

Annual Research Summary

January - December 2013

Kamatlab Research
University of Notre Dame



Summer 2013

Prashant V. Kamat

Rev. John A. Zahm Professor of Science
Department of Chemistry & Biochemistry and Radiation Laboratory
Concurrent Professor, Chemical & Biomolecular Eng.
Notre Dame, IN 46556-5674, USA

Tel. (574) 631-5411 Fax (574) 631-8068
E-mail: PKAMAT@nd.edu;
Website: <http://www.nd.edu/~kamatlab>

Research Group

Graduate Students

Sean Murphy (Chemistry)
Sachi Krishnamurthy (Chemistry)
James Radich (Chem. Eng.)
Douglas Hines (Chemistry)
Jeff Christians (Chem. Eng.)
Joseph Manser (Chem. Eng.)
Yong-Siou Chen (Chemistry)
Jacob Hoffman (Chemistry)
Danilo Jara-Quinteros (Chemistry)
Seogjoon Yoon (Chemistry)

Incoming Students Victoria Bridewell (Chemistry)
Steven Kobosko (Chem. Eng.)

Undergraduate Students

Spring 2013

Raymond Fung (Waterloo)
Tim Siegler (CBE,UND)
Jack Olding
Anthony Krenselewski
Brandon Dunham
Andrew Neils

Summer 2013

Julian Pilate-Hutcherson
Justin Waller
Nick Hamilton
David O'Shaughnessy
Anthony Krenselewski
Jack Olding

Fall 2013

Tim Siegler (CBE,UND)
Andrew Neils (CBE, UND)
Jack Olding (Physics, UND)
Anthony Krenselewski(CBE, UND)
Mia Eppler (CBE, UND)
Lynda Smith (RET)

Postdoctoral Research Associate

G. Ramesha (July 2012-June 2013)
Pralay Santra (Mar 2011 February 2012))
Hyunbong Choi (Nov 2010-)
Rabeka Alam (Aug 2013)
Kevin Stamplecoskie (May 2013)

Visiting Scientists

Julie Peller (IUN)
Roxana Nicolaescu (Serim Corporation)
J. P. Kim (Korea Basic Science Institute)
Santosh Haram (Fulbright Scholar)

Graduation/Fellowships/Recognition

Sean Murphy, Ph.D. (Dept. of Chemistry, University of Notre Dame, April 2013)
Metal Nanoparticle-Graphene Oxide Composites: Photophysical Properties and Sensing Applications

Awards/Honors

PVK: Langmuir Lectureship Award (ACS Fall Meeting) Sept 2013
Adjunct Faculty, University of Wisconsin, Madison
h-index- Crosses the milestone of 100

Group: James Radich and Jeff Christians Eiler Graduate Fellowship
James Radich Bayer Environmental Research Fellowship
Joe Manser, Participant in ACS Publications multimedia workshop
Tim Siegler,,ND Nano Fellowship & Statt Fellowship
Alex Mobashery 1st place in the Energy and Transportation category in the Northern Indiana Regional Science Fair and participant in International Sustainable World Project Olympiad in Houston, TX.

Professional Activities

- **Deputy Editor**, Journal of Physical Chemistry Letters (2009-present)
- **Editorial Advisory Boards**
 - Langmuir (2000-present)
 - Interface (1999-present)
 - Electrochemical and Solid State Letters (September 2006-present)
 - International Journal of Photoenergy (2001-2008)
 - Applied Electrochemistry (2009-present)
- **ND committees**
 - Member of the COS-COS (2008-present)
 - CAP –Chemistry & Biochemistry (Fall 2009-)
 - Sustainable Energy Institute Leadership Team (2010-)
- **Symposium Organizer**
 - Co-Organizer, Nanostructures for Energy Conversion, 223 ECS Meeting Toronto, May, 2013

Invited Seminar/Colloquium

Rutgers University, February 14, 2013

Quantum Dot Architectures for Next Generation Solar Cells

North Texas University, Dallas, March 1, 2013

Quantum Dot Solar Cells. Next Big Thing in Photovoltaics?

Michigan State University, April 19, 2013

Semiconductor Nanostructures for Light Energy Conversion

University of Illinois, Urbana-Champaign, Inorganic/Materials/Physical Chemistry seminar, May 1, 2013

Quantum Dot Architectures for Next Generation Photovoltaics

McGill University, May 14, 2013

Nanostructure Architectures for Next Generation Photovoltaics

Seminar at the Korea Advanced Institute of Science and Technology, Daejeon, Korea, July 5

Chasing the Photovoltaic Race with Quantum Dot Solar Cells

Virginia Tech, Blacksburg, Virginia, Chemistry Department seminar September 6

Semiconductor Quantum Dots and Light Energy Conversion

Invited seminar at the Institute of Chemical Sciences and Eng., EPFL, in Lausanne, Switzerland, Oct 10

Harvesting Photons with Semiconductor Quantum Dots

Conference Presentations (2013)

Meeting Presentations:

Spring Meeting of the American Chemical Society, New Orleans, April 7-11, 2013

Graphitic design: Graphene-based assemblies for solar energy conversion

Electrochemical Society Meeting, Toronto, Canada, May 12-16, 2013

Photocatalysis with Semiconductor-Graphene Oxide- Metal Cluster Assembly

Ian Lightcap, Sean Murphy, Sachidananda Krishnamurthy and Prashant V. Kamat

Tuning Photoresponse with CdSSe Quantum Dots. Towards the Design of Rainbow Solar Cell

Pralay Santra and Prashant V. Kamat

E-MRS 2013 Spring Meeting, Strasbourg, France May 27-31

Emerging Strategies for High Efficiency Quantum Dot Solar Cells (Invited)

Prashant V. Kamat

Tandem Layered Quantum Dot Solar Cells

Prashant V. Kamat Pralay Santra

Photocatalysis with Semiconductor-Graphene Oxide- Metal Cluster Assembly

Prashant V. Kamat, Sachidananda Krishnamurthy, Ian Lightcap

- Department of Energy Solar Photochemistry Conference, Annapolis, Maryland, June 2-5
Modulation of Light Harvesting Properties of Semiconductor Quantum Dot Assemblies
- Sungkyun International Solar Forum in Seoul, Korea July 1-3
Quantum Dot Solar Cells. Modulation of Photoresponse with Ternary Metal Chalcogenides (Invited)
- Plenary lecture, at the International Photochemistry conference in Leuven, Belgium, July 21-26
Manipulation of Photoinduced Charge Transfer Processes in Quantum Dot Solar Cells (Invited)
- Telluride Conference in Colorado, August 4-10
Emerging Strategies for Boosting Light Harvesting Efficiency in Quantum Dot Solar Cells (Invited)
- Fall ACS National Meeting in Indianapolis, September 8-12
Designing tandem layered quantum dot solar cells with CdSeS nanocrystals (Invited)

Emergence of quantum dot solar cells as next generation photovoltaics (Invited)

Meeting the clean energy challenge with semiconductor nanostructures, Langmuir Award Lecture
- Workshop on Photocatalysis as a tool for sustainability, Portoroz, Slovenia, September 23-24
Semiconductor Assisted Photocatalysis and Energy Conversion (Invited)

How to Make Your Next Publication Scientifically Effective (Invited)
- The 3rd European Symposium on Photocatalysis ; Portoroz, Slovenia, September 24-25.
Many Faces of Metal Nanoparticles. Understanding Their Role in Photocatalysis (Invited)
- CB Filtration Strategies and Multifunctional Materials Development Workshop, ARO, Belcamp, Maryland Oct 8,9
Designing Graphene-Semiconductor-Metal Catalysts MAT (Invited)
- SCILOG conference organized by the Research Corporation, Oracle, Arizona, October 16-18
Harvesting Light Energy with Semiconductor Nanostructures (Keynote lecture)
- American Vacuum Society Meeting. Long Beach, CA, Oct. 27-Nov 1
Chasing the Photovoltaic Race with Quantum Dot Solar Cells (Invited)



Lamguir Lectureship Awarded (ACS Fall Meeting)

Presentation by Students and Postdocs

246th Meeting of the American Chemical Society, Indianapolis, IN. 9/9/2013

J. Christians and P. V. Kamat

Hole Transfer Dynamics of Sb₂S₃ Solar Cells

S. Krishnamurthy and P. V. Kamat

Rainbow CdSe- Graphene Oxide Assembly: Size Dependent Electron Transfer and Enhanced Light Energy Conversion

D. A. Hines and P. V. Kamat

Influence of Surface Chemistry on Electron Transfer at the CdSe-TiO₂ Interface

J. G. Radich and P. V. Kamat

Gold Nanoparticle-Mediated OH Attack on Reduced Graphene Oxide: The Evolution of Holey Graphene*

Graduate Student Union Research Symposium, University of Notre Dame, Notre Dame, IN. 2/27/2013.

J. Christians and P. V. Kamat

Antimony Sulfide Solar Cells. A Spectroscopic Investigation of the Hole Transfer Process

Climate Change and the Common Good, University of Notre Dame, Notre Dame, IN. 4/9/2013.

J. Christians and P. V. Kamat

Antimony Sulfide Solar Cells - Toward a Brighter Energy Future

D. A. Hines and P. V. Kamat

Implications of Quantum Dot Surface Chemistry on Photovoltaic Device Applications

Notre Dame Spark Conference, University of Notre Dame, Notre Dame, IN. 4/16/2013.

J. Christians and P. V. Kamat

Painting the Future: Brining Solar Power to the People

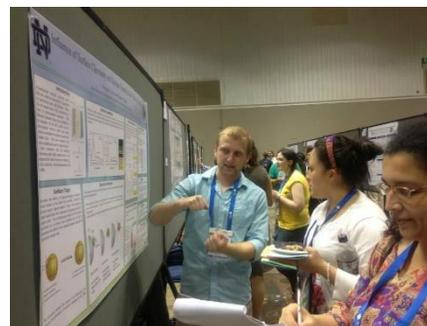
Calvin College Engineering Seminar, Calvin College, Grand Rapids, MI. 10/4/2013.

J. Christians and P. V. Kamat
Solar Paint, Notre Dame, and Surviving Graduate School

PINDU 2013, West Lafayette, IN. November 2013.

S. Krishnamurthy and P. V. Kamat
Rainbow CdSe- Graphene Oxide Assembly: Size Dependent Electron Transfer and Enhanced Light Energy Conversion

D. JaraQuinteros and P. V. Kamat
Size-Dependent Excited-State Dynamic and Photovoltaic Performance in CuInS₂ Quantum Dots Sensitized Solar Cells



Doug Hines explaining his poster at the ACS National Meeting in Indianapolis

Energy week 2013, University of Notre Dame, Notre Dame, IN. October 2013.

S. Krishnamurthy and P. V. Kamat
Rainbow CdSe- Graphene Oxide Assembly: Size Dependent Electron Transfer and Enhanced Light Energy Conversion

D. A. Hines and P. V. Kamat
Influence of Surface Chemistry on Electron Transfer at the CdSe-TiO₂ Interface

Gordon Conference on Photochemistry, Easton, MA. 7/14/2013

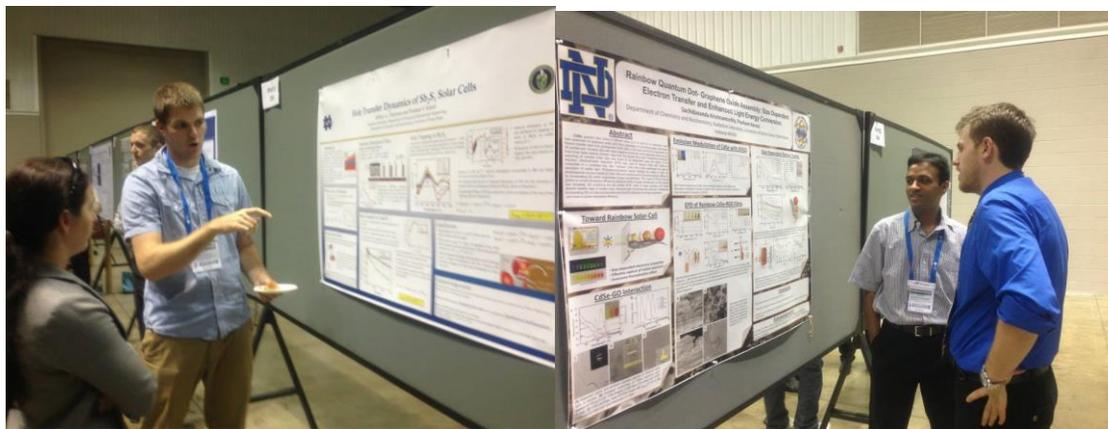
K. G. Stamplecoskie, Y. S. Chen and P. V. Kamat
Excited State Dynamics of Gold Clusters and How They Sensitize TiO₂ Delivering >2% Solar Cell Efficiency

17th Annual Conference of the Chinese American Chemical Society, Chicago, IL 5/4/2013

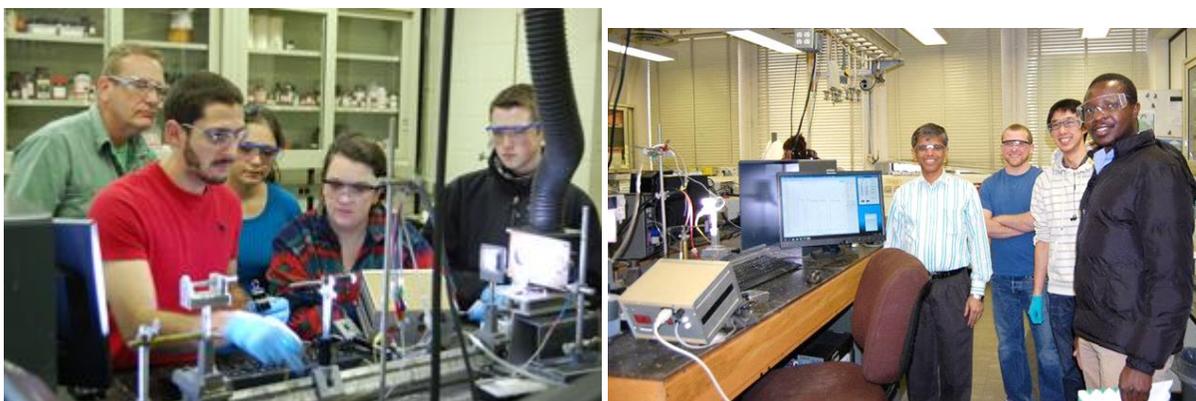
L. Sun and P. V. Kamat
Electrochemical Reduction of CO₂ Assisted by Ionic Liquids

AICHE National Meeting, San Francisco, CA, 11/5/13

J. G. Radich and P. V. Kamat
Fundamental Studies on the Origin of Reduced Graphene Oxide Enhancements in Energy Storage Electrodes



Poster presentations by Jeff Christians and Sachi Krihnamurthy at the ACS National Meeting in Indianapolis



Joe Manser (Left) demonstrating the solar cell characterization

Research Papers

1. Yokomizo, Y.; Krishnamurthy, S.; Kamat, P. V., *Photoinduced Electron Charge and Discharge of Graphene-ZnO Nanoparticle Assembly*. *Catal. Today*, 2013, 199, 36-41. doi:10.1016/j.cattod.2012.04.045
2. Lightcap, I. V.; Kamat, P. V., *Graphitic Design: Prospects of Graphene-Based Nanocomposites for Solar Energy Conversion, Storage, and Sensing*. *Accounts of Chemical Research*, 2013, 46 (10), 2235–2243. doi:10.1021/ar300248f
3. Krishnamurthy, S.; Kamat, P. V., *Galvanic Exchange on Reduced Graphene Oxide. Designing a Multifunctional Two-Dimensional Catalyst Assembly*. *J. Phys. Chem. C*, 2013, 117, 571–577. doi:10.1021/jp309529b
4. Santra, P.; Kamat, P. V., *Tandem Layered Quantum Dot Solar Cells. Tuning the Photovoltaic Response with Luminescent Ternary Cadmium Chalcogenides*. *J. Am. Chem. Soc.*, 2013, 135, 877–885. doi:10.1021/ja310737m
5. Murphy, S.; Huang, L.; Kamat, P. V., *Reduced Graphene Oxide-Silver Nanoparticle Composite as an Active SERS Material*. *J. Phys. Chem. C*, 2013, 117, 4740–4747. doi:10.1021/jp3108528
6. Choi, H.; Kuno, M.; Hartland, G. V.; Kamat, P. V., *CdSe Nanowire Solar Cells using a Carbazole as Surface Modifier*. *J. Mater. Chem. A*, 2013, 1, 5487–5491. doi:10.1039/C3TA10387K

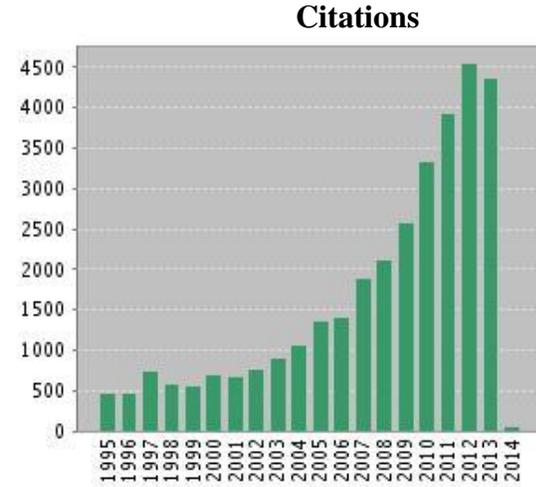
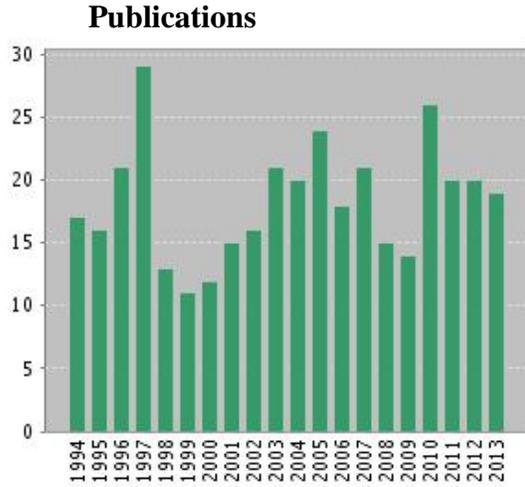
7. Kamat, P. V., *Quantum Dot Solar Cells. The Next Big Thing in Photovoltaics*. *J. Phys. Chem. Lett.*, 2013, 4, 908–918. doi:http://dx.doi.org/10.1021/jz400052e
8. Santra, P. K.; Nair, P. V.; Thomas, K. G.; Kamat, P. V., *CuInS₂ Sensitized Quantum Dot Solar Cell. Electrophoretic Deposition, Excited State Dynamics and Photovoltaic Performance*. *J. Phys. Chem. Lett.*, 2013, 4, 722-729. doi:10.1021/jz400181m
9. Radich, J. G.; Kamat, P. V., *Making Graphene Holey. Gold Nanoparticle-Mediated Hydroxyl Radical Attack on Reduced Graphene Oxide*. *ACS Nano*, 2013, 7, 5546-5557. doi:10.1021/nn401794k
10. Chen, Y.-S.; Choi, H.; Kamat, P. V., *Metal Cluster Sensitized Solar Cells. A New Class of Thiolated Gold Sensitizers Delivering Efficiency Greater Than 2%*. *J. Am. Chem. Soc.*, 2013, 135, 8822–8825. doi:10.1021/ja403807f
11. Hines, D. A.; Kamat, P. V., *Quantum Dot Surface Chemistry: Ligand Effects and Electron Transfer Reactions*. *J. Phys. Chem. C*, 2013, 117, 14418–14426. doi: 10.1021/jp404031s
12. Christians, J. A.; Kamat, P. V., *Trap and Transfer. Two-Step Hole Injection Across the Sb₂S₃/CuSCN Interface in Solid State Solar Cells*. 2013, 7, 7967–7974. doi: 10.1021/nn403058f
13. Radich, J. G.; Chen, Y.-S.; Kamat, P. V., *Ni-Doped MnO₂ Nanowire-Reduced Graphene Oxide Composite for Rapid Cycling Cathode in Lithium Ion Batteries*. *ECS JSS*, 2013, 2, M3178-M3181. doi: 10.1149/2.023310jss
14. Eltom, A.; McDonald, M. P.; Vietmeyer, F.; Thapa, J.; Morozov, Y. V.; Sokolov, D. A.; Hodak, J. H.; Vinodgopal, K.; Kamat, P. V.; Kuno, M., *Direct observation of heterogeneous single layer graphene oxide reduction kinetics*. *Nano Lett.*, 2013, 13, 5777–5784. doi: 10.1021/nl402057j
15. Choi, H.; Kamat, P. V., *CdS Nanowire Solar Cells. Dual Role of Squaraine Dye as a Sensitizer and a Hole Transporter.*, *J. Phys. Chem. Lett.*, 2013, 4, 3983–3991. doi: 10.1021/jz402306j
16. Choi, H.; Radich, J. G.; Kamat, P. V., *Sequentially Layered CdSe/CdS Nanowire Architecture for Improved Nanowire Solar Cell Performance*, *J. Phys. Chem. C, ASAP*. doi: 10.1021/jp410235s
17. Christians, J. A.; RCM, F.; Kamat, P. V., *An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide*. *J. Am. Chem. Soc.* 2014, ASAP. doi: 10.1021/ja411014k
18. Stamplecoskie, K; Chen, Y-S.; Kamat, P. V. *Excited State Behavior of Luminescent Glutathione Protected Gold Clusters*, *J. Phys. Chem. C, ASAP*. doi: 10.1021/410856h

Editorials

- Kamat, P. V.; Schatz, G. C. *Emerging Research Frontiers in Physical Chemistry*, *J. Phys. Chem. Lett.*, 2013, 4 (1), pp 233–234, doi: 10.1021/jz301955f
- Kamat, P. V.; Schatz, G. C. *Increasing the Impact of Published Work. Introducing ACS LiveSlides*, *J. Phys. Chem. Lett.*, 2013, 4 (14), pp 2377–2378; doi: 10.1021/jz401301z
- Kamat, P.; Schatz, G. C., *How to Make Your Next Paper Scientifically Effective*. *J. Phys. Chem. Lett.*, 2013, 4, 1578-1581. doi: 10.1021/jz4006916
- Kamat, P. V., *Energy Outlook for Planet Earth*. *J. Phys. Chem. Lett.*, 2013, 4, 1727-1729. doi: 10.1021/jz400902s
- Kamat, P. V. *Evolution of Perovskite Photovoltaics and Decrease in Energy Payback Time* *J. Phys. Chem. Lett.*, 2013, 4, 3733–3734 doi: 10.1021/jz402141s

Publication Analysis

Source: Thomson ISI, Dec 19, 2013



Results found: 487

Sum of the Times Cited : 34000+

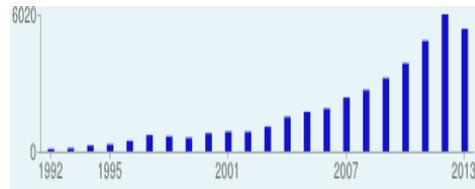
Average Citations per Item : 70

h-index : 101



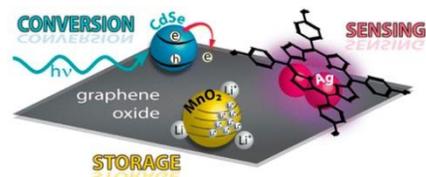
Citation indices

	All	Since 2008
Citations	41480	20949
h-index	110	79
i10-index	346	272



Graphitic Design: Prospects of Graphene-Based Nanocomposites for Solar Energy Conversion, Storage, and Sensing

Lightcap, I. V.; Kamat, P. V.,
Acc. Chem. Res., 2013, 46, 2235–2243.
 DOI: 10.1021/ar300248f

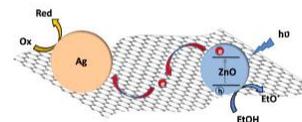


Abstract

The promising field of graphene nanocomposites for sensing and energy applications is based on fundamental studies that explain the electronic interactions between semiconductor or metal nanoparticles and graphene. In particular, reduced graphene oxide is a suitable composite substrate because of its two-dimensional structure, outstanding surface area, and electrical conductivity. In this Account, we describe common assembly methods for graphene composite materials and examine key studies that characterize its excited state interactions. We also discuss strategies to develop graphene composites and control electron capture and transport through the 2D carbon network. In addition, we provide a brief overview of advances in sensing, energy conversion, and storage applications that incorporate graphene-based composites. With these results in mind, we can envision a new class of semiconductor– or metal–graphene composites sensibly tailored to address the pressing need for advanced energy conversion and storage devices.

Photoinduced electron charge and discharge of graphene–ZnO nanoparticle assembly

Yokomizo, Y.; Krishnamurthy, S.; Kamat, P. V.,
Catal. Today 2013, 199, 36–41.
 DOI: 10.1016/j.cattod.2012.04.045

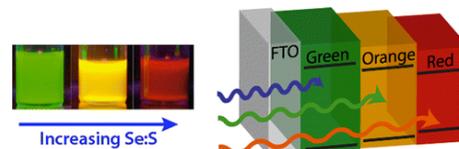


Abstract

Graphene oxide (GO) serves as a two-dimensional carbon nano-mat to anchor catalyst nanoparticles. We have developed a photocatalyst assembly by anchoring ZnO and Ag nanoparticles on graphene oxide sheets suspended in ethanol. Upon photoirradiation, the electrons are transferred from ZnO to GO to produce reduced graphene oxide (RGO). The ZnO–RGO composites are further decorated with Ag nanoparticles by reducing Ag^+ ions quantitatively with excess electrons stored in RGO. Under continuous UV-illumination we observe charging of ZnO nanoparticles as evidenced by the shift in absorption edge. However, no shift in the band edge is seen for ZnO–RGO or ZnO–RGO–Ag composites under UV irradiation indicating the quick discharge of electrons on RGO surface. Such charge–discharge phenomenon on the graphene oxide sheet was further probed by carrying out reduction of methyl viologen. Improved charge separation and selectivity in the reduction process was achieved in these graphene based photocatalytic assemblies.

Tandem-Layered Quantum Dot Solar Cells: Tuning the Photovoltaic Response with Luminescent Ternary Cadmium Chalcogenides

Santra, P; Kamat, P. V.,
J. Am. Chem. Soc., 2013, 135, 877–885
 DOI: 10.1021/ja310737m

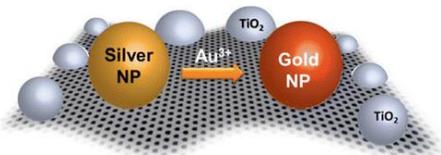


Abstract

Photon management in solar cells is an important criterion as it enables the capture of incident visible and infrared photons in an efficient way. Highly luminescent CdSeS quantum dots (QDs) with a diameter of 4.5 nm were prepared with a gradient structure that allows tuning of absorption and emission bands over the entire visible region without varying the particle size. These crystalline ternary cadmium chalcogenides were deposited within a mesoscopic TiO₂ film by electrophoretic deposition with a sequentially-layered architecture. This approach enabled us to design tandem layers of CdSeS QDs of varying band gap within the photoactive anode of a QD solar cell (QDSC). An increase in power conversion efficiency of 1.97–2.81% with decreasing band gap was observed for single-layer CdSeS, thus indicating varying degrees of photon harvesting. In two- and three-layered tandem QDSCs, we observed maximum power conversion efficiencies of 3.2 and 3.0%, respectively. These efficiencies are greater than the values obtained for the three individually layered photoanodes. The synergy of using tandem layers of the ternary semiconductor CdSeS in QDSCs was systematically evaluated using transient spectroscopy and photoelectrochemistry.

Galvanic Exchange on Reduced Graphene Oxide: Designing a Multifunctional Two-Dimensional Catalyst Assembly

Krishnamurthy, S.; Kamat, P. V.
J. Phys. Chem. C, 2013, 117, 571–577
 DOI: 10.1021/jp309529b



Abstract

The two-dimensional network of reduced graphene oxide (RGO) is decorated with silver and gold nanoparticles. The silver nanoparticles deposited on RGO by photocatalytic reduction are subjected to galvanic exchange with Au³⁺ ions to transform them into gold nanoparticles. This compositional change on the RGO surface demonstrates RGO's versatile ability to anchor a wide array of nanoparticles and facilitate chemical transformations. Coupled with RGO's unique ability to capture and transport electrons, galvanic exchange is used to contrive a two-dimensional nanocatalyst mat. Raman studies show that metal nanoparticles anchored on reduced graphene oxide facilitate enhancement of Raman bands. Using methyl viologen as a probe we elucidate the photocatalytic activity of the semiconductor–RGO–metal nanoassembly and highlight the mediation of RGO in charge transfer processes

Reduced Graphene Oxide–Silver Nanoparticle Composite as an Active SERS Material

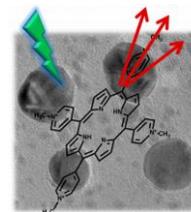
Murphy, S.; Huang, L.; Kamat, P. V...

J. Phys. Chem. C, 2013, 117, 4740–4747

DOI: 10.1021/jp3108528

Abstract

Selectivity and enhanced sensitivity for SERS measurements are highly desirable for environmental and analytical applications. Interaction of a target molecule with SERS substrate plays a pivotal role in determining the magnitude of enhancement and spectral profile of the SERS signal. A reduced graphene oxide–Ag nanoparticle (RGO-Ag NP) composite has been designed to boost SERRS sensitivity of a porphyrin derivative. Complexation between 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP) porphyrin and the RGO-Ag NP composite is evidenced by a red-shifted porphyrin absorption band. Results indicate complexation is influential in improved surface-enhanced resonance Raman (SERRS) signal for TMPyP and thus offers an advantage for target molecule detection at low concentration levels. The combined effects of RGO and Ag NPs in the enhancement of SERS signal of TMPyP are discussed.



Synchronized Energy and Electron Transfer Processes in Covalently Linked CdSe-Squaraine Dye-TiO₂ Light Harvesting Assembly.

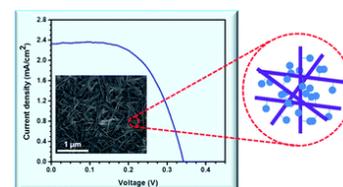
Choi, H.; Kuno, M. K.; Hartland, G. H.; Kamat, P. V.,

J. Mater. Chem. A, 2013, 1, 5487–5491

DOI: 10.1039/C3TA10387K

Abstract

Carbazole molecules containing thiol functional groups, when attached to CdSe nanowires (NWs), facilitate hole transport across semiconductor interfaces. The improved hole transfer rate is evidenced by increased electron lifetimes and better photovoltaic performance. Nanowire solar cells (NWSCs) with carbazole treatment delivered a power conversion efficiency of 0.46%, which is an order of magnitude improvement over untreated films. The illumination of the sample during the electrophoretic deposition of nanowires also had a profound effect in obtaining stable and higher photocurrents.



Quantum Dot Solar Cells. *The Next Big Thing* in Photovoltaics

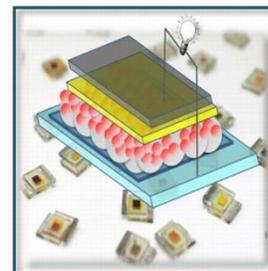
Kamat, P. V.

J. Phys. Chem. Lett., 2013, 4, 908–918

DOI: 10.1021/jz400052e

Abstract

The recent surge in the utilization of semiconductor nanostructures for solar energy conversion has led to the development of high-efficiency solar cells. Some of these recent advances are in the areas of synthesis of new semiconductor materials and the ability to tune the electronic properties through size, shape, and composition and to assemble quantum dots as hybrid assemblies. In addition, processes such as hot electron injection, multiple exciton generation (MEG), plasmonic effects, and energy-transfer-coupled electron transfer are gaining momentum to overcome the efficiency limitations of energy capture and conversion. The recent advances as well as future prospects of quantum dot solar cells discussed in this perspective provide the basis for consideration as “*The Next Big Thing*” in photovoltaics.



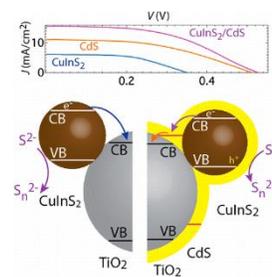
CuInS₂-Sensitized Quantum Dot Solar Cell. Electrophoretic Deposition, Excited-State Dynamics, and Photovoltaic Performance.

Santra, P. K.; Nair, P. V.; Thomas, K. G.; Kamat, P. V.,

J. Phys. Chem. Lett., 2013, 4, 722–729

DOI: 10.1021/jz400181m

Ternary metal chalcogenides such as CuInS₂ offer new opportunities to design quantum dot solar cells (QDSC). Chemically synthesized CuInS₂ quantum dots (particle diameter, 2.6 nm) have been successfully deposited within the mesoscopic TiO₂ film using electrophoretic deposition (150 V cm⁻¹ dc field). The primary photoinduced process of electron injection from excited CuInS₂ into TiO₂ occurs with a rate constant of $5.75 \times 10^{11} \text{ s}^{-1}$. The TiO₂/CuInS₂ films are photoactive and produce anodic photocurrent with a power conversion efficiency of 1.14%. Capping the TiO₂/CuInS₂ film with a CdS layer decreases the interfacial charge recombination and thus offers further improvement in the power conversion efficiency (3.91%). The synergy of using CdS as a passivation layer in the composite film is also evident from the increased external quantum efficiency of the electrode in the red region where only CuInS₂ absorbs the incident light.

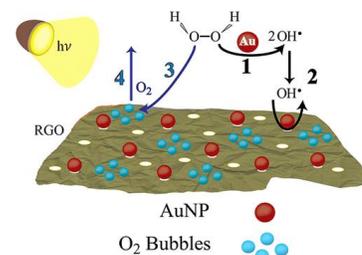


Making Graphene *Holey*. Gold-Nanoparticle-Mediated Hydroxyl Radical Attack on Reduced Graphene Oxide

Radich, J. G.; Kamat, P. V.
ACS Nano, 2013, 7, 5546–5557
 DOI: 10.1021/nm401794k

Abstract

Graphene oxide (GO) and reduced graphene oxide (RGO) have important applications in the development of new electrode and photocatalyst architectures. Gold nanoparticles (AuNPs) have now been employed as catalyst to generate OH^\bullet and oxidize RGO *via* hydroxyl radical attack. The oxidation of RGO is marked by pores and wrinkles within the 2-D network. Nanosecond laser flash photolysis was used in conjunction with competition kinetics to elucidate the oxidative mechanism and calculate rate constants for the AuNP-catalyzed and direct reaction between RGO and OH^\bullet . The results highlight the use of the AuNP-mediated oxidation reaction to tune the properties of RGO through the degree of oxidation and/or functional group selectivity in addition to the nanoporous and wrinkle facets. The ability of AuNPs to catalyze the photolytic decomposition of H_2O_2 as well as the hydroxyl radical-induced oxidation of RGO raises new issues concerning graphene stability in energy conversion and storage (photocatalysis, fuel cells, Li-ion batteries, *etc.*).

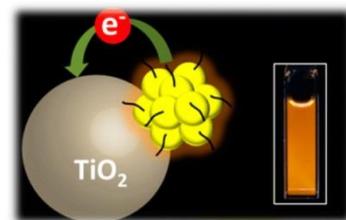


Metal-Cluster-Sensitized Solar Cells. A New Class of Thiolated Gold Sensitizers Delivering Efficiency Greater Than 2%

Chen, Y.-S., Choi, H.; Kamat, P. V.,
J. Am. Chem. Soc., 2013, 135, 8822–8825
 DOI: 10.1021/ja403807f

Abstract

A new class of metal-cluster sensitizers has been explored for designing high-efficiency solar cells. Thiol-protected gold clusters which exhibit molecular-like properties have been found to inject electrons into TiO_2 nanostructures under visible excitation. Mesoscopic TiO_2 films modified with gold clusters deliver stable photocurrent of 3.96 mA/cm^2 with power conversion efficiencies of 2.3% under AM 1.5 illumination. The overall absorption features and cell performance of metal-cluster-sensitized solar cells (MCSCs) are comparable to those of CdS quantum-dot-based solar cells (QDSCs). The relatively high open-circuit voltage of 832 mV and fill factor of 0.7 for MCSCs as compared to QDSCs show the viability of these new sensitizers as alternatives to semiconductor QDs and sensitizing dyes in the next generation of solar cells.



Hines, D. A.; Becker, M. A.; Kamat, P. V., Photoinduced Surface Oxidation and Its Effect on the Exciton Dynamics of CdSe Quantum Dots.

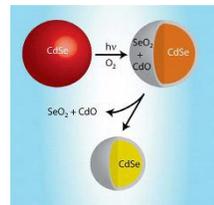
Hines, D. A.; Kamat, P. V.,

J. Phys. Chem. C, 2013, 117, 14418–14426..

DOI: 10.1021/jp404031s

Abstract

With the increased interest in quantum dot sensitized solar cells (QDSCs) there comes a need to better understand how surface modification of quantum dots (QDs) can affect the excited state dynamics of QDs, electron transfer at the QD–metal oxide (MO) interface, and overall photoconversion efficiency of QDSCs. We have monitored the surface modification of solution based QDs via the steady state absorption and emission characteristics of colloidal CdSe passivated with β -alanine (β -Ala). The trap-remediating nature of the β -Ala molecule, arising from the Lewis basicity of the amine group, is realized from the hypsochromic shifts seen in excitonic absorption and emission bands as well as an increase in fluorescence quantum yield. Transient absorption measurements of CdSe–TiO₂ films prepared with and without β -Ala as a linker molecule further reveal the role of the surface modifier in influencing excited state electron transfer processes.



Trap and Transfer: Two-Step Hole Injection Across the Sb₂S₃/CuSCN Interface in Solid-State Solar Cells

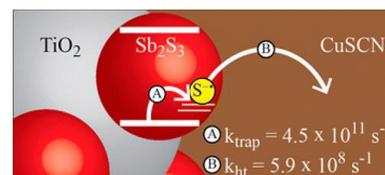
Christians, J.; Kamat, P. V.

ACS Nano, 2012, 7, 7967–7974.

DOI: 10.1021/nn403058f

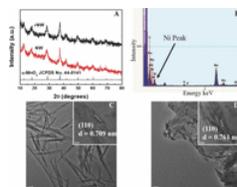
Abstract

In solid-state semiconductor-sensitized solar cells, commonly known as extremely thin absorber (ETA) or solid-state quantum-dot-sensitized solar cells (QDSCs), transfer of photogenerated holes from the absorber species to the p-type hole conductor plays a critical role in the charge separation process. Using Sb₂S₃ (absorber) and CuSCN (hole conductor), we have constructed ETA solar cells exhibiting a power conversion efficiency of 3.3%. The hole transfer from excited Sb₂S₃ into CuSCN, which limits the overall power conversion efficiency of these solar cells, is now independently studied using transient absorption spectroscopy. In the Sb₂S₃ absorber layer, photogenerated holes are rapidly localized on the sulfur atoms of the crystal lattice, forming a sulfide radical (S⁻) species. This trapped hole is transferred from the Sb₂S₃ absorber to the CuSCN hole conductor with an exponential time constant of 1680 ps. This process was monitored through the spectroscopic signal seen for the S⁻ species in Sb₂S₃, providing direct evidence for the hole transfer dynamics in ETA solar cells



Nickel-Doped MnO₂ Nanowires Anchored onto Reduced Graphene Oxide for Rapid Cycling Cathode in Lithium Ion Batteries

Radich, J. G.; Chen, Y.-S., Kamat, P. V.,
ECS JSS, 2013, **2**, M3178-M3181.
DOI: 10.1149/2.023310jss



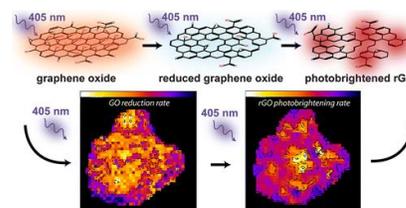
Abstract

Nickel-doped MnO₂ nanowires were synthesized directly onto reduced graphene oxide (RGO) to generate a composite cathode material with improved high-rate cycling characteristics. The presence of RGO improves the electrochemical characteristics of the cathode in Li-ion half-cell architecture. Cyclic voltammetry, electrochemical impedance spectroscopy, and electrode cycling are confirm that RGO plays a major role in enhancing the ability of the Ni_xMn_(1-x)O₂ to reversibly intercalate lithium ions at 1C rate. The chronocoulometric response of the RGO-based electrode shows the improvements originate from faster reaction kinetics and transport of Li⁺ coupled with increased specific capacitance and Li⁺ adsorption.

Direct Observation of Spatially Heterogeneous Single-Layer Graphene Oxide Reduction Kinetics

Eltom, A.; McDonald, M. P.; Vietmeyer, F.; Thapa, J.; Morozov, Y. V.; Sokolov, D. A.; Hodak, J. H.; Vinodgopal, K.; Kamat, P. V.; Kuno, M.

2013, *13*, 5777–5784
DOI: 10.1021/jp30



Abstract

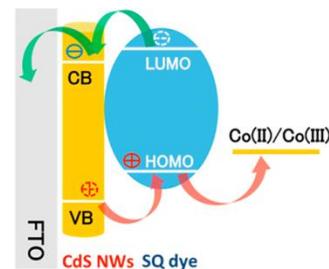
Graphene oxide (GO) is an important precursor in the production of chemically derived graphene. During reduction, GO's electrical conductivity and band gap change gradually. Doping and chemical functionalization are also possible, illustrating GO's immense potential in creating functional devices through control of its local hybridization. Here we show that laser-induced photolysis controllably reduces individual single-layer GO sheets. The reaction can be followed in real time through sizable decreases in GO's photoluminescence efficiency along with spectral blueshifts. As-produced reduced graphene oxide (rGO) sheets undergo additional photolysis, characterized by dramatic emission enhancements and spectral redshifts. Both GO's reduction and subsequent conversion to photobrightened rGO are captured through movies of their photoluminescence kinetics. Rate maps illustrate sizable spatial and temporal heterogeneities in sp² domain growth and reveal how reduction "flows" across GO and rGO sheets. The observed heterogeneous reduction kinetics provides mechanistic insight into GO's conversion to chemically derived graphene and highlights opportunities for overcoming its dynamic, chemical disorder..

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
 DOI: 10.1021/jz402306j

Abstract

Nickel-doped MnO_2 nanowires were synthesized directly onto reduced graphene oxide (RGO) to generate a composite cathode material with improved high-rate cycling characteristics. The presence of RGO improves the electrochemical characteristics of the cathode in Li-ion half-cell architecture. Cyclic voltammetry, electrochemical impedance spectroscopy, and electrode cycling are confirm that RGO plays a major role in enhancing the ability of the $\text{Ni}_x\text{Mn}_{(1-x)}\text{O}_2$ to reversibly intercalate lithium ions at 1C rate. The chronocoulometric response of the RGO-based electrode shows the improvements originate from faster reaction kinetics and transport of Li^+ coupled with increased specific capacitance and Li^+ adsorption.



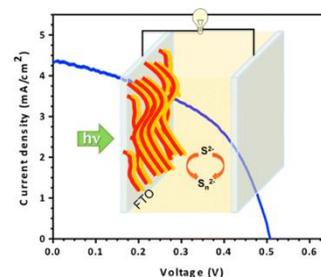
Sequentially Layered CdSe/CdS Nanowire Architecture for Improved Nanowire Solar Cell Performance

Choi, H; Radich J. G.; Kamat, P. V.

J. Phys. Chem. C, Article ASAP
 DOI: 10.1021/jp410235s

Abstract

The power conversion efficiency of semiconductor nanowire (NW) based solar cells as compared to quantum dot solar cell (QDSC) has remained lower, and efforts to improve the photovoltaic performance of semiconductor NWs continue. We have now succeeded in using a layered architecture of CdS and CdSe NWs for improving the photovoltaic performance of nanowire solar cell (NWSC). The photoanode designed with sequentially deposited films of CdSe and CdS NWs delivered a power conversion efficiency of 1%. This efficiency of CdSe/CdS composite is an order of magnitude improvement over single nanowire system (CdS or CdSe) based solar cell. The improvement seen in the CdSe/CdS composite film is attributed to charge rectification and improvement of electron and hole separation and transport in the opposite direction. Impedance spectroscopy demonstrates the beneficial effect of type II structure in CdSe/CdS sequential deposition through lower transport resistance, which remains a dominating effect in dictating the overall performance of the NWSC..

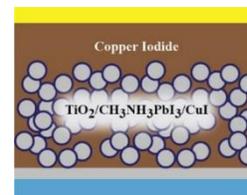


An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide

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

J. Am. Chem. Soc. ASAP

DOI: 10.1021/ja411014k.



Abstract

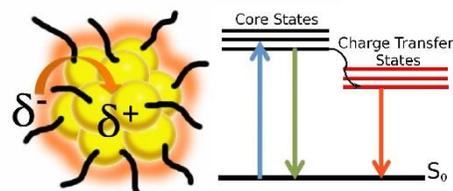
Organo-lead halide perovskite solar cells have emerged as one of the most promising candidates for the next generation of solar cells. To date, these perovskite thin film solar cells have exclusively employed organic hole conducting polymers which are often expensive and have low hole mobility. In a 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.

Excited State Behavior of Luminescent Glutathione Protected Gold Clusters

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

J. Phys. Chem. C. ASAP

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 ($\tau = 780$ 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 ($\tau < 3$ 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..



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