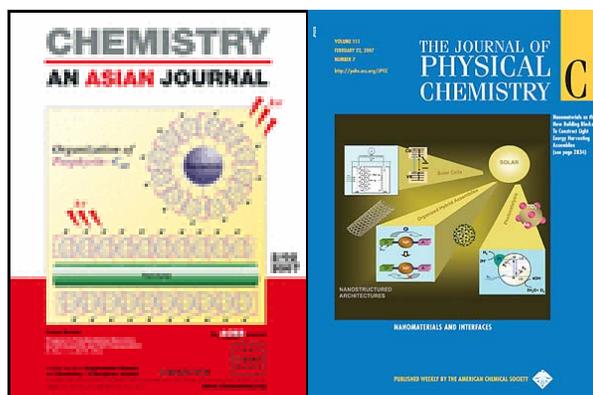


Annual Research Summary

January - December 2007

Prashant V. Kamat



Summer 2007

Prashant V. Kamat

Professor, Chemistry & Biochemistry
Concurrent Professor, Chemical & Biomolecular Eng.
Senior Scientist, Radiation Laboratory
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Website: <http://www.nd.edu/~pkamat>

Research Program

The goal of DOE sponsored research is to improve charge separation efficiencies in novel inorganic-organic hybrid assemblies and at solid interfaces by elucidating the chemical interactions, the rates and yields of interfacial charge transfer and charge recombination processes that take place on them.

In addition, part of the research group is active in exploring new ways to utilize carbon nanostructures and nanotubes in energy conversion systems.

External Collaborators

K. George Thomas (NIIST, Trivandrum, India)
D. Ramaiah (NIIST, Trivandrum, India)
S. Fukuzumi (Osaka University)
T. Akasaka (Tsukuba University)

S. Hotchandani (U. of Quebec)
D. D. Sarma (IACS, Kolkata, India)
Val Vulev (Univ. California, Riverside)
Kevin O'Shea (Florida International Univ.)

Collaborators at Notre Dame

Bruce Bunker (Physics),
Ken Kuno (Chemistry)
Bradley Smith (Chemistry)

Joan Brennecke (Chem. Eng.)
Paul McGinn (Chem. Eng.)

Visiting Scientists

Taicheng An (Guangzhou Inst. of Geochem., CAS)
Kensuke Takechi (Toyota Central R&D, Nagoya)
Kevin O'Shea (Florida International Univ.)

J. Peller (Indiana U., N. W.)
K. Vinodgopal (Indiana U., N. W.)

Postdoctoral Research Associate

Sandy Moisan (Feb –Jul 2007)
Yoichiro Matsunaga (March 2006- Sept 2007)
Toshihiro Diamon (Oct 2007- Jan 2008)

Aunsorn Kongkanad (Jan 2006 – Aug 2007)
Masataka Ohtani (Oct- Nov 2007)

Graduate Students

David Baker (Chem. Eng., U. Of Notre Dame)
Clifton Harris (Chemistry)
Kevin Tvrdy (Chemistry)

Matt Becker (Physics, Jointly with Prof. Bunker)
Brian Seger (Chem. Eng. U. of Notre Dame)
Yanghai Yu (Chem. Eng. Jointly with Prof. Kuno)

First Year Graduate Students Ben Meekins (Chem. Eng.) and Ian Lightcap (Chemistry) will be joining the group soon.

Undergraduate Students

Patrick Brown (Chem. & Biochem, U. Notre Dame)
Meghan Jebb (Chem. & Biochem, U. Notre Dame)
Caitlin Lambert (Summer REU student)
Edema Ojomo (Summer REU jointly with S. Brown)

Chris Beesley (Chem. & Biochem, U. Notre Dame)
Sohaib Hashmi (Chem. & Biochem, U. Notre Dame)
Ryan Muszynski (Waterloo Co-op student)
Tom Hauch (Adams high School student)

Visitors to conduct experiments or extend scientific collaboration

Kenji Saito (Prof. Fukuzumi group, Osaka University)
Tilian Xu and Prof. Kevin O'Shea (Florida International University)
Prof. Jaesang Lee/ Prof. Jaehong Kim (Georgia Tech.)
Prof. Junhong Chen (University of Wisconsin-Milwaukee)
Prof. Yoshio Nosaka (Nagaoka University)

Research Funding

Department of Energy, BES
 US Army
 Toyota Central R&D, Japan

Honors/Awards

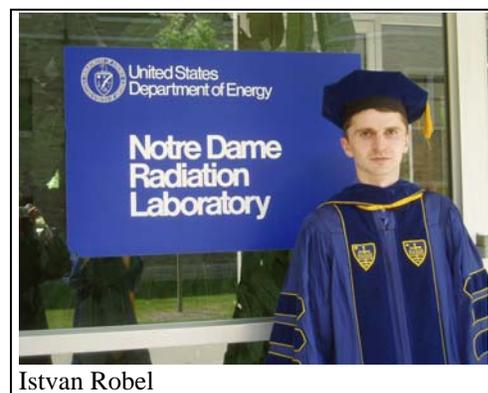
Rajendralal Mitra Professorship Lecture
 Indian Association for the Cultivation of Science, Kolkata, India

Degrees Awarded

Istvan Robel (Ph. D.) *Molecularly Wired Nanocomposites: Charge Transfer in Semiconductor, Metal, and Carbon Nanotube Architectures*
 Ben Merritt (M.S.) *The Effect of 1,4-Diaminoanthraquinone as a Conductive Linker in Chromophore Functionalized Gold Nanoparticles*

Professional Activities

- **Senior Editor**, *Journal of Physical Chemistry A/B/C*
- **Member**, Editorial Advisory Board, *Langmuir*
- **Member**, Editorial Board, *Research on Chemical Intermediates*
- **Member**, Editorial Board, *International Journal of Photoenergy*
- **Member**, Editorial Board, *Interface*
- **Member**, Editorial Board *Electrochemical and Solid State Letters*
- **Treasurer**, *Fullerenes, Nanotubes and Carbon Nanostructures Division* (The Electrochemical Society) May 2004-2008
- **Symposium Organizer** of the Nanotechnology symposium at the Spring (Chicago) and Fall (Washington, DC) meetings of the Electrochemical Society.
- **Panels/Workshops**
 - Workshop on nanotechnology and water treatment. Rice Univ., Houston, TX, February 25-27, 2007
 - DOE Catalysis Panel Review, March 12, 13, 2007
 - NSF/IC Workshop on Power Sources, Washington, DC, April 24-25, 2007
 - GCEP Review Panel May 4, 2007
 - NSF Catalysis and Biocatalysis Panel May 15, 2007
 - DOE Basic Research Needs in Catalysis for Energy workshop, Washington, DC August 6-8, 2007
 - NSF Solar/PV Panel on Dec. 3 & 4



Istvan Robel

Invited Lectures

Prashant V. Kamat

Chemistry Department Colloquium, University of Toronto, November 16, 2007
Nanostructure Architectures for Light Energy Conversion

Physical Chemistry/Chemical Physics Colloquium University of Colorado, Boulder, CO, November 2, 2007
Quantum Dot Archetexture for Solar Cells

Chemistry Department Colloquium, Department of Chemistry, Univ. North Carolina, Charlotte
Semiconductor Quantum Dot Architectures for Solar Energy Conversion

Rajendralal Mitra Professorship Lecture, Indian Association for the Cultivation of Science, Kolkata, India, September 25-28, 2007, (i) *Meeting Clean Energy Demand with Nanotechnology*, (ii) *Nanotube Architecture for Solar Cells and Fuel Cells*,” and (iii) *Quantum Dot Solar Cells*.

Indian Institute of Science, Bangalore October 3, 2007
(i) *Nanostructure Hybrid Architectures for Solar Energy Conversion* and (ii) *Scientific Publications – Issues, and Ethics*.”

Chemistry Department Seminar, Andrews University, Barrien Springs, September 4, 2007
Harvesting Light Energy with Carbon Nanotube-Semiconductor Hybrids

Materials Research Laboratory Seminar, University of Illinois at Urbana-Champaign, May 25 2007
Nanostructure Hybrid Architectures for Solar Energy

Meeting Presentations

Third JNU Conference on Chemistry of Materials, Munnar, Kerala, India, September 28-October 1, 2006

Charge Separation and Charge Collection in Semiconductor-Carbon Nanotube Hybrid Assemblies, P. V. Kamat

Fall Meeting of the American Chemical Society, Boston, August 19-23, 2007

Semiconductor Quantum Dot Architectures for Solar Energy Conversion, P. V. Kamat

Second Energy Center Hydrogen Initiative (ECHI-II) Symposium. Purdue University, April 12-13, 2007.

Nanostructure hybrid architectures for solar energy conversion. P. V. Kamat

29th Department of Energy (DOE) Solar Photochemistry Research Conference will be held June 4-7, 2007, Airlie Conference Center, in Airlie, Virginia

Swcnt-semiconductor architectures for photoelectrochemical solar cells, P. V. Kamat and A. Kongkanand

2nd Annual Hydrogen Symposium, Purdue University April 12-13, 2007.

Nanostructure Hybrid Architectures for Solar Energy Conversion, P. V. Kamat

211th Electrochemical Society Meeting, Chicago, IL, May 6-10, 2007.

Probing Exchangeable Protons in a Nafion Film using Thiazine Dyes B. J. Seger, P. V. Kamat and K. Vinodgopal
SWCNT-Semiconductor Composites. Excited State Interactions, Charge Equilibration and Photocurrent Generation
P. V. Kamat, F. Vietmeyer and A. Kongkanand

Solar Energy Conversion Properties of Carbon Nanotubes-Porphyrins Composite Assemblies T. Hasobe (JAIST), S. Fukuzumi (Osaka University) and P. V. Kamat

Single-Walled Carbon Nanotube Scaffold for improving Charge Transport Efficiency in Nanostructured Titanium Dioxide Films A. Kongkanand, R. Martínez Domínguez and P. V. Kamat

Organic Solar Cells Composed of Composite Molecular Assemblies of Porphyrins and Fullerenes with Metal and Semiconductor Nanomaterials T. Hasobe (JAIST), S. Fukuzumi (Osaka University) and P. V. Kamat

Titanium Dioxide Nanotube Array as a Support for Platinum Electrocatalyst A. Kongkanand and P. V. Kamat

Symposium on Synthesis and Self-assembly of Nanomaterials, CNM Workshop on Nanomaterials for Energy., Argonne National Laboratory, Argonne, May 10, 2007

Molecularly Wired Nanostructured Assemblies for Solar Energy Conversion. P. V. Kamat

Spring Meeting of the American Chemical Society, Chicago, March 25-29, 2007.

Meeting clean energy demand with nanostructure architectures., P. V. Kamat,

Single wall carbon nanotube scaffolds for photoelectrochemical solar cells. P. V. Kamat, F. Vietmeyer and A. Kongkanand

SWCNT based nanostructured hybrid assemblies for next generation solar cells P. V. Kamat, F. Vietmeyer and A. Kongkanand

Workshop on nanotechnology and water treatment. Invited: Rice Univ., Houston, TX, February 25-27, 2007.

Semiconductor nanostructures for environmental remediation. P. V. Kamat,

Group Achievements/News

- David Baker, Clifton Harris and Kevin Tvrdy (First year graduate students) joined the group in January.
- Ben Meritt completed his Master of Science degree and received the diploma at the commencement.
- Istvan Robel received his Ph. D. degree at the commencement
- Kensuke Takechi (Toyota Central R&D), Taicheng An (Guangzhou Inst. of Geochem., CAS), Sandy Moisan, and Yoichi Matsunaga (Tsukuba Univ.) returned to their host institutions.
- Anusorn Kongkanand joined GM Research, Rochester, NY in August.
- Kevin and Jessica got married in June 2007.
- Brian Seger spent two summer months at Osaka University, Japan (Fellowship from Osaka University) to conduct research in Prof. Fukuzumi's laboratory.
- Patrick Brown was awarded Statt Fellowship of Univ. of Notre Dame to conduct summer research.
- Meghan Jebb returned from Study Abroad (Ireland) program and continued her research in the Fall semester.



Break from work: Caitlin with her tuba during a summer afternoon



David Baker getting ready for hydrothermal synthesis

Research Publications

1. Sudeep, P. K.; Takechi, K.; Kamat, P. V., *Harvesting Photons in the Infrared. Electron Injection from Excited Tricarbocyanine dye (IR 125) into TiO₂ and Ag@TiO₂ core-shell nanoparticles.* **J. Phys. Chem. C**, **2007**, *111*, 488-494.
2. Hasobe, T.; Saito, K.; Kamat, P. V.; Troiani, V.; Qiu, H.; Solladié, N.; Kim, K. S.; Park, J. K.; Kim, D.; D'Souza, F.; Fukuzumi, S., *Organic Solar Cells. Supramolecular Composites of Porphyrins and Fullerenes Organized by Polypeptide Structures as Light Harvesters.* **J. Mater. Chem.**, **2007**, *17*, 4160-4170.
3. Arunkumar, E.; Sudeep, P. K.; Kamat, P. V.; Noll, B. C.; Smith, B. D., *Singlet Oxygen Generation Using Iodinated Squaraine and Squaraine-Rotaxane Dyes.* **New J. Chem.**, **2007**, *31*, 677 - 683.
4. Kongkanand, A.; Domínguez, R. M.; Kamat, P. V., *Single Wall Carbon Nanotube Scaffolds for Photoelectrochemical Solar Cells. Capture and Transport of Photogenerated Electrons.* **Nano Lett.**, **2007**, *7*, 676-680.
5. Hasobe, T.; Fukuzumi, S.; Hattori, S.; Kamat, P. V., *Shape- and Functionality-Controlled Organization of TiO₂-Porphyrin-C₆₀ Assembly for Improved Performance of Photochemical Solar Cells.* **Chemistry, Asian J.**, **2007**, *2*, 265-272.
6. Kamat, P. V., *Meeting the Clean Energy Demand: Nanostructure Architectures for Solar Energy Conversion.* **J. Phys. Chem. C**, **2007**, *111*, 2834 - 2860.
7. Vietmeyer, F.; Seger, B.; Kamat, P. V., *Anchoring ZnO Particles on Functionalized Single Wall Carbon Nanotubes. Excited State Interactions and Charge Collection.* **Adv. Mater.**, **2007**, *19*, 2935-2940.
8. Seger, B.; Vinodgopal, K.; Kamat, P. V., *Proton activity in Nafion films. Probing exchangeable protons with methylene blue.* **Langmuir**, **2007**, *23*, 5471 -5476.
9. Hasobe, T.; Fukuzumi, S.; Kamat, P. V.; Murata, H., *Porphyrin based molecular architectures for light energy conversion.* **Mol. Cryst. Liq. Cryst.**, **2007**, *471*, 39-51.
10. Robel, I.; Kuno, M.; Kamat, P. V., *Size-Dependent electron Injection from Excited CdSe Quantum Dots into TiO₂ Nanoparticles.* **J. Am. Chem. Soc.**, **2007**, *129*, 4136 -4137.
11. Jebb, M.; Sudeep, P. K.; Pramod, P.; Thomas, K. G.; Kamat, P. V., *Ru(II)trisbipyridine Functionalized Gold Nanorods. Morphological Changes and Excited-State Interactions.* **J. Phys. Chem. B**, **2007**, *111*, 6839 - 6844.
12. Kongkanand, A.; Kamat, P. V., *Interactions of Single Wall Carbon Nanotubes with Methyl Viologen Radicals. Quantitative Estimation of Stored Electrons.* **J. Phys. Chem. C**, **2007**, *111*, 9012-9015.
13. Kongkanand, A.; Kamat, P. V., *Electron Storage in Single Wall Carbon Nanotubes. Fermi Level Equilibration in Semiconductor-SWCNT Suspensions.* **ACS Nano**, **2007**, *1*, 13-21.
14. Hasobe, T.; Kamat, P. V., *Photoelectrochemistry of stacked cup carbon nanotube films. Tube-Length dependence and charge transfer with excited porphyrin.* **J. Phys. Chem. C**, **2007**, *111*, 16626 - 16634.
15. Xu, T.; Kamat, P. V.; Joshi, S.; Mebe, A. M.; Cai, Y.; O'Shea, K. E., *Hydroxyl Radical Mediated Degradation of Phenylarsonic Acid.* **J. Phys. Chem. A**, **2007**, *111*, 7819 -7824.

The paper "Photovoltaic Cells using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles, Hasobe, T., Imahori, H., Kamat, P. V. and Fukuzumi, S., **J. Am. Chem. Soc.**, **2005**, *127*, 1216-1228" is included as one of the **five most cited paper in the area of Solar Cells** during last two years. This paper was also quoted as the "**Hot Paper**" for the month of Sept-Oct 2006 by the **ISI**. (Hot paper list is based on increased frequency of citations)

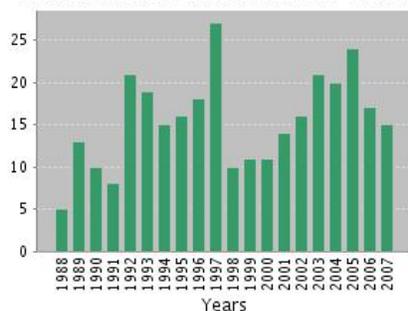
Submitted/Accepted for Publication

1. Takechi, K.; Kamat, P. V.; Avira, R. R.; Jyothi, K.; Ramaih, D., *Harvesting Infrared Photons with Croconate Dyes*. **Chem. Mater.**, **2007**, in press.
2. Seger, B.; Kongkanand, A.; Vinodgopal, K.; Kamat, P. V., *Platinum Dispersed on Silica Nanoparticles for PEM Fuel Cells*. **J. Electroanal. Chem.**, **2007**, in press (published on web).
3. Hasobe, T.; Fukuzumi, S.; Kamat, P. V.; Murata, H., *Fullerene-Based Supramolecular Nanoclusters with poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV) for Light Energy Conversion*. **Jap. J. Appl. Phys.**, **2007**, in press.
4. Zhang, Z.; Meisel, D.; Kamat, P.; Kuno, M., *Layer-by-layer self-assembly of colloidal gold-silica multilayers*. **J. Chem. Ed.**, **2007**, submitted.
5. Wan, J.; Ferreira, A.; Xia, W.; Chow, C. H.; Takechi, K.; Kamat, P. V.; Guilford Jones, I.; Vullev, V. I., *Solvent Dependence of the Charge-Transfer Properties of a Quaterthiophene-Anthraquinone Dyad*. **J. Phys. Chem. B**, **2007**, *111*, submitted.
6. Kongkanand, A.; Tvrđy, K.; Takechi, K.; Kuno, M. K.; Kamat, P. V., *Quantum Dot Solar Cells. Tuning Photoresponse through Size and Shape Control of CdSe-TiO₂ Architecture*. **J. Am. Chem. Soc.**, **2007**, submitted.
7. Brown, P. R.; Takechi, K.; Kamat, P. V., *Single-Walled Carbon Nanotube Scaffolds for Dye-Sensitized Solar Cells*. **J. Phys. Chem. C**, **2007**, submitted.

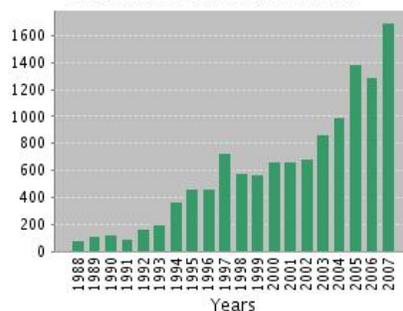
The paper . *Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO₂ Films*. Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V., *J. Am. Chem. Soc.*, **2006**, *128*, 2385-2393.” is cited as the “**Hot Paper in the field of Chemistry**” for the month of **Oct 2007** by the **ISI Web of Knowledge**. (*Hot paper list is based on increased frequency of citations*)

Publicationa Analysis (1988-2007)

Published Items in Each Year



Citations in Each Year



Results found: 348
 Sum of the Times Cited 12,344
 Average Citations per Item 35.47
 h-index 60

Source: ISI Web of Knowledge, December 7, 2007

Abstracts of Publications

J. Phys. Chem. C, 2007. 111, 2834 - 2860. <http://dx.doi.org/10.1021/jp066952u>

Meeting the Clean Energy Demand: Nanostructure Architectures for Solar Energy Conversion.

Kamat, P. V.,

The increasing energy demand in the near future will force us to seek environmentally clean alternative energy resources. The emergence of nanomaterials as the new building blocks to construct light energy harvesting assemblies has opened up new ways to utilize renewable energy sources. This article discusses three major ways to utilize nanostructures for the design of solar energy conversion devices: (i) Mimicking photosynthesis with donor-acceptor molecular assemblies or clusters, (ii) semiconductor assisted photocatalysis to produce fuels such as hydrogen, and (iii) nanostructure semiconductor based solar cells. This account further highlights some of the recent developments in these areas and points out the factors that limit the efficiency optimization. Strategies to employ ordered assemblies of semiconductor and metal nanoparticles, inorganic-organic hybrid assemblies, and carbon nanostructures in the energy conversion schemes are also discussed. Directing the future research efforts toward utilization of such tailored nanostructures or ordered hybrid assemblies will play an important task in achieving the desired goal of cheap and efficient fuel production (e.g., solar hydrogen production) or electricity (photochemical solar cells).

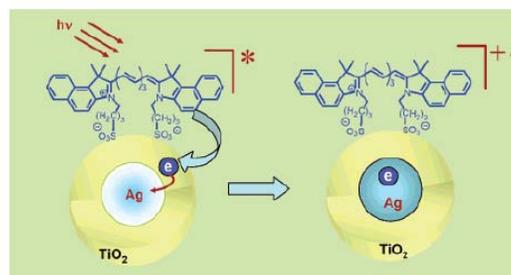


J. Phys. Chem. C, 2007. 111, 488-494. <http://dx.doi.org/10.1021/jp066502z>

Harvesting Photons in the Infrared. Electron Injection from Excited Tricarbocyanine dye (IR 125) into TiO₂ and Ag@TiO₂ core-shell nanoparticles.

Sudeep, P. K.; Takechi, K.; Kamat, P. V.,

TiO₂ and Ag@TiO₂ core shell nanoparticles have been modified with a carbocyanine dye (IR-125) to extend the photoresponse in the near-infrared. Upon binding dye molecules to TiO₂, we observe a sharp decrease in the fluorescence yield. The electron injection into TiO₂ was found to dominate the deactivation of the excited singlet state. The rate constant for the charge injection process as determined from the decay of the excited singlet is $\sim 10^{11}$ s⁻¹. In the case of Ag@TiO₂, the electrons injected into the TiO₂ layer are quickly transferred to the Ag core. The metal core in Ag@TiO₂ did not alter the forward charge-transfer kinetics, but it influenced the back electron transfer. The regeneration of the dye involving the reaction between the oxidized dye and injected electron was a factor of 2 slower for Ag@TiO₂ than the TiO system. Use of composite nanoparticles comprised of a metal core semiconductor shell may provide new ways to modulate charge recombination processes in dye-sensitized solar cells.

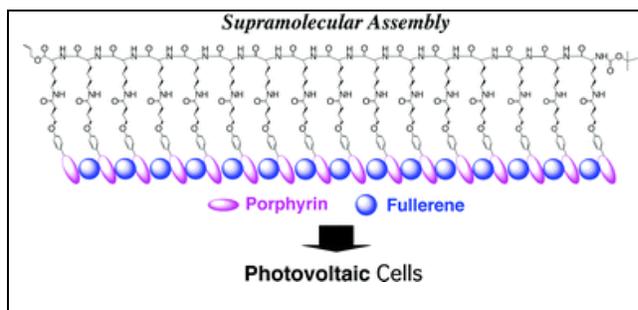


J. Mater. Chem., 2007. 17, 4160-4170. <http://dx.doi.org/10.1039/b706678c>

Organic Solar Cells. Supramolecular Composites of Porphyrins and Fullerenes Organized by Polypeptide Structures as Light Harvesters.

Hasobe, T.; Saito, K.; Kamat, P. V.; Troiani, V.; Qiu, H.; Solladié, N.; Kim, K. S.; Park, J. K.; Kim, D.; D'Souza, F.; Fukuzumi, S.,

We have constructed supramolecular solar cells composed of a series of porphyrin-peptide oligomers [porphyrin functionalized -polypeptides, P(H₂P)_n or P(ZnP)_n (n = 1, 2, 4, 8, 16)], and fullerenes assembled on a nanostructured SnO₂ electrode using an electrophoretic deposition method. Remarkable enhancement in the photoelectrochemical performance as well as the broader photoresponse in the visible and near-infrared regions is seen with increasing the number of porphyrin units in -polypeptide structures. Formation of supramolecular clusters of porphyrins and fullerenes prepared in acetonitrile-toluene = 3 : 1 has been confirmed by transmission electron micrographs (TEM) and the absorption spectra. The highly colored composite clusters of porphyrin-peptide oligomers and fullerenes have been



assembled as three-dimensional arrays onto nanostructured SnO₂ films using an electrophoretic deposition method. A high power conversion efficiency, η of 1.6% and the maximum incident photon-to-photocurrent efficiency (IPCE = 56%) were attained using composite clusters of free base and zinc porphyrin-peptide hexadecamers [P(H₂P)₁₆ and P(ZnP)₁₆] with fullerenes, respectively. Femtosecond transient absorption and fluorescence measurements of porphyrin-fullerene composite films confirm improved electron-transfer properties with increasing number of porphyrins in a polypeptide unit. The formation of molecular assemblies

between porphyrins and fullerenes with a polypeptide structure controls the electron-transfer efficiency in the supramolecular complexes, meeting the criteria required for efficient light energy conversion.

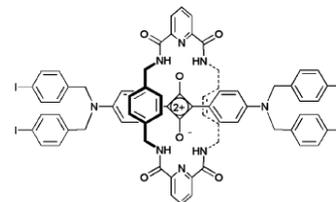
New J. Chem., 2007, 31, 677 - 683. <http://dx.doi.org/10.1039/b616224j>

Singlet Oxygen Generation Using Iodinated Squaraine and Squaraine-Rotaxane Dyes.

Arunkumar, E.; Sudeep, P. K.; Kamat, P. V.; Noll, B. C.; Smith, B. D.,

The goal of this study was to assess the ability of squaraine-rotaxanes to generate singlet oxygen

for potential application in photodynamic therapy (PDT). Specifically, we compare the aggregation and photophysical properties of an iodinated squaraine dye and an iodinated squaraine-rotaxane. Even under strongly aggregating conditions, the absorption spectra of both remain relatively sharp. An X-ray crystal structure of the iodinated squaraine dye shows that it adopts perpendicular, end-to-face orientations in the solid state. Singlet oxygen generation efficiency was measured by trapping with 1,3-diphenylisobenzofuran. The triplet state of the rotaxane was characterized using laser flash photolysis. The results of this study suggest that heavily halogenated squaraine-rotaxanes have potential as singlet oxygen photosensitizers for PDT.

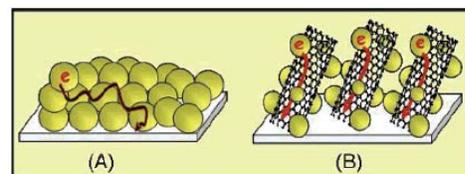


Nano Lett., 2007, 7, 676-680. <http://dx.doi.org/10.1021/nl0627238>

Single Wall Carbon Nanotube Scaffolds for Photoelectrochemical Solar Cells. Capture and Transport of Photogenerated Electrons.

Kongkanand, A.; Domínguez, R. M.; Kamat, P. V.,

Single wall carbon nanotube (SWCNT) architecture when employed as conducting scaffolds in a TiO₂ semiconductor based photoelectrochemical cell can boost the photoconversion efficiency by a factor of 2. Titanium dioxide nanoparticles were dispersed on SWCNT films to improve photoinduced charge separation and transport of carriers to the collecting electrode surface. The shift of ~ 100 mV in apparent Fermi level of the SWCNT-TiO₂ system as compared to the unsupported TiO₂ system indicates the Fermi level equilibration between the two systems. The interplay between the TiO₂ and SWCNT of attaining charge equilibration is an important factor for improving photoelectrochemical performance of nanostructured semiconductor based solar cells. The feasibility of employing a SWCNT-TiO₂ composite to drive the water photoelectrolysis reaction has also been explored.

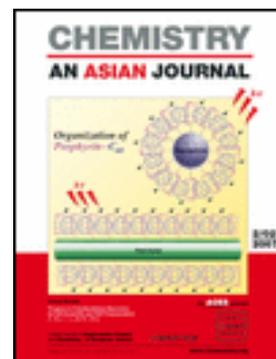


Chemistry, Asian J., 2007, 2, 265-272. <http://dx.doi.org/10.1002/asia.200600358>

Shape- and Functionality-Controlled Organization of TiO₂-Porphyrin-C₆₀ Assembly for Improved Performance of Photochemical Solar Cells.

Hasobe, T.; Fukuzumi, S.; Hattori, S.; Kamat, P. V.,

Shape- and functionality-controlled organization of porphyrin derivatives-C₆₀ supramolecular assemblies using TiO₂ nanotubes and nanoparticles has been achieved for the development of photochemical solar cells. The differences in the efficiency of light-energy conversion of these solar cells are explained on the basis of the geometrical orientation of the porphyrins with respect to the TiO₂ surface and the supramolecular complex formed with C₆₀. The maximum photon-conversion efficiency (IPCE) of 60 % obtained with TiO₂ nanotube architecture is higher than the value obtained with nanoparticle architecture. The results presented in this study show the importance of substrate morphology in promoting electron transport within the mesoscopic semiconductor film.

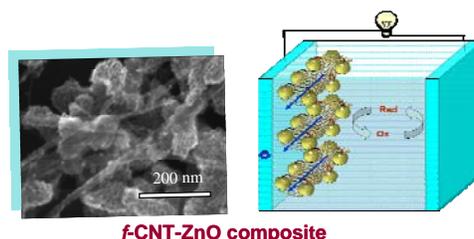


Adv. Mater., 2007, 19, 2935-2940. <http://dx.doi.org/10.1002/adma.200602773>

Anchoring ZnO Particles on Functionalized Single Wall Carbon Nanotubes. Excited State Interactions and Charge Collection.

Vietmeyer, F.; Seger, B.; Kamat, P. V.,

Excited state interaction between functionalized carbon nanotubes (*f*-CNT) and ZnO nanoparticles has been probed by emission spectroscopy and photoelectrochemistry. A decrease in the emission yield of ZnO nanoparticles parallels the decrease in emission lifetime as they bind to *f*-CNT. Based on the decrease in emission lifetime we obtain an average rate constant of 1×10^8 s⁻¹ for the electron transfer between excited ZnO and *f*-CNT. The *f*-CNT-ZnO composite films cast on conducting glass electrode by electrophoretic deposition or drop cast method exhibit photocurrent response in the UV-region with a maximum photon conversion efficiency (IPCE) of 16% at 360 nm. The ability of carbon nanotube scaffold to collect and transport photogenerated electrons is described.

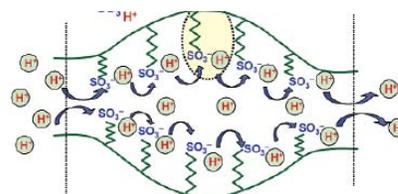


Langmuir, 2007. 23, 5471 -5476. <http://dx.doi.org/10.1021/la0636816>

Proton activity in Nafion films. Probing exchangeable protons with methylene blue.

Seger, B.; Vinodgopal, K.; Kamat, P. V.,

A simple approach to monitor the H^+ activity of a proton-exchange membrane (Nafion) is introduced by incorporating methylene blue as an indicator dye. The dye exhibits characteristics absorption maxima at 665 and 745 nm corresponding to its singly and doubly protonated forms, respectively. The apparent proton activity of Nafion as monitored from the appearance of doubly protonated methylene blue absorption is equivalent to 1.2 M H_2SO_4 . By monitoring the spectral changes associated with the protonation equilibrium of the dye, it is possible to probe the rate and the exchangeable proton sites within the Nafion film. For the Nafion 117 film, we estimate the total exchangeable proton sites to be 2.5×10^{19} sites/cm² or 4.2×10^{-5} mols/cm². The equilibrium constant for the H^+/Na^+ exchange for the bound sites is determined to be 2.2. The feasibility of methylene blue as a probe to monitor proton activity during the operation of a direct methanol fuel cell has been explored.



Mol. Cryst. Liq. Cryst., 2007. 471, 39-51.

Porphyrin based molecular architectures for light energy conversion.

Hasobe, T.; Fukuzumi, S.; Kamat, P. V.; Murata, H.

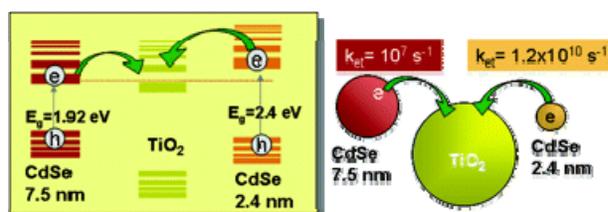
We have constructed a series of supramolecular photovoltaic cells composed of multi-porphyrin arrays such as porphyrin-alkanethiolate monolayer protected gold nanoparticles [H_2PC_nMPC : n is the number of methylene groups in the spacer], porphyrin dendrimers [D_nP_n], and porphyrin-peptide oligomers [$P(H_2P)_{(n)}$] and fullerene (C_{60}) on nanostructured SnO_2 electrodes (OTE/ SnO_2). These multi-porphyrin arrays form complexes with fullerene molecules and they form clusters in acetonitrile/toluene mixed solvent. The highly colored composite clusters are assembled as three-dimensional arrays onto nanostructured SnO_2 films [denoted as OTE/ SnO_2 /(multi-porphyrin array + C_{60})_(m)] using an electrophoretic deposition method. These highly organized molecular assembly films attain drastic enhancement of light energy conversion properties as compared to the non-organized reference system. The maximum power conversion efficiency (η) of OTE/ SnO_2 =($H_2PC_{15}MPC + C_{60}$)_(m) reaches 1.5%, which is 45 times higher than that of the reference system (0.035%).

J. Am. Chem. Soc., 2007. 129, 4136 -4137. <http://dx.doi.org/10.1021/ja070099a>

Size-Dependent electron Injection from Excited CdSe Quantum Dots into TiO_2 Nanoparticles.

Robel, I.; Kuno, M.; Kamat, P. V.,

Electron injection from excited CdSe quantum dots into TiO_2 nanoparticles can be easily modulated by controlling the particle size. Femtosecond transient absorption studies indicate that the rate constant for electron transfer from the thermalized s-state of CdSe quantum dots increases with decreasing particle size. The energy difference between the conduction bands of the two semiconductor systems acts as a driving force for the electron transfer in the normal Marcus region. An increase in the interparticle electron transfer rate constant by 3 orders of magnitude (from $\sim 10^7$ to 10^{10} s⁻¹) has been achieved by decreasing the CdSe particle diameter from 7.5 to 2.4 nm.

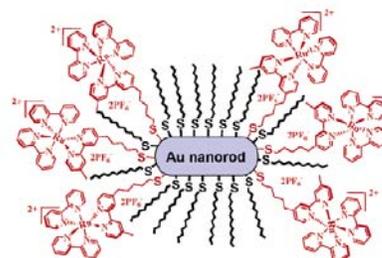


J. Phys. Chem. B, 2007. 111, 6839 - 6844. <http://dx.doi.org/10.1021/jp070701j>

Ru(II)trisbipyridine Functionalized Gold Nanorods. Morphological Changes and Excited-State Interactions.

Jebb, M.; Sudeep, P. K.; Pramod, P.; Thomas, K. G.; Kamat, P. V.,

Gold nanorods synthesized using cetyltrimethylammonium bromide and tetraoctylammonium bromide as stabilizers are functionalized with a thiol derivative of ruthenium(II) trisbipyridyl complex [$(Ru(bpy)_3^{2+}-C_5-SH)$] in dodecanethiol using a place-exchange reaction. The changes in the plasmon absorption bands and transmission electron micrographs indicate significant changes in the gold rod morphology during the place-exchange reaction. The $(Ru(bpy)_3^{2+}-C_5-SH)$ in its excited state undergoes quick deactivation when bound to gold nanorods. More than 60% of the emission was quenched when [$(Ru(bpy)_3^{2+}-C_5-SH)$] was bound to gold nanorods. Emission decay analysis indicates that the energy transfer rate constant is greater than 10^{10} s⁻¹.

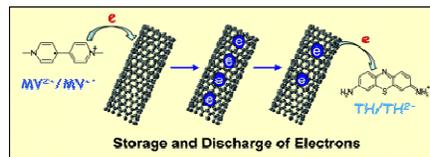


J. Phys. Chem. C, 2007. 111, 9012-9015. <http://dx.doi.org/10.1021/jp0726541>

Interactions of Single Wall Carbon Nanotubes with Methyl Viologen Radicals. Quantitative Estimation of Stored Electrons.

Kongkanand, A.; Kamat, P. V.,

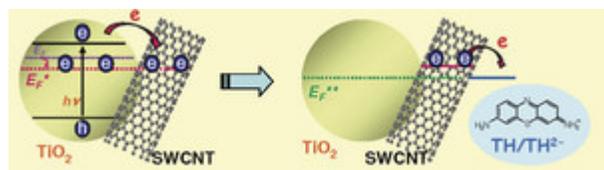
The electron storage and discharge properties of single wall carbon nanotubes (SWCNTs) are probed by their interaction with radiolytically and photolytically produced methyl viologen ($MV^{•+}$) radicals. Quantitative estimation of stored electrons amounts to one electron per ~ 100 carbon atoms of SWCNT. These stored electrons are readily discharged on demand by introducing an electron acceptor such as thionine ($E_{TH/TH^{\bullet-}}^0 = 0.064$ V vs NHE). On the basis of the charge equilibration experiments, we estimate the apparent Fermi level of SWCNT as 0.039 V versus NHE.



ACS Nano, 2007. 1, 13-21. <http://dx.doi.org/10.1021/nn700036f>

Electron Storage in Single Wall Carbon Nanotubes. Fermi Level Equilibration in Semiconductor-SWCNT Suspensions.

Kongkanand, A.; Kamat, P. V.,



The use of single wall carbon nanotubes (SWCNTs) as conduits for transporting electrons in a photoelectrochemical solar cell and electronic devices requires better understanding of their electron-accepting properties. When in contact with photoirradiated TiO_2 nanoparticles, SWCNTs accept and store electrons. The Fermi level equilibration with photoirradiated TiO_2 particles indicates storage of up to 1 electron per 32 carbon atoms in the SWCNT. The stored electrons are readily

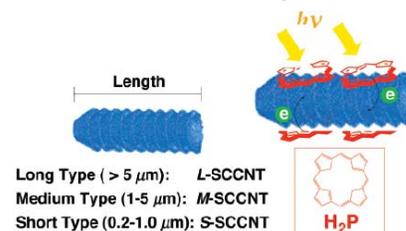
discharged on demand upon addition of electron acceptors such as thiazine and oxazine dyes (reduction potential less negative than that of the SWCNT conduction band) to the TiO_2 -SWCNT suspension. The stepwise electron transfer from photoirradiated TiO_2 nanoparticles \rightarrow SWCNT \rightarrow redox couple has enabled us to probe the electron equilibration process and determine the apparent Fermi level of the TiO_2 -SWCNT system. A positive shift in apparent Fermi level (20–30 mV) indicates the ability of SWCNTs to undergo charge equilibration with photoirradiated TiO_2 particles.

J. Phys. Chem. C, 2007. 111, 16626 - 16634. <http://dx.doi.org/10.1021/jp074995k>

Photoelectrochemistry of stacked cup carbon nanotube films. Tube-Length dependence and charge transfer with excited porphyrin.

Hasobe, T.; Kamat, P. V.,

Photoelectrochemical solar cells are constructed with stacked-cup carbon nanotubes (SCCNT) on optically transparent electrodes (OTE). Three SCCNT samples with different tube lengths (long type, L-SCCNT; medium type, M-SCCNT; and short type, S-SCCNT) were electrophoretically deposited on OTE/ SnO_2 electrodes to probe the tube-length dependence of the photoelectrochemical behavior. The maximum incident photon-to-photocurrent efficiency (IPCE) of 19% is attained at an applied bias potential of 0.2 V vs SCE in OTE/ SnO_2 /L-SCCNT. The power conversion efficiencies (η) of SCCNT-modified electrodes increase with increasing tube length. Improved efficiency of the photocurrent generation is ascribed to the ability of SCCNT in promoting photoinduced charge separation by accepting electrons from excited H_2P and transporting to the collecting electrode surface.



J. Phys. Chem. A, 2007. 111, 7819 -7824. <http://dx.doi.org/10.1021/jp072135y>

Hydroxyl Radical Mediated Degradation of Phenylarsonic Acid.

Xu, T.; Kamat, P. V.; Joshi, S.; Mebe, A. M.; Cai, Y.; O'Shea, K. E.,

Phenyl-substituted arsonic acids have been widely used as feed additives in the poultry industry. While very few studies have been reported on the environmental impact of these compounds, they have been introduced into the environment through land application of poultry litter in large quantities (about 10^6 kg/year). Phenylarsonic acid (PA) was used as a model for problematic arsonic acids. Dilute aqueous solutions of PA were subjected to radiolysis under hydroxyl radical generating conditions, which showed rapid degradation of PA. Product studies indicate addition of $\cdot OH$ to the phenyl ring forms the corresponding phenols as the primary products. Arsenite, $H_3As^{III}O_3$, and arsenate, $H_3As^V O_4$, were also identified as products. The optimized structures and relative calculated energies (using GAUSSIAN 98, the B3LYP/6-31G(d) method) of the various transient intermediates are consistent with the product studies. Pulse radiolysis was used to determine the rate constants of PA with $\cdot OH$ ($k = 3.2 \times 10^9 M^{-1} s^{-1}$) and $SO_4^{\cdot-}$ ($k = 1.0 \times 10^9 M^{-1} s^{-1}$). PA reacts slower toward $O^{\cdot-}$ ($k = 1.9 \times 10^7 M^{-1} s^{-1}$) and $N_3^{\cdot-}$ (no detectable transient), due to the lower oxidation potential of these two radicals. Our results indicate advanced oxidative processes employing $\cdot OH$ and $SO_4^{\cdot-}$ can be effective for the remediation of phenyl-substituted arsonic acids.

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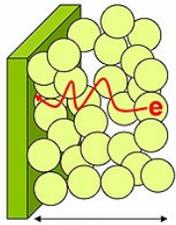
Monday, March 05, 2007

Cheap Nano Solar Cells

Carbon nanotubes could help make nanoparticle-based solar cells more efficient and practical.

By Kevin Bullis

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Escape route: Electrons created in a nanoparticle-based solar cell have to follow a circuitous path (red line) to reach an electrode. Many don't make it, lowering the efficiency of these cells. Researchers at Notre Dame have used carbon nanotubes to help the electrons reach the electrode, improving efficiency. Credit: Prashant Kamat

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TECHNOLOGY UPDATE

Mar 7, 2007

New look for solar cells

Researchers in the US have shown that carbon nanotubes can significantly improve the efficiency of solar cells made of titanium dioxide, a readily available and cheap chemical routinely used in paint and sunscreen. Prashant Kamat and colleagues at the University of Notre Dame, Indiana, anchored titanium dioxide nanoparticles on single-walled carbon nanotubes and found that the efficiency of converting ultraviolet light into current was doubled compared to that using the nanoparticles alone.

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Now, Kamat and colleagues have used carbon nanotubes to direct the flow of photogenerated charge carriers so that they can reach an electrode more easily, where they can then



Nanostructured films

<http://www.technologyreview.com/Nanotech/18259/>

<http://nanotechweb.org/articles/news/6/3/7/1>



Posted: February 28, 2007

Carbon nanotubes can double the efficiency of photoelectrochemical solar cells

(Nanowerk Spotlight) The photocatalytic activity of nanostructured semiconductor films has been widely explored in designing solar cells, solar hydrogen production, and environmental remediation. Of particular interest is the **dye-sensitized solar cell (DSSC)** which uses nanostructured titanium dioxide films modified with sensitizing dyes. Despite the initial success of achieving 10% solar conversion efficiency, the effort to further improve their performance has not been very successful. A major hurdle in attaining higher photoconversion efficiency in such nanostructured electrodes is the transport of electrons across the particle network. The photogenerated electrons in nanostructured films for example have to travel through the network of semiconductor particles and encounter many grain boundaries during the transit. Such a random transit path for the photogenerated electrons increases the probability of their recombination with oxidized sensitizer. With the recent advance in the design of nanotube and nanowire architecture, it should be possible to use such one-dimensional nanostructures to direct the flow of photogenerated charge carriers. The obvious challenge is to use nanowire or nanotube networks as support to anchor light-harvesting semiconductor particles and facilitate the electron transport to the collecting electrode surface in a solar cell. Researchers now have demonstrated that single wall carbon nanotube (SWCNT) architecture when employed as conducting scaffolds in a titanium dioxide semiconductor based photoelectrochemical cell can boost the photoconversion efficiency by a factor of 2.

There was a lot of interest in our last week's Nanowerk Spotlight "[The impact of carbon nanotubes on the use of solar energy](#)" so we are following up today with a detailed look at new research that improves the efficiency of solar cells with carbon nanotubes.

Dr. **Prashant V. Kamat**, a professor of chemistry and biochemistry at Notre Dame University and a senior scientist at the university's Radiation Laboratory, and his team have developed a semiconductor nanoparticle-carbon nanotube hybrid assembly to improve the photoconversion efficiency of solar cells

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NanoParticles TiO₂ Improve Solar Cell Efficiency

http://www.greentechlog.com/2007/03/nanoparticles_tio2_improve_solar_cell_efficiency.html

Univ of Notre Dame researchers experiment with nanotechnology to evaluate the effectiveness of solar cell conversion. Professor Prashant V. Kamat is leading this research effort on nanotech and [light energy conversion](#), and shares this [recent presentation](#) (PPS), "Meeting the Clean Energy Challenge with Nanotechnology." ...

... "The researchers added single-walled carbon nanotubes to a film made of titanium-dioxide nanoparticles, doubling the efficiency of converting ultraviolet light into electrons when compared with the performance of the nanoparticles alone." ...



Via Technology Review: [Nanotechnology for Solar Cell Efficiency](#)

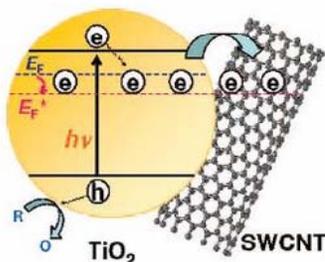
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Published: 07:50 EST, August 27, 2007

Carbon nanotubes' electronic properties optimized for future applications

By Lisa Zyga



Electron transfer between a TiO₂ semiconductor nanoparticle and SWCNT is caused by the system striving toward charge equilibration. Reprinted with permission from Anusorn Kongkanand, et al. ©2007 American Chemical Society.

While researching the unique electrical properties of single-walled carbon nanotubes (SWCNTs), it demonstrated the nanotubes' ability to capture and store one electron per 32 carbon atoms in a SWCNT. These electrons can be readily discharged on demand with the addition of an electron-accepting dye, significantly increasing the photocurrent and photoconductivity of electrical systems.

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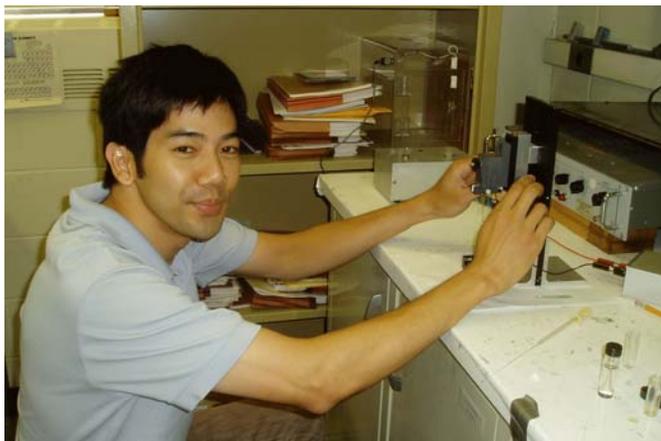
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University of Notre Dame [scientists](#) Anusorn Kongkanand and Prashant Kamat monitored the transfer of electron semiconductor particles to SWCNTs as the composite system strained to achieve charge equilibrium. The *ACS Nano*, will be useful for the design of nanotubes as a way to direct the flow charge and boost photoelectric performance for applications including electronic devices and solar cells.

<http://www.physorg.com/news107419836.html>



Anusorn carrying out electrophoretic deposition



Pat and Kensuke during a photoelectrochemical measurement

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Solar Cells

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Total Cites: 60

Article Title: Photovoltaic cells using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles

Authors: Hasobe, T, Imahori, H, Kamat, PV, Ahn, TK, Kim, SK, Kim, D, Fujimoto, A, Hirakawa, T, Fukuzumi, S

Journal: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Volume: 127

Page: 1216-1228

Year: 2005

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ESI Special Topics, October 2007

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<http://www.esi-topics.com/fbp/2007/october07-PrashantVKamat.html>



At the ECS meeting in Chicago

Field: Chemistry



Fast Breaking Comments by: Prashant V. Kamat

Article Title: Quantum dot solar cells. Harvesting light energy with CdSe nanocrystals molecularly linked to mesoscopic TiO₂ films

Authors: Robel, I; Subramanian, V; Kuno, M; Kamat, PV

Journal: J AM CHEM SOC

Volume: 128

Issue: 7

Page: 2385-2393

Year: FEB 22 2006

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