Annual Research Summary

January - December 2014

Kamatlab Research
University of Notre Dame

Prashant V. Kamat

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Research Group

Graduate Students
Sachi Krishnamurthy (Chemistry)
James Radich (CBE)
Douglas Hines (Chemistry)
Jeff Christians (CBE)
Joseph Manser (CBE)
Yong-Siou Chen (Chemistry)
Jacob Hoffman (Chemistry)
Danilo JaraQuinteros (Chemistry)
Seogjoon Yoon (Chemistry)
Victoria Bridewell (Chemistry)
Steven Kobosko (CBE)

Incoming Students Christian Telavera (Chemistry)
Sebastian Snowberger (CBE)

Visiting Student: Ivan Grigioni

Undergraduate Students

Spring 2014
Tim Siegler (CBE)
Jack Olding (CBE)
Mia Epler (CBE)
Anthony Krenselewski (CBE)
Andrew Niels (CBE)
Grace Meikle (Physics)

Summer 2014
Abigail Swint, ND Nano Fellowship
Pierre Miranda, iSURE Fellowship
Barry Reid Naughton Fellowship
John.J.Johnstone, URAP Fellowship
Katherine.A.Andreasen URAP Fellowship

Fall 2014
Andrew Niels (CBE)
Jack Olding (Physics)
Abigail Swint (CBE)
Rose Bernier (CBE)

Summer RET: Mark Wilson (RET)

Postdoctoral Research Associate
Christopher Tuinenga (March 2014 – present)
Hyunbong Choi (Nov 2010 - Feb 2014)
Rebaka Alam (Aug 2013 – present)
Kevin Stamplecoskie (May 2013 – present)

Visiting Scientists Julie Peller (IUN)
Roxana Nicolaescu (Serim Corporation)
Santosh Haram (Fulbright Scholar)

Graduation/Fellowships/Recognition

Sachi Krishnamurthy Department of Chemistry, University of Notre Dame, April 2014
Graphene-Based Assemblies: Electron Transfer Processes and Energy Conversion Applications
James Radich Dept. of Chemical & Biomolecular Eng, University of Notre Dame, April 2014 .
Reduced Graphene Oxide-Based Nanoassembiles for Energy Storage

Awards/Honors

PVK: University of Notre Dame Annual Research Award (Presented by the President, U. of Notre Dame)
Most cited Chemist by Thomson Reuters
Elected to Indian National Science Academy as Preavasi Fellow

Group: James Radich, Bayer Fellowship
Rabeka Alam, Postdoc to Faculty Workshop sponsored by the ACS
Jeff Christians, Eilers Fellowship, Bayer Fellowship
Abigail Swint, ND Nano Fellowship
Pierre Miranda, iSURE Fellowship
Barry Reid Naughton Fellowship
Tim Siegler, Statt Fellowship
Danilo Jara to attend The 6th International Conference on Excited State Processes in Electronic and Bionanomaterials, Santa Fe, New Mexico, Jeff Christians, via the GSU Professional Development Award and the GSU CPGt, to attend the 2014 MRS Spring Meeting & Exhibit in San Francisco CA, and Joseph Manser to attend KAUST Solar Future 2014 meeting in Thuwal, Saudi Arabia

Professional Activities

- **Deputy Editor,** Journal of Physical Chemistry Letters (2009-present)
- **Editorial Advisory Boards**
  Langmuir (2000-present)
  Research on Chemical Intermediates (2003-present)
  Electrochemical and Solid State Letters (September 2006-present)
  Applied Electrochemistry (2009-present)
- **ND committees**
  Member of the COS-COS (2008-present)
  Member, SEI Leadership Team, 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, 225th ECS Meeting Orlando, May, 2014

Invited Seminar/Colloquium

University of California at Berkeley October 17, 2014
Quantum Dots and Organic-Metal Halide Perovskites for Transformative Photovoltaics

University of Florida, Gainesville, September 16, 2014
Transformative Photovoltaics with Quantum Dots and Organic-Metal Halide Perovskites

Marquette University, Milwaukee, September 12, 2014
Quantum Dots and Organic-Metal Halide Perovskites for Next Generation Solar Cells

University of California, Riverside May 19, 2014
Emergence of Quantum Dots and Organometal Halide Perovskites in Thin Film Photovoltaics.

Case Western University, May 2, 2014
Quantum Dots and Organometal Halide Perovskites for Thin Film Photovoltaics

Temple University April 3, 2014
Making Electrons Cheaper. Quantum Dots and Organometal Halide Perovskites for Next Generation Solar Cells

University of North Carolina at Chapel Hill April 2, 2014
Light Energy Conversion with Semiconductor Quantum Dots and Organometal Halide Perovskites

University of Colorado, Boulder April 22, 2014
Thin Film Photovoltaics with Quantum Dots and Organometal Halide Perovskites

Conference Presentations (2014)

Schulich Graduate Students Chemistry Symposium, Haifa, Israel, Dec 11, 2014
Next Generation Photovoltaics with Quantum Dots and Organic Metal Halide Perovskites
Prashant V. Kamat (Plenary Speaker)

MRS Fall Meeting Boston, Nov 30- Dec 5, 2014
Insights into the Charge Carrier Dynamics of $CH_3NH_3PbI_3$ *Films and Evolution of Perovskite Structure*
J. Manser, Jeffrey Christians, K. Stamplecoskie, P. V. Kamat
Beyond Plasmons Thiolated Gold Clusters Exhibit Photosensitizing Property in the Visible
P.V. Kamat (Invited Speaker)

Nanocordoba 2014, Cordoba, Argentina October 22-24, 2014
Designing Next Generation Solar Cells with Quantum Dots and Organometal Halide Perovskite
Prashant V. Kamat (Invited Speaker)

CB Filtration Strategies and Multifunctional Materials Working Group. Army Research Office, Arlington, VA, on 21-22 October 2014.
Graphene Oxide Based Multifunctional Catalyst Mat for Simultaneous Sensing and Degradation of Nitroaromatics
P. V. Kamat, Rabeka Alam, and Ian Lightcap (Invited)

5th Annual Scialog Conference on Solar Energy Conversion, Tucson, Arizona, October 14-17, 2014
Organic Metal Halide Peroviskite Photovoltaics. Beyond the Hype
P. V. Kamat (KEYNOTE Speaker)

Indo-US Nanomaterials for Energy Workshop 17-18 Sept Purdue, West Lafayette, September 17- 18, 2014
Emergence of Quantum Dot and Organic Metal Halide Photovoltaics.
P. V. Kamat and Jeffry Christians (Invited)

ECOSS30 –European Conference on Surface Science August 31-Sept 5
Quantum Dot and Organometal Halide Perovskite Solar Cells. Interfacial Charge Transfer Processes in Thin Film Photovoltaics
P. V. Kamat, Jeffry Christians, and Joseph Manser (Invited)

248th meeting of the American Chemical Society, August 10-14, San Francisco
Thiolated metal clusters as new class of photosensitizers in light energy conversion
P. V Kamat, Yong Siou Chen, Kevin Stamplecoskie.
How stable is graphene oxide for photocatalytic applications? Reactivity toward hydroxyl radicals
J. Radich, P. V Kamat. (Invited)
Building BRICK by BRICK sometimes works: How ACS Editors' participation in ACS on Campus has brought publishing best practices to thousands of authors in BRICKS countries, an overview of challenges and successes
S. Sara Rouhi, Kirk S. Schanze, Prashant V. Kamat. (Invited)
Hole transfer limitations in thin film solid state solar cells
P. V Kamat, Jeffrey Christians, Joseph Manser.

20th International Conference on Photochemical Conversion and Storage of Solar Energy, Berlin, July 27 – August 1, 2014
Hole Transfer Processes in Quantum Dot and Organometalhalide Solar Cells”
P. V. Kamat (Plenary)

Sungkyun International Solar Forum, Seoul July 3-5, 2014
Quantum-Dot and Organometal halide Perovskite Solar Cells. New Insights into the Hole Transfer Processes
J. Christians, J. Manser and P. V. Kamat (Invited)

36th DOE Solar Photochemistry Meeting, Annapolis, June 1-4, 2014
Visible Light Induced Electron Transfer with Thiolated Gold Clusters
Y.-S. Chen, K. Stamplecoskie and P. V. Kamat (Invited)

2014 MRS Spring Meeting, San Francisco, April 21-25, 2014
San Francisco Semiconductor Quantum Dot and Perovskite Photovoltaics: Tracking the Hole Transport in Thin Film Solid State Solar Cells
P. V. Kamat, Jeffrey Christians.

247th meeting of the American Chemical Society, March 16-20, Dallas,
Nanomaterial assemblies with energy and environmental implications
P. V Kamat
Catching the photovoltaic power of quantum dots and organometal halide perovskites
P. V Kamat, D.Jara-Quinteros, Jeffrey Christians. (Invited)

Presentation by Students and Postdocs

2014 AIChE Annual Meeting, November 16-21st, Atlanta, GA
Organometal Halide Perovskite Solar Cells Featuring Inorganic Hole Conductors
Jeffrey A Christians, Prashant V Kamat.

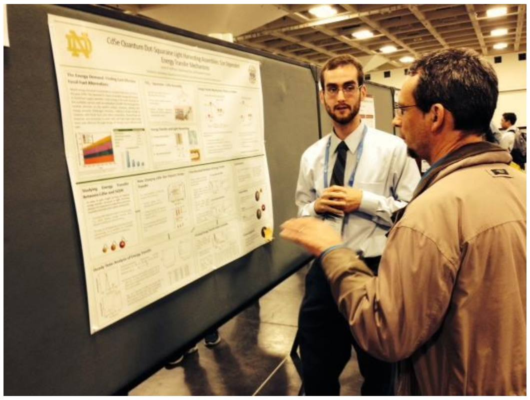
2014 AIChE Annual Meeting, November 16-21st, Atlanta, GA
Charge Carrier Dynamics in Thin Film Solid-State Solar Cells
Jeffrey A Christians, Prashant V Kamat.

2014 Solar Future Meeting, November 8-11th, Thuwal, Saudi Arabia
Elucidation of Excited State Species and Ultrafast Light-Induced Processes in Lead Halide Hybrid Perovskites
Joseph S. Manser, Kevin G. Stamplecoskie, Prashant V. Kamat

248th Meeting of the American Chemical Society, August 10-14th, San Francisco, CA
Surface modification and hole stabilization: Investigating the role of Na2S in liquid junction photovoltaic
Douglas A Hines, Prashant V Kamat.

248th Meeting of the American Chemical Society, August 10-14th, San Francisco, CA
Detection and degradation of low level contaminants using hybrid graphene based sensors
Rabeka Alam, Ian V Lightcap, Prashant V Kamat.

248th Meeting of the American Chemical Society, August 10-14th, San Francisco, CA
CdSe quantum dot-squaraine light harvesting assemblies: Size dependent energy transfer mechanisms
Jacob B Hoffman, Hyunbong Choi, Prashant V Kamat.



Summer Undergraduate Research Symposium, August 1st, Notre Dame, IN
Stability of the Solar Cell Absorber Methylammonium Lead Iodide Perovskite During Exposure in Humidified Air
Pierre A Miranda Herrera, Jeffrey A Christians, Prashant V Kamat.

Summer Undergraduate Research Symposium, August 1st, Notre Dame, IN
Photovoltaics: Cu2S Synthesis, Solar Cell Efficiencies, and Applications
Mark Wilson, Jeffrey A Christians, Prashant V Kamat.

Summer Undergraduate Research Symposium, August 1st, Notre Dame, IN
Structural and Crystallization Characteristics of Organic-Inorganic Perovskite Materials
Barry Reid, Joseph S. Manser, Prashant V. Kamat

97th Canadian Chemistry Conference, Vancouver, Canada, June 1-5th, 2014
Size Dependent Excited State Properties of Nano-Gold: From Plasmons to Molecule-Like Transitions and their Applications in Light Harvesting
Kevin Stamplecoskie, Prashant V. Kamat

IEEE Mini Symposium, March 14th, Notre Dame, IN
Charge Carrier Dynamics in Light-Harvesting Hybrid Perovskites
Joseph S. Manser, Prashant V. Kamat

6th Annual AIChE Midwest Regional Conference, March 10-11th, Chicago, IL
Determination of the Limiting Mechanism of Hole Transfer in Sb_2S_3/CuSCN Solid-State Solar Cells
Jeffrey A Christians, David T Leighton Jr., Prashant V Kamat.

6th Annual AIChE Midwest Regional Conference, March 10-11th, Chicago, IL
Insight into the Nature of Charge Carriers in Hybrid Perovskites for Light-Harvesting Applications
Joseph S. Manser, Prashant V. Kamat

6th Graduate Student Union Research Symposium, February 27th, Notre Dame, IN
Improved Hole Conductivity and Lower Cost for Perovskite Solar Cells with Copper Iodide
Jeffrey A Christians, Prashant V Kamat.

Summer Undergraduate Research Symposium, August 1st, Notre Dame, IN
Explorations into the Adsorption of Nitro Molecules to Graphene Oxide in Solution for the Design of Smart Materials
John J. Johnstone, Rabeka Alam, Prashant V Kamat.

Summer Undergraduate Research Symposium, August 1st, Notre Dame, IN
Creating Multifunctional Semiconductor-Graphene-Metal Smart Films on Flexible Substrates for the Detection of Nitroaromatic and Organophosphate Compounds
Katherine Andreasen, Rabeka Alam, Prashant V Kamat.

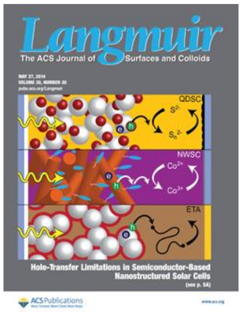
Midwest Imaging and Microanalysis Workshop at Notre Dame, May 19st, Notre Dame, IN
Visible Light-Driven Hydrogen Production from Neutral Water Using Glutathione-Capped Gold Nanoclusters as Photosensitizers
Yong-Siou Chen, Prashant V Kamat.

The 5th Midwest Graduate Research Symposium, March 29th, Toledo, OH
Glutathione-Protected Gold Cluster: A Newly Discovered Visible Light Active Photosensitizer for Hydrogen Generation
Yong-Siou Chen, Prashant V Kamat.

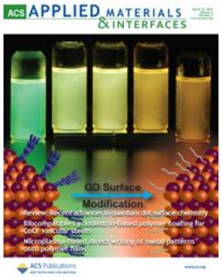
The 6th International Conference on Excited State Processes in Electronic and Bio nanomaterials, June 9-12th, Santa Fe, New Mexico.
Light Energy Conversion with Size Quantized $CuInS_2$ Pyramidal Nanoparticles.
Danilo H. Jara, Prashant V. Kamat.

Research Papers

1. *Surface Oxidation as a Cause of High Open-Circuit Voltage in CdSe ETA Solar Cells.* Kirmayer, S; Edri, E.; Hines, D.; Klein-Kedem, N.; Cohen, H.; Niitsoo, O.; Pinkas, I.; Kamat, P. V.; Hodes, G. Adv. Mater. Interf. 2014, ASAP.
2. *Size-Dependent Photovoltaic Performance of CuInS$_2$ Quantum Dots Sensitized Solar Cells* Jara, D. H.;Yoon, S.; Stamplecoskie, K. G.; Kamat, P. V. Chem. Mater. 2014, ASAP.
3. *Dual Nature of the Excited State in Organic-Inorganic Lead Halide Perovskites* Stamplecoskie, K. G.; Manser, J. S.; Kamat, P. V. Energy Environ. Sci. 2014, ASAP.



4. *The Origin of Catalytic Effect in the Reduction of CO$_2$ at Nanostructured TiO$_2$ Films* Ramesha, G. K.; Brennecke, J. F.; Kamat, P. V. *ACS Catal.* 2014, 4 (9), 3249–3254.
5. *Band Filling with Free Charge Carriers in Organometal Halide Perovskites* Manser, J. S.; Kamat, P. V. *Nat. Photon.* 2014, 8, 737–743.
6. *Is Graphene a Stable Platform for Photocatalysis? Mineralization of Reduced Graphene Oxide with UV-Irradiated TiO$_2$ Nanoparticles* Radich J. G.; Krenselewski, A.; Zhu, J.; Kamat, P. V. *Chem. Mater.* 2014, 26 (15), 4662–4668.
7. *Size-Dependent Excited State Behavior of Glutathione-Capped Gold Clusters and Their Light-Harvesting Capacity* Stamplecoskie, K. G.; Kamat, P. V. *J. Am. Chem. Soc.* 2014, 136 (31), 11093–11099.
8. *Size-Dependent Energy Transfer Pathways in CdSe Quantum Dot–Squaraine Light-Harvesting Assemblies: Förster versus Dexter* Hoffman, J. B.; Choi, H.; Kamat, P. V. *J. Phys. Chem. C* 2014, 118 (32), 18453–18461.
9. *Sense and Shoot: Simultaneous Detection and Degradation of Low Level Contaminants using Graphene Based Smart Material Assembly* Alam, R.; Lightcap, I. V.; Karwacki, C. J.; Kamat, P. V. *ACS Nano* 2014, 8 (7), 7272–7278.
10. *Switching the Reaction Course of Electrochemical CO$_2$ Reduction with Ionic Liquids* Sun, L.; Ramesha, G. K.; Kamat, P. V.; Brennecke, J. F. *Langmuir* 2014, 30 (21), 6302–6308.
11. *How Does a SILAR CdSe Film Grow? Tuning the Deposition Steps to Suppress Interfacial Charge Recombination in Solar Cells* Becker, M. A.; Radich, J. G.; Bunker, B. A.; Kamat, P. V. *J. Phys Chem. Lett.* 2014, 5, 1575–1582.



12. *Glutathione Capped Gold Nanoclusters as Photosensitizers. Visible Light Induced Hydrogen Generation in Neutral Water* Chen, Y.-S.; Kamat, P. V. *J. Am. Chem. Soc.* 2014, 136 (16), 6075–6082.
13. *CdSe-Graphene Oxide Light Harvesting Assembly. Size Dependent Electron Transfer and Light Energy Conversion Aspects* Krishnamurthy, S.; Kamat, P. V. *ChemPhysChem* 2014, 15, 2129–2135.
14. *Quantum Dot Solar Cells. Hole Transfer as a Limiting Factor in Boosting Photoconversion Efficiency* Kamat, P. V.; Christians, J. A.; Radich, J. G. *Langmuir* 30 (20), 5716-5725 (Feature Article).
15. *CdSeS Nanowires. Compositionally Controlled Band Gap and Exciton Dynamics* Kim J.-P.; Christians, J. A.; Choi, H.; Krishnamurthy, S.; Kamat, P. V. *J. Phys. Chem. Lett.* 5, 1103-1109.
16. *Carbon Nanohoops: Excited Singlet and Triplet Behavior of [9]- and [12]-cycloparaphenylene* Hines, D. A.; Darzi, E. R.; Jasti, R.; Kamat, P. V. *J. Phys. Chem. A* 2014, 118 (9), 1595–1600.

17. *Charge Transfer Mediation Through Cu_xS. The Hole Story of CdSe in Polysulfide*
    Radich, J.G.; Peeples, N. R.; Santra, P. K.; Kamat, P. V. *J. Phys. Chem. C* 2014, 118 (30), 16463–16471.
18. *Recent Advances in Quantum Dot Surface Chemistry*
    Hines, D. A.; Kamat, P. V. *ACS Appl. Mater. Interfaces* 2014, 6 (5), 3041–3057.
19. *Driving Charge Separation for Hybrid Solar Cells: Photo-induced Hole Transfer in Conjugated Copolymer and Semiconductor Nanoparticle Assemblies*
    Wang, Y.; Liu, K.; Mikherjee, P.; Hines, D. A.; Santra, P.; Shen, H. Y.; Kamat, P. V.; Waldeck, D. H. *Phys. Chem. Chem. Phys.* 2014, 16, 5066-5070.
20. *Rate Limiting Interfacial Hole Transfer in Sb_2S_3 Solid-State Solar Cells*
    Christians, J. A.; Leighton Jr., D. T.; Kamat, P. V. *Energy and Environ. Sci.* 2014, 7, 1148-1158.
21. *Kinetics and Mechanism of $^{\bullet}OH$ Mediated Degradation of Dimethyl Phthalate in Aqueous Solution: Experimental and Theoretical Studies*
    An T.; Gao, Y.; Li, G.; Kamat, P. V.; Peller, J.; Joyce, M. V. *Environ. Sci. Technol.* 2014, 48 (1), 641–648.
22. *Excited State Behavior of Luminescent Glutathione Protected Gold Clusters*
    Stamplecoskie, K. G.; Chen, Y.-S.; Kamat, P. V. *J. Phys. Chem. C* 2014, 118 (2), 1370-1376.
23. *An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide*
    Christians, J. A.; Fung, R. C. A.; Kamat, P. V. *J. Am. Chem. Soc.* 2014, 136 (2), 758-764.
24. *Direct Observation of Spatially Heterogeneous Single-Layer Graphene Oxide Reduction Kinetics*
    McDonald, M. P.; Eltom, A.; Vietmeyer, F.; Thapa, J.; Morozov, Y. V.; Sokolov, D. A.; Hodak, J. H.; Vinodgopal, K.; Kamat, P. V.; Kuno, M. *Nano Lett.* 2013, 13 (12), 5777-5784.
25. *Sequentially Layered CdSe/CdS Nanowire Architecture for Improved Nanowire Solar Cell Performance*
    Choi, H.; Radich, J. G.; Kamat, P. V. *J. Phys. Chem. C* 2013, 118 (1), 206–213.
26. *CdS Nanowire Solar Cells: Dual Role of Squaraine Dye as a Sensitizer and a Hole Transporter*
    Choi, H.; Kamat, P. V. *J. Phys. Chem. Lett.* 2013, 4, 3983–3991.

Independent Publication by Postdoc/Grad Students

27. Role of Mn^{2+} in Doped Quantum Dot Solar Cell. Santra, P. K.; Chen, Y.-S., *Electrochim. Acta* **2014,** *146*, 654-658.
28. Stamplecoskie, K. G.; Manser, J. S., Facile SILAR Approach to Air-Stable Naked Silver and Gold Nanoparticles Supported by Alumina. *ACS Appl. Mater Interfac.* **2014,** *6*, 17489-17495.

Editorials

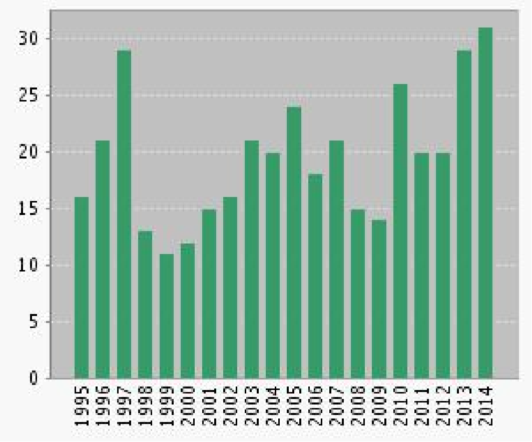
Kamat, P. V., Emergence of New Materials for Light–Energy Conversion: Perovskites, Metal Clusters, and 2-D Hybrids. J. Phys. Chem. Lett. 2014, 5, 4167-4168.
Mastering the Art of Scientific Publication: Twenty Papers with 20/20 Vision on Publishing
Kamat, P. V.; Buriak, J. M.; Schatz, G. C.; Weiss, P. S. J. Phys. Chem. Lett. 2014, 5 (20), 3519-3521.
What's in a Name?
Kamat, P. V.; Schatz, G. C. J. Phys. Chem. Lett. 2014, 5 (16), 2879–2879.
Best practices for reporting on heterogeneous photocatalysis
Buriak, J. M.; Kamat, P. V.; Schanze, K. S. ACS Appl. Mater. Interfaces 2014, 6 (15), 11815–11816.
Why Did You Accept My Paper?
Kamat, P. V.; Prezhdo O. V.; Shea, J.-E.;Scholes, G.; Zaera, F.; Zwier, T. S.; Schatz, G. C.
J. Phys.Chem. Lett. 2014, 5 (14), 2443-2443.

Graphical Excellence
Kamat, P. V.; Hartland, G. V.; Schatz, G. C. J. Phys. Chem. Lett. 2014, 5 (12), 2118-2120.
Cite with a Sight
Kamat, P. V.; Schatz, G. C. J. Phys. Chem. Lett. 2014, 5 (7), 1241–1242.
Organometal Halide Perovskites for Transformative Photovoltaics
Kamat, P. V. J. Am. Chem. Soc. 2014, 136 (10), 3713–3714.
Overcoming the Myths of the Review Process and Getting Your Paper Ready for Publication
Kamat, P. V.; Scholes, G.; Prezhdo O. V.; Zaera, F.; Zwier, T. S.; Schatz, G. C.
J. Phys. Chem. Lett. 2014, 5, 896-899.
The Increasing Impact of Multimedia and Social Media in Scientific Publications
Kamat, P. V.; Schatz, G. C. J. Phys. Chem. Lett. 2014, 1, 233-234.
Evolution of Perovskite Photovoltaics and Decrease in Energy Payback Time
Kamat, P. V. J. Phys. Chem. Lett. 2013, 4, 3733-3734.

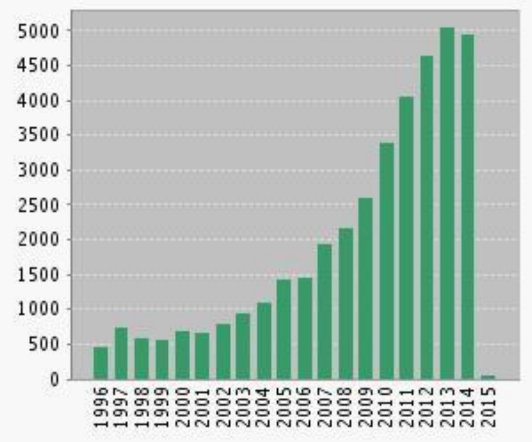
Publication Analysis

Source: Thomson ISI , Dec 18, 2014

Publications



Citations



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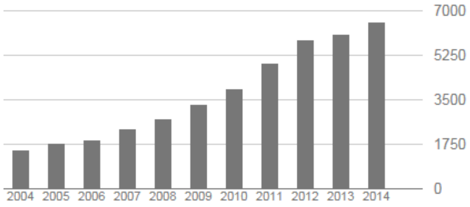
Sum of the Times Cited : 40300+

Average Citations per Item : 76

h-index : **107**

Google scholar



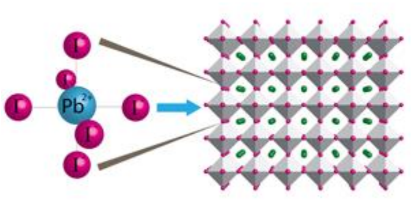
Citation indices

	All	Since 2008
Citations	48818	20949
h-index	**117**	86
i10-index	372	290

2013 Impact Factor of Kamatlab Papers = (2013 Citations of 2011-12 papers)/(No. of 2011-12 papers)
= 708 citations/28 papers
= **25.28**

Dual Nature of the Excited State in Organic-Inorganic Lead Halide Perovskites

Stamplecoskie, K. G.; Manser, J. S.; Kamat, P. V.
Energy Environ. Sci. **2015**, *8*, 208 - 215
DOI: 10.1039/C4EE02988G

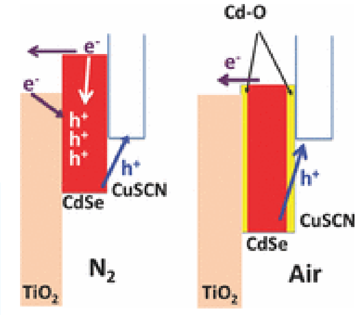


Abstract

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 $CH_3NH_3^+$ organic cation is known to yield the $CH_3NH_3PbI_3$ perovskite structure upon annealing. In examining the precursor solution used in the processing of $CH_3NH_3PbI_3$ solar cells, we find that Pb_2^+ readily forms plumbate complexes in the presence of excess iodide ions and exhibits characteristic absorption bands at 370 (PbI_3^-) and 425 nm (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 $CH_3NH_3PbI_3$ 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 $CH_3NH_3PbI_3$ excited state. Characterization of this unique dual excited state nature provides further insight into the optoelectronic behavior of hybrid lead halide perovskite films and thus aids in elucidating their exceptional photovoltaic properties.

Surface Oxidation as a Cause of High Open-Circuit Voltage in CdSe ETA Solar Cells

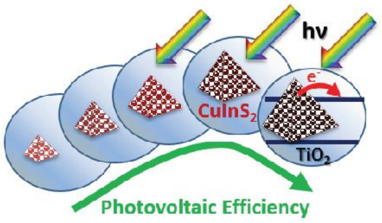
Kirmayer, S; Edri, E.; Hines, D.; Klein-Kedem, N.; Cohen, H.; Niitsoo, O.; Pinkas, I.; Kamat, P. V.; Hodes, G.
Adv. Mater. Interf. 2014, Art No. 1400346
DOI: 10.1002/admi.201400346



Abstract

Upon annealing in air, extremely thin absorber solar cells based on CdSe--sensitized titania show relatively high values of open-circuit voltage but low currents. This stems from the fact that while oxidation impedes electron injection from the CdSe to the TiO_2, the balance between hole extraction and recombination is improved in favor of the former.

Size-Dependent PV Performance of $CuInS_2$ Quantum Dots Sensitized Solar Cells

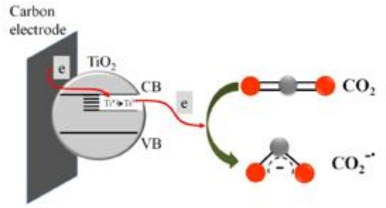


Jara, D. H.;Yoon, S.; Stamplecoskie, K. G.; Kamat, P. V.
Chem. Mater. 2014, ASAP.
DOI: 10.1021/cm5040886

Abstract

The optical and electronic properties of quantum dots (QDs) which are drastically affected by their size have major impact on their performance in devices like solar cells. We now report the size dependent solar cell performance for $CuInS_2$ QDs capped with 1-dodecanethiol. Pyramidal shaped $CuInS_2$ QDs with diameter between 2.9 nm and 5.3 nm have been synthesized and assembled on mesoscopic TiO_2 films by electrophoretic deposition. Time resolved emission and transient absorption spectroscopy measurements have ascertained the role of internal and surface defects in determining the solar cell performance. An increase in power conversion efficiency (PCE) was observed with increasing size of QDs, with maximum values of 2.14 and 2.51% for 3.9 and 4.3 nm size particles, respectively. The drop in PCE observed for larger QDs (5.3 nm) is attributed to decreased charge separation following bandgap excitation. Since the origin of photocurrent generation in $CuInS_2$ QDSC arises from the defect dominated charge carriers it offers the opportunity to further improve the efficiency by controlling these defect concentrations.

The Origin of Catalytic Effect in the Reduction of CO_2 at Nanostructured TiO_2 Films

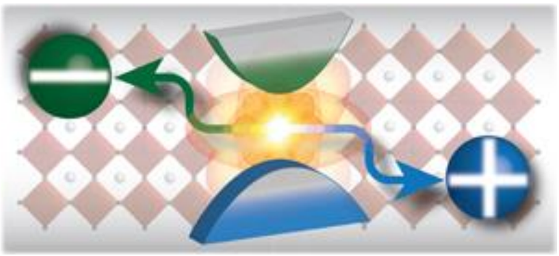


Ramesha, G. K.; Brennecke, J. F.; Kamat, P. V.
ACS Catal. 2014, 4 (9), 3249–3254.
DOI:10.1021/cs500730w

Abstract

Electrocatalytic activity of mesoscopic TiO_2 films towards the reduction of CO_2 is probed by depositing a nanostructured film on a glassy carbon electrode. The one-electron reduction of CO_2 in acetonitrile seen at an onset potential of -1.1 V (vs. NHE) is ~0.5 V lower than the one observed with a glassy carbon electrode. The electrocatalytic role of TiO_2 is elucidated through spectroelectrochemistry and product analysis. Ti^{3+} species formed when TiO_2 film is subjected to negative potentials have been identified as active reduction sites. Binding of CO_2 to catalytically active Ti^{3+} followed by the electron transfer facilitates the initial one-electron reduction process. Methanol was the primary product when the reduction was carried out in wet acetonitrile.

Band Filling with Free Charge Carriers in Organometal Halide Perovskites



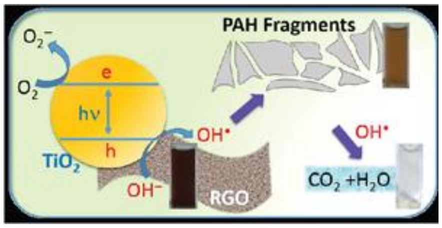
Manser, J. S.; Kamat, P. V.
Nat. Photon. 2014, 8, 737–743.
DOI: **10.1038/nphoton.2014.171**

Abstract

The unique and promising properties of semiconducting organometal halide perovskites have brought these materials to the forefront of solar energy research. Here, we present new insights into the excited-state properties of $CH_{3>}NH_3PbI_3$ thin films through femtosecond transient absorption spectroscopy measurements. The photoinduced bleach recovery at 760 nm reveals that band-edge recombination follows second-order kinetics, indicating that the dominant relaxation pathway is via recombination of free electrons and holes. Additionally, charge accumulation in the perovskite films leads to an increase in the intrinsic bandgap that follows the Burstein–Moss band filling model. Both the recombination mechanism and the band-edge shift are studied as a function of the photogenerated carrier density and serve to elucidate the behaviour of charge carriers in hybrid perovskites. These results offer insights into the intrinsic photophysics of semiconducting organometal halide perovskites with direct implications for photovoltaic and optoelectronic applications.

Is Graphene a Stable Platform for Photocatalysis? Mineralization of Reduced Graphene Oxide with UV-Irradiated TiO_2 Nanoparticles

Radich J. G.; Krenselewski, A.; Zhu, J.; Kamat, P. V.
Chem. Mater. 2014, 26 (15), 4662–4668
DOI: 10.1021/cm5026552

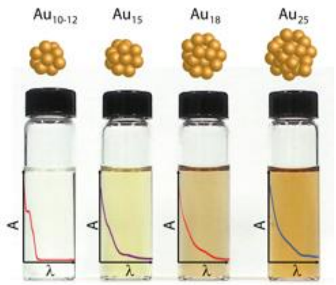


Abstract

The recent thrust in utilizing reduced graphene oxide (RGO) as a support for nanostructured catalyst particles has led to the claims of improved efficiency in solar cells, fuel cells, and photocatalytic degradation of pollutants. Specifically, the robust TiO_2 system is often coupled with RGO to improve charge separation and facilitate redox reactions. Here we probe the stability of RGO in the presence of UV-excited TiO_2 in aqueous media and establish its reactivity towards $OH^{\bullet}$ radicals, a primary oxidant generated at the TiO_2 surface. By probing changes in absorption, morphology and total organic carbon content (TOC) we conclusively demonstrate the vulnerability of RGO towards $OH^{\bullet}$ attack and raise the concern of its use in many applications where $OH^{\bullet}$ are likely to be formed. On the other hand, the $OH^{\bullet}$ radical-mediated mineralization could also enable new approaches in tackling environmental remediation of nanocarbons such as RGO, carbon nanotubes, and fullerenes.

Size-Dependent Excited State Behavior of Glutathione-Capped Gold Clusters and Their Light-Harvesting Capacity

Stamplecoskie, K. G.; Kamat, P. V.
J. Am. Chem. Soc. 2014, 136 (31), 11093–11099
DOI: 10.1021/ja505361n

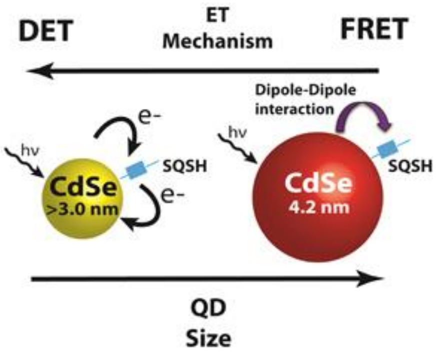


Abstract

Glutathione protected gold clusters exhibit size dependent excited state and electron transfer properties. Larger size clusters (e.g., Au25GSH18) with core-metal atoms display rapid (<1 ps) as well as slower relaxation (~200 ns) while homoleptic clusters (e.g., Au10-12GSH10-12) exhibit only slower relaxation. These decay components have been identified as metal-metal transition and ligand-to-metal charge transfer respectively. The short lifetime relaxation component becomes less dominant as the size of the gold cluster decreases. The long-lived excited state and ability to participate in electron transfer are integral for these clusters to serve as light harvesting antennae. A strong correlation between the ligand-to-metal charge-transfer excited state lifetime and photocatalytic activity was evidenced from

the electron transfer to methyl viologen. The photoactivity of these metal clusters show increasing photocatalytic reduction yield (0.05 - 0.14) with decreasing cluster size, Au25 < Au18 < Au15 < Au10-12. Gold clusters, Au18GSH14, were found to have the highest potential as a photosensitizer based on the quantum yield of electron transfer and good visible light absorption properties.

Size-Dependent Energy Transfer Pathways in CdSe Quantum Dot–Squaraine Light-Harvesting Assemblies: Förster versus Dexter

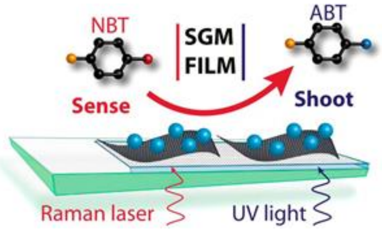


Hoffman, J. B.; Choi, H.; Kamat, P. V.
J. Phys. Chem. C 2014, 118 (32), 18453–18461
DOI: 10.1021/jp506757a

Abstract

Energy transfer coupled with electron transfer is a convenient approach to mimic photosynthesis in light energy conversion. Better understanding of mechanistic details of energy transfer processes is important to enhance the performance of dye or quantum dot sensitized solar cells. Energy transfer through both long range dipole based Förster Resonance Energy Transfer (FRET), and short range Dexter Energy Transfer (DET) mechanisms have been identified to occur between CdSe quantum dots (QDs) linked to a red-infrared absorbing squaraine dye through a short thiol functional group (SQSH). Solutions of SQSH linked to CdSe were investigated through steady-state and time resolved spectroscopy experiments to explore both mechanisms. Photoluminescence studies revealed that smaller QDs had higher energy transfer efficiencies than predicted by FRET, and femtosecond transient absorption experiments revealed faster energy transfer rates in smaller donor QD sizes. These findings supported A DET process dominating at small donor sizes. The presence of both processes illustrates multiple strategies for utilizing energy transfer in light harvesting assemblies and the required considerations in device design to maximize energy transfer gains through either mechanism.

Sense and Shoot: Simultaneous Detection and Degradation of Low Level Contaminants using Graphene Based Smart Material Assembly

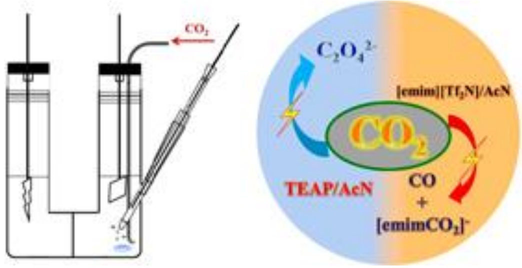


Alam, R.; Lightcap, I. V.; Karwacki, C. J.; Kamat, P. V.
ACS Nano 2014, 8 (7), 7272–7278.
DOI: 10.1021/nn502336x

Smart material nanoassemblies that can simultaneously sense and shoot low level contaminants from air and water are important for overcoming the threat of hazardous chemicals. Graphene oxide (GO) sheets deposited on mesoscopic TiO_2 films that underpin the deposition of Ag nanoparticles with UV-irradiation provide the foundation for the design of a smart material. The Ag particle size is readily controlled through precursor concentration and UV irradiation time. These semiconductor – graphene oxide – metal (SGM) films are SERS active and hence capable of sensing aromatic contaminants such as nitrobenzenethiol (NBT) in nanomolar range. Increased local concentration of organic molecule achieved through interaction with 2D carbon support (GO) facilitates low-level detection of contaminants. Upon UV irradiation of the NBT loaded SGM film, one can induce photocatalytic transformations. Thus, each component of the SGM film plays a pivotal role in aiding the detection and degradation of a contaminant dispersed in aqueous solutions. The advantage of using SGM films as multipurpose "detect and destroy" systems for nitroaromatic molecule is discussed.

Switching the Reaction Course of Electrochemical CO2 Reduction with Ionic Liquids

Sun, L.; Ramesha, G. K.; Kamat, P. V.; Brennecke, J. F.
Langmuir 2014, 30 (21), 6302–6308
DOI:10.1021/la5009076

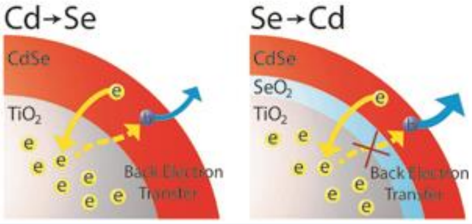


Abstract

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]) offers new ways to modulate the electrochemical reduction of carbon dioxide. [emim][Tf_2N], when present as the supporting electrolyte in acetonitrile, decreases the reduction overpotential at a Pb electrode by 0.18 V as compared to tetraethylammonium perchlorate as the supporting electrolyte. More interestingly, the ionic liquid shifts the reaction course during the electrochemical reduction of carbon dioxide by promoting the formation of carbon monoxide instead of oxalate anion. With increasing concentration of [emim][Tf_2N], a carboxylate species with reduced CO_2 covalently bonded to the imidazolium ring is formed along with carbon monoxide. The results highlight the catalytic effects of the medium in modulating the CO_2 reduction products.

How Does a SILAR CdSe Film Grow? Tuning the Deposition Steps to Suppress Interfacial Charge Recombination in Solar Cells

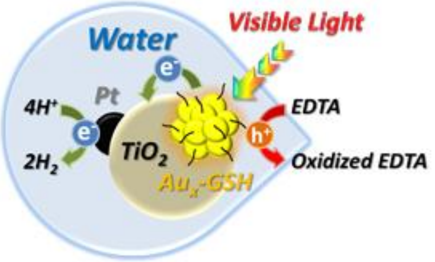
Becker, M. A.; Radich, J. G.; Bunker, B. A.; Kamat, P. V.
J. Phys Chem. Lett. 2014, 5, 1575–1582
DOI: 10.1021/jz500481v



Abstract

Successive Ionic Layer Adsorption and Reaction (SILAR) is a popular method of depositing the metal chalcogenide semiconductor layer on the mesoscopic metal oxide films for designing quantum dot sensitized solar cell (QDSSC) or Extremely Thin Absorber (ETA) solar cells. While this deposition method exhibits higher loading of light absorbing semiconductor layer than direct adsorption of pre-synthesized colloidal quantum dots, the chemical identity of these nanostructures and evolution of interfacial structure are poorly understood. We have now analyzed step-by-step SILAR deposition of CdSe films on mesoscopic TiO_2 nanoparticle films using x-ray absorption near-edge structure analysis and probed the interfacial structure of these films. The film characteristics interestingly show dependence on the order in which the Cd and Se are deposited, and the CdSe-TiO_2 interface is affected only during the first few cycles of deposition. Development of SeO_2 passivation layer in the SILAR-prepared films to form TiO_2/SeO_2/CdSe junction facilitates an increase in photocurrents and power conversion efficiencies of quantum dot solar cells when these films were integrated as photoanodes in a photoelectrochemical solar cell.

Glutathione Capped Gold Nanoclusters as Photosensitizers. Visible Light Induced Hydrogen Generation in Neutral Water



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

J. Am. Chem. Soc. 2014, 136 (16), 6075–6082.

DOI: 10.1021/ja5017365

Abstract

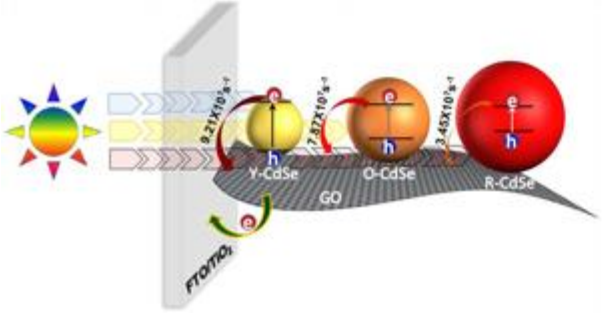
Glutathione capped metal nanoclusters (Aux-GSH NCs) which exhibit molecular like properties are employed as a photosensitizer for hydrogen generation in a photoelectrochemical cell (PEC) and a photocatalytic slurry reactor. The reversible re-duction (E0= -0.63 V vs. RHE) and oxidation (E0= 0.97 V and 1.51 V vs. RHE) potentials of these metal nanoclusters make them suita-ble for driving the water splitting reaction. When a mesoscopic TiO_2 film sensitized by Au_x-GSH NCs was used as the pho-toanode with a Pt counter electrode in aqueous buffer solution (pH = 7), we observe significant photocurrent activity under visible light (400 - 500 nm) excitation. Additionally, sensitizing Pt/TiO_2 nanoparticles with Au_x-GSH NCs in an aqueous slurry system and irradiating with visible light produced H_2 at a rate of 0.3 mmole of hydrogen/hr/gram of Au_x-GSH NCs. The rate of H_2 evolution was significantly enhanced (~5 times) when a sacrificial donor, such as EDTA, was introduced into the sys-tem. Using metal nanoclusters as a photosensitizer for hydrogen generation lays the foundation for the future exploration of other metal nanoclusters with well controlled numbers of metal atoms and capping ligands.

CdSe-Graphene Oxide Light Harvesting Assembly. Size Dependent Electron Transfer and Light Energy Conversion Aspects

Krishnamurthy, S.; Kamat, P. V.

ChemPhysChem 2014, 15, 2129–2135

DOI: 10.1002/cphc.201301189

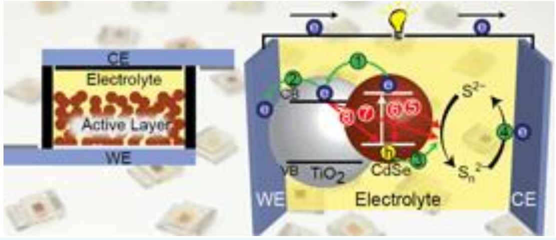


Abstract

Excited state interaction between CdSe quantum dots (QD) of different sizes (2.3, 3.2 and 4.2 nm diameter) and graphene oxide (GO) has been probed by depositing them as films on conducting glass electrodes. The emission of smaller CdSe QDs (2.3 nm) is quenched by GO three times faster than that of larger QDs (4.2 nm). Electrophoretic deposition method has allowed us to sequentially deposit single or multiple layers of different sized QDs and GO assemblies on conducting glass electrode and achieve the modulation of photoresponse in photoelectrochemical solar cells. Superior photoconversion efficiency through the incorporation of GO is attributed to the improved charge separation in the composite assembly.

Quantum Dot Solar Cells. Hole Transfer as a Limiting Factor in Boosting Photoconversion Efficiency

Kamat, P. V.; Christians, J. A.; Radich, J. G.
Langmuir 30 (20), 5716-5725 (Feature Article),
DOI: 10.1021/la500555w

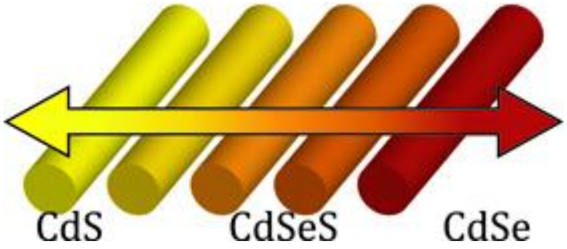


Abstract

Semiconductor nanostructures are attractive for designing low cost solar cells with tunable photoresponse. The recent advances in size and shape selective synthesis have enabled the design of quantum dot solar cells with photoconversion efficiencies greater than 5%. In order to make them competitive with other existing thin film or polycrystalline photovoltaic technologies, it is important to overcome kinetic barriers for charge transfer at semiconductor interfaces. This feature focuses on the limitations imposed by slow hole transfer in improving solar cell performance and its role in the stability of metal chalcogenide solar cells. Strategies to improve the rate of hole transfer through surface modified redox relays offer new opportunities to overcome the hole transfer limitation. The mechanistic and kinetic aspects of hole transfer in Quantum Dot Solar Cells (QDSCs), Nanowire Solar Cells (NWSCs) and Extremely Thin Absorber (ETA) solar cells are discussed..

CdSeS Nanowires. Compositionally Controlled Band Gap and Exciton Dynamics

Kim J.-P.; Christians, J. A.; Choi, H.; Krishnamurthy, S.; Kamat, P. V.
J. Phys. Chem. Lett. 5, 1103- 1109
DOI: 10.1021/jz500280g

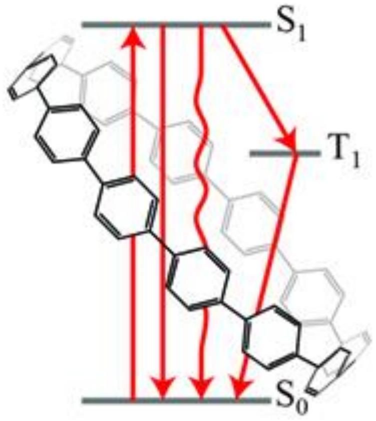


Abstract

CdS, CdSe and ternary $CdSe_xS_{(1-x)}$ are some of the most widely studied II-VI semiconductors due to their wide range of applications and promising performance in numerous systems. One-dimensional semiconductor nanowires offer the ability to conduct charges efficiently along the length of the wire which has potential charge transport benefits compared to nanoparticles. Herein, we report a simple, inexpensive synthetic procedure for high quality CdSeS nanowires where the composition can be easily modulated from pure CdSe to pure CdS by simply adjusting the Se:S precursor ratio. This allows for tuning of the absorption and emission properties of the nanowires across the visible spectrum. The CdSeS nanowires have a wurtzite crystal structure and grow along the [001] direction. As measured by femtosecond transient absorption spectroscopy, the short component of the excited state lifetime remains relatively constant at ~10 ps with increasing Se; however the contribution of this short lifetime component increased dramatically from 8.4% to 57.7% with increasing Se content. These CdSeS nanowires offer facile synthesis and widely adjustable optical properties, characteristics which give them broad potential applications in the fields of optoelectronics, and photovoltaics.

Carbon Nanohoops: Excited Singlet and Triplet Behavior of [9]- and [12]-cycloparaphenylene

Hines, D. A.; Darzi, E. R.; Jasti, R.; Kamat, P. V.
J. Phys. Chem. A 2014, 118 (9), 1595–1600
DOI: 10.1021/jp4123562



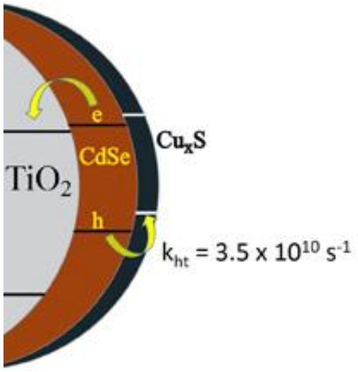
Abstract

Cycloparaphenylene molecules, commonly known as 'carbon nanohoops,' have the potential to serve as building blocks in constructing carbon nanotube architectures. The singlet and triplet excited state characteristics of [9]-cycloparaphenylene ([9]CPP) and [12]-cycloparaphenylene ([12]CPP) have now been elucidated using time resolved transient absorption and emission techniques. The fluorescence quantum yields (Φ) of [9]CPP and [12]CPP were determined to be 0.46 and 0.83 respectively. Rates of non-radiative recombination (k_{nr}), radiative recombination (k_r) and intersystem crossing (kisc) determined in this study indicate that radiative decay dominates in these nanohoop structures. The triplet quantum yields determined through energy transfer with excited biphenyl triplet were 0.18 and 0.13 for [9]CPP and [12]CPP respectively. The rate of triplet state quenching by oxygen was measured to be 1.7×10^3 s^{-1} ([9]CPP) and 1.9×10^3 s^{-1} ([12]CPP). The excited state dynamics established in this study enable us to understand the behavior of a carbon nanotube-like structure on a single subunit level.

Charge Transfer Mediation Through CuxS. The Hole Story of CdSe in Polysulfide

Radich, J.G.; Peeples, N. R.; Santra, P. K.; Kamat, P. V.

J. Phys. Chem. C 2014, 118 (30), 16463–16471.
DOI: 10.1021/jp4113365

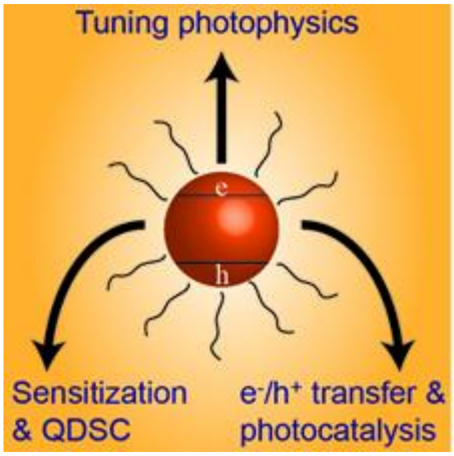


Abstract

Hole transfer to dissolved sulfide species in liquid junction CdSe quantum dot sensitized solar cells is relatively slow when compared to electron transfer from CdSe to TiO_2. Controlled exposure of cadmium chalcogenide surfaces to copper ions followed by immersion in sulfide solution promotes development of interfacial CuxS layer, which mediates hole transfer to polysulfide electrolyte by collection of photogenerated holes from CdSe. In addition, Cu_xS was also found to interact directly with defect states on the CdSe surface and quench emission characteristic of electron traps resulting from selenide vacancies. Together these effects were found to work in tandem to deliver 6.6% power conversion efficiency using Mn-doped CdS and CdSe co-sensitized quantum dot solar cell. Development of n-p interfacial junction at the photoanode-electrolyte interface in quantum dot solar cells unveils new means for designing high efficiency liquid junction solar cells.

Recent Advances in Quantum Dot Surface Chemistry

Hines, D. A.; Kamat, P. V.
ACS Appl. Mater. Interfaces 2014, 6 (5), 3041–3057
DOI: 10.1021/am405196u

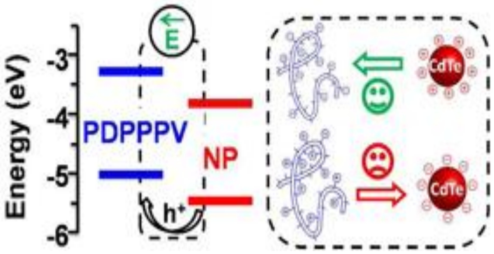


Abstract

Quantum dot (QD) surface chemistry is an emerging field in semiconductor nanocrystal related research. Along with size manipulation, the careful control of QD surface chemistry allows modulation of the optical properties of a QD suspension. Even a single molecule bound to the surface can introduce new functionalities. Herein, we summarize the recent advances in QD surface chemistry and the resulting effects on optical and electronic properties. Specifically, the feature article focuses addresses three main issues: (i) How surface chemistry affects the optical properties of QDs, (ii) How it influences the excited state dynamics and (iii) How one can manipulate surface chemistry to control the interactions between QDs and metal oxides, metal nanoparticles and in self-assembled QD monolayers.

Driving Charge Separation for Hybrid Solar Cells: Photo-induced Hole Transfer in Conjugated Copolymer and Semiconductor Nanoparticle Assemblies

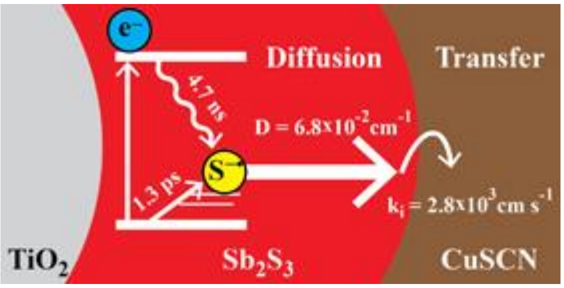
Wang, Y.; Liu, K.; Mikherjee, P.; Hines, D. A.;
Santra, P.; Shen, H. Y.; Kamat, P. V.; Waldeck, D. H.
Phys. Chem. Chem. Phys. 2014, 16, 5066-5070.
DOI: 10.1039/C3CP55210A



Abstract

This work reports on the use of an internal electrostatic field to facilitate charge separation at inorganic-organic interfaces, analogous to those in hybrid solar cells. Systematic charge transfer studies show that the donor-acceptor charge transfer rate is highly sensitive to the direction of the internal electric field.

Rate Limiting Interfacial Hole Transfer in Sb2S3 Solid-State Solar Cells



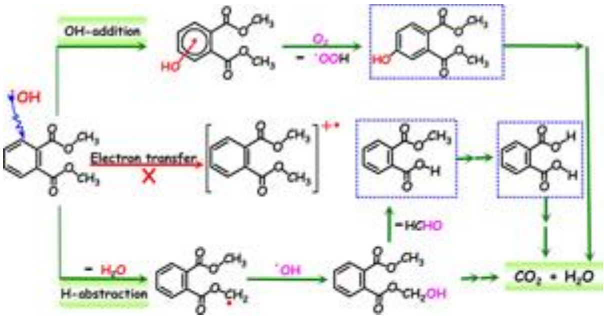
Christians, J. A.; Leighton Jr., D. T.; Kamat, P. V.
Energy and Environ. Sci. 2014, 7, 1148-1158.
DOI: http://dx.doi.org/10.1039/C3EE43844A

Abstract

Transfer of photogenerated holes from the absorber species to the p-type hole conductor is fundamental to the performance of solid-state sensitized solar cells. In this study, we comprehensively investigate hole diffusion in the Sb_2S_3 absorber and hole transfer across the Sb_2S_3–CuSCN interface in the TiO_2/Sb_2S_3/CuSCN system using femtosecond transient absorption spectroscopy, carrier diffusion modeling, and photovoltaic performance studies. Transfer of photogenerated holes from Sb_2S_3 to CuSCN is found to be dependent on Sb_2S_3 film thickness, a trend attributed to diffusion in the Sb_2S_3 absorber. However, modeling reveals that this process is not adequately described by diffusion limitations alone as has been assumed in similar systems. Therefore, both diffusion and transfer across the Sb_2S_3–CuSCN interface are taken into account to describe the hole transfer dynamics. Modeling of diffusion and interfacial hole transfer effects reveal that interfacial hole transfer, not diffusion, is the predominate factor dictating the magnitude of the hole transfer rate, especially in thin (< 20 nm) Sb_2S_3 films. Lastly, the implications of these results are further explored by photovoltaic measurements using planar TiO_2/Sb_2S_3/CuSCN solar cells to elucidate the role of hole transfer in photovoltaic performance.

Kinetics and Mechanism of ·OH Mediated Degradation of Dimethyl Phthalate in Aqueous Solution: Experimental and Theoretical Studies

An T.; Gao, Y.; Li, G.; Kamat, P. V.; Peller, J.; Joyce, M. V.
Environ. Sci. Technol. 2014, 48 (1), 641–648
DOI: 10.1021/es404453v



Abstract

The hydroxyl radical (•OH) is one of the main oxidative species in aqueous phase advanced oxidation processes, and its initial reactions with organic pollutants are important to understand the transformation and fate of organics in water environments. Insights into the kinetics and mechanism of •OH mediated degradation of the model environmental endocrine disruptor, dimethyl phthalate (DMP), have been obtained using radiolysis experiments and computational methods. The bimolecular rate constant for the •OH reaction with DMP was determined to be (3.2 ± 0.1) × 109 $M^{-1}s^{-1}$. The possible reaction mechanisms of radical adduct formation (RAF), hydrogen atom transfer (HAT), and single electron transfer (SET) were considered. By comparing the experimental absorption spectra with the computational results, it was concluded that the RAF and HAT were the dominant reaction pathways, and OH-adducts (•$DMPOH_1$, •$DMPOH_2$) and methyl type radicals •DMP(-H)α were identified as dominated intermediates. Computational results confirmed the identification of transient species with maximum absorption around 260 nm as •$DMPOH_1$ and •DMP(-H)α, and these radical intermediates then converted to monohydroxylated dimethyl phthalates and monomethyl phthalates. Experimental and computational analyses which elucidated the mechanism of •OH-mediated degradation of DMP are discussed in detail.

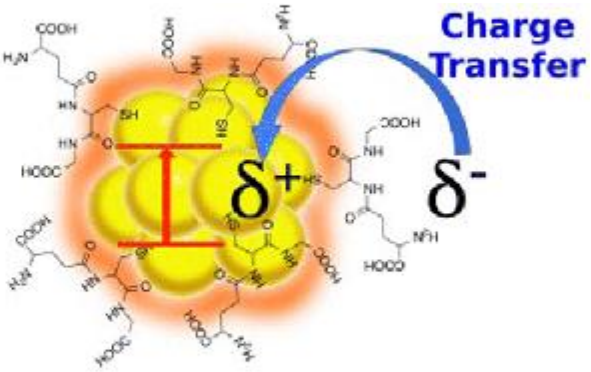
Excited State Behavior of Luminescent Glutathione Protected Gold Clusters

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

J. Phys. Chem. C 2014, 118 (2), 1370-1376.
DOI: 10.1021/jp410856h

Abstract

The excited state behavior of luminescent gold clusters provide new insights in understanding their photocatalytic activity in the visible region. The excited state of glutathione protected gold nanoclusters (AuGSH) which is characterized by the long-lived excited state (τ = 780 ns) arises from the ligand-to-metal type transition. These AuGSH clusters are in a partially oxidized state, (Au(I))and are readily reduced by chemical or electrochemical methods. Interestingly a metal core transition with short lived lifetime (τ <3 ps) appears along with a longer lifetime in reduced AuGSH clusters. The role of oxidation state of gold clusters in dictating the photocatalytic reduction of methyl viologen is discussed.



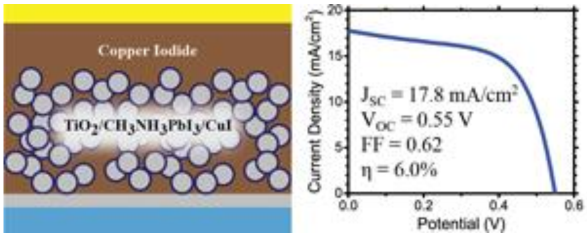
An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide

Christians, J. A.; Fung, R. C. A.; Kamat, P. V.

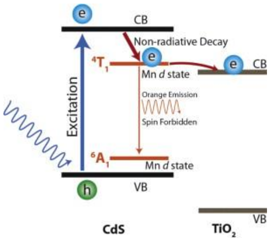
J. Am. Chem. Soc. 2014, 136 (2), 758-764
DOI: 10.1021/ja411014k

Abstract

Organo-lead halide perovskite solar cells have emerged as one of the most promising candidates for the next generation of solar cells. To date, these perovskite thin film solar cells have exclusively employed organic hole conducting polymers which are often expensive and have low hole mobility. In a quest to explore new inorganic hole conducting materials for these perovskite based thin film photovoltaics, we have identified copper iodide as a possible alternative. Using copper iodide, we have succeeded in achieving a promising power conversion efficiency of 6.0% with excellent photocurrent stability. The open-circuit voltage, compared to the best spiro-OMeTAD devices, remains low and is attributed to higher recombination in CuI devices as determined by impedance spectroscopy. However, impedance spectroscopy revealed that CuI exhibits two orders of magnitude higher electrical conductivity than spiro-OMeTAD which allows for significantly higher fill factors. Reducing the recombination in these devices could render CuI as a cost effective competitor to spiro-OMeTAD in perovskite solar cells.



Role of Mn^{2+} in Doped Quantum Dot Solar Cell



Santra, P. K.; Chen, Y.-S..

Electrochim. Acta 2014, *146*, 654-658.
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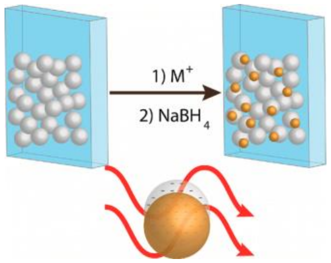
Abstract

In recent times, Mn doped quantum dot sensitized solar cells (QDSSCs) have shown a lot of interest as it provides a different strategy to improve the photovoltaic performances. In this work, we have systematically studied the effect of Mn^{2+} dopant concentration on the photovoltaic performances of CdS based QDSSCs. The open circuit potential increases systematically with increase in Mn^{2+} dopant concentration. The efficiency of the solar cell increases from 1.63% to 2.53% from undoped to 7.5% doped CdS. The role of Mn^{2+} in enhancing the photovoltaic performances was further probed by open circuit voltage decay and the energy levels were studied using transient absorption spectroscopy. Both spin and orbital forbidden Mn *d-d* transition ($^4T_1 – ^6A_1$) helps in reducing the recombination inside the solar cell, which improves the overall photovoltaic performances.

Facile SILAR Approach to Air-Stable Naked Silver and Gold Nanoparticles Supported by Alumina



Stamplecoskie, K. G.; Chen, Y.-S..

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Abstract

A synthetically convenient and scalable SILAR (successive ion layer adsorption and reaction) method is used to make air-stable films of silver and gold nanoparticles supported on alumina scaffolds. This solution-based deposition technique yields particles devoid of insulating capping agents or ligands. The optical properties of the nanoparticle films were investigated using femtosecond transient absorption spectroscopy. A linear absorption arising from intraband excitation (775 nm laser pulse) is seen only for Au nanoparticles at low intensity. However, both Au and Ag particles exhibit plasmon resonance responses at high excitation intensity via two photon absorption of the 775 nm pump pulse. The difference in optical response to near-IR laser excitation is rationalized based on the known density of states for each metal. To demonstrate the potential applications of these films, alumina-supported Ag nanoparticles were utilized as substrates for surface enhanced Raman spectroscopy, resulting in a 65-fold enhancement in the Raman signal of the probe molecule rhodamine 6G. The exceptional stability and scalability of these SILAR films opens the door for further optical and photocatalytic studies and applications, particularly with ligand-free Ag nanoparticles that typically oxidize under ambient conditions. Additionally, isolating plasmonic and interband electronic excitations in stable AgNP under visible light irradiation could enable elucidation of the mechanisms that drive noble metal-assisted photocatalytic processes.

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