Annual Research Summary

January - December 2010

Kamat Research Group
University of Notre Dame

Prashant V. Kamat

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2010 Activities/ Highlights

Research Group

Graduate Students

Yunghai Yu (Chem. Eng. -coadvisior Ken Kuno)
David Baker (Chem. Eng.)
Kevin Tvrdy (Chemistry)
Clifton Harris (Chemistry)
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.)
Thibaut Viguier (Chem. Eng. –till Summer 2010)

Incoming Students

Douglas Hines (Chemistry)
Jeff Christians (Chem. Eng.)

Undergraduate Students

Spring 2010

Peter Lobaccaro (CBE, UND)
Ryan P. Dwyer (Chemistry, UND)
Veronica Tsou (Waterloo)

Summer 2010

Ryan P. Dwyer (Chemistry, UND)
Peter Lobaccaro (CBE, UND)
Tim Schumer (CBE, UND)
Sarah Schubert (Chemistry, UND)

Fall 2010

Douglas Pernik (Chemistry, UND)
Ryan P. Dwyer (Chemistry, UND)
Peter Lobaccaro (CBE, UND)
Sarah Schubert (Chemistry, UND)
Susan Garabedian (CBE, UND)

Postdoctoral Research Associate

Jin Ho Bang (Jan-July 2010)
Alexsandra Wojcik (Jan-Aug 2010)
Yoon-Ho Jun (June 2010-)
Hyunbong Choi (Nov 2010-)

Visiting Scientists K. Vinodgopal and Julie Peller (IUN)
Roxana Nicolaescu (Serim Corporation)
Azusa Takai (Waseda University)
Ken-ichi Matsuoka (Kyushu Univeristy)

Awards/Fellowships/Recognition

Yanghai Yu, Successful completion of his Ph. D. Thesis (July 2010)

Douglas Pernik, Slatt Fellowship for undergraduate research (2010-2011)

Ian Lightcap, Winner of 2009-10 Notre Dame Graduate Student Research Symposium (Science Div, Jan 22, 2010).

Prashant Kamat, recognition by the provost at the home football game against Tulsa.

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)

  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**

  Symposium Organizer: Coorganizer, Nanostructures for Energy Conversion, , 217th ECS Meeting Vancouver, Canada April 25-30, 2010

  2010 International Chemical Congress of Pacific Basin Societies, (Pacifichem)**,** *Nanostructure-Enhanced Photochemical Reactions Symposium*, , December 15-20, 2010, Honolulu, Hawaii

Invited Seminar/Colloquium

Kyoto University September 1-7, 2010.

Kamat, P. V. *How to communicate your research effectively.*

Kamat, P. V. *Light energy conversion with nanostructured semiconductor.*

Kamat, P. V. *Solar cells by design. Manipulating charge transfer at semiconductor interfaces*

National Taiwan University, Taiwan. August 3, 2010.

Kamat, P. V. (2010). *How to communicate your research effectively?*

Kamat, P. V. (2010). *Solar cells by design, manipulating charge transfer at nanostructure interfaces*

National Chung Cheng University, Dept. Chem. Biochem., Minhsiung Township, Taiwan. August 2, 2010.

Kamat, P. V. *Manipulation of semiconductor nanoarchitectures for light energy conversion.*

Jawaharial Nehru Center for Adv. Sci. Research, India. October 5-6, 2010

Kamat, P. V. *Carbon nanostructures for energy conversion*.

Kamat, P. V. *Publish or perish: Ethics of scientific publication*.

IGERT Seminar, Univ. of Massachusetts, Amherst, Dec. 3, 2009

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

Recognition by the Provost Tom Burrish at the ND home football game against Tulsa.

Conference Presentations (2010):

International Workshop on Advanced Materials, RAK-CAM, UAE, February 22-24, 2010

Kamat, P. V. Nanostructure Nanoassemblies for Next Generation Solar Cells

NSF Advanced Studies Institute on "Nanomaterials and Nanocatalysis for Energy Photochemicals and Environmental Applications", Cairo, Egypt.

Kamat, P. V. *Nanostructure nanoassemblies to next generation solar cells.*

Spring Meeting of the Electrochemical Society Meeting, Vancouver, Canada April 25-30, 2010

Kamat, P. V. *Graphene oxide as 2-D carbon support to anchor semiconductor and metal nanoparticles.*

Keynote Speaker, Graduae Student Symposium, University of Buffallo, May 14, 2010

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

NSF Advanced Studies Institute on "Nanomaterials and Nanocatalysis for Energy, Photochemicals and Environmental Applications", Cairo, Egypt. March 27-April 5, 2010

Kamat, P. V. *Carbon nanostructures for energy conversion.*

Kamat, P. V. *Ethics of scientific research.*

DOE Solar Photochemistry Conference, Annapolis, June 2010

Kamat, P. V., Tvrdy, K., Meekins, B., Lightcap, I., Baker, D., Bang J. H. *Manipulation of Charge Transfer Processes in Semiconductor Quantum Dot Based Nanoarchitectures*

Fullerene-nanotubes General Symposium, Kyoto, Japan. Sept 5-7, 2010

Kamat, P. V. *Carbon nanostructures for energy conversion.*

Midwest Regional Conference, AIChE, Chicago, IL, October 1, 2010

Baker, D. and Kamat, P. V. *Overcoming losses at the counter electrode in quantum dot solar cells by salt bridge isolation*

445th ACS Midwest Regional Meeting, Wichita, Kansas. Oct 27-29, 2010

Kamat, P. V. *Excited state dynamics of quantum dot sensitized solar cells.*

National Institute for Materials Science (NIMS Conference), Tsukuba, Japan, July 12-14, 2010

Kamat, P. V. *Exploitation of nanostructure interface for light energy conversion.*

18th International Conf. on Photochemical Conversion and Storage of Solar Energy, Seoul, Korea, July 25-30, 2010

Kamat, P. V. *Quantum dot solar cells, exploitation of nanostructure for efficient charge transfer.*

Gordon Reaearch Conference on Radiation Chemistry, Andover, NH, July 18-23, 2010

Wojcik, A. and P. V. Kamat *Spectroscopic and photoelectrochemical characterization of near-infrared responsive squaraine dyes.*

Postdoctorate to Faculty Workshop. Sponsored by ACS and NSF, August 21, 2010.

Kamat, P. V. (2010). *Publish or perish.*

American Chemical Society Fall Meeting, Boston, MA, August 22-26, 2010

Kamat, P. V. *Modulating interparticle electron transfer in quantum dot solar cells.*

Kamat, P. V. *Quantum dot sensitized solar cells, mapping photoinduced charge transfer processes.*

Murphy, S. J., Postnikoff, C., Huang, L., Kamat, P. V. *Ultrafast transient absorption and surface enhanced Raman of photosynthetic reaction centers linked to silver nanoparticles*

Sixth JNC Research Conference on Chemistry of Materials, Cochin, Kerala, India, Oct 2-4, 2010

Kamat, P. V., J. H. Bang, Tvrdy, K, Baker, D. *Understanding charge transfer processes at nanostructured semiconductor interface.*

Research Papers

(1) Gassensmith, J. J.; Matthys, S.; Wojcik, A.; Kamat, P. V.; Smith, B. D. Squaraine Rotaxane as Optical Chloride Sensor *Chemistry, European J.* **2010**, *16*, 2916-2921.

(2) Kamat, P. V., Photosensitization of SnO_2 and Other Dyes, in *Dye Sensitized Solar Cells*, K. Kalyansundaram, Editor. 2010, EPFL Press, Switzerland: Laussane.

(3) 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**, *20*, 582-587.

(4) 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.* **2010**, *10*, 577–583.

(5) Yu, Y.; Kamat, P. V.; Kuno, M. A CdSe Nanowire/Quantum Dot Hybrid Architecture for Improving Solar Cell Performance *Adv. Funct. Mater.* **2010**, *20*, 1464-1472.

(6) Chakrapani, V.; Tvrdy, K.; Kamat, P. V. Modulation of Electron Injection in CdSe-TiO_2 System through Medium Alkalinity *J. Am. Chem. Soc.* **2010**, *132*, 1228-1229.

(7) Kamat, P. V. Graphene based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a 2-Dimensional Carbon Support *J. Phys. Chem. Lett.* **2010**, *1*, 520-527.

(8) Bang, J. H.; Kamat, P. V. Solar Cell by Design. Photoelectrochemistry of TiO_2 Nanorod Arrays Decorated with CdSe *Adv. Funct. Mater.* **2010**, *20*, 1970-1976.

(9) Wojcik, A.; Nicolaescu, R.; Kamat, P. V.; Patil, S. Photochemistry of Far Red Responsive Tetrahydroquinoxaline-Based Squaraine Dyes *J. Phys. Chem. A* **2010**, *114*, 2744-2750.

(10) Tvrdy, K.; Kamat, P. V., Quantum Dot Solar Cells, in *Comprehensive Nanoscience and Technology* G. Wiederrecht, Editor. 2010, Elsevier: Oxford, U.K.

(11) Baker, D. R.; Kamat, P. V. Tuning the Emission of CdSe Quantum Dots by Controlled Trap Enhancement *Langmuir* **2010**, *26*, 11272-11276.

(12) Kamat, P. V. Revealing Surface Interactions in Quantum Dot Based Photovoltaic Architectures (A Perspective on the Article, Electronic Energy Alignment at the PbSe Quantum Dots/ZnO(1010) Interface by Timp and Zhu) *Surf. Sci.* **2010**, *604*, 1331-1332

(13) Vinodgopal, K.; Neppolian, B.; Lightcap, I. V.; Grieser, F.; Ashokkumar, M.; Kamat, P. V. Sonolytic Design of Graphene Au Nanocomposites. Simultaneous and Sequential Reduction of Graphene Oxide and Au(III) *J. Phys. Chem. Lett.* **2010**, 1987-1993.

(14) Ng, Y. H.; Lightcap, I. V.; Goodwin, K.; Matsumura, M.; Kamat, P. V. To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO_2 Nanostructured Films? *J. Phys. Chem. Lett.* **2010**, *1*, 2222–2227.

(15) Tvrdy, K.; Frantszov, P.; Kamat, P. V. Electron Transfer from Quantum Dots to Metal Oxide Nanoparticles: Theory, Experiment, and Implications *Proc. Natl. Acad. Sci. U. S. A.* **2010**, in press.

(16) Kamat, P. V.; Tvrdy, K.; Baker, D. R.; Radich, J. G. Beyond photovoltaics: semiconductor nanoarchitectures for liquid junction solar cells *Chem. Rev.* **2010**, *110*, 6689–6735.

(17) Kamat, P. V. Capturing Hot Electrons *Nature Chemistry* **2010**, *2*, 809-810.

(18) Wojcik, A.; Kamat, P. V. Reduced Graphene Oxide and Porphyrin. An Interactive Affair in 2-D *ACS Nano* **2010**, *4*, 6697–6706.

(19) Zhang, J.; Bang, J. H.; Tang, C.; Kamat, P. V. Tailored TiO_2–$SrTiO_3$ Heterostructure Nanotube Arrays for Improved Photoelectrochemical Performance, *ACS Nano* **2010**, *4*, 387-395

(20) Harris, C.; Kamat, P. V. Photocatalytic Events of CdSe Quantum Dots in Confined Media. Electrodic Behavior of Coupled Platinum Nanoparticles *ACS Nano* **2010**, *4*, in press.

Editorials

(1) Schatz, G.; Kamat, P.; Hammes-Schiffer, S.; Zwier, T. A New High-Profile Journal for Cutting-Edge Research across Physical Chemistry *J. Phys. Chem. Lett.* **2010**, *1*, 1-1.

(2) Kamat, P. V. Graphene: A Physical Chemistry Perspective *J. Phys. Chem. Lett.* **2010**, *1*, 587-588.

(3) Kamat, P. Material Science by Design. Chemical and Energy Conversion Research in the New Decade *J. Phys. Chem. Lett.* **2010**, *1*, 673-673.

(4) Kamat, P. V. Meeting the Challenges of Energy Sustainability *J. Phys. Chem. Lett.* **2010**, *1*, 1018-1019.

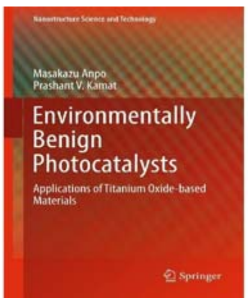
(5) Kamat, P. V. Revealing the Art of Nanoscience *J. Phys. Chem. Lett.* **2010**, *1*, 1283-1283.

(6) Kamat, P. V. Emerging Faces of Carbon *J. Phys. Chem. Lett.* **2010**, *1*, 2606-2606.

(7) Kamat, P. V. Electrochemistry in the Driver's Seat *J. Phys. Chem. Lett.* **2010**, *1*, 2220-2221.

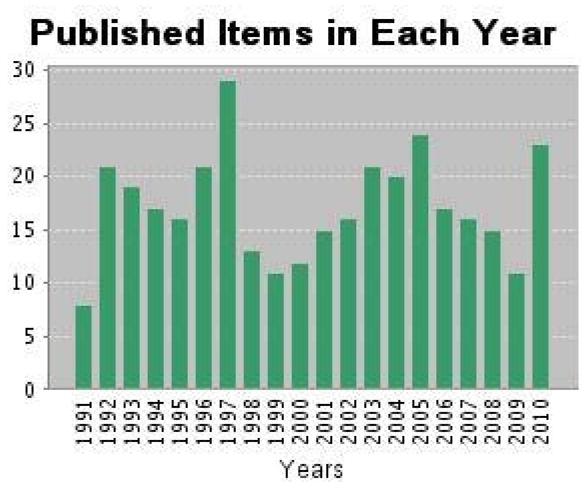
(8) Kamat, P. V. Solar Cells by Design *J. Phys. Chem. Lett.* **2010**, *1*, 3147-3148.

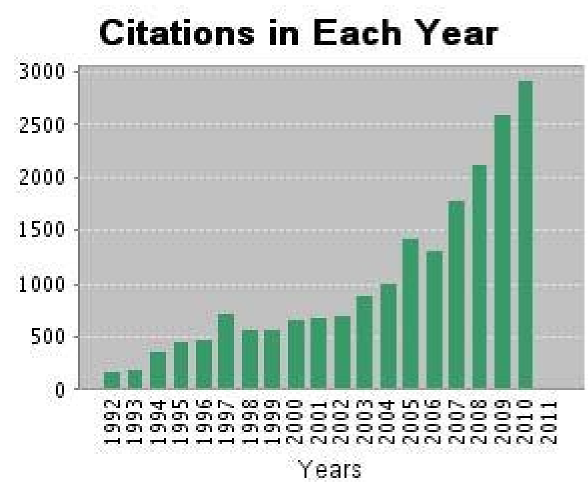
Edited Book



Environmentally Benign Photocatalysts: Applications of Titanium Oxide-based Materials: The Development of Highly Active Photocatalysts for the Generation
Masakazu Anpo and Prashant V. Kamat (Editors) Springer Publisher

Publication Analysis





Results found: 417

Sum of the Times Cited : 20400+

Average Citations per Item : ~50

h-index : **80**

Ten most cited publications of previous two years (2008-2009)

Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO2 architecture
Kongkanand A, Tvrdy K, Takechi K, et al. J. AM. CHEM. SOC. 130, 4007-4015 2008
Times Cited: 183

2. Title: Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters
Kamat PV JOURNAL OF PHYSICAL CHEMISTRY C Volume: 112, 18737-18753 2008
Times Cited: 162

3. TiO_2-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide
Williams G, Seger B, Kamat PV ACS NANO 2, 1487-1491 2008
Times Cited: 139

4. Decorating graphene sheets with gold nanoparticles
Muszynski R, Seger B, Kamat PV JOURNAL OF PHYSICAL CHEMISTRY C 112, 5263-5266 2008
Times Cited: 96

5. Electrocatalytically Active Graphene-Platinum Nanocomposites. Role of 2-D Carbon Support in PEM Fuel Cells Seger B, Kamat PV JOURNAL OF PHYSICAL CHEMISTRY C 113, 7990-7995, 2009
Times Cited: 48

6. Photosensitization of TiO_2 Nanostructures with CdS Quantum Dots: Particulate versus Tubular Support Architectures Baker DR, Kamat PV ADVANCED FUNCTIONAL MATERIALS 19, 805-811, 2009
Times Cited: 47

7. Quantum dot solar cells. Electrophoretic deposition of CdSe-C-60 composite films and capture of photogenerated electrons with nC(60) cluster shell
Brown P, Kamat PV JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 130, 8890-8891, 2008
Times Cited: 41

8. Quantum Dot Sensitized Solar Cells. A Tale of Two Semiconductor Nanocrystals: CdSe and CdTe
Bang JH, Kamat PV ACS NANO 3, 1467-1476, 2009
Times Cited: 34

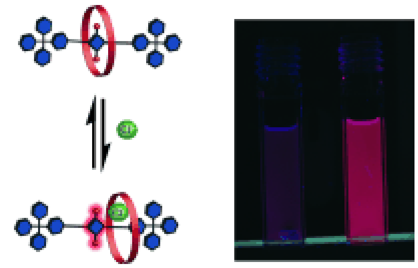
9. Title: Single-walled carbon nanotube scaffolds for dye-sensitized solar cells
Brown P, Takechi K, Kamat PV JOURNAL OF PHYSICAL CHEMISTRY C Volume: 112, 4776-4782, 2008
Times Cited: 33

10. Title: CdSe Quantum Dot Sensitized Solar Cells. Shuttling Electrons Through Stacked Carbon Nanocups
Farrow B, Kamat PV J. AM. CHEM. SOC. Volume: 131, 11124-11131, 2009
Times Cited: 26

(Source Web of Science as of December 24, 2010)

Squaraine Rotaxane as Optical Chloride Sensor

Gassensmith, J. J.; Matthys, S.; Wojcik, A.; Kamat, P. V.; Smith, B. D.
Chemistry, European J. **2010**, *16*, 2916-2921
DOI: 10.1002/chem.200902547

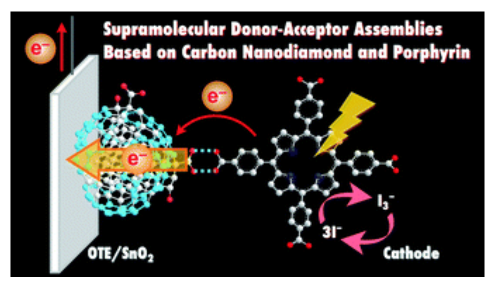


Abstract

A mechanically interlocked squaraine rotaxane is comprised of a deep-red fluorescent squaraine dye inside a tetralactam macrocycle. NMR studies show that Cl^- binding to the rotaxane induces macrocycle translocation away from the central squaraine station, a process that is completely reversed when the Cl^- is removed from the solution. Steady-state fluorescence and excited-state lifetime measurements show that this reversible machine-like motion modulates several technically useful optical properties, including a three-fold increase in deep-red fluorescence emission that is observable to the naked eye. The fluorescence intensity of a dipstick increased eighteen-fold upon dipping in an aqueous solution of tetrabutylammonium chloride (300 mM) and was subsequently reversed by washing with pure water. It is possible to develop the dipsticks for colorimetric determination of Cl^- levels by the naked eye.

Supramolecular Donor-Acceptor Assemblies Composed of Carbon Nanodiamond and Porphyrin for Photoinduced Electron Transfer and Photocurrent Generation

Ohtani, M.; Kamat, P. V.; Fukuzumi, S.
J. Mater. Chem. **2010**, *20*, 582-587
DOI: 10.1039/B916634C

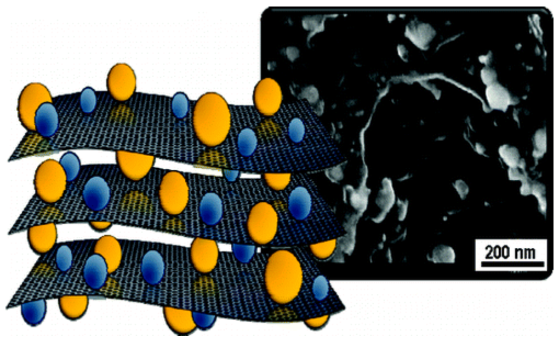


Abstract

Supramolecular donor–acceptor assemblies composed of carbon nanodiamond (ND) and porphyrin (Por) are constructed through interensemble hydrogen bonding and π–π interactions. Formation of the supramolecular clusters composed of ND and porphyrin has been confirmed by transmission electron microscopy (TEM), dynamic light scattering (DLS), and IR spectroscopy. The resulting supramolecular clusters have been assembled as three-dimensional arrays onto nanostructured SnO_2 films using an electrophoretic deposition method for the test of photoelectrochemical properties. Enhancement in the photoelectrochemical performance as well as the broader photoresponse in the visible region is seen with formation of the supramolecular clusters between ND and porphyrins as compared with the reference system without porphyrins..

Anchoring Semiconductor and Metal Nanoparticles on a 2-Dimensional Catalyst Mat. Storing and Shuttling Electrons with Reduced Graphene Oxide

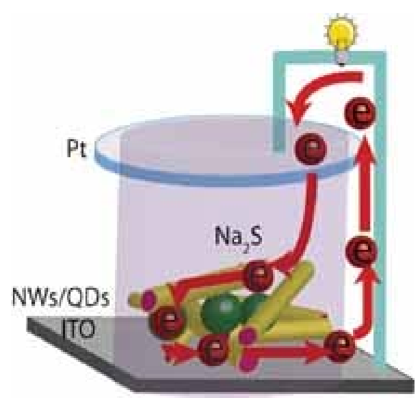
Lightcap, I. V.; Kosel, T. H.; Kamat, P. V.
Nano Lett. **2010**, *10*, 577–583
DOI: 10.1021/nl9035109



Abstract
Using reduced graphene oxide (RGO) as a two-dimensional support, we have succeeded in selective anchoring of semiconductor and metal nanoparticles at separate sites. Photogenerated electrons from UV-irradiated TiO_2 are transported across RGO to reduce silver ions into silver nanoparticles at a location distinct from the TiO_2 anchored site. The ability of RGO to store and shuttle electrons, as visualized via a stepwise electron transfer process, demonstrates its capability to serve as a catalyst nanomat and transfer electrons on demand to adsorbed species. These findings pave the way for the development of next generation catalyst systems and can spur advancements in graphene-based composites for chemical and biological sensors.

A CdSe Nanowire/Quantum Dot Hybrid Architecture for Improving Solar Cell Performance

Yu, Y.; Kamat, P. V.; Kuno, M.
Adv. Funct. Mater. **2010**, *20*, 1464-1472
DOI: 10.1002/adfm.200902372

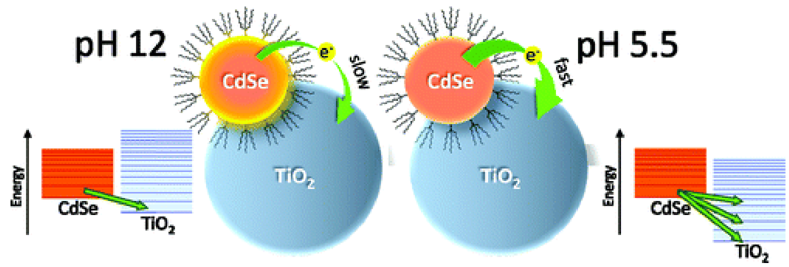


Abstract
Incorporating colloidal CdSe quantum dots (QDs) into CdSe nanowire (NW)-based photoelectrochemical solar cells increases their incident-photon-to-carrier conversion efficiencies (IPCE) from 13% to 25% at 500 nm. While the effect could, in principle, stem from direct absorption and subsequent carrier generation by QDs, the overall IPCE increase occurs across the entire visible spectrum, even at wavelengths where the dots do not absorb light. This beneficial effect originates from an interplay between NWs and QDs where the latter fill voids between interconnected NWs, providing electrically accessible conduits, in turn, enabling better carrier transport to electrodes. The presence of QDs furthermore reduces the residual polarization anisotropy of random NW networks. Introducing QDs therefore addresses an important limiting constraint of NW photoelectrochemical solar cells. The effect appears to be general and may aid the future design and implementation of other NW-based photovoltaics.

Modulation of Electron Injection in CdSe-TiO_2 System through Medium Alkalinity

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

J. Am. Chem. Soc. **2010**, *132*, 1228-1229
DOI: 10.1021/ja909663r



Abstract

Charge injection from excited CdSe quantum dots into nanostructured TiO_2 film can be modulated by varying solution pH. At increasing solution pH, the conduction band of TiO_2 shifts 59 mV/pH unit to a more negative potential, thereby decreasing the driving force and thus decreasing the rate of nonradiative electron transfer from excited CdSe. The emission yield and the average emission lifetime increase with increasing pH, thus providing a way to monitor the variation in medium pH.

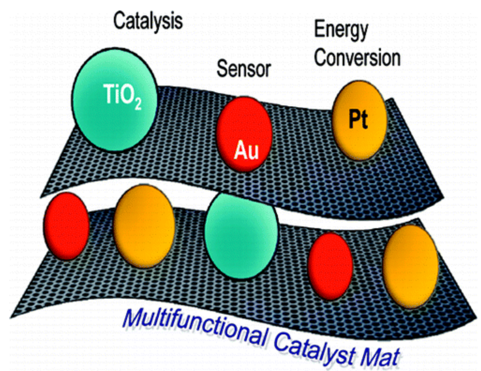
Graphene based Nanoarchitectures. Anchoring Semiconductor and Metal Nanoparticles on a 2-Dimensional Carbon Support

Kamat, P. V.

J. Phys. Chem. Lett. **2010**, *1*, 520-527
DOI: 10.1021/jz900265j

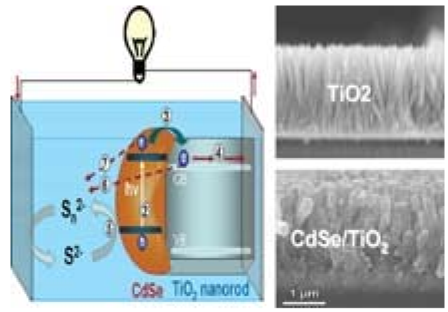
Abstract

Graphene based two-dimensional carbon nanostructures serve as a support to disperse catalyst nanoparticles. Reduced graphene oxide is used as a support to anchor semiconductor and metal nanoparticles. Such a design strategy would enable the development of a multifunctional catalyst mat. This Perspective focuses on the interaction between graphene oxide−semiconductor (TiO_2, ZnO) and graphene oxide−metal (Au, Pt) nanoparticles and discusses potential applications in catalysis, light energy conversion, and fuel cells.



Solar Cell by Design. Photoelectrochemistry of TiO_2 Nanorod Arrays Decorated with CdSe

Bang, J. H.; Kamat, P. V.
Adv. Funct. Mater. **2010**, *20*, 1970-1976
DOI: 10.1002/adfm.200902234

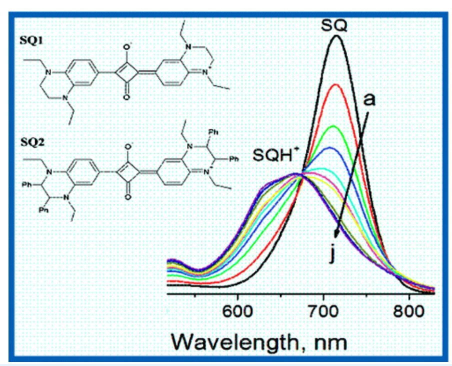


Abstract

One-dimensional (1D) nanostructures of TiO_2 are grown directly on transparent, conductive glass substrate using hydrothermal/solvothermal methods. When employed as a photoanode in photoelectrochemical cells, the vertically aligned TiO_2 nanorod array exhibits slower charge recombination at electrolyte interface as compared to mesoscopic TiO_2 particulate film. Electrochemical deposition of CdSe onto TiO_2 nanorod array is carried out to extend absorption into visible light region. The role of CdSe-sensitized, 1D rutile TiO_2 architecture in the solar cell design is discussed.

Photochemistry of Far Red Responsive Tetrahydroquinoxaline-Based Squaraine Dyes

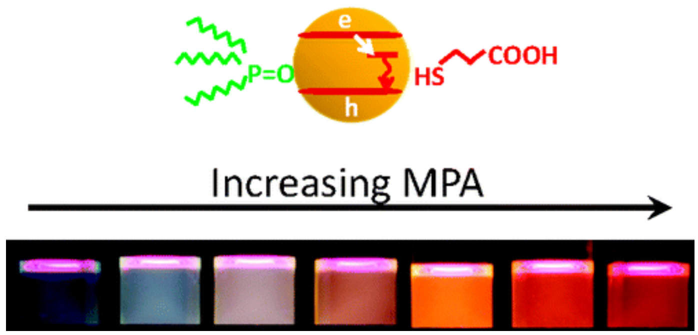
Wojcik, A.; Nicolaescu, R.; Kamat, P. V.; Patil, S.
J. Phys. Chem. A **2010**, *114*, 2744-2750
DOI: 10.1021/jp9118887



The photochemical and redox properties of two newly synthesized tetrahydroquinoxaline-based squaraine dyes (SQ) are investigated using femto- and nanosecond laser flash photolysis, pulse radiolysis, and cyclic voltammetry. In acetonitrile and dichloromethane, these squaraines exist as monomers in the zwitterionic form ($\lambda_{max} \approx 715$ nm, $\varepsilon_{max} \approx 1.66 \times 10^5$ M^{-1} cm^{-1} in acetonitrile). Their excited singlet states ($^1SQ^*$) exhibit a broad absorption band at 480 nm, with singlet lifetimes of 44 and 123 ps for the two dyes. The excited triplet states of the squaraine dyes exhibit a broad absorption band at ca. 560 nm ($\varepsilon_{triplet} \approx 4.2 \times 10^4$ M^{-1} cm^{-1}) and undergo deactivation via triplet−triplet annihilation and ground-state quenching processes. The oxidized forms of the investigated squaraines ($SQ^{\bullet+}$) exhibit absorption maxima at 510 and 610 nm.

Tuning the Emission of CdSe Quantum Dots by Controlled Trap Enhancement

David R. Baker and Prashant V. Kamat*
Langmuir **2010**, *26*, 11272-11276
DOI: 10.1021/la100580g

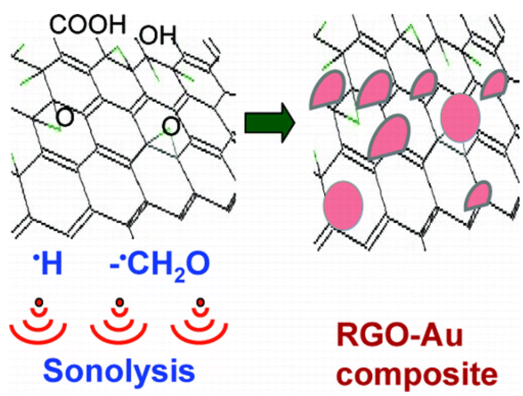


Abstract

Ligand exchange with 3-mercaptopropionic acid (MPA) has been successfully used to tune the emission intensity of trioctylphosphineoxide/dodecylamine-capped CdSe quantum dots. Addition of 3-mercaptopropionic acid (MPA) to CdSe quantum dot suspension enhances the deep trap emission with concurrent quenching of the band edge emission. The smaller sized quantum dots, because of larger surface/volume ratio, create a brighter trap emission and are more easily tuned. An important observation is that the deep trap emission which is minimal after synthesis is brightened to have a quantum yield of 1−5% and can be tuned based on the concentration of MPA in solution with the quantum dots. Photoluminescence decay and transient absorption measurements reveal the role of surface bound MPA in altering the photophysical properties of CdSe quantum dots.

Sonolytic Design of Graphene Au Nanocomposites. Simultaneous and Sequential Reduction of Graphene Oxide and Au(III)

Vinodgopal, K.; Neppolian, B.; Lightcap, I. V.; Grieser, F.; Ashokkumar, M.; Kamat, P. V.
J. Phys. Chem. Lett. **2010**, 1987-1993
DOI: 10.1021/jz1006093

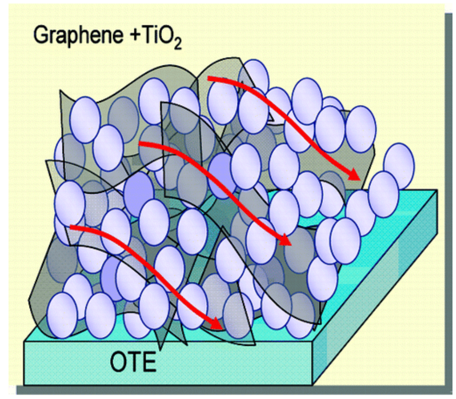


Abstract

High-frequency ultrasound at 211 kHz is effective in developing graphene-based nanoarchitectures. Both simultaneous and sequential reduction steps have been employed to reduce the graphene oxide (GO) and a gold precursor, $HAuCl_4$. Characterization of the composites by transmission electron microscopy following the reduction process revealed well-dispersed Au nanoparticles on the reduced GO (RGO) sheets that are no more than a few layers thick (1−4 layers). The Raman spectra of the RGO−Au composites showed a distinct surface enhancement of the graphene Raman bands upon increasing the surface coverage of gold nanoparticles. The merits of sonolytic reduction in developing graphene-based composites are discussed.

To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO_2 Nanostructured Films?

Ng, Y. H.; Lightcap, I. V.;Goodwin, K.; Matsumura, M.; Kamat, P. V.
J. Phys. Chem. Lett. **2010**, *1*, 2222–2227
DOI: 10.1021/jz100728z

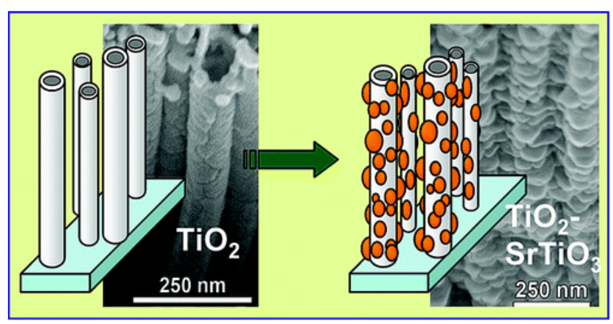


Abstract

Graphene−TiO_2 nanocomposites synthesized via a solution-based method involving photocatalytic reduction of graphene oxide have been employed as photoanodes. Nearly 90% enhancement in the photocurrent is seen as reduced graphene oxide serves as electron collector and transporter. Additionally, the graphene−TiO_2 nanocomposite electrodes exhibit significant activity for the complete photocatalytic decomposition of 2,4-dichlorophenoxyacetic acid (2,4-D). Combined with safe, solution-based synthetic practices, the promising photocurrent and photocatalytic degradation rates provide the framework and motivation for the implementation of graphene−TiO_2 nanocomposites on larger scales.

Tailored TiO_2–$SrTiO_3$ Heterostructure Nanotube Arrays for Improved Photoelectrochemical Performance,

Zhang, J.; Bang, J. H.; Tang, C.; Kamat, P. V.
ACS Nano, **2010**, *4* (1), pp 387–395
DOI: 10.1021/nn901087c

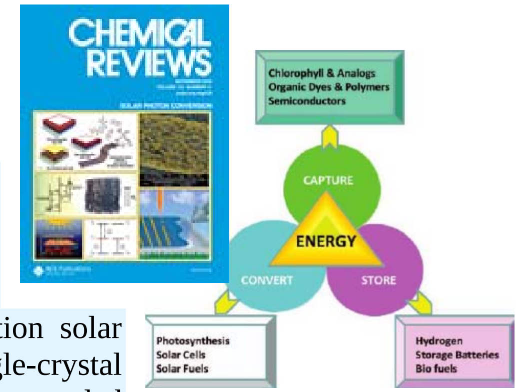


Abstract

TiO_2 nanotube arrays formed on Ti substrate by electrochemical anodization have been converted into TiO_2−$SrTiO_3$ heterostructures by controlled substitution of Sr under hydrothermal conditions. The growth of $SrTiO_3$ crystallites on the nanotube array electrode was probed by electron microscopy and X-ray diffraction. As the degree of Sr substitution increases with the duration of hydrothermal treatment, an increase in the size of $SrTiO_3$ crystallites was observed. Consequently, with increasing $SrTiO_3$ fraction in the TiO_2−$SrTiO_3$ nanotube arrays, we observed a shift in the flat band potential to more negative potentials, thus confirming the influence of $SrTiO_3$ in the modification of the photoelectrochemical properties. The TiO_2−$SrTiO_3$ composite heterostructures obtained with 1 h or less hydrothermal treatment exhibit the best photoelectrochemical performance with nearly 100% increase in external quantum efficiency at 360 nm. The results presented here provide a convenient way to tailor the photoelectrochemical properties of TiO_2−$SrTiO_3$ nanotube array electrodes and employ them for dye- or quantum-dot-sensitized solar cells and/or photocatalytic hydrogen production.

Beyond photovoltaics: semiconductor nanoarchitectures for liquid junction solar cells

Kamat, P. V.; Tvrdy, K.; Baker, D. R.; Radich, J. G.
Chem. Rev. **2010**, *110*, 6689–6735
DOI: 10.1021/cr100243p

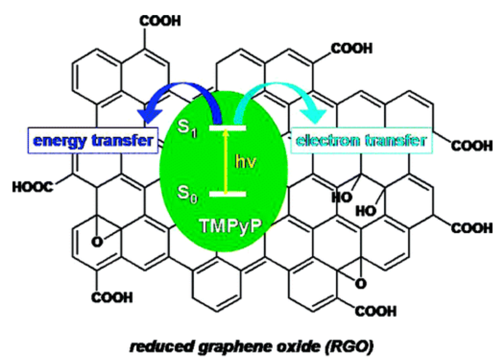


Abstract

Liquid-junction photoelectrochemical solar cells make use of the principles of photochemistry, electrochemistry, and semiconductor physical chemistry. The field of photoelectrochemistry has nurtured the development and design of next-generation solar cells. This field, which originated with single-crystal semiconductor electrochemistry in the 1960s, has now expanded to nanostructured semiconductor electrodes. Basic research at the semiconductor/electrolyte interface continues to draw the attention of scientists around the world. The recent technological advances in the commercialization of dye sensitized solar cells have provided a further boost to the development of photoelectrochemical solar cells.

Reduced Graphene Oxide and Porphyrin. An Interactive Affair in 2-D

Wojcik, A.; Kamat, P. V.
ACS Nano **2010**, *4*, 6697–6706
DOI: 10.1021/nn102185q

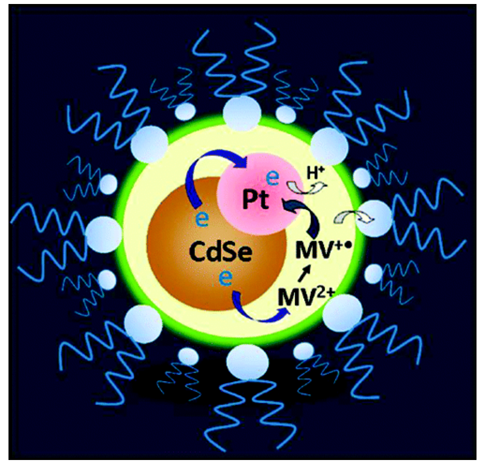


Abstract

Photoexcited cationic 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP) undergoes charge-transfer interaction with chemically reduced graphene oxide (RGO). Formation of the ground-state TMPyP−RGO complex in solution is marked by the red-shift of the porphyrin absorption band. This complexation was analyzed by Benesi−Hildebrand plot. Porphyrin fluorescence lifetime reduced from 5 to 1 ns upon complexation with RGO, indicating excited-state interaction between singlet excited porphyrin and RGO. Femtosecond transient absorption measurements carried out with TMPyP adsorbed on RGO film revealed fast decay of the singlet excited state, followed by the formation of a longer-living product with an absorption maximum around 515 nm indicating the formation of a porphyrin radical cation. The ability of TMPyP−RGO to undergo photoinduced charge separation was further confirmed from the photoelectrochemical measurements. TMPyP−RGO coated conducting glass electrodes are capable of generating photocurrent under visible excitation. These results are indicative of the electron transfer between photoexcited porphyrin and RGO. The role of graphene in accepting and shuttling electrons in light-harvesting assemblies is discussed.

Photocatalytic Events of CdSe Quantum Dots in Confined Media. Electrodic Behavior of Coupled Platinum Nanoparticles

Harris, C.; Kamat, P. V.
ACS Nano **2010**, *4,* 7321–7330.
DOI: 10.1021/nn102564x

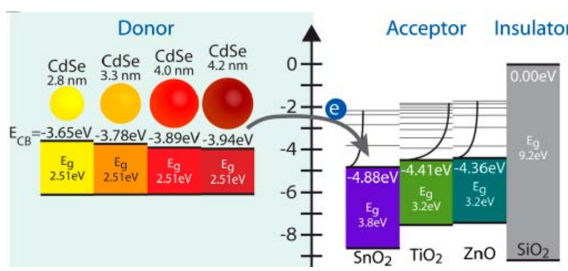


Abstract

The electrodic behavior of platinum nanoparticles (2.8 nm diameter) and their role in influencing the photocatalytic behavior of CdSe quantum dots (3.4 nm diameter) has been evaluated by confining both nanoparticles together in heptane/dioctyl sulphosuccinate/water reverse micelles. Electron transfer from CdSe to Pt is found to occur with a rate constant of 1.22×10^9 s^{-1}. With the use of methyl viologen (MV^{2+}) as a probe molecule, the role of Pt in the photocatalytic process is established. Ultrafast oxidation of the photogenerated $MV^{+\bullet}$ radicals indicates that Pt acts as an electron sink, scavenging electrons from $MV^{+\bullet}$ with a rate constant of 3.1×10^9 s^{-1}. The electron transfer between $MV^{+\bullet}$ and Pt, and a drastically lower yield of $MV^{+\bullet}$ under steady state irradiation, confirms the ability of Pt nanoparticles to discharge electrons quickly. The kinetic details of photoinduced processes in CdSe−Pt assemblies and the electrodic behavior of Pt nanoparticles provide important information for the development of light energy conversion devices.

Photoinduced Electron Transfer from Semiconductor Quantum Dots to Metal Oxide Nanoparticles.

Kevin Tvrdy.; Pavel A. Frantsuzov.; Prashant V. Kamat
Proc. Nat. Acad. Sci, USA **2011**, in press
doi:10.1073/pnas.1011974107.



Abstract

Quantum dot-metal oxide junctions are an integral part of next generation solar cells, light emitting diodes, and nanostructured electronic arrays. We present for the first time 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 4.2nm) and metal oxide nanoparticle acceptors (SnO_2, TiO_2, 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.

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