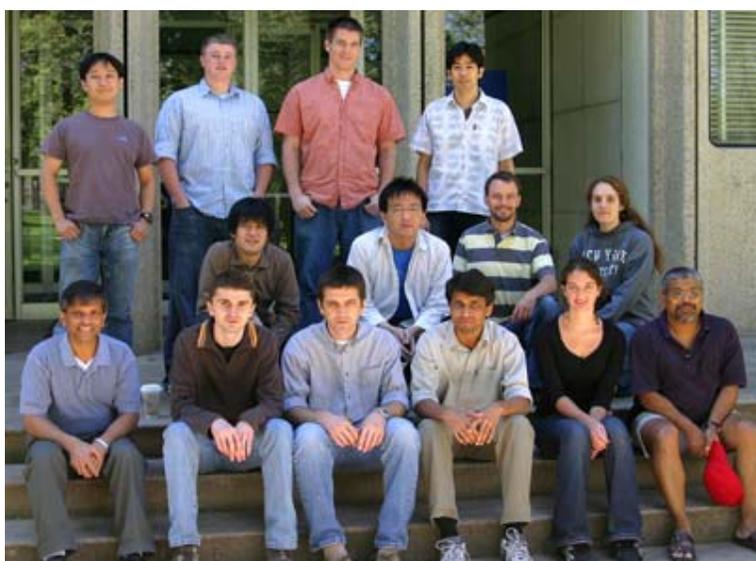


# Annual Research Summary

January - December 2006

Prashant V. Kamat



Summer 2006

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## Prashant V. Kamat

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

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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 such as fuel cells (Support from US Army)

## External Collaborators

K. George Thomas (RRL, Trivandrum)

S. Hotchandani (U. of Quebec)

T. Ebessen, (Université Louis Pasteur, France)

K. Takagi (Nagoya University)

S. Fukuzumi (Osaka University)

Kevin O'Shea (Florida International Univ.)

T. Akasaka (Tsukuba University)

## Collaborators at Notre Dame

Bruce Bunker(Physics),

Joan Brennecke (Chem. Eng.)

Ken Kuno (Chemistry)

Paul McGinn (Chem. Eng.)

Bradley Smith(Chemistry)

## Visiting Scientists

Taicheng An (Guangzhou Inst. of Geochem., CAS)

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

Taku Hasobe (AIST, Japan)

Kensuke Takechi (Toyota Central R&D, Nagoya)

K. Takagi (Nagoya University)

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

## Postdoctoral Research Associate

P. K. Sudeep (July 2004 –Aug 2005)

Aunsorn Kongkanad (Jan 2004 – present)

Yoichiro Matsunaga (March 2006- present)

Theodoros Triantis (April-May 2006)

Said Barazzouk (May-Sept. 2006)

## Graduate Students

Istvan Robel (Physics, Jointly with Prof. Bunker)

Brian Seger (Chem. Eng. U. of Notre Dame)

Matt Becker (Physics, Jointly with Prof. Bunker)

David Baker (Chem. Eng., U. Of Notre Dame)

Ben Merritt (Chemistry, U. of Notre Dame)

Yanghai Yu (Chem. Eng. Jointly with Prof. Kuno)

Clifton Harris, and Kevin Tvrdy (Chemistry) will be joining the group soon.

## Undergraduate Students

Felix Vietmeyer (University of Bielefeld, Germany)

Lucy Summerville (Mech. Eng. UND)

Meghan Jebb (Chem. & Biochem, U. Notre Dame )

Edema Ojomo (REU student)

Rebeca Martínez Domínguez (REU student)

Alice Gelio (Indiana U. NW)

Ben Edquist (Indiana U. NW)

## Visitors to conduct experiments or extend scientific collaboration

K. Takagi (Nagoya University), Taku Hasobe (AIST, Japan) and Theodoros Triantis (Greece)  
Jaesang Lee and Prof. Jaehong Kim (Georgia Tech.)

## Research Funding

Department of Energy, BES

US Army

Indiana 21<sup>st</sup> Century Research and Technology Fund (ended in Aug 2006)

Toyota Central R&D, Japan

## Award

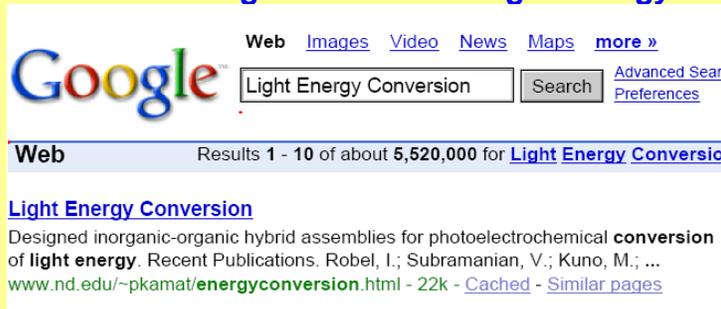
**First Honda-Fujishima Lectureship Award** was presented by the Japanese Photochemistry Association at its Annual meeting in Sendai, September 9-12, 2006

## 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 (Denver) and Fall (Cancun) meetings of the Electrochemical Society.

*Did you know....*

**Which site appears as #1 in Google Search for “Light Energy Conversion”?**



<http://www.nd.edu/~pkamat/energyconversion.html>

## Invited Lectures

### Prashant V. Kamat

#### **Molecularly Wired Hybrid Assemblies for Solar Energy Conversion**

Ohio State University, Analytical Division Seminar, May 26, 2006

#### **Meeting Energy Demand. Nanostructure Architectures for Solar Energy Conversion**

Toyota Central, R& D, Nagoya, Japan, March 29, 2006

## Meeting Presentations

### **JNU Conference on Chemistry of Materials, Aquasareen, Kerala, India, October 29-31, 2006**

*Organized Hybrid Assemblies for Light Energy Conversion*

### **210<sup>th</sup> Electrochemical Society Meeting, Cancun, Mexico, October-29-November 3, 2006**

*Presentations by K. Takechi, T. Hasobe and K. Vinodgopal*

### **Southwest Regional Meeting of the American Chemical Society, Houston, October, 19-21 2006**

Symposium on Chemical Utilization of Solar Energy

*Organized assemblies for light energy conversion. P. V. Kamat*

### **Japanese Photochemistry Association Annual Meeting, Sendai, September 10-13, 2006**

*Nanostructured Hybrid Assemblies for Light Energy Conversion*

### **Fall Meeting of the American Chemical Society, San Francisco, September 2006**

*Semiconductor-SWCNT Hybrid Assemblies for Light Energy Conversion, P. V. Kamat*

### **16th International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-16), Uppsala, Sweden, July 2-7, 2006.**

*"Harvesting Infrared Photons with Cyanine Dye Clusters" K. Takechi, P. K. Sudeep and P. V. Kamat*

### **Chinese Chemical Society Meeting, Changchun, China, July 10-12, 2006**

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

### **Symposia at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing, July 7-9, 2006**

*Getting involved in the scientific publishing process: what does it take? Robin D. Rogers, Leonard V. Interrante, David Whitten, Prashant V Kamat and John Ochs*

### **28<sup>th</sup> Department of Energy (DOE) Solar Photochemistry Research Conference will be held June 4-7, 2006, Airlie Conference Center, in Airlie, Virginia**

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

### **209<sup>th</sup> Electrochemical Society Meeting, Denver, CO, May 7-12, 2006.**

*Platinum Nanoparticles Anchored on Single-Wall Carbon Nanotubes, P. V. Kamat, A. Kongkanand, S. Kubata, G. Grishkumar*

*Photoinduced Charge Transfer Processes in Chromophore Functionalized Metal Nanoparticles, P. V. Kamat, P.K. Sudeep and K. George Thomas.*

*Single Wall and Stacked-Cup Carbon Nanotubes for Light Energy Conversion, P. V. Kamat, T. Hasobe and S. Fukuzumi*

*CdSe Quantum Dot Solar Cells, P. V. Kamat, V. Subramanian, I. Robel and M. Kuno.*

*Enhanced Photoelectrochemical property of Shape and Functionality Controlled Organization of TiO<sub>2</sub>-Porphyrin- C<sub>60</sub> Assembly, Taku Hasobe, S. Fukuzumi and P.V. Kamat*

*Ordered Structures of Porphrins and Carbon Nanotubes and their role in Light Energy Conversion*, **Taku Hasobe**, S. Fukuzumi and P.V. Kamat.

*Cyanine Dye Aggregates for Photocurrent Generation in Near-IR Region*, **K. Takechi**, P.K. Sudeep, I. Robel and P.V. Kamat.

*Single Wall Carbon Nanotube Supports for Portable Direct Methanol Fuel Cells*, **K. Vinodgopal**, G. Grishkumar and P.V. Kamat

**CNM Workshop on Nanomaterials for Energy., Argonne National Laboratory, Argonne, May 2, 2006**

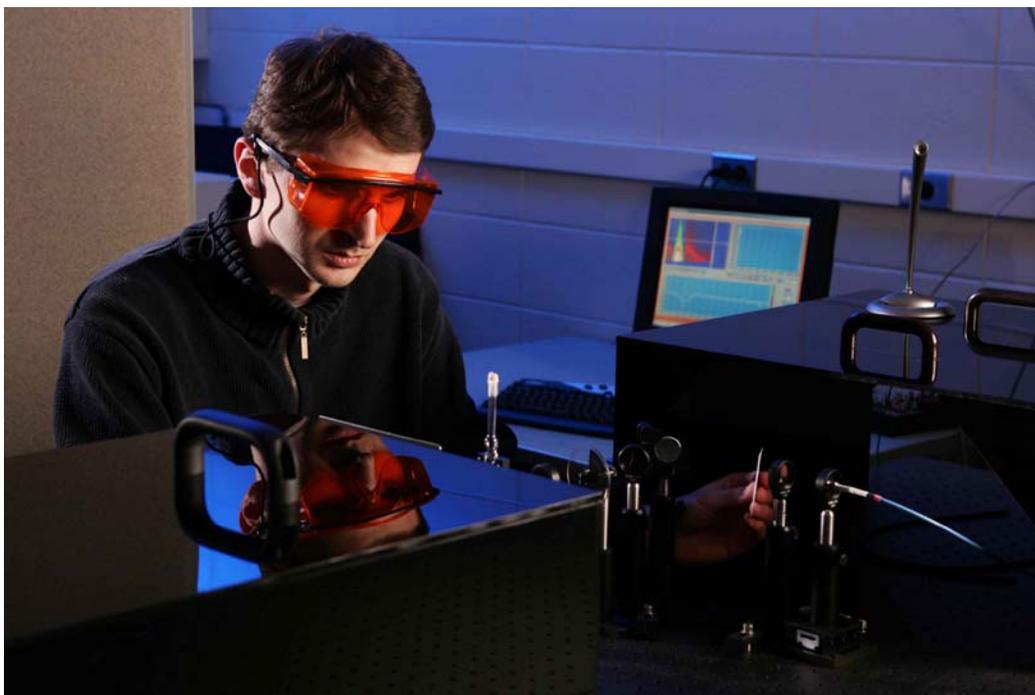
*Molecularly Wired Nanostructured Assemblies for Solar Energy Conversion*. P. V. Kamat

**Symposium on Supramolecular Photochemistry for Intelligent and Functional Materials, Nagoya University, Japan. May 30, 2006**

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

**International Conference on Nano Science and Technology New Delhi, India March 15-18, 2006**

- *Nanostructure Architectures for Solar Energy Conversion.*



Istvan Robel carrying out femtosecond pump-probe spectroscopy experiment. He successfully defended his Ph. D. thesis and has joined Argonne National Laboratory as a Postdoctoral Research Associate.

## Research Publications

1. Hasobe, T., Hattori, S., Kamat, P. V. and Fukuzumi, S., *Supramolecular nanostructured assemblies of different types of porphyrins with fullerene using TiO<sub>2</sub> nanoparticles for light energy conversion*. **Tetrahedron**, 2006. 62: 1937-1946.
2. Hasobe, T., Fukuzumi, S. and Kamat, P. V., *Stacked-Cup Carbon Nanotubes for Photoelectrochemical Solar Cells*. **Angew. Chem. (Int. Ed.)**, 2006. 45: 755-759.
3. Robel, I., Girishkumar, G., Bunker, B. A., Kamat, P. V. and Vinodgopal, K., *Structural changes and catalytic activity of platinum nanoparticles supported on C60 and carbon nanotube films during the operation of direct methanol fuel cells*. **Appl. Phys. Lett.**, 2006. 88: 073113.
4. Girishkumar, G., Hall, T. D., Vinodgopal, K. and Kamat, P. V., *Single Wall Carbon Nanotube Supports for Portable Direct Methanol Fuel Cells*. **J. Phys. Chem. B**, 2006. 110: 107-114.
5. Robel, I., Subramanian, V., Kuno, M. and Kamat, P. V., *Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO<sub>2</sub> Films*. **J. Am. Chem. Soc.**, 2006. 128: 2385-2393.
6. Kongkanand, A., Kuwabata, S., Girishkumar, G. and Kamat, P., *Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity of Oxygen Reduction*. **Langmuir**, 2006. 21: 2392 - 2396.
7. Kikuchi, H., Kitano, M., Takeuchi, M., Matsuoka, M., Anpo, M. and Kamat, P. V., *Extending the Photoresponse of TiO<sub>2</sub> to the Visible Light Region: Photoelectrochemical Behavior of TiO<sub>2</sub> Thin Films Prepared by RF-Magnetron Sputtering Deposition Method*. **J. Phys. Chem. B**, 2006. 110: 5537 - 5541.
8. Sudeep, P. K., James, P. V., Thomas, K. G. and Kamat, P. V., *Singlet and Triplet Excited State Interactions and Photochemical Reactivity of Phenyleneethynylene Oligomers*. **J. Phys. Chem. A**, 2006. 110: 5642 - 5649.
9. Kamat, P. V., *Carbon Nanomaterials: Building Blocks in Energy Conversion Devices*. **Interface**, 2006. 15: 45-47.
10. Robel, I., Kamat, P. V. and Kuno, M. K., *Exciton Recombination in CdSe nanowires. Bimolecular to three-particle Auger Kinetics*. **Nano Lett.**, 2006. 6: 1344-1349.
11. Dintinger, J., Robel, I., Kamat, P. V., Genet, C. and Ebbesen, T. W., *Terahertz All-Optical Molecule-Plasmon Modulation* **Advanced Materials**, 2006. 18: 1645-1648.
12. Lahiri, D., Subramanian, V., Bunker, B. A. and Kamat, P. V., *Probing photochemical transformations at TiO<sub>2</sub>/Pt and TiO<sub>2</sub>/Ir interfaces using x-ray absorption spectroscopy* **J. Chem. Phys.**, 2006. 124: 204720.
13. Kongkanand, A., Vinodgopal, K., Kuwabata, S. and Kamat, P. V., *Highly-dispersed Pt catalysts on Single-Walled Carbon Nanotubes and Their Role in Methanol Oxidation*. **J. Phys. Chem. B**, 2006. 110: 16185-16192.
14. Takechi, K., Sudeep, S. and Kamat, P. V., *Harvesting Infrared Photons with Tricarbocyanine Dye Clusters*. **J. Phys. Chem. B**, 2006. 110: 16169-16173.
15. Hasobe, T., Fukuzumi, S. and Kamat, P. V., *Hierarchical Assembly of Porphyrins and Fullerenes for Solar Cells*. **Interface**, 2006. 15: 47-51.
16. Hasobe, T., Fukuzumi, S. and Kamat, P. V., *Organized Assemblies of Single-Wall Carbon Nanotube (SWCNT) and Porphyrin for Photochemical Solar Cells. Charge Injection from Excited Porphyrin into SWCNT* **J. Phys. Chem. B**, 2006. 110, 25477 - 25484 (Nozik Festschrift issue).
17. Pramod, P., Sudeep, P. K., Thomas, K. G. and Kamat, P. V., *Photochemistry of Ruthenium trisbipyridine Functionalized on Gold Nanoparticles*. **J. Phys. Chem. B**, 2006. 110: 20737-20741.
18. Kamat, P. V., *Harvesting photons with carbon nanotubes*. **Nanotoday**, 2006. 1: 20-27.

## Submitted/Accepted for Publication

1. Hasobe, T., Saito, K., Kamat, P. V., Troiani, V., Qiu, H., Solladié, N., Kim, K. S., Park, J. K., Kim, D., D'Souza, F. and Fukuzumi, S., *Organic Solar Cells. Supramolecular Composites of Porphyrins and Fullerenes Organized by Polypeptide Structures as Light Harvesters*. **Chemistry, Asian J.**, 2006: submitted.
2. Sudeep, P. K., Takechi, K. and Kamat, P. V., *Harvesting Photons in the Infrared. Electron Injection from Excited Tricarbocyanine dye (IR 125) into TiO<sub>2</sub> and Ag@TiO<sub>2</sub> core-shell nanoparticles*. **J. Phys. Chem. C**, 2007: in press.
3. Kamat, P. V. *Meeting the Clean Energy Demand: Nanostructured Architectures for Light Energy Conversion (Feature Article)* **J. Phys. Chem. C**, 2006: 111, in press.
4. 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.** 2006, submitted.
5. Hasobe, T.; Fukuzumi, S.; Hattori, S.; Kamat, P. V. *Shape- and Functionality-Controlled Organization of TiO<sub>2</sub>-Porphyrin-C<sub>60</sub> Assembly for Improved Performance of Photochemical Solar Cells* **Chemistry, Asian J.**, 2007. 2 in press,.
6. 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 submitted,
7. 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 submitted,
8. Seger, B, Vinodgopal, K; Kamat, P. V. Proton activity in Nafion films. Probing exchangeable protons with methylene blue, **Langmuir**, 2007, submitted

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 the “Hot Paper” for the month of Sept-Oct 2006 by the **ISI**. (Hot paper list is based on increased frequency of citations)



P.K. Sudeep conducting a nanosecond laser flash photolysis experiment. After spending two years at Notre Dame he recently joined Univ. of Massachusetts at Amherst to continue his postdoctoral research.

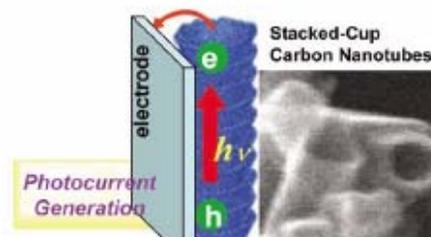
## Abstracts of Publications

*Angewandte Chemie International Ed.* 45( 5), 755-759, (2006) <http://dx.doi.org/10.1002/anie.200502815>

### Stacked-Cup Carbon Nanotubes for Photoelectrochemical Solar Cells

Taku Hasobe, Shunichi Fukuzumi, Prashant V. Kamat

An interesting property of carbon nanostructures is their optical response, and their utilization in light energy conversion devices. Herein we present the optical properties of stacked-cup carbon nanotubes (SCCNT), and the effectiveness of their semiconducting properties to generate photocurrent in a photoelectrochemical cell with high photoconversion efficiency. On the basis of the results presented in this study that the SCCNTs exhibit photocurrents two orders of magnitude greater than SWCNTs.

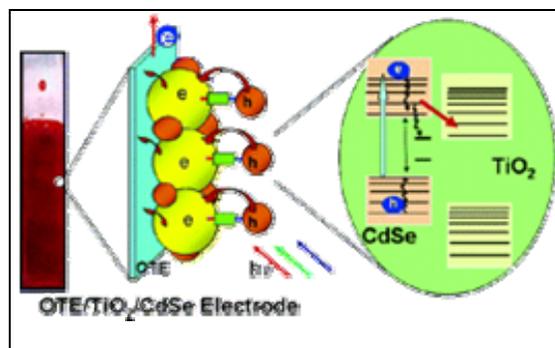


*J. Am. Chem. Soc.*, 128 (7), 2385 -2393, 2006. <http://dx.doi.org/10.1021/ja056494n>

### Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO<sub>2</sub> Films

István Robel, Vaidyanathan Subramanian, Masaru Kuno, and Prashant V. Kamat

By using bifunctional surface modifiers (SH-R-COOH), CdSe quantum dots (QDs) have been assembled onto mesoscopic TiO<sub>2</sub> films. Upon visible light excitation, CdSe QDs inject electrons into TiO<sub>2</sub> nanocrystallites. Femtosecond transient absorption as well as emission quenching experiments confirm the injection from the excited state of CdSe QDs into TiO<sub>2</sub> nanoparticles. Electron transfer from the thermally relaxed s-state occurs over a wide range of rate constant values between  $7.3 \times 10^9$  and  $1.95 \times 10^{11} \text{ s}^{-1}$ . The injected charge carriers in a CdSe-modified TiO<sub>2</sub> film can be collected at a conducting electrode to generate a photocurrent. The TiO<sub>2</sub>-CdSe composite, when employed as a photoanode in a photoelectrochemical cell, exhibits a photon-to-charge carrier generation efficiency of 12%. Significant loss of electrons occurs due to scattering as well as charge recombination at TiO<sub>2</sub>/CdSe interfaces and internal TiO<sub>2</sub> grain boundaries.



*J. Phys. Chem. A*, 110 (17), 5642 -5649, 2006. <http://dx.doi.org/10.1021/jp0603637>

### Singlet and Triplet Excited-State Interactions and Photochemical Reactivity of Phenyleneethynylene Oligomers

P. K. Sudeep, P. V. James, K. George Thomas, and Prashant V. Kamat

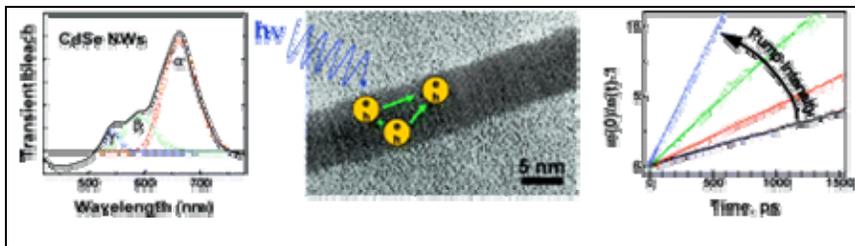
The rigid rodlike character of phenyleneethynylenes and their ability to communicate charge/excitation energy over long distances have made them useful as molecular linkers in the light energy harvesting assemblies and molecular electronics devices. These linker molecules themselves possess rich photochemistry as evident from the relatively large yields of the excited singlet (0.5-0.66) and triplet (0.4-0.5) states of two model oligomers, 1,4-bis(phenylethynyl)-2,5-bis(hexyloxy)benzene (**OPE-1**) and 1,4-bis((4-phenylethynyl)phenylethynyl)-2,5-bis(hexyloxy)benzene (**OPE-2**). In particular, the long-lived triplet excited state is capable of undergoing deactivation by self-quenching processes such as ground-state quenching and triplet-triplet (T-T) annihilation. The T-T annihilation occurs with a nearly diffusion-controlled rate ( $\sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), and ground-state quenching occurs with a rate constant of  $\sim 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The electron transfer from the excited **OPE-1** and **OPE-2** to benzoquinone as characterized from the transient absorption spectroscopy illustrates the ability of these molecules to shuttle the electrons to acceptor moieties. In addition, pulse radiolysis experiments confirm the spectroscopic fingerprint of the cation radical (or "trapped hole") with absorption bands in the 500-600 nm region.

*Nano Lett.*, **6** (7), 1344 -1349, 2006. <http://dx.doi.org/10.1021/nl060199z>

## Exciton Recombination Dynamics in CdSe Nanowires: Bimolecular to Three-Carrier Auger Kinetics

István Robel, Bruce A. Bunker, Prashant V. Kamat, and Masaru Kuno

Ultrafast relaxation dynamics of charge carriers in CdSe quantum wires with diameters between 6 and 8 nm are studied as a function of carrier density. At high electron-hole pair densities above  $10^{19} \text{ cm}^{-3}$  the dominant process for carrier cooling is the "bimolecular" Auger recombination of one-dimensional (1D) excitons. However, below this excitation level an unexpected transition from a bimolecular (exciton-exciton) to a three-carrier Auger relaxation mechanism occurs. Thus, depending on excitation intensity, electron-hole pair relaxation dynamics in the nanowires exhibit either 1D or 0D (quantum dot) character. This dual nature of the recovery kinetics defines an optimal intensity for achieving optical gain in solution-grown nanowires given the different carrier-density-dependent scaling of relaxation rates in either regime.



*J. Phys. Chem. B*, **110** (11), 5537 -5541, 2006. <http://dx.doi.org/10.1021/jp058262g>

## Extending the Photoresponse of TiO<sub>2</sub> to the Visible Light Region: Photoelectrochemical Behavior of TiO<sub>2</sub> Thin Films Prepared by the Radio Frequency Magnetron Sputtering Deposition Method

Hisashi Kikuchi, Masaaki Kitano, Masato Takeuchi, Masaya Matsuoka, Masakazu Anpo, and Prashant V. Kamat

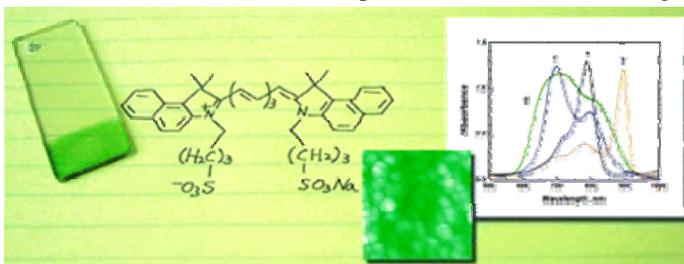
TiO<sub>2</sub> thin films prepared by a radio frequency magnetron sputtering (RF-MS) deposition method were found to show an enhanced photoelectrochemical response in the visible light region. By controlling the temperature and the gaseous medium during the deposition step, it was possible to control the properties of these films. The photoelectrochemical behavior of the sputtered TiO<sub>2</sub> thin films was compared with that of a commercial TiO<sub>2</sub> sample, and the sputtered films showed higher incident photon to the charge carrier generation efficiency (IPCE of 12.6% at 350 nm) as well as power conversion efficiency (0.33% at 1.84 mW/cm<sup>2</sup>) than the commercial TiO<sub>2</sub> sample. Femtosecond transient absorption spectroscopy experiments have revealed that a major fraction of photogenerated electrons and holes recombine within a few picoseconds, thus limiting photocurrent generation efficiency. The mechanistic insights obtained in the present study should aid in designing semiconductor nanostructures that will maximize the charge separation efficiency and extend the response of the large band gap semiconductor TiO<sub>2</sub> into visible light regions.

*J. Phys. Chem. B*, **110** (33), 16169 -16173, 2006. <http://dx.doi.org/10.1021/jp063651b>

## Harvesting Infrared Photons with Tricarboyanine Dye Clusters

Kensuke Takechi, P. K. Sudeep, and Prashant V. Kamat

The absorption of 4,5-benzoindotricarboyanine dye (IR125) in the infrared can be tuned by controlling the type of aggregation in different media. Molecular clusters of this dye formed in a mixed solvent show broad absorption in the 550-950 nm region as compared to the absorption bands of J- and H-type aggregates. The molecular clusters of the carboyanine dye are electrophoretically deposited as thin film on optically transparent electrodes using a dc electric field. These tricarboyanine dye cluster films are photoactive in the infrared region and produce cathodic current when employed as photocathode in a photoelectrochemical cell. Transient absorption spectroscopy of the molecular clusters show short-lived singlet state in the picosecond time scale (lifetime 6 ps) and a charge separated state in the nanosecond time scale. Implication of such dye cluster films for harvesting infrared photons in a photoelectrochemical cell is discussed.

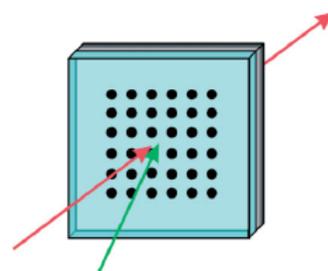


*Adv. Mater.* **18**, 1645-1648 (2006) <http://dx.doi.org/10.1002/adma.200600366>

## Terahertz All-Optical Molecule- Plasmon Modulation

J. Dintinger, I. Robel, P. V. Kamat, C. Genet, T. W. Ebbesen

The combination of molecular-excited states and refractive-index-sensitive surface plasmon structures are attractive for the development of ultrafast all-optical active plasmonic devices. While J-aggregates are suitable for rapid terahertz index switching, photochromic molecules can also be used to generate a more permanent refractive-index change controllable by light.



*J. Phys. Chem B.*, **110** (1), 107 -114, 2006. <http://dx.doi.org/10.1021/jp054764i>

## Single Wall Carbon Nanotube Supports for Portable Direct Methanol Fuel Cells

G. Girishkumar, Timothy D. Hall, K. Vinodgopal, and Prashant V. Kamat

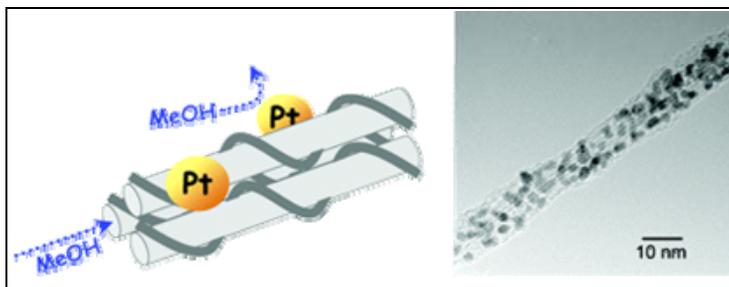
Single-wall and multiwall carbon nanotubes are employed as carbon supports in direct methanol fuel cells (DMFC). The morphology and electrochemical activity of single-wall and multiwall carbon nanotubes obtained from different sources have been examined to probe the influence of carbon support on the overall performance of DMFC. The improved activity of the Pt-Ru catalyst dispersed on carbon nanotubes toward methanol oxidation is reflected as a shift in the onset potential and a lower charge transfer resistance at the electrode/electrolyte interface. The evaluation of carbon supports in a passive air breathing DMFC indicates that the observed power density depends on the nature and source of carbon nanostructures. The intrinsic property of the nanotubes, dispersion of the electrocatalyst and the electrochemically active surface area collectively influence the performance of the membrane electrode assembly (MEA). As compared to the commercial carbon black support, single wall carbon nanotubes when employed as the support for anchoring the electrocatalyst particles in the anode and cathode sides of MEA exhibited a ~30% enhancement in the power density of a single stack DMFC operating at 70 °C.

*J. Phys. Chem. B.*, **110** (33), 16185 -16188, 2006. <http://dx.doi.org/10.1021/jp064054s>

## Highly Dispersed Pt Catalysts on Single-Walled Carbon Nanotubes and Their Role in Methanol Oxidation

Anusorn Kongkanand, K. Vinodgopal, Susumu Kuwabata, and Prashant V. Kamat

Well-dispersed Pt catalysts with very high utilization efficiencies for fuel cell reactions have been prepared by ethylene glycol reduction on polymer-wrapped single-walled carbon nanotubes (SWCNTs). By wrapping the SWCNTs in a polymer such as polystyrene sulfonate, we are able to break up the nanotube bundles to achieve better dispersion. These polymer-wrapped SWCNTs with platinum nanoparticles deposited on them show very high electrochemically active surface areas. The increase in utilization efficiencies for platinum catalysts on these SWCNT supports can be attributed to the increased surface areas and the well-dispersed nature of the carbon support and catalyst. The catalyst dispersion facilitates diffusion of reactant species which in turn results in higher methanol oxidation currents and more positive potentials for oxygen reduction.

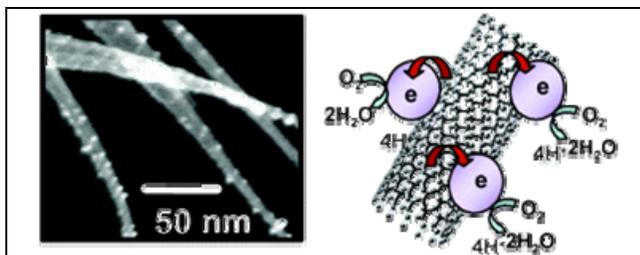


*Langmuir*, **22** (5), 2392 -2396, 2006. <http://dx.doi.org/10.1021/la052753a>

## Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity for Oxygen Reduction Reaction

Anusorn Kongkanand, Susumu Kuwabata, G. Girishkumar, and Prashant Kamat

Significant enhancement in the electrocatalytic activity of Pt particles toward oxygen reduction reaction (ORR) has been achieved by depositing them on a single wall carbon nanotubes (SWCNT) support. Compared to a commercial Pt/carbon black catalyst, Pt/SWCNT films cast on a rotating disk electrode exhibit a lower onset potential and a higher electron-transfer rate constant for oxygen reduction. Improved stability of the SWCNT support is also confirmed from the minimal change in the oxygen reduction current during repeated cycling over a period of 36 h. These studies open up ways to utilize SWCNT/Pt electrocatalyst as a cathode in the proton-exchange-membrane-based hydrogen and methanol fuel cells.



*J. Phys. Chem. B*, **110** (50), 25477-25484, 2006 <http://dx.doi.org/10.1021/jp064845u>

## Organized Assemblies of Single Wall Carbon Nanotubes and Porphyrin for Photochemical Solar Cells: Charge Injection from Excited Porphyrin into Single-Walled Carbon Nanotubes

Taku Hasobe, Shunichi Fukuzumi, and Prashant V. Kamat

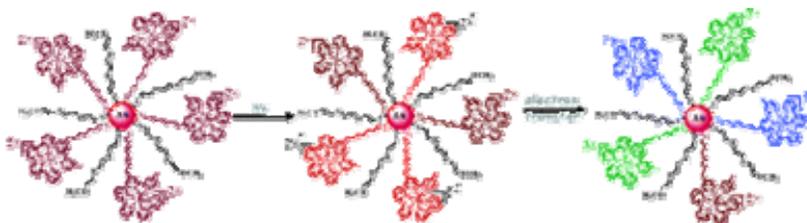
Photochemical solar cells have been constructed from organized assemblies of single-walled carbon nanotubes (SWCNT) and protonated porphyrin on nanostructured SnO<sub>2</sub> electrodes. The protonated form of porphyrin (H<sub>4</sub>P<sup>2+</sup>) and SWCNT composites form 0.5-3.0 μm-sized rodlike structures and they can be assembled onto nanostructured SnO<sub>2</sub> films [optically transparent electrode OTE/SnO<sub>2</sub>] by an electrophoretic deposition method. These organized assemblies are photoactive and absorb strongly in the entire visible region. The incident photon to photocurrent efficiency (IPCE) of OTE/SnO<sub>2</sub>/SWCNT-H<sub>4</sub>P<sup>2+</sup> is ~13% at an applied potential of 0.2 V versus saturated calomel electrode. Femtosecond pump-probe spectroscopy experiments confirm the decay of the excited porphyrin in the SWCNT-H<sub>4</sub>P<sup>2+</sup> assembly as it injects electrons into SWCNT. The dual role of SWCNT in promoting photoinduced charge separation and facilitating charge transport is presented

*J. Phys. Chem. B*, **110** (42), 20737 -20741, 2006. <http://dx.doi.org/10.1021/jp064878+>

## Photochemistry of Ruthenium Trisbipyridine Functionalized on Gold Nanoparticles

P. Pramod, P. K. Sudeep, K. George Thomas, and Prashant V. Kamat

Design of nanohybrid systems possessing several ruthenium trisbipyridine (Ru(bpy)<sub>3</sub><sup>2+</sup>) chromophores on the surface of gold nanoparticles, by adopting a place exchange reaction, was reported and their photophysical properties were tuned by varying the density of chromophores. The charge shift between the excited and ground-state Ru(bpy)<sub>3</sub><sup>2+</sup> chromophores was reported for the first time, leading to the formation of Ru(bpy)<sub>3</sub><sup>+</sup> and Ru(bpy)<sub>3</sub><sup>3+</sup>. Electron-transfer products were not observed on decreasing the concentration of Ru(bpy)<sub>3</sub><sup>2+</sup> functionalized on Au nanoparticles or in a saturated solution of unbound chromophores. The close proximity of the chromophores on periphery of the gold core may lead to an electron transfer reaction and the products sustained for several nanoseconds before undergoing recombination, probably due to the stabilizing effect of the polar ethylene glycol moieties embedded between the chromophore groups.



*Appl. Phys. Lett.* 88 (7): Art. No. 073113 (2006) <http://dx.doi.org/10.1063/1.2177354>

## Structural changes and catalytic activity of platinum nanoparticles supported on C-60 and carbon nanotube films during the operation of direct methanol fuel cells

Robel I, Girishkumar G, Bunker BA, Kamat PV, Vinodgopal K

Comparison of the structure and activity of Pt nanoparticles anchored on two nanostructured carbon supports, C<sub>60</sub> and carbon nanotubes (CNTs) provides insight into their electrocatalytic activity in direct methanol fuel cells. The local structure of platinum atoms during the initial stages of the catalytic oxidation of methanol was probed using x-ray absorption spectroscopy. A large fraction of the Pt atoms in the Pt-C<sub>60</sub> nanocomposite continuously undergoes structural changes during the initial stages of methanol oxidation. The Pt-CNT system, however, proves to be more robust in maintaining its initial morphology and higher electrocatalytic activity. These observations reflect the importance of the carbon support in controlling the catalyst morphology and activity during methanol oxidation.

*J. Chem. Phys.* 124, 204720 (2006) <http://dx.doi.org/10.1063/1.2198193>

## Probing photochemical transformations at TiO<sub>2</sub>/Pt and TiO<sub>2</sub>/Ir interfaces using x-ray absorption spectroscopy

Debdutta Lahiri . V. Subramanian Bruce A. Bunker, Prashant V. Kamat

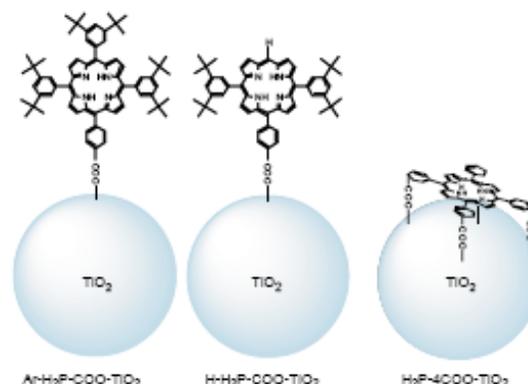
Structural transformations at the TiO<sub>2</sub>/Pt and TiO<sub>2</sub>/Ir interfaces during UV-irradiation have been probed by X-ray absorption spectroscopy. Oxidation by the photogenerated holes results in the intercalation of Pt and Ir into the Titania matrix. The structural transformations observed with Pt and Ir nanoparticles anchored on TiO<sub>2</sub> is different than the clustering of gold atoms observed in the TiO<sub>2</sub>/Au system. Implications of such structural transformations on the photocatalytic activity of semiconductor photocatalysts are discussed.

*TETRAHEDRON* 62 (9): 1937-1946 (2006) <http://dx.doi.org.lib-proxy.nd.edu/10.1016/j.tet.2005.05.113>

## Supramolecular nanostructured assemblies of different types of porphyrins with fullerene using TiO<sub>2</sub> nanoparticles for light energy conversion

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

TiO<sub>2</sub> nanoparticles were modified with porphyrin derivatives, 5-[4-benzoic acid]-10,15,20-tris[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (**Ar-H<sub>2</sub>P-COOH**), 5-[4-benzoic acid]-10,20-tris[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (**H-H<sub>2</sub>P-COOH**), and 5,10,15,20-tetra[4-benzoic acid]-21*H*,23*H*-porphyrin (**H<sub>2</sub>P-4COOH**). The porphyrin-modified TiO<sub>2</sub> nanoparticles were deposited on nanostructured OTE/SnO<sub>2</sub> electrode together with nanoclusters of fullerene (C<sub>60</sub>) in acetonitrile-toluene (3/1, v/v) using an electrophoretic deposition technique to afford the porphyrin-modified TiO<sub>2</sub> composite electrode denoted as OTE/SnO<sub>2</sub>/(porphyrin-modified TiO<sub>2</sub> nanoparticle+C<sub>60</sub>)<sub>n</sub>. The porphyrin-modified TiO<sub>2</sub> composite electrodes have efficient light absorbing properties in the visible region, exhibiting the photoactive response under visible light excitation using  $\text{[Fe}^{2+}/\text{Fe}^{3+}]$  redox couple. The incident photon-to-photocurrent efficiency (IPCE) values of supramolecular nanostructured electrodes of porphyrin-modified TiO<sub>2</sub> nanoparticles with fullerene [OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub>, and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub>] are much larger than those of the reference systems of porphyrin-modified TiO<sub>2</sub> nanoparticles without C<sub>60</sub> [OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub>]. In particular, the maximum IPCE value (41%) is obtained for OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub> under the bias potential of 0.2 V versus SCE.



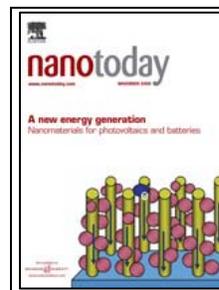
## Review Articles in Popular Magazines

Nanotoday 1, 20-27 (2006) [http://dx.doi.org/10.1016/S1748-0132\(06\)70113-X](http://dx.doi.org/10.1016/S1748-0132(06)70113-X)

### Harvesting photons with carbon nanotubes

**Prashant V. Kamat**

New initiatives are needed to harvest solar light energy with greater efficiency. Carbon nanotubes have emerged as new architectures for designing light-harvesting assemblies. Ways to utilize carbon nanotube assemblies as photoresponsive electrode materials and their role in the conversion of light energy into electricity are discussed

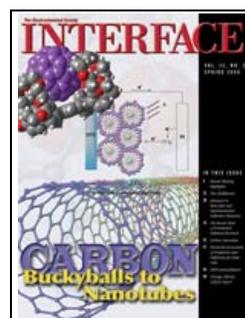


Interface, 15 (2), 47-51 (Summer issue 2006)

### Hierarchical Assembly of Porphyrins and Fullerenes for Solar Cells

**Taku Hasobe, Shunichi Fukuzumi, and Prashant V. Kamat**

The supramolecular chemistry approach as a means of assembling donor (porphyrin) and acceptor (C60) for light energy conversion has been studied extensively by us and this article represents an overview of earlier published work. 9-12 Composites of donor and acceptor moieties (e.g., porphyrin and fullerene) in the form of clusters when assembled as a 3D network on a conducting surface provide a means to achieve efficient photocurrent generation.



Interface, 15 (1), 47-51 (Spring issue 2006)

### Carbon Nanomaterials: Building Blocks in Energy Conversion Devices

**Prashant Kamat**

Carbon nanotubes, fullerenes, and mesoporous carbon structures constitute a new class of carbon nanomaterials with properties that differ significantly from other forms of carbon such as graphite and diamond. The ability to custom synthesize nanotubes with attached functional groups or to assemble fullerene (C<sub>60</sub> and analogues) clusters into three-dimensional (3D) arrays has opened up new avenues to design high surface area catalyst supports and materials with high photochemical and electrochemical activity. Unlike the conventional graphite phase, carbon nanostructures possess metallic or semiconductor properties that can induce catalysis by participating directly in the charge transfer process. Further, the electrochemical properties of these materials facilitate modulation of their charge transfer properties and aid in the design of catalysts for hydrogenation, sensors, and fuel cells.



Domer 10K Run, Sept. 23 2006

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# Heart Cut

April 3, 2006

**Use quantum dots as light-harvesting “antennae”.** Ordered assemblies of semiconductor nanoparticles with narrow band gaps have been used to harvest visible light energy in photoelectrochemical cells. However, the photocurrents obtained from these assembly systems are often low because fast charge recombination limits photocurrent generation.

M. Kuno, P. V. Kamat, and co-workers at the University of Notre Dame (IN) have prepared a semiconductor heterojunction structure by linking two kinds of nanoparticles with tailored band offsets through a group of bifunctional surface modifiers. This assembly exhibits high photon-to-charge carrier generation efficiency.

**Laser Focus World**

The Magazine for the Photonics & Optics  
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Volume: 42, Issue: 4, April 2006

## PHOTOVOLTAICS: Quantum Dots promise - next-generation solar cells

A promising tool for enabling more widespread use of solar energy is the use of nanotechnology to improve the efficiency of a photovoltaic cell's conversion of energy from visible photons to electrons. In 2001, power-conversion efficiencies of 11% were reported from photoelectrochemical cells constructed from nanocrystalline materials and conducting polymer films.<sup>1</sup> Now, researchers at the University of Notre Dame (Notre Dame, IN) have developed a solar cell made from cadmium selenide (CdSe) quantum dots assembled onto titanium dioxide (TiO<sub>2</sub>) films.<sup>2</sup>

The use of quantum dots (QDs) in the fabrication of solar cells promises not only high power-conversion efficiencies, but also offers spectral tunability. Because the absorption properties of semiconductor quantum dots are size-dependent, CdSe particles can be tuned from the red to the blue region (from 650 to 400 nm) by decreasing the particle diameter. By assembling the particles in an orderly fashion, the photoresponse of the photovoltaic cell can be tuned, optimizing the spectral response as a function of wavelength.

Economist.com

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## Solar energy

## Powering up

Sep 14th 2006

From The Economist print edition

## Improved devices may make better use of sunlight

The third technique, being developed by Prashant Kamat of the University of Notre Dame, Indiana, and his colleagues, uses that fashionable scientific tool, the carbon nanotube. This is a cylinder composed solely of carbon atoms, and one of its properties is good electrical conductivity. In effect, nanotubes act as wires a few billionths of a metre in diameter.

Dr Kamat and his team covered the surface of an experimental cell made of cadmium sulphide, zinc oxide and titanium dioxide with nanotubes, so that the tubes stuck up from the surface like hairs. The tu



## Solar Energy: Charged For The Future

Once regarded as costly and impractical, solar technology is now poised to play a larger role in the future, thanks to new developments that could result in lower costs and improved efficiency. Potential applications include cellphones, computers, automobiles, homes and office buildings.

say they have found a new and promising way to boost the efficiency of solar cells. In preliminary studies, carbon nanotubes that were engineered into the architecture of semiconductor solar cells (composed of cadmium sulfide, zinc oxide and titanium dioxide) resulted in a doubling of the cells' photoconversion efficiencies (converting light into energy). In some cases, the efficiency of solar cells jumped from 5 percent to 10 percent in the presence of carbon nanotubes, according to Prashant Kamat, Ph.D., a professor of chemistry at the University. Carbon nanotubes also could be added to other types of solar cells, such as dye-sensitized solar cells and organic solar cells based on conducting polymers, to create similar or even stronger efficiency boosts, he says.

CHEMICAL  
& Engineering News

September 18, 2006

Volume 84, Number 38

p. 35



## ACS Journals Tap Chinese Scientists

Editors aim to strengthen their interactions with a country that is a top generator of submissions

[Jean-François Tremblay](#)

On Aug. 1, for the first time, a Chinese academic became an associate editor of the ACS monthly journal *Crystal Growth & Design*. Maochun Hong, director of the Fujian Institute of Research on the Structure of Matter, joined a virtual team of four associate editors based in the U.S., the U.K., and now China.