metabolism of living organisms. It is the prime energy source for most endergonic biological systems and participates in numerous enzymatic reactions. As we presented in our preliminary report,[7] the HOESY experiment is able to evaluate solvent and intramolecular proton dipolar relaxation for the three phosphates in ATP. We ran the HOESY experiment for 0.5 M ATP in fully deuterated phosphate buffer (100% D_2O, repeated lyophilizations). Figure 7 shows individual slices at three phosphorus signals along the F_1 dimension (proton chemical shift) in the HOESY experiment. Each phosphorus slice has a small peak corresponding to the HOD peak, due to the small number of residual solvent protons in the sample. The γ-phosphorus slice gives the highest HOD intensity which may be due to (a) the terminal phosphorus being most accessible to the water and (b) in the buffer (pH 5.6), there still being one proton attached to the γ-phosphorus through oxygen (pK_as for γ-phosphorus in ATP are 4.1 and 6.5[25]).

In the α-phosphorus slice, two intramolecular dipolar interactions are indicated: (a) with H-5' protons, close to the sugar ring, and (b) with the H-8 proton of the base. This is consistent with the anti conformation being populated, which is expected for solutions of ATP.[26]

Conclusions

The heteronuclear 2-D NOE experiment should prove to be a powerful albeit sometimes demanding experiment for structural elucidation and conformational analysis, both in ^{13}C and ^{31}P NMR spectroscopy. It should be noted that this experiment gives information through space (dipolar interaction) rather than through bonds (*J* coupling). For carbon-13, it provides information about dipolar interactions between quaternary carbons and nearby protons. A disadvantage of the HOESY experiment for relatively weak NMR nuclei (e.g., ^{15}N, ^{13}C) is that in order to detect cross peaks a concentrated sample may be necessary. This is especially true for nonprotonated sp[2] or sp- hybridized atoms at high magnetic fields, where NOEs may be quite small.

The HOESY technique should prove useful for the study of molecular conformation and solvent–solute interactions in a variety of chemical and biological systems. Since the observed nucleus is not limited to ^{13}C or ^{31}P, HOESY experiments are also expected to have significant potential in studies of peptides (^{15}N), organometallics and metalloenzymes[8] (spin $^1/_2$ metals), and solvation studies of inorganic spin $^1/_2$ ions.

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H$_2$ Photoproduction by Nafion/CdS/Pt Films in H$_2$O/S^{2-} Solutions

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Abstract: We report the construction, characterization, and evaluation of a novel system for photocatalytic hydrogen generation that comprises semiconductor (CdS) crystallites embedded in a polymer (Nafion) matrix that also contains a hydrogen-evolution catalyst (Pt). Hydrogen-production efficiencies from water containing a sacrificial electron donor (sulfide ion) were greater than those commonly obtained with unsupported colloidal or powdered semiconductors under similar conditions. Several factors dramatically influence performance: the crystalline form and surface composition of the semiconductor and the extent of catalyst dispersion throughout the film.

Photocatalytic and photosynthetic reactions at semiconductor particles provide the possibility of the utilization of solar energy for the promotion of useful chemical reactions.[1,2] Photoreactions at these particles are based on the production of electrons and holes (e^-h^+) upon absorption of light; these can react with species in solution to produce oxidized and reduced forms. These particulate systems are of interest because they are generally easy to fabricate, are potentially inexpensive, and have a large surface area which facilitates efficient light absorption and heterogeneous charge (e^- and h^+) transfer to solution species. CdS is an interesting semiconductor material that has been studied as an electrode material; many studies of particulate systems involving CdS have also been reported.[3–12]

Particle systems have several disadvantages, however. Since they are dispersed in the solvent system, they are inconvenient to use in continuous-flow systems. They may also tend to flocculate and settle out with time. A previous brief communication[13]

described the production and immobilization of CdS in a polymer (Nafion) matrix and its use for the photocatalyzed reduction of

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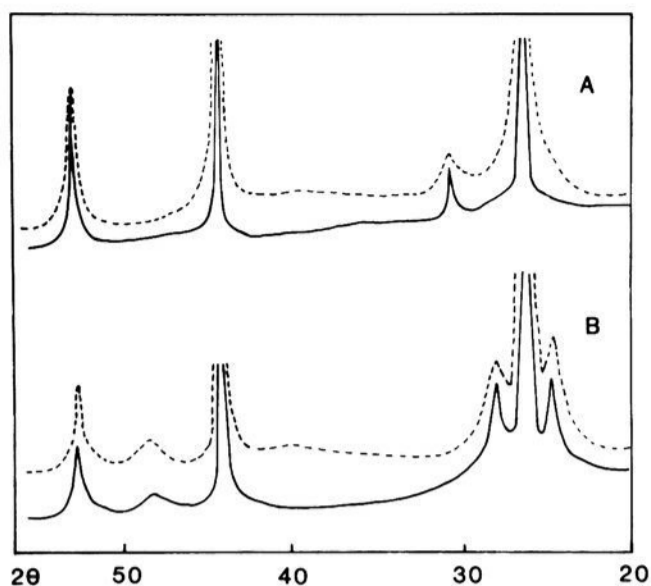
Figure 1. XRD spectra of cubic (curve A) and hexagonal CdS (curve B). The dashed lines are those of CdS incorporated in the Nafion film and the solid lines are commercial CdS powders.
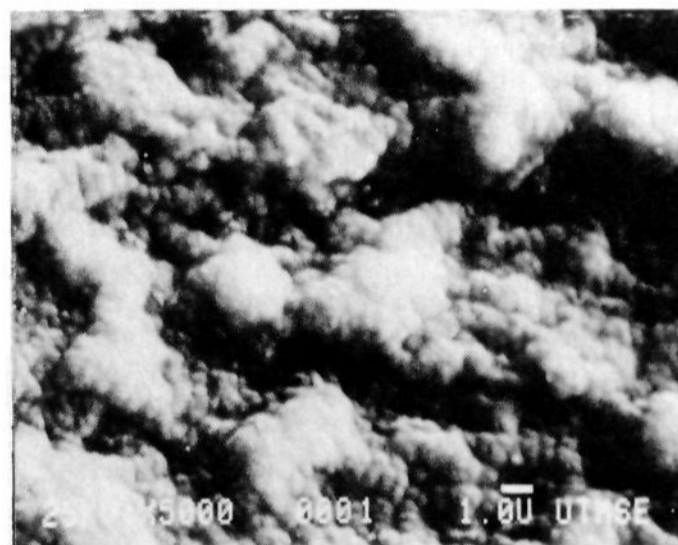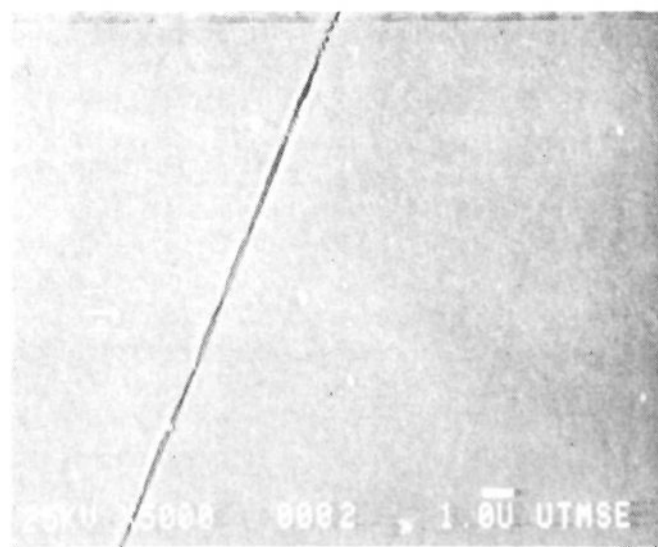
methyl viologen. In this report we discuss the incorporation of platinum as a catalyst in this Nafion/CdS system and the use of this "integrated chemical system" for the photocatalytic production of hydrogen. These polymer-immobilized semiconductor systems have several advantages. The photoactive system is held in place and so is useful in flow systems. The Nafion/CdS system can be removed for more facile analysis of the reaction solution and regeneration of the semiconductor particles. Moreover, the dispersed semiconductor particles do not tend to flocculate or settle. These membrane systems also offer the potential for "vectorial" charge transfer with separation of the oxidized and reduced products. In addition the polymer matrix itself may play a role in the operation of the system, e.g., by its ion-exchange properties, concentrating some solution reactants and rejecting others. Finally, it is a useful substrate for fabrication of a multicomponent system.

Experimental Section

1. Platinization of the Nafion Membrane. Nafion (117 DuPont, equivalent weight 1100, 180 μm nominal thickness) perfluorinated cation exchange membranes were used for all experiments reported herein. All Nafion films were cleaned by boiling in concentrated HNO_3 and then washing with boiling distilled water.

The homogeneous deposition of Pt into Nafion films was carried out by soaking in a dilute solution of $Pt(NH_3)_2I_2$ (0.1–0.5 mM)[14] for several hours. The amount of Pt complex incorporated into the Nafion films was determined by optical absorption spectroscopy and, depending on the soaking time, was in the range 0.01–0.6 mg/cm². The Nafion films with incorporated Pt complex were immersed in 0.1 M $NaBH_4$ solution overnight. Under these conditions the complex was reduced to produce Pt-metal particles throughout the Nafion films. The platinized Nafion films were washed two times with boiling distilled water or until the water was neutral. The concentration of Pt in the Nafion film could be controlled by varying the soaking time in the Pt-complex solution. The incorporated Pt crystallite size was determined by X-ray powder diffraction (XRD) line broadening methods to be ca. 100 Å.[15] Note that this homogeneous platinization always preceded CdS incorporation (see next subsection). The effect of the H_2S treatment on the Pt will be discussed below.

Pt was also deposited onto Nafion films *after* CdS incorporation by RF sputtering at 2×10^{-2} torr under Ar flow with a Materials Research Corp. Model MRC8620 triple shutter R&D sputtering module. The rate of Pt deposition was calibrated by measuring the optical absorption of Pt sputtered onto glass plates under similar conditions. This calibration provides our estimates of Pt film thickness, since for sputtered Pt the

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Figure 2. SEM photographs of the surface of α-CdS/Nafion and β-CdS/Nafion.

XRD and SEM were of insufficient intensity to provide an estimate of particle size or thickness.

2. Preparation of CdS-Impregnated Nafion Films and Control of the Crystal Form of CdS. Nafion films, with or without incorporated Pt, were soaked in 0.5 M $Cd(NO_3)_2$ for 1 h and then washed in distilled H_2O. The Cd^{2+} ion is strongly bound at the anion sites in the Nafion. The crystal form of CdS (α-hexagonal or β-cubic) in Nafion depended on the method of preparation. The XRD data for these different CdS forms are presented in Figure 1. As will be described below the crystal structure affected the efficiency of hydrogen production.

Method I: β-CdS (Cubic). The Nafion film was soaked in boiling, dilute HNO_3 (pH 2.1) and H_2S gas bubbled for 10 min. The films were then washed with boiling H_2O. These films are bright orange, and from the XRD widths the average CdS crystal size was estimated as ca. 200 Å ($\approx$20 Å).[15]

Method II: α-CdS (Hexagonal). The Nafion was soaked in distilled H_2O and bubbled with H_2S gas for 10 min, all at room temperature. The films were then washed with boiling H_2O. These films were bright yellow, and the XRD line widths gave an average crystal size of ca. 200 Å ($\approx$20 Å).[15] We note that in an earlier report with use of $CdCl_2$ and Method II[13] only α-CdS was formed.

Scanning electron microscopy (SEM) revealed a striking difference in the surface roughness of α- and β-CdS in Nafion (Figure 2). Cross-sectional SEM of CdS/Nafion did not demonstrate any morphological difference in these two crystal forms in the interior of the membrane. X-ray fluorescence detection of Cd demonstrated that Cd was essentially homogeneously distributed throughout the Nafion, with a slightly higher concentration near the outer surfaces.

As will be discussed later, the β-CdS (cubic) is much more active with respect to H_2 photoproduction than α-CdS (hexagonal). The extreme disparity in the appearance of the surface is the only morphological difference we have found for these two preparations. One may speculate that the observed difference in activity is a result of surface area at the CdS–solution interface; however, the light that penetrates quite deeply into the CdS layer is as photoactive as light absorbed near the surface (see Results and Discussion).

The total CdS content of these Nafion films was determined by leaching out the CdS with acid (1.0 M HCl) followed by polarographic analysis for Cd^{2+}. The maximum CdS content in the Nafion for these studies was 1.3 mg/cm² ($\approx$0.5 M). Unlike our earlier report,[13] in the studies reported here the CdS was distributed essentially uniformly throughout the Nafion.

H₂ Photoproduction by Nafion/CdS/Pt Films

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3. Photolysis. For most experiments two different irradiation systems were used: (1) a single lens system with a 1-kW xenon lamp (1.0 W/cm²) or (2) a multiple station system with a 450-W xenon lamp (0.15 W/cm²). Both used a water filter to remove IR radiation. Light intensities were measured by an EG&G Model 500-1 radiometer. Wavelength studies utilized an argon ion laser (Coherent Radiation Model CR6-UV). This laser has variable output power for the various wavelengths of interest.

All the experiments reported herein use 0.1 M Na₂S as a sacrificial reagent (pH 13); this prevents or minimizes oxidation of lattice S²⁻ ions in CdS by photogenerated holes.[6] Most irradiations were carried out at slightly above room temperature, after we determined there to be little temperature effect on the H₂ production rates. In most studies the Nafion/CdS membrane (ca. 1 cm × 1 cm) was supported in the bulk 0.1 M Na₂S solution. It is also possible to use Nafion/CdS membranes in a "two-cell" configuration, in which the membrane acts as a separator between two different solutions. Results for systems of this type are currently under investigation.

For most experiments the irradiated sample was supported in a 10-mL test tube and was immersed in 3 mL of the Na₂S solution. All solutions were thoroughly outgassed with N₂ before irradiation. Gaseous products were analyzed by gas chromatography (Autoprep A-700) with a 15-ft Porapak Q column at room temperature.

To assess the reproducibility of our measurements, simultaneous irradiations of three identically prepared samples were carried out. The relative standard deviation of these measurements was 10%.

Quantum yields were measured by using the blue-green lines of the argon ion laser. The power incident on the sample was measured with a laser power meter, and the hydrogen yield was measured as described above. No corrections were made for light absorption or scattering by the film.

4. Reagents. The chemicals used are commercially available: H₂S (Linde); nitric acid (MCB); Na₂S·9H₂O (Alfa); CdCl₂·2.5H₂O (Aldrich); Cd(NO₃)₂·4H₂O (Mallinckrodt); K₂PtCl₄ (Aldrich); H₂PtCl₆·6H₂O (Alfa); α-CdS (Aldrich, 99.999%); β-CdS (Aldrich, 98.88%); and NaBH₄ (Alfa).

Results and Discussion

In our experiments we have identified three primary effects on the rate of photogeneration of H₂: (1) CdS crystal structure and the film pretreatment or irradiation history; (2) method of Pt loading and the weight percent of Pt; and (3) excitation wavelength. A subsection is devoted to each of these. In the last subsection we compare the rate of H₂ production for the Nafion/β-CdS/Pt system with several other CdS/Pt systems.

1. Effect of Crystal Structure and Film Treatment. For most of the results discussed in this subsection the Pt was deposited homogeneously (see Experimental Section) before CdS impregnation. On the basis of smaller set of experiments we believe that the effect of CdS crystal structure is similar with sputtered Pt. One of the most striking findings in our work on Nafion/CdS is the much greater activity of β-CdS (cubic) toward H₂ production than α-CdS (hexagonal). The *best* Nafion/α-CdS system approached two-thirds of the activity of a typical Nafion/β-CdS preparation. The Nafion/β-CdS preparation also had the advantage of being very reproducible with respect to the rate of H₂ production, while different Nafion/α-CdS preparations varied by several orders of magnitude. It was verified by XRD that the β-CdS, which is thermodynamically less stable than α-CdS,[16] retained its cubic form after a series of irradiations. No H₂ is produced in the absence of light up to 70 °C. Temperature had little effect on the H₂ yield under photolysis over the range 30–50 °C; at 70 °C the photolysis yield decreased. All the results discussed in detail were obtained within the temperature range 35–45 °C.

The rate of H₂ production always diminished with irradiation time. This loss of activity was not simply the result of consumption of the S²⁻ in solution nor the inner filter effect of the generated S₂²⁻ ion, since replacement of the irradiated Na₂S solution with fresh Na₂S did not restore the initial H₂ production rate. A grey-blue deposit was observed to build up on the surface of the Nafion/β-CdS during irradiation. This deposit could be removed by washing the membrane with boiling H₂O, after which the activity was *higher* than in the initial run. The history of a
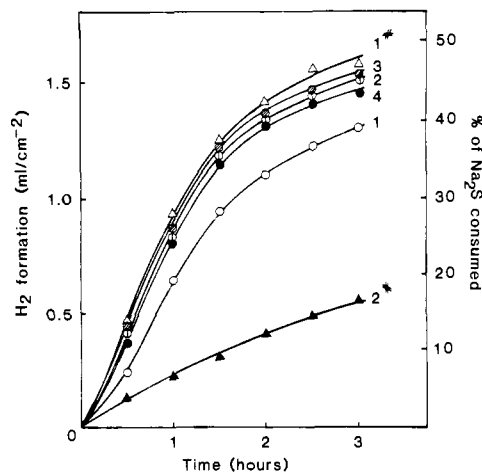
Figure 3. Time dependence of hydrogen production in a 1-cm² Nafion film containing CdS and Pt (0.02 mg/cm²). The integers are successive runs with the same film. Curves 1# and 2# are for a different film pretreatment. See text for details.

particular Nafion/β-CdS sample is presented in Figure 3. The percent consumption of Na₂S in Figure 3 is based on the following assumed stoichiometry:

$$2h\nu + 2S^{2-} + 2H_2O \xrightarrow{CdS} S_2^{2-} + H_2 + 2OH^- \qquad (1)$$
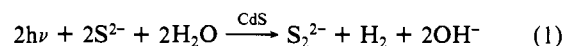
In a recent publication Aspnes and Heller[17] demonstrated a strong effect of adsorbed H₂ on platinum-group metal–semiconductor contacts. With their results in mind, Nafion/β-CdS was pretreated with H₂ at room temperature, followed by at least 0.5 h of outgassing with N₂, before use. Except for this H₂ pretreatment this film was identical with the film used to generate curves 1 through 4 in Figure 3. A comparison of a H₂-treated (1#) film to one with no H₂ treatment (1) in Figure 3 illustrates the overall improvement in the H₂ production rate for 1#. In particular the initial rate of H₂ production is improved (there is no hint of an "induction period"), consistent with the Aspnes–Hiller hypothesis that some H₂ production is required before contact potentials are favorable for subsequent H₂ formation. In Figure 3, 2# refers to the same film as 1#, after it was washed in boiling H₂O and restored to the same Na₂S solution.

The results of H₂ pretreatment suggested the following experiment to test the effect of irradiation history on the H₂ production rate (see Figure 4). A Nafion/β-CdS membrane was irradiated for 1 h with the low-power xenon lamp (0.15 W/cm²) yielding an initial H₂ production rate of 3.9 μmol/(cm²·h), and when the low-power lamp was replaced with the higher-power xenon lamp (1.0 W/cm²) and the membrane irradiated for 6 min and then returned to the low-power system, the H₂ production rate increased by a factor of about 2.

Surface analysis by XPS (VG ESCA-5) indicates that the oxidation state of Pt may be altered by this H₂ treatment. The Pt(4f₇/₂) binding energy (BE) was 72.1 eV on fresh films. After irradiation in the manner described above, the BE dropped to 71.3 eV, essentially the same as that for a Pt foil (BE = 71.2 eV). We conclude that Pt was partially oxidized in the fresh films and that during the early stages of hydrogen production, it was reduced to Pt°. This change in oxidation state is, we believe, related to the change in H₂ production activity.

To investigate this effect further, we probed the state of Pt before CdS incorporation into the film. After Pt incorporation and reduction with NaBH₄, the Pt(4f₇/₂) BE indicated that Pt²⁺ complexes were completely reduced to Pt°. Thus the oxidized Pt species is formed at some point during the CdS incorporation process. Thus while not excluding the process proposed by Aspnes and Heller,[17] we consider the reduction of partially oxidized Pt as responsible, in part, for the observed induction period.

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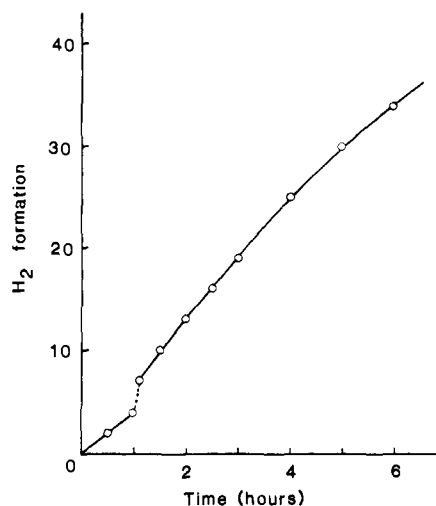
Figure 4. Hydrogen production of the CdS–Pt (0.04 mg/cm²)–Nafion film by a low-power (0.15 W/cm²) xenon lamp. The dashed line corresponds to a 6-min irradiation by a high-power (1 W/cm²) xenon lamp.
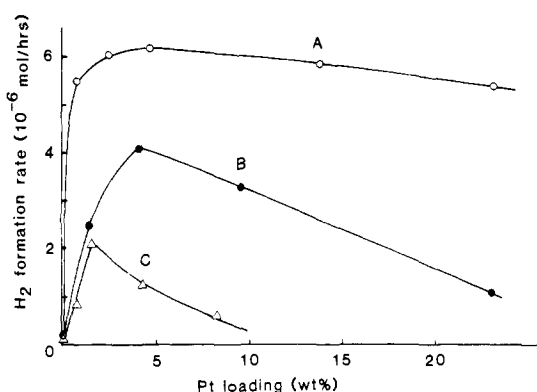

Figure 5. Effect of Pt loading on hydrogen production for different Pt–CdS systems (for 3 h of irradiation). Curve A: chemically reduced Pt:Nafion/β-CdS film. Curve B: photoreduced colloidal Pt–Colloidal CdS. Curve C: sputtered Pt:Nafion/β-CdS film.

2. Effects of Platinum Deposition and Loading. As discussed in the Experimental Section, two modes of platinization were used: (1) chemical reduction, which is presumed to disperse Pt homogeneously in the Nafion preceding CdS impregnation, and (2) Pt sputtering after CdS impregnation. In the second case the H₂ production was very inefficient unless the Pt side of the Nafion/CdS membrane was irradiated. Clearly there must exist some inverse dependence of H₂ yield on the average separation between the site of photon absorption and the Pt catalyst (this point will be discussed further in the next subsection). The H₂ yield was greatest for a sputtered Pt coating on the order of 100 Å in thickness; at greater thicknesses, the yield declined approximately exponentially with the thickness of the coating. We interpret this as a simple "filter effect" by the Pt metal.

For a comparison of different CdS/Pt systems, the H₂ yield as a function of Pt loading was measured for Nafion/β-CdS with chemically reduced Pt or with sputtered Pt and CdS colloid with photoreduced Pt (following the method of Buhler et al.).[18] In all cases 1.3 mg of CdS was used with identical irradiation conditions; the results are presented in Figure 5. For the cases of chemically reduced Pt with Nafion/β-CdS or photoreduced Pt–CdS colloid, the optimum loading was ~4 wt %. For sputtered Pt with Nafion/β-CdS, the optimal loading was ~1.5 wt %. Note that for Nafion/β-CdS the optimal H₂ yield for the sputtered Pt is approximately one-third that of chemically deposited Pt. We ascribe this to a simple geometric effect, i.e., the average separation between an absorbed photon and the Pt is larger for the "layered" sputtered Pt:β-CdS system. We do not have an explanation for the much stronger decrease in H₂ yield for Pt > 4 wt % for the CdS colloid system relative to Nafion/β-CdS.
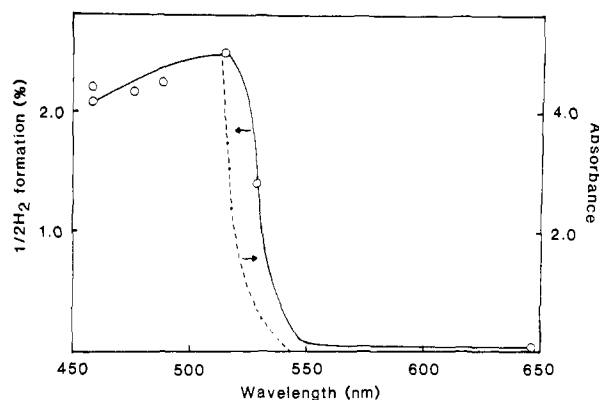
Figure 6. Photoaction spectrum of the CdS–Pt (0.04 mg/cm²) film (obtained by laser excitation (50 mW)). The dashed line is the UV spectrum of the CdS–Pt film.
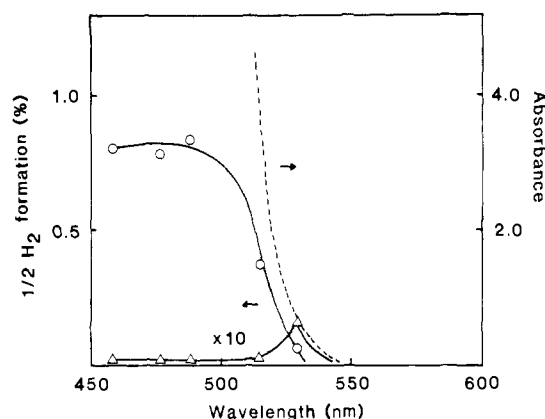

Figure 7. Photoaction spectra of the CdS–Pt (100 Å thick) film (obtained by laser excitation (50 mW)) with irradiation from the Pt side (O) and the bare CdS side (△). The dashed line is the UV absorption of the CdS–Pt film.

3. Effect of Irradiation Wavelength and Intensity. For all the experiments discussed in this subsection an Ar ion laser was used as an excitation source. This excitation source has several emission lines that can be selected in the region of the CdS band gap, and the power of all lines can be adjusted to be the same. In Figure 6 the action spectrum for H₂ production is compared to the Nafion/β-CdS (chemically deposited Pt) absorption edge. As expected, the H₂ yield increases sharply at the band edge (note the absence of H₂ production at the 647.1-nm Kr ion laser line). There is a slight decrease in H₂ yield at the shorter wavelengths, where the light absorption by the CdS colloids is known to be increasing. This implies that H₂ production near the illuminated surface is slightly less efficient than deeper in the Nafion/β-CdS membrane.

Analysis of the effect of penetration depth of the radiation is more straightforward for Nafion/β-CdS with the sputtered Pt coating (Figure 7). In this case the H₂ yield does not rise as rapidly at the band edge as with the chemically deposited Pt and reaches a clear plateau at shorter wavelengths. Also shown in Figure 7 is the wavelength dependence of H₂ production with irradiation from the Pt-free side of the Nafion/β-CdS. There is no appreciable H₂ yield except at the longest wavelength. At this wavelength some light reaches the platinized side of the membrane, although it is much attenuated. These results reemphasize that CdS must be excited in the vicinity of the Pt catalyst.

It is interesting to consider the relation between the light-penetration depth and H₂ yield for a sputtered Pt coating in more detail. For purposes of discussion we adopt a model in which the rate constant of H₂ formation from an excitation event a distance x from the CdS–Pt interface, $r(x)$, is a step function, i.e.

$$r(x) = r_0 \qquad x < L$$
$$r(x) = 0 \qquad x > L \qquad\qquad (2)$$
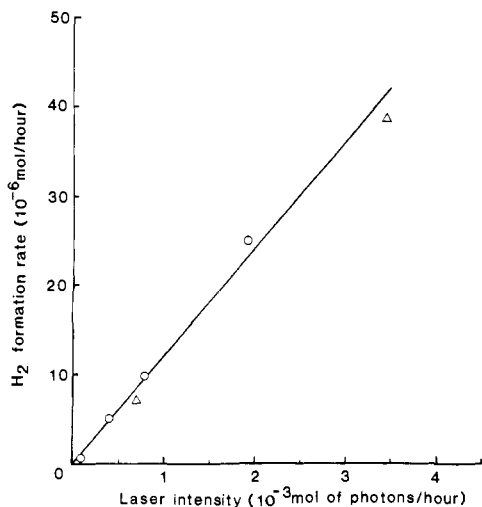
Figure 8. Light-intensity dependence of the rate of hydrogen production in a Nafion film containing CdS and Pt (0.04 mg/cm^2) at 514.5 (O) and 457.9 nm (△).

Thus for constant photon flux the rate of H$_2$ formation per cm^2 of irradiated surface for any wavelength, R_λ, is related to the fraction of incident light that is absorbed in the region $0 \leq x \leq L$, i.e.

$$R_\lambda = I_{ex}r_0(1 - e^{-\alpha_\lambda L}) = I_{ex}r_0(1 - 10^{-\epsilon_\lambda ML}) \qquad (3)$$

where α_λ is the extinction coefficient in cm^{-1} and I_{ex} is the photon flux per cm^2. In the second term M is the molarity and ϵ_λ the decadic molar extinction coefficient of the CdS. If $\epsilon_\lambda ML \gg 1$ then R_λ reaches a constant value, as observed for $\lambda < 500$ nm. The relative rate of H$_2$ formation for band edge excitation ($R_{\lambda e}$) to the limiting yield for deep band excitation ($r_0 I_{ex}$) yields an equation for L

$$R_{\lambda e}/r_0 I_{ex} = 1 - 10^{-\epsilon_{\lambda e} ML} \qquad (4)$$

Taking either our values for ϵ based on the Nafion/β-CdS absorption spectrum or published values for CdS colloids,[19] we estimate L to be in the range 10–30 μm. Thus our results are consistent with extensive charge or energy migration from the point of initial excitation to the CdS–Pt interface. This calculation does assume a homogeneous Pt coating on the outside region of the Nafion/CdS membrane. If there is significant sputtered Pt migration into the Nafion (on the order of 10 μm) then L in the previous equations would correspond to this migration length. However, we have not been able to directly detect Pt in the interior using Ar ion sputtering/XPS techniques.

Extensive charge or energy migration *could* lead to nongeminate electron-hole recombination or excited-state annihilation. This would result in a sublinear dependence of H$_2$ formation rate on light intensity. This does not seem to be the case, since the rate of H$_2$ production is linear with laser intensity at either 514.5 or 457.9 nm for Nafion/β-CdS/sputtered Pt (see Figure 8).

4. Comparison of Nafion/β-CdS with Other Sacrificial CdS:Pt Systems. It is difficult to establish absolute rates of H$_2$ production, because different workers use different irradiation geometries and/or sources (including filtering). We have approached this problem by comparing our Nafion/β-CdS system (with chemically deposited or sputtered Pt) with two other CdS:Pt systems reported in the literature. We have tried to reproduce the method of CdS:Pt preparation based on these published reports and have compared the rate of H$_2$ production under identical irradiation conditions. We have also compared the ratio of the H$_2$ production rate with and without Pt catalyst, as a kind of internal calibration. These results are given in Table I (also see Figure 4 and the discussion in subsection 2). Our optimum Nafion/β-CdS system with chemically deposited Pt is slightly more efficient than the dispersed

Table I. Comparison of H$_2$ Production by Different CdS/Pt Preparations

system	wt % of Pt	H$_2$ rate,[a] μmol/(cm^2·h)	rate with Pt/ rate Pt free
CdS colloid,[b] photoreduced Pt	2.5	4.0	10
CdS powder,[c] Pt powder	4.0	1.0	2.5
Nafion/β-CdS, chem-reduced Pt	1.3	4.2	100
Nafion/β-CdS, sputtered Pt	1.5	2.1	33
Nafion/α-CdS, chem-reduced Pt	1.3	2.5	100

[a] Irradiation source: xenon lamp, 0.15 W/cm^2. [b] Preparation according to Buhler et al.[18] [c] Preparation according to Matsumura et al.[9b]

CdS colloid system of Buhler et al.[18] and significantly more efficient than the CdS powder system of Matsumura et al.[9b] Perhaps the most interesting difference between our Nafion/CdS system and colloid or powder systems is the very large enhancement factor induced by the Pt catalyst, i.e., the Nafion/CdS system is inefficient for H$_2$ production in the absence of Pt catalyst.

We note that the number of moles of H$_2$ produced with a typical Nafion/β-CdS system exceeds the moles of CdS present by a factor greater than 100. Clearly this system does not involve extensive oxidation of the CdS itself. If the sacrificial reagent Na$_2$S is eliminated, only a very small amount of H$_2$ is produced; for the pH range 6–12 under these experimental conditions we estimate the quantum yield of H$_2$ production to be ~5 × 10^{-6} (i.e., 1/2 × 5 × 10^{-6} mol of H$_2$ produced for each mol of photons absorbed).

Conclusions

Thus, we have developed a new technique for the support of highly reactive, small dimension semiconductor particles within a polymeric membrane. When the semiconductor particles of this integrated system are metallized to provide a catalytic reduction site, these materials function as effective photoelectrochemical interfaces for photoinduced electron transfer. Upon photolysis of platinized CdS particles supported within Nafion in the presence of a sacrificial electron donor (Na$_2$S), the production of hydrogen gas by water reduction can be observed.

The efficiency of hydrogen production by this integrated chemical system is comparable to the best colloidal or powdered CdS preparations that have been reported, under the same experimental conditions. The crystal structure of the photoactive semiconductor particle greatly influences the yield of hydrogen, with cubic β-CdS acting as a more active catalyst than hexagonal α-CdS. Also critical for efficient operation of the system was the method of dispersal of platinum on the semiconductor surface. Either homogeneous chemical deposition throughout the membrane or surface coverage by metal vapor deposition could be used to achieve metal–semiconductor contact.

A study of the effect of average separation between the photoactive interface and the metallic reduction center implies that either charge or energy migration occurs over an appreciable distance (upwards of 10 μm) or that appreciable diffusion of metal into the polymeric membrane during deposition has occurred. The observation of an induction period before evolution of hydrogen begins is consistent with the Aspnes–Heller[17] hypothesis requiring surface hydrogenation in order to establish the requisite contact potential for efficient gas production. However, using XPS we have also demonstrated that this induction period may be related to the reduction of Pt to the zerovalent state.

These integrated systems seem to be robust, although after prolonged use the rate of hydrogenation decreases. The photoactivity of a used membrane system can be restored by washing with boiling water to remove surface coatings. Stoichiometric consumption of surface-dispersed CdS is clearly not responsible for the decreased hydrogenation rate, for on a molar basis many more equivalents of hydrogen can be evolved from this integrated system than are present as photoactive semiconductor.

Efforts are continuing to understand the effect of the semiconductor crystal structure, of the degree of dependence on the

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mode of dispersal of platinum on the semiconductor particle, and of the optimum geometry in the integrated system on the efficiency of gas evolution.

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One-Electron Reduction of Nitrobenzenes by α-Hydroxyalkyl Radicals via Addition/Elimination. An Example of an Organic Inner-Sphere Electron-Transfer Reaction

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Abstract: The reactions in aqueous solution of α-hydroxyalkyl radicals with para-substituted nitrobenzenes were studied by using product analysis, electron spin resonance, and pulse radiolysis techniques. At neutral pH the α-hydroxyalkyl radicals are quantitatively oxidized to yield the corresponding ketones or aldehydes and H^+, and the nitrobenzenes are reduced to the radical anions. The mechanism of this redox reaction depends strongly on the substituents on the α-hydroxyalkyl radical (the electron donor) and on the nitrobenzene (the electron acceptor). In the case of α-hydroxymethyl radical, the reaction proceeds by addition to the nitro group to produce an alkoxynitroxyl radical which can undergo an OH^--catalyzed heterolysis to give formaldehyde and the radical anion of the nitrobenzene. With the α-hydroxyethyl radical, both addition and "electron transfer" take place, the fraction of electron transfer increasing with increasing electron-withdrawing power of the substituent. The nitroxyl-type adducts undergo a spontaneous unimolecular heterolysis to give acetaldehyde, H^+, and nitrobenzene radical anion. The rate constants k_s (from $<10^2$ to 5×10^4 s^{-1}) for this heterolysis increase with increasing electron-withdrawing strength of the substituent if it is on the benzene, and they decrease if the substituent is on the methyl carbon of the nitroxyl. The heterolysis reaction is characterized by low (5–10 kcal/mol) activation enthalpies and strongly negative (–5 to –25 eu) activation entropies, which originate from hydration of a proton in the transition state. From the effect on the activation parameters exerted by substituents on the electron acceptor and on the electron donor parts of the nitroxyl radical it is concluded that the heterolysis reaction proceeds by a push–pull mechanism and is entropy controlled. In the reaction of the α-hydroxyprop-2-yl radical with substituted nitrobenzenes, the lifetimes of potential adducts of the nitroxyl type are ≤ 1 μs if the substituent R is less electron donating than OH. However, if R = NH_2, an adduct is formed which undergoes spontaneous heterolysis with $k_s = 2.1 \times 10^3$ s^{-1}. The heterolysis reaction can also be slowed down by making the solvent less polar than water: in 95% propan-2-ol/5% water $k_s = 1.5 \times 10^4$ s^{-1} for R = CN as compared to $>10^6$ s^{-1} in water.

The one-electron reduction of nitro compounds has received considerable attention, particularly as a result of the interest in structure–reactivity correlations concerning radicals[2] and also in view of the application of nitro aromatics as radiosensitizers in radiotherapy.[3] In order to reduce the nitro compounds, these have often been reacted with α-hydroxyalkyl radicals, which generally behave as potent one-electron donors.[2] However, as shown[4] as early as 1968 by ESR measurements, the mechanism of interaction of α-hydroxyalkyl radicals and nitro compounds is more complicated than expected on the basis of simple electron transfer between the reactants. Depending on the nature of the

α-hydroxyalkyl radical and on solvent or pH, nitroxide-type radicals, formed by addition rather than electron transfer, were detected.[4,5] These observations were supported by the results of pulse radiolysis experiments using optical detection,[6] and it was concluded[4,6] that it is the stability of the conjugate carbonium ions[7] that determines whether the reaction between an α-hydroxyalkyl radical and the nitro compound proceeds by electron transfer or by addition. On the other hand, it has been pointed out[8] also that the redox potential of the nitro compound may determine the probability of radical addition or electron transfer. However, the dependence of the reaction pattern on the structure of the reactants has not been systematically studied. Furthermore, the potential influence of solvent and of pH has not received the necessary attention, although it was demonstrated[4] already in 1968 that, e.g., the adduct of the hydroxymethyl radical to nitrobenzene

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