

Annual Research Summary

January - December 2009

Kamat Research Group
University of Notre Dame



Prashant V. Kamat

Professor, Chemistry & Biochemistry
Concurrent Professor, Chemical & Biomolecular Eng.
Senior Scientist, Radiation Laboratory
Notre Dame, IN 46556-5674, USA

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

2008 Activities/ Highlights

Research Group

Graduate Students

- David Baker (Chem. Eng.)
- Matt Becker (Physics - coadv. Bruce Bunker)
- Clifton Harris (Chemistry)
- Ian Lightcap (Chemistry)
- Ben Meekins (Chem Eng.)
- Sean Murphy (Chemistry - coadv. Libai Huang)
- James Radich (Chem. Eng.)
- Brian Seger (Chem. Eng.)
- Thibaut Viguiere (Chem. Eng.)
- Kevin Tvrdy (Chemistry)
- Yunghai Yu (Chem. Eng. -coadvisor Ken Kuno)
- Sachi Krishnamurthy (Chemistry)

Undergraduate Students

Spring 2009

- Patrick Brown (Chemistry, UND)
- Chris Rodriguez (CBE, UND)
- Patrick Yee (CBE, UND)
- Blake Farrow (U. Waterloo)

Summer 2009

- Kevin Goodwin (NDNano summer fellow)

Fall 2009

- Douglas Pernik (Chemistry, UND)
- Ryan P. Dwyer (Chemistry, UND)
- Peter Lobaccaro (CBE, UND)

Postdoctoral Research Associate

- Jin Ho Bang
- Alexsandra Wojcik
- Vidhya Chakrapani

Visiting Scientists

- K. Vinodgopal and Julie Peller (Indiana Univ. Northwest)
- Roxana Nicolaescu (Serim Corporation)
- Hironobu Hayashi (Kyoto University)
- Jun Zhang (Huazhong Normal University, Wuhan)
- M. Ashokkumar & N. Bernaudshaw (Univ. of Melbourne)

Awards/Fellowships/Recognition

Brian Seger, Successful completion of his Ph. D. Thesis (June 2009)

Kevin Tvrdy, Summer Fellowship Award, College of Science, U. Notre Dame.

Patrick Brown, William R. Wischerath Outstanding Chemistry Major Award. Also received Outstanding Physics Major award.

Blake Farrow, Runner up, Video contest, "What is Nano" sponsored by ACS (March 2009)

Patrick Brown, Co-winner Student Presentation, 2009 AAAS Meeting, Chicago (March 2009)

Professional Activities

- **Deputy Editor**, Journal of Physical Chemistry Letters (2009-present)
- **Executive Editor**, Journal of Physical Chemistry A/B/C (2008-present)
- **Editorial Advisory Boards**
 - Langmuir (2000-present)
 - Interface (1999-present)
 - Electrochemical and Solid State Letters (September 2006-present)
 - International Journal of Photoenergy (2001-2008)
- **Committees**
 - Awards and Honors Committee of the Electrochemical Society (2007-2011)
 - Treasurer, Fullerene, Nanotubes and Carbon Nanostructures Division, (2004-2008)
- **ND committees**
 - Member of the COS-COS (2008-present)
 - Awards Committee—Chemistry & Biochemistry (Spring 2009)
 - CAP—Chemistry & Biochemistry (Fall 2009-)
 - ND Nano Executive Committee (Spring-Summer 2009)
- **Symposium Organizer**
 - 2009 First International Symposium on Graphene** (Spring meeting of the Electrochemical Society, San Francisco)
 - 2009 Symposium on Metal and Semiconductor Nanoparticles** (Spring Meeting of the Electrochemical Society, San Francisco)

Seminar Presentations

Univ. Massachusetts, Amherst, December 3, 2009

Solar Cell By Design. Manipulating Charge Transfer at Nanostructure Interfaces

Hokkaido University, Chemistry Department Seminar, October 29, 2009

Solar Cells by Design. Harvesting Light Energy with Nanostructure Assemblies.

University of Wisconsin, Madison, Chemistry Department seminar, October 15, 2009

Got Nanotubes? 1-D Architecture based light harvesting assemblies for next generation solar cells.

Indiana University, Bloomington, IN Chemistry Department Colloquium, September 22, 2009 *Nanostructure Architectures for Next generation Solar Cells.*

Northern Illinois University , DeKalb, IL, Chemistry department Colloquium, September 14, 2009 *Nanostructure Architectures for solar Energy Conversion,*

Washington University in St. Louis, Department of Energy, Environmental & Chemical Engineering Departmental seminar, September 11, 2009.

Solar Cells by Design. Harvesting Light Energy with Nanostructure Assemblies.

Osaka University, SANKEN (The Institute of Scientific and Industrial Research), September 2, 2009 *Carbon Nanostructures for Energy Conversion..*

University of Castilla La Mancha, Toledo Spain, May 15, 2009.

Photoinduced charge transfer processes in CdSe quantum dot based composites

Academic lectures

Dept. of Materials Science, The Royal Institute of Technology, Stockholm, Sweden. May 7, 8, 2009

Quantum Dot Solar Cells,

Carbon Nanostructures for Energy Conversion

Ethics of scientific Publication

Graduate School of Chemistry and Materials Science (AGS), Hokkaido University, Sapporo, Japan October 27-31, 2009

The Adventures of Nanoscience”

Carbon Nanostructures for Energy Conversion.

Applications and Environmental Impact of Nanotechnology

Ethics of Scientific Publications

Conference Presentations (2008)

Gordon Research Conference, Chemical Reactions at Surfaces,, Ventura, CA, February 8-13, 2009.

Kamat, P. V. Quantum Dot Solar Cells. *Semiconductor Nanocrystals as Light Harvestors* **Invited**

International Symposium for Environmental Innovation Driven by Chemistry and Catalytic Science, Sapporo, Japan, March 18-19, 2009.

Kamat, P. V. *Solar Cells by Design. Manipulating Charge Transfer at Nanostructure Interfaces* **Invited**

Hybrid and Organic Photovoltaics Conference, Benidorm, Spain, May 10-13, 2009.

Kamat, P. V. *Solar Cells by Design. Harvesting Light Energy with Semiconducting Quantum Dots.* **Invited**

Workshop on Quantum Dot Solar Cells, University of Alicante, Alicante, May 14, 2009

Kamat, P. V. *Photoelectrochemical aspects of CdSe and CdTe semiconductor nanocrystals.* **Invited**

DOE Solar Energy Contractor Meeting, Baltimore, MD, June 8-20, 2009,

Kamat, P. V., Bang, J. H. *Quantum dot sensitized solar cells. A tale of two semiconductor nanocrystals: CdSe and CdTe.* **Invited**

238th American Chemical Society National Meeting, August 16-20, 2009, Washington, DC. September 1-3, 2009

Kamat, P. V. and Bang, J. H. *Quantum dot sensitized solar cells. Tale of two semiconductor nanocrystals: CdSe And CdTe.* **Invited**

Kamat, P. V. and Seger, B. *TiO₂-Carbon nanostructure based proton exchange membrane assembly for Photocatalytic hydrogen production.* **Invited**

5th Handai Nanoscience and Nanotechnology Internation Symposium Nano-Advanced Materials Design, Icho-Kanikan, Osaka University, Japan. September 2, 2009

Kamat, P. V. *Nanostructure Architectures for Light Energy Conversion.* **Invited**

Surface Science Society Japan Meeting, Tokyo. October 27, 2009

Kamat, P. V., *Nanostructure Assemblies for Light Energy Conversion.* **Invited**

QUIM-UNAM, National Autonomous University of Mexico, November 18-20, 2009

Kamat, P. V. *Nanostructure Assemblies for Next Generation Solar Cells*

Material Research Society Meeting, Boston, November 30-Dec 4, 2009

Chakrapani, Vidhya Bang, Jin Ho and Kamat, P. V. *Role of Redox Electrolyte on the Performance of CdSe based Quantum Dot Solar Cell.*

Meekins, Benjamin and Kamat, P. V. *Amplification of photocurrent generation by Lithium Ion Intercalation*

Tvrdy, Kevin and Kamat, P. V. *Size Dependent Electron Transfer from CdSe Colloidal Nanoparticles to Various Metal Oxide Colloids within Thin Films*

Prashant V. Kamat, Kevin Tvrdy and David Baker, *Quantum Dot Sensitized Solar Cells. Manipulating Photoresponse Through Size Control.* **Invited**

Prashant V. Kamat and Blake Farrow *CdSe Quantum Dots Anchored on TiO₂ and Carbon Nanotubes. 1-D Architectures as Scaffolds to Improve the Efficiency of Solar Cells.* **Invited**

Research Papers

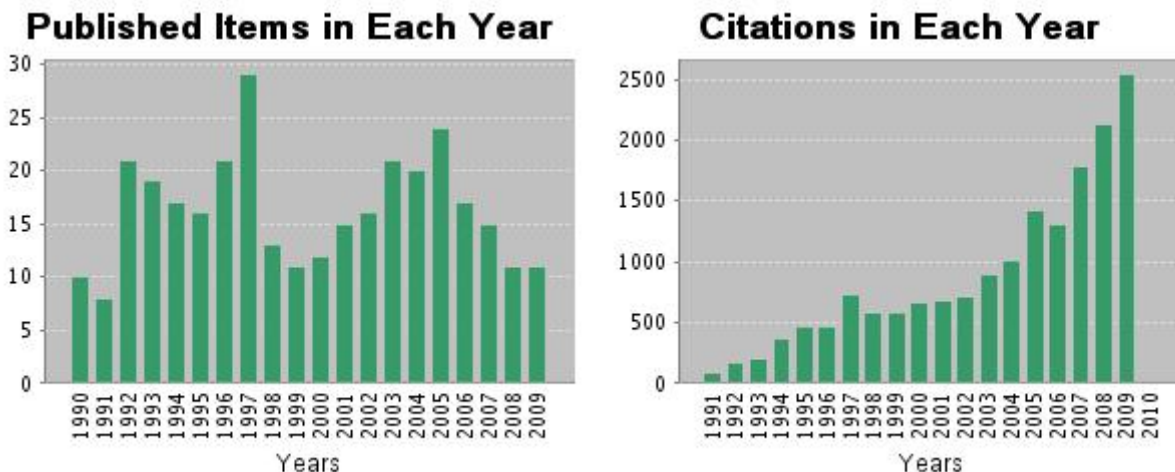
- (1) Bang, J. H.; Kamat, P. V., *Solar Cell by Design. Photoelectrochemistry of TiO₂ Nanorod Arrays Decorated with CdSe*. **Adv. Funct. Mater.** 2009, submitted.
- (2) Wojcik, A; Nicolaescu, R.; Kamat, P. V.; Patil, S. *Photochemistry of Far Red Responsive Tetrahydroquinoxaline-Based Squaraine Dyes*, **J. Phys. Chem. A** 2009 submitted.
- (3) Kamat, P. V., *Graphene based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a 2-Dimensional Carbon Support*. **J. Phys. Chem. Lett.** 2010, 1, (doi: 10.1021/jz900265j) -Perspective.
- (4) Chakrapani, V.; Tvrđy, K.; Kamat, P. V., *Modulation of Electron Injection in CdSe-TiO₂ System through Medium Alkalinity*. **J. Am. Chem. Soc.** 2009, submitted.
- (5) Yu, Y.; Kamat, P. V.; Kuno, M., *CdSe Nanowire Photoelectrochemical Solar Cells Enhanced with Colloidal CdSe Quantum Dots*. **2009**, submitted.
- (6) Lightcap, I. V.; Kosel, T. H.; Kamat, P. V., *Anchoring Semiconductor and Metal Nanoparticles on a 2-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide*. **Nano Lett.** **2009**, submitted.
- (7) Zhang, J.; Bang, J. H.; Tang, C.; Kamat, P. V. *Tailored TiO₂-SrTiO₃ Heterostructure Nanotube Arrays for Improved Photoelectrochemical Performance*, **ACS Nano** 2010, in press (doi:10.1021/nn901087c).
- (8) Ohtani, M.; Kamat, P. V.; Fukuzumi, S. *Supramolecular Donor-Acceptor Assemblies Composed of Carbon Nanodiamond and Porphyrin for Photoinduced Electron Transfer and Photocurrent Generation*, **J. Mater. Chem.** 2010, in press. (doi: 10.1039/b918527e)
- (9) Tvrđy, K.; Kamat, P. V., *Quantum Dot Solar Cells*, in *Comprehensive Nanoscience and Technology* G. Wiederrecht, Editor. 2010, Elsevier: Oxford, U.K.
- (10) Kamat, P. V.; Schatz, G. *Nanotechnology for Next Generation Solar Cells* **J. Phys. Chem. C** 2009, 113, 15473–15475. (doi:10.1021/jp905378n) –Editorial.
- (11) Meekins, B. H.; Kamat, P. V. *Got TiO₂ Nanotubes? Lithium Ion Intercalation can Boost Their Photoelectrochemical Performance Three-Fold.*, **ACS Nano** 2009, 3, 3437–3446. (doi:10.1021/nn900897r)
- (12) Seger, B.; Kamat, P. V. *Fuel Cell Geared in Reverse. Photocatalytic Hydrogen Production using a TiO₂/Nafion/Pt Membrane Assembly with No Applied Bias.*, **J. Phys. Chem. C** 2009, 113, 18946–18952 (doi: 10.1021/jp907367k)
- (13) Kamat, P. V. *Photosensitization of SnO₂ and Other Dyes*. In *Dye Sensitized Solar Cells*; Kalyansundaram, K., Ed.; EPFL Press, Switzerland: Laussane, 2010.
- (14) Gassensmith, J. J.; Matthys, S.; Wojcik, A.; Kamat, P. V.; Smith, B. D. *Squaraine Rotaxane as Optical Chloride Sensor*, **Chemistry, European J.** 2010, in press.
- (15) Williams, G.; Kamat, P. V. *Graphene-Semiconductor Nanocomposites. Excited State Interactions between ZnO Nanoparticles and Graphene Oxide*, **Langmuir** 2010, 25, 13869–13873 (doi:10.1021/la900905h).
- (16) Baker, D. R.; Kamat, P. V. *Disassembly, Reassembly and Photoelectrochemistry of Etched TiO₂ Nanotubes*, **J. Phys. Chem. C** 2009, 113, 17967–17972. (doi: 10.1021/jp9065357)

- (17) Farrow, B.; Kamat, P. V. *CdSe Quantum Dot Sensitized Solar Cells. Shuttling Electrons through Stacked Carbon Nanocups* **J. Am. Chem. Soc.** 2009, 131, 11124-11131. (doi:10.1021/ja903337c)
- (18) Bang, J. H.; Kamat, P. V. *Quantum Dot Sensitized Solar Cells. CdTe versus CdSe Nanocrystals*, **ACS Nano** 2009, 3, 1467-1476. (doi:10.1021/nn900324q)
- (19) Harris, C. T.; Kamat, P. V. *Photocatalysis with CdSe Nanoparticles in Confined Media: Mapping Charge Transfer Events in the Subpicosecond to Second Timescales*, **ACS Nano** 2009, 3, 682-690. (doi:10.1021/nn800848y)
- (20) Koch, M.; Nicolaescu, R.; Kamat, P. V. *Photodegradation of Polythiophene Based Polymers. Excited State Properties and Radical Intermediates.*, **J. Phys. Chem. C** 2009, 113, 11507-11513. (doi:10.1021/jp808141u)
- (21) Seger, B.; Kamat, P. V. *Electrocatalytically Active Graphene-Platinum Nanocomposites. Role of 2-D Carbon Support in PEM Fuel Cells*, **J. Phys. Chem. C** 2009, 113, 7990-7995. (doi:10.1021/jp900360k)
- (22) Tvrdy, K.; Kamat, P. V. *Substrate Driven Photochemistry of CdSe Quantum Dot Films: Charge Injection and Irreversible Transformation on Oxide Surfaces*, **J. Phys. Chem. A.** 2009, 113, 3765-3772. (doi:10.1021/jp808562x)
- (23) Baker, D. R.; Kamat, P. V. *Photosensitization of TiO₂ Nanostructures with CdS Quantum Dots. Particulate versus Tubular Support Architectures*, **Adv. Funct. Mater.** 2009, 19, 805-811. (doi:10.1002/adfm.200801173)



Runner Up - ACS Nanotube Video Contest Spring 2009
Featured in Wired Magazine and other blogs

Publication Analysis



Results found: 382

Sum of the Times Cited : 17,310

Average Citations per Item : 45.31

h-index : 74

Five most cited 2007-2008 publications

[Meeting the clean energy demand: Nanostructure architectures for solar energy conversion](#)

Kamat PV

JOURNAL OF PHYSICAL CHEMISTRY C 111 2834-2860 **2007 Times Cited 228**

[Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture](#)

Kongkanand A, Tvrdy K, Takechi K, et al.

Source: **JOURNAL OF THE AMERICAN CHEMICAL SOCIETY** 130 4007-4015 **2008 Times Cited 80**

[Single wall carbon nanotube scaffolds for photoelectrochemical solar cells. Capture and transport of photogenerated electrons](#)

Kongkanand A, Dominguez RM, Kamat PV

NANO LETTERS 7 676-680 **2007 Times Cited 58**

[Size-dependent electron injection from excited CdSe quantum dots into TiO₂ nanoparticles](#)

Robel I, Kuno M, Kamat PV

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 129 4136-4137 **2007 Times Cited 55**

[Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters](#)

Kamat PV

JOURNAL OF PHYSICAL CHEMISTRY C 112 18737-18753 **2008 Times Cited 55**

(Source Web of Science as of December 18, 2009)

CdSe Quantum Dot Sensitized Solar Cells. Shuttling Electrons Through Stacked Carbon Nanocups

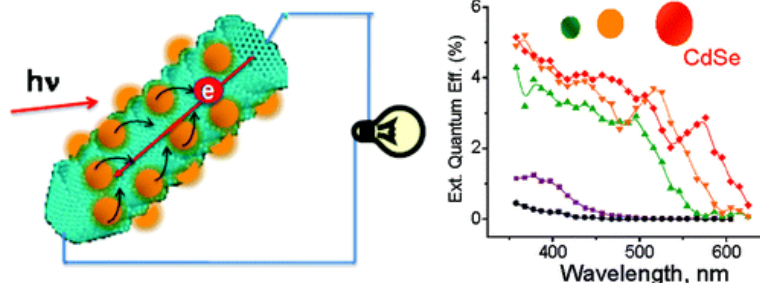
Blake Farrow and Prashant V. Kamat*

J. Am. Chem. Soc., 2009, 131 (31), pp 11124–11131

DOI: 10.1021/ja903337c

Abstract

The charge separation between excited CdSe semiconductor quantum dots and stacked-cup carbon nanotubes (SCCNTs) has been successfully tapped to generate photocurrent in a quantum dot sensitized solar cell (QDSC). By employing an electrophoretic deposition technique we have cast SCCNT–CdSe composite films on optically transparent electrodes (OTEs). The quenching of CdSe emission, as well as transient absorption measurements, confirms ultrafast electron transfer to SCCNTs. The rate constant for electron transfer increases from $9.51 \times 10^9 \text{ s}^{-1}$ to $7.04 \times 10^{10} \text{ s}^{-1}$ as we decrease the size of CdSe nanoparticles from 4.5 to 3 nm. The ability of SCCNTs to collect and transport electrons from excited CdSe has been established from photocurrent measurements. The morphological and excited state properties of SCCNT–CdSe composites demonstrate their usefulness in energy conversion devices.



Substrate Driven Photochemistry of CdSe Quantum Dot Films: Charge Injection and Irreversible Transformations on Oxide Surfaces[†]

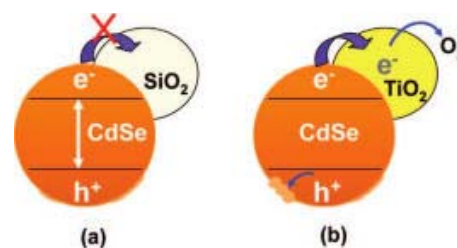
Kevin Tvrdy and Prashant V. Kamat*

J. Phys. Chem. A, 2009, 113 (16), pp 3765–3772

DOI: 10.1021/jp808562x

Abstract

The photochemical behavior of CdSe quantum dots anchored to different surfaces was probed through their deposition on glass, SiO₂, and TiO₂ films. Following visible light irradiation under ambient conditions, CdSe quantum dots deposited on semiconducting TiO₂ surface degraded, where no such degradation was observed when deposited on inert SiO₂ surface or glass. Fluorescence decay and transient absorption experiments confirmed that charge injection from excited CdSe into TiO₂ occurs with an apparent rate constant of $5.62 \times 10^8 \text{ s}^{-1}$ and is the primary event responsible for photodegradation. In the presence of air, injected electrons are scavenged by surface adsorbed oxygen leaving behind reactive holes which induce anodic corrosion of CdSe quantum dots. In a vacuum environment, minimal CdSe degradation was observed as electron scavenging by oxygen is replaced with charge recombination between injected electrons and holes in CdSe nanocrystals. Spectroscopic measurements presented in this study highlight the role of both substrate and medium in dictating the photochemistry of CdSe quantum dots.



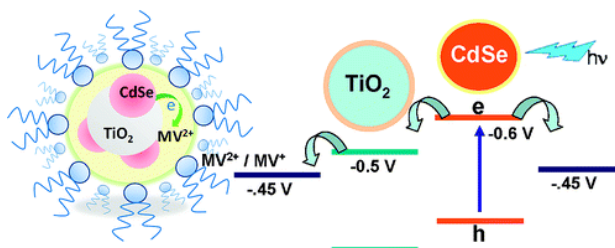
Photocatalysis with CdSe Nanoparticles in Confined Media: Mapping Charge Transfer Events in the Subpicosecond to Second Timescales

Clifton Harris and Prashant V. Kamat*
ACS Nano, 2009, 3 (3), pp 682–690
 DOI: [10.1021/nn800848y](https://doi.org/10.1021/nn800848y)

Abstract

Photoinduced charge transfer events between 3 nm diameter CdSe semiconductor nanocrystals and an electron acceptor, MV^{2+} , have been probed in the subpicosecond–microseconds–seconds time scale by confining the reactants in an AOT/heptane reverse micelle. The probe molecule, methyl viologen (MV^{2+}) interacts with the excited CdSe nanoparticle and quenches its emission effectively. The ultrafast electron transfer to MV^{2+} , as monitored from the exciton bleaching recovery of CdSe and the formation of MV^{+} radical, is completed with an average rate constant of $2.25 \times 10^{10} \text{ s}^{-1}$.

Under steady state irradiation (450 nm) the accumulation of MV^{+} is seen with a net quantum yield of 0.1. Mediation of the electron transfer through TiO_2 nanoparticles is achieved by coupling them with the CdSe- MV^{2+} system within the reverse micelle. This coupling of two semiconductor nanoparticles increases the quantum yield of MV^{2+} reduction by a factor of 2. The dual roles of TiO_2 as an electron shuttle and a rectifier are elucidated by transient absorption spectroscopy and steady state photolysis. The presence of both TiO_2 and MV^{2+} in the reverse micelle creates a synergistic effect to enhance the electron transfer rate constant by an order of magnitude. The time-resolved events that dictate the production and stabilization of electron transfer product provide an insight into the photocatalytic systems that are potentially important in solar hydrogen production and photocatalytic remediation.

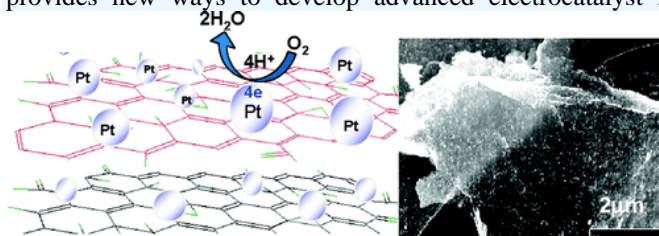


Electrocatalytically Active Graphene-Platinum Nanocomposites. Role of 2-D Carbon Support in PEM Fuel Cells

Brian Seger and Prashant V. Kamat*
J. Phys. Chem. C, 2009, 113 (19), pp 7990–7995
 DOI: [10.1021/jp900360k](https://doi.org/10.1021/jp900360k)

Abstract

The use of a 2-D carbon nanostructure, graphene, as a support material for the dispersion of Pt nanoparticles provides new ways to develop advanced electrocatalyst materials for fuel cells. Platinum nanoparticles are deposited onto graphene sheets by means of borohydride reduction of H_2PtCl_6 in a graphene oxide (GO) suspension. The partially reduced GO-Pt catalyst is deposited as films onto glassy carbon and carbon Toray paper by drop cast or electrophoretic deposition methods. Nearly 80% enhancement in the electrochemically active surface area (ECSA) can be achieved by exposing



partially reduced GO-Pt films with hydrazine followed by heat treatment (300 °C, 8 h). The electrocatalyst performance as evaluated from the hydrogen fuel cell demonstrates the role of graphene as an effective support material in the development of an electrocatalyst.

Fuel Cell Geared in Reverse: Photocatalytic Hydrogen Production Using a TiO₂/Nafion/Pt Membrane Assembly with No Applied Bias

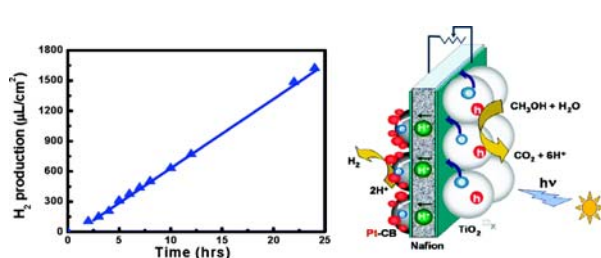
Brian Seger and Prashant V. Kamat*

J. Phys. Chem. C, 2009, 113 (43), pp18946–18952

DOI: 10.1021/jp907367k

Abstract

Renewed interest in graphene architectures has opened up new avenues to utilize them in electronic and optoelectronic applications. The desire to design graphene–metal nanohybrid assemblies has led us to explore a solution-based approach of chemical reduction of AuCl₄[−] ions in graphene suspensions. The gold particles anchored on octadecylamine functionalized graphene are readily suspendable in THF medium. The dependence of particle stability on the graphene concentration and SEM analysis indicate that the gold nanoparticles are well dispersed on graphene sheets. Transient absorption spectroscopy measurements suggest that the ultrafast disappearance of plasmon absorption and its recovery are unaffected by the presence of graphene.



the gold nanoparticles are well dispersed on graphene sheets. Transient absorption spectroscopy measurements suggest that the ultrafast disappearance of plasmon absorption and its recovery are unaffected by the presence of graphene.

Graphene–Semiconductor Nanocomposites: Excited-State Interactions between ZnO Nanoparticles and Graphene Oxide[†]

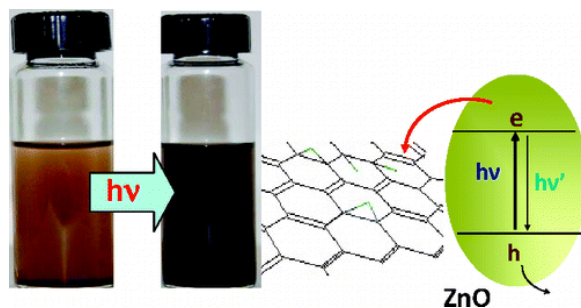
Graeme Williams[‡] and Prashant V. Kamat*

Langmuir, 2010, 25(24), pp13869–13873

DOI: 10.1021/la900905h

Abstract

Graphene oxide sheets suspended in ethanol interact with excited ZnO nanoparticles and undergo photocatalytic reduction. The luminescence quenching of the green emission of ZnO serves as a probe to monitor the electron transfer from excited ZnO to graphene oxide. Anchoring of ZnO nanoparticles on 2-D carbon nanostructures provides a new way to design semiconductor–carbon nanocomposites for catalytic applications.



Got TiO₂ Nanotubes? Lithium Ion Intercalation Can Boost Their Photoelectrochemical Performance

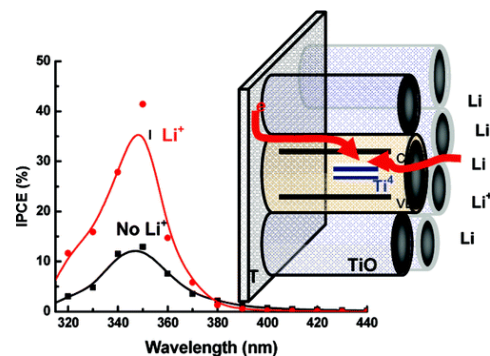
Benjamin H. Meekins and Prashant V. Kamat*

ACS Nano, **2009**, 3, pp 3437–3446

DOI: 10.1021/nn900897r

Abstract

Cations such as H⁺ and Li⁺ are intercalated into TiO₂ nanotube arrays by subjecting them to short-term electrochemical pulses at controlled potentials (<−1.0 V vs Ag/AgCl). The intercalation of these small cations has a profound effect toward enhancing photocurrent generation under UV light irradiation. A nearly three-fold increase in the photoconversion efficiency (IPCE) was observed upon intercalation of Li⁺ ions into TiO₂ nanotube arrays. The intercalation process is visualized by the color change from gray to blue. Spectroelectrochemical measurements were carried out to monitor the absorption changes at different applied potentials. The analysis of the V_{oc} decay following termination of UV light shows a significant decrease in the rate of recombination of accumulated electrons upon Li⁺ ion intercalation.



Nanotechnology for Next Generation Solar Cells

Prashant V. Kamat and George C. Schatz

J. Phys. Chem. C, 2009, 113 (35), pp 15473–15475

DOI: 10.1021/jp905378n

We are pleased to present this Virtual Issue of *Journal of Physical Chemistry C*, "Nanotechnology for Next Generation Solar Cells", the first in a series of Virtual Issues from the *Journal of Physical Chemistry*. Several additional Virtual Issues will be released in 2009 and 2010. We hope they will be a valuable resource for the scientific community.



Disassembly, Reassembly, and Photoelectrochemistry of Etched TiO₂ Nanotubes

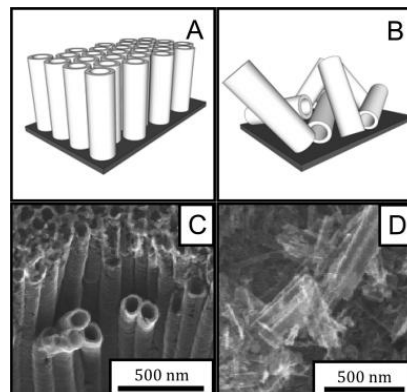
David R. Baker and Prashant V. Kamat*

J. Phys. Chem. C, 2009, 113 (41), pp 17967–17972

DOI: 10.1021/jp9065357

Abstract

Etched TiO₂ nanotubes are removed from the titanium foil substrate by sonication and are reassembled onto new electrodes for photovoltaic applications. CdS nanocrystallites were deposited on the restructured electrodes to compare their performance as quantum dot-sensitized solar cells to aligned nanotube electrodes. The sensitized photoresponses of the photoelectrochemical cell created from reassembled TiO₂ nanotubes are very similar to aligned TiO₂ nanotube arrays. Transient absorption spectroscopy of dispersed tubes indicates that electron transfer from excited CdS nanocrystallites into TiO₂ nanotubes occurs at a rate of $2.0 \times 10^{10} \text{ s}^{-1}$. BET surface area analysis is investigated on etched nanotube powder without the need for weight approximation and was found to be $77.0 \pm 2.9 \text{ m}^2/\text{g}$. The importance of nanotube orientation and porosity on the electrode surface in stabilizing accumulated electrons in TiO₂ nanotubes is elucidated from the open circuit voltage decay. Nanotube orientation was also seen to affect electron transport in photocurrent experiments.



Quantum Dot Sensitized Solar Cells. A Tale of Two Semiconductor Nanocrystals: CdSe and CdTe

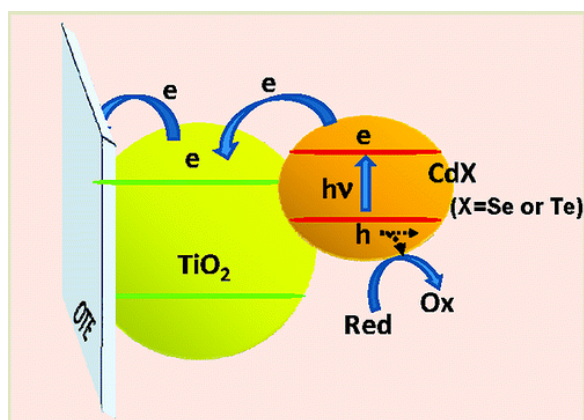
Jin Ho Bang and Prashant V. Kamat*

ACS Nano, 2009, 3 (6), pp 1467–1476

DOI: 10.1021/nn900324q

Abstract

CdSe and CdTe nanocrystals are linked to nanostructured TiO₂ films using 3-mercaptopropionic acid as a linker molecule for establishing the mechanistic aspects of interfacial charge transfer processes. Both these quantum dots are energetically capable of sensitizing TiO₂ films and generating photocurrents in quantum dot solar cells. These two semiconductor nanocrystals exhibit markedly different external quantum efficiencies ($\sim 70\%$ for CdSe and $\sim 0.1\%$ for CdTe at 555 nm). Although CdTe with a more favorable conduction band energy ($E_{\text{CB}} = -1.0 \text{ V vs NHE}$) is capable of injecting electrons into TiO₂ faster than CdSe ($E_{\text{CB}} = -0.6 \text{ V vs NHE}$), hole scavenging by a sulfide redox couple remains a major bottleneck. The sulfide ions dissolved in aqueous solutions are capable of scavenging photogenerated holes in photoirradiated CdSe system but not in CdTe. The anodic corrosion and exchange of Te with S dominate the charge transfer at the CdTe interface. Factors that dictate the efficiency and photostability of CdSe and CdTe quantum dots are discussed.



Photodegradation of Polythiophene-Based Polymers: Excited State Properties and Radical Intermediates[†]

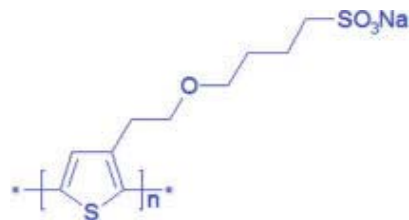
Marius Koch[‡], Roxana Nicolaescu and Prashant V. Kamat^{*}

J. Phys. Chem. C, 2009, 113 (27), pp 11507–11513

DOI: 10.1021/jp808141u

Abstract

Polythiophene-based polymers are an important class of organic semiconductors that serve as the building blocks for polymer-based hybrid solar cells. These polymers are susceptible to oxidative photodegradation in air. A model water-soluble polymer, the sodium salt of poly[2-(3-thienyl)ethoxy-4-butylsulfonate], was employed to investigate the role of excited-state and singlet-state properties in the photodegradation of the polymer. The singlet excited state produces characteristic absorption at 770 nm with a lifetime of 22 ps. The triplet state exhibits a broad absorption in the 650–800 nm region and has a lifetime of 18.7 μ s in deaerated water. The excited triplets are readily quenched by oxygen with a rate constant of $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ via both electron and energy transfer pathways. Pulse radiolysis experiments have been conducted to verify the identity of the cation radical and hydroxyl adduct of the polymer. It is evident from the photochemical experiments that the high photochemical reactivity of triplets with oxygen is responsible for the photodegradation. .



Photosensitization of TiO₂ Nanostructures with CdS Quantum Dots: Particulate versus Tubular Support Architectures[†]

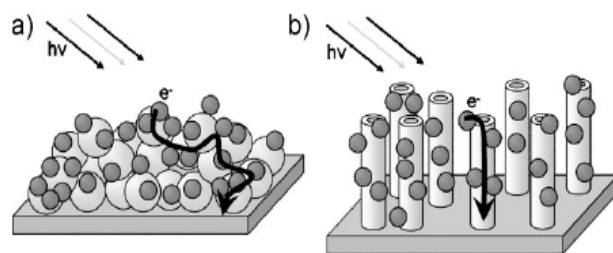
David R. Baker², Prashant V. Kamat

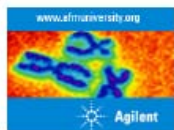
Advanced Functional Materials **2009**, 19, 805-811

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Abstract

TiO₂ nanotube arrays and particulate films are modified with CdS quantum dots with an aim to tune the response of the photoelectrochemical cell in the visible region. The method of successive ionic layer adsorption and reaction facilitates size control of CdS nanocrystals, upon excitation with visible light, inject electrons into the TiO₂ nanotubes and particles and thus enable their use as photosensitive electrodes. Maximum incident photon to charge carrier efficiency (IPCE) values of 55% and 26% are observed for CdS sensitized TiO₂ nanotube and nanoparticulate architectures respectively. The nearly doubling of IPCE observed with the TiO₂ nanotube architecture is attributed to the increased efficiency of charge separation and transport of electrons.





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Photoactive graphene-semiconductor composites

(Nanowerk Spotlight) The electrical properties of graphene have been the topic of recent interest from various disciplines because this novel carbon material offers exciting opportunities to develop nanocomposites with unusual electronic catalytic properties. Most of these studies involve mechanical peeling of individual graphene sheets – one at a time – from a block of graphite.

The requirement to obtain graphene as individual sheets and to maintain it in the reduced form introduces a certain level of complexity into the process of designing composite systems where, for instance, semiconductor or metal nanoparticle are anchored on graphene sheets. Without some form of intervention, the strong van der Waals interactions between reduced graphene sheets would cause them to collapse and aggregate.

Researchers have now developed a simple photocatalytic method to anchor semiconductor nanoparticles on a single sheet of graphene using a solution-based process.

"Following our recent report ("Decorating Graphene Sheets with Gold Nanoparticles") on the formation of a graphene-gold composite system that is suspendable in an aqueous medium using a chemical reduction method, we have now designed an on-demand reduction strategy to obtain graphene semiconductor composite nanostructures," Dr. Prashant V. Kamat tells Nanowerk. "We successfully carried out UV-induced photocatalytic reduction of graphene oxide and maintained well-separated graphene-semiconductor composite sheets."

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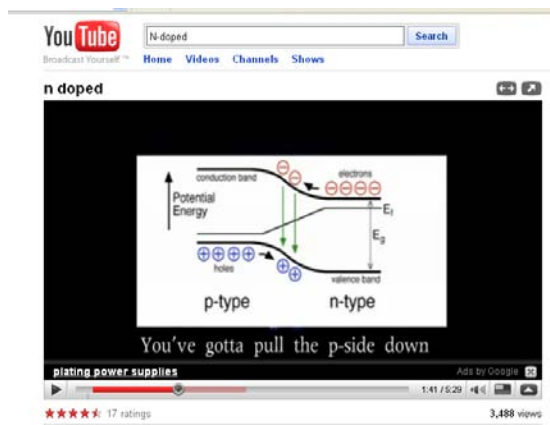
Nano-technology for Next Generation Solar Cells

Prashant V. Kamat, senior scientist at the Radiation Laboratory and professor of Chemistry and Biochemistry, recently reported on developments in the utilization of semiconductor quantum dots for light energy

Notre Dame Science, College News



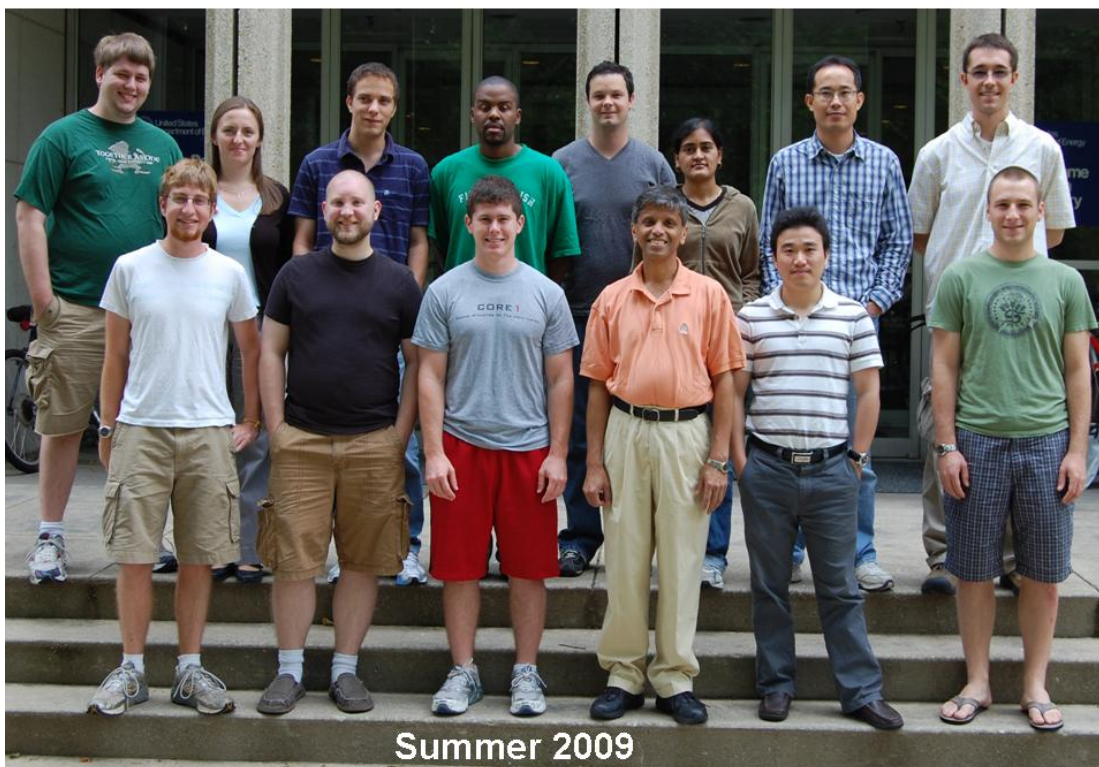
Nanogirls
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Winner of ACS Nanotube contest



N-DOPED
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Congratulations. Brian Seger successfully defended his Ph D thesis in June 2010.



Summer 2009