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SEMICONDUCTORS IN MEMBRANE MIMETIC SYSTEMS

JANOS H. FENDLER*

Department of Chemistry
Syracuse University
Syracuse, New York 13244-1200

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Abstract - *In situ* generation and stabilization of colloidal semiconductors in synthetic single-bilayer surfactant and polymerized surfactant vesicles are described. Vesicles provide sites for the formation of controllable-sized semiconductors; shift the equilibrium between nucleation and particle growth in favor of the former; effect band gaps, reduction and oxidation potentials; and influence electron transfer to and from donors and acceptors located on, or in close proximity to, the semiconductor. A brief description of the properties of surfactant vesicles and polymerized surfactant vesicles is provided. Quantum size effects in, and water photoreduction by, vesicle-stabilized, colloidal CdS are then discussed in some detail.

I. Introduction

Electrical conductivities of semiconductors are intermediate between those of insulators and metals. Properties of semiconductors are best described in terms of the band theories of solids.[1] This theory can be explained either by chemical or physical arguments. The chemical approach considers the broadening of discreet energy levels and the formation of bands upon the overlap of the atoms constituting the solid. The higher energy band, normally occupied by electrons, is called the conduction band, CB, while the band containing valence electrons is referred to as the valence band, VB. The energy difference between the conduction and valence bands is defined by the bandgap.

Description of energy levels for semiconductors associated with ions in solution is more complex. The electric field set up at the solid semiconductor-redox couple containing solution interface results, in the language of semiconductor photoelectrochemistry,[2] in band bending. Simply stated, band bending implies the development of VB and CB energies at the surface of the semiconductor which differ from those present in its interior. An important consequence of band bending is that VB and CB energies determined in solid-state devices are expected to change upon placing the semiconductor in a polar solution.

Up to fairly recently, preparations, characterizations and utilizations of semiconductors have been restricted to solid-state, crystalline, microcrystalline and amorphous systems. The entry of photophysical chemists has been signaled by their studies in dispersed colloidal semiconductors. Their interest has primarily centered on semiconductor-mediated oxidations and reductions, particularly those related to water splitting.[3-5] Dispersed colloidal semiconductors offer a number of advantages. They have broad absorption spectra and high extinction coefficients at appropriate band energies. They are relatively inexpensive and can be sensitized by doping or by physical or chemical modifications. Dispersed colloidal semiconductors have high surface areas and can, therefore, function as efficient light harvesters. Subsequent to photoexcitation, colloidal semiconductors function as pools of electrons and holes (Figure 1) which, in principle, allow for multielectron transfer processes. Colloidal semiconductors can be prepared small enough to minimize interference due to scattered light and allow direct flash photolytic investigations of electron transfers.

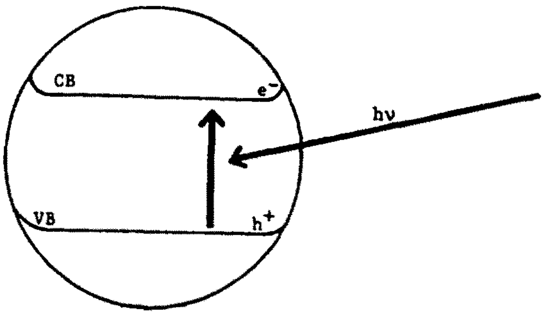


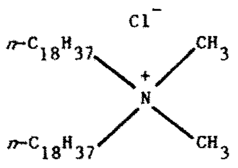
Figure 1: Schematic illustration of a colloidal semiconductor. Bandgap excitation promotes electrons from the valence band, VB, to the conduction band, CB. In the absence of electron donors and/or acceptors of appropriate potential at the semiconductor surface or close to it, most of the charge-separated, conduction-band electrons, e^-_{CB}, and valence band holes, h^+_{VB}, non-productively recombine. Notice the band bending at the semiconductor interface.

Unfortunately, colloidal semiconductors also suffer from a number of disadvantages. Until recently, they could not be reproducibly prepared as small (less than 20 nm in diameter), monodispersed particles. Small and uniform particles are needed to diminish non-productive electron-hole recombinations. The smaller the semiconductor particle, the greater the chance of the escape of the charge carriers to the semiconductor surface where electron transfer can occur. There is a minimum size, however, which semiconductors must reach before absorption occurs at the bulk bandgap (i.e., before the polymolecular particle becomes a semiconductor). The onset of semiconducting properties for CdS has been estimated to occur for particles whose diameters reach 6 nm. Semiconductors are difficult to maintain in solution for extended times in the absence of stabilizers. Stabilizers are bound to affect, of course, the photoelectrical behavior of semiconductors. Their modification, and their coating by catalysts are, at present, more of an art than a science. Furthermore, the lifetime of electron-hole pairs in semiconductors is orders of magnitude shorter than the excited-state lifetime of typical organic sensitizers. This is due to the very much faster undesirable electron-hole recombinations than those observed in homogeneous solutions. Quantum yields for charge separations in colloidal semiconductors are, therefore, disappointingly low.

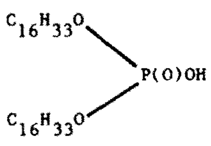
Some of these difficulties have been overcome by incorporating colloidal semiconductors into polyurethane films,[6] Nafion membranes[7] and reversed micelles.[8,9] Emphasis will be placed in the present article on the use of organized surfactant bilayers as media for the *in situ* generation, size control and stabilization of dispersed colloidal semiconductors. Prior to presenting our recent results, physical-chemical properties of bilayer surfactant vesicles[10,11] and polymerized vesicles[12] will be discussed.

II. Surfactant Vesicles and Polymerized Surfactant Vesicles

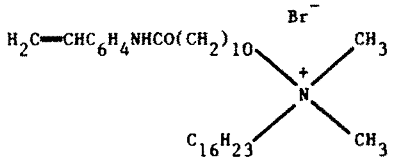
Relatively simple surfactants of the type **1-6** have been shown to form closed bilayer structures, called vesicles (Figure 2).[10]



DODAC, **1**



DHP, **2**



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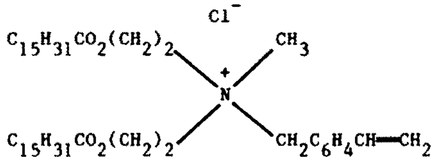

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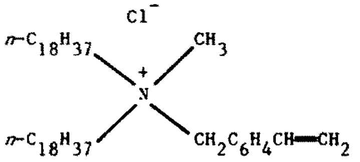

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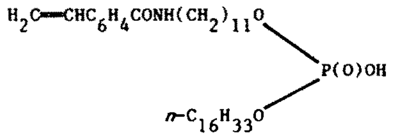

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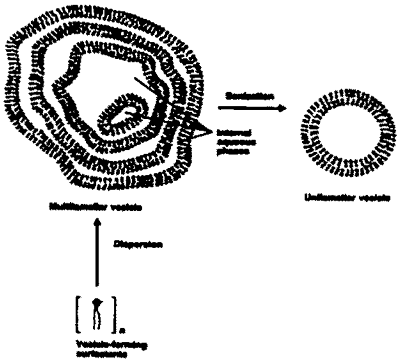

Figure 2: Formation of surfactant vesicles

Vesicles can be prepared in a number of types and sizes. Small unilamellar vesicles (SUVs), with diameters of 200 to 500 Å; large unilamellar vesicles (LUVs), with diameters of 1000 to 10,000 Å; and multilamellar vesicles (MLVs), with diameters of 1000 to 8000 Å, have been characterized.

LUVs are prepared by injecting an ether solution of phospholipids into warm water, by removing, under reduced pressure, the organic solvents from water-in-oil microemulsions of phospholipids, or by adding calcium ion and ethylenediaminetetraacetic acid, EDTA, to SUVs. MLVs form when dried phospholipids or surfactants swell in water.

Sonicating MLVs above the temperature at which they are transformed from a gel to a liquid causes SUVs to form. SUVs also can be prepared by injecting a solution of the phospholipid or surfactant in alcohol through a small-bore syringe into water, by diluting phospholipid detergent micelles, by gel filtration or dialysis, or by dispersing swollen phospholipids through a press. Uniform SUVs are prepared by ultracentrifugation and gel filtration. Most quantitative investigations of vesicles have been carried out on SUVs prepared from well-characterized phospholipids.

Both SUVs and MLVs undergo temperature-induced phase transitions. At low temperature, phospholipids are arranged in tilted one-dimensional lattices. At temperatures just below the transition, two-dimensional arrangements form. Above the main phase transition temperature, phospholipids revert to one-dimensional arrangements, separated somewhat from each other, and assume liquid-like configurations.

Surfactant vesicles are in highly ordered gel (solid) states below their phase transition temperatures, but they are in a fluid (liquid) state above it. The temperature and range of the phase transition are affected by the nature of the phospholipid or surfactant forming the vesicle or by adding electrolytes and substrates.

Below their phase transition temperatures, SUVs with diameters of about 300 Å grow spontaneously to vesicles with diameters of about 900 Å. The larger vesicles remain stable for several weeks.

Electrolytes and certain hydrophobic substances in moderate concentrations (about 10^{-2} M) also can cause vesicles to grow. Higher concentrations of electrolytes, ethanol, and detergents destroy vesicles.

Vesicles are dynamic structures. They undergo phase transitions and fusion, and they shrink if electrolytes are externally added and swell if placed in a solution that is more dilute than the internal electrolyte concentration inside the vesicles. Molecular motions of individual phospholipids in vesicles are quite varied. Kink formation, rotational and segmental motions, lateral diffusion, and transverse motion from one interface of the bilayer to the other (flip-flop) have been recognized.

Vesicles interact with, transport, and are permeable to substrates. Hydrophobic molecules can be distributed among vesicle bilayers. Alternatively, they can be anchored by a long chain terminating in a polar head group. Polar molecules, particularly those that are electrostatically repelled from the inner surface, move freely in water pools trapped within vesicles.

Once large substrates are trapped they remain within the vesicles for days to weeks. Small ions either can diffuse across the bilayers or be transported through the bilayers with the aid of pores or carriers.

The need for enhanced stability and greater permeability control leads to the development of polymerized vesicles.[12] Vesicles prepared from polymerizable surfactants (**3**-**6**, for example) become substantially more stable upon polymerization by ultraviolet light or by the addition of initiators (Figure 3). Polymerized vesicles have shelf lives of several months and remain stable in solutions of up to 25% alcohol. Polymerization does not alter the size of vesicles. It is possible to prepare stable polymerized vesicles of diameters that range from 300 to 3000 Å. Furthermore, vesicles prepared from surfactants with polymerizable moieties in the head groups (**4** and **5**, for example) can be selectively "zipped up" at their inner or outer surfaces, or at both. Selective polymerization allows a fine control of acid and base transport from the bulk solution to the vesicle interior, or vice versa. These species permeate unpolymerized vesicles almost instantaneously.

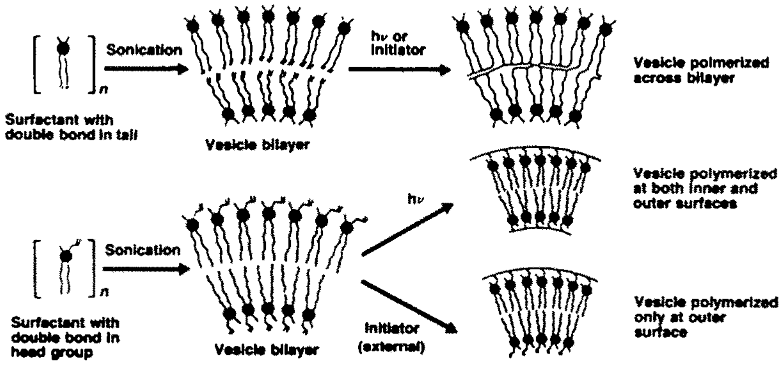

Figure 3: Vesicle formation and polymerization.

In partially polymerized vesicles, acid or base transfer occurs in the minute-to-hour time scale. Conversely, a pH gradient of several orders of magnitude can be maintained for many hours in completely polymerized vesicles. Photopolymerization of vesicles prepared from surfactants that contain styrene in their head groups (**4** and **5**, for example) results in pulling together approximately 20 monomers, thereby creating 15-Å-diameter surface clefts. Due to this relatively low degree of linking, vesicle fluidities and osmotic activities are retained upon polymerization.

III. Quantum Size Effects of Surfactant Vesicle Stabilized Colloidal Semiconductors

Renewed interest in ultrasmall (50 Å diameter or less) colloidal semiconductors has focused upon the investigations of the physical chemical consequences of transitions between cluster-like and bulk-like properties.[13-22] Colloidal particles in the range of size distributions at which they are about to become semiconductors have many unique, as yet incompletely understood, properties. They have been termed by

Henglein[13] as the modern equivalent of Ostwalt's "world of neglected dimensions."[23] Initial decrease in the size of dispersed colloidal semiconductors (say to 40-60 Å diameter for CdS or ZnS)[14-17] results only in a decrease in the density of states in the conduction band and, hence, in the absorption coefficient. Until the exciton state, lying just below the edge of the conduction band, is not appreciably affected, decrease in the semiconductor size will only manifest in a modest ultraviolet shift of the absorption. Development of a shoulder at the blue edge of the band gap corresponds to electronic transition from the valence band to the exciton state. Further decreases in the semiconductor size lead to ultrasmall particles in which the charge carriers are confined in a small volume. Band gaps of semiconductors in this "Q-state" are shifted dramatically to higher energy. It has been possible, for example, to prepare colorless dispersed CdS colloids.[13] Most importantly, colloidal semiconductors in their "Q-state" have been shown to have enhanced redox potentials with respect to their larger analogs.[20] Band gap irradiation of CO_2 saturated solutions of dispersed colloidal CdSe particles in sizes smaller than 50 Å produced formic acid. Conversely, excitation of large particle sized CdSe colloids under identical conditions, did not yield formic acid.[20]

Advantage has been taken of organic solvents, low temperatures and carefully controlled nucleation to form ultrasmall dispersed colloidal particles.[13-20] Small sized CdS semiconductors have also been prepared and embedded in Nafion membranes[7] and in porous vycor glass.[24] It has not yet been possible, however, to generate and maintain controlled sized colloidal particles in their "Q-state" in aqueous solution in the absence of stabilizers.

Recently, we have reported marked size effects in CdS colloids generated *in situ* in negatively charged DHP (**2**) surfactant vesicles.[21] We argued that surfactant vesicles provide containers for generating colloidal particles in controllable sizes.[11,25] CdS particles can be localized at the outer, the inner, or at both surfaces of single bilayer vesicles (Figure 4). Each of these arrangements has certain advantages. Semiconductors on outer vesicles surfaces are more accessible to reagents and can, therefore, more readily undergo photosensitized electron transfer. Highest yields of sacrificial water photoreductions were obtained in vesicles which contained rhodium-coated colloidal CdS at both their inner and outer surfaces.[25] Smaller and more monodispersed CdS particles can be prepared and maintained for longer times in the interior of vesicles than at any other arrangements.

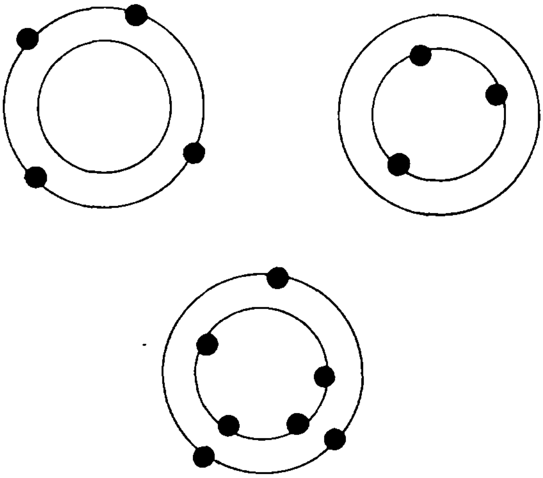

Figure 4: Schematics of available sizes for organizing colloidal semiconductors in single-bilayer surfactant vesicles.

Sizes of semiconductors in vesicles can be controlled by adjusting the number of precursors (Cd^{2+} ions, for example) per vesicle and/or by regulating the amount and rate of addition of H_2S. Vesicles are also efficient in maintaining colloidal particles over extended periods of time (for several months).[12] Spatial confinements in the bilayers preclude particle growth either by nucleation or Ostwald ripening. Different populations of semiconductors were shown to be generated at the inner and at the outer surface of DHP vesicles.[21]

More precise control of CdS particle sizes was obtained in DODAC vesicles.[26] Four different methods of preparations were investigated. In **Preparation A**, CdS particles were generated from $CdEDTA^{2-}$ distributed both at the inner and outer surfaces of DODAC vesicles. CdS particles were localized only in the inner, or at the outer, surfaces of DODAC vesicles in **Preparations B** and **C**, respectively. **Preparation** of **D** involved the generation of CdS from Cd^{2+} ions electrostatically repulsed from the DODAC vesicle surfaces.

CdS particles were formed in **Preparations A**, **B**, **C**, and **D** by the careful addition of controlled amounts of H_2S. Particle sizes and size distributions have been assessed from their absorption spectra. The parameters used are defined in Figure 5. Thus, the onset of absorption (o) is defined as the wavelength at which the absorption becomes zero. The absorption edge (s) is the intersection of the base line with the tangent drawn to the absorption maximum (m, or in the case of two maxima, m_1 and m_2) or to the shoulder (sh). In the case of a pronounced maximum, the half width of the band at the base line ($d_{1/2}$) is also determined. It should be emphasized that the obtained $d_{1/2}$ values do not correspond to sizes. They provide, however, an assessment of size distribution. The smaller the $d_{1/2}$ value, the more monodispersed are the colloid particles.

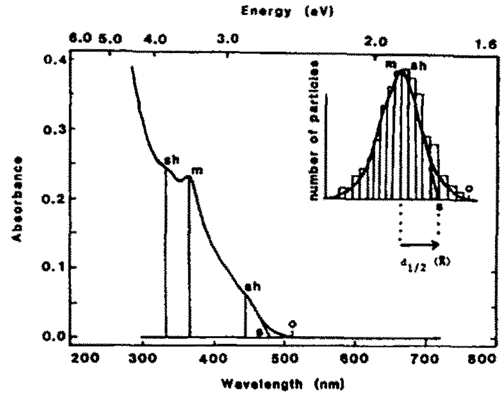

Figure 5: Absorption spectrum of CdS particles, *in situ* generated at the outer and inner surfaces of DODAC vesicles (**Preparation A**); sh = shoulder, m = maximum, s = absorption edge, o = onset of absorption. As shown in the insert, each $d_{1/2}$ value was obtained by taking the difference in Å (read off from a size vs. absorption maximum absorption edge calibration curve[27]) between m and s.

Absorption spectra of CdS, formed by the addition of increasing amounts of H_2S to vesicles prepared by cosonicating $CdEDTA^{2-}$ and DODAC (**Preparation A**), are shown in Figure 6. Addition of H_2S, in slight stoichiometric excess, gave structured spectra with absorption maximum at 340 nm and a maximum, or shoulder, of 380 nm (Figure 6). Further addition of H_2S caused the disappearance of the absorption

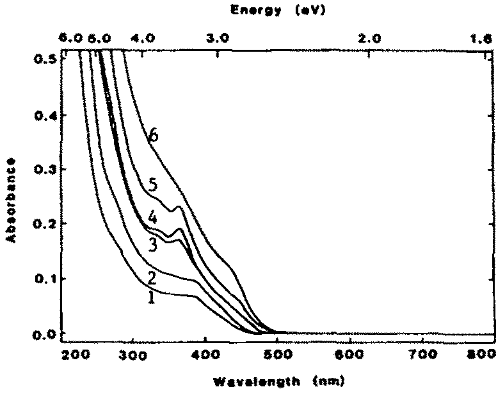

Figure 6: CdEDTA2- adsorbed on outer and inner surface of DODAC vesicles: [CdEDTA] = 2 x 10-4 M, [DODAC] = 2.0 x 10-3 M, pH = 9.5; 10 (1), 20 (2), 30 (3), 40 (4), 50 (5), and 100 (6) μL of H_2S injected into an argon stream with a flow rate of 10 mL/min to 3.0 ml sample solution.

maxima. Importantly, these absorption edges, if present, remained independent of the amounts of H_2S added. Figure 7 shows the comparison of CdS spectra of particles generated on inner, outer, and on both sides of DODAC vesicles.

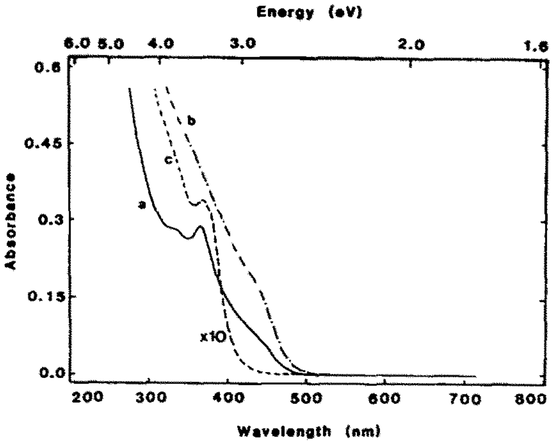

Figure 7: CdS absorption spectra formed on outer and inner (a), outer (b), and inner surface (c) alone: [DODAC] = 2.0×10^{-3} M in all systems; [$CdEDTA^{2-}$] = 2.0×10^{-4} M (a), 1.0×10^{-4} M (b) and (c); pH = 9.5 (a) and (b), 10.0 (c); the spectrum of (c) is ten times enlarged.

Strictly speaking, absorption edges can only be associated with band gaps in macrocrystalline semiconductors. For particles in the 20-30 Å diameter, the first and second excited states generally lie at energies greater than the range at which their absorption were taken.[14] Furthermore, sizes of dispersed colloidal semiconductors vary and their dispersity depends on the method of preparation.

Distribution of CdS particles formed in the different systems are summarized in Figure 8. In the absence of vesicles, addition of H_2S to Cd^{2+} led to broad distribution of relatively large semiconductor particles. Structureless spectra and the presence of shoulders indicated the presence of macrocrystalline particles. As seen, the smallest particles are produced in the presence of electrolytes.

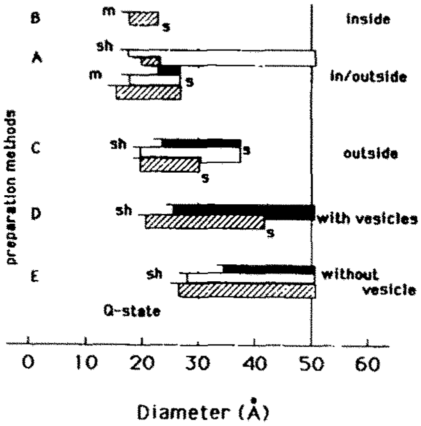

Figure 8: Sizes and size distribution of CdS particles prepared in the different systems. Bars indicate size ranges from the absorption maximum (m) or shoulder (sh) to the absorption edge (s). Open bars on the right-hand side imply absorption edges beyond 50 Å (the limit of validity on the calibration curve[27]). The "Q-state" range lies below 30 Å particle diameter.

Electron-transfer efficiencies were investigated by taking advantage of methylviologen, MV^{2+}, as an acceptor. Amounts of $MV^{\dot{+}}$ formed upon 354 nm excitation of CdS, *in situ* generated on the outer surfaces of DODAC vesicles (**Preparation C**), were measured at 600 nm. The left-hand side of Figure 9 shows the absorption spectra of two CdS samples which differed only in the amounts of H_2S used in their preparation. These samples had absorption edges of 416 nm and 485 nm. The right-hand side of Figure 9 shows time-dependent absorption changes at 605 nm for these two samples in the presence of 4.0×10^{-4} M MV^{2+} following excitation by a 15 nsec laser pulse. Particles with shorter wavelength absorption edges are seen to have photoreduced MV^{2+} more efficiently than those with longer wavelength absorption edges. Taking $\varepsilon_{606\ nm} = 13700\ M^{-1}\ cm^{-1}$, amounts of $MV^{\dot{+}}$ formed in these two samples were calculated to be 2.9×10^{-6} M and 7.2×10^{-6} M, corresponding to quantum yields of 0.4% and 1.0%, respectively.

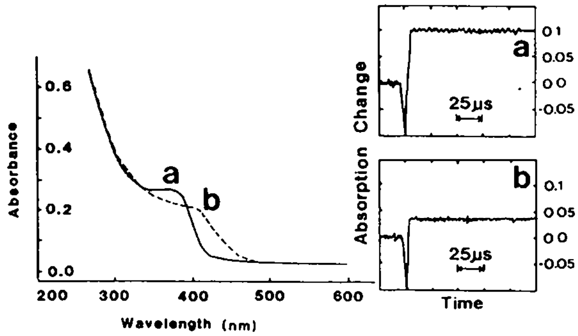

Figure 9: Electron transfer from excited CdS particles to MV^{2+} as acceptor: [DODAC] = 2.0×10^{-3} M, [$CdEDTA^{2-}$] = 1.0×10^{-4} M (outside); [MV^{2+}] = 4.0×10^{-4} M; 50 (a) and 30 (b) µL of H_2S injected in an argon stream with a flow rate of 10 mL/min to 3.0 ml sample solution.

Enhanced electron transfer efficiencies in smaller CdS particles can be accounted by:

(1) The photogenerated electrons and holes are produced closer to the surface with smaller particles. They, therefore have a greater chance to migrate to the surface and undergo electron-transfer reactions than they do in larger particles. In other words, non-productive, electron-hole recombinations (competing with electron transfer) are more prevalent in larger CdS particles than in smaller ones.

(2) Smaller particles have larger surface areas than larger ones (surface area is proportional to reciprocal diameter if other factors, like total weight of the semiconductor, remain constant). Hence, there are more surface-absorbed MV^{2+} present in vesicles which contain smaller particles, rather than larger CdS particles.

(3) With smaller particles the conduction-band electrons become of higher energy. This results in increased electron-transfer rates and, hence, in increased yields of reduced methylviologen.

Surfactant vesicles have been shown to have a myriad of advantages in the generation and stabilization of semiconductors. They provide sites for CdS formation and shift the equilibrium between nucleation and particle growth in favor of the former. Electrostatic effects may well alter band gaps and reduction potential, as well as influence electron transfer to and from donors and acceptors located on, or in, close proximity to the semiconductor. Positively-charged ammonium headgroups on DODAC attract negative ions (Cl^-, OH^-, S^{2-}, $EDTA^{3-}$) in sufficient amounts to assume partial covering of CdS particles prior and subsequent to their incorporation into the potential field of DODAC vesicles. These anionic coatings decrease the lateral mobility of CdS particles and stop, therefore, their growth.

IV. Surfactant-Vesicle-Stabilized, Semiconductor-Mediated Water Photoreduction

The potential of catalyst-coated colloidal semiconductor particles in solar energy conversion has been recognized by a rapidly growing number of laboratories worldwide.[5] Many different strategies have been considered for the generation and the stabilization of these colloids. They include the use of aqueous polymers or polyelectrolytes,[3-5, 12, 14] inorganic oxide particles,[6-9] macroscopic synthetic membranes,[15-17] water-in-oil microemulsions,[18] non-aqueous solvents[9,12,13] or aqueous surfactant vesicles.[19-21] Because of its optimum characteristics among many available semiconductor materials, CdS has been the most popular and the best described.[6-8,21,25,28]

Band gap excitation of CdS by visible light ($\lambda < 520$ nm for macroscopic CdS), resulted in promotion of electrons from the valence to the conduction band, and hence in charge separation. CdS conduction band electrons, under favorable conditions, could then reduce water at the catalyst/semiconductor interface.[4]

1. H_2 generation and electron transfer with CdS in DHP (**2**) vesicles

The activity of vesicle-stabilized, catalyst-coated colloidal CdS was first demonstrated in DHP vesicles, using Rh as catalyst and thiophenol (PhSH) as sacrificial electron donor.[33] Figure 10 illustrates the mechanism of this photosensitized H_2 generation. The proposed position of the CdS particle (partially buried in the vesicle bilayer) was supported by the following observations:

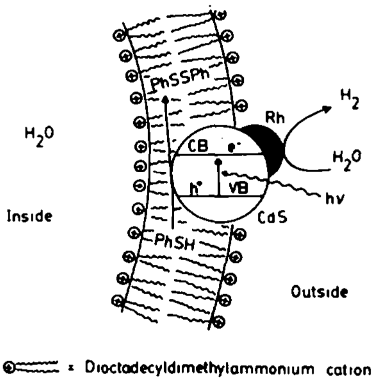

Figure 10: An idealized model for CdS-sensitized water photoreduction by PhSH in aqueous DHP vesicles. The position of the colloid in the vesicle (represented here as generated on the outside surface) is based on fluorescence quenching experiments.

(a) CdS particles generated from externally adsorbed Cd^{2+} ions did not precipitate, even after months; therefore, they had to remain bound to the vesicle interface; (b) CdS fluorescence was efficiently quenched by PhSH, which was located in the hydrophobic membrane; therefore, the colloidal CdS particles had a direct contact with the inner part of the membrane; (c) The CdS particle retained access to the surface where it originated, since entrapped polar electron acceptors such as methylviologen (MV^{2+}), while unable to penetrate the DHP membrane, could also quench the fluorescence of inner-surface-generated CdS particles. However, this quenching decreased with time, showing a gradual penetration of the CdS toward the middle of the bilayer; (d) CdS particles at the vesicle interiors remained at the inner surface of the membrane, since externally added quencher such as MV^{2+} and Rh^{3+}, while adsorbed at the outer surface of DHP vesicles, did not quench inner-surface CdS fluorescence, even after several weeks.

Although CdS could be located selectively at the inner or outer surface of the vesicles, symmetrically organized samples were found easiest to prepare most reproducibly. No significant effect of CdS location upon the photochemical activity for H_2 generation was observed.

2. Hydrogen generation in vesicles prepared from DODAC (**1**), **4** and polymerized **4**

Positively charged vesicles prepared from **1** and **4** were found to be better media for CdS-mediated water photoreduction than that prepared from DHP (**2**).

Polymerization of **4** vesicles affected the capability of EDTA to act as an electron donor for Rh-coated CdS particles. The role of EDTA was first to reverse the charge of Cd^{2+} and Rh^{3+} ions in order to control the growth of the CdS particles at the surfaces of the vesicles. It was hoped that EDTA could subsequently be used as electron donor in the CdS-photosensitized water reduction. However, EDTA was found inefficient in DODAC and unpolymerized 4 vesicles. On the other hand, EDTA was efficient in polymerized vesicles. This effect was understood as an increased access to CdS of the aqueous phase and EDTA, resulting from the cleft formation upon polymerization of 4. Unfortunately, the EDTA amounts were still severely limited by their destabilizing effect on the cationic vesicles. To overcome this problem, several alcohols were tried as electron donors, and among them benzylalcohol was found to be by far the the most efficient. It could be added up to saturation in water (ca. 4% vol.) without destroying the vesicles. Only 1% benzylalcohol gave a maximum rate, at 40% of over 200 μmol H_2/h (4.5 ml H_2/h) from 25 ml samples containing only 0.82 mg of CdS/Rh catalyst ($2 \cdot 10^{-4}$ M CdS and $4 \cdot 10^{-5}$ M Rh). Figure 11 illustrates the mechanism and proposed structure of the polymerized 4 vesicle system under visible light irradiation. Quantum efficiency of H_2 production in the different vesicles is summarized in Table 1.

Table 1. Quantum Yield of Hydrogen Formation at 400 nm,[a] Hydrogen Production Rates, and CdS Bandgaps in Different Vesicular Systems at 40°C

medium[b]	CdS band gap[c]	rates of H_2 production, μmol/h: full spectrum (λ>350 nm)	rates of H_2 production, μmol/h: monochromatic (400 nm)	Φ (400 nm),%
HMP/water	487/100	5	1.3	0.5
DHP	490/63.3	5	1.4	1.2
DODAC	488/93.1	164	18.1	10.0
unpolymerized 1	463/67.1	120	9.9	7.3
polymerized 1	498/58.8	205	12.4	10.1

[a] Φ = 1/2 H_2 molecule produced per photon absorbed. [b] Surfactant concentration 2×10^{-3} M, CdS 2×10^{-4} M, Rh 4×10^{-5} M, benzyl alcohol 1%, 25-mL sample, 16.1-mL gas phase. [c] CdS bandgap (nm)/fractions of 400-nm light absorbed (%) vs. light absorbed and scattered (determined from the absorbance spectrum).

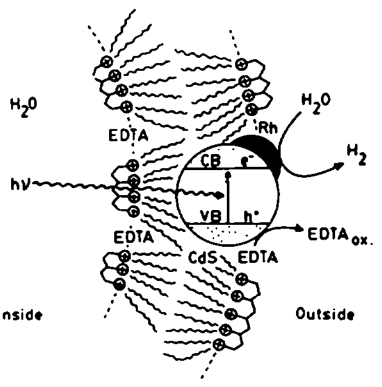

Figure 11: An idealized scheme for hydrogen generation with benzylalcohol as sacrificial electron donor, in polymerized 4-vesicle-stabilized, Rh-coated, colloidal CdS.

V. Conclusion

Within a relatively short time, dispersed colloidal semiconductors have become the subject of important areas of research. Questions like "how many individual molecules need to assemble to manifest band and semiconducting properties?", "what is the mechanism of the assembly processes?", and "what physical and chemical properties are influenced by particle size changes, particularly at the region and just below the point of their becoming semiconductors?" are increasingly being asked by physicists and physical chemists.

Finding answers to these questions is motivated by the expectation of discovering new phenomena and unique properties which may well lead to innovative applications. Successful experimentation on dispersed colloidal semiconductors requires good reproducibility under relatively controllable conditions. The tenet of this summary has been that organized assemblies, in general, and vesicles and polymerized vesicles, in particular, provide such conditions. Clearly we are just at the beginning of a major breakthrough. It is up to us to realize the full potential of this intellectually stimulating and highly relevant chemistry.

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REFERENCES AND NOTES

(1) Kittel, C. "Introduction to Solid State Physics"; John Wiley & Sons, Inc.: New York, 1980.

(2) Gerischer, H.; Willig, F. *Top. Curr. Chem.* **1976**, *61*, 33-56.

(3) Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314-321.

(4) Grätzel, M. "Energy Resources Through Photochemistry and Catalysis"; Academic Press: New York, 1983.

(5) Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 2730-2740.

(6) Meissner, D.; Memming, R.; Kastening, B. *Chem. Phys. Lett.* **1983**, *96*, 34-37.

(7) Krishnan, M.; White, J. R.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 7002-7003. Mau, A. W. H.; Huang, C. B.; Kakuta, B.; Bard, A. J.; Campion, A. C.; Fox, M. A.; White, M.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537-6542.

(8) Meyer, M.; Wallberg, C.; Kurihara, K.; Fendler, J. H. *J. Chem. Soc., Chem. Commun.* **1984**, 90-91.

(9) Kuczynski, J.; Thomas, J. K. *Langmuir* **1985**, 158-163.

(10) Fendler, J. H. *Acc. Chem Res.* **1980**, *13*, 7-13.

(11) Fendler, J. H. "Membrane Mimetic Chemistry, Characterizations and Applications of Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host-Guest Systems and Polyions"; Wiley: New York, 1982. Fendler, J. H. *Chem. Eng. News*, **1984** (Jan 2) *62*, 25-38. Fendler, J. H. *Science* **1984**, *223*, 888-894. Fendler, J. H. *Chemtech.* **1985**, *15*, 686-691.

(12) Fendler, J. H.; Tundo, P. *Acc. Chem. Res.* **1984**, *17*, 3-8. Fendler, J. H. In "Surfactants in Solution", Mittal, K. L., Lindman, B., Eds.; Plenum Press: New York, 1984; pp 1947-1989. Gros, L.; Ringsdorf, H.; Schupp, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 305-325. Fuhrhop, J. H.; Mathieu, J. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 100-113.

(13) Weller, H.; Koch, V.; Gutierrez, M.; Henglein, A. *Ber Bunsenges. Phys. Chem.* **1984**, *88*, 649-656.

(14) Fojtik, A.; Weller, H.; Koch, V.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 969-977.

(15) Rosetti, R.; Nakahara, S.; Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 1086-1088.

(16) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403-4409. Brus, L. E. In "Dynamics on Surfaces," Pullman, B., Ed.; Reidel: New York, 1984; pp. 431-435.

(17) Rosetti, R.; Ellison, J. L.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4464-4469.

(18) Rosetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1985**, *82*, 552-559.

(19) Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Rajh, T.; Micic, O. I. *J. Phys. Chem.* **1985**, *89*, 397-399.

(20) Nemeljkovic, J. M.; Nenadovic, M. T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1986**, *90*, 12-13.

(21) Tricot, Y.-M.; Fendler, J. H. *J. Phys., Chem.* **1986**, *90*, 0000-0000.

(22) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555-2560.

(23) Ostwald, W. "Die Welt der vernachlassigten Dimensiomen;" Steinkopff, Dresden, 1920.

(24) Kuczynski, J.; Thomas, J. K. *J. Phys. Chem.* **1985**, *89*, 2720-2721.

(25) Tricot, Y.-M.; Emeren, Å; Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 4721-4726.

(26) Watzke, H.; Fendler, J. H. *J. Phys. Chem.*, submitted.

(27) Weller, H.; Smidt, H. M.; Koch, U.; Fojtik, A.; Baral, S.; Henglein, A.; Kunath, W.; Weiss, K.; Dieman, E. *Chem. Phys. Lett.* **1986**, *124*, 557-560.

(28) Ramsden, J. J.; Grätzel, M. *J. Chem. Soc. Far. Trans. I* **1984**, *80*, 919-933.

(29) Serpone, N.; Sharma, D. K.; Maieson, M. A.; Grätzel, M.; Ramsden, J. J. *Chem. Phys. Lett.* **1985**, *115*, 473-476.

(30) Henglein, A. *Ber. Buns. Phys. Chem.* **1982**, *86*, 302-305.

(31) Ramsden, J. J.; Webber, S. E.; Grätel, M. *J. Phys. Chem.* **1985**, *89*, 2740-2743.

(32) Kuczynski, J. P.; Milosajevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1984**, *88*, 890-896.

(33) Tricot, Y.-M.; Fendler, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7359-7366.

(34) Rafaeloff, R.; Tricot, Y.-M.; Nome, F.; Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 533-537.