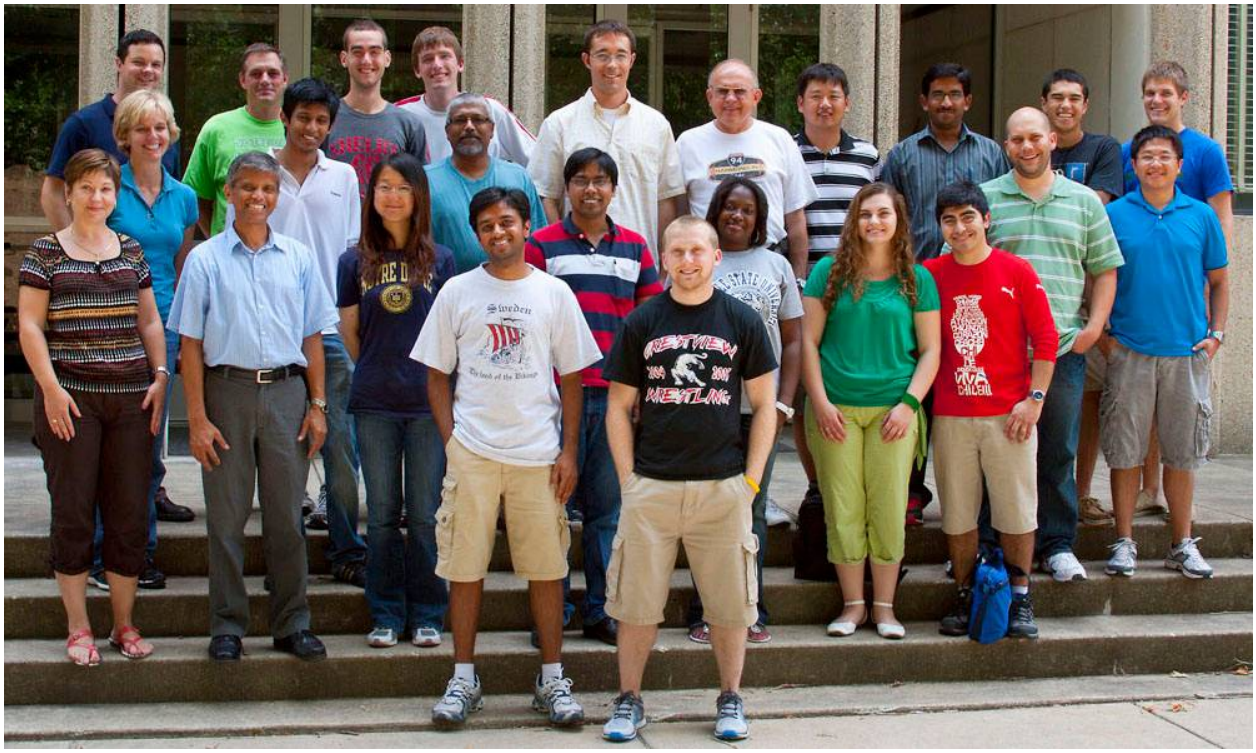
Annual Research Summary

January - December 2012

Kamatlab

University of Notre Dame

(kamatlab.com)



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

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

Research Group

Graduate Students

Matt Becker (Physics - coadvisor Bruce Bunker)
Ian Lightcap (Chemistry)
Ben Meekins (Chem Eng.)
Sachi Krishnamurthy (Chemistry)
Sean Murphy (Chemistry - coadvisor Libai Huang)
James Radich (Chem. Eng.)
Douglas Hines (Chemistry)
Jeff Christians (Chem. Eng.)
Joseph Manser (Chem Eng)
Yuan-Sioux Chen (Chemistry)
Lyuan Sun (CBE, Advisor Joan Brennecke)
Brandon Daley (Esteem Student)

Incoming Students
Jacob Hoffman (Chemistry)
Danilo JaraQuinteros (Chemistry)
Anshumaan Bajapai (Chem Eng. (co-advisor with M. Kuno)

Undergraduate Students

Spring 2012
Grace Meikle (Physics, UND)
Justin Hintz (Chemistry, UND)
Lisa Edwards(Sci Bus UND)
Nevin Peeples (CBE, UND)
Stephanie Weber (CBE, UND)

Summer 2012
Tim Siegler (ND Nano)
Owen Abe (Chemistry, UMaryland)
Jerrin Thomas (ND Nano, UND)

Fall 2012
Grace Meikle (Physics)
Tim Siegler (Chemistry)
Andrew P. Neils (CBE)
Chris Rodriguez (CBE, UND)
Brandon Dunham (CBE, UND)
Raymond Fung (Waterloo)
Lisa Edwards(Sci Bus UND)

Teachers Patrick Kurowski, Peter Hoffman, Kasi Bolden, and John Bogucki

Participants of Summer Research Experience for Teachers program

Postdoctoral Research Associates

G. Ramesha (July 2012-)
Pralay Santra (Mar 2011-)
Hyunbong Choi (Nov 2010-)

Visiting Scientists Julie Peller (IUN)
Roxana Nicolaescu (Serim Corporation)
J. P. Kim (Korea Basic Science Institute)
Alex Mobashery (Penn High School)

Graduation/Fellowships/Recognition

1. **Matthew Becker, Ph.D.** (Dept. of Physics, University of Notre Dame, December 2011)
   Toward the Structural Understanding and Improved Performance of Quantum Dot Solar Cells
2. **Benjamin Meekins, Ph.D.** (Dept. of Chemical & Biomolecular Eng., University of Notre Dame, April 2012)
   Controlling Interfacial Transfer Processes for Improved Photoelectrochemical Performance
3. **Ian Lightcap, Ph.D.** (Dept. of Chemistry & Biochem., University of Notre Dame, April 2012) *Excited State Interactions in Graphene Oxide-Semiconductor/Metal Nanoparticle Architectures for Sensing and Energy Conversion*
4. **Brandon Daley, M.S. (**Esteem Program)
   Commercialization Strategy for a Quantum Dot Solar Cell Paint Coating

Awards/Honors

PVK: Visiting Professor at Indian Institute of Science, Bangalore, India (Dec 2011-Jan 2012)
Visiting Professor, Kyoto University, Japan
Adjunct Faculty, University of Wisconsin, Madison
Cited among top 500 living chemists with highest *h*-index (Chemistry World)
Cited among the 100 Top Chemists of last decade (ISI)

Group:Ian Lightcap, 2011- 2012 Rohm & Haas Outstanding Graduate student award
Jeff Christians, Participant in ACS Publications multimedia workshop
Tim Siegler,ND Nano Fellowship & Statt Fellowship.
Grace Meikle, NanoJapan: International Research Experience for Undergraduates Program

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- present)
  Sustainable Energy Institute Leadership Team (2010- present)
- **Symposium Organizer**
  Co-Organizer, Nanostructures for Energy Conversion, , 221st ECS Meeting Seattle, May 1-4, 2012

Invited Seminar/Colloquium

Quantum dot architectures for the next generation solar cells
NRL Chemistry Colloquium Lecture Series. Washington, DC, February 16

Tapping semiconductor quantum dots for next generation solar cells.
University of Miami, Miami, FL. Chemistry Department Seminar February 24

Designing next generation solar cells with quantum dot architectures.
Purdue University, Chemistry Department and Birck Nanotechnology Center joint seminar. March 16

Light energy conversion with nanostructure assemblies
University of Pittsburgh, Pittsburgh, PA, Chemistry Department Seminar April 26

Quantum dot solar cells
Iowa State University, Ames, IA, Chemistry Department Seminar, April 27

Lecture series on nanotechnology and energy conversion
Royal Institute of Technology, Stockholm, Sweden. May 28-29

Nanostructure architectures for light energy conversion
Publish or perish
Hong Kong, University of Science and Technology. June 28-29

Designing next generation solar cells with semiconductor quantum dots
CTO Solar Print Ltd. Dublin, Ireland. August 31

Semiconductor quantum dots for next generation photovoltaics
Georgia Institute of Technology, School of Materials Science & Engineering Seminar. September 10

Quantum dot solar cells
Pennsylvania State University, University Park, PA. Physical Chemistry Seminar, September 11

Here comes the sun. Exploiting semiconductor quantum dots for next generation solar cells
Indian Institute of Technology, Kanpur, India. ACS India Outreach Seminar October 8

Many Faces of Gold. Charge Equilibration versus Plasmonic Effects in Metal-Semiconductor Nanocomposites
Hokkaido Univ Sapporo, Japan, Chemistry Department seminar November 8

Quantum dot-based and sensitized photovoltaic cells; its relation to artificial photosynthesis
Toin University of Yokohama, Yokohama, Japan. November 10

Nanostructure architectures for light energy conversion
Nagoya, Japan, Nagoya University, Department of Crystalline Materials Science seminar, Nov. 16

Conference Presentations (2012)

Indian-US Workshop on Nanophotonics and Nanoplasmonics, Indian Inst. Sci., Bangalore, Jan 9-12. *(Invited Lecture)*
Excited state interactions of graphene-metal nanocomposites.

4th International Symposium on Advanced Plasma Science and Its Applications for Nitrides and nanomaterials (ISPlasma2012). Chubu Univ., Aichi, Japan, January 28-February 1 (Invited Lecture)
Light energy conversion with nanostructure assemblies.

243rd Meeting of the American Chemical Society. San Diego, CA. March 25-29 (Invited Lecture)
Role of metal co-catalyst in semiconductor assisted photocatalysis. Charge equilibration versus plasmonic effects.

Annual Meeting of the Electrochemical Society. Seattle, WA, May 1-4
Chemistry and physics of graphene and 2D nanostructures.
Strategies to design high efficiency quantum dot sensitized solar cells.
Capture store and discharge of electrons in graphene based assemblies.

Gordon Research Conference, Chemistry and Physics of Graphitic Carbon materials, Davidson, NC, June 17-22.
Graphene based assemblies for light energy conversion. (Invited Lecture)

DOE Solar Photochemistry Conference,. Annapolis, MD. June 3-6
Tracking excited state interactions in graphene oxide-semiconductor mesoscale architectures.

19th International Conference on Photochemical Conversion and Storage of Solar Energy. California Institute of Technology, Pasadena, CA. July 29-August 3 (Plenary Talk)
Quantum dot sensitized solar cells.

244th Meeting of the American Chemical Society. Philadelphia, PA. August 19-23
Shuttling electrons with graphene oxide in quantum dot solar cells. (Invited Lecture)
Strategies to design graphene-semiconductor-metal catalyst mat. (Invited Lecture)

8th JNC Conference on Chemistry of Materials. Trivandrum, India. Sept 30-Oct 2 (Invited Lecture)
Semiconductor-metal composites for light energy conversion. Charge equilibration versus plasmonic effects.

3rd Plasmonic Chemistry Symposium. Tokyo, Japan November 10 (Invited Lecture)
Light energy conversion with semiconductor-metal composites. Charge equilibration versus plasmonic effects

7th Asian Photochemistry Conference 2012, Osaka University, Osaka, Japan. November 12-15 (Plenary Talk)
Role of metal nanoparticles in semiconductor assisted photocatalysis.

Symposium on Artificial Photosynthesis, Kyoto University. Kyoto, Japan, November 20 (Invited Lecture)
Synchronizing energy and electron transfer processes in quantum dot solar cells

Presentation by Students and Postdocs

Indo-US Bilateral Workshop on Nanophotonics and Nanoplasmonics, Bangalore, India. Jan 9-12

S. Krishnamurthy and P. V. Kamat .
Galvanic exchange on reduced graphene oxide. Designing multifunctional two-dimensional nano assembly.

243rd Meeting of the American Chemical Society. San Diego, CA. March 25-29

I. V. Lightcap, and P. V. Kamat
Graphene based semiconductor composites for light energy conversion.

7th International Conference on Quantum Dots, Santa Fe, NM May 13-18

Pralay Santra
Boosting the Efficiency of Quantum Dot Sensitized Solar Cells by Mn Doping

19th International Conference on Photochemical Conversion and Storage of Solar Energy. California Institute of Technology, Pasadena, CA. July 29-August 3

Douglas Hines and P. V. Kamat
Modulating Electron Transfer at the CdSe-TiO_2 Interface through Linker Functional Groups

S. Krishnamurthy
Galvanic Exchange on Reduced Graphene Oxide. Designing Multifunctional Two-Dimensional Nano assembly.

Ian Lightcap, Sean Murphy, Lebai Huang, P. V. Kamat
Photoinduced Charge Transfer Interactions Between Porphyrin-Ag Nanoparticle and Porphyrin-RGO-Ag Nanoparticle Composites

Plasmonics, Gordon Research Seminar, June 9,10

Sean Murphy
Charge-Transfer and Surface Interactions: Metal Nanoparticle-Porphyrin and Graphene-Metal Nanoparticle-Porphyrin Composites

5th Annual Argonne Postdoctoral Research Symposium, Argonne, IL, September 20-21

Radich, J.G. and Kamat, P. V.
Reduced Graphene Oxide for Energy Storage Composites

Santra, P. K. and Kamat, P. V.
Boosting the Efficiency of Quantum Dot Sensitized Solar Cells by Mn Doping

Murphy, S.; Lightcap, I.; Huang, L.; Kamat, P
Metal Nanoparticle and Graphene-Metal Nanoparticle Composites: Charge Transfer and Surface Interactions with Target Molecules.

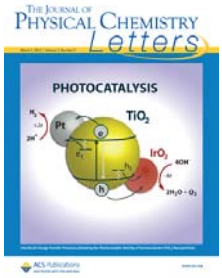
PINDU 2012, University of Notre Dame, December 1

S. Krishnamurthy and P. V. Kamat .
Galvanic Exchange on Reduced Graphene Oxide. Designing a Multifunctional Two-Dimensional Catalyst Assembly

Book Chapters

Santra, P. K.; Kamat, P. V., Quantum Dot Solar Cells Research at Notre Dame, in *Frontiers of Quantum Dot Solar Cells*, T. Toyoda, Editor. 2012, CMC Publishing, Tokyo, Japan. p. 156-161.

Radich, J. G.; Kamat, P. V., Future Prospects of Quantum Dot Solar Cells in *Frontiers of Quantum Dot Solar Cells*, T. Toyoda, Editor. 2012, CMC Publishing, Tokyo, Japan. p. 156-161..



Research Papers

(1) Genovese, M. P.; Lightcap, I. V.; Kamat, P. V., *Sun-Believable Solar Paint. A Transformative One-Step Approach for Designing Nanocrystalline Solar Cells.* ACS Nano, 2012, *6*, 865–872.

(2) Santra, P. K.; Kamat, P. V., *Mn-Doped Quantum Dot Sensitized Solar Cells. A Strategy to Boost Efficiency over 5%* J. Am. Chem. Soc., 2012, *134*, 2508–2511.

(3) Kamat, P. V., *Manipulation of Charge Transfer Across Semiconductor Interface. A Criterion that Cannot be Ignored in Photocatalyst Design.* J.Phys. Chem. Lett., 2012, *3*, 663-672.

(4) Yokomizo, Y.; Krishnamurthy, S.; Kamat, P. V., *Photoinduced Electron Charge and Discharge of Graphene-ZnO Nanoparticle Assembly.* Catal. Today, 2012, *199*, 36-41.

(5) Kamat, P. V., *Boosting the Efficiency of Quantum Dot Sensitized Solar Cells Through Modulation of Interfacial Charge Transfer.* Acc. Chem. Res., 2012, *45,* 1906–1915

(6) Choi, H.; Santra, P. K.; Kamat, P. V., *Synchronized Energy and Electron Transfer Processes in Covalently Linked CdSe-Squaraine Dye-TiO_2 Light Harvesting Assembly.* ACS Nano, 2012, *6,* 5718–5726.

(7) Lightcap, I. V.; Kamat, P. V., *Fortification of CdSe Quantum Dots with Graphene Oxide. Excited State Interactions and Light Energy Conversion.* J. Am. Chem. Soc., 2012, *134*, 7109–7116.

(8) Radich, J. G.; Kamat, P. V., *Origin of Reduced Graphene Oxide Enhancements in Electrochemical Energy Storage.* ACS Catalysis, 2012, *2*, 807-816.

(9) Lightcap, I. V.; Murphy, S.; Schumer, T.; Kamat, P. V., *Electron Hopping Through Single-to-Few Layer Graphene Oxide Films. Photocatalytically Activated Metal Nanoparticle Deposition.* J. Phys. Chem. Lett., 2012, *3*, 1453-1458.

(10) Choi, H.; Chena, W. T.; Kamat, P. V., *Know Thy Nano Neighbor. Plasmonic versus Electron Charging Effects of Gold Nanoparticles in Dye Sensitized Solar Cells.* ACS Nano, 2012, *6*, 4418–4427.

(11) Hines, D. A.; Becker, M. A.; Kamat, P. V., *Photoinduced Surface Oxidation and Its Effect on the Exciton Dynamics of CdSe Quantum Dots.* J. Phys. Chem. C, 2012, *116*, 13452–13457.

(12) Vinodgopal, K.; Neppolian, B.; Salleh, N.; Lightcap, I. V.; Grieser, F.; Ashokkumar, M.; Ding, T. T.; Kamat, P. V., *Dual-Frequency Ultrasound for Designing Two Dimensional Catalyst Surface: Reduced Graphene Oxide-Pt Composite.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012, *409*, 81-87.

(13) Chen, W.-T.; Hsu, Y.-J.; Kamat, P. V., *Realizing Visible Photoactivity of Metal Nanoparticles. Excited State Behavior and Electron Transfer Properties of Silver (Ag_8) Clusters* J. Phys. Chem. Lett., 2012, *3*, 2493–2499.

(14) Krishnamurthy, S.; Kamat, P. V., *Galvanic Exchange on Reduced Graphene Oxide. Designing a Multifunctional Two-Dimensional Catalyst Assembly.* J. Phys. Chem. C, 2012, *116*, (ASAP).

(15) Lightcap, I. V., *Graphitic Design: Prospects of Graphene-Based Nanocomposites for Solar Energy Conversion, Storage, and Sensing.* Accounts of Chemical Research, 2012, in press (ASAP).

Editorials

(1) Kamat, P. V.; *Virtual Issue: TiO_2 Nanostructures: Recent Physical Chemistry Advances. J. Phys. Chem. C* **2012**, *116*, 11849−11851 .

(2) Kamat, P. V.; Schatz, G. C. *Advancing the Frontiers of Physical Chemistry, J. Phys. Chem. Lett.* **2012**, *3*,38-39.

(3) Kamat, P. V.; Schatz, G. C. *The Journal of Physical Chemistry Letters, The FIRST Impact*, *J. Phys. Chem. Lett.* **2012**, *3*, 1934-1935.

(4) Kamat, P. V.; Schatz, G. C.; *Getting the submission Right and Avoiding Rejection J. Phys. Chem. Lett.* **2012**, 3, 3088−3089.

(5) Kamat, P. V *The Magic of Electrocatalysts, J. Phys. Chem. Lett.* **2012**, 3, 3404

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Publication Analysis

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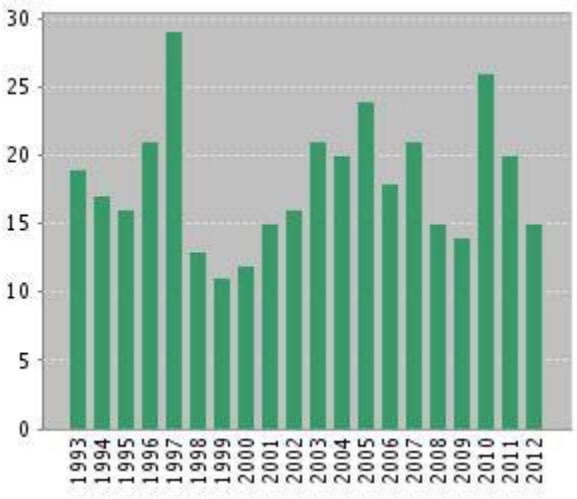
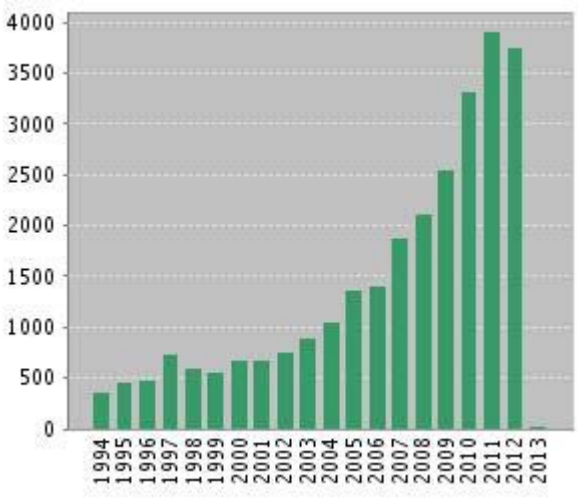
Publications



Citations



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i10-index	321	254

Sun-Believable Solar Paint. A Transformative One-Step Approach for Designing Nanocrystalline Solar Cells.

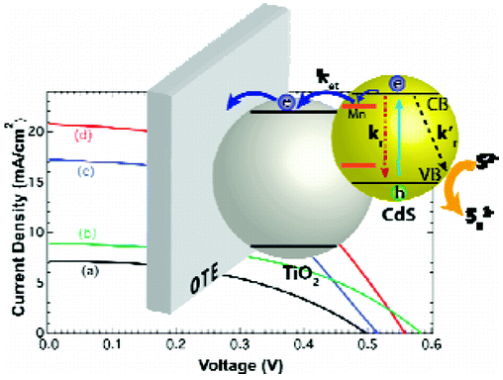
Genovese, M. P.; Lightcap, I. V.; Kamat, P. V.
ACS Nano, 2012, **6**, 865–872
DOI: 10.1021/nn204381g

Abstract

A transformative approach is required to meet the demand of economically viable solar cell technology. By making use of recent advances in semiconductor nanocrystal research, we have now developed a one-coat solar paint for designing quantum dot solar cells. A binder-free paste consisting of CdS, CdSe, and TiO_2 semiconductor nanoparticles was prepared and applied to conducting glass surface and annealed at 473 K. The photoconversion behavior of these semiconductor film electrodes was evaluated in a photoelectrochemical cell consisting of graphene–Cu_2S counter electrode and sulfide/polysulfide redox couple. Open-circuit voltage as high as 600 mV and short circuit current of 3.1 mA/cm^2 were obtained with CdS/TiO_2–CdSe/TiO_2 electrodes. A power conversion efficiency exceeding 1% has been obtained for solar cells constructed using the simple conventional paint brush approach under ambient conditions. Whereas further improvements are necessary to develop strategies for large area, all solid state devices, this initial effort to prepare solar paint offers the advantages of simple design and economically viable next generation solar cells.

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

Santra, P. K.; Kamat, P. V.
J. Am. Chem. Soc., 2012, 134, 2508–2511
DOI: 10.1021/ja211224s



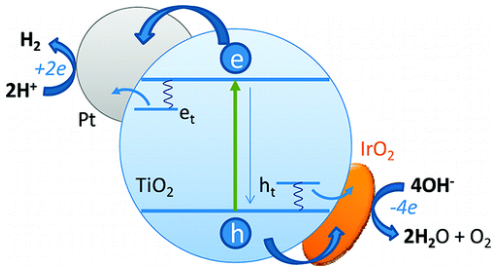
Abstract

To make Quantum Dot Sensitized Solar Cells (QDSC) competitive, it is necessary to achieve power conversion efficiencies comparable to other emerging solar cell technologies. By employing Mn^{2+} doping of CdS, we have now succeeded in significantly improving QDSC performance. QDSC constructed with Mn-doped-CdS/CdSe deposited on mesoscopic TiO_2 film as photoanode, Cu_2S/Graphene Oxide composite electrode, and sulfide/polysulfide electrolyte deliver power conversion efficiency of 5.4%.

Manipulation of Charge Transfer Across Semiconductor Interface. A Criterion that Cannot be Ignored in Photocatalyst Design.

Kamat, P. V.

J. Phys. Chem. Lett., 2012, **3**, 663-672
DOI: **1021/jz201629p**



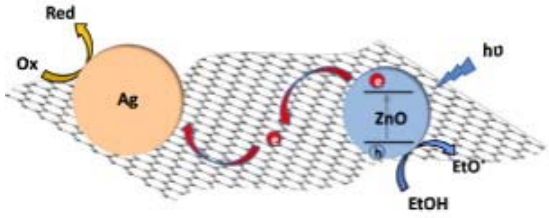
Abstract

The Perspective focuses on photoinduced electron transfer between semiconductor–metal and semiconductor–semiconductor nanostructures and factors that influence the rate of electron transfer at the interface. The storage and discharge properties of metal nanoparticles play an important role in dictating the photocatalytic performance of semiconductor–metal composite assemblies. Both electron and hole transfer across the interface with comparable rates are important in maintaining high photocatalytic efficiency and stability of the semiconductor assemblies. Coupled semiconductors of well-matched band energies are convenient to improve charge separation. Furthermore, semiconductor and metal nanoparticles assembled on reduced graphene oxide sheets offer new ways to design multifunctional catalyst mat. The fundamental understanding of charge-transfer processes is important in the future design of light-harvesting assemblies..

Photoinduced Electron Charge and Discharge of Graphene-ZnO Nanoparticle Assembly

Yokomizo, Y.; Krishnamurthy, S.; Kamat, P. V.

Catal. Today, 2012, **199**, 36-41
DOI:10.1016/j.cattod.2012.04.045



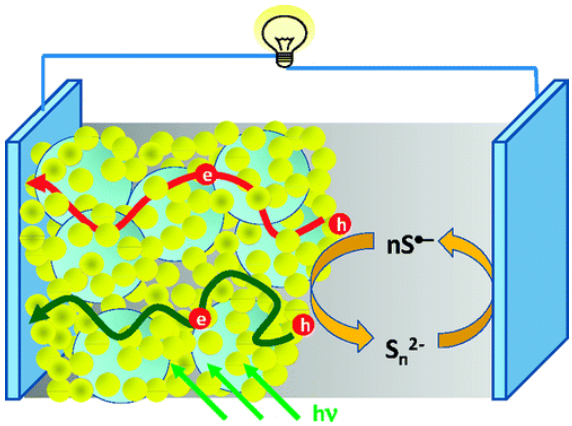
Abstract

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.

Boosting the Efficiency of Quantum Dot Sensitized Solar Cells Through Modulation of Interfacial Charge Transfer.

Kamat, P. V.

Acc. Chem. Res. 2012, 45, 1906–1915
DOI: 10.1021/ar200315d



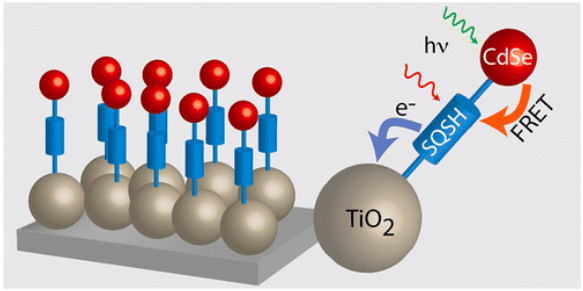
Abstract

This Account focuses on photoinduced electron transfer processes in quantum dot sensitized solar cells (QDSCs) and discusses strategies to overcome the limitations of various interfacial electron transfer processes. The heterojunction of two semiconductor nanocrystals with matched band energies (e.g., TiO_2 and CdSe) facilitates charge separation. Disparity between the electron and hole scavenging rate leads to further accumulation of holes within the CdSe QD and increases the rate of electron–hole recombination. To overcome the losses due to charge recombination processes at the interface, researchers need to accelerate electron and hole transport.

Synchronized Energy and Electron Transfer Processes in Covalently Linked CdSe-Squaraine Dye-TiO_2 Light Harvesting Assembly.

Choi, H.; Santra, P. K.; Kamat, P. V.

ACS Nano, 2012, **6**, 5718–5726
DOI: 10.1021/nn301982e

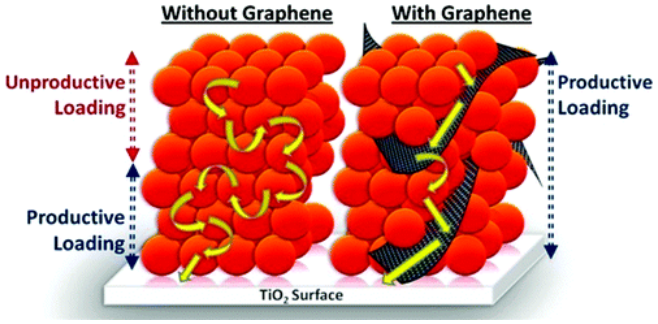


Abstract

Manipulation of energy and electron transfer processes in a light harvesting assembly is an important criterion to mimic natural photosynthesis. We have now succeeded in sequentially assembling CdSe quantum dot (QD) and squaraine dye (SQSH) on TiO_2 film and couple energy and electron transfer processes to generate photocurrent in a hybrid solar cell. When attached separately, both CdSe QDs and SQSH inject electrons into TiO_2 under visible–near-IR irradiation. However, CdSe QD if linked to TiO_2 with SQSH linker participates in an energy transfer process. The hybrid solar cells prepared with squaraine dye as a linker between CdSe QD and TiO_2 exhibited power conversion efficiency of 3.65% and good stability during illumination with global AM 1.5 solar condition. The synergy of covalently linked semiconductor quantum dots and near-IR absorbing squaraine dye provides new opportunities to harvest photons from selective regions of the solar spectrum in an efficient manner.

Electron Transfer Cascade by Organic/Inorganic Ternary Composites of Porphyrin, Zinc Oxide Nanoparticles, and Reduced Graphene Oxide on a Tin Oxide Electrode that Exhibits Efficient Photocurrent Generation

Lightcap, I. V.; Kamat, P. V.
J. Am. Chem. Soc., 2012, **134**, 7109–7116
DOI: 10.1021/ja3012929

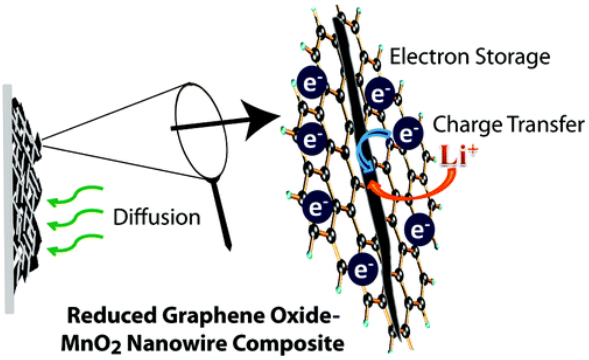


Abstract

Graphene based 2-D carbon nanostructures provide new opportunities to fortify semiconductor based light harvesting assemblies. Electron and energy transfer rates from photoexcited CdSe colloidal quantum dots (QDs) to graphene oxide (GO) and reduced graphene oxide (RGO) were isolated by analysis of excited state deactivation lifetimes as a function of degree of oxidation and charging in (R)GO. Apparent rate constants for energy and electron transfer determined for CdSe–GO composites were 5.5×10^8 and 6.7×10^8 s^{-1}, respectively. Additionally, incorporation of GO in colloidal CdSe QD films deposited on conducting glass electrodes was found to enhance the charge separation and electron conduction through the QD film, thus allowing three-dimensional sensitization. Photoanodes assembled from CdSe–graphene composites in quantum dot sensitized solar cells display improved photocurrent response (~150%) over those prepared without GO.

Origin of Reduced Graphene Oxide Enhancements in Electrochemical Energy Storage.

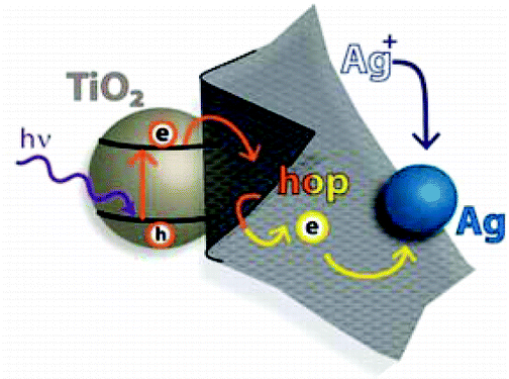
Radich, J. G.; Kamat, P. V.
ACS Catalysis, 2012, **2**, 807-816.
DOI: 10.1021/cs3001286



Reduced graphene oxide (RGO) has become a common substrate upon which active intercalation materials are anchored for electrochemical applications such as supercapacitors and lithium ion batteries. The unique attributes of RGO, including high conductivity and porous macrostructure, are often credited for enhanced cycling and capacity performance. Here we focus on probing the electrochemical response of α-MnO_2/RGO composite used as an electrode in a lithium ion battery cell and elucidating the mechanistic aspects of the RGO on the commonly observed improvements in cycling and capacity. We find that electron storage properties of RGO enables better electrode kinetics, more rapid diffusion of Li^+ to intercalation sites, and a greater capacitance effect during discharge. Further investigation of the length of the one-dimensional nanowire morphology of the α-MnO_2 has allowed us to differentiate between the innate characteristics of the MnO_2 and those of the RGO.

Electron Hopping Through Single-to-Few Layer Graphene Oxide Films. Photocatalytically Activated Metal Nanoparticle Deposition.

Lightcap, I. V.; Murphy, S.; Schumer, T.; Kamat, P. V.
J. Phys. Chem. Lett., 2012, **3**, 1453-1458.
DOI: 10.1021/jz3004206

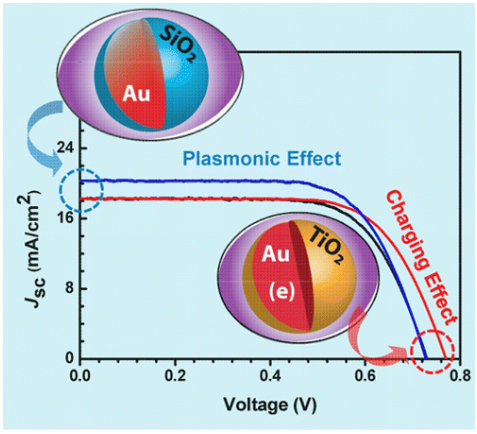


Abstract

Single- to few-layer graphene oxide (GO) sheets have been successfully anchored onto TiO_2 films using electrophoretic deposition. Upon UV illumination of TiO_2–GO films, photogenerated electrons from TiO_2 are captured by GO. These electrons are initially used in GO's reduction, while additional electron transfer results in storage across its sp^2 network. In the presence of silver ions, deposition of silver nanoparticles (NPs) is accomplished on the GO surface opposite the TiO_2, thus confirming the ability of GO to transport electrons through its plane. Illumination-controlled reduction of silver ions allows for simple selection of particle size and loading, making these semiconductor–graphene–metal (SGM) films ideal for custom catalysis and sensor applications. Initial testing of SGM films as surface-enhanced resonance Raman (SERRS) sensors produced significant target molecule signal enhancements, enabling detection of nanomolar concentrations.

Know Thy Nano Neighbor. Plasmonic versus Electron Charging Effects of Gold Nanoparticles in Dye Sensitized Solar Cells.

Choi, H.; Chena, W. T.; Kamat, P. V.
ACS Nano, 2012, **6**, 4418–4427
DOI: 10.1021/nn301137r

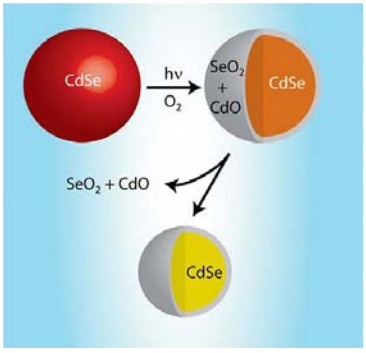


Abstract

Neighboring metal nanoparticles influence photovoltaic and photocatalytic behavior of semiconductor nanostructures either through Fermi level equilibration by accepting electrons or inducing localized surface plasmon effects. By employing SiO_2- and TiO_2-capped Au nanoparticles we have identified the mechanism with which the performance of dye-sensitized solar cells (DSSC) is influenced by the neighboring metal nanoparticles. The efficiency of an N719 dye-sensitized solar cell (9.3%) increased to 10.2% upon incorporation of 0.7% Au@SiO_2 and to 9.8% upon loading of 0.7% Au@TiO_2 nanoparticles. The plasmonic effect as monitored by introducing Au@SiO_2 in DSSC produces higher photocurrent. However, Au nanoparticles undergo charge equilibration with TiO_2 nanoparticles and shift the apparent Fermi level of the composite to more negative potentials. As a result, Au@TiO_2 nanoparticle-embedded DSSC exhibit higher photovoltage.

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.; Becker, M. A.; Kamat, P. V.
J. Phys. Chem. C, 2012, **116**, 13452–13457
DOI: 10.1021/jp303659g

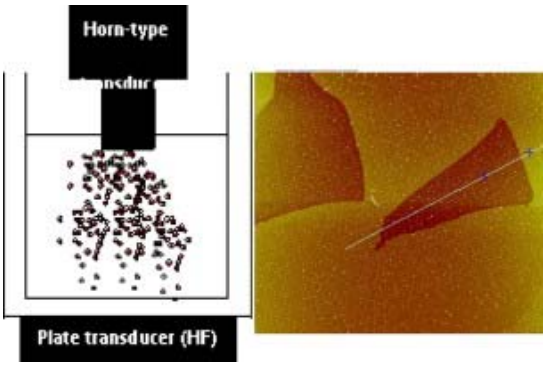


Abstract

With increased interest in semiconductor nanoparticles for use in quantum dot solar cells there comes a need to understand the long-term photostability of such materials. Colloidal CdSe quantum dots (QDs) were suspended in toluene and stored in combinations of light/dark and N_2/O_2 to simulate four possible benchtop storage environments. CdSe QDs stored in a dark, oxygen-free environment were observed to better retain their optical properties over the course of 90 days. The excited state lifetimes, determined through femtosecond transient absorption spectroscopy, of air-equilibrated samples exposed to light exhibit a decrease in average lifetime (0.81 ns) when compared to samples stored in a nitrogen/dark environment (8.3 ns). A photoetching technique commonly used for controlled reduction of QD size was found to induce energetic trap states to CdSe QDs and accelerate the rate of electron–hole recombination. X-ray absorption near edge structure (XANES) analysis confirms surface oxidation, the extent of which is shown to be dependent on the thickness of the ligand shell.

Dual-Frequency Ultrasound for Designing Two Dimensional Catalyst Surface: Reduced Graphene Oxide-Pt Composite

Vinodgopal, K.; Neppolian, B.; Salleh, N.; Lightcap, I. V.; Grieser, F.; Ashokkumar, M.; Ding, T. T.; Kamat, P. V.
Colloids and Surfaces A, 2012, **409**, 81-87.
DOI: 10.1016/j.colsurfa.2012.06.006

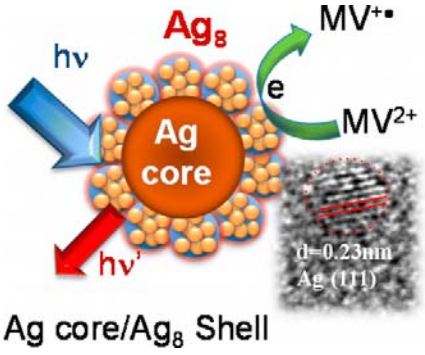


Abstract

Few-layered reduced graphene oxide–Pt composites are prepared using a combination of two ultrasound frequencies at 20 kHz and 211 kHz. Such a unique dual frequency arrangement operating in tandem, yields large exfoliated graphene sheets with platinum nanoparticles dispersed on them. The extent of reduction achieved by the use of this dual frequency sonication arrangement is evaluated by XPS, IR, and Raman spectroscopies. Transmission electron and atomic force microscopies confirm the morphology of resulting assemblies to be bi- and single layered sheets. These composites show good electrocatalytic activity towards methanol oxidation.

Realizing Visible Photoactivity of Metal Nanoparticles. Excited State Behavior and Electron Transfer Properties of Silver (Ag_8) *Clusters*

Chen, W.-T.; Hsu, Y.-J.; Kamat, P. V.
J. Phys. Chem. Lett., 2012, **3**, 2493–2499.
DOI:10.1021/jz300940c

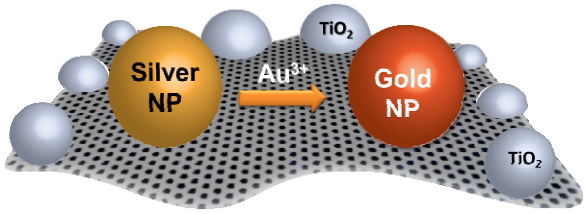


Abstract

Silver nanoclusters complexed with dihydrolipoic acid (DHLA) exhibit molecular-like excited-state properties with well-defined absorption and emission features. The 1.8 nm diameter Ag nanoparticles capped with Ag_8 clusters exhibit fluorescence maximum at 660 nm with a quantum yield of 0.07%. Although the excited state is relatively short-lived (τ 130 ps), it exhibits significant photochemical reactivity. By introducing MV^{2+} as a probe, we have succeeded in elucidating the interfacial electron transfer dynamics of Ag nanoclusters. The formation of $MV^{+\bullet}$ as the electron-transfer product with a rate constant of 2.74×10^{10} s^{-1} confirms the ability of these metal clusters to participate in the photocatalytic reduction process. Basic understanding of excited-state processes in fluorescent metal clusters paves the way toward the development of biological probes, sensors, and catalysts in energy conversion devices.

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

J Krishnamurthy, S.; Kamat, P. V.
J. Phys. Chem. C, 2012, **116**, ASAP
DOI: 10.1021/jp30



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 Au^{3+} 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 nano-particles and facilitate chemical transformations. Coupled with RGO's unique ability to capture and transport electrons, galvanic exchange is used to contrive a two-dimensional nano catalyst 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.

Experimental facilities at Notre Dame Radiation Laboratory
For additional information please refer to Kamatlab.com