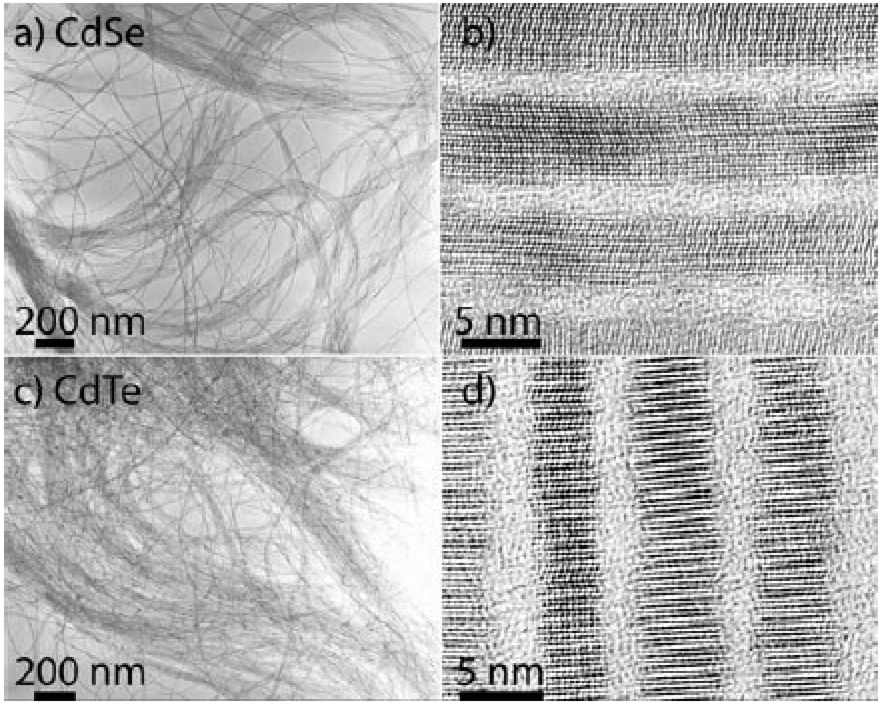
III. Issues and Challenges

1. To design tailored Interfaces with different size particles



….towards the design of a Rainbow Solar Cell

2. 1-D Semiconductor Architectures for Solar Cells



In collaboration with Prof. Ken Kuno

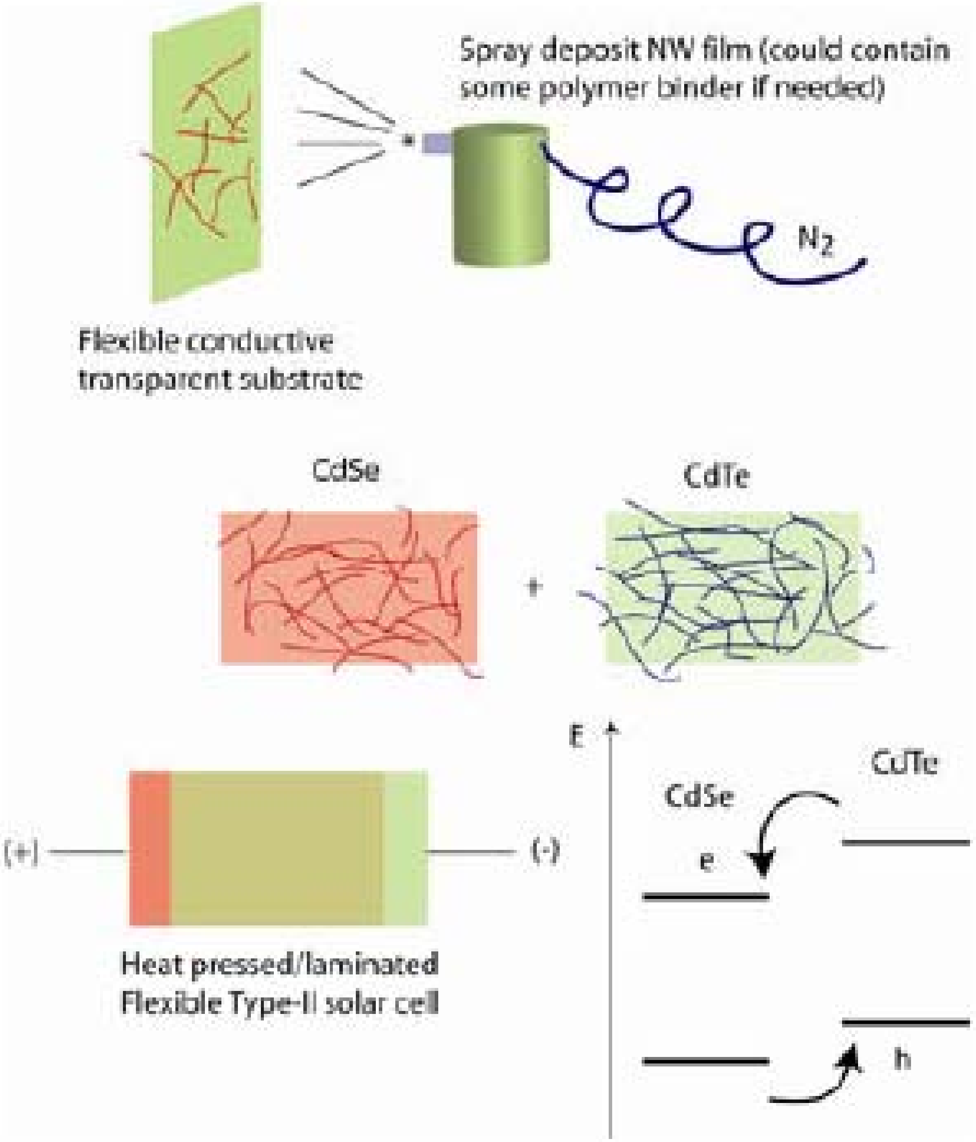
Low and high resolution TEM images of (a, b) CdSe and (c, d) CdTe nanowires.

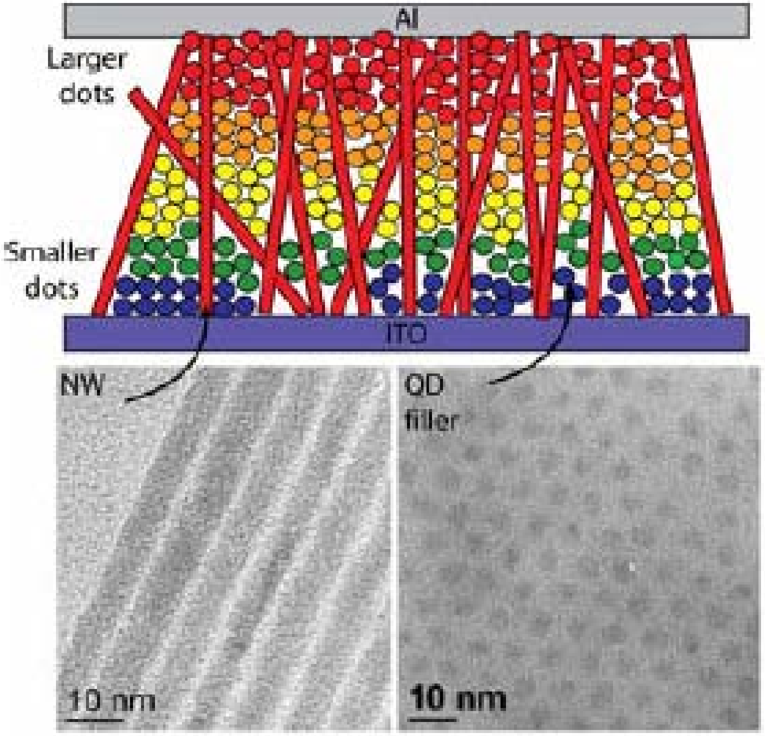
An overview of solution-based semiconductor nanowires M. Kuno, *Phys. Chem. Chem. Phys.* ***2008, 10, 620***

Solution-based straight and branched CdTe nanowires, M. Kuno, O. Ahmad, V. Protasenko, D. Bacinello, T. Kosel, *Chem. Mater.* ***2006, 18, 5722.***

Solution-liquid-solid growth of semiconductor nanowires, F. Wang, A. Dong, J. Sun, R. Tang, H. Yu, W. E. Buhro, *Inorg. Chem.* ***2006, 45, 7511.***

.. . to employ 1-D architectures in solar cells
… to understand the wire/wire or wire dot interfaces –size and shape effects



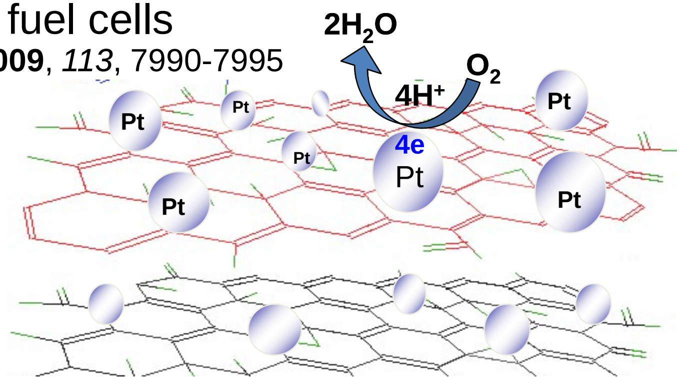


Graphene as 2-D Carbon Support

Towards the development of a 2-D catalyst mat (Ian Lightcap, Brian Seger)

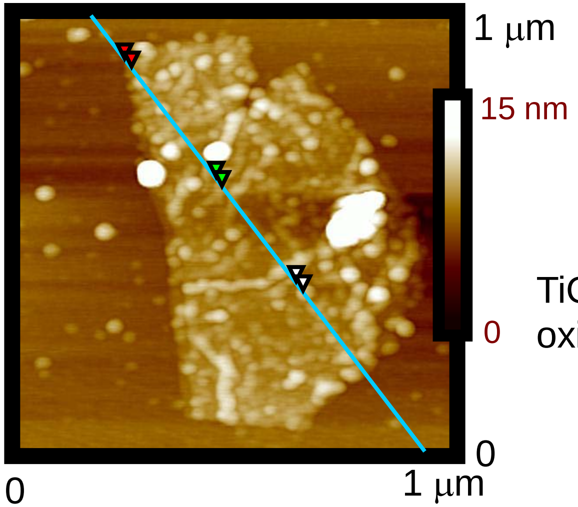
Graphene-Pt in fuel cells

J. Phys. Chem. C **2009**, *113*, 7990-7995



Photocatalytic reduction of graphene oxide

ACS Nano **2008**, *2*, 1487-1491



TiO_2- graphene oxide composite

Summary

- Unique properties of quantum dots can assist in developing low-cost and high efficiency solar cells
- Size and shape of support plays an important role in dictating interfacial charge transfer processes .
- Opportunities exist for carbon nanotubes and other 1-D nanomaterials 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, 18737-18753*

Researchers/Collaborators

Support: US DOE (BES)

Graduate students

Brian Seger (Chem. Eng.)
David Baker (Chem. Eng.)
Kevin Tvrdy (Chemistry)
Clifton Harris (Chemistry)
Matt Baker (Physics)
Ian Lightcap (Chemistry)
Sean Murphy (Chemistry)
Yanghai Yu (Chem. Eng.)
Anusorn Kongkanand
Istvan Robel

Undergraduate students

Pat Brown
Blake Farrow

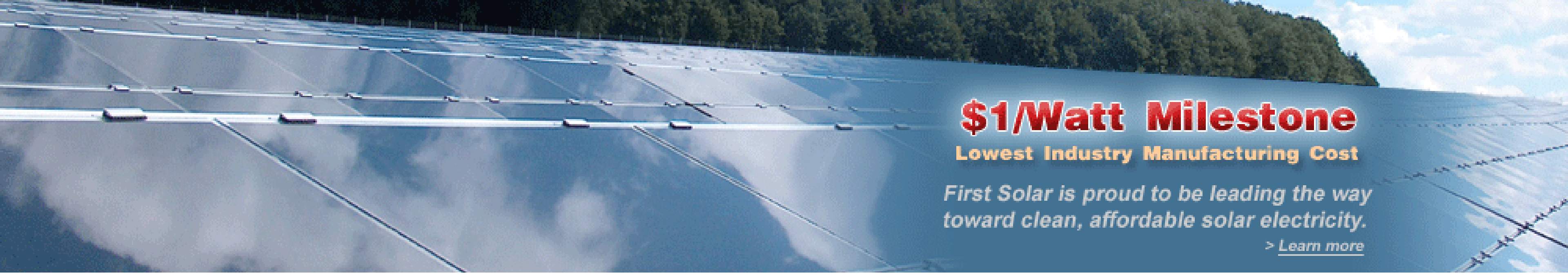
Post-Docs/Visiting Scientists

Jin Ho Bang
Alexsandra Wojcik
Vidya Chakapani

Collaborators

Dr. K. G. Thomas (India)
Prof Ken Kuno (UND)
Prof. Val Vulev (UC Riverside)


SPRING 2009



The semiconductor material used in First Solar PV Modules is primarily sourced from the byproducts of mining operations.

First Solar PV Modules incorporate micron amounts of cadmium telluride (CdTe) – about 1-2% of the semiconductor material used in typical crystalline silicon solar modules.

The semiconductor material is effectively sequester within the module throughout its 25+ year lifetime.

ENVIRONMENTAL EFFECTS OF CdTe -- *Large-scale use of CdTe PV modules does not present any risks to health and the environment, and recycling the modules at the end of their useful life completely resolves any environmental concerns. During their operation, these modules do not produce any pollutants, and furthermore, by displacing fossil fuels, they offer great environmental benefits. CdTe PV modules appear to be more environmentally friendly than all other current uses of Cd.**
RENEWABLE & SUSTAINABLE ENERGY REVIEWS", Vol 8, 2004, pp 303 – 334, V M Fthenakis, "Life Cycle Impact Analysis of Cadmium in CdTe PV Production", with permission from Elsevier

youtube nanogirls

NanoGirls

http://www.youtube.com/watch?v=MubNtDwjJ2w

delicious solar cell

A Delicious New Solar Cell Technology

★★★★★ 165 ratings

52,394 views

http://www.youtube.com/watch?v=bVwzJEhMmD8