

# Annual Research Summary

January - December 2011

**Kamat Research Group**  
**University of Notre Dame**



Summer 2011

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## **Prashant V. Kamat**

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## 2011 Activities/ Highlights

### Research Group

#### Visiting Scientists

Prof. Julie Peller (Indiana University, Northwest)  
Dr. Roxana Nicolaescu (Serim Corporation)  
Mr. Yuji Yokomizo (Ritsumeikan University, Japan)  
Dr. Lorena Barrientos Poblete (UMCE,Santiago-Chile)  
Mr. Wei-Ta Chen, ( National Chiao Tung University in Taiwan)

#### Postdoctoral Associates

Dr. Yoonho Jun  
Dr. Hyunbong Choi  
Dr. Pralay Santra

#### Graduate Students

Matt Becker (Physics - coadv. Bruce Bunker)  
Ian Lightcap (Chemistry)  
Ben Meekins (Chem. Eng.)  
Sean Murphy (Chemistry - coadv. Libai Huang)  
James Radich (Chem. Biomol. Eng.)  
Sachi Krishnamurthy (Chemistry)  
Douglas Hines (Chemistry)  
Jeff Christians (Chem. Biomol.Eng.)  
Brandon Daly (ESTEEM, ND)

#### Undergraduate Students

##### Spring 2011

Douglas Pernik (CBE, UND) -Slatt Fellow  
Ryan P. Dwyer (Chemistry, UND)  
Peter Lobaccaro (CBE, UND)  
Tim Schumer (CBE, UND)  
Susan Garabedian (CBE, UND)

##### Summer 2011

Nevin Peeples (CBE, UND) NURF Fellow  
Stephanie Weber (CBE, UND) -Slatt Fellow  
Lisa Edwards (Science Buisness) - NURF Fellow  
Blake Weaver (UND)

##### Fall 2011

Douglas Pernik (CBE, UND)  
Justin Hintz (Chemistry, UND)  
Grace Heikle (Physics, UND)  
Nevin Peeples (CBE, UND)  
Stephanie Weber (CBE, UND)  
Tim Siegler (CBE, UND)

## Awards/Fellowships/Recognition

1. **Kevin Tvrdy** Department of Chemistry, University of Notre Dame, March 2011  
*Electron Transfer Reactions in Quantum Dot Sensitized Solar Cells*
2. **David Baker** Dept. of Chemical & Biomolecular Eng, University of Notre Dame, March 2011  
*On the Advancement of Quantum Dot Solar Cell Performance Through Enhanced Charge Carrier Dynamics.*
3. **Cliffton Harris** Department of Chemistry, University of Notre Dame, March 2011  
*Photoinduced Electron Transfer Processes of Semiconductor Quantum Dots in Confined Media*
4. **Yanghai Yu** who defended his Ph. D. thesis in 2010 received his formal degree at 2011 commencement

### Awards/Honors (PVK):

Fellow of the American Chemical Society (2011)

Chemical Research Society of India (CRSI) Lectureship Award 2011

Visiting Professor at Marie Curie University, Paris and a symposium in honor of the award of Professorship

Cited among top 500 living chemists with highest *h*-index (Chemistry World)

Cited among the 100 Top Chemists of last decade (ISI)

## 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)
- **Committees**
  - Awards and Honors Committee of the Electrochemical Society (2007-2011)
- **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, , 219<sup>th</sup> ECS Meeting Montreal, Canada May 1-4, 2011

## Invited Seminar/Colloquium

University of Louisville September 23, 2011 Chemical Engineering Department Seminar

*Nanostructure Assemblies for Next Generation Solar Cells*

CNRS - Universite Lyon 1, Departmental Seminar, July 22, 2011

*Role of Metals in Semiconductor Assisted Photocatalysis*

Centre Microélectronique de Provence, Ecole Nationale Supérieure des Mines de Saint Etienne, July 21, 2011

*Nanostructure Assemblies for Light Energy Conversion*

Marie Curie University, Paris, July 4-31, 2011. *Lecture Series.*

*Strategies to Harvest Light Energy with Semiconductor Nanostructures*

*Controlling photoinduced charge transfer processes at semiconductor interface*

*Graphene based assemblies for energy conversion*

*Understanding the role of metals in semiconductor assisted photocatalysis*

*Publish or Perish (The art of scientific writing)*

University of Texas at Austin, TX May 12, 2011 Chemistry Department Seminar

*Manipulation of Photoinduced Charge Transfer Events in Semiconductor Nanoassemblies*

University of California Davis, May 17, 2011, Chemistry Department Seminar

*Quantum Dot Solar Cells*

University of California Riverside, March 30, 2011 Chemical Engineering Department Seminar

*Light Energy Conversion with Semiconductor Quantum Dots*

Ottawa University, Canada, Chemistry Department seminar, March 16, 2011

*Strategies to Harvest Light Energy with Semiconductor Nanostructures*

Kansas State University, Manhattan, Kansas, on February 17, 2011 (PLU Distinguished Speaker)

*Semiconductor Nanostructures for Next Generation Solar Cells*

**Conference Presentations (2011):**

Bunsen-Colloquium and Discussions, Heidelberg Oct 12-14, 2011 (Invited Speaker)

*Nanostructure Architectures for Energy Conversion*

Colloquium on Intelligent Systems (Invited talk) University of Stuttgart, October 11, 2011

*Exploitation of nanostructure assemblies for light energy conversion (Invited speaker)*

2nd International Conference on Semiconductor Sensitized Solar Cells, Mallorca, Spain, Sept 18-20 2011

*Tailoring Nanostructured Semiconductor Interface for Quantum Dot Sensitized Solar Cells*

242<sup>nd</sup> American Chemical Society Meeting, Denver, August 28 - September 1, 2011 (Invited Speaker)

*Mapping the kinetics of charge transfer processes responsible for the photocatalytic activity of semiconductor-Pt catalyst*

*Modulating charge injection between CdSe quantum dots and oxide nanoparticles*

ICP 2011 (International Conference of Photochemistry), Beijing, China, August 7-12, 2011 (Plenary Speaker)

*Quantum Dot Solar Cells. Photoinduced Charge Transfer at Nanostructure Interface*

XXXIII REUNIÓN BIENAL DE LA SOCIEDAD ESPAÑOLA DE QUÍMICA Valencia, July 24th - 28th 2011 (Plenary Speaker)

*Nanostructure Assemblies for Solar Energy Conversion*

Sungkyun Solar Forum, Korea, June 26-28, 2011 (Invited speaker)

*Mechanistic Insights into the Operation of Quantum Dot Sensitized Solar Cells (Invited Speaker)*

Workshop on Nanoplasmonics for Energy and the Environment, Vigo, Spain, June 11-14, 2011 (Invited Speaker)

*Graphene Based Hybrid Assemblies for Energy Conversion*

33<sup>rd</sup> DOE Solar Photochemistry Research Meeting, Wintergreen, VA, June 2011

*Photoinduced Electron Transfer between CdSe Quantum Dots and Oxide Nanoparticles*

219<sup>th</sup> Meeting of the Electrochemical Society, Montreal, May 1-6, 2011

*Graphene Oxide Semiconductor Nanocomposites*

*A 2-D Interactive Affair between Excited Porphyrin and Graphene Oxide*

*Interfacial Charge Transfer Dynamics in Quantum Dot Solar Cells*

2011 Spring MRS Meeting, San Francisco, April 2011 (Invited Speaker)

*Graphene-Semiconductor Composites as Next Generation Photocatalysts*

*Interfacial Charge Transfer Processes at Nanostructured Semiconductor Interface*

American Physics Society Meeting, Dallas, TX, March 21 – 25, 2011 (Invited Speaker)

*Quantum Dot Solar Cells. Understanding Charge Transfer at Nanostructure Interface*

241<sup>st</sup> American Chemical Society Meeting, Anaheim, CA, March 27-31, 2011 (Invited Speaker)

*Quantum Dot Solar Cells. Exploitation of Nanostructure Interface for Efficient Charge Transfer*

*Designing TiO<sub>2</sub>-SrTiO<sub>3</sub> composites for photocatalytic water splitting processes*

Lo Mejor de la Universidad de Notre Dame en Mexico, March 2, 2011 (Invited Speaker)

*Semiconductor Architectures for Next Generation Solar Cells*

3<sup>rd</sup> Annual Workshop on Electrochemistry at the University of Texas at Austin, February 19, 20, 2011

Kamat, P. V. “*Beyond Photovoltaics. Nanostructure Architecture for Liquid Junction Solar Cells*” (Invited)

13th CRSI and 5th RSC Symposium in Chemistry in Bhubaneswar, India, February 4-6, 2011

Kamat, P. V. “*Nanostructure Semiconductor Assemblies for Next Generation Solar Cells*” (Award Lecture)

PACIFICHEM, Symposium on The Nanostructure-Enhanced Photochemical Reactions. Honolulu Dec 15-20, 2010.

*Manipulation of photochemical processes on a graphene oxide sheet*

### **Presentation by Students and Postdocs**

**H. Choi**, 2nd International Conference on Semiconductor Sensitized Solar Cells, Mallorca, Spain, Sept 18-20 2011

*Supersensitization of Quantum Dot Sensitized Solar Cells with NIR Organic Dye*

**B. Meekins**, Graduate Student Union Research Symposium, University of Notre Dame, February 8, 2011  
*Enhanced Photovoltaic Properties of SrTiO<sub>3</sub>-TiO<sub>2</sub> Heterostructures for Solar Cell and Hydrogen Generation Applications*

**I. Lightcap**, Gordon Research Conference: Chemical Reactions at Surfaces, Ventura, CA; Feb. 6-11  
*Next Generation Catalysts and Sensors: A 2D Solution* (poster presentation and one of 6 graduate students selected to give an oral presentation for the "hot topics" segment).

**I. Lightcap**, Global School For Advanced Studies, Graphene Fundamentals and Applications, Grenoble, France; June 20-26 (One of 24 international graduate students or post-docs selected as a scholar and received full NSF support),

*Band gap engineering and piezoresistive properties of graphene for gas sensing applications*

**J. Radich**, 2209<sup>th</sup> Meeting of the Electrochemical Society, Boston, October 10-14, 2011

*Reduced Graphene Oxide-Copper Sulfide Nanocomposites as Electrocatalysts in Quantum Dot Solar Cells: Overcoming the Platinum-Sulfur Relationship*

## Research Papers

- (1) Tvrdy, K.; Frantszov, P.; Kamat, P. V. Photoinduced Electron Transfer from Semiconductor Quantum Dots to Metal Oxide Nanoparticles. *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 29-34.
- (2) Kamat, P. V. Graphene-based Nanoassemblies for Energy Conversion. *J. Phys. Chem. Lett.* **2011**, *2*, 242–251.
- (3) Krishnamurthy, S.; Lightcap, I. V.; Kamat, P. V. Electron Transfer between Methyl Viologen Radicals and Graphene Oxide: Reduction, Electron Storage and Discharge *J. Photochem. Photobiol. A: Chem.* **2011**, *221*, 214-219.
- (4) Radich, J. G.; McGinn, P. J.; Kamat, P. V. Graphene-based Composites for Electrochemical Energy Storage. *Interface* **2011**, *Spring Issue*, 63-66.
- (5) Pernik, D.; Tvrdy, K.; Radich, J. G.; Kamat, P. V. Tracking the Adsorption and Electron Injection Rates of CdSe Quantum Dots on TiO<sub>2</sub>: Linked Versus Direct Attachment. *J. Phys. Chem. C* **2011**, *115*, 13511–13519.
- (6) Chakrapani, V.; Baker, D.; Kamat, P. V. Understanding the Role of the Sulfide Redox Couple (S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup>) in Quantum Dot Sensitized Solar Cells. *J. Am. Chem. Soc.* **2011**, *133*, 9607–9615.
- (7) Hayashi, H.; Lightcap, I. V.; Tsujimoto, M.; Takano, M.; Umeyama, T.; Kamat, P. V.; Imahori, H. 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. *J. Am. Chem. Soc.* **2011**, *133*, 7684–7687.
- (8) Takai, A.; Kamat, P. V. Capture, Store and Discharge. Shuttling Photogenerated Electrons across TiO<sub>2</sub>-Silver Interface. *ACS Nano* **2011**, *4*, 7369–7376.
- (9) Meekins, B. H.; Kamat, P. V. Role of Water Oxidation Catalyst, IrO<sub>2</sub> in Shuttling Photogenerated Holes Across TiO<sub>2</sub> Interface. *J. Phys. Chem. Lett.* **2011**, *2*, 2304-2310.
- (10) Radich, J. G.; Dwyer, R.; Kamat, P. V. Cu<sub>2</sub>S -Reduced Graphene Oxide Composite for High Efficiency Quantum Dot Solar Cells . Overcoming the Redox Limitations of S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup> at the Counter Electrode. *J. Phys. Chem. Lett.* **2011**, *2*, 2453–2460.
- (11) Choi, H.; Nicolaescu, R.; Paek, S.; Ko, J.; Kamat, P. V. Supersensitization of CdS Quantum Dots with NIR Organic Dye: Towards the Design of Panchromatic Hybrid-Sensitized Solar Cells. *ACS Nano* **2011**, *in press*.
- (12) Murphy, S.; Huang, L.; Kamat, P. V. Charge-Transfer Complexation and Excited State Interactions in Porphyrin-Silver Nanoparticle Hybrid Nanostructures". *J. Phys. Chem. C* **2011**, *115*, *in press*.

## Book Chapter

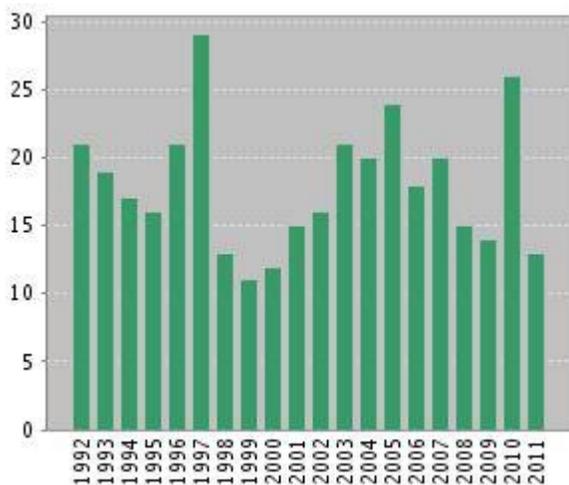
Tvrdy, K.; Kamat, P. V., Quantum Dot Solar Cells, in *Comprehensive Nanoscience and Technology*, D. L. Andrews; Scholes, G. D. and Wiederrecht, G. P., Editors. 2011, Oxford: Academic Press. p. 257-275.

## Editorials

- (1) Schatz, G. C.; Kamat, P. V.; Hammes-Schiffer, S.; Zwier, T. S. Looking Beyond the First Anniversary. *J. Phys. Chem. Lett.* **2011**, 2, 34-35.
- (2) Prezhdo, O. V.; Kamat, P. V.; Schatz, G. C. Virtual Issue: Graphene and Functionalized Graphene. *J. Phys. Chem. C* **2011**, 115, 3195-3197.
- (3) Kamat, P. V. Dominance of Metal Oxides in the Era of Nanotechnology. *J. Phys. Chem. Lett.* **2011**, 2, 839-840.
- (4) Kamat, P. V. Semiconductor Nanocrystals: To Dope or Not To Dope. *J. Phys. Chem. Lett.* **2011**, 2,

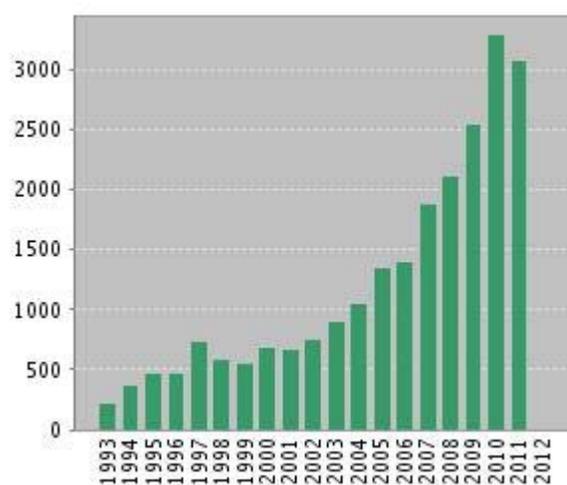
## Publication Analysis (Source: Thomson ISI)

### Published Items



Results found: 442  
Average Citations per Item: 55

### Citations



Sum of the Times Cited : 24000+  
h-index : 88

### Ten most cited publications of previous two years (2009-2010)

Electrocatalytically Active Graphene-Platinum Nanocomposites. Role of 2-D Carbon Support in PEM Fuel Cells  
Segar Brian; Kamat Prashant V. *JOURNAL OF PHYSICAL CHEMISTRY C*, 2009, 113, 7990-7995 DOI:  
10.1021/jp900360k Times Cited: [114](#)

Photosensitization of TiO<sub>2</sub> Nanostructures with CdS Quantum Dots: Particulate versus Tubular Support  
Architectures Baker David R.; Kamat Prashant V. *ADVANCED FUNCTIONAL MATERIALS* 2009, 19 805-  
811 DOI: 10.1002/adfm.200801173 MAR 10 2009 Times Cited: [107](#)

Graphene-Based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional  
Carbon Support Kamat Prashant V. *JOURNAL OF PHYSICAL CHEMISTRY LETTERS* 2010, 1 520-527 DOI:  
10.1021/jz900265j Times Cited: [94](#)

Graphene-Semiconductor Nanocomposites: Excited-State Interactions between ZnO Nanoparticles and Graphene  
Oxide Williams Graeme; Kamat Prashant V. *LANGMUIR* 2009, 25, 13869-13873 DOI: 10.1021/la900905h

Times Cited: [71](#)

Anchoring Semiconductor and Metal Nanoparticles on a Two-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide Lightcap Ian V.; Kosel Thomas H.; Kamat Prashant V. NANO LETTERS 2010, 10, 577-583 DOI: 10.1021/nl9035109 Times Cited: [71](#)

Quantum Dot Sensitized Solar Cells. A Tale of Two Semiconductor Nanocrystals: CdSe and CdTe Bang Jin Ho; Kamat Prashant V. ACS NANO 3 6 1467-1476 DOI: 10.1021/nn900324q JUN 2009 Times Cited: [57](#)

CdSe Quantum Dot Sensitized Solar Cells. Shuttling Electrons Through Stacked Carbon Nanocups Farrow Blake; Kamat Prashant V. JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2009, 131, 11124-11131 DOI: 10.1021/ja903337c Times Cited: [51](#)

To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO<sub>2</sub> Nanostructured Films? Ng Yun Hau; Lightcap Ian V.; Goodwin Kevin; et al. JOURNAL OF PHYSICAL CHEMISTRY LETTERS 2010, 1 15 2222-2227 DOI: 10.1021/jz100728z Times Cited: [34](#)

Photocatalysis with CdSe Nanoparticles in Confined Media: Mapping Charge Transfer Events in the Subpicosecond to Second Timescales Harris Clifton; Kamat Prashant V. ACS NANO 2009, 3 682-690 DOI: 10.1021/nn800848y Times Cited: [33](#)

Substrate Driven Photochemistry of CdSe Quantum Dot Films: Charge Injection and Irreversible Transformations on Oxide Surfaces Tvrdy Kevin; Kamat Prashant V. JOURNAL OF PHYSICAL CHEMISTRY A 2009, 113 16 3765-3772 DOI: 10.1021/jp808562x Times Cited: [28](#)

(Source Web of Science as of November 14, 2010)

## Photoinduced Electron Transfer from Semiconductor Quantum Dots to metal Oxide Nanoparticles.

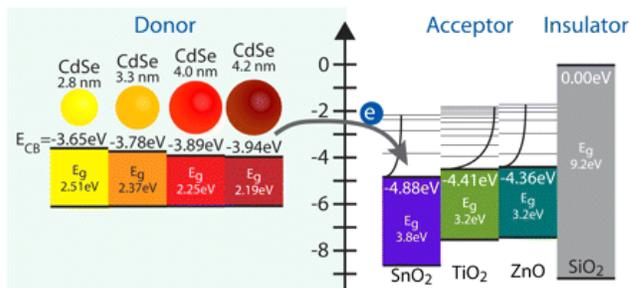
Tvrdy, K.; Frantszov, P.; Kamat, P. V.

*Proc. Nat. Acad. Sci. USA* **2011**, *108*, 29-34

DOI: [10.1073/pnas.1011972107](https://doi.org/10.1073/pnas.1011972107)

### Abstract

Quantum dot-metal oxide junctions are an integral part of next-generation solar cells, light emitting diodes, and nanostructured electronic arrays. Here we present a comprehensive examination of electron transfer at these junctions, using a series of CdSe quantum dot donors (sizes 2.8, 3.3, 4.0, and 4.2 nm in diameter) and metal oxide nanoparticle acceptors (SnO<sub>2</sub>, TiO<sub>2</sub>, and ZnO). Apparent electron transfer rate constants showed strong dependence on change in system free energy, exhibiting a sharp rise at small driving forces followed by a modest rise further away from the characteristic reorganization energy. The observed trend mimics the predicted behavior of electron transfer from a single quantum state to a continuum of electron accepting states, such as those present in the conduction band of a metal oxide nanoparticle. In contrast with dye-sensitized metal oxide electron transfer studies, our systems did not exhibit unthermalized hot-electron injection due to relatively large ratios of electron cooling rate to electron transfer rate. To investigate the implications of these findings in photovoltaic cells, quantum dot-metal oxide working electrodes were constructed in an identical fashion to the films used for the electron transfer portion of the study. Interestingly, the films which exhibited the fastest electron transfer rates (SnO<sub>2</sub>) were not the same as those which showed the highest photocurrent (TiO<sub>2</sub>). These findings suggest that, in addition to electron transfer at the quantum dot-metal oxide interface, other electron transfer reactions play key roles in the determination of overall device efficiency.



## Graphene-based Nanoassemblies for Energy Conversion.

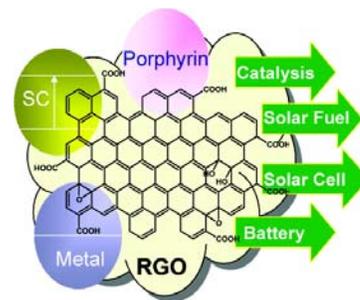
Kamat, P. V.

*J. Phys. Chem. Lett.* **2011**, *2*, 242–251

DOI: [10.1021/jz101639v](https://doi.org/10.1021/jz101639v)

### Abstract

Graphene-based assemblies are gaining attention as a viable alternate to boost the efficiency of various catalytic and storage reactions in energy conversion applications. The use of reduced graphene oxide has already proved useful in collecting and transporting charge in photoelectrochemical solar cells, photocatalysis and electrocatalysis. In many of these applications the flat carbon serves as a scaffold to anchor metal and semiconductor nanoparticles and assists in promoting selectivity and efficiency of the catalytic process. Covalent and noncovalent interaction with organic molecules is another area that is expected to provide new frontiers in graphene research. Recent advances in manipulating graphene-based 2-D carbon architecture for energy conversion are described.

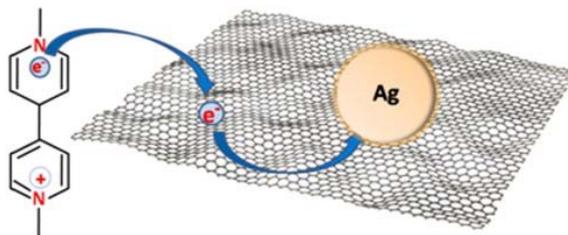


## Electron Transfer between Methyl Viologen Radicals and Graphene Oxide: Reduction, Electron Storage and Discharge

Krishnamurthy, S.; Lightcap, I. V.; Kamat, P. V.  
*J. Photochem. Photobiol. A: Chem.* **2011**, *221*, 214-219.  
 DOI: [10.1016/j.jphotochem.2011.02.024](https://doi.org/10.1016/j.jphotochem.2011.02.024)

### Abstract

Photochemically generated methyl viologen radicals undergo electron transfer with graphene oxide (GO) in ethanol suspensions. This charge transfer interaction results in the reduction of GO as well as storage of electrons. The stored electrons can be utilized to reduce  $\text{Ag}^+$  ions and thus anchor silver nanoparticles on reduced graphene oxide (RGO). The spectroscopic experiments that elucidate the quantitative electron transfer and transmission electron microscopy that highlights the potential of designing metal-RGO assemblies are discussed.

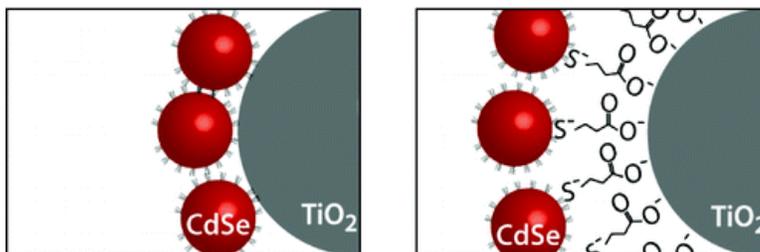


## Tracking the Adsorption and Electron Injection Rates of CdSe Quantum Dots on $\text{TiO}_2$ : Linked Versus Direct Attachment

Pernik, D.; Tvrđy, K.; Radich, J. G.; Kamat, P. V..  
*J. Phys. Chem. C* **2011**, *115*, 13511–13519.  
 DOI: [10.1021/jp203055d](https://doi.org/10.1021/jp203055d)

### Abstract

Understanding CdSe quantum dot (QD) adsorption phenomena on mesoscopic  $\text{TiO}_2$  films is important for improving the performance of quantum dot sensitized solar cells (QDSSCs). A kinetic adsorption model has been developed to elucidate both Langmuir-like submonolayer adsorption and QD aggregation processes. Removal of surface-bound trioctylphosphine oxide as well as the use of 3-mercaptopropionic acid (MPA) as a molecular linker improved the adsorption of toluene-suspended QDs onto  $\text{TiO}_2$  films. The adsorption constant  $K_{\text{ad}}$  for submonolayer coverage was  $(6.7 \pm 2.7) \times 10^3 \text{ M}^{-1}$  for direct adsorption and  $(4.2 \pm 2.0) \times 10^4 \text{ M}^{-1}$  for MPA-linked assemblies. Prolonged exposure of a  $\text{TiO}_2$  film to a CdSe QD suspension resulted in the assembly of aggregated particles regardless of the method of adsorption. A greater coverage of  $\text{TiO}_2$  was achieved with smaller QDs due to reduced size constraints. Ultrafast transient absorption spectroscopy demonstrated faster electron injection into  $\text{TiO}_2$  from directly adsorbed QDs ( $k_{\text{ET}} = 7.2 \times 10^9 \text{ s}^{-1}$ ) compared with MPA-linked QDs ( $k_{\text{ET}} = 2.3 \times 10^9 \text{ s}^{-1}$ ). The adsorption kinetic details presented in this study are useful for controlling CdSe QD adsorption on  $\text{TiO}_2$  and designing efficient photoanodes for QDSSCs.



## Graphene-based Composites for Electrochemical Energy Storage

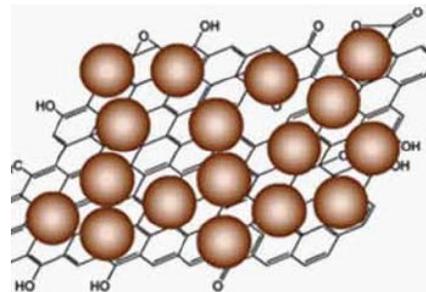
Radich, J. G.; McGinn, P. J.; Kamat, P. V...

*Interface* **2011**, *Spring Issue*, 63-66

[Link:](#)

### Abstract

Graphene presents unique opportunities to the scientific community through its diverse and varied properties, which show promise to enhance many catalytic, photoelectrochemical, and electrochemical processes. The inexpensive route to RGO from GO and selective binding properties exhibited by the latter open doors to the creation of composite materials for these applications. Synergistic effects are already observed in the multiple facets of graphene-based composites, and lithium ion batteries stand to benefit considerably through further understanding of the interactions of intercalation materials lithium ions, and graphene.



## Understanding the Role of the Sulfide Redox Couple ( $S^{2-}/S_n^{2-}$ ) in Quantum Dot Sensitized Solar Cells.

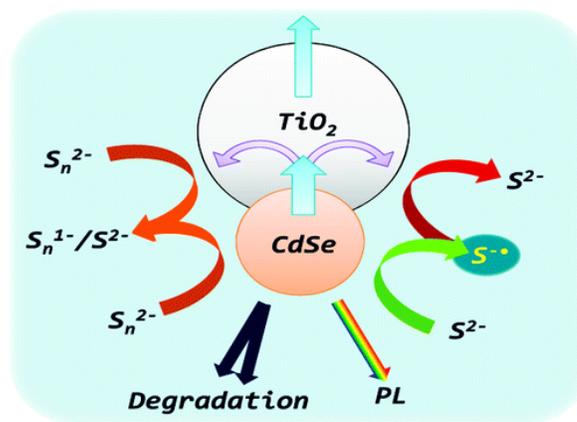
Chakrapani, V.; Baker, D.; Kamat, P. V.

*J. Am. Chem. Soc.* **2011**, *133*, 9607-9615

[DOI: 10.1021/ja203131b](https://doi.org/10.1021/ja203131b)

### Abstract

The presence of sulfide/polysulfide redox couple is crucial in achieving stability of metal chalcogenide (e.g., CdS and CdSe)-based quantum dot-sensitized solar cells (QDSC). However, the interfacial charge transfer processes play a pivotal role in dictating the net photoconversion efficiency. We present here kinetics of hole transfer, characterization of the intermediates involved in the hole oxidation of sulfide ion, and the back electron transfer between sulfide radical and electrons injected into  $TiO_2$  nanoparticles. The kinetic rate constant ( $10^7-10^9 s^{-1}$ ) for the hole transfer obtained from the emission lifetime measurements suggests slow hole scavenging from CdSe by  $S^{2-}$  is one of the limiting factors in attaining high overall efficiency. The presence of the oxidized couple, by addition of S or Se to the electrolyte, increases the photocurrent, but it also enhances the rate of back electron transfer.

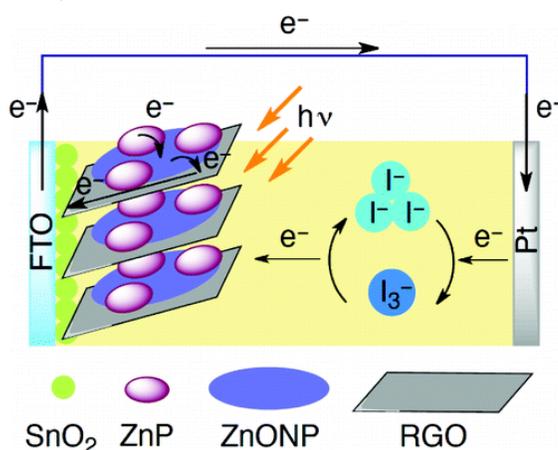


## Electron Transfer Cascade by Organic/Inorganic Ternary Composites of Porphyrin, Zinc Oxide Nanoparticles, and Reduced Graphene Oxide on a Tin Oxide Electrode that Exhibits Efficient Photocurrent Generation

Hayashi, H.; Lightcap, I. V.; Tsujimoto, M.; Takano, M.; Umeyama, T.; Kamat, P. V.; Imahori, H.  
*J. Am. Chem. Soc.* **2011**, *133*, 7684–7687  
 DOI: [10.1021/ja201813n](https://doi.org/10.1021/ja201813n)

### Abstract

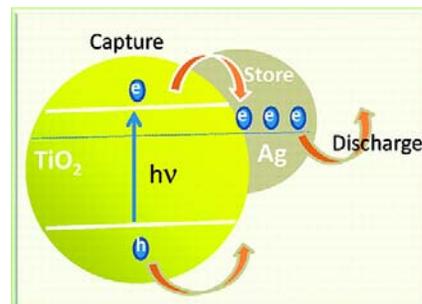
A bottom-up strategy has been developed to construct a multiple electron transfer system composed of organic/inorganic ternary composites (porphyrin, zinc oxide nanoparticles, reduced graphene oxide) on a semiconducting electrode without impairing the respective donor-acceptor components. The hierarchical electron transfer cascade system exhibited remarkably high photocurrent generation with an incident-photon-to-current efficiency of up to ca. 70%.



## Capture, Store and Discharge. Shuttling Photogenerated Electrons across TiO<sub>2</sub>-Silver Interface.

Takai, A.; Kamat, P. V.  
*ACS Nano* **2011**, *4*, 7369–7376  
 DOI: [10.1021/nn202294b](https://doi.org/10.1021/nn202294b)

UV irradiation of TiO<sub>2</sub> nanoparticles in the presence of Ag<sup>+</sup> ions results in the quantitative reduction and deposition of silver on its surface. Continued UV irradiation following the deposition of Ag on the TiO<sub>2</sub> surface causes a blue shift in the surface plasmon peak from 430 to 415 nm as these particles become charged with excess electrons. Under UV irradiation, both the charging and discharging of electrons occur at different rates, thus allowing the system to attain a steady state. Upon stopping the UV irradiation, a fraction of these electrons remain stored. The electron storage is dependent on the amount of Ag deposited on TiO<sub>2</sub> nanoparticles with maximum capacity seen at 8.6 μM of Ag in a suspension containing 5.8 mM of TiO<sub>2</sub>. Such electron charging and discharging processes in semiconductor–metal composites need to be taken into account while evaluating the plasmon resonance induced effects in photocatalysis and photoelectrochemistry.

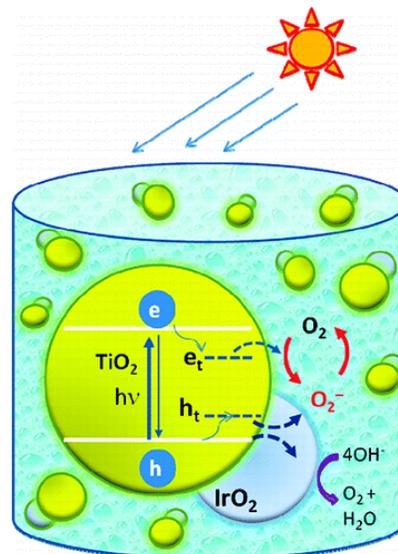


## Role of Water Oxidation Catalyst, IrO<sub>2</sub> in Shuttling Photogenerated Holes Across TiO<sub>2</sub> Interface

Meekins, B. H.; Kamat, P. V  
*J. Phys. Chem. Lett.* **2011**, 2, 2304-2310  
[DOI: 10.1021/jz200852m](https://doi.org/10.1021/jz200852m)

### Abstract

Iridium oxide, a water oxidation cocatalyst, plays an important role in mediating the hole transfer process of a UV-irradiated TiO<sub>2</sub> system. Spectroscopic identification of trapped holes has enabled their characterization in colloidal TiO<sub>2</sub> suspension and monitoring of the transfer of trapped holes to IrO<sub>2</sub>. Titration of trapped holes with potassium iodide yields an estimate of three holes per particle during 7 min of UV irradiation of TiO<sub>2</sub> suspension in ethanol containing 5% acetic acid. The hole transfer to IrO<sub>2</sub> occurs with a rate constant of  $6 \times 10^5 \text{ s}^{-1}$ . Interestingly, IrO<sub>2</sub> also catalyzes the recombination of trapped holes with reduced oxygen species. The results discussed here provide a mechanistic and kinetic insight into the catalytic role of IrO<sub>2</sub> in the photogenerated hole transfer process.

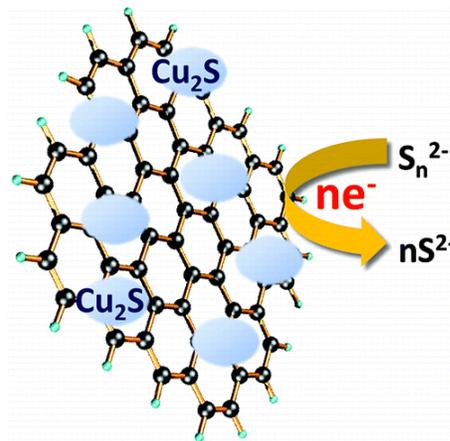


## Cu<sub>2</sub>S-Reduced Graphene Oxide Composite for High Efficiency Quantum Dot Solar Cells . Overcoming the Redox Limitations of S<sup>2-</sup>/S<sub>n</sub><sup>2-</sup> at the Counter Electrode.

Radich, J. G.; Dwyer, R.; Kamat, P. V. *J. Phys. Chem. Lett.* **2011**, 2, 2453–2460  
*J. Phys. Chem. Lett.* **2011**, 2, 2453–2460  
[DOI: 10.1021/jz201064k](https://doi.org/10.1021/jz201064k)

### Abstract

Polysulfide electrolyte that is employed as a redox electrolyte in quantum dot sensitized solar cells provides stability to the cadmium chalcogenide photoanode but introduces significant redox limitations at the counter electrode through undesirable surface reactions. By designing reduced graphene oxide (RGO)-Cu<sub>2</sub>S composite, we have now succeeded in shuttling electrons through the RGO sheets and polysulfide-active Cu<sub>2</sub>S more efficiently than Pt electrode, improving the fill factor by 75%. The composite material characterized and optimized at different compositions indicates a Cu/RGO mass ratio of 4 provides the best electrochemical performance. A sandwich CdSe quantum dot sensitized solar cell constructed using the optimized RGO-Cu<sub>2</sub>S composite counter electrode exhibited an unsurpassed power conversion efficiency of 4.4%.



## Supersensitization of CdS Quantum Dots with NIR Organic Dye: Towards the Design of Panchromatic Hybrid-Sensitized Solar Cells.

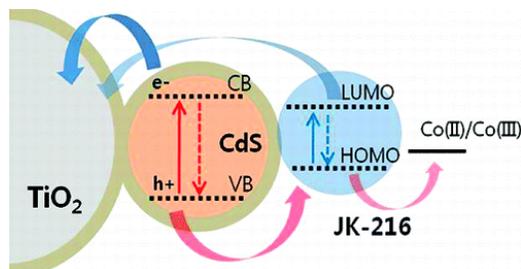
Choi, H.; Nicolaescu, R.; Paek, S.; Ko, J.; Kamat, P. V.

*ACS Nano* **2011**, *in press*.

DOI: [10.1021/nn2035022](https://doi.org/10.1021/nn2035022)

### Abstract

The photoresponse of quantum dot solar cells (QDSCs) has been successfully extended to the near-IR (NIR) region by sensitizing nanostructured TiO<sub>2</sub>-CdS films with a squaraine dye (JK-216). CdS nanoparticles anchored on mesoscopic TiO<sub>2</sub> films obtained by successive ionic layer adsorption and reaction (SILAR) exhibit limited absorption below 500 nm with a net power conversion efficiency of 1% when employed as a photoanode in QDSC. By depositing a thin barrier layer of Al<sub>2</sub>O<sub>3</sub>, the TiO<sub>2</sub>-CdS films were further modified with a NIR absorbing squaraine dye. Quantum dot sensitized solar cells supersensitized with a squaraine dye (JK-216) showed good stability during illumination with standard global AM 1.5 solar conditions, delivering a maximum overall power conversion efficiency ( $\eta$ ) of 3.14%. Transient absorption and pulse radiolysis measurements provide further insight into the excited state interactions of squaraine dye with SiO<sub>2</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>/CdS/Al<sub>2</sub>O<sub>3</sub> films and interfacial electron transfer processes. The synergy of combining semiconductor quantum dots and NIR absorbing dye provides new opportunities to harvest photons from different regions of the solar spectrum.



## Charge-Transfer Complexation and Excited State Interactions in Porphyrin-Silver Nanoparticle Hybrid Nanostructures

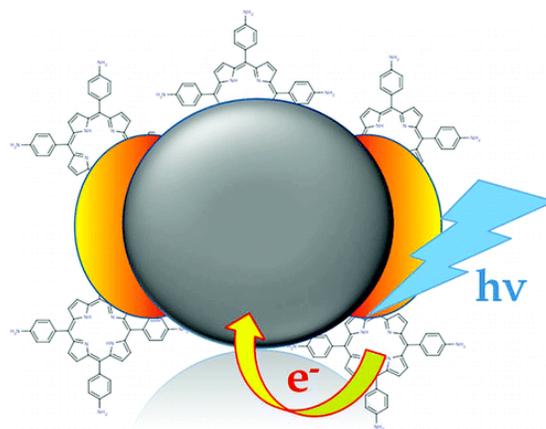
Murphy, S.; Huang, L.; Kamat, P. V.

*J. Phys. Chem. C* **2011**, *115*, *in press*.

DOI: [10.1021/jp205711x](https://doi.org/10.1021/jp205711x)

### Abstract

Highly photoactive porphyrin is shown to form charge-transfer complex with silver nanoparticles. Complexation of tetra(4-aminophenyl) porphyrin (TAPP) with Ag nanoparticles is confirmed by ground-state absorption and Raman spectroscopy. Strong Raman enhancement indicates both electromagnetic and chemical enhancement. Evidence of chemical enhancement includes a selective enhancement of porphyrin Raman bands. Fast charge separation in the complex is indicated by ultrafast transient absorption and fluorescence upconversion measurements. The charge-separated state is shown to have a lifetime of  $116 \pm 6$  ps. Porphyrin substituents are shown to play a role in the formation of charge-transfer complex.



## CdSe Quantum Dot–Fullerene Hybrid Nanocomposite for Solar Energy Conversion: Electron Transfer and Photoelectrochemistry

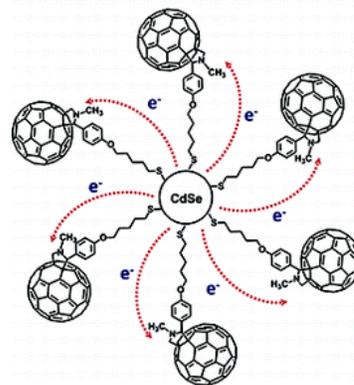
Jin Ho Bang and Prashant V. Kamat

*ACS Nano* **2011**, *5*, in press.

DOI: 10.1021/nn204350w

### Abstract

The development of organic/inorganic hybrid nanocomposite systems that enable efficient solar energy conversion has been important for applications in solar cell research. Nanostructured carbon-based systems, in particular C<sub>60</sub>, offer attractive strategies to collect and transport electrons generated in a light harvesting assembly. We have assembled CdSe–C<sub>60</sub> nanocomposites by chemically linking CdSe quantum dots (QDs) with thiol-functionalized C<sub>60</sub>. The photoinduced charge separation and collection of electrons in CdSe QD–C<sub>60</sub> nanocomposites have been evaluated using transient absorption spectroscopy and photoelectrochemical measurements. The rate constant for electron transfer between excited CdSe QD and C<sub>60</sub> increased with the decreasing size of the CdSe QD ( $7.9 \times 10^9 \text{ s}^{-1}$  (4.5 nm),  $1.7 \times 10^{10} \text{ s}^{-1}$  (3.2 nm), and  $9.0 \times 10^{10} \text{ s}^{-1}$  (2.6 nm)). Slower hole transfer and faster charge recombination and transport events were found to dominate over the forward electron injection process, thus limiting the deliverance of maximum power in CdSe QD–C<sub>60</sub>-based solar cells. The photoinduced charge separation between CdSe QDs and C<sub>60</sub> opens up new design strategies for developing light harvesting assemblies.



Harvesting Solar Energy at Notre Dame.

50 kW photovoltaic panels installed on the roof of Stinson Remick Hall went on operation in 2010. This new building is also the home of Sustainable Energy Institute and ND Nano