Quantum Dot Solar Cells

Lecture 4

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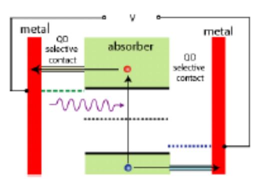
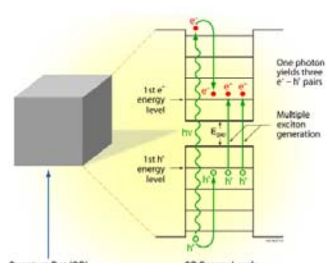
Department of Chemistry and Biochemistry

Quantum Dot Solar Cells

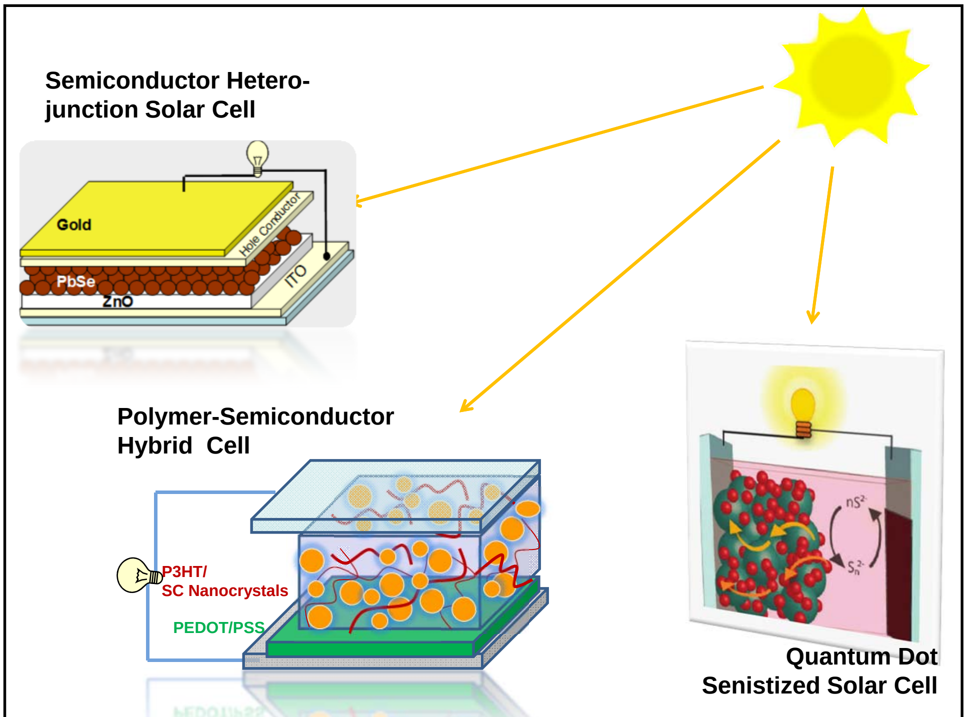
Tunable band edge
- Offers the possibility to harvest light energy over a wide range of visible-ir light with selectivity



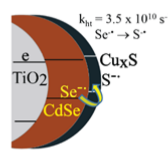
Hot carrier injection from higher excited state
- (minimizing energy loss during thermalization of excited state)



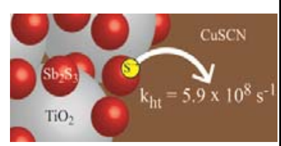
Multiple carrier generation solar cells.
- Utilization of high energy photon to multiple electron-hole pairs



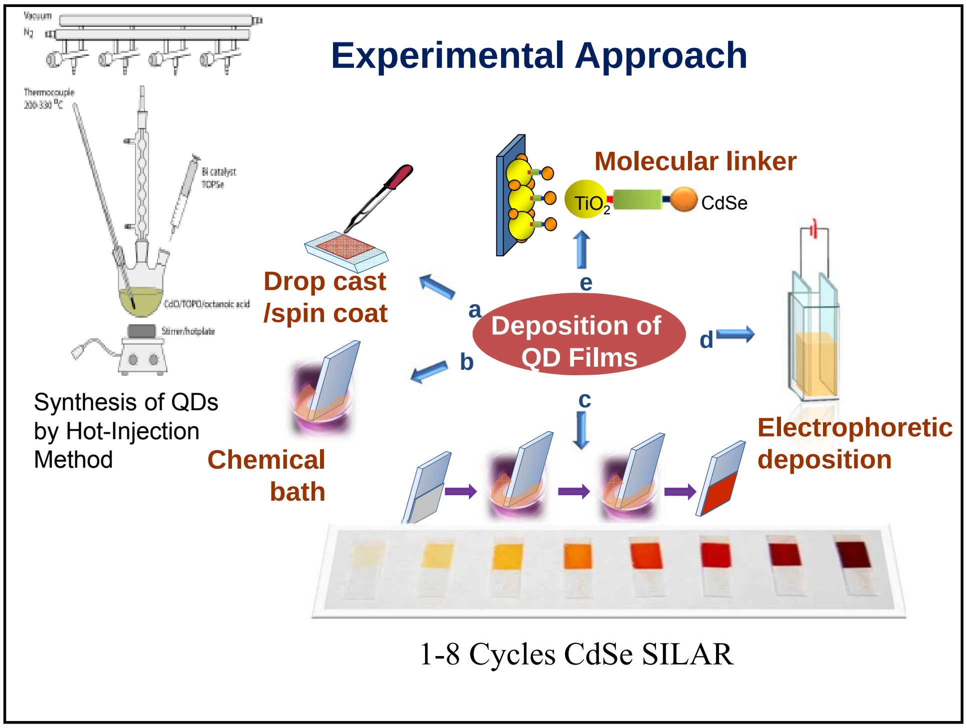
Outline

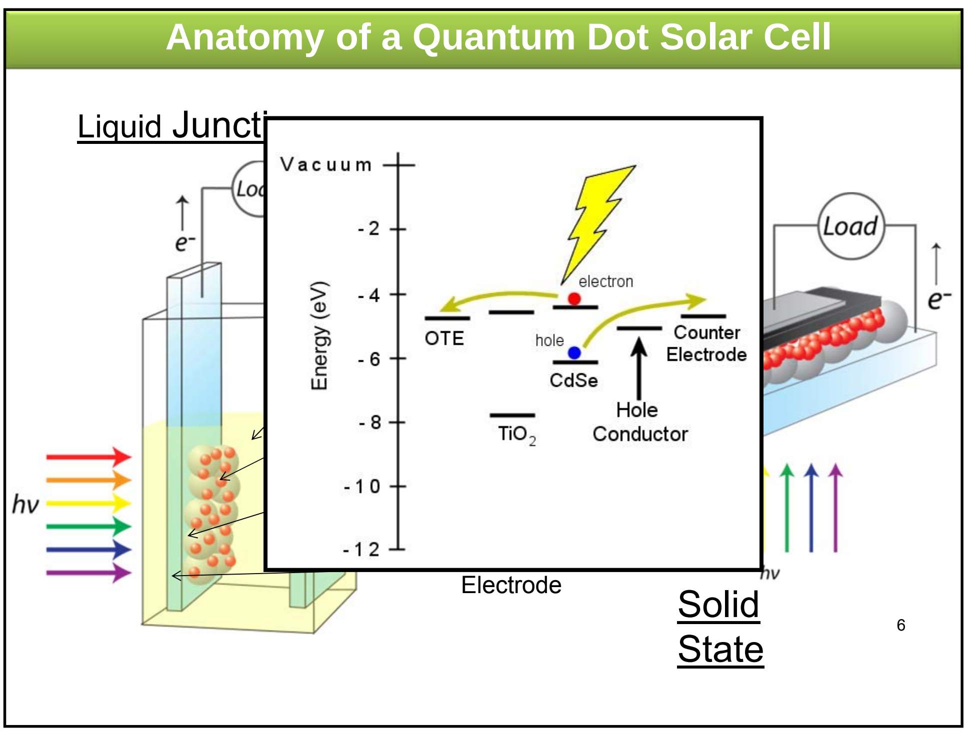


1. **QD Sensiized Solar Cells**
   - Principle of operation
   - Sulfide/polysulfide redox system



2. **Thin Film Solar Cells**
   - Sb_2S_3 ETA Solar Cells
   - Hole transfer in solid state solar cells

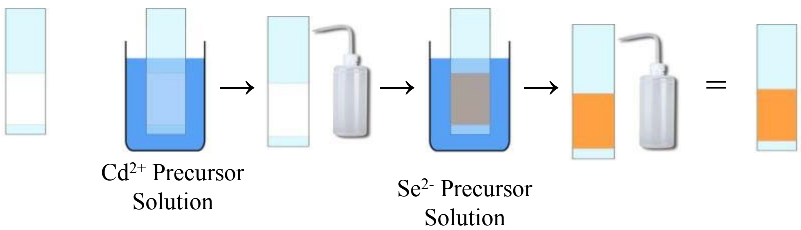

Experimental Approach
Vacuum
N2
Thermocouple
200-330 °C
Bi catalyst
TOPSe
CdO/TOPO/octanoic acid
Stirrer/hotplate
Synthesis of QDs
by Hot-Injection
Method
Molecular linker
TiO2
CdSe
Drop cast
/spin coat
a
b
c
d
e
Deposition of
QD Films
Chemical
bath
Electrophoretic
deposition
1-8 Cycles CdSe SILAR


Anatomy of a Quantum Dot Solar Cell
Liquid Juncti
e-
hv
Load
e-
hv
Vacuum
-2
-4
-6
-8
-10
-12
Energy (eV)
electron
hole
OTE
CdSe
TiO2
Counter
Electrode
Hole
Conductor
Electrode
Solid
State
6

Successive Ionic Layer Adsorption and Reaction

- Common method for achieving good sensitizer loading for quantum dot solar cells
- Any insight into the structure could lead to better control of deposition and ultimately better-performing solar cells

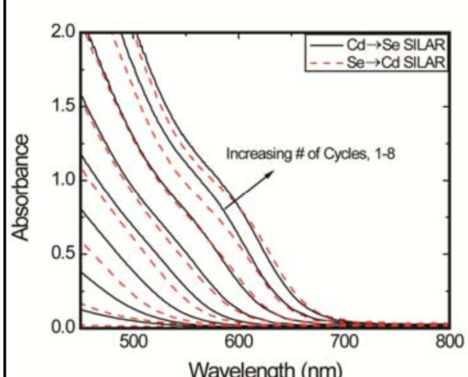
$$[Cd^{2+} \text{ dip} \rightarrow \text{wash} \rightarrow Se^{2-} \text{ dip} \rightarrow \text{wash}] = 1 \text{ Cycle}$$



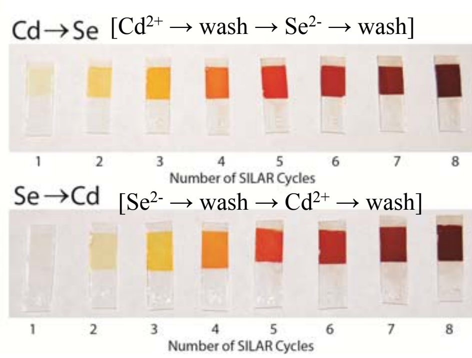
1-8 Cycles CdSe SILAR

7

Progressive *SILAR* Deposition

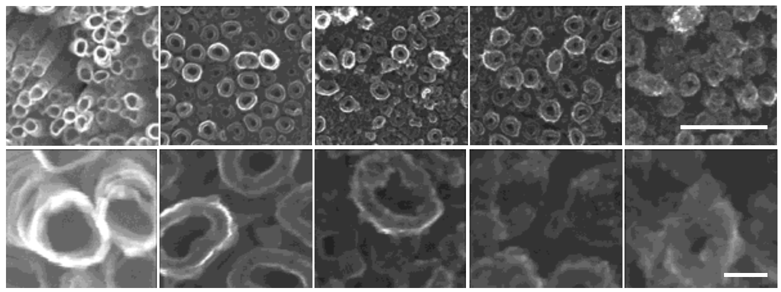


- Nearly identical at 5+ cycles
- Less light absorbed for Se-initiated films with fewer than 5 cycles



Growth of CdS QDs on TiO_2 nanotubes during SILAR

Unsonicated TiO_2 NT | 0 dip | 5 dip | 10 dip | 20 dip



100kX

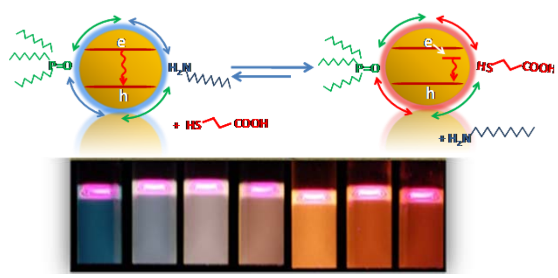
500kX

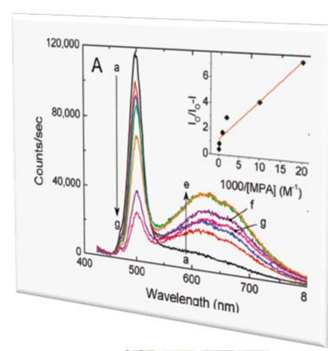
Scale bars: Top 500nm, bottom 50nm

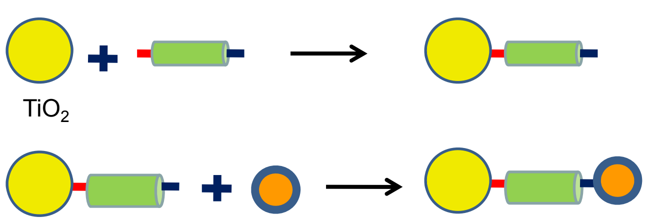
$(TiO_2) \xrightarrow{Cd^{2+}} (TiO_2)Cd^{2+} \longrightarrow$ Wash $\xrightarrow{S^{2-}} (TiO_2)CdS \longrightarrow$ Wash

1 dip cycle

TiO_2- CdSe Assembly Using a Bifunctional Linker Molecule







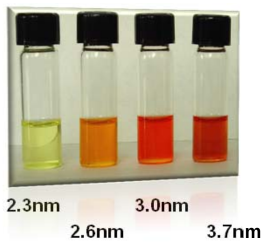
TiO_2

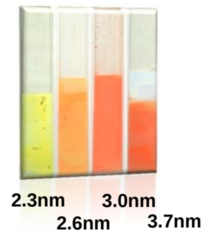
CdSe

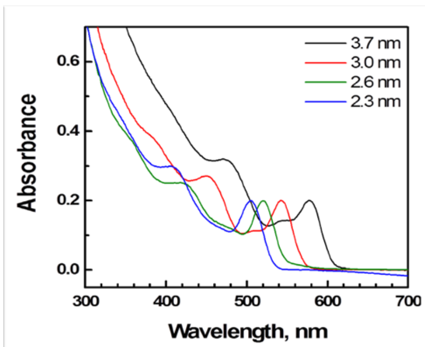
TiO_2/CdSe

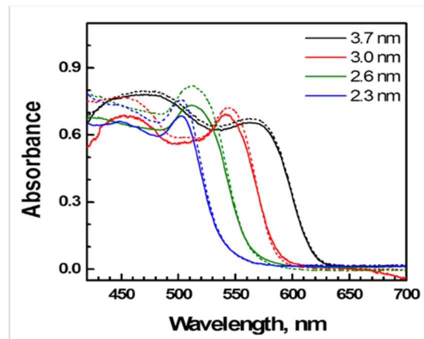
Baker & Kamat Langmuir **2010,** 26, 11272-11276**.**

Modification of TiO_2 Films with Different Size CdSe Particles

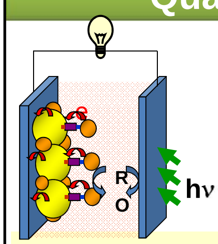




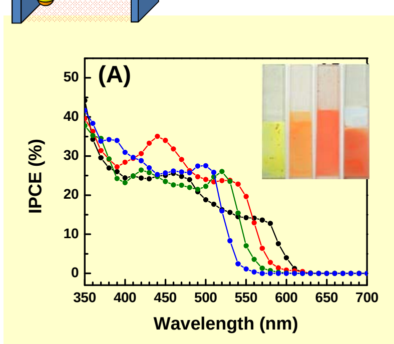


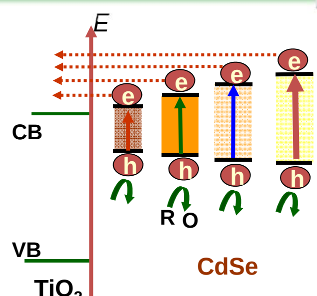


Quantum Dot Solar Cells



- Size selective deposition of CdSe QDs to TiO_2 films
- Ability to tune the photoresponse of QDSC
- Higher efficiency with smaller size QDs





IPCE or Ext. Quantum Eff.
= (1240/λ) x (Isc/Iinc) x 100

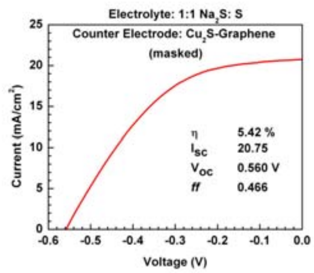
J|A|C|S
ARTICLES
Published on Web 03/01/2008

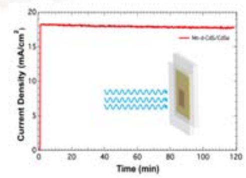
Quantum Dot Solar Cells. Tuning Photoresponse through Size and Shape Control of CdSe–TiO_2 Architecture

Anusorn Kongkanand,† Kevin Tvrdy,†‡ Kensuke Takechi,† Masaru Kuno,†‡ and Prashant V. Kamat*†‡§

Improving the performance of QDSC

Power Conversion Efficiency of 5.4%
Is among the highest for QD Solar Cells





Working Electrode:
(Mn doped CdS/CdSe/ZnS) (SILAR method)
Cell configuration: Sandwich Cell
Actual Electrode Area: 0.22 cm²
masked to remove any scattering effects

JACS 2012, 134, 2508–2511

Mn-Doped Quantum Dot Sensitized Solar Cells: A Strategy to Boost Efficiency over 5%

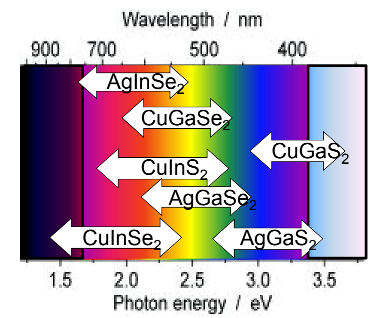
Pralay K. Santra and Prashant V. Kamat

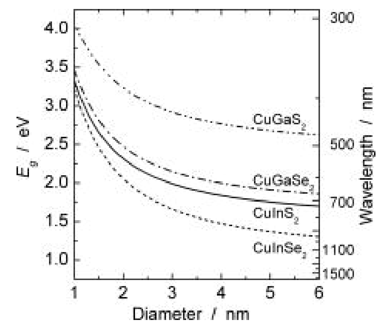
Can we design environmentally safe solar cell technology with Metal Chalcogenides?

150 year old lead acid battery still dictates the operation of a modern automobile!

Ternary semiconductor nanocrystals

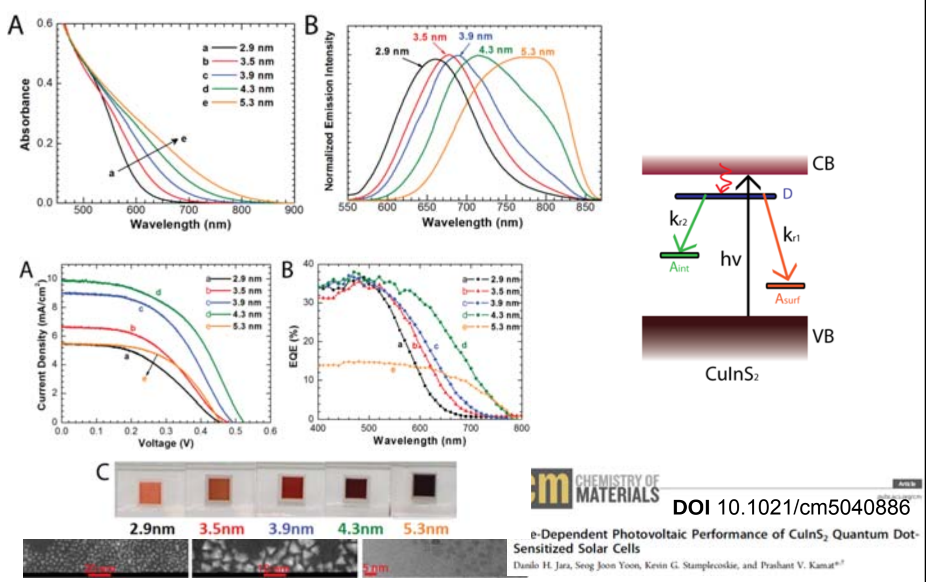
- The I-III-VI chalcopyrite structure is derived from the fact that the group II element in the II-VI zinc blende structure is substituted by group I and III elements.
- Optical band gap of the QDs covers a wide wavelength range from near-infrared to ultraviolet.
- Bulk $CuInS_2$ has a direct bandgap of 1.53 eV with size tunable absorption and emission (Bohr radius ~4.1 nm).





Omata, T. et al. Size dependent optical band gap of ternary I-III-VI(2) semiconductor nanocrystals. *J. Appl. Phys.* **2009**, *105*, Art no 073106.

Size Quantized $CuInS_2$ Nanoparticles



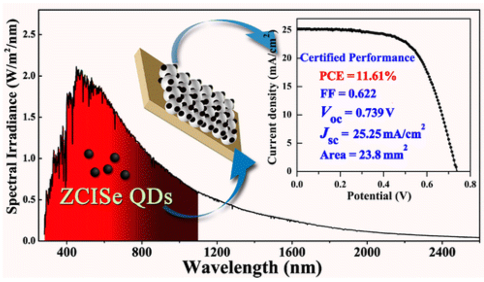
DOI 10.1021/cm5040886

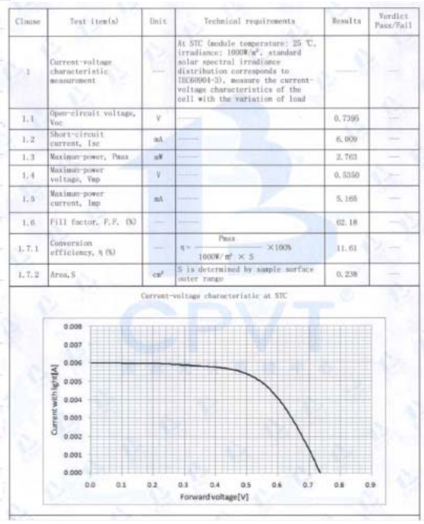
Zn–Cu–In–Se Quantum Dot Solar Cells with a Certified Power Conversion Efficiency of 11.6%

JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Jun Du†, Zhonglin Du†, Jin-Song Hu§, Zhenxiao Pan†, Qing Shen∥⊥, Jiankun Sun§, Donghui Long‡, Hui Dong#, Litao Sun#, Xinhua Zhong*†, and Li-Jun Wan§

DOI: 10.1021/jacs.6b00615





Clause	Test item(s)	Unit	Technical requirements	Results	Verdict Pass/Fail
1	Current-voltage characteristic measurement	—	At STC (module temperature: 25 ℃, irradiance: 1000W/m², standard solar spectral irradiance distribution corresponds to IEC60904-3), measure the current-voltage characteristics of the cell with the variation of load	—	—
1.1	Open-circuit voltage, Voc	V	—	0.7395	—
1.2	Short-circuit current, Isc	mA	—	6.009	—
1.3	Maximum-power, Pmax	mW	—	2.763	—
1.4	Maximum-power voltage, Vmp	V	—	0.5350	—
1.5	Maximum-power current, Imp	mA	—	5.165	—
1.6	Fill factor, F.F. (%)	—	—	62.18	—
1.7.1	Conversion efficiency, η (%)	—	$\eta = \frac{P_{max}}{1000W/m^2 \times S} \times 100\%$	11.61	—
1.7.2	Area, S	cm²	S is determined by sample surface outer range	0.238	—

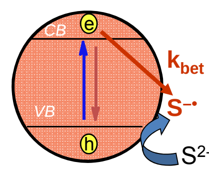
Current-voltage characteristic at STC

Addressing the Issues of Sulfide/Polysulfide Couple

Hole scavenging versus anodic corrosion

$CdSe\ (h) + S^{2-} \longrightarrow CdSe + S^{-\bullet}$

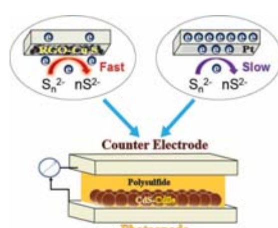
$CdSe(h+) \longrightarrow Cd^{2+} + Se^{0}$ $Cd^{2+} + S^{2-} \longrightarrow CdS$



Back electron transfer between oxidized couple and injected electrons

Redox activity at counter electrode

S^{2-}/S_n^{2-} couple -oxidation potential of +0.5 V vs. NHE

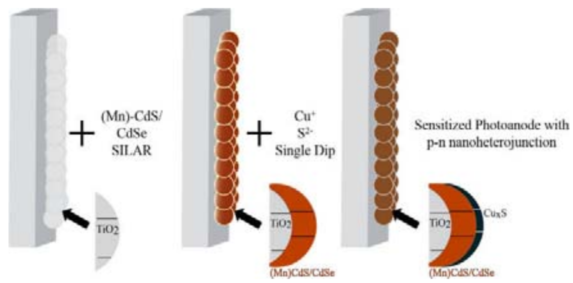


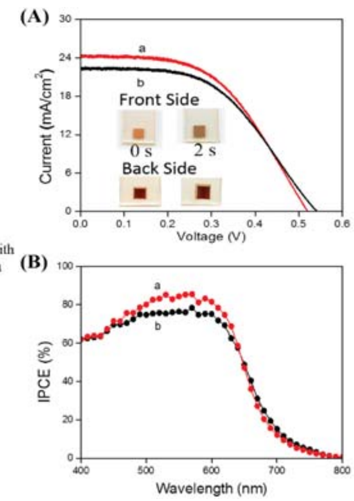
Chakrapani, V.; Baker, D.; Kamat, P. V. Understanding the Role of the Sulfide Redox Couple (S^{2-}/S_n^{2-}) in Quantum Dot Sensitized Solar Cells. *J. Am. Chem. Soc.* ***2011, 133, 9607–9615.***

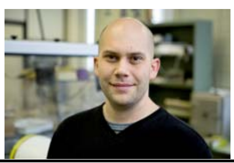
Radich, J. G.; Dwyer, R.; Kamat, P. V. Cu_2S -Reduced Graphene Oxide Composite for High Efficiency Quantum Dot Solar Cells . Overcoming the Redox Limitations of S^{2-}/S_n^{2-} at the Counter Electrode. *J. Phys. Chem. Lett.* ***2011, 2, 2453–2460.***

Hole transfer at the interface

- Cu_xS mediates hole transfer to polysulfide
- Improves efficiency from 5.9% to 6.6%







J. G. Radich; N. R. Peeples; P. K. Santra; P. V Kamat, *J. Phys. Chem. C* **2014**, DOI: 10.1021/jp4113365.

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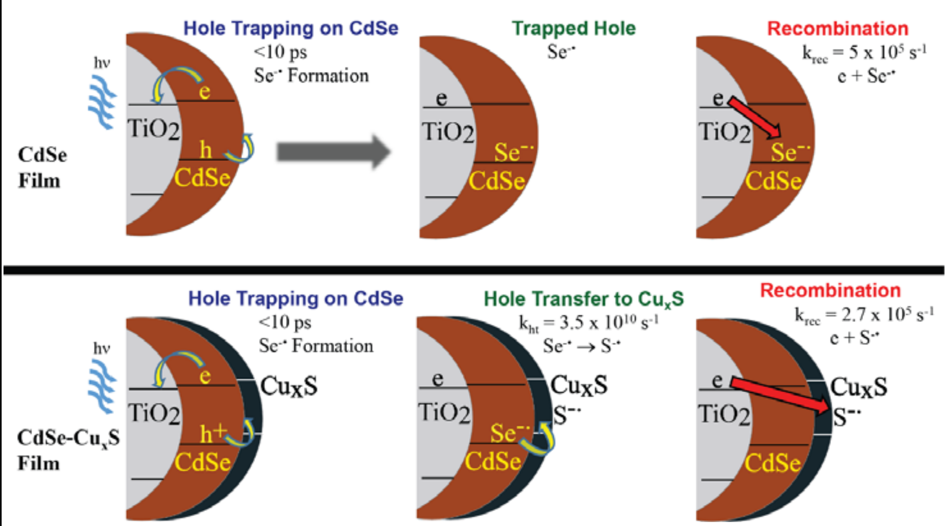
Cu_xS Mediated Hole Transfer



J. G. Radich; N. R. Peeples; P. K. Santra; P. V Kamat, *J. Phys. Chem. C* **2014**, DOI: 10.1021/jp4113365.

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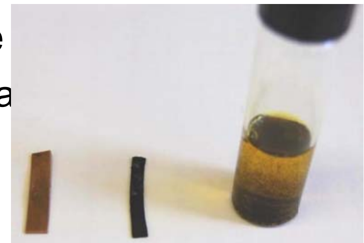
Stable, Regenerative, PEC Cells



- Brass counter electrode
  - Forms Cu_2S and eventua[lly]
    disintegrates
- Methanol in electrolyte
  - Methanol is a sacrificial hole scavenger
- Na_2SO_3 or S^{2-} electrolyte
  - Only one member of the redox couple present

Radich, J. et. al, *J. Phys. Chem. Lett.*, **2011**, *2* (19), pp 2453–2460
Hodes, G., *J. Phys. Chem. Lett.,* **2012**, *3* (9), pp 1208–1213

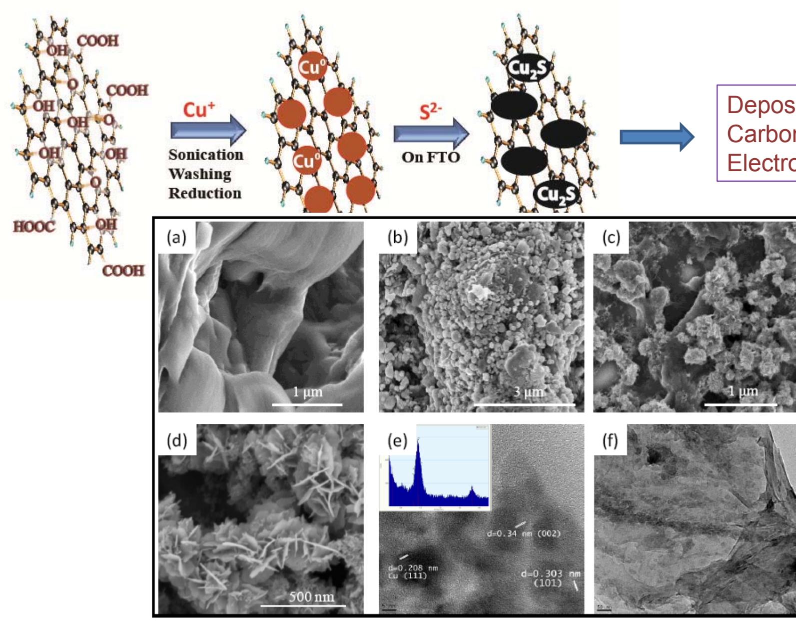
Overcoming Counter Electrode Issue

Pt electrode gets poisoned in sulfide mediu,m

Sulfides of Co, Ni have show good electrochemical activity in sulfide medium

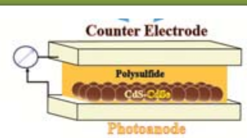
Need to design a stable counter electrode

Counter Electrode Design to Improve Fill Factor

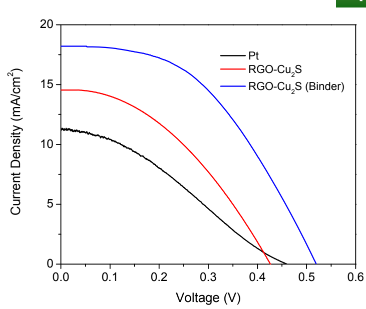


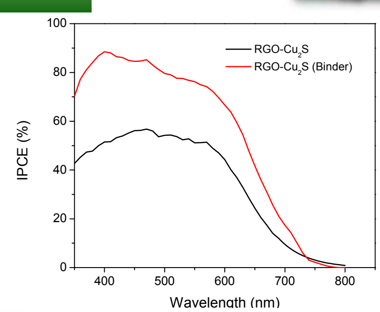
Deposit on Carbon Paper Electrode

QDSC Performance with Cu_2S/Graphene Counter Electrode



Voc =0.55 V
Isc = 18 mA/cm^2
ff = 0.5
η = 4.4 %





TiO_2/CdSe/CdS Photoanode
Cu_2S/Graphene Electrode
1M Na_2S, 0.1 M S in water
100 mW/cm^2 Area 0.25 cm^2

Binder: poly(vinylidene) fluoride (PVDF)

The Journal of Physical Chemistry Letters 2011, 2, 2453–2460

Cu_2S Reduced Graphene Oxide Composite for High-Efficiency Quantum Dot Solar Cells. Overcoming the Redox Limitations of S_2^-/S_n^{2-} at the Counter Electrode

James G. Radich, Ryan Dwyer, and Prashant V. Kamat

Emerging Strategies

Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

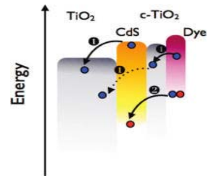
Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4]* Matthew C. Beard[1]*

DOI: 10.1126/science.1209845
Science **334**, 1530 (2011);

The Journal of Physical Chemistry Letters pubs.acs.org/JPCL
2010, *1* (7), pp 1134–1138

Quantum Dot−Dye Bilayer-Sensitized Solar Cells: Breaking the Limits Imposed by the Low Absorbance of Dye Monolayers

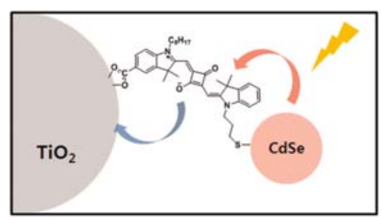
Menny Shalom, Josep Albero, Zion Tachan, Eugenia Martínez-Ferrero, Arie Zaban,* and Emilio Palomares*



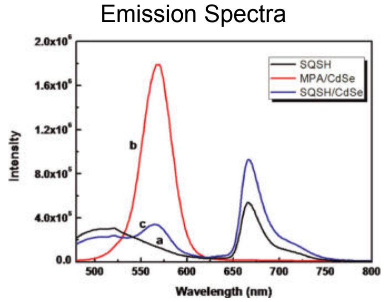
Synchronized Energy and Electron Transfer Processes in Covalently Linked CdSe−Squaraine Dye−TiO$_2$ Light Harvesting Assembly

Hyunbong Choi, Pralav K. Santra, and Prashant V. Kamat*

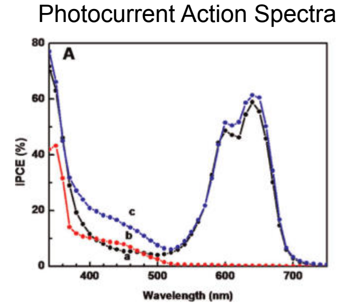
VOL. 6 ▪ NO. 6 ▪ 5718–5726 ▪ 2012 ACSNANO



Emission Spectra

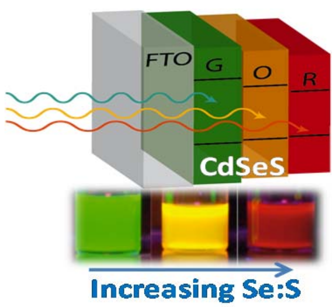


Photocurrent Action Spectra

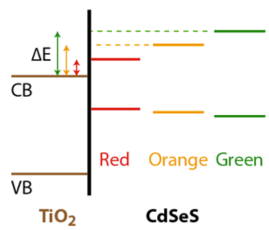


Towards the design of *Rainbow Solar Cell*

…. semiconductor QDs in a tandem fashion

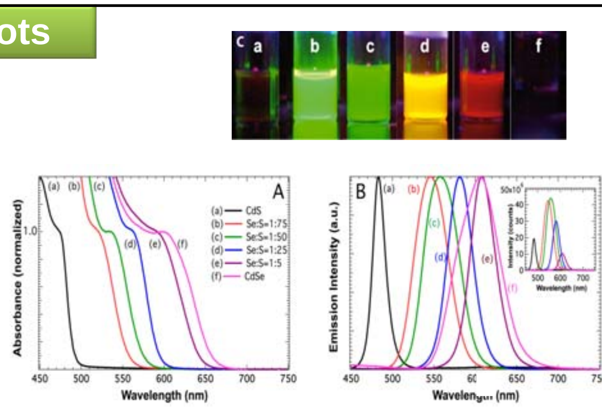


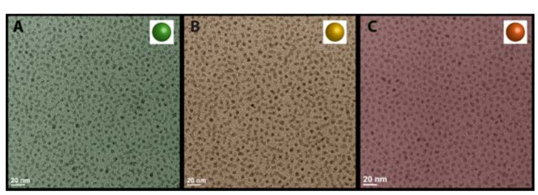
- To broaden the photoresponse of QDSC
- To explore the synergy of layered QDs in capture and conversion of incident photons
- To minimize the energy loss associated with higher energy excitations



CdSSe quantum dots

- Bandgap can be tuned by varying S:Se composition
- Emission Quantum yield of CdSeS is as high as 0.62
- CdSSe has been shown to have graded alloy structure
- Inject electrons into metal oxide semiconductors and can be employed in QDSC
- Enables design of Tandem layered QDSC

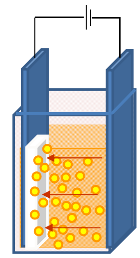


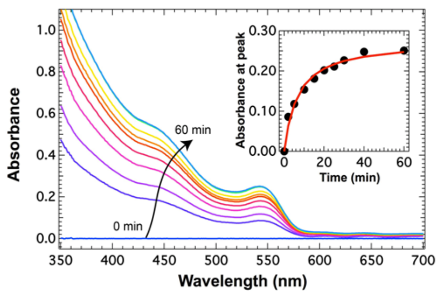


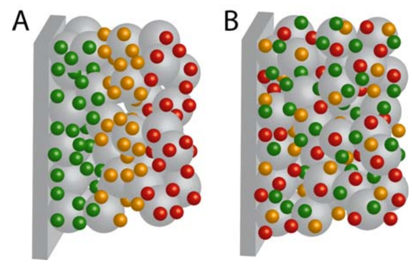
Santra & Kamat JACS 2013, 135, 877–885

Electrophoretic Deposition of QDs

- Semiconductor QDs in mixed solvents become charged and can be driven to the electrode surface with an externally applied bias.
- Following the increase in absorption, one can quantitatively deposit QDs within mesoscopic TiO_2 film



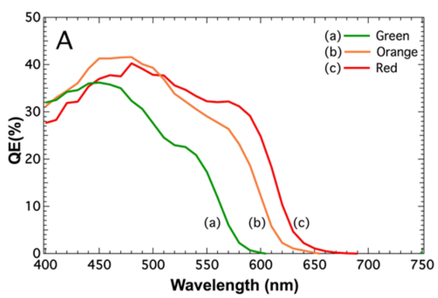


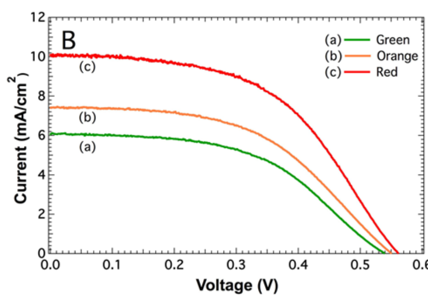


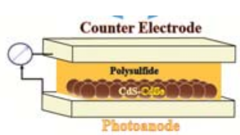
Sequential vs. Mixed

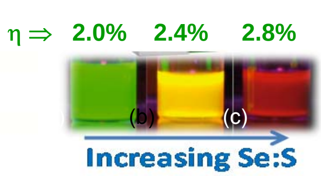
Santra and Kamat, JACS 2013,

External quantum efficiency and J-V characteristics of CdSSe QDs



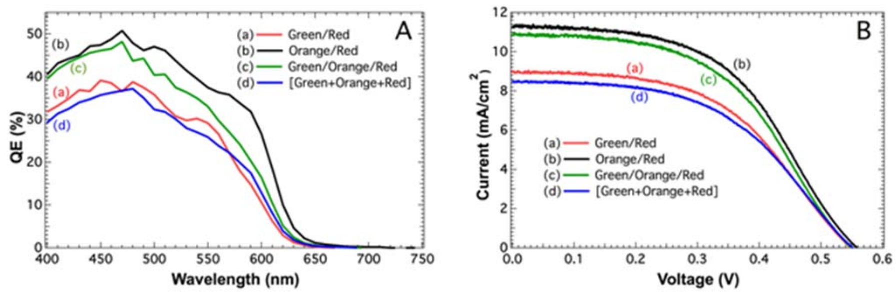




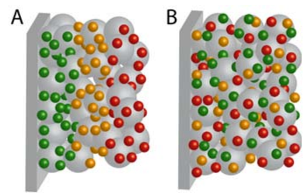


Higher current and efficiencies are seen for red QDs

Photovoltaic performance of tandem layered quantum dot solar cells

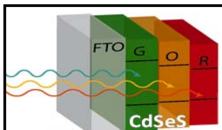


	η % Expt	Calc.
Green + Red	2.49	2.14
Orange + Red	3.19	2.44
Green + Orange + Red	3.00	2.13
Green, Orange, Red (Mixed)	2.34	2.40

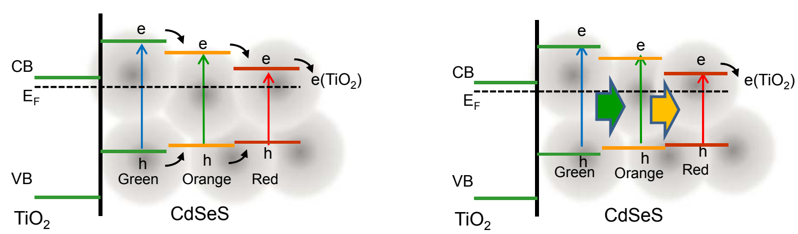


Sequential vs. Mixed

Santra and Kamat, JACS 2013, 135, 877–885



Coupling energy and electron transfer at mesoscale



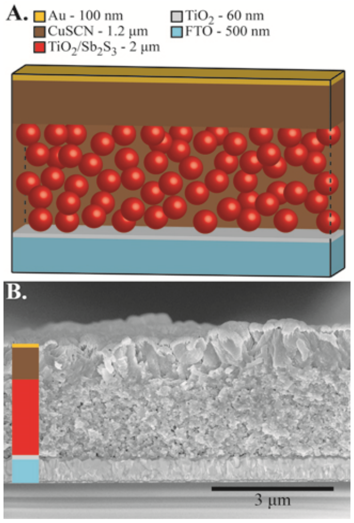
Currently experiments are underway

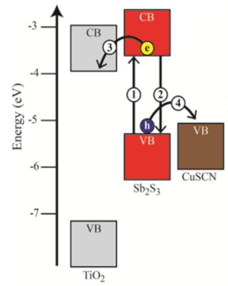
•To establish the synergy of tandem layered quantum dot solar cells.

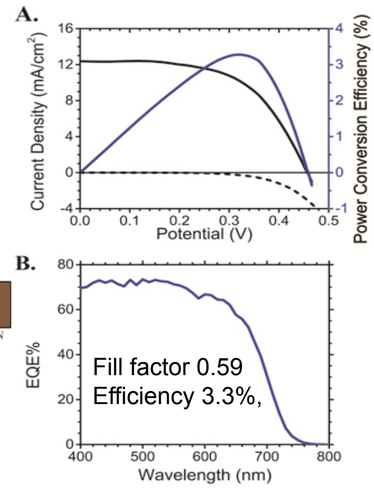
•To elucidate energy transfer and/or electron transfer processes

(Transient absorption and emission measurements to probe the excited state deactivation)

Sb_2S_3/CuSCN Based Solid State Solar Cells





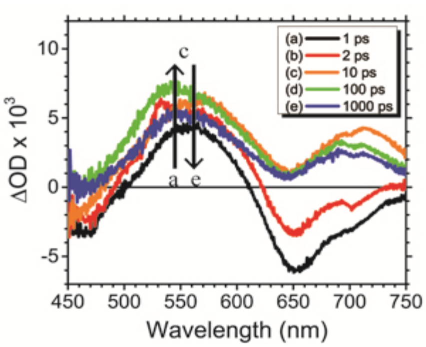


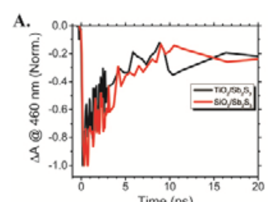
Christians and Kamat ACS Nano 2013, **7**, 7967–7974

Establishing Two Step Hole Transfer Process

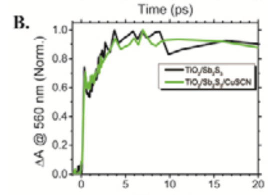
1. Hole Trapping in Sb_2S_3 Films

$$Sb_2S_3(h) \longrightarrow Sb_2S_2S^{-\bullet}$$





460 nm



560 nm

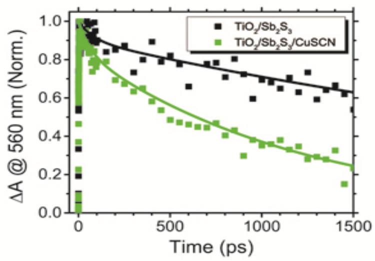
The hole trapping process proceed s with a rate constant of $4.5 \times 10^{11}\ s^{-1}$.

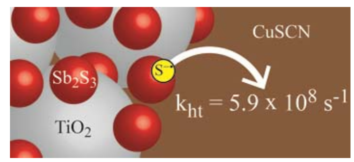
Establishing Two Step Hole Transfer Process

2. Hole Transfer to CuSCN

$Sb_2S_2S^{-\bullet}$ + e ⟶ Sb_2S_3 + heat

$Sb_2S_2S^{-\bullet}$ + CuSCN ⟶ Sb_2S_3 + CuSCN(*h*)



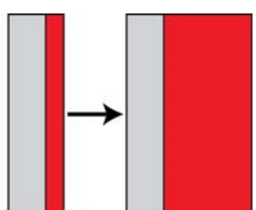


Hole transfer to CuSCN occurs with a rate constant of k_{ht} = 5.9 × 10^8 s^{-1}

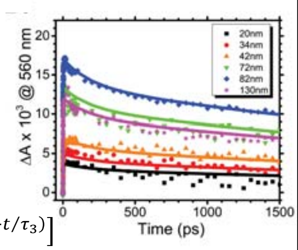
- The transfer of photogenerated holes from the absorber species to the p-type hole conductor is a two step process and plays a critical role in the charge separation process.
- Hole transfer is 2-3 order of magnitude slower than the electron injection process

ACS Nano 2013, **7**, 7967–7974

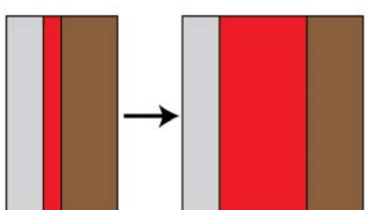
Hole Diffusion in Sb_2S_3



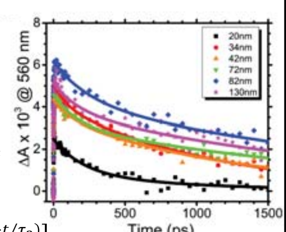
Similar rate constants



$$y = C\left[-e^{(-t/\tau_1)} + Ae^{(-t/\tau_2)} + (1-A)e^{(-t/\tau_3)}\right]$$



Different kinetic rate constants



$$y = C\left[Ae^{(-t/\tau_2)} + (1-A)e^{(-t/\tau_3)}\right]$$

J. A. Christians; D. T. Leighton Jr.; P. V. Kamat, *Energy Environ. Sci.* **2014**, 7, 1148-1158.

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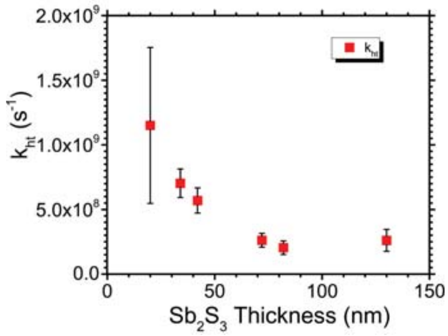
Investigating Hole Diffusion

- k_{ht} strongly depends on Sb_2S_3 film thickness



(1) Trapping: $Sb_2S_3(h) \longrightarrow Sb_2S_2S^{-\bullet}$

(2) Diffusion: $Sb_2S_2S^{-\bullet} + CuSCN \longrightarrow [Sb_2S_2S^{-\bullet}{-}CuSCN]$

(3) Transfer: $[Sb_2S_2S^{-\bullet}{-}CuSCN] \longrightarrow Sb_2S_3 + Cu(SCN^{-\bullet})$

J. A. Christians; D. T. Leighton Jr.; P. V. Kamat, *Energy Environ. Sci.* **2014**, 7, 1148-1158.

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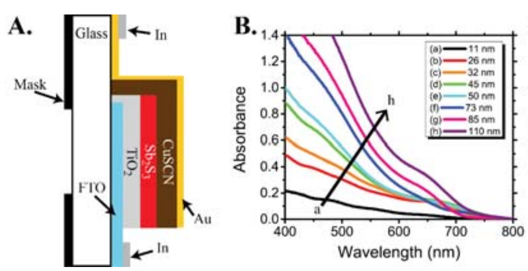
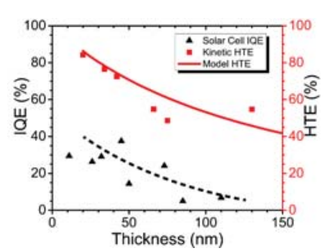
HT Rate and Photovoltaics



- Maximum photocurrent at ~ 45 nm
- Confirms hole transfer limitations
- Other factors also contribute
  - back electron transfer, charge collection, etc.



$IQE = EQE/LHE \quad HTE = k_{ht}/(\langle\tau\rangle_{Sb_2S_3}^{-1} + k_{ht})$

J. A. Christians; D. T. Leighton Jr.; P. V. Kamat, *Energy Environ. Sci.* **2014**, 7, 1148-1158.

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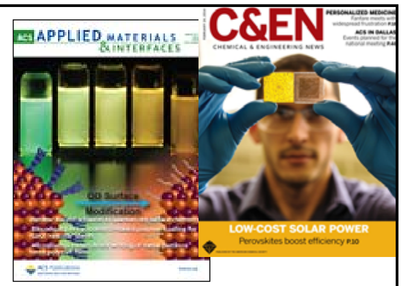
Summary

- Unique properties of organic metal halide perovskites offer new opportunities to develop low-cost and high efficiency solar cells
- CuI as a hole conductor provides excellent opportunity to develop thin film perovskite solar cells
- Excited state properties offer new insights into the charge separation dynamics within the perovskite film.
- Need to overcome stability issues -susceptibility to humid atmosphere



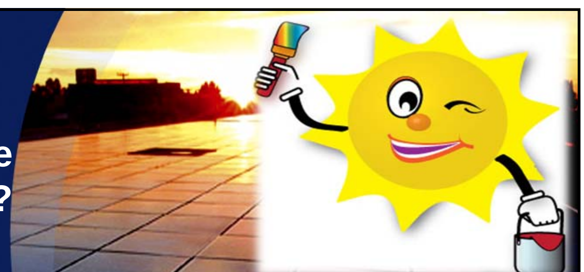
Band Filling with Free Charge Carriers in Organometal halide Perovskites
J. S. Manser and P. V. Kamat
Nature Photonics, 2014, 8, 737-743

An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. J. A. Christians R. Fung and P. V. Kamat J. Am. Chem. Soc., 2014, **136**, 758–764

Quantum Dot Solar Cells: Hole Transfer as a Limiting Factor in Boosting the Photoconversion Efficiency
P. V. Kamat, J. A. Christians, J. G. Radich
Langmuir, 2014, **30**, 5716–5725

What will the future hold?

Over the last twenty years, the per-kWh price of photovoltaics has dropped from about $500 to ~ $2; think of what the next twenty years will bring.



It is *Sun-Believable*

OUR Solar Power FUTURE

The U.S. Photovoltaics Industry Roadmap Through 2030 and Beyond