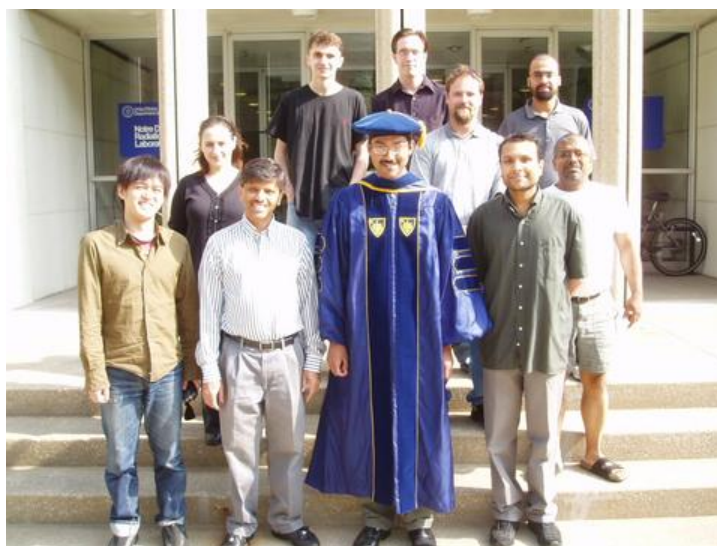


Research Activities

January - December 2004

Prashant V. Kamat



Research Group, May 2004

Contact Information: Tel. (574) 631-5411 Fax (574) 631-8068
E-mail: PKAMAT@nd.edu; 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 and Indiana 21st Century Research Fund)

External Collaborators

K. George Thomas (RRL, Trivandrum)
S. Hotchandani (U. of Quebec)
S. Fukuzumi (Osaka University)
M. Anpo (Osaka Prefecture University)
Kevin O'Shea (Florida International Univ.)

Collaborators at Notre Dame

Kamat: Bruce Bunker(Physics), Olaf Wiest (Chemistry), Paul McGinn (Chem. Eng.) Joan Brennecke (Chem. Eng.) and Eduardo Wolf (Chem. Eng.)

Visiting Scientists

K. Vinodgopal (Indiana U., N. W.)
J. Peller (Indiana U., N. W.)
K. George Thomas (RRL. India)

Postdoctoral Research Associate

Tsutomo Hirakawa (Jan- May 2004)
P. K. Sudeep (July 2004 –present)
G. Girish Kumar (Jan – present)
Taku Hasobe (Nov – present)

Graduate Students

Roxana Nicolaescu (Chemistry, U. of Notre Dame)
Ravi Vaidyanathan (Chem. Eng. U. of Notre Dame)
Istvan Robel (Physics, U. of Notre Dame)

Visiting students with independent support, Ella Jacob (Hebrew University), Said Barazzouk (U. Quebec, Trois Rivières, Canada). H. Kikuchi (Osaka Prefecture University) Taku Hasobe (Osaka University), and Tilian Xu (Florida International University) returned to their parent institutions after conducting the collaborative work on photoinduced charge transfer processes in semiconductor films, functionalized metal clusters and self assembled organic clusters.

Visitors to conduct experiments or extend scientific collaboration

Kevin O'Shea (Florida International University) Hugh Hillhouse (Purdue University)
Chris Bardeen (U. Illinois, Urbana) S Thayumanavan (U. of Massachusetts)
Tomoyoshi Motohiro (TOYOTA Central R&D Labs.,Inc.)

Undergraduate Students

Kristine Drew (Co-Op student, Univ. Waterloo)
Matt Rettker (Indiana University, NW)
Rob Heilweil (Indiana University, NW)

Ph. D. Dissertations

Ravi Vaidyanathan (Chemical Engineering, UND, Graduated in May 2004), “*Photoelectrochemical and photocatalytic aspects of semiconductor-metal Nanocomposites*”.

Roxana Nicolaescu (Chemistry, UND, Defended Thesis, June 2, 2004), “Radical induced Oxidative transformations of N-Heterocyclic Compounds”

Awards and Recognitions of Research Group

Ravi Subramanian received the 2004 William D. Manly Award for excellence in materials research for his thesis work conducted at Radiation Laboratory. This award is presented by the College of Engineering. Ravi has joined U. of Illinois-Urbana Champaign to carry out postdoctoral research.

Roxana Nicolaescu has defended her Ph. D. thesis. She has joined Serim Research Corporation, Elkhart.

Professional Activities/Honors

- **Senior Editor**, *Journal of Physical Chemistry*
- **Member**, Editorial Advisory Board, *Langmuir*
- **Member** Editorial Board, *Fullerene Science & Technology*
- **Member**, Editorial Board, *Research on Chemical Intermediates*
- **Member**, Editorial Board, *International Journal of Photoenergy*
- **Member**, Editorial Board, *Interface*
- **Chairman**, *Fullerenes, Nanotubes and Carbon Nanostructures Division* (The Electrochemical Society) May 2002-2004
- **Treasurer**, *Fullerenes, Nanotubes and Carbon Nanostructures Division* (The Electrochemical Society) May 2002-2004
- **Panel member** of INSERC Review Committee, Canada
- **Member**, Discussion Panel, Energy & Nanotechnology Workshop I: Prospects for Solar Energy
- **Symposium Organizer** of the Nanotechnolgy symposium at the Spring (San Antonio) and Fall (Honolulu) meetings of the Electrochemical Society.
- **Symposium Organizer** of the Fundamental Science and Technology of Photofunctional Interfaces at the Fall meetings of the Electrochemical Society, Honolulu, Hawaii.

Research Highlights

- Both core@shell and coupled-type semiconductor-metal composite systems were used to improve the energetics and photoinduced charge separation in light energy harvesting assemblies. The size-dependent shift in the apparent Fermi level of the TiO₂-Au composite shows the ability of Au nanoparticles to influence the energetics and improve the photoinduced charge separation. Reversible photoinduced electron storage and dark discharge have been achieved in Ag core@TiO₂ shell systems. The photoinduced charge separation in the TiO₂ shell is followed by electron injection into the silver core. Interestingly, the charging of the silver core is associated with the shift in surface plasmon band from 460 to 430 nm. The stored electrons could be readily discharged on demand by reacting the charged Ag@TiO₂ composite with an electron acceptor. As the electrons from silver core are discharged the original surface plasmon absorption of Ag core can be restored.
- Novel organic solar cells have been prepared using self-organization of porphyrin (donor) and fullerene (acceptor) moieties with gold nanoparticles and assembling these composite clusters on SnO₂ electrodes (in collaboration with Prof. Fukuzumi's group). The photoinduced charge separation in the cluster film has been successfully utilized for the photocurrent generation with spectral response extending upto 1000 nm and a maximum incident photon-to-photocurrent efficiency (IPCE) of 54%. A net power conversion efficiency of 1.5%, which was achieved using porphyrin-Au-C₆₀ assemblies, is one of the highest efficiencies achieved using supramolecular donor-acceptor systems.
- Photoelectrochemical cells constructed with single-wall carbon nanotube (SWCNT) film electrodes generate photocurrent upon visible excitation. A low photon-to-current conversion efficiency of 0.15% indicated that most of the photogenerated charge carriers are lost in the recombination process. Relaxation of photogenerated charge carriers in the SWCNT to the lowest energy gap was estimated to be in <1 ps.
- Single wall carbon nanotube based proton exchange membrane has been constructed for hydrogen and direct methanol fuel cells. The electrophoretic method developed in our laboratory provides a convenient way to assemble SWCNT bundles from solution on electrode surfaces under the influence of a dc electric field. These SWCNT-Pt films improve electrocatalytic performance and enhance power putput in hydrogen fuel cells.

A Femtosecond Transient Absorption Spectrometer has been successfully installed. Using 775, 387 or 258 nm laser pulses (1 kHz, 150 fs pulse width) as the excitation source, we can now probe transients formed in an ultrafast photochemical event (subpicosecond to nanosecond time scale). Preliminary studies have established ultrafast electron transfer between excited porphyrin and C₆₀ ($k=3\times 10^{12} \text{ s}^{-1}$) in a composite cluster system. Photoinduced electron transfer within the composite clusters is currently being used to elucidate the mechanism of photocurrent generation in organic solar cells.

Two graduate students successfully defended their Ph. D theses: Ravi Vaidyanathan (Chemical Engineering, UND, January 2004, thesis title: "Photoelectrochemical and Photocatalytic Aspects of Semiconductor-metal Nanocomposites") and Roxana Nicolaescu (Chemistry, UND, June 2004, thesis title: "Radical induced Oxidative transformations of N-Heterocyclic Compounds").

Invited Lectures

- Prashant Kamat, *Charge separation in semiconductor nanocomposites*. University of Notre Dame, Condensed Physics Seminar
- Prashant Kamat, *Photoinduced charge separation in organic-inorganic hybrid nanostructures* Clemson University, Clemson, February 16, 2004
- Prashant Kamat, *Photoresponsive Inorganic-organic Hybrid Nanoassemblies*, Center for Nanoscience and Nanotechnology, Rice University, Houston, April 16, 2004
- Prashant Kamat, *Nanostructured Architectures for energy conversion*, Colloquium, Dept. of Materials Science and Engineering, Purdue University, September 27, 2004
- Prashant Kamat, *Photoinduced charge separation in organic-inorganic nano hybrids*. Invited lecture was presented at the Advanced Science Institute on the theme "New Frontiers of Functional Materials" Miyagi, Japan, July 26-31, 2004
- Prashant Kamat, Energy & Nanotechnology Workshop, Rice University, Houston, October 15-17, 2004
- Prashant Kamat, Distinguished Lectures at Universidad Nacional Autonoma de Mexico, 1. *Photoresponsive Organic- Inorganic Hybrid Nanoassemblies*; 2. *Nanostructure Architectures for Energy Conversion*; 3. *Advanced Oxidation Processes for Environmental Remediation*, October 25-30, 2004.

Meeting Presentations

- Kamat, P. V. and Tsutomu Hirakawa, "Combining Semiconductor-metal nanocomposites for improving the efficiency of advanced oxidation processes". Annual Meeting of the American Chemical Society Anaheim, CA, March 28-April 1, 2004, **(Invited)**.
- Kamat, P. V., and George Thomas, K. "Chromophore functionalized metal nanoparticles", Annual Meeting of the American Chemical Society Anaheim, CA, March 28-April 1, 2004 **(Invited)**.
- Hirakawa, T., Subramanian, N. and Kamat, P. V. *Charge transfer from excited semiconductor to metal nanoparticles*. 205th Meeting of the Electrochemical Society San Antonio, TX May 9-14, 2004 **(Invited)**.
- Haria, M. and Kamat, P. V. *C₆₀ Cluster as an electron shuttle in a photochemical solar cell*. 205th Meeting of the Electrochemical Society San Antonio, TX May 9-14, 2004 **(Invited)**.
- Hasobe, T., Kashiwagi, Y., Absalom, M.A., Hosomizu, K., Crossley, M.J., Imahori, H., Kamat, P.V. and Fukuzumi, S. *Supramolecular photovoltaic cells composed of clusterized fullerenes with porphyrin dendrimers and porphyrin-alkanethiolate protected-gold nanoparticles*. 205th Meeting of the Electrochemical Society San Antonio, TX May 9-14, 2004
- Kamat, P. V., Hasobe, T. and Haria, M. *Molecular clusters as light harvesting antennas and electron shuttles*. DOE Solar Photochemistry Conference Airlie Conference Center, Airlie, VA Invited June 6-9, 2004

Nicolaescu, R., Olaf Wiest, O. and Kamat, P. V., *Hydroxyl Radical induced transformations of N-heterocycles*, Gordon Research Conferene on Radiation Chemistry, Colby College, Maine, June 20-25, 2004

Kamat, P. V. and Hirakawa, T., *Photoinduced Charge Separation in Semiconductor-Metal and chromophore-metal nanoassemblies*, Fall meeting of the American Chemical Society, Philadelphia, August 22-26, 2004 (**Invited**).

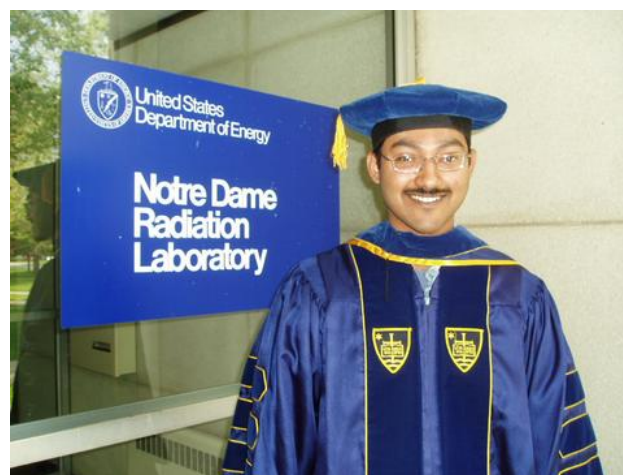
Kamat, P. V. *Nanohybrid Architectures for Organic Photovoltaics*, KCIST-2004 Conference on New Frontiers in Photovoltaics, Gyongju, Korea, August 31-September 3, 2004

K. Vinodgopal, G. Kumar, M. Rettker, R. Underhile, D. Meisel, and P. Kamat, Carbon Nanotube Electrodes for Methanol Fuel Cells -205th Meeting of the Electrochemical Society San Antonio, TX May 9-14, 2004 (**Keynote**).

T. Hasobe, S. Hattori, H. Kotani, K. Ohkubo, K. Hosomizu, H. Imahori , P. Kamat, and S. Fukuzumi Photovoltaic Cells Composed of Fullerene Clusters and a Molecular Dyad with an Extremely Long Lifetime of the Electron-Transfer State - 205th Meeting of the Electrochemical Society San Antonio, TX May 9-14, 2004

Proceeding Papers

1. Nelson, T., Vinodgopal, K., Kumar, G. G. and Kamat, P. One Step Metal Particle Deposition and Solubilization of Single Wall Carbon Nanotubes for fuel cell applications. in Annual meeting of the Electrochemical Society. 2004. San Antonio, TX: The Electrochemical Society, p 152-159
2. Hasobe, T., Kashiwagi, Y., Absalom, M. A., Sly, J., Hosomizu, K., Crossley, M. J., Imahori, H., Kamat, P. V. and Fukuzumi, S. *Supramolecular Photovoltaic Cells Composed of Clusterized Fullerenes with Porphyrin Dendrimers and Porphyrin-Alkanethiolate Protected-Gold Nanoparticles*. in Annual meeting of the Electrochemical Society. 2004. San Antonio, TX: The Electrochemical Society, p. 51-70.
3. Kumar, G., Meisel, D., Kamat, P. V. and Vinodgopal, K. Nanostructured Carbon Electrodes Based on Fullerenes and Carbon Nanotubes for Methanol Oxidation Reaction. in Annual meeting of the Electrochemical Society. 2004. San Antonio, TX: The Electrochemical Society, p. 298-306.



Research Publications

1. Peller, J., Wiest, O. and Kamat, P. V., *Hydroxyl Radical's Role in the Remediation of a Common Herbicide, 2,4-Dichlorophenoxyacetic acid (2,4-D) -Feature Article*. J. Phys. Chem. A, **2004**, *108*, 10925-10933 (**Feature Article**)
2. Subramanian, V., Wolf, E. E. and Kamat, P. V., *Catalysis with TiO₂/Au Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration*. J. Am. Chem. Soc., 2004, **126**, 4943-4950.
3. Vinodgopal, K., Subramanian, V. and Kamat, P. V., *The Selective Electrochemical Detection of Model Pollutant Species Using Films of Naturally Occurring Humic Acid*. Environ. Sci. Technol., 2004, **38**, 2161-2166.
4. Pillai, Z. S. and Kamat, P. V., *What Factors Control the Size and Shape of Silver Nanoparticles in the Citrate Ion Reduction Method*. J Phys. Chem. B, 2004, **108**, 945-951.
5. Kamat, P. V., Haria, M. and Hotchandani, S., *C₆₀ Cluster as an Electron Shuttle in a Ru(II)-Polypyridyl Sensitizer Based Photochemical Solar Cell*. J. Phys. Chem. B, 2004, **108**, 5166-5170.
6. Hasobe, T., Kashiwagi, Y., Absalom, M. A., Hosomizu, K., Crossley, M. J., Imahori, H., Kamat, P. V. and Fukuzumi, S., *Supramolecular Photovoltaic Cells of Porphyrin Dendrimers and Fullerene*. Adv. Mater., 2004, **16**, 975-978.
7. George Thomas, K., Barazzouk, S., Ipe, B. I., Shibu Joseph, S. T. and Kamat, P. V., *Unidirectional Plasmon Coupling through Longitudinal Self-assembly of Gold Nanorods*. J. Phys. Chem. B, 2004, **108**, 13066-13068.
8. Hasobe, T., Hattori, S., Kotani, H., Ohkubo, K., Hosomizu, K., Imahori, H., Kamat, P. V. and Fukuzumi, S., *Photoelectrochemical Properties of Supramolecular Composite of Fullerene Nanoclusters and 9-Mesityl-10-Carboxymethyl-acridinium Ion on SnO₂*. Org. Lett., 2004, **6**, 3103-3106.
9. Hirakawa, T. and Kamat, P. V., *Electron Storage and Surface Plasmon Modulation in Ag@TiO₂ Clusters*. Langmuir, 2004, **20**, 5645-5647.
10. Hasobe, T., Kamat, P. V., Absalom, M. A., Kashiwagi, Y., Sly, J., Crossley, M. J., Hosomizu, K., Imahori, H. and Fukuzumi, S., *Supramolecular Photovoltaic Cells Based on Composite Molecular Nanoclusters: Dendritic Porphyrin and C₆₀, Porphyrin Dimer and C₆₀, and Porphyrin-C₆₀ Dyad*. J. Phys. Chem. B, 2004, **108**, 12865-12872.
11. Kamat, P. V., *Photochemistry and Electrochemistry of Nanoassemblies*, in *Chemistry of Nanomaterials*, C. N. R. Rao, A. Muller, and A.K. Cheetham, Editors. 2004, John Wiley Interscience: New York.
12. Barazzouk, S., Hotchandani, S., Vinodgopal, K. and Kamat, P. V., *Single wall carbon nanotube films for photocurrent generation. A prompt response to visible light irradiation*. J. Phys. Chem. B, 2004, **108**, 17015-17018.
13. Fukuzumi, S., Hasobe, T., Ohkubo, K., Crossley, M. J., Kamat, P. V. and Imahori, H., *□-Complex formation in electron-transfer reactions of porphyrins*. J. Porphyrins and Phthalocyanines, 2004, **8**, 191.
14. Kamat, P. V., Thomas, K. G., Barazzouk, S., Girishkumar, G., Vinodgopal, K. and Meisel, D., *Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their Alignment and Deposition as a Film in a DC-Field*. J. Am. Chem. Soc., 2004, **126**, 10757-10762.
15. Vinodgopal, K., Haria, M., Meisel, D. and Kamat, P., *Fullerene Based Carbon Nanostructures for Methanol Oxidation*. Nano Lett., 2004, **4**, 415-418.

1. Hirakawa, T. and Kamat, P. V., *Charge Separation and Catalytic Activity of Ag@TiO₂ Core-Shell Composite Clusters under UV-Irradiation*. J. Am. Chem. Soc., 2004, submitted
2. Hasobe, T., Imahori, H., Kamat, P. V. and Fukuzumi, S., *Photovoltaic Cells using composite nanoclusters of porphyrins and fullerenes with gold nanoparticles*. J. Am. Chem. Soc., 2004, 126, in press.
3. Barazzouk, S., Kamat, P. V. and Hotchandani, S., *Photoinduced Electron Transfer between Chlorophyll a and Gold Nanoparticles*. J. Phys. Chem. B, 2005, **109**, in press.
4. Hasobe, T., Hattori, S., Kamat, P. V., Wada, Y. and Fukuzumi, S., *Organization of supramolecular assembly of 9-mesityl-10-carboxymethylacridinium ion and fullerene clusters on TiO₂ nanoparticles for light energy conversion*. J. Mater. Chem., 2005, in press.
5. Nicolaescu, A. R., Wiest, O. and Kamat, P. V., *Mechanistic pathways of the hydroxyl radical reactions of quinoline. 1. Identification, distribution and yields of hydroxylated products*. J. Phys. Chem. A, 2004, **108**, submitted.
6. Nicolaescu, A. R., Wiest, O. and Kamat, P. V., *Mechanistic pathways of the hydroxyl radical reactions of quinoline. 2. Computational analysis of .OH attack at C-atoms*. J. Phys. Chem. A, 2004, **108**, submitted.
7. Girishkumar, G., Vinodgopal, K., Meisel, D. and Kamat, P. V., *CNT films for methanol oxidation*. J. Phys. Chem. B, 2005, **108** in press.



Femtosecond transient spectrophotometer (See page 14)

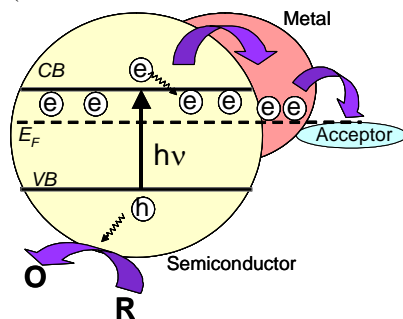
Abstracts of Published Papers

J. Am. Chem. Soc., 2003, **126**, 4943-4950

Catalysis with TiO₂/Au Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration

Subramanian, V., E.E. Wolf, and P.V. Kamat

Photoexcited semiconductor nanoparticles undergo charge equilibration when they are in contact with metal nanoparticles. Such a charge distribution has direct influence in dictating the energetics of the composite by shifting the Fermi level to more negative potentials. The transfer of electrons to Au nanoparticles has now been probed by exciting TiO₂ nanoparticles under steady state and laser pulse excitation. Equilibration with the C₆₀/C₆₀⁻ redox couple provides a means to determine the apparent Fermi level of the TiO₂-Au composite system. The size-dependent shift in the apparent Fermi level of the TiO₂-Au composite (20 mV for 8 nm diameter and 40 mV for 5 nm and 60 mV



for 3 nm gold nanoparticles) shows the ability of Au nanoparticles to influence the energetics by improving the photoinduced charge separation. Isolation of individual charge transfer steps from

UV-excited TiO₂ → Au → C₆₀ has provided mechanistic and kinetic information on the role of metal in semiconductor-assisted photocatalysis and size-dependent catalytic activity of metal-semiconductor nanocomposites.

Environ. Sci. Technol., 2004, **38**, 2161-2166.

The Selective Electrochemical Detection of Model Pollutant Species Using Films of Naturally Occurring Humic Acid

K. Vinodgopal, K., V. Subramanian, and P.V. Kamat

An electroanalytical method has been developed to investigate the uptake of redox active species by the naturally occurring humic acid substances. The Suwannee river humic acid (SHA) films were first cast on a glassy carbon electrode using an electrophoretic approach. The binding of a series of redox active species to these SHA films was then probed using cyclic voltammetry at a rotating disc electrode. Neutral molecules like hydroquinone and

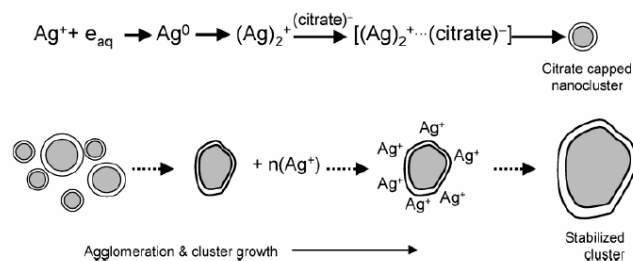
cationic species such as methyl viologen are able to bind with the humic membrane and exhibit high redox activity within the film. On the other hand anionic species like ferrocyanide are unable to attach themselves to the SHA films and thus exhibit negligible electrochemical activity. Cyclic voltammetric study of SHA films has also facilitated the determination of the partitioning constants and identifying the effect of coadsorbed ions (Ca²⁺) on the binding of redox species. The electroanalytical method described in this study opens up new avenues to examine the interactions and transport of charged species in a humic acid environment.

J. Phys. Chem. B, 2004, **108**, 945-951

What Factors Control the Size and Shape of Silver Nanoparticles in the Citrate Ion Reduction Method?

Zeena Pilai and P.V. Kamat

Citrate ion, a commonly used reductant in metal colloid synthesis, undergoes strong surface interaction with silver nanocrystallites. The slow crystal growth observed as a result of the interaction between the silver surface and the citrate ion makes this reduction process unique compared to other chemical and radiolytic synthetic methods. Addition of citrate ions to preformed silver colloids (Ag-capped SiO₂) results in the complexation of citrate with silver colloids. The difference absorption spectra of SiO₂-Ag colloids in the presence of citrate ions show an increase in the absorption at 410 nm with increase in concentration of citrate. The apparent association constant as determined from these absorption changes is 220 M⁻¹. Pulse-radiolysis studies show that citrate ions complex with the silver seeds and influence the particle growth. For example, one of the primary intermediates, Ag₂⁺ produced in the radiolytic reduction of silver ions, readily interacts with citrate to form a complex absorbing in the 410-nm region. The complex, [Ag₂⁺-citrate], undergoes slower transformations compared to uncomplexed Ag₂⁺. This slow transformation of the citrate complex eventually leads to the formation of larger clusters of silver. Steady-state and pulse-radiolysis experiments provide evidence for the multiple roles of citrate ions as a reductant, complexant, and stabilizer that collectively dictate the size and shape of silver nanocrystallites.

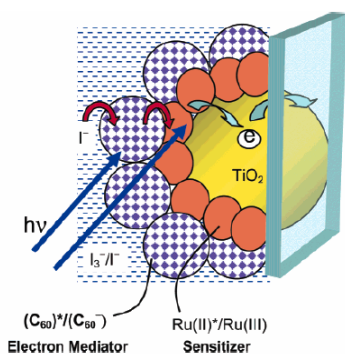


J. Phys. Chem. B, 2004, **108**, 5166-5170.

C₆₀ Cluster as an Electron Shuttle in a Ru(II)-Polypyridyl Sensitizer-Based Photochemical Solar Cell

Prashant V. Kamat*, Mehul Haria, and Surat Hotchandani

The interaction between the excited sensitizer and the redox couple in a photochemical solar cell is an important factor that can decrease the photon-conversion efficiency. We have now employed C₆₀ clusters to separate the Ru(bpy)₂(dcbpy)²⁺ (Ru(II) complex) and I₃⁻/I⁻ couple to minimize the sensitizer-redox couple interactions. The C₆₀-modified electrodes (viz., OTE/SnO₂/Ru(II)/C₆₀ and OTE/TiO₂/Ru(II)/C₆₀) delivered photocurrent with greater efficiency than did the SnO₂ and TiO₂ films modified with only a Ru(II) dye (viz., OTE/SnO₂/Ru(II) and OTE/TiO₂/Ru(II)).



The luminescence quenching of Ru(II)* by I₃⁻, which occurs with a rate constant of 1.9 (10¹⁰ M⁻¹ s⁻¹), is suppressed following the deposition of a layer of C₆₀ clusters. This paper presents a novel concept of employing a redox-active molecular assembly as an

electron relay that greatly minimizes the interaction with the excited dye while maintaining the effectiveness of the regeneration cycle.

J. Phys. Chem., 2004, **108**, 10925-33-Feature Article.

Hydroxyl Radical's Role in the Remediation of a Common Herbicide, 2,4-Dichlorophenoxyacetic acid

J. Peller, O. Wiest, Prashant V. Kamat

The massive use of herbicides in the agricultural industry has led to measurable levels in natural bodies of water, many of which supply the human population with fresh drinking water. Advanced oxidation processes such as photocatalysis, sonolysis, and radiolysis show promise in eliminating the dangers of exposure to herbicides and the products of their natural breakdown. A basic understanding of the mechanistic details involved in the oxidative transformations remains the key for improving the effectiveness of the advanced oxidation processes. The role of the hydroxyl radical in the breakdown of the common herbicide 2,4-D (2,4-dichlorophenoxyacetic acid), its breakdown product 2,4-DCP (2,4-dichlorophenol), and related compounds is elucidated through the determination of degradation rates, analyses of the transformation intermediates, and studies using computational chemistry methods.

Adv. Mater. 2004, **16**, 975

Supramolecular Photovoltaic Cells Using Porphyrin Dendrimers and Fullerene

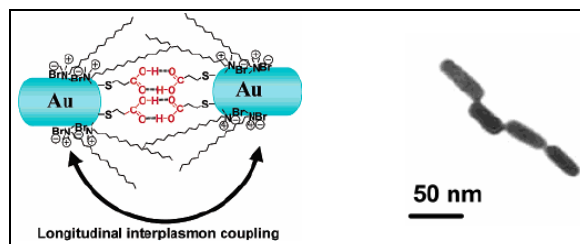
T. Hasobe, Y. Kashiwagi, M. A. Absalom, J. Sly, K. Hosomizu, M. J. Crossley*, H. Imahori*, P. V. Kamat*, S. Fukuzumi*

A new type of solar cells have been prepared using nanoclusters of fullerene and a molecular dyad (9-mesityl-10-methylacridinium ion) with an extremely long lived electron-transfer state as well as a high energy (2.37 eV), which are assembled on optically transparent nanostructured SnO₂ electrodes. The organic photovoltaic cell composed of both 9-mesityl-10-methylacridinium ion and fullerene nanoclusters exhibits significant enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions as compared with the reference system containing only each component.

J. Phys. Chem. B 2004, **108**, 13066-13068.

Unidirectional Plasmon Coupling through Longitudinal Self-assembly of Gold Nanorods.

George Thomas, K.; Barazzouk, S.; Ipe, B. I.; Shibu Joseph, S. T.; Kamat, P. V.



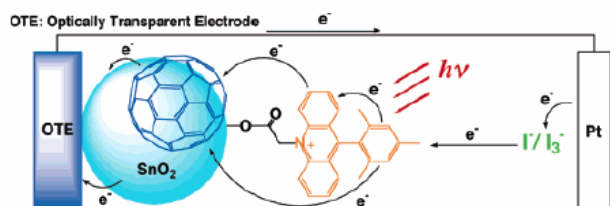
We report a new paradigm for tuning the optical properties of gold nanorods by organizing them longitudinally, using thioalkylcarboxylic acid based bifunctional molecules. The rationale behind the selection of the bifunctional molecule is based on the fact that the thiol group binds to the ends of the nanorods, which further assembles in a longitudinal fashion through cooperative hydrogen bonding between the carboxylic groups. A generalized procedure for uniaxial plasmon coupling through longitudinal self-assembly of Au nanorods, initially to dimers and further to linear assemblies, is presented. Uniaxial modulation of interplasmon coupling through stepwise self-assembly of Au nanorods will have application in nanoelectronics and plasmonics.

Org. Lett., 2004, 6, 3103-3106

Photoelectrochemical Properties of Supramolecular Composite of Fullerene Nanoclusters and 9-Mesityl-10-Carboxymethyl-acridinium Ion on SnO₂.

Hasobe, T., Hattori, S., Kotani, H., Ohkubo, K., Hosomizu, K., Imahori, H., Kamat, P. V. and Fukuzumi, S.

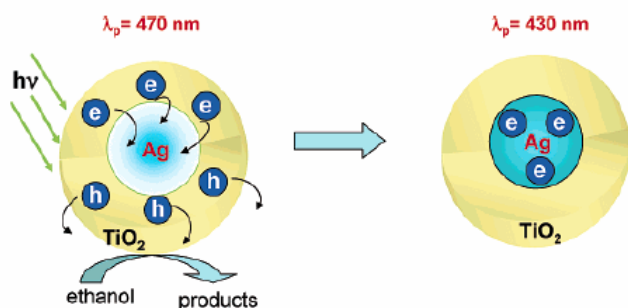
The photovoltaic cell composed of both fullerene nanoclusters and 9-mesityl-10-carboxymethylacridinium ion exhibits significant enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions as compared with the reference system containing only each component.



Langmuir, 2004, 20, 5645-5647.

Electron Storage and Surface Plasmon Modulation in Ag@TiO₂ Clusters.

Hirakawa, T. and Kamat, P. V.



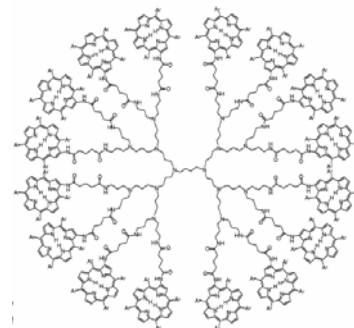
The reversible charging and discharging effects associated with photoexcitation of a TiO₂ shell in a Ag@TiO₂ composite are described. The photoinduced charge separation in the TiO₂ shell is followed by electron injection into the silver core. Interestingly, the charging of the silver core is associated with the shift in the surface plasmon band from 460 to 430 nm. The stored electrons are discharged upon exposure of the charged Ag@TiO₂ composite to an electron acceptor. As the electrons from the silver core are discharged, the original surface plasmon absorption of the Ag core is restored.

J. Phys. Chem. B, 2004, 108, 12865-12872.

Supramolecular Photovoltaic Cells Based on Composite Molecular Nanoclusters: Dendritic Porphyrin and C₆₀, Porphyrin Dimer and C₆₀, and Porphyrin-C₆₀ Dyad.

Hasobe, T., Kamat, P. V., Absalom, M. A., Kashiwagi, Y., Sly, J., Crossley, M. J., Hosomizu, K., Imahori, H. and Fukuzumi, S.

Novel organic solar cells have been prepared using molecular clusters of porphyrin dendrimer (donor) and fullerene (acceptor) dye units assembled on SnO₂ electrodes. The molecular clusters of porphyrin with dendritic structure and fullerene exhibit



controlled size and shape in contrast with the reference systems (a porphyrin dimer and a porphyrin-fullerene dyad) without dendritic structure in TEM images, which show rather irregular and smaller clusters. The composite molecular nanoclusters of dendritic porphyrin and fullerene prepared in acetonitrile/toluene mixed solvent absorb light over entire spectrum of visible light. The comparison of photoelectrochemical properties of composite molecular cluster of porphyrin and fullerene with that of molecular cluster of porphyrin-C₆₀ dyad with covalent linkage shows the importance of interpenetrating structure in each network to transport hole and electron efficiently. Furthermore, organic photovoltaic cells using clusters of supramolecular complexes of V-shaped porphyrin dimer and porphyrin dendrimers with fullerene exhibit remarkable enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions as compared with the reference system. This clearly indicates that the π - π interaction between porphyrins and fullerenes in the supramolecular clusters plays an important role in improving the light energy conversion efficiency.

In *Chemistry of Nanomaterials*, C. N. R. Rao, A. Muller, and A.K. Cheetham, Editors. 2004, John Wiley Interscience: New York

Photochemistry and Electrochemistry of Nanoassemblies

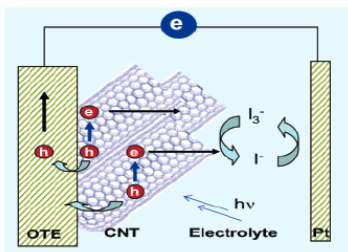
Kamat, P. V.

J. Phys. Chem. B, 2004, **108**, 17015-17018

Single wall carbon nanotube films for photocurrent generation. A prompt response to visible light irradiation.

Barazzouk, S., Hotchandani, S., Vinodgopal, K. and Kamat, P. V.

Electrophoretically deposited single-wall carbon nanotube (SWCNT) films on optically transparent electrodes are photoelectrochemically active and generate photocurrent upon visible



excitation. A low photon-to-current conversion efficiency of 0.15% suggests that most of the photogenerated charge carriers are lost in the recombination process. Time-resolved transient absorption experiments confirm the charge separation following the laser-pulse excitation of SWCNTs. Relaxation of photogenerated charge carriers in the SWCNT to the lowest energy gap occurs in <1 ps.

J. Porphyrins and Phthalocyanines, 2004, **8**, 191

π -Complex formation in electron-transfer reactions of porphyrins.

Shunichi Fukuzumi, Taku Hasobe, Ohkubo, K., Crossley, M. J., Kamat, P. V. and Imahori, H.

π -Complex formation between porphyrins and their radical cations plays an important role in self-exchange electron transfer between neutral porphyrins and the radical cations, leading to negative activation enthalpies when the stabilization energy of the π -complex is larger than the activation energy for the intracomplex electron transfer in the π -complex. A number of porphyrin molecules are self-organized on three-dimensional gold nanoclusters to form monolayer-protected gold nanoclusters (MPCs) that act as an efficient photocatalyst for the uphill reduction of HV^{2+} by BNAH to produce 1-benzyl nicotinamidinium ion (BNA^+) and hexyl viologen radical cation (HV^+). Such three-dimensional architectures of porphyrin MPCs with large surface area allow supramolecular π -complexation between MPCs and HV^{2+} , resulting in fast electron transfer from the singlet excited state of porphyrin to HV^{2+} on MPCs. The π -interaction is exploited to develop efficient photovoltaic devices consisting of porphyrin and fullerene assemblies which have an enhanced light-harvesting efficiency throughout the solar spectrum together with a highly efficient conversion of the harvested light into electrical energy.

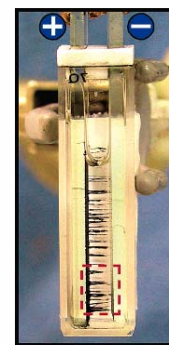
J. Am. Chem. Soc., 2004, **126**, 10757-10762

Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their Alignment and Deposition as a Film in a DC-Field.

Kamat, P. V., Thomas, K. G., Barazzouk, S., Girishkumar, G., Vinodgopal, K. and Meisel, D.

A one-step process of solubilization of single wall carbon nanotubes (SWCNT) in an organic solvent has enabled us to polarize them asymmetrically in a dc electric field. Quaternary ammonium ion-capped SWCNTs readily suspend in organic solvents; under the influence of a dc electric field, they assemble as stretched bundles anchored on the positive electrode.

At low dc applied field (<40 V), all of the SWCNTs from the suspension are deposited on the electrode, thus providing a simple methodology to design robust SWCNT films. At higher applied voltages (>100 V), the SWCNT bundles stretch out into the solution and orient themselves perpendicular to the electrode surface. The alignment of these bundles is responsive to the ON-OFF cycles of the applied electric field. The possibility of modulating the alignment of SWCNT in an electric field opens new ways to achieve electrical contacts in nano- to micro-devices.



Nano Lett., 2004, **4**, 415-418

Fullerene Based Carbon Nanostructures for Methanol Oxidation

Vinodgopal, K., Haria, M., Meisel, D. and Kamat, P.

Films of C_{60} clusters were electrophoretically deposited on optically transparent electrode surfaces. These C_{60} films constitute a new class of carbon electrodes with properties that differ from graphite and diamond electrodes. The electrophoretically deposited C_{60} cluster film is highly porous and is quite stable to oxidative potentials. Hence C_{60} film provides an electrochemical window to carry out oxidation processes. Upon electrodeposition of platinum particles, these nanostructured carbon films show remarkable activity toward methanol oxidation. The dependence of methanol oxidation on the amount of platinum and C_{60} in a half-cell reaction demonstrates the role of fullerene nanoclusters as a new form of carbon support.

In Popular Press



materialstoday
the magazine for tomorrow's technology

A Materials Today supplement
nanotoday

[home](#) [about mt](#) [recent issues](#) [product guides](#) [on the web](#) [conferences](#)

April 2004



Research News

Prashant V. Kamat and colleagues from the University of Notre Dame and Indiana University Northwest have shown that fullerene clusters can improve the performance of electrodes for direct methanol fuel cells (DMFCs) [Vinodgopal et al., Nano Lett. (2004) doi: 10.1021/nl035028y]. "Most DMFC anodes, where the oxidation of ethanol is carried out, are based on electrocatalysts," explains Kamat, "in which metal nanoparticles such as a 1:1 mixture of Pt and Ru are deposited on electrically conducting, high-surface area carbon films."

Making smaller fuel cells for portable electronic devices will require submicron-sized carbon electrode supports that minimize the use of noble metals but retain suitable catalytic activity. "Carbon nanotubes and fullerene nanoclusters are the most suitable candidates for designing such miniaturized electrodes," says Kamat. Films of C_{60} nanoclusters are stable to oxidative potentials, highly porous, exhibit electrocatalytic properties, and have a high surface area, all of which could make them useful for fuel cell applications. The researchers deposited C_{60} clusters onto optically transparent electrodes using electrophoresis to form a nanostructured film. Pt nanoparticles were then loaded onto the C_{60} film by electrodeposition. This electrode was tested for methanol oxidation in a half-cell reaction. The C_{60} clusters promote methanol oxidation at the Pt crystallites. Kamat attributes the enhancement to the high-surface area provided by the C_{60} support. "We are currently working towards optimizing the performance of fullerene and carbon nanotube-based electrodes," says Kamat.

Jonathan Wood

Source:
http://www.materialstoday.com/pdfs_7_4/resnews.pdf

Femtosecond Transient Spectrometer

Femtosecond Transient Absorption Spectrometer installation is now complete and it is now operational for carrying out transient absorption experiments using 775, 387 and 258 nm laser pulse excitation. The software developed by Ultrafast Systems is user friendly and allows the user to monitor the kinetics at different wavelengths and spectral evolution at different times during data acquisition. ASCII files can be exported to ORIGIN or other platforms.

The current capabilities

Excitation wavelength: 775, 387 and 258 nm, pulse width 150 fs, 1 kHz, 1 mJ/pulse @ 775 nm.

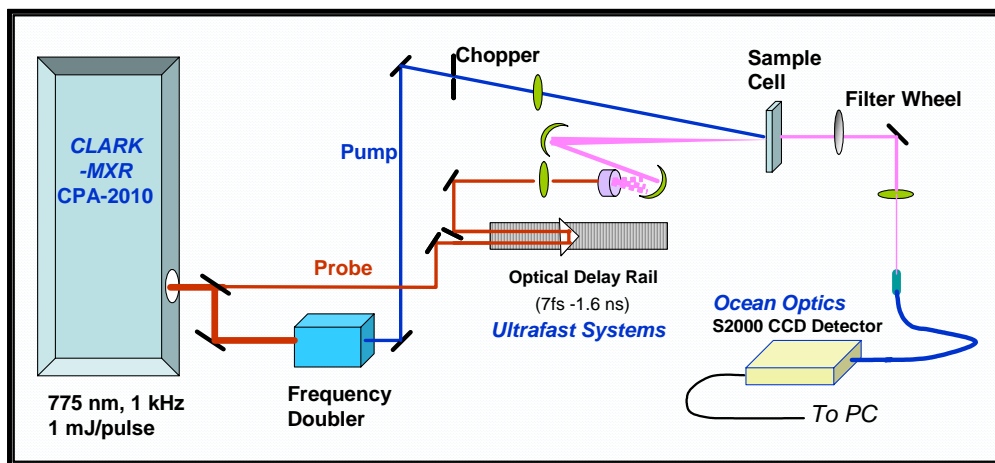
Current Detection Range for Absorption: 420-750 nm (Will be extended to IR when the detection system becomes available from Ultrafast Systems)

Detection Limit: Delta Abs of ~0.0005

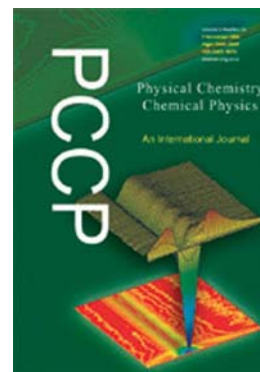
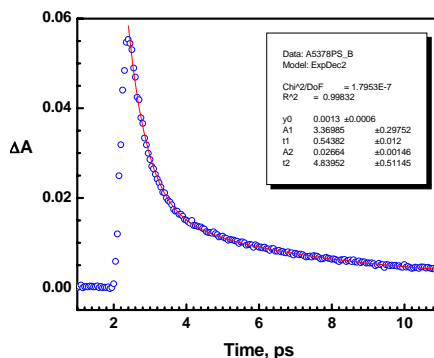
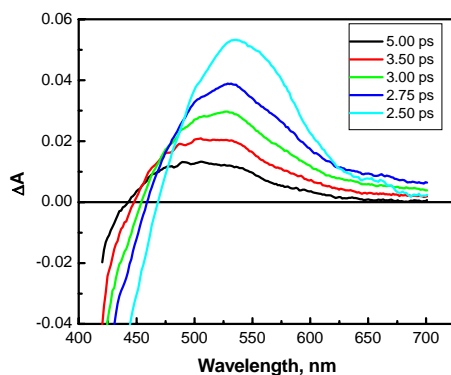
Delay Times.: Upto 1.6 ns with delay increments of 10 fs or greater. Each delay setting averages 2500 shots in 5 seconds (collection time can be reduced for faster acquisition).

The delay times can be varied during the experiment to cover both short and long times in a single experiment.

Sample Cell: Currently employs a 1 or 2 mm cuvette (static or flow mode). Less than 1 ml of sample is sufficient, if it is stable under laser excitation. Tracking the absorption using reverse delay allows one to check the stability of the sample and the accuracy of detection.



The preliminary results shown below is a representative example of the spectral detection range, sensitivity and timescale capability of the current apparatus.



Left: Time-resolved spectra obtained following the 387 nm laser pulse excitation of Ag@TiO₂ core@shell particles. The positive absorption at 540 nm arises from the hot electrons and negative absorption below 460 nm arises from the bleaching of the plasmon absorption of silver core.

Middle: The decay of the transient at 537 nm corresponding to the relaxation of hot electrons via electron-phonon coupling ($t=0.54$ ps) and phonon-phonon relaxation (4.84 ps) of the silver core.

Right: PCCP cover page (2004, 6, 5263) illustrating Prof. Greg Hartland (Dept. Chemistry, UND) transient spectroscopy measurements of gold nanoparticles,