

"(10 ± 5 ± n)-jump" perimetal processes; $n = 0 \rightarrow 5$. For example, the "3-jump" process of Figure 2 belongs to $n = 2$, a set that also includes 7-, 13-, and 17-jump processes, all of them now excluded. Four more sets, $n = 0, 1, 3$, and 5, are all incompatible with the high-temperature average spectrum. Within the sole remaining set, $n = 4$, the C_3 symmetry of **1a** allows allylic alkylation to be described equally well as 1-jump or 19-jump. Neither these nor any other NMR data, however, can exclude an alternative 9 (or 11)-jump process, nor can they exclude multistep equivalents. The transient carbocations within each equivalent, however, are limited to those that introduce no new elements of structural or permutational symmetry.

The exclusion of **1b**, both as a static structure and as a transient intermediate, now removes the only isolobal⁸ metallocene analogue from hydrocarbon chemistry.⁹ It will be interesting to see how many other polyhedral carbocations¹⁰ can survive a comparably stringent experimental test.

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Supplementary Material Available: A -164 °C ¹³C NMR spectrum and the derivation of its peak assignments (10 pages). Ordering information is given in any current masthead page.

(9) The 1,3-dehydroallyl cation ligands of **1b** have, however, since reappeared as "open cyclopropenium" cation ligands in organometallic chemistry: Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570.

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Visible Light Induced Hydrogen Production from in Situ Generated Colloidal Rhodium-Coated Cadmium Sulfide in Surfactant Vesicles

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Macrodispersed and colloidal semiconductors are utilized increasingly in photochemical solar energy conversion.¹ Band-gap excitation produces an electron-hole pair whose recombination can be intercepted by catalysts, which may, in turn, lead directly to water splitting.² However, charge recombination renders such a system inefficient.³ Separate development of sacrificial oxidation and reduction half-cells and their subsequent coupling, through space or time, provides an alternative approach. Such an approach has been fruitfully employed in homogeneous solutions using organized surfactant assemblies to compartmentalize sensitizers, relays, and catalysts and hence to aid charge separation.⁴ The present communication reports the first use of surfactant vesicle-stabilized, in situ formed, catalyst-coated, colloidal semiconductor in artificial photosynthesis. Band-gap excitation by visible light ($\lambda > 350$ nm) of rhodium-coated colloidal cadmium sulfide,

in dihexadecylphosphate (DHP) surfactant vesicles, produced hydrogen in the presence of thiophenol.

Preparation and characterization of DHP surfactant vesicles have been described.⁵ CdCl₂, RhCl₃, or methylviologen (MV²⁺) were incorporated by cosonicated these ions with DHP and then removing externally adsorbed or nonadsorbed cations by cation-exchange chromatography.⁶ Entrapment rates of 45–50% CdCl₂⁷ corresponded to the adsorption of Cd²⁺ on the inner walls of negatively charged DHP vesicles.⁸ Exposure of vesicle-entrapped CdCl₂ to excess gaseous H₂S resulted in CdS formation. Assuming complete reaction, the absorbance of vesicle-entrapped CdS at 400 nm corresponds to $\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 1A). Ultraviolet irradiation with a 450-W xenon lamp under Ar bubbling for 60 min mediated the reduction of Rh³⁺ to Rh⁰ in the presence of CdS. Rhodium reduction was monitored by absorption spectroscopy (Figure 1A).

Air-saturated, vesicle-entrapped, colloidal CdS showed the characteristic weak fluorescence emission due, primarily, to electron-hole recombination.⁹ Fluorescence intensity maximum (ca. 500 nm)¹⁰ corresponded to full band-gap emission. The fluorescence intensity is strongly reduced in the presence of Rh³⁺ (Figure 1B) and disappears completely after reduction of Rh³⁺ to Rh⁰. However, UV irradiation under Ar bubbling in the absence of Rh³⁺ does not affect the intensity of CdS fluorescence. Quenching of CdS fluorescence by coentrapped Rh³⁺ appears to be Stern-Volmer as a function of the initial concentration of Rh³⁺ (Figure 2).¹¹ Coentrapped MV²⁺ strongly quenches CdS fluorescence and deviates from a Stern-Volmer quenching, indicating the possibility of a static quenching (Figure 2). Interestingly, externally adsorbed MV²⁺ does not quench vesicle-entrapped CdS fluorescence, even several days after being added to CdS-containing vesicles. This is consistent, with the CdS being located completely inside of the vesicles and with neither MV²⁺ nor CdS leaking through the DHP vesicles under the present experimental conditions. Thiophenol, PhSH, also quenches the fluorescence of reversed micelle-entrapped CdS fluorescence.¹²

The hydrodynamic radius of the vesicles, after CdS formation, was found to be $550 \pm 50 \text{ \AA}$.¹³ Vesicle sizes were not affected

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(6) Typically 49.2 mg of DHP were sonicated in 30 mL of triply distilled water to give stoichiometric concentrations of $3.0 \times 10^{-3} \text{ M}$ DHP, $3 \times 10^{-4} \text{ M}$ CdCl₂, and $1.0 \times 10^{-4} \text{ M}$ RhCl₃ at pH 7 (with $3.0 \times 10^{-3} \text{ M}$ NaOH during sonication). Under the present experimental conditions, essentially all cations (Cd²⁺ and Rh³⁺) were adsorbed on either side of the vesicles. After cation-exchange chromatography, 45–50% of the initial amount of Cd²⁺ was retained inside of the vesicles,⁷ which corresponded to the fraction of Cd²⁺ adsorbed on the inner walls of negatively charged DHP vesicles.⁸ Entrapment rates in the absence of adsorption would be controlled by the inner volume fraction, which is approximately 0.5% of the total volume of the vesicle dispersion. The amount of Cd²⁺ ions entrapped in a single vesicle is proportional to the number of DHP surfactants forming the inside layer. As these vesicles have a rather broad size distribution,⁸ this will be reflected on the sizes of CdS particles formed inside of the vesicles. Typically, for an aggregation number of 50 000 DHP surfactants per vesicle, approximately 22 000 surfactant molecules will form the inside layer, entrapping by adsorption 2200 Cd²⁺ ions under the present experimental conditions and the same amount of CdS molecules will be produced in such a vesicle after exposure to H₂S. It is believed that these CdS molecules eventually agglomerate in one single particle per vesicle. However, no trace of CdS precipitation is observed after several weeks, thus indicating the efficiency of the DHP vesicles to stabilize the colloidal CdS dispersion.

(7) Determined by atomic absorption spectroscopy.

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(10) No correction was made for the photomultiplier response.

(11) Concentrations of Rh³⁺ shown in Figure 2 refer to those added initially, since the amounts entrapped were not directly determined. Entrapment rates of Rh³⁺, by analogy with Cd²⁺ and other adsorbates,⁸ are assumed to be 45–50%.

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(13) A Malvern 2000 light-scattering system and a Spectra Physics 171 Ar⁺ laser were used. Data were collected at $\theta = 90^\circ$, at 23 °C. Q values (polydispersities) were in the order of 0.3.

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(3) Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 172.

(4) Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley-Interscience: New York, 1982.

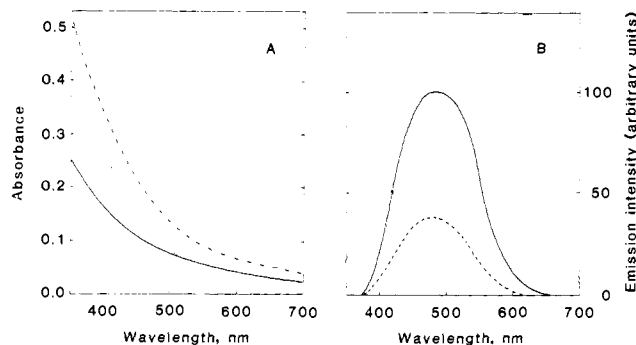


Figure 1. (A) Absorption spectra of 2×10^{-3} M DHP vesicle-entrapped 1×10^{-3} M Cd^{2+} and approximately 3.2×10^{-5} M Rh^{3+} : (—) after removal of external cations, (---) after exposure to H_2S (formation of CdS), (---) after 60 min of UV irradiation (formation of Rh^0). (B) Fluorescence emission spectra of 2×10^{-3} M DHP vesicle-entrapped 1×10^{-4} M colloidal CdS , under 330-nm excitation: (—) in the absence (before and after UV irradiation under Ar bubbling) (---) and in the presence of approximately 3.2×10^{-5} M Rh^{3+} .

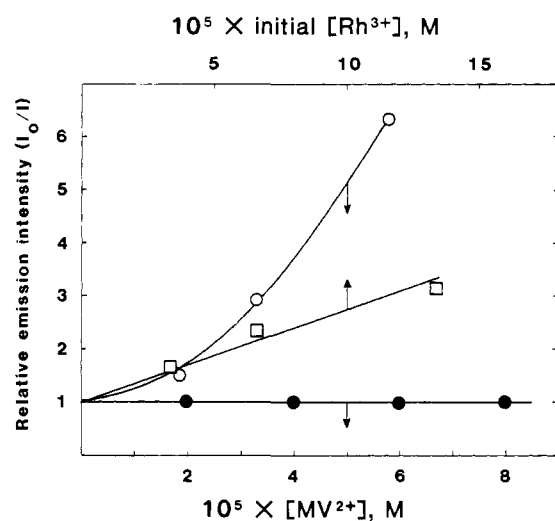


Figure 2. Stern-Volmer plots for the quenching of 2×10^{-3} M DHP vesicle-entrapped 1×10^{-4} M colloidal CdS by coentrapped MV^{2+} (O), coentrapped Rh^{3+} (□), and externally adsorbed MV^{2+} (●).

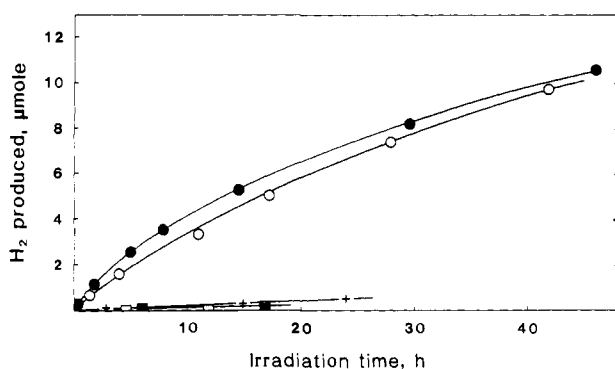


Figure 3. Hydrogen production in deaerated solution as a function of irradiation time using 350-nm cutoff and water filters at 30°C . Plotted are the amount of hydrogen produced by a 25-mL DHP vesicle solution and measured in the gas phase (16 mL) by GPLC: 2×10^{-3} M DHP, 1×10^{-4} M CdS , rhodium coated as described in the text. In the presence of 10^{-3} M PhSH and at pH approximately 7, adjusted before irradiation (●, ○; separate samples, indicating our reproducibility); same sample in the absence of CdS and Rh (+) or in the absence of PhSH only (■) or in the absence of PhSH only (□).

by varying the initial concentration of CdCl_2 from 0 to 7×10^{-4} M. Irradiation of degassed, vesicle-entrapped, rhodium-coated, colloidal CdS by visible light (450-W xenon lamp, 350-nm cutoff filter) in the presence of 10^{-3} M PhSH resulted in hydrogen formation, which could be sustained for approximately 48 h

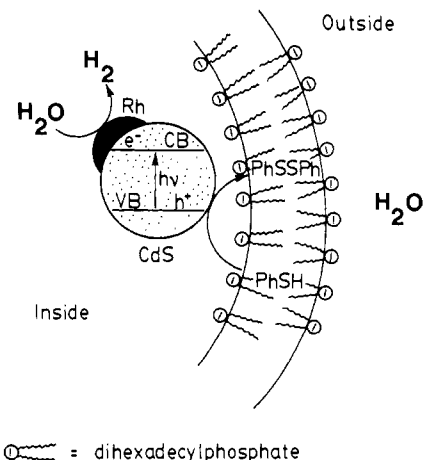


Figure 4. An idealized model for CdS -sensitized water photoreduction by PhSH in aqueous DHP vesicles. The position of the colloid in the vesicles should not be taken for granted, however.

(Figure 3). After 48 h, more than 90% of PhSH was consumed. Sustained hydrogen formation is the consequence of electron transfer from PhSH , presumably located in the DHP membranes, to the positive holes in the colloidal CdS . This, in turn, diminishes undesirable electron-hole recombinations and allows electron transfer to the surface of the semiconductor where Rh^0 -catalyzed water reduction occurs (Figure 4). In the absence of either CdS , Rh^0 , or PhSH , no or very little amount of H_2 is produced. Optimization of surfactant vesicle-entrapped catalyst-coated semiconductors is the objective of our current scrutiny. These systems, along with polymer membrane incorporated semiconductors,^{14,15} may well provide means for viable solar energy conversion.

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Registry No. Dihexadecyl phosphate, 2197-63-9; thiophenol, 108-98-5; rhodium, 7440-16-6; cadmium sulfide, 1306-23-6; hydrogen, 1333-74-0.

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Isolation from Pistacia Resins of a Bicyclic Triterpenoid Representing an Apparent Trapped Intermediate of Squalene 2,3-Epoxyde Cyclization

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Following the establishment of the role of squalene and more specifically (3S)-squalene 2,3-epoxide^{2,3} in the biosynthesis of polycyclic triterpenoids, we have found that there has been considerable interest and speculation concerning the exact nature of this remarkable biotransformation. The cyclization was originally envisaged as a completely concerted process,⁴ a view supported by the failure to trap or otherwise detect any intermediates. However, the most recent work of van Tamelen and his co-workers

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