Photoelectrochemistry
and
Nanoparticle Research

Research Activity
January 2003 - December 2003

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Research Funding
Office of Basic Energy Sciences, U.S. Department of Energy
Research Program

Photoelectrochemical Processes for Light Energy Conversion

- Charge transfer processes in semiconductor and metal nanostructures
- Semiconductor-metal nanocomposites
- Photochemical and radiation chemical processes on surfaces
- Excited state & redox processes of novel molecular assemblies
- Environmental remediation

External Collaborators

K. George Thomas (RRL, Trivandrum)
S. Hotchandani (U. of Quebec)
K. Vinodgopal (Indiana U., N. W.)
S. Padmaja (Unilever Research)
S. Fukuzumi (Osaka University)
H. Imahori (Kyoto University)
M. Anpo (Osaka Prefecture University)

Collaborators at Notre Dame

Joan Brennecke, Bruce Bunker, Olaf Wiest, and Eduardo Wolf

Visiting Scientists

K. Vinodgopal (Indiana U., N. W.)
K. George Thomas (RRL, India)
S. Hotchandani (U. of Quebec)

Postdoctoral Research Associate

Zeena S. Pillai (August 2001-Sept 2003)
Shailesh Sharma (April 2002-March 2003)
Tsutomu Hirakawa (April 2003-present)
Girish Kumar (Aug. 2003-present)
Mariko Hirakawa (Oct. 2003-present)

Graduate Students

Roxana Nicolaescu (Chemistry, U. of Notre Dame)
Julie Peller (Chemistry, U. of Notre Dame)
Ravi Vaidyanathan (Chem. Eng. U. of Notre Dame)
Said Barazzouk (Chemistry, U. of Quebec)
Taku Hasobe (Chemistry, Osaka U)
Hisashi Kikuchi (Osaka Prefecture Univ.)

Undergraduate Students

M. Haria (Co-op student, McMaster U.) Jan-Aug 2003

Ph. D. Dissertations

Julie Peller (Chemistry, UND, May 2003), “Hydroxyl radical mediated transformations of Herbicide, 2,4-Dichlorophenoxyacetic acid and related compounds”.

Professional Activities

- Senior Editor/Editorial Board Member, Journal of Physical Chemistry
- Editor/Editorial Board Member, Research on Chemical Intermediates
- Editorial Board Member, Langmuir
- Editorial Board Member, Fullerene Science & Technology
- Editorial Board Member, International Journal of Photoenergy
- Editorial Board Member, Interface
- Chairman, Fullerenes, Nanotubes and Carbon Nanostructures Division (The Electrochemical Society)
- Co-Editor, Book on Fullerenes Volume 13, 2003 (The Electrochemical Society)
- Panel member of NSF-SBIR Review Committee
- Panel member of EPA Grand Challenge Workshop
Significant Accomplishments

**Fermi Level Equilibration in Semiconductor-Metal Nanocomposites.** Oxide semiconductor colloids (TiO$_2$, and ZnO) are capable of undergoing charge storage under UV-irradiation. By making use of this electron accumulation property and the ability to titrate the stored electrons with a redox couple (C$_{60}^-$/C$_{60}$), we succeeded in determining the Fermi level of TiO$_2$ and TiO$_2$-Au nanoparticulate systems. The charge distribution between the semiconductor and metal nanoparticles was found to shift Fermi level to more negative potentials. A Fermi level shift of $-22$ mV observed for the Au-TiO$_2$ nanocomposite is indicative of improved charge separation in semiconductor-metal systems and demonstrates its usefulness for improving the efficiency of photocatalytic reactions.

**Surface Interactions of CdSe Quantum Dots:** The excited state interaction between CdSe nanocrystals and a hole acceptor, $p$-phenylenediamine (PPD), was elucidated using emission and transient absorption spectroscopies. The changes in the photophysical properties of CdSe nanocrystals arising from the interaction with PPD were different than those obtained with an aliphatic amine, $n$-butylamine ($n$-BA). At low concentrations (<0.5 mM) $n$-butylamine enhances the emission of CdSe quantum dots whereas PPD effectively quenches the emission at similar concentrations. The low oxidation potential of PPD ($E^{\circ} = 0.26$ V vs NHE) enables it to act as an effective scavenger for photogenerated holes. A surface bound complexation equilibrium model was proposed to explain the quenching phenomenon. The transient absorption measurements confirmed the formation of PPD cation radical and subsequent formation of coupling product. Formation of such charged species at the surface extends the bleaching recovery over several microseconds.

**Assembly of Molecular Clusters on Electrode Surfaces for Photocurrent Generation.** Composite molecular nanoclusters of fullerene and porphyrin were prepared in acetonitrile/toluene mixed solvent to absorb light over entire spectrum of visible light. Both tubular shaped or square shaped microcrystallites were obtained by varying composition and evaporation conditions. The highly colored composite clusters were further assembled as 3 dimensional array onto nanostructured SnO$_2$ films using electrophoretic deposition approach. The composite cluster films exhibit an incident photon-to-photocurrent efficiency (IPCE) as high as 17 % at an applied potential of 0.2 V vs. SCE which is significantly higher than the additive effect observed from either porphyrin (IPCE = 1.6 %) or fullerene clusters (IPCE = 5.0 %) under similar photoelectrochemical conditions. The high IPCE observed with porphyrin and C$_{60}$ clusters demonstrate the synergy of these systems towards yielding efficient photoinduced charge separation within these composite nanoclusters.

**Environmental Remdiation:** By simultaneously carrying out high frequency sonolysis and photocatalysis we have succeeded in achieving faster and complete mineralization with no build up of toxic intermediates even at very low catalyst loadings. Whereas sonolysis is quite effective in the initial degradation of chlorinated aromatic molecules, complete mineralization is difficult to achieve. Photocatalysis is selective towards the degradation of polar aromatics and causes the build up of undesirable chemical intermediates. The synergy of combining the two advanced oxidation processes was established using 2,4 dichlorophenoxo acetic acid as a model compound. The primary events of the oxidative transformation of N-heterocycles, e.g. Quinoline, by different radicals, was elucidated using radiolysis and sonolysis. The hydroxyl radical reacts by adding to both rings of quinoline to form the OH adducts. On the other hand, SO$_4$ oxidizes the quinoline to its radical cation, which further undergoes hydrolysis to yield also the OH adducts.

Nanostructured humic acid membranes on optically transparent electrodes (OTE) were prepared by electrophoretic deposition from a solution of Suwanee River Humic acid (SHA) in ethanol/acetonitrile. The thickness of the film and the rate of deposition of SHA are dependent on the applied voltage and the concentration of the solution. Tapping mode Atomic Force Microscopy (TM-AFM) confirmed the presence of a three-dimensional, porous, assembly of SHA clusters on the electrode surface. The ability of these membranes to incorporate redox-active species such as ferrocene from solution opens new ways to probe binding properties of various chemical species present in the environment.
Awards and Recognition

Served as **Editor** of the scientific journal, Research on Chemical Intermediates (2001-Sep 2003); Serving as **Senior Editor** of the Journal of Physical Chemistry starting October 2003.

**Member** of Board of Directors (2002-2004) and Finance committee (2003-2008) of the Electrochemical Society

Serving the term as a **Chairman** of the Fulerenes, Nanotubes and Carbon Nanostructures Division of the Electrochemical Society (2000-2004)

Japan Society for Promotion of Science (JSPS) Fellowship, July-August 2003

Delivered Plannary/invited lectures at the meetings and chaired sessions at the International Photochemical Society Conference, Nara, Japan; 11th International Conference on Colloid and Surface Science, Brazil; MPND Conference Orleans, France; The American Chemical Society Meeting, New Orleans, and The Electrochemical Society meeting, Paris, France.

Panel member, Grand Challenge Workshop organized by EPA


Invited Lectures


Luminescent semiconductor nanostructures for monitoring low level contaminants. **Grand Challenge Workshop** sponsored by Environmental Protection Agency Washington, DC Invited May 8-9, 2003


Photoresponsive Hybrid Nanostructures , **Univ. of Notre Dame** (Chem. Eng. Sept. 2, 2003)

Photoinduced charge separation in organic - inorganic hybrid nanostructures, **Marquette University** (Chemistry, Sept. 5, 2003)

Photoresponsive Hybrid Nanostructures, **Auburn University** (Chemistry Dept., Oct. 2, 2003)

Inorganic-organic hybrid nanostructures for light energy conversion, **Univ. of Missouri at St. Louis** (Chemistry Dept., Oct. 20, 2003)
Meeting Presentations


Kamat, P. V. 2003 Photoinduced charging events in semiconductor-metal and metal-fluorophore hybrid nanoassemblies. XXI International Photochemistry Conference Nara, Japan Invited July 16-20, 2003


Graduate Research Presentations

Annual Meeting of the American Chemical Society
Nicolaescu, R.
Radiolytic transformations of Quinoline

Notre Dame Environmental Education Research (NDEER) symposium Wednesday, November 12, 2003.
Peller, J.
OH: A strong oxidant for the remediation of chlorinated organic contaminants in water.
Nicolaescu, R.
Radiolytic transformations of Quinoline
Subramanian, V.
Analysis of a Semiconductor - Metal Photocatalyst Using a Continuous Batch Flow Photocatalytic Reactor

AIChE annual meeting, San Francisco, November 2003

Subramanian, V.
Photoinduced Transformations at the Semiconductor -Metal Interface in Films and Solutions
Subramanian, V.
Photophysical, Photocatalytic and Electrochemical Aspects of Semiconductor - Metal Nanocomposite Systems
Subramanian, V.
Fermi Level Equilibration in TiO₂/Au Nanocomposites. Effect of Particle Size
Publications

Published Articles


Submitted/Accepted for Publication


Monographs/Special Volumes


Abstracts of Some Recent Submissions


Chromophore Functionalized Gold Nanoparticles.
George Thomas, K. and P.V. Kamat,

We report in this account the design of chromophore functionalized metal nanoparticles and the detailed investigation of the ground as well as excited state interactions between the metal nanoparticles and the photoactive molecules. Mechanistic details of various deactivation channels of the photoexcited chromophores, such as energy and electron transfer, to the metal nanoparticle are presented. The methodologies adopted for organizing chromophore functionalized gold nanoparticles on to two-dimensional surfaces and their possible applications in photovoltaics and fluorescent display devices are described.


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.


Nanostructured assembly of porphyrin clusters for light energy conversion.
Hasobe, T., H. Imahori, S. Fukuzumi, and P.V. Kamat

Free base porphyrin molecules form well-defined and ordered nanoclusters in mixed solvents with absorption characteristics that significantly differ from those of the monomer form. These self-assembled crystallites in acetonitrile/toluene (9:1, v/v) can be deposited as thin films on nanostructured TiO₂ electrode using an electrophoretic technique. These porphyrin cluster assembly is highly photoactive and capable of undergoing charge separation under visible light excitation. Photoexcitation of the porphyrin film electrode assembly in a photoelectrochemical cell with visible light produces relatively high photocurrent generation. A maximum photocurrent of 0.15 mA cm⁻² and a photovoltage of 250 mV were attained using I₃⁻/I⁻ redox couple. The electron flow to TiO₂ electrode can be facilitated by application of a positive potential. An incident photon-to-current conversion efficiency (IPCE) of 2.0 % has been achieved at an applied bias potential of 0.2 V vs. SCE. The broad photoresponse of these crystallites throughout the visible range as well as the ease of assembling them on the electrode surface opens up new avenues for harvesting a wide wavelength range of solar light.


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.
Hasobe, T., H. Imahori, S. Fukuzumi, and P.V. Kamat

**Efficient Photocurrent Generation using Electrophoretic Deposition**

Composite molecular nanoclusters of fullerene and porphyrin prepared in acetonitrile/toluene mixed solvent absorb light over entire spectrum of visible light. Upon slow evaporation of the solvent on the copper grid, these mixed nanoclusters undergo close packed stacking to produce either tubular shaped or square shaped microcrystallites and differ from those obtained from single component clusters. The highly colored composite clusters can be assembled as 3 dimensional array onto nanostructured SnO2 films using electrophoretic deposition approach. The composite cluster films exhibit an incident photon-to-photocurrent efficiency (IPCE) as high as 17 % at an applied potential of 0.2 V vs. SCE which is significantly higher than the additive effect observed from either porphyrin (IPCE = 1.6 %) or fullerene clusters (IPCE = 5.0 %) under similar photoelectrochemical conditions. The high IPCE observed with porphyrin and C60 clusters demonstrate the synergy of these systems towards yielding efficient photoinduced charge separation within these composite nanoclusters.

**Adv. Mater. 2003, submitted.**

*Supramolecular Photovoltaic Cells of Porphyrin Dendrimers and Fullerene.*

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

Organic photovoltaic cells using supramolecular complexes of porphyrin dendrimers with fullerene demonstrate remarkable enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and infrared regions relative to the reference system. This demonstrates that molecular assemblies of C60 and porphyrins with dendric structures are effective in light energy conversion systems.


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

Zeena Pilai and P.V. Kamat

We have investigated the early reduction steps using pulse radiolysis to understand the role of sodium citrate towards the growth of particles. 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.


*Fullerene Based Carbon Nanostructures for Methanol Oxidation*

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

Films of C60 clusters were electrophoretically deposited on optically transparent electrode surfaces. These C60 films constitute a new class of carbon electrodes with properties that differ from graphite and diamond electrodes. These films are quite stable to oxidative potentials and hence provide an electrochemical window to carry out oxidation processes. The electrophoretically deposited C60 cluster film is highly porous and consists of C60 clusters that are assembled in orderly fashion. Upon electrophoresis of platinum particles, these nanostructured carbon films show remarkable activity towards methanol oxidation. The dependence of methanol oxidation on the amount of platinum and C60 in a half cell reaction demonstrates the role of fullerene nanoclusters as new form of carbon support.

**Comptes Rendus Chimie, 2003 6, 999-1007**

*Nanoscience Opportunities in Environmental Remediation*

P. V. Kamat and D. Meisel

Semiconductor nanostructures play an important role in developing smart materials that can simultaneously sense and destroy harmful chemical contaminants from our environment. This review article highlights some recent advances of nanoscience in the area of environmental remediation. The potential for improving the effectiveness of photocatalytic processes by means of semiconductor-metal nanocomposites and merits of combining two advanced oxidation processes are discussed.
Quaternary Self-Organization of Porphyrin and Fullerene Units by Clusterization with Gold Nanoparticles on SnO2 Electrodes for Organic Solar Cells.

Hasobe, T., H. Imahori, S. Fukuzumi, and P.V. Kamat

Herein we report novel organic solar cells prepared using quaternary self-organization of porphyrin (donor) and fullerene (acceptor) dye units by clusterization with gold nanoparticles on SnO2 electrodes. Remarkable enhancement of fullerene (acceptor) dye units by clusterization with gold using quaternary self-organization of porphyrin (donor) and computational studies of the formation of the dichlorophenoxyl radical.

Mechanism of Hydroxyl Radical-Induced Breakdown of the Herbicide 2,4-Dichlorophenoxyacetic Acid

J. Peller, O. Wiest and P. V. Kamat

Oxidative transformations by the hydroxyl radical are significant in advanced oxidation processes for the breakdown of organic pollutants, yet mechanistic details of the reactions are lacking. A combination of experimental and computational methods has been employed in this study to elucidate the reactivity of the hydroxyl radical with the widely used herbicide 2,4-D. The experimental data on the reactivity of the hydroxyl radical in the degradation of the herbicide 2,4-D was attained from \( \gamma \)-radiolysis experiments using both \( ^{18} \text{O} \)-labeled water and unlabeled water. This was complemented by computational studies of the \( \cdot \text{OH} \) attack on 2,4-D and 2,4-DCP (2,4-dichlorophenol) in gas phase and in solution. These studies established the main reaction pathway of \( \cdot \text{OH} \) on 2,4-D. In addition, the majority of the early intermediates in the reaction between the hydroxyl radical and 2,4-DCP, the major intermediate, were identified experimentally. While the hydroxyl radical attacks 2,4-D by \( \cdot \text{OH} \)-addition to the aromatic ring, the oxidative breakdown of 2,4-DCP occurs through both \( \cdot \text{OH} \)-addition and the formation of the dichlorophenoxyl radical.

Charge Transfer on the Nanoscale


This is the report of a DOE sponsored workshop organized to discuss the status of our understanding of charge transfer processes on the nanoscale and to identify research and other needs for progress in nanoscience and nanotechnology. The current status of basic electron-transfer research, both theory and experiment, is addressed, with emphasis on the distance dependent measurements, and we have attempted to integrate terminology and notation of solution electron transfer kinetics with that of conductance analysis. The interface between molecules or nanoparticles and bulk metals is examined and new research tools that advance description and understanding of the interface are presented. The state of the art efforts in the area of molecular electronics is summarized along with further research needs. Finally, novel strategies of nanoscale architectures based on photochemistry, catalysis and electrocatalysis are presented for enhancing the efficiencies of energy conversion.
Electrophoretic Assembly of Naturally Occurring Humic Substances as Membranes
K. Vinodgopal, V. Subramanian, S. Carrasquillo, P. V. Kamat

Nanostructured humic acid membranes on optically transparent electrodes (OTE) have been prepared by electrophoretic deposition from a solution of Suwanee River Humic acid (SHA) in ethanol/acetonitrile. The thickness of the film and the rate of deposition of SHA are dependent on the applied voltage and the concentration of the solution. Tapping mode Atomic Force Microscopy (TM-AFM) confirms the presence of a three-dimensional, porous, assembly of SHA clusters on the electrode surface. The ability of these membranes to incorporate redox-active species such as ferrocene from solution has been demonstrated by cyclic voltammetry experiments. A linear dependence of the peak current for the oxidation of ferrocene as a function of scan rate indicates that the ferrocene is incorporated into the humic membrane.

Photoinduced Transformations at Semiconductor/Metal Interface: EXAFS Investigation of UV-irradiated Au-TiO2 Films
D. L. Dey V. Subramanian, T. Shibata, E. E. Wolf, B. A. Bunker, and P. V. Kamat

Nanostructured TiO2 films modified with gold nanoparticles are photoelectrochemically active under UV-excitation and deliver photocurrent when used as a photoanode in a photoelectrochemical cell. The photogenerated holes are capable of oxidizing gold at the TiO2 interface and cause the overall photoelectrochemical performance of the composite film to decrease. As gold ions generated during photooxidation interact with the TiO2 nanoparticles, the band edge shifts into the visible. X-ray absorption fine structure (XAFS) of pre- and post- UV-irradiated TiO2/Au samples have provided quantitative local structural information for these samples. We have observed a remarkable change of the near neighbor species between these samples. The Au ions which are coordinated mostly with Ti and oxygen atoms prior to UV illumination exhibits clustered gold atom features following UV-illumination.

Synergy of Combining Sonolysis and Photocatalysis in the Degradation and Mineralization of Chlorinated Aromatic Compounds
J. Peller, O. Wiest, and P. V. Kamat

Merits of using advanced oxidation processes such as sonolysis and photocatalysis as well as a combination of the two have been explored using model herbicides such as 2,4-dichlorophenoxy acetic acid and 2,4-dichlorophenoxypropionic acid and the chlorinated phenols 2,4-dichlorophenol and 2,4,6-trichlorophenol. Whereas sonolysis is quite effective in the initial degradation of chlorinated aromatic molecules, complete mineralization is difficult to achieve. Photocatalysis is selective towards the degradation of polar aromatics and causes the build up of undesirable chemical intermediates. In contrast to sonolytic degradation, photocatalysis is very effective towards achieving complete mineralization. By simultaneously carrying out high frequency sonolysis and photocatalysis we have succeeded in achieving faster and complete mineralization with no build up of toxic intermediates even at very low catalyst loadings. The synergy of combining the two advanced oxidation processes is discussed.

Radical Induced Oxidative Transformation of Quinoline
R. Nicolaescu, O. Wiest, P. V. Kamat

The primary events of the oxidative transformation of Quinoline, an environmental pollutant, by different radicals, have been investigated using pulse radiolysis. The hydroxyl radical react by adding to both rings of quinoline to form the OH adducts. On the other hand, SO4°* oxidizes the quinoline to its radical cation, which further undergoes hydrolysis to yield also the OH adducts. The possibility of the quinoline radical cation to undergo hydrolysis was independently verified by generating the radical cation under laser induced photoionization conditions. The quinoline radical cation produced in acetonitrile shows high reactivity towards water. The rate for OH reaction is higher (k = 1 x 10^10 M^-1 s^-1) than that found for SO4°* reaction (k = 3.5 x 10^8 M^-1 s^-1). Quinoline is much less reactive towards N3° and O° radicals. Mechanistic understanding of the primary oxidation pathway of quinoline could aid in designing strategies for the abatement of pollutants containing nitrogen heterocycles.

Assembling Fullerenes as Nanoclusters and Films
P. V. Kamat and K. George Thomas

Fullerenes and their derivatives readily form self-assembled molecular clusters in mixed solvents. These molecular clusters are optically transparent and thermodynamically stable. Furthermore, one can dope these spherical fullerene assemblies with electron donors such as Ferrocene, amines, phenothiazine. The size and shape of these clusters can be altered with structural modifications. These clusters can be readily assembled as 3-dimensional array on a conducting glass electrode. These interesting fullerene nanostructures show unusual electrochemical sensing and light energy conversion properties. Salient features of these nanostructures are described here.

Photoinduced charge transfer between CdSe nanocrystals and p-phenylenediamine.
S. Sharma, Z.S. Pillai, and P.V. Kamat

The excited state interaction between CdSe nanocrystals and a hole acceptor, p-phenylenediamine (PPD), is probed using emission and transient absorption spectroscopies. The changes in the photophysical properties of CdSe nanocrystals arising from the interaction with PPD are compared with an aliphatic amine, n-butylamine (n-BA). At low concentrations (~0.5 mM) n-butylamine enhances the emission of CdSe quantum dots whereas PPD effectively quenches the emission at similar concentrations. The low oxidation potential of PPD (\(E^\circ = 0.26\) V vs NHE) enables it to act as an effective scavenger for photogenerated holes. A surface bound complexation equilibrium model has been proposed to explain the quenching phenomenon. The transient absorption measurements confirm the formation of PPD cation radical and subsequent formation of coupling product.


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

Photoinduced electron accumulation in ZnO nanoparticles results in the bleaching of the exciton band as well as quenching of green emission. In the absence of an electron scavenger, photogenerated electrons are stored near the conduction band edge and promote charge recombination via a nonradiative process. When gold nanoparticles are added to pre-UV-irradiated ZnO colloids, only partial recovery of the emission is seen. Pt nanoparticles on the other hand caused almost complete recovery of the quenched emission as the electrons are discharged into the solution. The charge distribution between UV-irradiated ZnO and gold nanoparticles results in equilibration of the Fermi level. Basic understanding of the interaction between the semiconductor and metal layers leading to Fermi-level equilibration is important for evaluating the role of noble metals in photocatalytic reactions.


Mass-Transfer and Kinetic Studies during the Photocatalytic Degradation of an Azo Dye on Optically Transparent Electrode Thin Film
Subramanian, V., P. V. Kamat and E. E. Wolf,

We have studied the various parameters that affect the kinetics of the degradation process for an azo dye in an aquatic flow system using a novel batch continuous-loop flow reactor with TiO\(_2\) colloids immobilized on a flat substrate. A detailed study of physical parameters including light intensity, flow rate, stirring, catalyst loading, dye concentration, and temperature has been performed to obtain the reaction kinetics independent of mass-transport limitations. We have studied the effect of metal nanoparticles on the photocatalytic activity of TiO\(_2\) under the optimized conditions of a flow reactor to determine the role of metal nanoparticles in the photocatalytic degradation of AO7.


Charge Distribution between UV-Irradiated TiO\(_2\) and Gold Nanoparticles. Determination of Shift in Fermi Level
Jakob, M., H. Levanon, and P.V. Kamat

TiO\(_2\) nanoparticles when subjected to UV irradiation exhibit blue coloration as electrons are stored within the particles. Upon contact with gold nanoparticles, a partial disappearance of the blue color is seen as the stored electrons are transferred from TiO\(_2\) to Au nanoparticles. The charge distribution between the semiconductor and metal nanoparticles causes the Fermi level to shift to more negative potentials. By employing C\(_{60}\)-C\(_{60}\) as a probe-redox couple, we were able to estimate the apparent Fermi levels of TiO\(_2\) and TiO\(_2\)/Au nanoparticles. A Fermi level shift of -22 mV observed for the Au-TiO\(_2\) nanocomposite is indicative of improved charge separation in semiconductor-metal systems and demonstrates its usefulness for improving the efficiency of photocatalytic reactions.


Photoinduced Electron Transfer Processes in Fullerene Based Dyads with Heteroaromatic Donors.
George Thomas, K., V. Biju, D.M. Guldi, P.V. Kamat, and M.V. George

Two classes of fullerene-based donor-bridge-acceptor (D-B-A) systems containing donors of varying oxidation potentials have been synthesized. An increase in the rate constant and quantum yield of charge separation (\(k_{cs}\) and \(\Phi_{cs}\)) has been observed for both classes of dyads, with decrease in the oxidation potentials of the donor groups. This observation indicates that the rates of the forward electron transfer fall in the normal region of the Marcus curve. The long-lived charge separation enabled the characterization of electron transfer products, namely, the radical cation of the donor and radical anion of the pyrroldinofullerene, by using nanosecond transient absorption spectroscopy. The small reorganization energy (\(\xi\)) of C\(_{60}\) coupled with large negative free energy changes (\(-\Delta G^\circ\)) for the back electron transfer places the back electron process in the inverted region of Marcus curve, thereby stabilizing the electron transfer products.
Summer of 2003 at Notre Dame

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