

Annual Research Summary

January - December 2005

Prashant V. Kamat



Summer 2005

Prashant V. Kamat

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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. Fukuzumi (Osaka University)
S. Kuwabata (Osaka University)

S. Hotchandani (U. of Quebec)
M. Anpo (Osaka Prefecture University)
Kevin O'Shea (Florida International Univ.)

Collaborators at Notre Dame

Bruce Bunker(Physics),
Ken Kuno (Chemistry)
Olaf Wiest (Chemistry)

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

Visiting Scientists

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

J. Peller (Indiana U., N. W.)
Kensuke Takechi (Toyota Central R&D, Nagoya)

Postdoctoral Research Associate

P. K. Sudeep (July 2004 –present)
G. Girish Kumar (Jan 2004– September 2005)
Taku Hasobe (Jan – June 2005)

Graduate Students

Istvan Robel (Physics, U. of Notre Dame)
Ben Merritt (Chemistry, U. of Notre Dame)
Brian Seger (Chem. Eng. U. of Notre Dame)

Visiting student with independent support Anusorn Kongkanand (Osaka University), carried out collaborative research on metal particles and returned to his parent institution. Visiting Scientists K. George Thomas (RRL, India), Taku Hasobe (Osaka University) and Kensuke Takechi (Toyota Central R&D) worked on the collaborative project of photochemical solar cells. Undergraduate Kaylie Young (Brown University) and Alicia Avila (UND) carried out their summer research. In addition undergraduate Lucy Summerville joined the group to carry out research related to energy conversion..

Undergraduate Students

Alicia Avila (Chem Biomol Eng, U. Notre Dame)
Kaylie Young (REU student, Brown Univ.)
Randy Orr (Indiana U. NW)

Kristine Drew (CoOp Student, Univ. of Waterloo)
Mariko Anderson (Indiana U. NW)
Lucy Summerville (Mech. Eng. UND)

Visitors to conduct experiments or extend scientific collaboration

Anusorn Kongkanand (Osaka Univ.) Jonathan Rochford (Rutgers University)

Research Funding

Department of Energy, BES

US Army

Indiana 21st Century Research and Technology Fund

Toyota Central R&D, Japan

Professional Activities/Honors

- **Senior Editor**, *Journal of Physical Chemistry*
- **Member**, Editorial Advisory Board, *Langmuir*
- **Member**, Editorial Board, *Research on Chemical Intermediates*
- **Member**, Editorial Board, *International Journal of Photoenergy*
- **Member**, Editorial Board, *Interface*
- **Treasurer**, *Fullerenes, Nanotubes and Carbon Nanostructures Division* (The Electrochemical Society) May 2004-2006
- **Panel member** NSF-SBIR/STTR Phase I, Photo & Electro-chemical Processes
- **Member**, Discussion Panel, Basic Research Needs for Solar Energy Utilization
- **Symposium Organizer** of the Nanotechnology symposium at the Spring (Quebec City) and Fall (Los Angeles) meetings of the Electrochemical Society.
- **Symposium Organizer** of the at the Fall meeting of the Materials Research Society, Boston, .

Impact Factor ...is it just a hype?

The impact factor (ISI) for most of the journals in the Physical Chemistry/Chemical Physics/Materials area range from 2 - 9. It is interesting to note that many of these journals have published significant number of papers with high impact (citations greater than 100) irrespective of their impact factor. If the scientific work is novel and significant, it is sure to make an impact in the long run.

Read more about an independent analysis of Citation Frequency and 30 most cited papers published in popular journals.

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

Research Highlights

Chromophore functionalized metal nanoparticles. The charge transfer interaction between gold nanoparticles and light harvesting chromophores (e.g., porphyrins and chlorophyll a) was explored to enhance the photoconversion efficiency. IPCE of ~60% was achieved using quaternary organization of porphyrin, C₆₀ and gold nanoparticles on electrode surfaces. The ability of gold nanoparticles in accepting and shuttling electrons from excited chlorophyll a (Chl_a) bound to mesoscopic TiO₂ film facilitates improved charge separation and enhanced photocurrent generation. Mechanistic aspects of dye sensitized silver particle formation using transient absorption spectroscopy was also elucidated.

Carbon nanotube-semiconductor composite as light harvesting assembly . The ability of the CdS-SWCNT nanocomposite system to undergo photoinduced charge separation was demonstrated for utilizing them as light harvesting assemblies. Deposition of CdS nanoparticles on single-walled carbon nanotubes produced a photoactive composite that initiated charge transfer interactions following excitation with visible light. Transient absorption experiments confirmed the quick deactivation of excited CdS on the SWCNT surface as the transient bleaching recovered in about 200 ps. Excitation of CdS deposited on SWCNT films produced photocurrent with a maximum incident photon to current generation efficiency of 0.5% and thus provided evidence for the electron transfer pathway in the composite.

Quantum Dot Solar Cells. Quantum dot solar cells have been constructed by assembling CdSe quantum dots (QDs) onto mesoscopic TiO₂ with the aid of a bifunctional linker molecule (SH-R-COOH). The charge injection from excited CdSe into TiO₂ nanoparticles is being investigated using transient absorption and photoelectrochemical measurements. The electron injection from the higher energy state occurs with a rate constant of $5 \times 10^{11} \text{ s}^{-1}$ and the electron transfer from the relaxed state occurs over a wide range of rate constant ($3.8 \times 10^9 \sim 9 \times 10^{10} \text{ s}^{-1}$). Preliminary studies indicate that ~12% incident photon to current conversion efficiency (IPCE) can be achieved using such quantum dot solar cells.

Hydroxyl radical attack on Chlorinated Aromatics. Hydroxyl radical addition was found to be the prominent reaction pathway for the chlorinated phenoxyacetic acids and also for the chlorinated phenols at pH values below the pK_a of the compounds. A very prominent change in $\cdot\text{OH}$ reactivity was observed with the chlorinated phenoxide ions in high pH solutions. Amid a greater electron-withdrawing presence on the aromatic ring (higher chlorinated phenoxide ions), the hydroxyl radical reacted preferably by way of addition to the aromatic ring. Steady state experiments utilizing gamma radiolysis also showed substantial slow down in oxidation with an increase in pH or concentration of substrate.

Single Wall Carbon Nanotubes For Fuel Cells. The electrophoretic deposition of SWCNT on a carbon fiber electrode (Toray paper) was employed to design a MEA for the fuel cell. Electrochemical studies demonstrate that hydrogen adsorption at SWCNT/Pt nanostructures plays an important role in improving the performance of H₂-based PEM fuel cell especially at higher pressures. Decrease in charge transfer resistance and greater adsorption of hydrogen makes the SWCNT based MEA attractive for developing next generation fuel cell devices.

TiO₂/Pt-Ru Hybrid Catalyst for Fuel Cells. A hybrid carbon fiber electrode (CFE) consisting of TiO₂ semiconductor photocatalyst and Pt-Ru catalyst has been developed to boost the performance of Direct Methanol Fuel Cells (DMFC). These two catalyst nanoparticles are deposited on opposite sides of the carbon fiber paper such that methanol oxidation is carried out catalytically on Pt-Ru and photocatalytically on TiO₂ under UV-light irradiation. The concept of incorporating a photocatalyst provides new ways to minimize precious metal content and enhance the performance of DMFCs. At low catalyst loadings (0.15 mg/cm²), a 25% enhancement in the peak power density is observed upon illumination with light.

Invited Lectures

Prashant V. Kamat

Meeting Energy Demand: Nanostructured Hybrid Assemblies for Catalysis and Solar Cells

The US-Egypt workshop on Nanostructured Materials and Nanotechnology, Alexandria, November 11-15, 2005

Meeting Energy Demand through Nanotechnology

Graduate Seminar, Department of Chemical Engineering, Univ. of Missouri, Rolla, October 4, 2005

The Clean Energy Challenge: Role of Solar Cells and Fuel Cells in the 21st Century

Environmental Engineering Seminar, University of Notre Dame, September 29, 2005

Panal Discussions, BES Solar Workshop, Washington, D.C. April 18-21, 2005

Energy Challenge and Nanotechnology

Chemistry Department Seminar, Western Michigan University, Kalamazoo, March 21, 2005

Ordered Nanoassemblies for Light Energy Conversion

Chemistry Department Seminar Series, Rutgers University, Newark, March 4, 2005

Nanostructure Architectures for Energy Conversion

Presidential Lecture, Florida International University, Miami, February 25, 2005

Istvan Robel

Carbon Nanotubes for Fuel Cell and Solar Cell Applications

Chemistry Department Seminar, Indiana University Northwest, Gary, February 10, 2005

Meeting Presentations

2005 Fall Meeting of the Materials Research Society, Boston, November 28- December 2, 2005

- Organized Assembly of Donor Acceptor Molecular Clusters for Next Generation Solar Cells, **Prashant V. Kamat**, Taku Hasobe and Shunichi Fukuzumi
- Semiconductor nanostructures as smart materials for simultaneous detection and degradation of organics from air and water, Vaidyanthan Subramanian, Istvan Robel, Kaylie Young, Joan Brennecke and **Prashant V. Kamat**
- Optical Effects in Chromophore Functionalized Metal Nanoparticles **Prashant V. Kamat** and K. George Thomas
- Interplasmon Coupling in Silver and Gold Nanorods, **K. George Thomas** and Prashant V. Kamat
- SWCNT-CdS Nanocomposite as Light Harvesting Assembly. Photoinduced Charge Transfer Interactions, **Istvan Robel**, Bruce Bunker and Prashant V. Kamat
- Ultrafast relaxation dynamics of charge carriers in CdSe quantum wires, **Istvan Robel**, Ken Kuno and Prashant V. Kamat

XXIIth International Conference On Photochemistry, Cairns Convention Centre, Queensland, Australia, 24 - 29th July, 2005

- Photoinduced Charge Separation in Chromophore Functionalized Metal Nanoparticles Organic Solar Cells, **Prashant V. Kamat**
- Organic-Inorganic Hybrid Nanostructures for Next Generation Solar Cells **Prashant V. Kamat**, Taku Hasobe and Shunichi Fukuzumi

207th Meeting of The Electrochemical Society, Quebec City, Canada, May 15 to May 20, 2005

- Electrophoretic Deposition of SWCNT Films and Photoelectrochemical Effects, **Prashant V. Kamat**, S. Barazzouk, S. Hotchandani and K. Vinodgopal
- Enhancement of Charge Separation in a Chlorophyll a Photoelectrochemical Cell by Gold Nanoparticles, **S. Hotchandani**, S. Barazzouk and P. Kamat
- Photoinduced Charge Separation in Ag@TiO₂ Core-Shell Nanostructures, **Prashant V. Kamat** and T. Hirakawa
- Photovoltaic Cells Composed of Supramolecular Clusters Based on Porphyrin-Peptide Oligomers and Fullerenes, **T. Hasobe**, P. Kamat, K. Saito, V. Troiani, N. Solladii, T. Ahn, S. Kim, D. Kim and F. D'Souza
- TiO₂/Pt-Ru/C Hybrid Catalyst for Methanol Oxidation", **Prashant V. Kamat**, K. Drew and K. Vinodgopal
- Electrophoretically Deposited Single Wall Carbon Nanotubes Electrodes for Fuel Cell Applications", **K. Vinodgopal**, G. Girishkumar, M. Rettker and Prashant V. Kamat

Annual Meeting of the Chemical Society Japan, Yokohama, Japan, March 26-29, 2005.

- Development of supramolecular photovoltaic cells by the composite clusters of porphyrin peptide oligomer and fullerene, **Taku Hasobe**, S. Fukuzumi and Prashant V. Kamat.

229th ACS National Meeting, in San Diego, CA, March 13-17, 2005

- ZnO nanostructures as smart materials for simultaneous detection and degradation of carboxylic acids, Vaidyanthan Subramanian and **Prashant V. Kamat**
- Photoinduced electron storage and transfer properties of metal-semiconductor composites, **Prashant V. Kamat** and Tustomu Hirakawa
- Mechanistic Evaluation of Arsenite Oxidation during TiO₂ photocatalysis, Tielian Xu, Prashant V. Kamat, and **Kevin E. O'Shea**
- Carbon nanotubes for fuel cell applications, **G. Girishkumar**, Matthew Rettker K. Vinodgopal, and Prashant V. Kamat
- Sonochemically prepared platinum nanoparticles for fuel cell applications, **K. Vinodgopal**, G. Girishkumar, Robert Underhile, and Prashant V. Kamat

Research Publications

1. 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.](#), **2005**, 127, 1216-1228.
2. Barazzouk, S., Kamat, P. V. and Hotchandani, S., *Photoinduced Electron Transfer between Chlorophyll a and Gold Nanoparticles*. [J. Phys. Chem. B](#), **2005**, 109, 716-723.
3. 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**, 15, 372-380.
4. 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](#), **2005**, 109, 2822-2828.
5. 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](#), **2005**, 109, 2829-2835.
6. 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.](#), **2005**, 127, 3928-3934.
7. Okamoto, K., Hasobe, T., Tkachenko, N. V., Lemmetyinen, H., Kamat, P. V. and Fukuzumi, S., *A Drastic Difference in Lifetimes of the Charge-Separated State of Formanilide-Anthraquinone Dyad vs Ferrocene-Formanilide- Anthraquinone Triad and Their Photoelectrochemical Properties of the Composite Films with Fullerene Clusters*. [J. Phys. Chem. A](#), **2005**, 109, 4662-4670.
8. Girishkumar, G., Rettker, M., Underhile, R., Binz, D., Vinodgopal, K., McGinn, P. and Kamat, P., *Single Wall Carbon Nanotube based Proton Exchange Membrane Assembly for Hydrogen Fuel Cells*. [Langmuir](#), **2005**, 21, 8487 - 8494.
9. Hasobe, T., Kamat, P. V., Troiani, V., Solladie, N., Ahn, T. K., Kim, S. K., Kim, D., Kongkanand, A., Kuwabata, S. and Fukuzumi, S., *Enhancement of Light-Energy Conversion Efficiency by Multi-Porphyrin Arrays of Porphyrin-Peptide Oligomers with Fullerene Clusters*. [J. Phys. Chem. B](#), **2005**, 109, 19-23.
10. Pillai, Z. S. and Kamat, P. V., *The spectroelectrochemistry of aromatic amine oxidation. An insight into the indo dye formation*. [Res. Chem. Intermed.](#), **2005**, 31, 103-112.
11. Drew, K., Girishkumar, G., Vinodgopal, K. and Kamat, P. V., *Boosting the Fuel Cell Performance with a Semiconductor Photocatalyst. TiO₂/Pt-Ru Hybrid Catalyst for Methanol Oxidation*. [J. Phys. Chem. B](#), **2005**, 109, 11851 - 11857.
12. Thomas, K. G., George, M. V. and Kamat, P. V., *Photoinduced Electron Transfer Processes in Fullerene-Based Donor-Acceptor Systems*. [Helv. Chim. Acta](#), **2005**, 88, 1291-1308.
13. Hasobe, T., Fukuzumi, S. and Kamat, P. V., *Ordered Assembly of Protonated Porphyrin Driven by Single Wall Carbon Nanotubes. J- and H-Aggregates to Nanorods*. [J. Am. Chem. Soc.](#), **2005**, 127, 11884 - 11885.
14. Robel, I., Bunker, B. and Kamat, P. V., *SWCNT-CdS nanocomposite as light harvesting assembly. Photoinduced charge transfer interactions*. [Adv. Mater.](#), **2005**, 17, 2458-2463.
15. Hasobe, T.;Hattori, S.;Kamat, P. V.;Urano, Y.;Umezawa, N.;Nagano, T.;Fukuzumi, S., *Organization of supramolecular assemblies of fullerene, porphyrin and fluorescein dye derivatives on TiO₂ nanoparticles for light energy conversion*. [Chem. Phys.](#), **2005**, 319, 243-252.
16. Peller, J. and Kamat, P. V., *Radiolytic Transformations of Chlorinated Phenols and Chlorinated Phenoxyacetic Acids*. [J. Phys. Chem. A](#), **2005**, 109, 9528-9535.
17. Sudeep, P. K. and Kamat, P. V., *Photosensitized Growth of Silver Nanoparticles under Visible Light Irradiation: A Mechanistic Investigation*. [Chem. Mater.](#), **2005**, 17, 5404 - 5410.
18. Xua, T., Kamat, P. V. and O'Shea, K. E., *Mechanistic Evaluation of Arsenite Oxidation in TiO₂ Assisted photocatalysis*. [J. Phys. Chem. A](#), **2005**, 109, 9070-9075.

Submitted/Accepted for Publication

1. Hasobe, T., Hattori, S., Kamat, P. V., Urano, Y., Umezawa, N., Nagano, T. and Fukuzumi, S., **Tetrahedron**, **2005**, in press.
2. Hasobe, T., Fukuzumi, S. and Kamat, P. V., *Stacked-Cup Carbon Nanotubes for Photoelectrochemical Solar Cells*. **Angew. Chem. (Int. Ed.)**, **2005**, in press.
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.**, **2005**, submitted.
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**, **2005**, 109,. Web (DOI: [10.1021/jp054764i](https://doi.org/10.1021/jp054764i))
5. Subramanian, V., Robel, I., Kuno, M. and Kamat, P. V., *Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO₂ Films*. **J. Am. Chem. Soc.**, **2005**, submitted.
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**, **2005**, 21, in press.



An IBH Single Photon Counting Spectrofluorimeter equipped with different excitation lasers has been successfully installed. The detection limit of our femtosecond transient absorption spectrometer has now been extended into the IR region. These new additions will assist in identifying the limiting factors in photoinduced electron transfer in molecular and semiconductor assemblies.

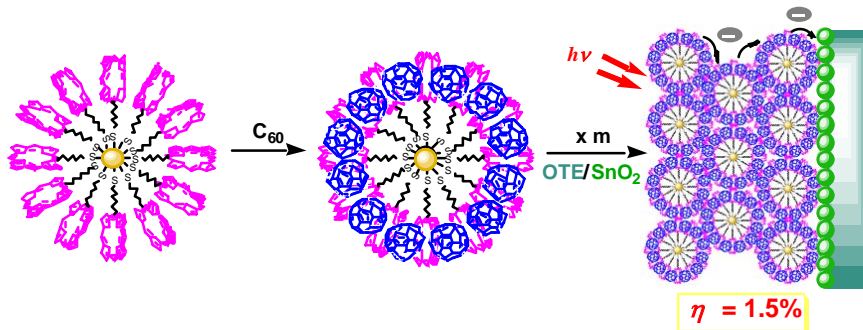
Abstracts of Publications

J. Am. Chem. Soc., **127** (4), 1216 -1228, 2005. (DOI: [10.1021/ja047768u](https://doi.org/10.1021/ja047768u))

Photovoltaic Cells Using Composite Nanoclusters of Porphyrins and Fullerenes with Gold Nanoparticles

Taku Hasobe, Hiroshi Imahori,*Prashant V. Kamat,*Tae Kyu Ahn, Seong Keun Kim, Dongho Kim,* Atsushi Fujimoto, Tsutomu Hirakawa, and Shunichi Fukuzumi*

Novel organic solar cells have been prepared using quaternary self-organization of porphyrin (donor) and fullerene (acceptor) units by clusterization with gold nanoparticles on nanostructured SnO₂ electrodes. First, porphyrin-alkanethiolate monolayer-protected gold nanoparticles (H₂PC_nMPC: *n* is the number of methylene groups in the spacer) are prepared (secondary organization) starting from the primary component (porphyrin-alkanethiol). These porphyrin-modified gold nanoparticles form complexes with fullerene molecules (tertiary organization), and they are clusterized in acetonitrile/toluene mixed solvent (quaternary organization). The highly colored composite clusters can then be assembled as three-dimensional arrays onto nanostructured SnO₂ films to afford the OTE/SnO₂/(H₂PC_nMPC+C₆₀)_m electrode using an electrophoretic deposition method. The film of the composite clusters with gold nanoparticle exhibits an incident photon-to-photocurrent efficiency (IPCE) as high as 54% and broad photocurrent action spectra (up to 1000 nm). The power conversion efficiency of the OTE/SnO₂/(H₂PC15MPC+C₆₀)_m composite electrode reaches as high as 1.5%, which is 45 times higher than that of the reference system consisting of the both single components of porphyrin and fullerene.



J. Phys. Chem. A, **109** (21), 4662 -4670, 2005. (DOI: [10.1021/jp045042e](https://doi.org/10.1021/jp045042e))

Drastic Difference in Lifetimes of the Charge-Separated State of the Formanilide-Anthraquinone Dyad versus the Ferrocene-Formanilide-Anthraquinone Triad and Their Photoelectrochemical Properties of the Composite Films with Fullerene Clusters

Ken Okamoto, Taku Hasobe, Nikolai V. Tkachenko,§ Helge Lemmetyinen,*§ Prashant V. Kamat,* and Shunichi Fukuzumi*

A long-lived charge-separated (CS) state, which can be observed even at 900 fs after laser excitation, has been attained in the formanilide-anthraquinone dyad (FA-AQ) in dimethyl sulfoxide, whereas the CS lifetime is shortened significantly to 20 ps in the ferrocene-formanilide-anthraquinone triad (Fc-FA-AQ). Such a drastic decrease in the CS lifetime by the addition of a ferrocene moiety to the FA-AQ dyad is ascribed to a decrease in the driving force of back electron transfer and an increase in the reorganization energy of electron transfer despite the longer charge-separation distance. The FA-AQ dyad and the Fc-FA-AQ triad have been employed as components of photovoltaic cells, where composite molecular nanoclusters of the FA-AQ dyad or the Fc-FA-AQ triad with fullerene (C₆₀) are assembled onto a SnO₂ electrode using an electrophoretic method. The composite films of the Fc-FA-AQ triad exhibit 10 times smaller values of an incident photon-to-photocurrent efficiency (IPCE) as compared with those of the FA-AQ dyad in accordance with a drastic decrease of the CS lifetime by addition of a ferrocene moiety to the FA-AQ dyad.

Chem. Phys. **319**, 243-252, 2005. <http://dx.doi.org/10.1016/j.chemphys.2005.06.035>

Organization of supramolecular assemblies of fullerene, porphyrin and fluorescein dye derivatives on TiO₂ nanoparticles for light energy conversion..

T. Hasobe, S. Hattori, P. V. Kamat, Y. Urano, N. Umezawa, T. Nagano and S. Fukuzumi

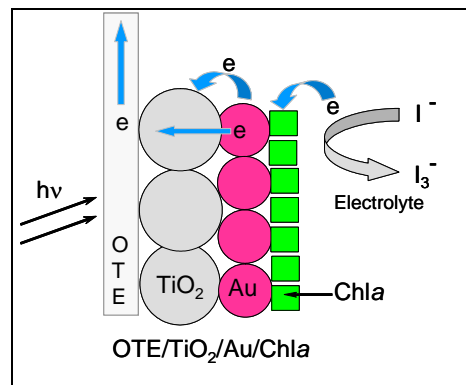
TiO₂ nanoparticles were modified with a porphyrin derivative, 5-[4-benzoic acid]-10,15,20-tris[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (H₂P-COOH), and fluorescein derivatives, 9-[2-(3-carboxy-9,10-diphenyl)anthryl]-2,7-difluoro-6-hydroxy-3*H*-xanthen-3-one (DPAX-COOH) and 2',7'-difluorofluorescein(FL-COOH). The dye-modified TiO₂ nanoparticles were deposited on nanostructured OTE/SnO₂ (OTE: optically transparent electrodes) together with nanoclusters of fullerene (C₆₀) from acetonitrile/toluene (3:1, v/v) using an electrophoretic deposition technique. The incident photon to photocurrent efficiency (IPCE) for these electrodes increases in order: OTE/SnO₂/(H₂P)_n < OTE/SnO₂/(H₂P-COO-TiO₂)_n < OTE/SnO₂/(H₂P-COO-TiO₂ + C₆₀). The IPCE value can be further improved by replacing H₂P-COOH with a fluorescein derivative containing an electron donor moiety: DPAX-COOH (DPA: diphenylanthracene). The maximum IPCE value (42%) is obtained for OTE/SnO₂/(DPAX-COO-TiO₂ + C₆₀)_n under the bias of 0.2 V vs. SCE.

J. Phys. Chem. B, **109** (2), 716-723, 2005. (DOI: [10.1021/jp046474s](https://doi.org/10.1021/jp046474s))

Photoinduced Electron Transfer between Chlorophyll *a* and Gold Nanoparticles

Saïd Barazzouk, Prashant V. Kamat, and Surat Hotchandani*

The emission intensity of Chla is quenched by gold nanoparticles. The dominant process for this quenching has been attributed to the process of photoinduced electron transfer from excited Chla to gold nanoparticles, although because of a small overlap between fluorescence of Chla and absorption of gold nanoparticles, the energy-transfer process cannot be ruled out. Photoinduced electron-transfer mechanism is supported by the electrochemical modulation of fluorescence of Chla. In absence of an applied bias, Chla cast on gold film, as a result of electron transfer, exhibits a very weak fluorescence. However, upon negatively charging the gold nanocore by external bias, an increase in fluorescence intensity is observed. The negatively charged gold nanoparticles create a barrier and suppress the electron-transfer process from excited Chla to gold nanoparticles, resulting in an increase in radiative process. Nanosecond laser flash experiments of Chla in the presence of gold nanoparticles and fullerene (C_{60}) have demonstrated that Au nanoparticles, besides accepting electrons, can also mediate or shuttle electrons to another acceptor. Taking advantage of these properties of gold nanoparticles, a photoelectrochemical cell based on Chla and gold nanoparticles is constructed.



J. Mater. Chem., **15**, 372-380, 2005. <http://dx.doi.org/10.1039/b413336f>

Organization of supramolecular assembly of 9-mesityl-10-carboxymethylacridinium ion and fullerene clusters on TiO₂ nanoparticles for light energy conversion

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

TiO₂ nanoparticles modified with composite nanoclusters of 9-mesityl-10-carboxymethylacridinium ion (**Mes-Acr⁺-COOH**) and fullerene (C_{60}) in acetonitrile/toluene (3:1, v/v) were deposited as thin films on nanostructured SnO₂ electrode using an electrophoretic technique. The composite TiO₂ films have broad as well as high absorbance properties, exhibiting photoactive response under visible light excitation using I₃/I redox couple as compared with the reference multilayer films composed of the single component. This indicates that the composite cluster TiO₂ film based on 9-mesityl-10-carboxymethylacridinium ion and fullerene harvests light widely in the visible region due to organization of the supramolecular assembly. In the case of a monolayer system of TiO₂ nanocrystallites modified with **Mes-Acr⁺-COOH**, however, no net photocurrent is observed in the photocurrent action spectrum. This indicates that TiO₂ nanoparticles act as materials to organize composite molecules rather than as those to accept electrons. An incident photon-to-photocurrent generation efficiency (IPCE) of 37% has been achieved at an applied bias potential of 0.2 V vs. SCE in the Mes-Acr⁺-COOH/ C_{60} composite system using TiO₂ nanoparticles.

Res. Chem. Intermed., **31**, 103-112, 2005.

<http://puck.ingentaconnect.com/vl=3433842/cl=26/nw=1/fm=docpdf/rpsv/cw/vsp/09226168/v31n1/s11/p103>

The spectroelectrochemistry of aromatic amine oxidation. An insight into the indo dye formation

Z. S. Pillai, and P. V. Kamat*

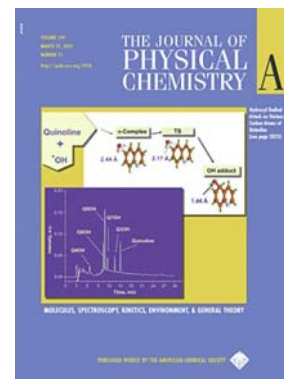
Mechanistic details of formation of two indo dyes have been investigated using spectroelectrochemistry. These dyes absorb strongly in the visible region and are formed when a primary amine such as *p*-phenylene diamine (PPD) is initiated electrochemically to form the radical cation. The PPD radical cation quickly couples with another coexisting aromatic amine, viz., *m*-phenylene diamine (MPD) or *p*-amino-*o*-cresol (PAOC) to yield a bright colored indo-amine or indo-cresol dyes. Unlike the conventional chemical oxidation methods, the electrochemical oxidation provides selectivity in oxidizing the desired aromatic amine (viz., PPD) and allows us to probe the pathways with which the bright colored dye is formed. Spectroelectrochemical studies that elucidate the indo dye formation and its dependence on the concentration of the color coupler are described. These *in situ* studies probe the reactivity of aromatic amines in self-coupling and cross coupling reactions. The electrochemical approach described in this study has also enabled us to synthesize pure form of these dyes.

J. Phys. Chem. A, **109** (12), 2822 -2828, 2005. (DOI: [10.1021/jp0450179](https://doi.org/10.1021/jp0450179))

Mechanistic Pathways of the Hydroxyl Radical Reactions of Quinoline. 1. Identification, Distribution, and Yields of Hydroxylated Products

A. Roxana Nicolaescu, Olaf Wiest,* and Prashant V. Kamat*

The mechanistic details of the hydroxyl radical-induced transformations of quinoline have been elucidated. The nature and distribution of the final products have provided insight into the preferential attack of the hydroxyl radicals at different sites on the aromatic rings. Hydroxylated products at all of the carbon atoms but one, C2, have been observed and quantified following controlled radiolysis of N_2O -purged aqueous quinoline solutions. The difference in the growth pattern and the lifetime of the monohydroxylated products under radiolytic conditions, as well as the formation of high-molecular-weight products (e.g., quinoline dimers), shows the complexity of the $\bullet OH$ reaction pathways. The radiolytic yields (G values) for the degradation of the quinoline and the formation of the hydroxylated products are calculated in the absence and in the presence of an oxidant, $K_3Fe(CN)_6$. The addition of $K_3Fe(CN)_6$ changes only the distribution of the hydroxylated products. These experiments indicate that the nature of the hydroxylated products is determined in the initial addition step of the reaction of the hydroxyl radical with quinoline, whereas the chemistry of the OH adducts is relevant to the distribution of the final products. The discrepancy between the products of γ -radiolysis and the photo-Fenton reaction of quinoline is also discussed.



J. Phys. Chem. A, **109** (12), 2829 -2835, 2005. (DOI: [10.1021/jp045016g](https://doi.org/10.1021/jp045016g))

Mechanistic Pathways of the Hydroxyl Radical Reactions of Quinoline. 2. Computational Analysis of Hydroxyl Radical Attack at C Atoms

A. Roxana Nicolaescu, Olaf Wiest,* and Prashant V. Kamat*

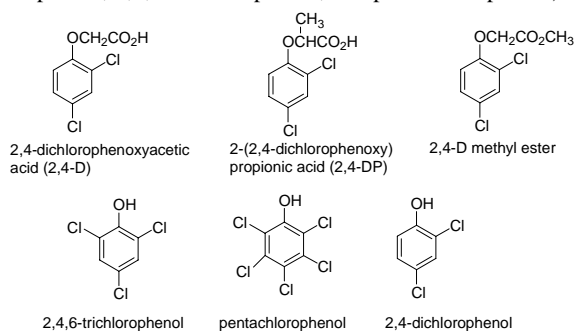
Density functional theory (DFT) calculations are employed to compare the mechanism of the $\bullet OH$ attacks at all carbon atoms in quinoline. The computational analysis of the energy surface for the reaction of $\bullet OH$ with quinoline reveals that the formation of OH adducts proceeds through exothermic formation of π -complexes/H-bonded complexes. The gas-phase reactions have activation energies ranging from <1.3 kcal/mol for the attack at positions C3 through C8 to 8.6 kcal/mol for the attack at the C2 position. Solvation, as described by the CPCM cavity model, lowers these activation barriers so that the attack at all carbon atoms except C2 is effectively barrierless. The $\bullet OH$ attack at C2 in solution is significantly different than at all other quinoline positions because it involves the only transition structure with energy higher than that of the starting materials and with an energetic barrier of 5.1 kcal/mol. The specific solvation approach also corroborates this finding because the attack at C2 was shown to have an energy barrier of 2.3 kcal/mol compared to the barrierless attack at C5. These results are in agreement with our recent experimental studies but differ from literature reports on the degradation of quinoline using the photo-Fenton reaction.

J. Phys. Chem. A, **109** (42), 9528 -9535, 2005. (DOI: [10.1021/jp053001s](https://doi.org/10.1021/jp053001s))

Radiolytic Transformations of Chlorinated Phenols and Chlorinated Phenoxyacetic Acids

Julie Peller* and Prashant V. Kamat

Hydroxyl radical reactions of selected chlorinated aromatic phenols (2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol) and chlorinated phenoxyacetic acids [2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-D methyl ester, 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP)] were studied using the radiolysis techniques of pulse radiolysis and γ -radiolysis. Hydroxyl radical addition was the prominent reaction pathway for the chlorinated phenoxyacetic acids and also for the chlorinated phenols at pH values below the pK_a of the compounds. A very prominent change in $\bullet OH$ reactivity was observed with the chlorinated phenoxide ions in high pH solutions. Two different reaction pathways were clearly present between the hydroxyl radical and the chlorinated phenoxide ions. One of the reaction pathways was suppressed when the concentration of chlorinated phenoxide ions was increased 10-fold. Amid a greater electron-withdrawing presence on the aromatic ring (higher chlorinated phenoxide ions), the hydroxyl radical reacted preferably by way of addition to the aromatic ring. Steady-state experiments utilizing γ -radiolysis also showed a substantial decrease in oxidation with an increase in pH of substrate.

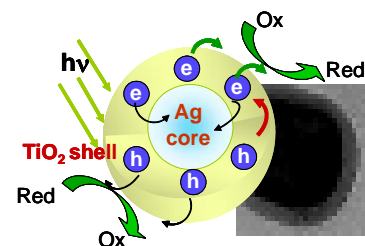


J. Am. Chem. Soc., **127** (11), 3928 -3934, 2005. (DOI: [10.1021/ja042925a](https://doi.org/10.1021/ja042925a))

Charge Separation and Catalytic Activity of Ag@TiO₂ Core-Shell Composite Clusters under UV-Irradiation

Tsutomu Hirakawa and Prashant V. Kamat*

Photocatalytic properties of Ag@TiO₂ composite clusters have been investigated using steady state and laser pulse excitations. Photoexcitation of TiO₂ shell results in accumulation of the electrons in the Ag core as evidenced from the shift in the surface plasmon band from 460 to 420 nm. The stored electrons are discharged when an electron acceptor such as O₂, thionine, or C₆₀ is introduced into the system. Charge equilibration with redox couple such as C₆₀/C₆₀^{•-} shows the ability of these core shell structures to carry out photocatalytic reduction reactions. The charge separation, charge storage, and interfacial charge-transfer steps that follow excitation of the TiO₂ shell are discussed.

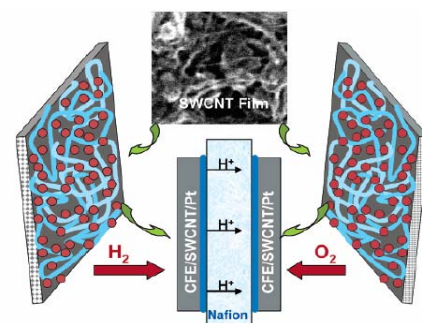


Langmuir, **21** (18), 8487 -8494, 2005. (DOI: [10.1021/la051499j](https://doi.org/10.1021/la051499j))

Single-Wall Carbon Nanotube-Based Proton Exchange Membrane Assembly for Hydrogen Fuel Cells

G. Girishkumar, Matthew Rettker, Robert Underhile, David Binz, K. Vinodgopal,* Paul McGinn, and Prashant Kamat*

A membrane electrode assembly (MEA) for hydrogen fuel cells has been fabricated using single-walled carbon nanotubes (SWCNTs) support and platinum catalyst. Films of SWCNTs and commercial platinum (Pt) black were sequentially cast on a carbon fiber electrode (CFE) using a simple electrophoretic deposition procedure. Scanning electron microscopy and Raman spectroscopy showed that the nanotubes and the platinum retained their nanostructure morphology on the carbon fiber surface. Electrochemical impedance spectroscopy (EIS) revealed that the carbon nanotube-based electrodes exhibited an order of magnitude lower charge-transfer reaction resistance (R_{ct}) for the hydrogen evolution reaction (HER) than did the commercial carbon black (CB)-based electrodes. The proton exchange membrane (PEM) assembly fabricated using the CFE/SWCNT/Pt electrodes was evaluated using a fuel cell testing unit operating with H₂ and O₂ as input fuels at 25 and 60 °C. The maximum power density obtained using CFE/SWCNT/Pt electrodes as both the anode and the cathode was ~20% better than that using the CFE/CB/Pt electrodes.

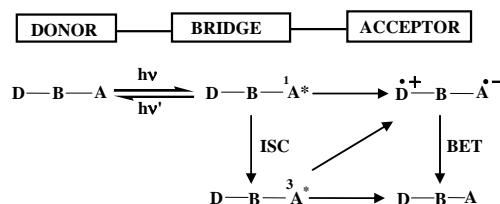


Helv. Chim. Acta, **88** 1291-1308, 2005. <http://dx.doi.org/10.1002/hlca.200590106>

Photoinduced Electron Transfer Processes in Fullerene-Based Donor-Acceptor Systems.

K. G. Thomas, M. V. George, and P. V. Kamat

Photoinduced electron transfer processes in fullerene-based donor-acceptor dyads (D-B-A) in homogeneous and cluster systems are summarized. Stabilization of charge has been achieved through the use of fullerene substituted-aniline/heteroaromatic dyads with tunable ionization potentials and also by using fullerene clusters. The rate constants for charge separation (k_{CS}) and charge recombination (k_{CR}) in fullerene substituted-aniline/heteroaromatic dyads show that forward electron transfer falls in the normal region of the Marcus curve and the back electron transfer in the inverted region of the Marcus parabola. Clustering of fullerene-based dyads assists in effective delocalization of the separated charge and thereby slows down the back electron transfer in these cases.

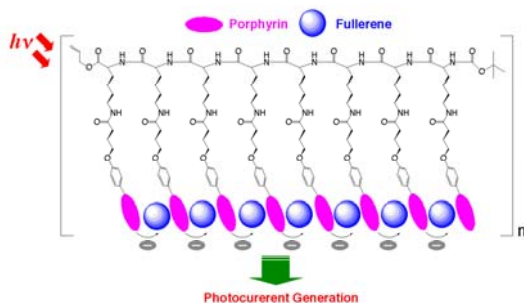


J. Phys. Chem. B, **109** (1), 19 -23, 2005. (DOI: [10.1021/jp045246v](https://doi.org/10.1021/jp045246v))

Enhancement of Light-Energy Conversion Efficiency by Multi-Porphyrin Arrays of Porphyrin-Peptide Oligomers with Fullerene Clusters

Taku Hasobe, Prashant V. Kamat,* Vincent Troiani, Nathalie Solladié,* Tae Kyu Ahn, Seong Keun Kim, Dongho Kim,* Anusorn Kongkanand, Susumu Kuwabata, and Shunichi Fukuzumi*

Organic photovoltaic cells using supramolecular complexes of porphyrin-peptide oligomers (porphyrin-functionalized α -polypeptides) with fullerene demonstrate remarkable enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions by increasing the number of porphyrin units in α -polypeptide structures. A high power conversion efficiency (η) of 1.3% and a maximum incident photon-to-photocurrent efficiency (IPCE) of 42% were attained using composite clusters of porphyrin-peptide octamer and fullerene. These results clearly show that the formation of a molecular assembly between fullerene and multi-porphyrin arrays with a polypeptide backbone controls the electron transfer efficiency in the supramolecular complex, which is essential for the light-energy conversion.

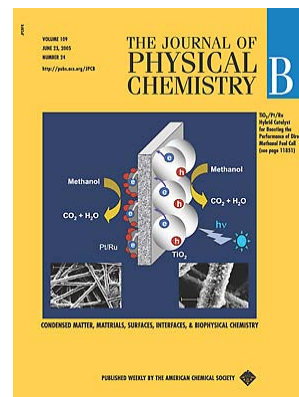


J. Phys. Chem. B, **109** (24), 11851 -11857, 2005. (DOI: [10.1021/jp051073d](https://doi.org/10.1021/jp051073d))

Boosting Fuel Cell Performance with a Semiconductor Photocatalyst: TiO₂/Pt-Ru Hybrid Catalyst for Methanol Oxidation

Kristine Drew, G. Girishkumar, K. Vinodgopal, and Prashant V. Kamat*

A hybrid carbon fiber electrode (CFE) consisting of TiO₂ semiconductor photocatalyst and Pt-Ru catalyst has been developed to boost the performance of direct methanol fuel cells (DMFC). These two catalyst nanoparticles are deposited on opposite sides of the carbon fiber paper such that methanol oxidation is carried out catalytically on Pt-Ru and photocatalytically on TiO₂ under UV-light irradiation. Since both catalysts carry out methanol oxidation independently, we observe an additive effect in the current generation. The carbon support fibers provide a large network to collect the electrons from both of these catalytic processes and thus assist in efficient current generation. In addition, TiO₂ improves the performance of the Pt-Ru catalyst in dark, indicating possible surface area improvement or diminished poisoning effects. The concept of incorporating a photocatalyst provides new ways to minimize precious metal content and enhance the performance of DMFCs. At low catalyst loadings (0.15 mg/cm²) at 295 K, a 25% enhancement in the peak power density is observed upon illumination with light.



J. Phys. Chem. A, **109** (40), 9070 -9075, 2005. (DOI: [10.1021/jp054021x](https://doi.org/10.1021/jp054021x))

Mechanistic Evaluation of Arsenite Oxidation in TiO₂ Assisted Photocatalysis

Tielian Xu, Prashant V. Kamat, and Kevin E. O'Shea*

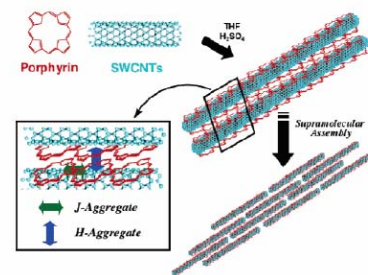
We report herein a detailed assessment of the roles of O₂, H₂O₂, \cdot OH, and O₂⁻ in the TiO₂ assisted photocatalytic oxidation (PCO) of arsenite. Although both arsenite, As(III), and arsenate, As(V), adsorb extensively onto the surface of TiO₂, past studies relied primarily on the analysis of the arsenic species in solution, neglecting those adsorbed onto the surface of TiO₂. We used extraction and analyses of the arsenic species adsorbed onto the surface of the TiO₂ to illustrate that the oxidation of As(III) to As(V) occurs in an adsorbed state during TiO₂ PCO. The TiO₂ photocatalytic oxidation (PCO) of surface adsorbed As(III) in deoxygenated solutions with electron scavengers, Cu²⁺, and polyoxometalates (POM) yields oxidation rates that are comparable to those observed under oxygen saturation, implying the primary role of oxygen is as a scavenger of the conduction band electron. Pulse radiolysis and competition kinetics were employed to determine a rate constant of $3.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of As(III) with O₂⁻. Transient absorption studies of adsorbed hydroxyl radicals, generated by subjecting colloidal TiO₂ to radiolytic conditions, provide convincing evidence that the adsorbed hydroxyl radical (TiO₂+ \cdot OH) plays the central role in the oxidation with As(III) during TiO₂ assisted photocatalysis. Our results suggest the reaction of superoxide anion radical does not contribute in the conversion of As(III) when compared to the reaction of As(III) with \cdot OH radical during TiO₂ PCO.

J. Am. Chem. Soc., **127** (34), 11884 -11885, 2005. (DOI: [10.1021/ja050687t](https://doi.org/10.1021/ja050687t))

Ordered Assembly of Protonated Porphyrin Driven by Single-Wall Carbon Nanotubes. J- and H-Aggregates to Nanorods

Taku Hasobe,[†] Shunichi Fukuzumi,^{*†} and Prashant V. Kamat^{*†}

Ordered assemblies of protonated porphyrin in the form of J- and H-type aggregates have been achieved on the single-wall carbon nanotube (SWCNTs) surface. This unusual molecular aggregation phenomenon driven by SWCNTs further enables macroscopic assembly in the form of linear bundles.

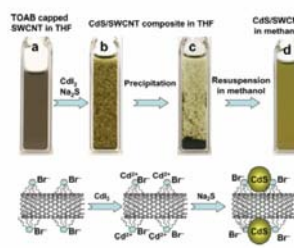


Adv. Mater. **17**, 2458-2463, 2005. (<http://dx.doi.org/10.1002/adma.200500418>)

SWCNT-CdS nanocomposite as light harvesting assembly. Photoinduced charge transfer interactions.

I. Robel, B. Bunker and P. V. Kamat

Deposition of CdS nanoparticles on single-walled carbon nanotubes produces a photoactive composite that undergoes charge transfer interactions following excitation with visible light. The luminescence of CdS is quenched by SWCNT. Transient absorption experiments confirm the quick deactivation of excited CdS on the SWCNT surface as the transient bleaching recovers in about 200 ps. Excitation of CdS deposited on SWCNT films produces photocurrent with a maximum incident photon to current generation efficiency of 0.5% and thus provides evidence for the electron transfer pathway in the composite. The ability of the CdS-SWCNT nanocomposite system to undergo photoinduced charge separation opens up new ways to design light harvesting assemblies.

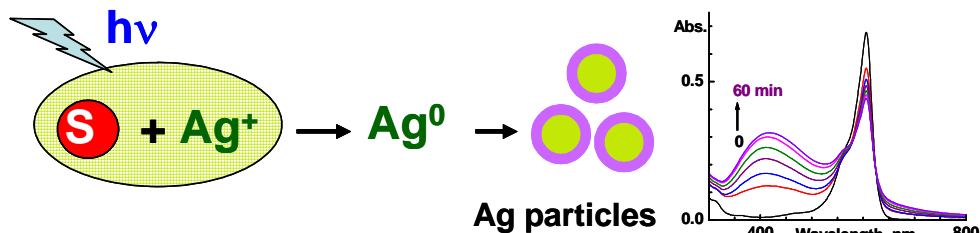


Chem. Mater., **17** (22), 5404 -5410, 2005. (DOI: [10.1021/cm0512777](https://doi.org/10.1021/cm0512777))

Photosensitized Growth of Silver Nanoparticles under Visible Light Irradiation: A Mechanistic Investigation

P. K. Sudeep and Prashant V. Kamat*

By employing thionine as a sensitizing dye, we have succeeded in inducing silver nanoparticle formation in ethanol/toluene medium. The particle size increases with the duration of photolysis, thus providing a simple experimental parameter to control the particle size. The photoinduced transformations as probed by steady state photolysis and transient absorption spectroscopy provide an insight into the charge-transfer processes leading to the formation of nanoparticles. Under visible light illumination, dye thionine undergoes self-quenching of the excited triplet to produce electron-transfer products in toluene/ethanol (1:1) mixture. The quenching of triplet excited dye by the ground state dye molecules ($k = 4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) occurs at a much faster rate than the quenching by Ag^+ ions ($k = 1.30 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$). Semithionine acts as a mild reductant to initiate reduction of silver ions ($k = 7.26 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and form silver seeds. These seeds grow with autocatalytic reduction of Ag^+ ions and by Ostwald ripening to produce larger size particles (10-30 nm diameter).



In Popular Press



Research News

New spin on carbon nanotube fibers

FABRICATION & PROCESSING

Individual single-walled carbon nanotubes (SWNTs) are known for their remarkable electrical, mechanical, and thermal properties, but it has proved difficult to reproduce these remarkable properties in macroscopic composite fibers. Fabrication has also proved tricky - either limited to short fibers produced by methods that cannot be easily scaled up or continuous fibers with high levels of impurities and little alignment. Researchers from Rice University, the University of Pennsylvania, and Carbon Consultants have succeeded in producing well-aligned, continuous macroscopic fibers consisting solely of SWNTs by conventional spinning (Erickson et al., *Science* (2004) 305, 1447). One of the main challenges to fabricating SWNT fibers has been the ability to disperse a sufficient concentration of the nanotubes for wet processing.

If a surfactant is used, it has to be removed during or after processing to produce pure SWNT fibers. The researchers get around this problem by dispersing the nanotubes in a 100% solution of sulfuric acid, which serves to positively charge the nanotubes and surround them with anions. This allows alignment of the SWNTs so that they can be extruded and coagulated into fibers by conventional spinning techniques. The fibers are made up of 200-600 nm "super-ropes", which themselves consist of densely packed 20 nm ropes. The SWNT fibers have a Young's modulus of 120x10 GPa, a tensile strength of 110x10 MPa, and electrical resistivities and thermal conductivities two-orders of magnitude higher than fibers produced with polymers.

Cynthia Sauty

New light on CNTs ENERGY GENERATION

Researchers at the University of Notre Dame have also demonstrated that SWNTs could be important to solar and fuel cells (Barazzouk et al., *J. Phys. Chem. B*(2004) doi: 10.1021/jp045840j). Prashant V. Kamat and coworkers deposited SWNT films on optically transparent electrodes using electrophoresis. When irradiated with visible light, these films generate a cathodic current. However, the light energy conversion efficiency of these materials needs to be improved significantly if they are to be used in solar cells. The researchers are now modifying the nanotubes with photoactive dye molecules and semiconductor quantum dots to improve efficiency.

Cordelia Sealy

<http://www.materialstoday.com/nanotoday2004/research.pdf>



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March 21, 2005

- Synthesize platinum-carbon cathodes by copolyrolysis
- Organofullerenes "harvest" light efficiently
- Organized composites efficiently convert light to electricity
- A catalyst for producing polyesters at room temperature
- Simulate the dissolution and growth of zeolite β C
- Observe growth defects in zeolite β directly
- Reduction by catalytic asymmetric transfer hydrogenation
- Trimethyltin hydroxide promotes mild ester hydrolysis

Organized composite nanoclusters efficiently convert light to electricity.

The development of efficient solar cells will benefit society because they convert solar energy, a no-cost light source, to much needed electrical power. An attractive strategy for developing such cells is mimicking photosynthesis, the natural energy conversion process. However, the photovoltaic devices developed so far have only limited degrees of self-organization, whereas the components in the natural system are highly organized into quaternary protein structures. An international team led by H. Imahori at Kyoto University, Japan, P. V. Kamat at the University of Notre Dame, IN, D. Kim at Yonsei University, Korea, and S. Fukuzumi at Osaka University, Japan, and including coauthors at Seoul National University, Korea, constructed hierarchically organized solar cells with nanocluster components ordered at up to the quaternary level. Porphyrinalkanethiol, fullerene, and gold nanoparticle were used as the primary building blocks for self-organization at these levels:

- Secondary organization: The porphyrinalkanethiol molecules self-assemble with the gold nanoparticles via metal-thiol bonds to give monolayer-protected gold nanoparticles.
- Tertiary organization: The peripheral porphyrin molecules form complexes with fullerene molecules by donor-acceptor interactions.
- Quaternary organization: The complexes are finally clustered into higher order structures using MeCN-toluene as the solvent.

The self-organized clusters are then assembled as 3-D arrays onto nanostructured tin oxide films by an electrophoretic deposition method to provide nanocomposite electrodes. The films of the composite nanoclusters exhibit broad photocurrent action spectra (up to 1 μ m) and incident photon-to-photocurrent efficiencies as high as 54%. The power conversion efficiency of the nanocomposite electrodes approaches 1.5%, 45 times greater than that of the nonorganized reference system. Such a remarkable enhancement of photovoltaic performance and the broader photoresponse in the visible and infrared spectra relative to the reference system demonstrate that quaternary organization of composite nanoclusters provides a novel entry for developing efficient organic solar cells. (*J. Am. Chem. Soc.* 2005, 127, 1216-1228) Ben Zhong Tang

The Hydrogen & Fuel Cell Letter

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July 2005

Illuminated Hybrid Platinum/ Semiconductor Electrode Delivers More Output In DMFC

NOTRE DAME, IN - By grafting a semiconductor photocatalyst carbon fiber paper electrode with a platinum-based catalyst, a team of scientists from the University of Notre Dame here and Indiana Tech Northwest in Gary has come up with a new hybrid electrode for methanol fuel cell that, with light shining on it, produces considerably more power than a straight platinum-catalyzed electrode.

But what's really surprising is that even in darkness, when the platinum is presumed to be non-active, the hybrid electrode combining the oxide semiconductor and the more or less conventional Pt-Ru (and ruthenium) catalyst performs better than the basic platinum

