**PHOTOCHEMICAL SOLAR ENERGY CONVERSION
UTILIZING SEMICONDUCTORS LOCALIZED
IN MEMBRANE-MIMETIC SYSTEMS**

Performance Report
DOE/ER/13506--37

April 1, 1989, to August 31, 1991

Janos H. Fendler
Department of Chemistry
Syracuse University
Syracuse, New York 13244-4100

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I. SUMMARY

Extending the frontiers of colloidal photochemistry and colloidal electrochemistry to solar photochemistry research had been the main objective of the research proposed to the Office of Basic Energy Sciences for the period of April 1, 1989, to March 31, 1992. More specific objectives of this proposal included the examination of semiconductor-particle-mediated photoelectron transfer and photoelectric effects in different membrane mimetic systems. Emphasis had been placed on developing bilayer lipid membranes (BLMs) and Langmuir-Blodgett (LB) films as new membrane-mimetic systems, as well as on the characterization and utilization of these systems. The major objectives of the proposed research have been accomplished. Work completed under this grant from April 1, 1989, to August 31, 1991, has led to 18 publications and 22 oral presentations at national and international meetings and institutions. A brief narrative summary of the published work is provided in the following pages, along with reprints of published papers and abstracts of manuscripts which are in press or have been submitted for publication.

II. SCIENTIFIC PROGRESS

A. *Semiconductor Particles in Vesicles*

Surfactant vesicles have continued to be utilized for the compartmentalization of the components of the artificial photosynthetic apparatus. The relative simplicity of surfactant vesicles rendered them to be useful for developing methodologies for the more complex bilayer lipid membranes (BLMs) and Langmuir-Blodgett (LB) films.

We have investigated dihexadecyl phosphate (DHP), vesicle-stabilized, *in situ*-generated, mixed CdS and ZnS semiconductor particles. Depending on the experimental conditions selected, either colloidal mixed crystals of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ or ZnS-coated CdS or CdS-coated ZnS particles were formed. Investigations of these vesicle-incorporated semiconductor particles by absorption and fluorescence spectroscopy, as well as by X-ray diffraction and laser-flash photolysis, revealed subtle and controllable changes in their bandgaps, reduction potentials, and photoelectron transfer efficiencies. Differences in the composition of the surfactant-vesicle-incorporated semiconductor particles have also manifested in different efficiencies of hydrogen generation in the presence of benzyl alcohol as a sacrificial electron donor.¹

Photocurrents have also been measured in aqueous solutions containing DHP-vesicle-incorporated CdS particles in the presence of methylviologen and glucose as a sacrificial electron donor (Figure 1). The ability of measuring photocurrent in microheterogeneous surfactant-vesicle solutions provided a means for the determination of Fermi levels at the surface of semiconductor particles. As expected, the flat-band potential varied significantly from preparation to preparation. Organized surfactant assemblies, thus, provided a convenient means for fine tuning semiconductor energy levels.³

Figure 1. Plot of photocurrent against irradiation time of a 2.0 mL solution of DHP- (2.0 mM) vesicle-incorporated CdS (0.2 mM) particles containing 1.0 mM glucose and 1.0 mM MV^{2+} at pH = 10. Arrows indicate the turning on and turning off of the 450 W Xenon lamp used for the irradiation (400 nm cut off and water filters). The lamp delivered 1.0 W/cm^2 radiant energy.

Methodologies have been developed for the *in situ* formation of cadmium, lead, indium, and zinc selenide particles on the surfaces of negatively charged DHP and positively charged dioctadecyldimethylammonium bromide (DODAB) vesicles. Two different chemical approaches have been taken. In the first method, the metal-selenide particles were generated from the metal-ion-coated vesicles by exposure to gaseous hydrogen selenide. In the second method, metal-selenide particles were formed by the chemical reduction of SeO_2 and M^{2+} in the presence of vesicles. Photoelectron transfer to methylviologen has been demonstrated for DODAB vesicles containing cadmium-selenide particles in the presence of sacrificial electron donors.⁶

B. *Semiconductor Particles in Bilayer Lipid Membranes*

Considerable progress has been made in the characterization of BLM-supported semiconductor and mixed-semiconductor particles and semiconductor junctions. Separation of two aqueous solutions by the BLM has allowed the convenient measurement of electrical and electrochemical properties by using macroscopic electrodes. Simultaneous electrical and spectroscopic monitoring of semiconductor particle formation on the BLM surface, as well as photoelectron transfer therein, afforded unprecedented fundamental insights.

Injection of an appropriate metal-ion precursor into one side (*cis* side) and hydrogen sulfide into the other side (*trans* side) of aqueous solutions bathing the opposites sides of a BLM has been shown to lead to the formation of cadmium, lead, zinc, mercury, and indium sulfide semiconductor particulate films. Depending on the concentration of H_2S and its infusion time, semiconductor particles of different thicknesses could be formed on the BLM surface. The proposed porous semiconductor particulate film formation and the arrangement of the working (E_W), reference (E_R), and counter (E_C) electrodes are illustrated schematically in Figure 2. Experimental conditions have been developed for the formation of a single composition of semiconductor particulate films deposited on only one side of a BLM, two different compositions of semiconductor particulate films sequentially deposited on the same side of a BLM, and two different compositions of semiconductor particulate films deposited on the opposite side of a BLM (Figure 3). Electrochemical measurements established current-rectifying behavior and the presence of n-type (CdS , ZnS , and In_2S_3) and p-type ($\text{Cu}_{2-(x+y)}\text{S}$) electrolyte-semiconductor (ES) junctions or semiconductor-semiconductor (SS') heterojunctions. Interestingly, prolonged voltammetric cycling converted the semiconductor particulate films on the BLM surfaces from n- to p-type behavior.⁵

Figure 2. Schematics of the semiconductor-particulate-film-coated BLM.

Figure 3. Schematic representation of the different semiconductor-coated BLMs. A single composition of particulate semiconductor deposited only on one side of the BLM constituted System A. Two different compositions of particulate semiconductors sequentially deposited on the same side of the BLM represent System B. Finally, two different compositions of particulates deposited on the opposite sides of the BLM made up System C.

Bandgap irradiation of a cadmium-sulfide semiconductor particulate film deposited on a glyceryl monooleate (GMO) BLM resulted in measurable photoelectric effects. The observed development of photovoltage has been rationalized in terms of generation of $O_2^{\cdot-}$ and H^+ in the opposite sides of the GMO BLM and that of its decay by the recombination of charges via mass transport of the ions across the BLM.⁴

C. *Semiconductor Particulate Films Formed at Monolayer Surfaces*

Perhaps the most significant accomplishment has been the development of a new versatile method for the formation of semiconductor particulate films which could be investigated both at monolayer surfaces and subsequent to their transfer onto solid supports in the solid state. The approach has been inspired by the formation of semiconductor particulate films at BLM interfaces.

Hydrogen sulfide or hydrogen selenide, introduced into an atmosphere, was allowed to infuse slowly across the compressed monolayer in contact with the aqueous metal counterion precursor of the semiconductor particulate film (Figure 4).^{8,9,11-13} Controlled infusion of the gas has resulted in the formation of covalent metal-sulfide or selenide bonds at a large number of sites at the compressed monolayer interface. The nascent metal sulfide microclusters grew laterally to linked, 30-50 Å diameter, 10-30 Å thick polyparticulates. With continued infusion of H₂S or H₂Se, these polyparticles formed an interconnected semiconductor particulate film whose thickness grew to several hundred angstroms (Figure 5). The growth of the semiconductor particulate films has been monitored by reflectivity measurements in the film balance. The semiconductor particulate films, at any stage of their growth, could be quantitatively transferred to a solid support. Absorption and emission spectroscopy, electron microscopy, X-ray diffraction, scanning tunneling microscopy, and scanning tunneling spectroscopy have been used for the characterization of semiconductor particulate films. Importantly, evidence has been obtained for size quantization and dimensionality reduction. Furthermore, photoelectron transfer has been shown to be dependent on the sizes of the semiconductor particles.

Incorporation of size-quantized semiconductor particles between the hydrophilic headgroups of Langmuir-Blodgett films has also been demonstrated.

Figure 4. Schematics of the experimental arrangements used for the generation of semiconductor particles at the negatively charged, surfactant headgroup-aqueous (1.0×10^{-3} M MCl_2) subphase interface and that used for the in situ monitoring of reflectivities: P, polarizer; D, detector; R, chart recorder.

Figure 5. Proposed schematics for the initial (a) and subsequent (b and c) growth of a monolayer-supported, porous, semiconductor particulate film.

More details on these studies are provided in the publications appended to this Performance Report.

III. SCIENTIFIC PERSONNEL

Dr. Janos H. Fendler
Principal Investigator

Dr. Subhash Baral
Research Assistant Professor

Dr. David Yogev
Postdoctoral Associate

Dr. Ottó Horváth
Postdoctoral Associate

Mrs. Kyunghee C. Yi
Graduate Student

Ms. Christine Dolan
Graduate Student

Mr. Jianping Yang
Graduate Student

IV. PUBLICATIONS

Dihexadecyl Phosphate, Vesicle-Stabilized and In-Situ-Generated Mixed CdS and ZnS Semiconductor Particles. Preparation and Utilization for Photosensitized Charge Separation and Hydrogen Generation, H.-C. Youn, S. Baral, and J. H. Fendler, J. Phys. Chem., 92, 6320-6327 (1988) (DOE/ER/13506--17).

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Size-Quantized Semiconductor Particles Formed at Monolayer Surfaces, X. K. Zhao, Y. Yuan, and J. H. Fendler, J. Chem. Soc. Chem. Commun., 1248-1252 (1990) (DOE/ER/13506--32).

In Situ Imaging of CdS and ZnS Semiconductor Particles in Surfactant Vesicles, B. R. Heywood, J. H. Fendler, and S. Mann, J. Coll. Interf. Sci., 138, 295-298 (1990) (DOE/ER/13506--33).

Membrane Mimetic Chemistry, J. H. Fendler, 1989 McGraw-Hill Encyclopedia of Science and Technology (1990) (DOE/ER/13506--38).

Semiconductor Particulate Films on Solid Supports, X. K. Zhao and J. H. Fendler, Chemistry of Materials, 3(1), 168-174 (1991) (DOE/ER/13506--39).

Size Quantization in Semiconductor Particulate Films, X. K. Zhao and J. H. Fendler, J. Phys. Chem., 95, 3716-3723 (1991) (DOE/ER/13506--40).

Electrical and Photoelectrochemical Characterization of CdS Particulate Films by Scanning Electrochemical Microscopy, Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy, X. K. Zhao, L. D. McCormick, and J. H. Fendler, Chemistry of Materials, in press (1991).

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Size-Quantized Particles at Artificial Membrane Interfaces, J. H. Fendler, "Proceedings of the Workshop on the Design and Processing of Materials by Biomimicking", in press (1991).

V. ORAL PRESENTATIONS

Year	Date	Place	Title
1989	June 12-15	Thirteenth Department of Energy Solar Photochemistry Research Conference Silver Creek, Colorado	Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane Mimetic Systems (DOE/ER/13506--24)
1989	July 23-28	III U.S./China/Japan Meeting on Macromolecule-Metal Complexes Lawrenceville, New Jersey	Bimolecular Thick Membranes as Supports for Semiconductors and Magnetic Particles: Characterization, Utilization, and Potential (DOE/ER/13506--25)
1989	October 19	Chemistry Department Rensselaer Polytechnic Institute Troy, New York	Size-Quantized Particles in Organized Assemblies
1989	November 6-9	International Symposium on Self-Assembly of Organic Compounds Kyushu University Fukuoka, Japan	Bilayer Lipid Membrane-Supported Electronic Devices (DOE/ER/13506--26)
1990	May 6-11	177th Meeting of the Electrochemical Society Montreal, Quebec, Canada	Bilayer Lipid Membrane-Supported Electronic Devices (DOE/ER/13506--34)
1990	June 4-10	Fourteenth Department of Energy Solar Photochemistry Research Conference Lake Harmony, Pennsylvania	Size-Quantized Semiconductor Particles Formed at Monolayer Surfaces (DOE/ER/13506--35)
1990	August 20-24	1990 International Congress on Membranes and Membrane Processes Chicago, Illinois	Surface Modified Bilayer Ultrathin Membranes (DOE/ER/13506--36)

Year	Date	Place	Title
1990	August 26-31	200th National Meeting of the American Chemical Society, Symposium of Past Kendall Laureates Washington, D.C.	Silver and Semiconductor Particle Formation at Monolayer Interfaces (DOE/ER/13506--41)
1990	October 2	Department of Chemical Engineering, Pennsylvania State University University Park, Pennsylvania	Membrane Mimetic Chemistry
1990	October 15	Institute of Biophysics Simmelweis Medical University Budapest, Hungary	Bilayer Lipid Membrane Supported Electronic Devices
1990	October 18	Hungarian Academy of Science Budapest, Hungary	Artificial Photosynthesis in Surfactant Vesicles - Physical Chemistry of Membrane Models
1990	October 19	ELTE, Department of Colloid Science Budapest, Hungary	Generation of Nanosized Two- Dimensional Particles at Monolayer Interfaces
1990	October 22	JATE, Department of Colloid Chemistry Szeged, Hungary	Interactions and Reactions in Reversed Micelles
1990	October 24	Academy of Szeged Szeged, Hungary	Preparation of Size-Quantized Semiconductor and Magnetic Particles in Model Membranes
1990	October 25	Lajos Kossuth University Debrecen, Hungary	Preparation and Characterization of Polymerized Surfactant Aggregates
1990	October 26	Institute of Biophysics, Biological Research Center Hungarian Academy of Sciences Szeged, Hungary	Mechanisms of Membrane Fusion
1990	November 6	Dow Lecture Series Bucknell University Lewisburg, Pennsylvania	Membrane Mimetic Chemistry

Year	Date	Place	Title
1991	March 5	La Societe Royale de Chimie Lecture, University of Namur, Belgium	Size-Quantized Silver and Semiconductor Particulate Films
1991	April 2-4	Workshop on the Design and Processing of Materials by Biomimicking, Seattle, WA	Size-Quantized Particles at Artificial Membrane Interfaces (DOE/ER/13506--42)
1991	May 5-10	179th Electrochemical Society Meeting, Washington, DC	Photoelectron Transfer at Size- Quantized Semiconductor Particles (DOE/ER/13506--43)
1991	June 2-6	Fifteenth Department of Energy Solar Photochemistry Research Conference, Snowmass, Colorado	Photochemical Solar Energy Conversion Utilizing Semiconductors Localized in Membrane Mimetic Systems (DOE/ER/13506--44)
1991	July 7-13	7th International Conference on Surface and Colloid Science Compiègne, France	Scanning Tunneling Microscopic, Optical, and Scanning Tunneling Spectroscopic Characterization of Size-Quantized Cadmium Selenide Particulate Films <i>In</i> <i>Situ</i> Generated at Monolayer Interfaces (DOE/ER/13506--45)

VI. STATEMENT OF REMAINING FUNDS

All funds from this grant will be spent by the end of the project period (March 31, 1992).

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