

# Annual Research Summary

January - December 2015

*Kamatlab*

University of Notre Dame



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## Prashant V. Kamat

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Website: <http://www.nd.edu/~kamatlab>

## Research Group

### Graduate Students

Douglas Hines (Chemistry) -Graduated in May 2015  
Jeff Christians (Chem. Eng.) -Graduated in May 2015  
Joseph Manser (Chem Eng)  
Yong-Siou Chen (Chemistry)  
Jacob Hoffman (Chemistry)  
Danilo JaraQuinteros (Chemistry)  
Seogjoon Yoon (Chemistry)  
Victoria Bridewell (Chemistry)  
Steven Kobosko (Chem Eng)  
Christian Telavera (Chemistry)  
Sebastian Snowberger (Chem Eng)

*Incoming Student* Anselme.Mucunguzi (Chemistry)

### Undergraduate Students

#### Spring 2015

Abigail Swint Tim Schumer  
Andrew P. Neils Molly Labine

#### Summer 2015

Tessa Ronan Sooraj Ben  
Molly Labine Christina Kappil  
Isaac Wrappes

#### Fall 2015

Christina Kappil Peter Chiang  
Isaac Wrappes Alexander Robinson

**Summer RET:** Thomas Adams (Summer RET - Lake Michigan Catholic)

### Postdoctoral Research Associate

Christopher Tuinenga (March 2014 – March 2015)  
Rebeka Alam (Aug 2013 – present)  
Kevin Stamplecoskie (May 2013 – June 2015)  
Gary Zaiats (July 2015 –present)  
Subila Balakrishnan (November 2015-present)

### Visiting Scientists

Julie Peller (IUN)  
Roxana Nicolaescu (Serim Corporation)  
Rodrigo Iglecias (Universidad Nacional de Cordoba, Chile)  
Ellen Raphael (Universidad Federal de SaoJoao del-Rei, Brazil)

## Graduation/Fellowships/Recognition

**Jeff Christians** Dept. of Chemical & Biomolecular Eng, University of Notre Dame, April 2015

*Mesostructured Thin Film Solar Cells: Examining Hole Transfer Mechanisms and Device Stability*

**Douglas Hines** Department of Chemistry, University of Notre Dame, April 2015 .

*Excited State Reactions at the Quantum Dot Surface*

### Awards/Honors

P. Kamat

Elected to Indian National Science Academy as Preavasi Fellow  
Recognition by Thomson Reuters among 2015-Most Cited Researchers

Jeffrey Christians

The 2014 Shaheen Award in Engineering

Douglas Hines

The 2014 Shaheen Award in Science

Joseph Manser

65th Lindau Nobel Laureate Meeting



Jeff Christians and Doug Hines Winners of Shaheen Award

### Fellowships

Yong-Siou Chen

ECS Travel Award to attend 227<sup>th</sup> the Electrochemical Soc. Meeting, Chicago May 24-28

Eilers Graduate Student Fellowship

CEST-Bayer fellowship

Jeffrey Christians

Eilers Graduate Student Fellowship

CEST-Bayer fellowship

### Undergraduate Fellowships

Naughton Fellowship for summer research was awarded to Tessa Ronan

ND Nano summer research fellowship was awarded to Isaac Wappes

Army Undergraduate Research fellowship was awarded to Christina Kappil and Abby Swint

## Professional Activities

- **Deputy Editor**, Journal of Physical Chemistry Letters (2009-present)
- **Editorial Advisory Boards**
  - Langmuir (2000-2014)
  - Research on Chemical Intermediates (2003-present)
  - Electrochemical and Solid State Letters (September 2006-2010)
  - Applied Electrochemistry (2009-present)
- **ND committees**
  - Member of the COS-COS (2008-present)
  - Member, SEI Fellow, University of Notre Dame (until June 2014)
  - Member, Steering Committee, Digitization of course work (Provost office)
  - Member: Solar Cell Panel (ND)
- **Symposium Organizer**
  - Co-Organizer, Nanostructures for Energy Conversion, , 227th ECS Meeting Chicago, May, 2014
  - Co-Organizer, Challenges in Plasmonic Photochemistry, Pacificchem, Honolulu, Dec 15-21, 2015

## Invited Seminar/Colloquium

### Seminars

**Kamat, P. V.**

Organic Metal Halide Perovskites for Next Generation Photovoltaics  
2015 Mahoney Seminar in the Department of Chemistry at the University of Massachusetts  
Amherst, November 19, 2015

Nanostructured Materials for Light Energy Conversion  
University of Texas at Austin, Materials Science Institute/Mechanical Engineering  
October 22, 2015

Semiconductor QDs and Perovskites for Next generation Photovoltaics  
Graphene Oxide based Multifunctional Catalyst Mat  
Looking Beyond Plasmonics. Light Harvesting Properties of Metal Nanoparticles and Clusters  
Lavoisier lectures, University of Paris, Diderot, Sept 28-Oct 1 2015

Next Generation Photovoltaics with Organic Metal Halide Perovskites  
University of Texas at Austin, Chemical Engineering Grad Student Seminar, April, 28, 2015

Quantum Dots to Perovskites. Exploring New Materials for Next Generation Solar Cells  
Harvard University, Applied Physics Colloquium, April 3, 2015

Making Electrons Cheaper with Next Generation Photovoltaic Materials  
University of Lund, Sweden, March 12, 2015

## Conference Presentations (2014)

*Chemical and Biomolecular Graduate Student Symposium, University of Notre Dame, Notre Dame, IN  
Mar 9*

Manser J.; Chen Y.-S.; Kamat P.V. *Hydrogen from sunlight: low-cost perovskite photovoltaics for tandem solar water splitting applications*

*249th Meeting of the American Chemical Society, Denver, CO Mar 22-26*

Kamat P.V.; Chen Y.-S.; Manser J.; Christians J. *Light energy conversion aspects of organic metal halide perovskites (Invited)*

Kamat P.V.; Alam R. *Simultaneous sensing and degradation of nitroaromatics with graphene based multifunctional catalyst mat (Invited)*

*2015 Materials Research Society Spring Meeting, San Francisco, CA Apr 6-10*

Kamat P.V.; Manser J.; Christians J. *excited state dynamics of plumbate perovskite solar cells (Invited)*

Kamat P.V.; Chen Y.-S.; Manser J. *Single junction perovskite-BiVO<sub>4</sub> tandem assembly for solar hydrogen production (Invited)*

Chen Y.-S.; Kamat P.V. *Bias-free photoelectrochemical hydrogen production using glutathione-capped gold nanoclusters as visible photosensitizers*

*20 Years of Quantum Dots at Los Alamos, Santa Fe, NM Apr 12-16*

Kamat P.V. *Quantum dots to perovskites. What can we learn from their excited state behavior?* (Invited)

*8th Argonne-Northwestern Solar Energy Research (ANSER) Center Symposium, Evanston, IL Apr 16-17*

Kamat P.V.; Manser J.; Christians J. *Revealing the intricacies of perovskites for next generation photovoltaics* (Invited)

*International Conference on Hybrid and Organic Photovoltaics, Rome, Italy May 10-13*

Manser J.; Chen Y.-S.; Kamat P.V. *Solar water splitting using an all solution-processed perovskite PV-photoanode tandem assembly*

Kamat P.V.; Manser J.; Christians J. *Semiconductor quantum dots and perovskites for next generation photovoltaics* (Invited)

*The 227th Electrochemical Society (ECS) Meeting, Chicago, IL May 24-28*

Chen Y.-S.; Manser J.; Kamat P.V. *An all solution-processed lead halide perovskite-BiVO<sub>4</sub> tandem architecture delivering STH of 2.5%*

Alam R.; Kamat P.V. *Anchoring semiconductor and metal nanoparticles on graphene oxide for simultaneous sensing and degradation of contaminants*

*American Chemical Society Great Lakes Central Regional Meeting, Grand Rapids, MI May 27-29*

Peller J.R.; Zhao C.; O'Shea K.; Mezyk S.P.; Kamat P.V. *Radiolysis studies to determine rate constants and reaction products of 4-methylcyclohexane methanol and propylene glycol phenyl ether with the hydroxyl radical in water*

*37th Department of Energy Solar Photochemistry PI Meeting, Gaithersburg, MD May 31-Jun 3*

Kamat P.V.; Chen Y.-S.; Manser J.; Stamplecoskie K.G.; Christians J. *Revealing the excited state intricacies of methyl ammonium lead halide perovskites* (Invited)

*Branching out with STEM Poster Session, University of Notre Dame, Notre Dame, IN Jun 9*

Bridewell V.L.; Alam R.; Karwacki C.J.; Kamat P.V. *CdSe/CdS nanorod photocatalysts: charge transfer optimization through shell length*

*Frontiers in Advanced Materials, Bangalore, India Jun 15-18*

Kamat P.V. *Designing perovskite solar cells for thin film photovoltaics: excitement and challenges* (Invited)

*Photochemistry Gordon Research Conference and Gordon Research Seminar, Stone Hill College, Easton, MA Jul 18-24*

JaraQuinteros D.; Stamplecoskie K.G.; Kamat P.V. *Unraveling the photophysical mechanism of CuInS<sub>2</sub> quantum dots by using Cu-deficient structures*

*7th Frontier Scientists Workshop, Korean Academy of Science & Technology, Atlanta, GA Jul 30-31*

Kamat P.V. *Next generation photovoltaics with organic metal halide perovskites* (Invited)

*250th Meeting of the American Chemical Society, Boston, MA Aug 16-20*

Kamat P.V.; Chen Y.-S.; Christians J. *Light energy conversion aspects of organic metal halide perovskites* (Invited)

Kamat P.V.; Alam R. *Simultaneous sensing and degradation of nitroaromatics with graphene oxide based multifunctional catalyst mat (Invited)*

Kamat P.V.; Alam R. *Multifunction chemical sensors designed on 2D nanomaterials for detection and degradation of low-level contaminants (Invited)*

Bartels D.M. *A simple ab initio model for the hydrated electron that matches experiment*

*International Symposium on Clusters and Nanomaterials, Richmond, VA Oct 25-29*

Kamat P.V.; Chen Y.-S.; Stamplecoskie K.G. *Looking beyond plasmonics. Exploring light harvesting properties of glutathione stabilized gold clusters (Invited)*

*International Workshop on "Nanomaterials for Energy and Biotechnology", Harbin Institute of Technology, Heilongjiang Province, China Nov 2-4*

Kamat P.V. *Quantum dots to perovskites. Nanostructure architectures for light energy conversion. (Plenary)*

*PINDU Inorganic Symposium, University of Notre Dame, Notre Dame, IN Dec 5*

Yoon S.J.; Stamplecoskie K.G.; Bernier R.T.; Kamat P.V. *Origin of  $CH_3NH_3PbBr_xI_{(3-x)}$  photophysical properties: effect of halide complexation*

Talavera C.; Kamat P.V. *Investigation of the excited states properties of glutathione capped gold nanoclusters upon ligand exchange with 2-phenylethanethiol*

Bridewell V.L.; Alam R.; Karwacki C.J.; Kamat P.V. *Size-tunable CdSe/CdS nanorods as photocatalysts*

*The International Chemical Congress of Pacific Basin Societies 2015, Honolulu, HI Dec 15-20*

Kamat P.V.; Manser J. *Excite state behavior of organic metal halide perovskite films and its influence on photovoltaic properties (Invited)*

Kamat P.V. *Visible photoactivity of gold clusters and their interaction with plasmonic nanoparticles*

Kamat P.V. *Multifunctional smart catalyst mat with graphene oxide and semiconductor nanostructures (Invited)*

## Research Papers

Chen Y.-S.; Manser J.; Kamat P.V.

*J. Am. Chem. Soc.* **2015**, *137*, 974-81

*All solution-processed lead halide perovskite-BiVO<sub>4</sub> tandem assembly for photolytic solar fuels production.*

Choi H.; Chen Y.-S.; Stamplecoskie K.G.; Kamat P.V.

*J. Phys. Chem. Lett.* **2015**, *6*, 217-23.

*Boosting the photovoltage of dye-sensitized solar cells with thiolated gold nanoclusters.*

Christians J.A.; Manser J.; Kamat P.V.

*J. Phys. Chem. Lett.* **2015**, *6*, 2086-95 (Perspective)

*Multifaceted excited state of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Charge separation, recombination, and trapping.*

Christians J.A.; Manser J.; Kamat P.V.

*J. Phys. Chem. Lett.* **2015**, *6*, 852-7 (Viewpoint)

*Best practices in perovskite solar cell efficiency measurements. Avoiding the error of making bad cells look good.*

Christians J.A.; Miranda Herrera P.A.; Kamat P.V.

*J. Am. Chem. Soc.* **2015**, *137*, 1530-8.

*Transformation of the excited state and photovoltaic efficiency of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite upon controlled exposure to humidified air.*

Grigioni I.; Stamplecoskie K.G.; Selli E.; Kamat P.V.

*J. Phys. Chem. C* **2015**, *119*, 20792–800.

*Dynamics of photogenerated charge carriers in WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction photoanodes.*

Guo Z.; Manser J.; Wan Y.; Kamat P.V.; Huang L.

*Nat Commun* **2015**, *6*.

*Spatial and temporal imaging of long-range charge transport in perovskite thin films by ultrafast microscopy.*

Hines D.A.; Darzi E.R.; Hirst E.; Jasti R.; Kamat P.V.

*J. Phys. Chem A* **2015**, *119*, 8083-9.

*Carbon nano hoops: excited singlet and triplet behavior of aza[8]cpp and 1, 15-diaza[8]cpp.*

Hines D.A.; Forrest R.P.; Corcelli S.A.; Kamat P.V.

*J. Phys. Chem B* **2015**, *119*, 7439-46.

*Predicting the rate constant of electron tunneling reactions at the CdSe-TiO<sub>2</sub> interface.*

Kirmayer S.; Edri E.; Hines D.A.; Klein-Kedem N.; Cohen H.; Niitsoo O.; Pinkas I.; Kamat P.V.; Hodes G.

*Adv. Mater. Interfaces* **2015**, *1400346*.

*Surface oxidation as a cause of high open-circuit voltage in CdSe ETA solar cells.*

Manser J.; Reid B.; Kamat P.V.

*J. Phys. Chem. C* **2015**, *119*, 17065-73.

*Evolution of organic-inorganic lead halide perovskite from iodoplumbate complexes.*

Stamplecoskie K.G.; Kamat P.V.

*J. Phys. Chem. Lett.* **2015**, *6*, 1870–5.

*Synergistic effects in the coupling of plasmon resonance of metal nanoparticles with excited gold clusters.*

Stamplecoskie K.G.; Manser J.; Kamat P.V.

*Energy Environ. Sci.* **2015**, *8*, 208-15.

*Dual nature of excited state of organic-inorganic lead halide perovskites.*

Bridewell, V. L.; Alam, R.; Karwacki, C. J.; Kamat, P. V.,

*Chemistry of Materials* **2015**, *27*, 5064-5071

[CdSe/CdS Nanorod Photocatalysts: Tuning the Interfacial Charge Transfer Process through Shell Length.](#)

Huang, W.; Manser, J. S.; Kamat, P. V.; Ptasinska, S.,

*Chemistry of Materials* **2015**. ASAP DOI: 10.1021/acs.chemmater.5b04122

[Evolution of Chemical Composition, Morphology, and Photovoltaic Efficiency of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Perovskite under Ambient Conditions.](#)

Itzhaik, Y.; Bendikov, T.; Hines, D. A.; Kamat, P. V.; Cohen, H.; Hodes, G.,

*The Journal of Physical Chemistry C* **2015** ASAP DOI: 10.1021/acs.jpcc.5b09233

[Band Diagram and Effects of the KSCN Treatment in TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/CuSCN ETA cells.](#)

Hodes, G.; Kamat, P. V.,

*J. Phys. Chem. Lett.* **2015**, *6*, 4090-4092(Viewpoint)

[Understanding the Implication of Carrier Diffusion Length in Photovoltaic Cells.](#)

## Editorials

[Know the Difference: Scientific Publications versus Scientific Reports.](#)

Kamat, P. V.; Schatz, G. C., *J. Phys. Chem. Lett.* **2015**, *6*, 858-859.

[Solar Cells versus Solar Fuels: Two Different Outcomes.](#)

Kamat, P. V.; Christians, J. A., *J. Phys. Chem. Lett.* **2015**, *6*, 1917-1918.

[Looking Beyond the Ph.D.](#)

Kamat, P. V., *J. Phys. Chem. Lett.* **2015**, *6*, 3139-3140.

[Journal Impact Factor and the Real Impact of Your Paper.](#)

Kamat, P. V.; Schatz, G. C., *J. Phys. Chem. Lett.* **2015**, *6*, 3074-3075.

[Recent Advances in Battery Science and Technology.](#)

Seshadri, R.; Persson, K.; Kamat, P. V.; Wu, Y., *Chemistry of Materials* **2015**, *27*, 4505-4506.

[Photons, Physical Chemistry, and the Year of Light – A Virtual Issue.](#)

Kamat, P. V.; Schatz, G. S.; Scholes, G.; Zwiernicki, T., *J. Phys. Chem. Lett.* **2015**, *6*, 1420-1422.

[Ten Reasons Why Peer Review Makes Sense.](#)

Kamat, P. V.; Schatz, G. C. *J. Phys. Chem. Lett.* **2015**, *6*, 2588-2589.

[Open Access Debate: On the Flip Side.](#)

Kamat, P. V., *J. Phys. Chem. Lett.* **2015**, *6*, 1238-1239.

[Know the Difference: Scientific Publications versus Scientific Reports.](#)

Kamat, P. V.; Schatz, G. C., *J. Phys. Chem. Lett.* **2015**, *6*, 858-859.

[What Is Hot in Physical Chemistry?](#)

Kamat, P. V., *J. Phys. Chem. Lett.* **2015**, *6*, 686-687.

[A Prolific First Five Years.](#)

Kamat, P. V.; Mennucci, B.; Prezhdo, O.; Scholes, G.; Zaera, F.; Zwiernicki, T.; Schatz, G. C.,

*J. Phys. Chem. Lett.* **2015**, *6*, 180-182

Kamat, P. V.,

[Back to the Photovoltaic Future with Perovskites](#), *J. Phys. Chem. Lett.* 2015, *6*, 4874–4875.

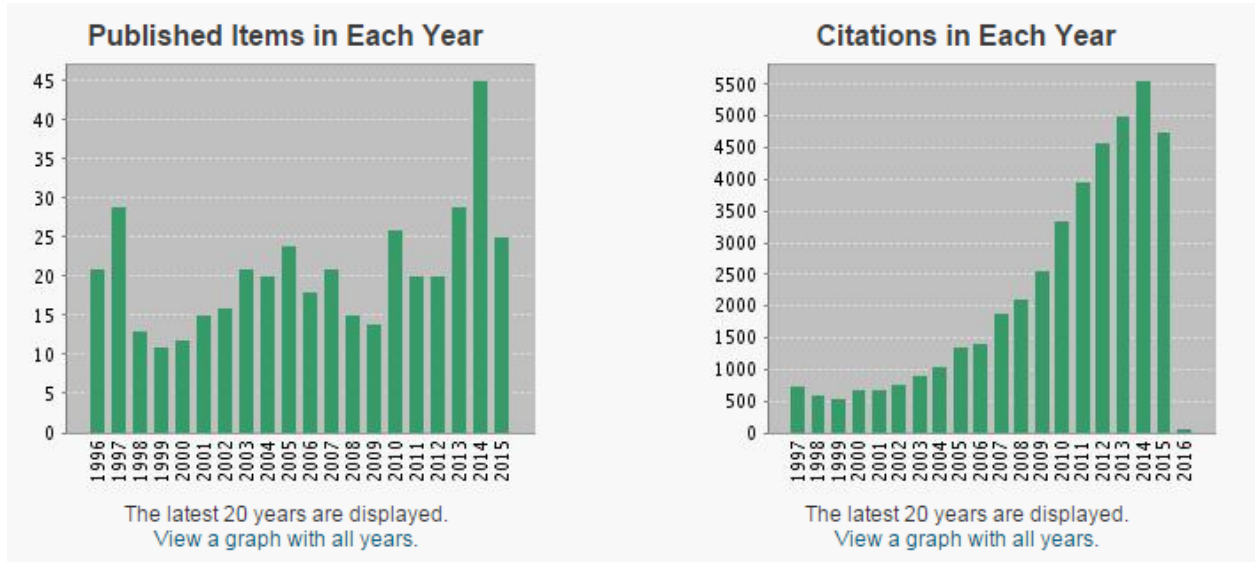
Kamat, P. V.,

[Physical Chemistry at the Interface](#). *J. Phys. Chem. Lett.* 2015, *6*, 5093-5093.



## Publication Analysis

Source: Thomson ISI, Dec 18, 2014

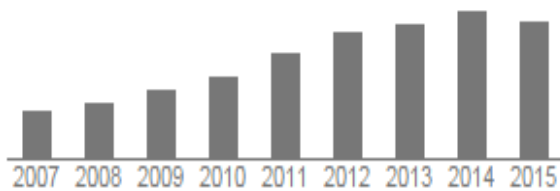


Results found: 568

Sum of the Times Cited : 45000+

Average Citations per Item : 79

h-index : 114



### Citation indices

	All	Since 2008
<a href="#">Citations</a>	55941	34469
<a href="#">h-index</a>	125	89
<a href="#">i10-index</a>	404	305

**2014 Article Impact of Kamatlab Papers** = (2014 Citations of 2012-13 papers)/(No. of 2012-13 papers)  
 = 778 citations/28 papers  
 = **27.78**

## All Solution-Processed Lead Halide Perovskite-BiVO<sub>4</sub> Tandem Assembly for Photolytic Solar Fuels Production.

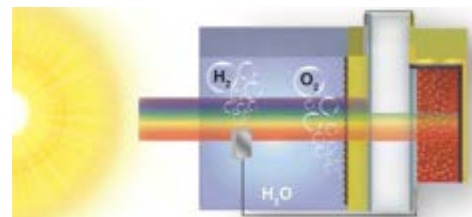
Chen, Y.-S.; Manser, J. S.; Kamat, P. V.

*J. Am. Chem. Soc.* 2015, 137, 974-981

<http://dx.doi.org/10.1021/ja511739y>

### Abstract

The quest for economic, large-scale hydrogen production has motivated the search for new materials and device designs capable of splitting water using only energy from the sun. Here we introduce an all solution-processed tandem water splitting assembly composed of a BiVO<sub>4</sub> photoanode and a single-junction CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> hybrid perovskite solar cell. This unique configuration allows efficient solar photon management, with the metal oxide photoanode selectively harvesting high energy visible photons, and the underlying perovskite solar cell capturing lower energy visible-near IR wavelengths in a single-pass excitation. Operating without external bias under standard AM 1.5G illumination, the photoanode?photovoltaic architecture, in conjunction with an earth-abundant cobalt phosphate catalyst, exhibits a solar-to-hydrogen conversion efficiency of 2.5% at neutral pH. The design of low-cost tandem water splitting assemblies employing single-junction hybrid perovskite materials establishes a potentially promising new frontier for solar water splitting research.



## Boosting the Photovoltage of Dye-Sensitized Solar Cells with Thiolated Gold Nanoclusters

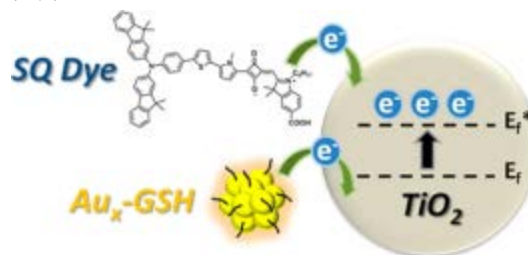
Choi, H.; Chen, Y.-S.; Stampeleskie, K. G.; Kamat, P. V.

*J. Phys. Chem. Lett.* 2015, 6, 217-223

<http://dx.doi.org/10.1021/jz502485w>

### Abstract

Glutathione-capped gold nanoclusters (Aux-GSH NCs) are anchored along with a sensitizing squaraine dye on a TiO<sub>2</sub> surface to evaluate the cosensitizing role of Aux-GSH NCs in dye-sensitized solar cells (DSSCs). Photoelectrochemical measurements show an increase in the photoconversion efficiency of DSSCs when both sensitizers are present. The observed photoelectrochemical improvements in cosensitized DSSCs are more than additive effects as evident from the increase in photovoltage ( $\Delta V$  as high as 0.24V) when Aux-GSH NCs is present. Electron equilibration and accumulation within gold nanoclusters increase the quasi-Fermi level of TiO<sub>2</sub> closer to the conduction band and thus decrease the photovoltage penalty. A similar beneficial role of gold nanoclusters towards boosting the Voc and enhancing the efficiency of Ru(II) polypyridyl complex-sensitized solar cells is also discussed.



## Best Practices in Perovskite Solar Cell Efficiency Measurements. Avoiding the Error of Making Bad Cells Look Good

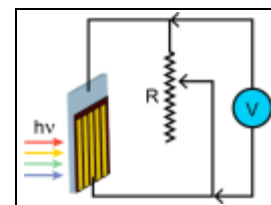
Christians J.A.; Manser J.; Kamat P.V.

*J. Phys. Chem. Lett.* 2015, 6, 852-7 (Viewpoint)

<http://dx.doi.org/10.1021/acs.jpcllett.5b00289>

### Abstract

In this Viewpoint, we will focus specifically on issues that we have observed firsthand in our laboratory related to the accurate measuring of perovskite solar cells.



## Multifaceted Excited State of $\text{CH}_3\text{NH}_3\text{PbI}_3$ . Charge Separation, Recombination, and Trapping

Jeffrey A. Christians, Joseph S. Manser, and Prashant V. Kamat\*

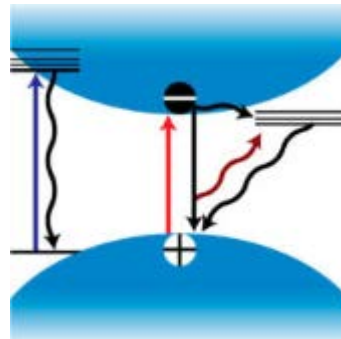
*J. Phys. Chem. Lett.* 2015, 6, 2086–2095 (Perspective)

<http://dx.doi.org/10.1021/acs.jpcllett.5b00594>

### Abstract

A need to understand the excited-state behavior of organic–inorganic hybrid perovskites, such as  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , has arisen due to the rapid development of perovskite solar cells. The photoinduced processes leading to the efficient charge separation observed in these materials remain somewhat elusive. This Perspective presents an overview of the initial attempts to characterize the excited-state and charge recombination dynamics in the prototypical material  $\text{CH}_3\text{NH}_3\text{PbI}_3$ .

While much has been accomplished in designing high-efficiency solar cells, the multifaceted nature of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  excited state offers ample challenges for the photovoltaic community to better comprehend. Building on this foundation may enable us to tackle the stability concerns that have shadowed the rise of perovskite solar cells. Furthermore, a better understanding of the excited-state properties can provide insight into the specific properties that have thrust this material to the forefront of photovoltaic research.



## Transformation of the excited state and photovoltaic efficiency of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite upon controlled exposure to humidified air

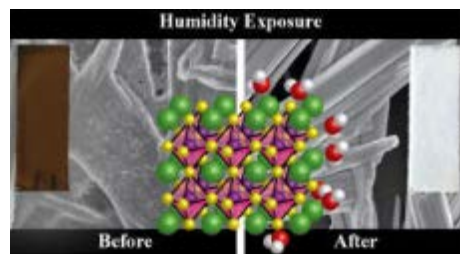
Christians J.A.; Miranda Herrera P.A.; Kamat P.V.

*J. Am. Chem. Soc.* 2015, 137, 1530-8.

<http://dx.doi.org/10.1021/ja511132a>

### Abstract

Humidity has been an important factor, in both negative and positive ways, in the development of perovskite solar cells and will prove critical in the push to commercialize this exciting new photovoltaic technology. The interaction between  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{H}_2\text{O}$  vapor is investigated by characterizing the ground-state and excited-state optical absorption properties and probing morphology and crystal structure. These undertakings reveal that  $\text{H}_2\text{O}$  exposure does not simply cause  $\text{CH}_3\text{NH}_3\text{PbI}_3$  to revert to  $\text{PbI}_2$ . It is shown that, in the dark,  $\text{H}_2\text{O}$  is able to complex with the perovskite, forming a hydrate product similar to  $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ . This causes a decrease in absorption across the visible region of the spectrum and a distinct change in the crystal structure of the material. Femtosecond transient absorption spectroscopic measurements show the effect that humidity has on the ultrafast excited state dynamics of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . More importantly, the deleterious effects of humidity on complete solar cells, specifically on photovoltaic efficiency and stability, are explored in the light of these spectroscopic understandings.

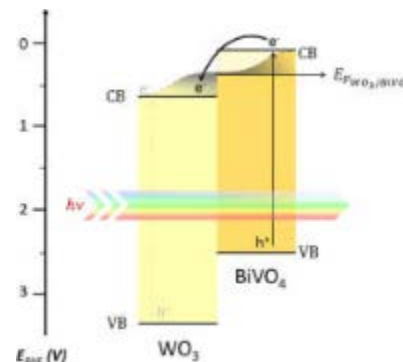


## Dynamics of photogenerated charge carriers in WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction photoanodes

Grigioni I.; Stamplecoskie K.G.; Selli E.; Kamat P.V.  
*J. Phys. Chem. C* **2015**, *119*, 20792–800.  
<http://dx.doi.org/10.1021/acs.jpcc.5b05128>

### Abstract

Bismuth vanadate (BiVO<sub>4</sub>) with a band gap of ~2.4 eV has emerged as one of the visible photocatalysts that can absorb light below 520 nm. The electron/ hole pairs that are generated following BiVO<sub>4</sub> band gap excitation are effective for water splitting, especially when BiVO<sub>4</sub> is combined with other metal oxides such as WO<sub>3</sub>. We report a solution processed method for designing transparent WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction electrodes and observe a synergistic effect on the photoelectrochemical activity of WO<sub>3</sub>/BiVO<sub>4</sub>, with the combined system performing dramatically better than either individual component. Using ultrafast transient absorption spectroscopy, we elucidated the electronic interaction between WO<sub>3</sub> and excited BiVO<sub>4</sub>. Moreover, the photocatalytic reduction of thionine by WO<sub>3</sub>/BiVO<sub>4</sub> as well as by each individual oxide component is used to track electron injection processes and determine the energetics of the studied systems. In the composite WO<sub>3</sub>/BiVO<sub>4</sub> film a shifted quasi-Fermi level results, due to electronic equilibration between the two materials. The better performance of WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction electrodes is thus a consequence of the electron injection from BiVO<sub>4</sub> into WO<sub>3</sub>, followed by back electron transfer from WO<sub>3</sub> to the holes in BiVO<sub>4</sub>.

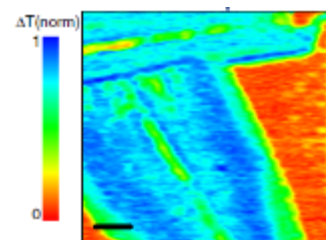


## Spatial and temporal imaging of long-range charge transport in perovskite thin films by ultrafast microscopy.

Guo Z.; Manser J.; Wan Y.; Kamat P.V.; Huang L.  
*Nat Commun* **2015**, *6*.  
<http://dx.doi.org/10.1038/ncomms8471>

### Abstract

Charge carrier diffusion coefficient and length are important physical parameters for semiconducting materials. Long-range carrier diffusion in perovskite thin films has led to remarkable solar cell efficiencies; however, spatial and temporal mechanisms of charge transport remain unclear. Here we present a direct measurement of carrier transport in space and in time by mapping carrier density with simultaneous ultrafast time resolution and B50-nm spatial precision in perovskite thin films using transient absorption microscopy. These results directly visualize long-range carrier transport of B220nm in 2 ns for solution-processed polycrystalline CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> thin films. Variations of the carrier diffusion coefficient at the mm length scale have been observed with values ranging between 0.05 and 0.08 cm<sup>2</sup> s<sup>-1</sup>. The spatially and temporally resolved measurements reported here underscore the importance of the local morphology and establish an important first step towards discerning the underlying transport properties of perovskite materials..



## Carbon nano hoops: excited singlet and triplet behavior of aza[8]cpp and 1, 15-diaza[8]cpp

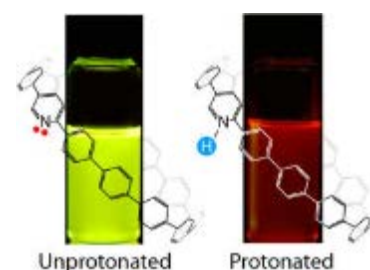
Hines D.A.; Darzi E.R.; Hirst E.; Jasti R.; Kamat P.V.

*J. Phys. Chem A* 2015, 119, 8083-9

<http://dx.doi.org/10.1021/acs.jpca.5b04404>

### Abstract

The excited state properties of two nitrogen-doped cycloparaphenylene molecules, or carbon nano hoops, have been studied using steady-state and time-resolved absorption and emission spectroscopies. Quantum yield of fluorescence ( $\Phi_f = 0.11$  and  $0.13$ ) and intersystem crossing ( $\Phi_{isc} = 0.45$  and  $0.32$ ) were determined for aza[8]CPP and 1,15-diaza[8]CPP, respectively. We also present the proton transfer reaction between trifluoroacetic acid and the nitrogen-doped nano hoops, which resulted in significant modifications to the steady-state absorption and emission spectra as well as the triplet-triplet absorption spectra. From fluorescence quenching data we determine the equilibrium constant for the proton transfer reaction between aza[8]CPP ( $K_{eq} = 1.39 \times 10^{-3}$ ) and 1,15-diaza[8]CPP ( $K_{eq} = 2.79 \times 10^{-3}$ ) confirming that 1,15-diaza[8]CPP is twice as likely to be protonated at a particular concentration of trifluoroacetic acid.



## Predicting the rate constant of electron tunneling reactions at the CdSe-TiO<sub>2</sub> interface.

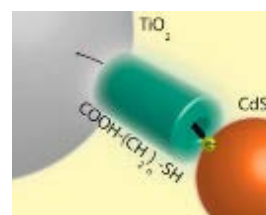
Hines D.A.; Forrest R.P.; Corcelli S.A.; Kamat P.V.

*J. Phy. Chem B* 2015, 119, 7439-46.

<http://dx.doi.org/10.1021/acs.jpca.5b04404>

### Abstract

Current interest in quantum dot solar cells (QDSCs) motivates an understanding of the electron transfer dynamics at the quantum dot (QD)-metal oxide (MO) interface. Employing transient absorption spectroscopy, we have monitored the electron transfer rate ( $k_{et}$ ) at this interface as a function of the bridge molecules that link QDs to TiO<sub>2</sub>. Using mercaptoacetic acid, 3-mercaptopropionic acid, 8-mercaptooctanoic acid, and 16-mercaptohexadecanoic acid, we observe an exponential attenuation of  $k_{et}$  with increasing linker length, and attribute this to the tunneling of the electron through the insulating linker molecule. We model the electron transfer reaction using both rectangular and trapezoidal barrier models that have been discussed in the literature. The one-electron reduction potential (equivalent to the lowest unoccupied molecular orbital) of each molecule as determined by cyclic voltammetry (CV) was used to estimate the effective barrier height presented by each ligand at the CdSe-TiO<sub>2</sub> interface. The electron transfer rate ( $k_{et}$ ) calculated for each CdSe-ligand-TiO<sub>2</sub> interface using both models showed the results in agreement with the experimentally determined trend. This demonstrates that electron transfer between CdSe and TiO<sub>2</sub> can be viewed as electron tunneling through a layer of linking molecules and provides a useful method for predicting electron transfer rate constants.



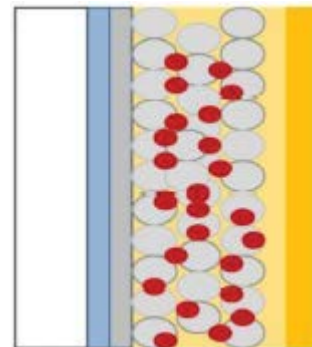
## Surface oxidation as a cause of high open-circuit voltage in CdSe ETA solar cells

Kirmayer S.; Edri E.; Hines D.A.; Klein-Kedem N.; Cohen H.; Niiitsoo O.; Pinkas I.; Kamat P.V.; Hodes G. *Adv. Mater. Interfaces* 2015, 1400346.

<http://dx.doi.org/10.1002/admi.201400346>

### Abstract

TiO<sub>2</sub>/CdSe/CuSCN extremely thin absorber (ETA) solar cells are found to give relatively high values of open-circuit voltage (>0.8 V) but low currents upon annealing the cadmium selenide (CdSe) in air (500 °C). Annealing in N<sub>2</sub> produces much lower photovoltages and slightly lower photocurrents. Band structure measurements show differences between the two annealing regimes that, however, appear to favor the N<sub>2</sub>-annealed CdSe. On the other hand, chemically resolved electrical measurements (CREM) of the cells reveal marked differences in photo-induced charge trapping, in particular at absorber grain boundaries of the air versus N<sub>2</sub>-annealed systems, correlated with the formation of Cd–O species at the CdSe surface. Using transient absorption and photovoltage decay, pronounced lifetime differences are also observed, in agreement with the strong suppression of charge recombination. The results point to a multiple role of grain surface-oxidation, which both impedes electron injection from the CdSe to the TiO<sub>2</sub>, but, much more significantly, enhances hole injection to the CuSCN via passivation of hole traps that act as efficient recombination centers.



## Evolution of organic-inorganic lead halide perovskite from iodoplumbate complexes

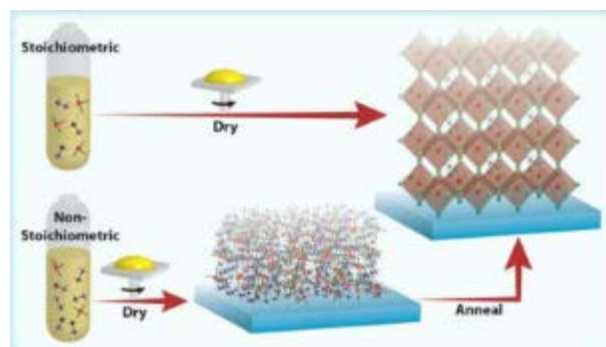
Manser J.; Reid B.; Kamat P.V.

*J. Phys. Chem. C* 2015, 119, 17065-73.

<http://dx.doi.org/10.1021/acs.jpcc.5b05898>

### Abstract

The optoelectronic properties of hybrid perovskites are a strong function of their physical structure, and understanding the fundamental steps involved in the formation of these films can aid in the optimization and rational design of devices with tailored properties. Here we investigate the structural and optical characteristics of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films prepared from solutions composed of stoichiometric and nonstoichiometric quantities of lead iodide and methylammonium iodide precursors. In the presence of excess organohalide salt, a precursor phase composed of various iodoplumbate complexes is stabilized. The complexes dominate the optical properties of as-deposited films. Upon thermal treatment, the iodoplumbate precursor phase gradually evolves into the final tetragonal perovskite structure. Employing transient absorption spectroscopy, we have succeeded in tracking this transformation and gain insight into the interplay between the solid-state precursor and perovskite phases at various stages of formation. Correlation between time-resolved spectroscopic data and structural character can aid in better defining the structure–property relationship of hybrid perovskite thin films.

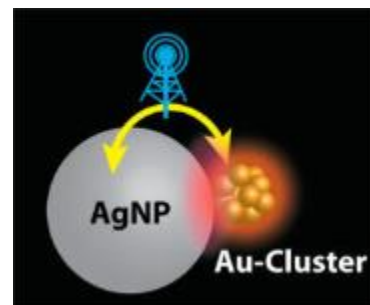


## Synergistic effects in the coupling of plasmon resonance of metal nanoparticles with excited gold clusters

Stamplecoskie K.G.; Kamat P.V.  
*J. Phys. Chem. Lett.* 2015, 6, 1870–5.  
<http://dx.doi.org/10.1021/acs.jpcllett.5b00665>

### Abstract

When molecules or clusters are within the proximity of metal particles, their electronic transitions can be drastically enhanced. We have now probed the off-resonance excitation of molecule-like, glutathione-capped gold clusters (Au-GSH) in the close proximity of larger (plasmonic) Au and Ag nanoparticles. The excited state absorption spectrum of Au-GSH\* is obtained with monophotonic excitation. The characteristic absorption of Au-GSH\* allows us to probe the influence of excited plasmonic nanoparticles coupled with the clusters. Although infrared (775 nm) laser pulses do not produce Au-GSH\*, the excited states of these clusters are formed when coupled with metal (Au, Ag) nanoparticles. Interestingly, the coupled excitation of Au-GSH/AgNP with 775 nm laser pulses also results in an enhanced field effect, as seen from increased plasmon response of the metal nanoparticles. Transient absorption measurements confirm the synergy between these two inherently different nanomaterials, causing them to display greater excitation features. Better understanding of metal cluster–metal nanoparticle interactions will have important implications in designing light harvesting systems, and optoelectronic devices.

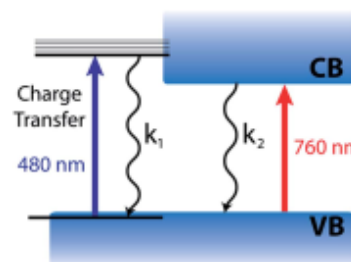


## Dual nature of excited state of organic-inorganic lead halide perovskites.

Stamplecoskie K.G.; Manser J.; Kamat P.V.  
*Energy Environ. Sci.* 2015, 8, 208-15.  
 DOI: 10.1002/cphc.201301189

### Abstract

The rapid increase in efficiency of methylammonium lead halide perovskite solar cells necessitates further investigation into the nature of perovskite absorption features and optical properties. Films obtained from the deposition of solutions containing lead halides and the  $\text{CH}_3\text{NH}_3^+$  organic cation is known to yield the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite structure upon annealing. In examining the precursor solution used in the processing of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solar cells, we find that  $\text{Pb}^{2+}$  readily forms plumbate complexes in the presence of excess iodide ions and exhibits characteristic absorption bands at 370 ( $\text{PbI}_3^-$ ) and 425 nm ( $\text{PbI}_4^{2-}$ ). Through comparative spectral analysis of the absorption features of charge transfer complexes in the solution phase and the final solid-state perovskite films, we are able to fully classify the absorption features in the excited state of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  across the transient absorption spectrum recorded following laser pulse excitation. In particular, we attribute the broad photoinduced absorption to a charge-transfer excited state, and show correlation between the photoinduced absorption and 480 nm bleach signals. These observations lead us to propose a band structure composed of two distinct transitions that is consistent with the various spectral features and kinetic behavior of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  excited state.



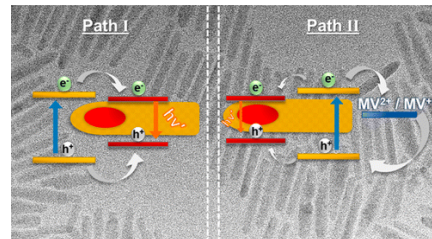
## CdSe/CdS Nanorod Photocatalysts: Tuning the Interfacial Charge Transfer Process through Shell Length.

Bridewell, V. L.; Alam, R.; Karwacki, C. J.; Kamat, P. V.,  
Chemistry of Materials 2015, 27, 5064-5071

<http://dx.doi.org/10.1021/acs.chemmater.5b01689>

### Abstract

CdSe/CdS core/shell semiconductor nanorods (NR) with rod-in-rod morphology offer new strategies for designing highly emissive nanostructures. The interplay between energetically matched semiconductors results in enhanced emission from the CdSe core. In order to further evaluate the cooperative role of these two semiconductors in a core/shell geometry, we have probed the photoinduced charge transfer between CdSe/CdS core/shell semiconductor NR and methyl viologen ( $MV^{2+}$ ). The quenching of the emission by the electron acceptor,  $MV^{2+}$ , as well as the production of electron transfer product  $MV^{\bullet+}$  depends on the aspect ratio ( $l/w$ ) of the NR thus pointing out the role of CdS shell in determining the overall photocatalytic efficiency. Transient absorption measurements show that the presence of  $MV^{2+}$  influences only the bleaching recovery of the CdS shell and not of the CdSe core recovery. Thus, optimization of shell aspect ratio plays a crucial role in maximizing the efficiency of this photocatalytic system.



## Evolution of Chemical Composition, Morphology, and Photovoltaic Efficiency of $CH_3NH_3PbI_3$ Perovskite under Ambient Conditions

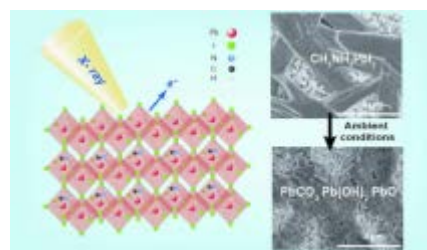
Huang, W.; Manser, J. S.; Kamat, P. V.; Ptasinska, S.,

Chemistry of Materials 2015. ASAP DOI: 10.1021/acs.chemmater.5b04122

<http://dx.doi.org/10.1021/acs.chemmater.5b04122>

### Abstract

The surface composition and morphology of  $CH_3NH_3PbI_3$  perovskite films stored for several days under ambient conditions were investigated by XPS, SEM, and XRD techniques. Chemical analysis revealed the loss of  $CH_3NH_3^+$  and I<sup>-</sup> species from  $CH_3NH_3PbI_3$  and its subsequent decomposition into lead carbonate, lead hydroxide, and lead oxide. After long-term storage under ambient conditions, morphological analysis revealed the transformation of randomly distributed defects and cracks, initially present in the densely packed crystalline structure, into relatively small grains. In contrast to  $PbI_2$  powder,  $CH_3NH_3PbI_3$  exhibits a different degradation trend under ambient conditions. Therefore, we propose a plausible  $CH_3NH_3PbI_3$  decomposition pathway that explains the changes in the chemical composition of  $CH_3NH_3PbI_3$  under ambient conditions. In addition, films stored under such conditions were incorporated into photovoltaic cells and their performances were examined. The chemical changes in the decomposed films were found to cause a significant decrease in the photovoltaic efficiency of  $CH_3NH_3PbI_3$ .



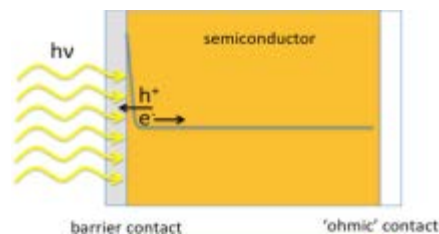


## Understanding the Implication of Carrier Diffusion Length in Photovoltaic Cells.

Hodes, G.; Kamat, P. V.,  
*J. Phys. Chem. Lett.* 2015, 6, 4090-4092 (Viewpoint)  
<http://dx.doi.org/10.1021/acs.jpcllett.5b02052>

### Abstract

The purpose of this Viewpoint is to dispel a commonly held misconception when comparing diffusion lengths and discuss how variation in the measuring techniques can bring about differences in the measured values..

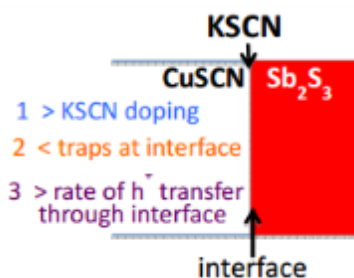


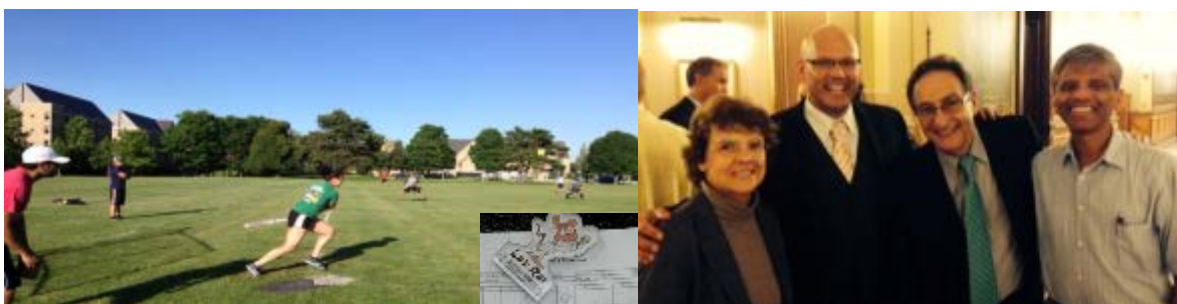
## Band Diagram and Effects of the KSCN Treatment in $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{CuSCN}$ ETA cells.

Itzhaik, Y.; Bendikov, T.; Hines, D. A.; Kamat, P. V.; Cohen, H.; Hodes, G.,  
*The Journal of Physical Chemistry C* 2015 ASAP  
 DOI:10.1021/acs.jpcc.5b09233  
<http://dx.doi.org/10.1021/acs.jpcc.5b09233>

### Abstract

Thiocyanate ion treatment, usually either LiSCN or KSCN, of the absorbing semiconductor before deposition of a CuSCN hole conducting layer is known to improve the performance of extremely thin absorber (ETA) solar cells by reducing the cell resistivity. However, in spite of several hypotheses, the mechanism behind this treatment outcome remains elusive. In this study, the interface between  $\text{Sb}_2\text{S}_3$  and CuSCN in an ETA cell is now investigated with surface spectroscopy and transient absorption spectroscopy to establish the mechanistic aspects of the KSCN treatment and role it plays in improving the photovoltaic performance. The prominent factors that dictate the cell performance are (a) doping the interfacial CuSCN and thus preventing the formation of a sub- $\mu\text{m}$  depleted layer and (b) passivating charge traps at the  $\text{Sb}_2\text{S}_3$  surface, which increases the rate of hole transfer from the absorber to the hole conductor. In addition we further show that the treatment works just as well in improving photovoltaic performance when carried out after CuSCN deposition (post-treatment).





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Science Sciences

