Photosensitized Charge Separation and Hydrogen Production in Reversed Micelle Entrapped Platinized Colloidal Cadmium Sulphide

Mauricio Meyer, Christer Wallberg, Kazue Kurihara, and Janos H. Fendler*

Department of Chemistry and Institute of Colloid and Surface Science, Clarkson College of Technology, Potsdam, New York 13676, U.S.A.

Irradiation of platinized colloidal cadmium sulphide, generated *in situ* in Aerosol-OT reversed micelle entrapped water pools in iso-octane, sensitized water photoreduction by thiophenol, dissolved in the organic phase.

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 separations.[4] The present communication reports the first use of a surfactant aggregate to facilitate charge separation in photolysed colloidal semiconductors. Platinized colloidal cadmium sulphide generated for the first time *in situ* in sodium bis-2-ethylhexylsulphosuccinate [Aerosol-OT (AOT)] reversed micelle entrapped water pools in iso-octane, sensitized water photoreduction by thiophenol, PhSH, dissolved in the organic solvent.

Colloidal cadmium sulphide was prepared from 3.2×10^{-4} M $CdCl_2$† and 2.0×10^{-5} M sodium hexametaphosphate, entrapped in 0.1 M AOT reversed micelles in iso-octane, by exposure to H_2S. The concentrations of colloidal CdS, formed in the reversed micelles, were determined to be 1.9×10^{-4} M by absorption spectroscopy.‡ Dynamic light scattering§ established the diameters of the reversed micelles to be 120 and 150 Å before and after colloid formation. Electron microscopy established the diameters of the CdS colloids to be smaller than 100 Å. These values correspond to water : surfactant ratios (*w*-values) of 18—20.[4] Platinization was carried out by adding 24 μl aqueous 0.05 M K_2PtCl_4 solution (to give stoicheiometric concentrations of 4.8×10^{-5} M in 25 ml without altering appreciably the *w*-values) to the reversed micelle entrapped colloidal CdS and irradiating it with a 450 W Xenon lamp under bubbling Ar for

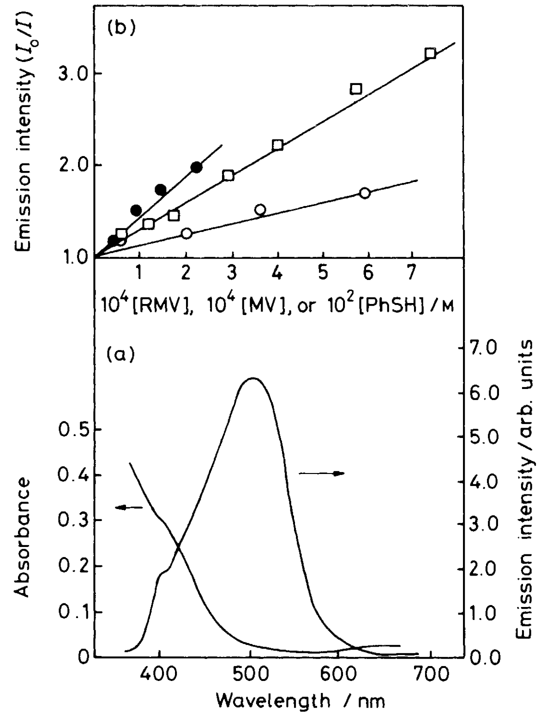

Figure 1. (a) Absorption and emission spectra of colloidal CdS in AOT entrapped water pools in iso-octane. (b) Stern–Volmer plots for the quenching of the fluorescence of colloidal CdS in AOT entrapped water pools in iso-octane by RMV^{2+} (●), MV^{2+} (□), and PhSH (○).

---

† All concentrations are stoicheiometric, *i.e.* related to the total volume of AOT reversed micelles.

‡ Taking $\varepsilon(400 \text{ nm}) = 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

§ A Malvern 2000 light scattering system and a Spectra Physics 171 Ar^+ laser were used. Data were collected at 90° and 23 °C. Typical sampling times were 0.5—3 μs. *Q*-values (polydispersities) were in the range of 0.2—0.5.

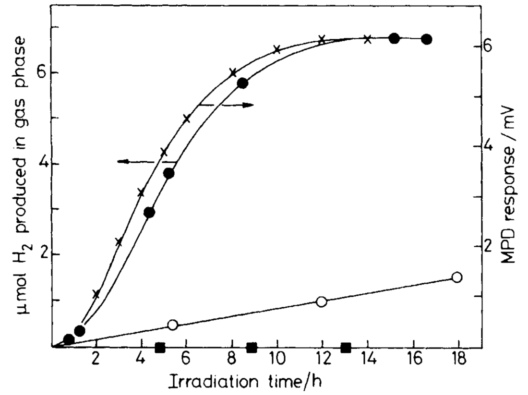

Figure 2. Hydrogen production in 1.9×10^{-4} M colloidal platinized CdS in 0.1 M AOT reversed micelle in iso-octane in the presence of 1.0×10^{-3} M PhSH in argon bubbled solution at 30 °C as a function of irradiation time, using 350 nm cut-off and water filters. Plotted are the amounts of H_2 formed in 25 ml solutions, measured in the gas phase (16 ml) by g.l.c. (●). MPD response in mV (×) corresponds to 3—4% of the amount of H_2 found in the gas phase. H_2 formation, determined by g.l.c., in the absence of PhSH (■) and in the absence of colloidal platinized CdS (○) are also given.

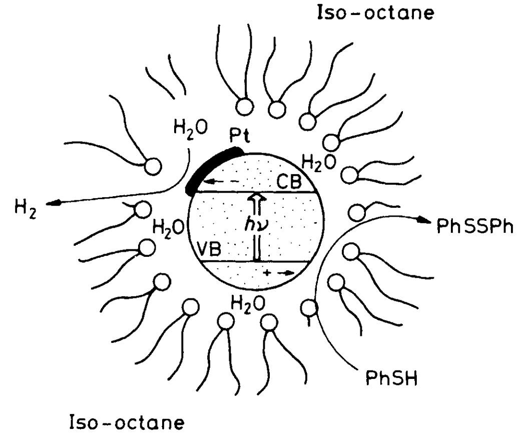

Figure 3. An idealized model for the CdS sensitized water photoreduction by PhS in AOT reversed micelles in iso-octane. VB = valence band, CB = conduction band.

30 min. Platinization was monitored by following the appearance of broad band absorbances, up to *ca.* 0.08 at 550 nm, due to colloidal Pt, possibly formed as in equation (1).[5]

$$\begin{aligned} \mathrm{PtCl_4^-} &\xrightarrow{h\nu} \mathrm{PtCl_3^-} + \mathrm{Cl\cdot} \\ \mathrm{2PtCl_3^-} &\longrightarrow \mathrm{Pt} + \mathrm{PtCl_4^{2-}} + \mathrm{Cl_2} \end{aligned} \qquad (1)$$

Unplatinized air saturated[6d] reversed micelle entrapped colloidal CdS showed the characteristic weak fluorescence emission, due primarily to the recombination of electrons with positive holes, previously observed in homogeneous solutions.[6] Fluorescence intensities of these solutions decayed biexponentially with lifetimes of 2.4 (25 ± 5%) and 28.5 (75 ± 5%) ns.¶ The fluorescence lifetimes of reversed micelle entrapped colloidal CdS are considerably longer than those observed in water (0.3 ns)[6a] indicating dramatic stabilization by decreasing the probability of electron–hole recombination. Addition of 2.3×10^{-4} M methylviologen, MV^{2+}, decreased the fluorescence lifetime of the longer lived component to 18.7 ns. Similarly, addition of a surface active viologen, $CH_2{=}C(Me)CO_2[CH_2]_{11}(C_5H_4N^+)_2Me$, RMV^{2+},[7] and PhSH, quenched the emission intensity of reversed micelle entrapped CdS presumably by removing electrons (MV^{2+}, RMV^{2+}) or holes (PhSH) (Figure 1). Apparent Stern–Volmer constants for quenching the fluorescence of colloidal CdS, entrapped in AOT reversed micelles by MV^{2+}, RMV^{2+}, and PhSH were calculated to be 2.6×10^3, 4.6×10^3, and 11.6 $dm^3\,mol^{-1}$, respectively.

Irradiation of degassed reversed micelle entrapped platinized CdS by visible light (450 W Xenon lamp, $\lambda > 350$ nm) resulted in hydrogen formation** upon addition of 1.0×10^{-3} M PhSH and it could be sustained for 12 h (Figure 2). This is the consequence of electron transfer from PhSH to the positive holes in the colloidal CdS, which diminish electron–hole recombinations (Figure 3).

Electron transfer in reversed micelle entrapped colloidal CdS has been substantiated by laser flash photolysis. Addition of 1.0×10^{-3} M RMV^{2+} resulted in the formation of the intermediate $RMV^{\cdot +}$.

Reversed micelles offer a number of advantages. They allow the convenient *in situ* formation and platinization of small uniform colloidal semiconductors and provide a means for their stabilization. Organic electron donors (*e.g.* PhSH) can be added in relatively high concentration and provide the means for charge separation by continuously removing the product (PhSSPh)[9] from the semiconductor, located in the water pool, to the organic solvent (Figure 3).

Support of this work by the U.S. Department of Energy is gratefully acknowledged.

Received, 15th August 1983; Com. 1111

References

1 M. Grätzel, *Acc. Chem. Res.*, 1981, **14**, 376; J. R. Darwent and G. Porter, *J. Chem. Soc., Chem. Commun.*, 1981, 145; J. R. Darwent, *J. Chem. Soc., Faraday Trans.* 2, 1981, **77**, 1703; K. Kalyanasundaram, E. Borgarello, and M. Grätzel, *Helv. Chim. Acta,* 1981, **64**, 362.
2 E. Borgarello, J. Kiwi, E. Pelizetti, M. Visca, and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 6324.
3 A. J. Bard, *J. Phys. Chem.*, 1982, **86**, 172.
4 J. H. Fendler, 'Membrane Mimetic Chemistry,' Wiley–Interscience, New York, 1982.
5 K. Kurihara and J. H. Fendler, *J. Am. Chem. Soc.*, 1983, **105**, 6152.
6 (a) D. Duonghong, J. Ramsden, and M. Grätzel, *J. Am. Chem. Soc.*, 1982, **104**, 2977; (b) A. Henglein, *J. Phys. Chem.*, 1982, **86**, 2291; (c) J. P. Kuczyuski, B. H. Milosavljevic, and J. K. Thomas, *J. Phys. Chem.*, 1982, **87**, 3368; (d) A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 301.
7 K. Kurihara, P. Tundo, and J. H. Fendler, *J. Phys. Chem.*, 1983, **87**, 3777.
8 A. Mills and G. Porter, *J. Chem. Soc., Faraday Trans.* 1, 1982, **78**, 3659.
9 I. Willner, C. Laane, J. W. Otvos, and M. Calvin, ACS Symposium Series, vol. 177, 1982, p. 71.

¶ Fluorescence lifetimes were determined on single photon counting equipment using a Sync.-pump frequency doubled pulsed laser as the excitation source (λ_{ex} = 290 nm). Emission observed at 490 nm.

** Hydrogen formation was monitored by a membrane polarographic detector (MPD) electrode and electrochemical processor (Applied Photophysics Ltd.) and quantified by gas–liquid partition chromatography (ref. 8).