

## Photoassisted hydrogen production using visible light and coprecipitated zinc sulfide.cntdot.cadmium sulfide without a noble metal

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ignored since transitions to them from the  $S_0$  ground state are not allowed by the symmetry selection rules.<sup>23</sup> The best-fit parameters for  $S_0$  are  $V_2 = -3980.0 \text{ cm}^{-1}$  and  $V_4 = -1023.0 \text{ cm}^{-1}$ , and those for  $S_1$  are  $V_2 = -2054.9 \text{ cm}^{-1}$  and  $V_4 = -1009.2 \text{ cm}^{-1}$ . These same potential parameters were used to calculate the 9PA- $d_5$  torsional frequencies which appear in the last column of Table II. Again, agreement is nearly within the experimental uncertainty. An independent fit of the 9PA- $d_5$  data gives the  $S_0$  potential parameters  $V_2 = -4209.2 \text{ cm}^{-1}$  and  $V_4 = -1094.4 \text{ cm}^{-1}$ , and the  $S_1$  parameters  $V_2 = -2465.2 \text{ cm}^{-1}$  and  $V_4 = -1122.2 \text{ cm}^{-1}$ . These potentials, shown as dotted lines in Figure 3, differ by less than about 10% from the potentials fitted to the 9PA data, which is probably less than the statistical uncertainty. Naturally, these potentials are to be regarded as valid only in the region near the minima, in which the experimentally determined vibrational levels lie. The inclusion of  $V_6$  potential terms results in only a slight improvement to the quality of the fits and negligible changes of the potentials in the well regions.

The fitting procedure we have employed leads to an arbitrary phase factor of  $90^\circ$  in the  $S_0$  and  $S_1$  torsional potentials. Fortunately, it is possible to establish the actual position of the potential in terms of  $\phi$  by employing additional evidence. First of all, an examination of a space-filling molecular model for 9PA shows that the planar ( $\phi = 0^\circ$ ) form is significantly destabilized by severe periplanar repulsions between the ortho-hydrogen atoms on the phenyl ring and the nearest hydrogens of the anthracene moiety. We therefore assign the torsional minimum of  $S_0$  to  $90^\circ$ . The phase of the  $S_1$  torsional potential can be established (relative to the  $S_0$  potential) by an analysis of the intensity pattern of the torsional transitions in Figure 2a. Franck-Condon factors calculated with the potentials as shown in Figure 3 are in good agreement with the observed intensities. In contrast, if the  $S_1$  potential is rotated by  $90^\circ$ , the predicted intensity pattern is

entirely inconsistent with experiment.

The  $S_0$  potential is relatively flat near the minimum compared to that of a harmonic oscillator. This shape is required to reproduce the negative anharmonicity in the  $S_0(a)$  spacings. The irregular positive anharmonicity in the  $S_1(A)$  spacings requires a double-minimum potential. The displacement of the equilibrium geometry in  $S_1$  compared to that in  $S_0$  correlates well with the observed maximum intensity of the  $A_0^n$  progression at  $n = 4$ . The Franck-Condon factors calculated for the best-fit potentials give an  $A_0^n$  peak at  $n = 5$ , in reasonably good agreement with experiment. A quantitative calculation of the line intensities for these transitions will require higher-order corrections to the simple Franck-Condon factors.<sup>23</sup>

In conclusion, it has been possible to determine the low-energy torsional potentials for 9PA in both  $S_0$  and  $S_1$  by analysis of the free-jet LIF spectra. These potentials reproduce quantitatively the experimental  $S_0(a)$  and  $S_1(A)$  transition frequencies in 9PA and 9PA- $d_5$ , and the calculated Franck-Condon factors are in qualitative agreement with the observed  $S_1(A)$  intensities. We expect that 9PA, along with the other prototype molecules for which data on torsional vibrations is becoming available, will serve as a valuable point of reference for photochemical and photophysical studies of molecules which exhibit large-amplitude vibrational motions.

*Acknowledgment.* The authors are indebted to Prof. Clayton F. Giese for providing the pulsed beam source used in these experiments and to Dr. Jaan Laane for giving us a copy of the computer code<sup>22</sup> which we used to determine the torsional potential parameters. This research was supported by the National Science Foundation, Grant Nos. CHE-8205769 and CHE-8351158, and by the Graduate School of the University of Minnesota.

*Supplementary Material Available:* Supplementary Material Available: Assignments of the 9PA and 9PA- $d_5$  fluorescence excitation spectrum, Tables I and II (6 pages). Ordering information is given on any current masthead page.

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## Photoassisted Hydrogen Production Using Visible Light and Coprecipitated ZnS·CdS without a Noble Metal

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ZnS and CdS coprecipitated into Nafion films and onto  $\text{SiO}_2$  have been used for photoassisted catalysis of  $\text{H}_2$  production in aqueous sulfide solution. With visible light and no noble metal catalyst, the ZnS·CdS catalyst is as active for  $\text{H}_2$  generation as Pt/CdS. There is no major difference in activity of the Nafion- and silica-supported catalysts.

### Introduction

Hydrogen production from water using semiconductor photocatalysts has been actively studied in recent years.<sup>1-4</sup> In previous papers,<sup>5,6</sup> we reported the advantages, construction, and operation of a photocatalyst system which consisted of platinized CdS in-

corporated in Nafion membranes. It was shown that this system compared favorably with the best systems reported to date for colloidal CdS dispersions.

Mixed semiconductor systems offer potential advantages for solar energy utilization because of the possibilities presented by interparticle electron transfer<sup>7</sup> and special properties (tuning of bandgap) of cofabricated systems.<sup>8</sup> In the present work, we report our initial results for hydrogen generation in a supported (Nafion and silica) mixed semiconductor system, ZnS·CdS, that does not require a noble metal catalyst. For this system, hydrogen generation is comparable to Pt/CdS/Nafion<sup>6</sup> and is much more

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efficient than for either semiconductor alone.

### Experimental Section

**ZnS·CdS/Nafion Preparation.** Prior to semiconductor incorporation, Nafion 117 membranes were cleaned as described earlier.<sup>6</sup> Single-component systems were prepared by soaking in either  $\text{Cd}(\text{NO}_3)_2$  or  $\text{Zn}(\text{NO}_3)_2$  solution (0.5 M) followed by treatment with  $\text{H}_2\text{S}$ . The mixed system was prepared by soaking in an equimolar solution of  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Cd}(\text{NO}_3)_2$  (0.5 M each). Soaking times of greater than 5 min saturated the films. The soaking was followed by rinsing in distilled water to remove excess and unbound metal ions. The films were then immersed in distilled water through which  $\text{H}_2\text{S}$  was bubbled for 10 min. The films are denoted ZnS·CdS/Nafion, CdS/Nafion, or ZnS/Nafion, depending on their composition.

The films were analyzed by X-ray powder diffraction (XRD). No XRD signals of ZnS were observed for either the ZnS·CdS/Nafion or the ZnS/Nafion. CdS/Nafion films, on the other hand, exhibited relatively strong XRD peaks corresponding to hexagonal CdS.<sup>6</sup> Although small peaks (presumably due to hexagonal CdS) were obtained for the mixed ZnS·CdS/Nafion system, the intensities were too weak to make a positive identification. These results show that CdS crystal growth is influenced by coprecipitation of ZnS and that crystallite sizes are very small (<30 Å). SEM of ZnS·CdS/Nafion showed a rough surface with particle sizes on the order of 0.5  $\mu\text{m}$ .

The films (1 × 1 cm when dry) were immersed in Pyrex glass cells containing 3 mL of 0.1 M  $\text{Na}_2\text{S}$ . The vessels were degassed under vacuum with sonication to remove gases from the interior of the membrane and were purged with  $\text{N}_2$ . Then the vessels were sealed with a rubber septum.

**ZnS·CdS/SiO<sub>2</sub> Preparation.** These catalysts were prepared by a conventional impregnation technique as follows: 1.00 g of  $\text{SiO}_2$  (Cab-O-Sil silica 300, Degussa) was immersed in 50 mL of aqueous solution containing  $2.31 \times 10^{-3}$  mol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $2.31 \times 10^{-3}$  mol of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , or a mixture of  $1.15 \times 10^{-3}$  mol of each of the nitrates. After the  $\text{SiO}_2$  powder was immersed, the solution was stirred for 2 h and then 50 mL of water saturated with  $\text{H}_2\text{S}$  was added and stirring continued for an additional 24 h. The resulting precipitates were filtered and dried in an oven at 110 °C. The fine powder thus obtained was either 24 wt % ZnS/SiO<sub>2</sub>, 26 wt % CdS/SiO<sub>2</sub>, or 11 wt % ZnS, 17 wt % CdS/SiO<sub>2</sub>, respectively, as determined by atomic absorption spectroscopy.

No XRD peaks were observed for these powders, indicating that the crystallite size was extremely small (<20 Å). Unsupported ZnS·CdS powder was also prepared for comparison by coprecipitation with  $\text{H}_2\text{S}$ -saturated water. The X-ray diffraction spectrum of this powder showed strong peaks corresponding to cubic ZnS and cubic CdS.

The photogeneration of hydrogen from water was carried out as follows: 50 mg of each catalyst was placed (not suspended) on the bottom of a 19 mL Pyrex glass vial. Then 12 mL of 0.1 M  $\text{Na}_2\text{S}$  aqueous solution was added as a sacrificial reagent, followed by deaeration assisted by ultrasonification and a purge with  $\text{N}_2$ .

**Photogeneration of Hydrogen.** A water-filtered 450-W Xe lamp and a glass filter (Corning 3-72) were used. The latter removes wavelengths shorter than 440 nm. Samples were taken with a gas syringe at periodic intervals for analysis by gas chromatography (using a Porapak Q column and  $\text{N}_2$  as the carrier gas). As the UV-visible absorption spectra of both ZnS·CdS/Nafion and ZnS·CdS/SiO<sub>2</sub> show sharp increases in optical density at the band edges of ZnS (340 nm) and CdS (510 nm) and no features attributable to a solid solution of the mixed sulfides, the filtered Xe lamp radiation is absorbed only by the CdS.

### Results

Figure 1 shows the results obtained for visible light irradiation ( $\lambda > 440$  nm) of the ZnS·CdS/Nafion and for a Pt/CdS/Nafion sample.<sup>6</sup> Neither the CdS/Nafion nor the ZnS/Nafion film showed any activity with visible light, even after 8 h of irradiation.

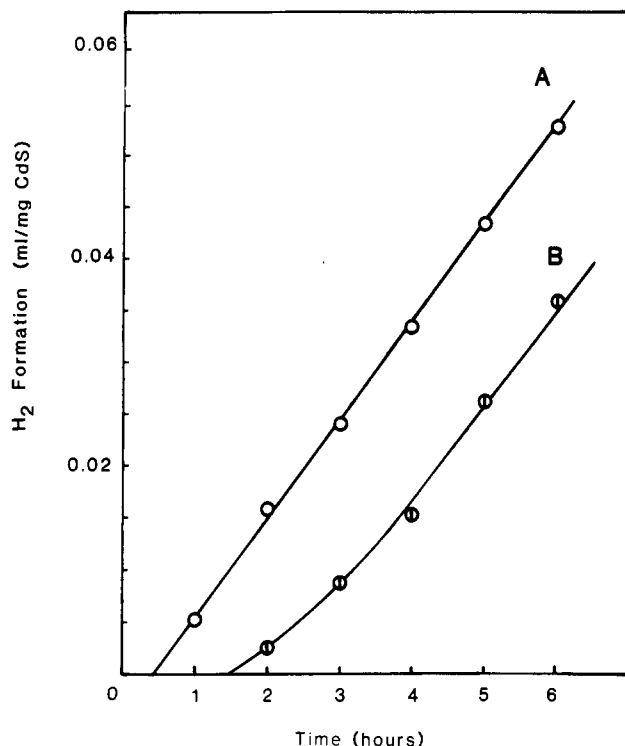


Figure 1. Photogeneration of  $\text{H}_2$  from Pt/CdS/Nafion (curve A) and ZnS·CdS/Nafion (curve B) films by visible light ( $\lambda > 440$  nm). The ordinate is in mL of  $\text{H}_2$  per mg of CdS per unit intensity.

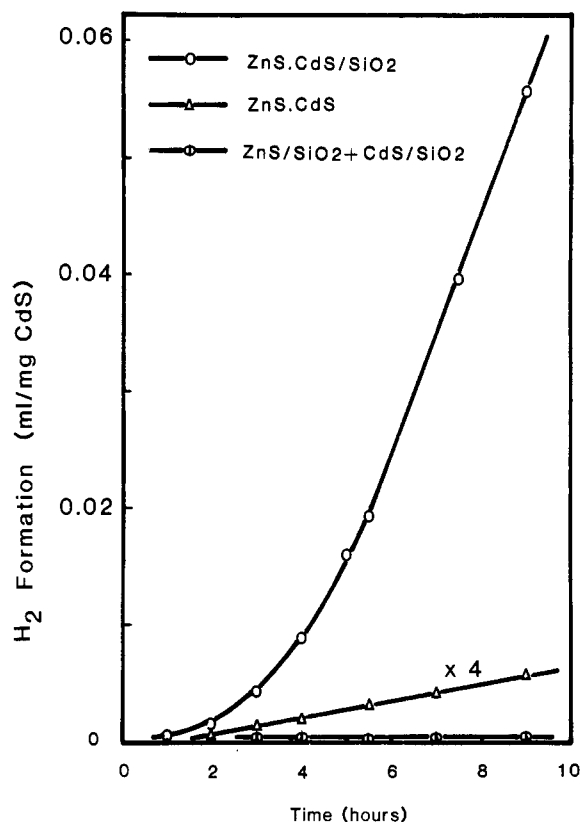


Figure 2. Hydrogen production by visible light irradiation of ZnS·CdS/SiO<sub>2</sub>, unsupported ZnS·CdS, and physically mixed ZnS/SiO<sub>2</sub> and CdS/SiO<sub>2</sub>. 50 mg of each catalyst in 12 mL of deaerated 0.1 M  $\text{S}^{2-}$  solution was used. The ordinate is in mL of  $\text{H}_2$  per mg of CdS per unit intensity.

Figure 2 shows comparable results for ZnS·CdS/SiO<sub>2</sub>, ZnS·CdS with no support, and a physical mixture of ZnS/SiO<sub>2</sub> and CdS/SiO<sub>2</sub>. The ZnS/SiO<sub>2</sub> and CdS/SiO<sub>2</sub> alone showed no activity over a 10-h irradiation period. Results were reproducible in each case to within 10%.

As discussed in detail elsewhere,<sup>9</sup> when the UV filter was removed, H<sub>2</sub> production rates increased by about a factor of 5, primarily because of the increased photon absorption rate. As compared to the ZnS-CdS systems, the UV-visible assisted H<sub>2</sub> production rates on either ZnS- or CdS-supported systems alone were more than a factor of 20 slower.

### Discussion

A comparison of the results shown in Figures 1 and 2 indicates several points of interest. (1) Except for a difference in induction time, a topic discussed elsewhere,<sup>9</sup> the activity of the ZnS-CdS/Nafion system is comparable to the Pt/CdS/Nafion system. (2) The activity of the ZnS-CdS/Nafion and ZnS-CdS/SiO<sub>2</sub> systems are comparable. (3) The activity of the ZnS-CdS/SiO<sub>2</sub> system is higher than that of the unsupported ZnS-CdS. (4) The activities of supported and unsupported ZnS-CdS systems are all significantly better than either the physical mixture of ZnS/SiO<sub>2</sub> and CdS/SiO<sub>2</sub> or the individual sulfides.

From these observations, we draw the following conclusions.

(1) Relatively efficient photoassisted catalytic hydrogen generation

can be realized without a noble metal catalyst. (2) The nature of the support is not a crucial element. (3) Intimate contact of ZnS and CdS is required for good activity.

A major issue is, of course, a detailed description of the intimate contact. As noted above, the UV-visible absorption spectra are dominated by features associated with bandgap excitation of separate phases of CdS and ZnS. The XRD data of the unsupported ZnS-CdS (which shows respectable activity) contain sharp diffraction peaks for both ZnS and CdS. These results and luminescence data<sup>9</sup> point to separate CdS and ZnS phases. Preliminary X-ray photoelectron spectroscopic data<sup>9</sup> suggest that the coprecipitated catalysts consist of particles with CdS-rich cores coated with a ZnS-rich exterior. This morphology gives a large interfacial area, maintains separate phases of CdS and ZnS, and leaves a large concentration of ZnS on the exterior. The latter point implies that ZnS interactions with solution species are catalytically important. The question of how CdS and ZnS interact through the CdS-ZnS interface to exhibit excellent catalytic properties is currently under investigation using surface science and photophysics techniques.

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## ARTICLES

### Photon Correlation Spectroscopy Using Resonance-Enhanced Light Scattering

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Resonance-enhanced Rayleigh light scattering (RRS) has been measured for iodine dissolved in several different solvents. Experimental techniques are described which avoid excessive heating and which permit corrections to be made for optical absorption by the sample. Measured RRS intensities show reasonable agreement with the predictions of semiclassical theory. Photon correlation spectroscopy has been used to measure RRS intensity fluctuations from very dilute solutions of iodine in viscous aprotic solvents. The mean hydrodynamic radius of iodine, obtained from the translational self-diffusion coefficient, is 0.23 nm. Some particular applications of RRS in dynamic light-scattering studies of translational diffusion are briefly discussed.

#### Introduction

Although the technique of dynamic light scattering (DLS) using intensity fluctuation analysis is well established in the fields of colloid chemistry as a method of measuring particle translational dynamics, development has been limited by difficulties of interpreting the data for all but the most dilute of systems.<sup>1</sup> Light scattering measures primarily the collective translational motions of particles in a liquid sample. In most cases what is observed is the relaxation of concentration gradients in the system by mutual diffusion. From the point of view of interpretations in terms of particle sizes and particle interactions, however, it is often more useful to know the self-diffusion coefficient which currently can be reliably obtained only by extrapolating to infinite dilution.<sup>2</sup> In cases where there is more than one solubilized component clear interpretation is often very difficult. It is desirable to develop

methods to make the experiment more selective or specific to chosen species or processes in the mixture.

Encouraging progress has been made recently regarding the use of optical matching techniques as a means of separating collective and self-diffusional motions in colloidal suspensions<sup>3</sup> and microemulsions.<sup>4</sup> Forced Rayleigh scattering from externally induced concentration gradients may also be used<sup>5</sup> to measure

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