Inorganica Chimica Acta, *90* (1984) 191–196

Effect of CdS Preparation on the Photo-catalyzed Decomposition of Hydrogen Sulfide in Alkaline Aqueous Media

NICK SERPONE*, ENRICO BORGARELLO

Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

MASSIMO BARBENI and EZIO PELIZZETTI

Istituto di Chimica Analitica, Università di Torino, 10125 Turin, Italy

Received March 17, 1984

Band-gap irradiation of CdS dispersions in alkaline aqueous media (pH 14) containing 0.1 M Na_2S produces hydrogen and sulfur. The reaction is photodecomposition of hydrogen sulfide by two quanta of visible light ($\lambda > 400$ nm). Various batches of commercially available cadmium sulfide, as well as CdS precipitated from nitrate, sulfate, and chloride solutions at neutral pH, produce different amounts of hydrogen. Electronically pure CdS (puratronic grade) generates almost no hydrogen. By contrast, CdS precipitates prepared in the presence of excess cadmium yield forty times more hydrogen than CdS prepared in the presence of excess sodium sulfide. Differences are rationalized in terms of possible surface modification and/or changes in the active sites by anions present as 'impurities' which could affect separation and recombination of the charge carriers, e_{CB}^- and h_{VB}^+, in CdS.

Introduction

Photochemical systems that generate hydrogen from water or hydrogen sulfide are based on redox reactions involving excited states of the light harvesting unit; such units can be dyes or semiconductor materials that absorb visible light in solar energy conversion schemes. One critical aspect that bears on the efficiency of the energy conversion process is the prevention of recombination of the redox species formed in the primary photo-redox event. In semiconductor materials, recombination of the electron/hole pairs formed from the light absorption act, leads to loss of chemical energy stored in the excited absorber. Thus, light-induced charge separation is an important step in converting photons to chemical energy. Recent work [2] from our laboratory has demonstrated electron transfer from the conduction band of CdS to that of TiO_2 semiconductor particulates in alkaline media containing bisulfide ions (or sulfide ions). This has led to effective charge separation by transferring e_{CB}^- of CdS onto the conduction band of TiO_2 and leaving the valence band holes on CdS. The process has been exploited to improve the performance of systems [3–8] achieving decomposition of H_2S by visible light excitation of CdS ($\lambda >$ 400 mn).

During the course of our investigations, we discovered that sample preparation of the cadmium sulfide semiconductor material has an important effect on the efficiency of hydrogen generation from the photo-cleavage of hydrogen sulfide in alkaline (pH 14) aqueous media. We report the effect of surface modification by chemical etching by acids, and we compare our results with those obtained using various batches of commercially available CdS. This study helps explain discrepant results from batch to batch, and results often differing from one laboratory to another.

Experimental

The three batches of CdS (*purissimum*, 99.999%) were purchased from Fluka and are denoted Fluka-1, Fluka-2, and Fluka-3. Anatase (145 m^2/g, elementary particle size ~100 Å, doped with Nb 600 ppm) was kindly provided by Dr. P. Panek, Bayer GmbH, West Germany. Puratronic grade CdS (99.998%) was purchased from Alfa-Ventron and was used as received. All other chemicals were at least reagent grade and employed as supplied by the vendor(s).

RuO_2-loading of TiO_2 particles was carried out by impregnating the powder with the desired amount of aqueous $RuCl_3$ solution; the slurry was then dried and calcined in air for 1 hour at 320 °C to form the ruthenium oxide. Loading was 0.5% w/w in RuO_2. Five different preparations of CdS were carried out. In the first three, a stoichiometric amount of a Na_2S solution was added to an aqueous solution of the cadmium salt ($CdCl_2$, $Cd(NO_3)_2$, or $CdSO_4$). The

---

*Author to whom correspondence should be addressed: Prof. N. Serpone [1], Department of Chemistry, Concordia University, 1455 deMaisonneuve Blvd. West Montreal, Que., H3G 1M8, Canada.

0020-1693/84/$3.00

mixtures were stirred for ~0.5 hour and the CdS was subsequently filtered by suction, washed 2–3 times with distilled water, and dried overnight *in vacuo* at ~60–70 °C. In the other two preparations, (a) to a 60-ml solution of 5×10^{-2} *M* Cd(NO$_3$)$_2$ was added a 140-ml solution 10^{-2} *M* in Na$_2$S (excess Cd^{2+} ions); or (b) to a 60-ml solution 5×10^{-2} *M* in Na$_2$S was added a 140-ml solution 10^{-2} *M* in Cd(NO$_3$)$_2$ (excess S^{2-} ions). The work-up of the two mixtures was carried out as above. Chemical etching of CdS was effected by adding 2–3 drops of concentrated nitric acid to an aqueous mixture of CdS, stirring manually for ~30 seconds and then drying the mixture in air at 320 °C for 1 hour.

Irradiations were carried out with samples of 25-ml contained (unless otherwise noted) in a pyrex glass vial with parallel flat surfaces or 5-ml volume contained in a round-walled pyrex glass vial closed with a septum. Solutions invariably contained 0.1 *M* Na$_2$S, 1 M NaOH, and 50 mg (or 10 mg) of CdS. Experiments with mixtures employed, in addition to CdS, 10 mg (in the 5-ml solutions) of RuO$_2$-loaded TiO$_2$ particles. The suspensions were argon-purged for ~10–15 minutes prior to irradiation with a 450-Watt Xe lamp equipped with a water jacket and a 400 nm cutoff filter to remove IR and UV radiation respectively. The global irradiance (>400 nm) of this lamp was 150–160 mW/cm^2 (unless otherwise noted) under the experimental conditions employed. Hydrogen was detected quantitatively by gas chromatography using a Carbosieve 5-Å column and argon as the carrier gas. The temperature of the solutions under irradiation was ~40 °C.

Results

Figure 1 illustrates the volume of H$_2$ produced by visible light irradiation ($\lambda > 400$ nm) of different batches of commercially available CdS. A comparison of CdS puratronic grade with CdS powders obtained from preparations using Na$_2$S and the sulfate, chloride, or nitrate salts of cadmium is depicted in Fig. 2 for 25-ml dispersions containing 0.1 *M* Na$_2$S and 1 *M* NaOH. Initial rates, r(H$_2$), of hydrogen generation are collected in Table I. Puratronic CdS produces very little hydrogen, r(H$_2$) = 0.002 ml/hr. Three different batches of CdS (Fluka, purissimum grade) produce H$_2$ at three different rates, differences between which are outside of experimental error; r(H$_2$) = 0.13 ml/hr (Fluka-2), 0.24 ml/hr (Fluka-1) and 0.41 ml/hr (Fluka-3). Of the three CdS materials prepared in our laboratory (see experimental for details), the naked CdS prepared from the sulfate salt gives the lowest rate of H$_2$ production, 0.12 ml/hr. Initial rates for the CdS prepared from the chloride and nitrate salts are 0.27 ml/hr and 0.50 ml/hr, respectively. In all cases (Figs. 1 and 2) there is an induction period of production of hydrogen which differs from sample to sample. It is evident in Fig. 2 that the r(H$_2$) is dependent on the sample preparation and, in particular, the nitrate preparation is intersting inasmuch as r(H$_2$) is nearly twice that from the chloride sample and nearly four times that from the sulfate sample. In addition, both the Fluka samples and our own CdS samples are far superior to the electronically-pure CdS (puratronic) material in generating hydrogen under visible light excitation. Figure 3 shows the volume of hydrogen produced against irradiation time for the CdS samples prepared in the presence of excess cadmium and excess sulfide ions. The former produces forty times more hydrogen (0.59 ml/hour; Table I) than the latter (0.015 ml/hour).

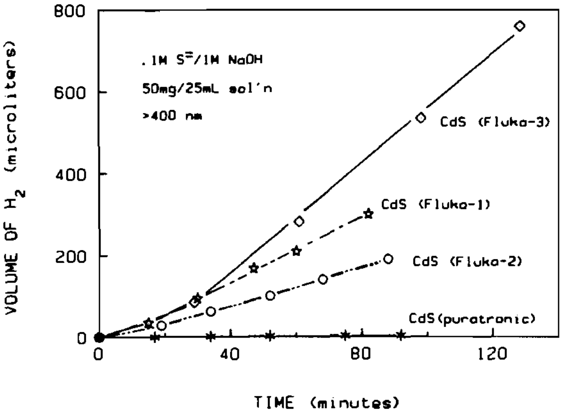

Fig. 1. Volume of hydrogen (STP) produced by visible light irradiation of various batches of commercially available CdS as a function of irradiation time; conditions: temperature ~40 °C, 0.1 *M* Na$_2$S/1 *M* NaOH, CdS present as 50 mg/25-ml solution.

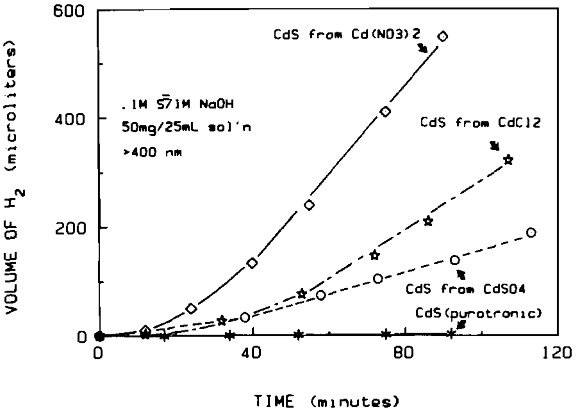

Fig. 2. Volume of hydrogen (STP) produced by visible light irradiation of various CdS precipitates obtained from different cadmium salts as a function of irradiation time; conditions as in Fig. 1.

In Fig. 4, which depicts the temporal evolution of hydrogen in 5-ml solutions containing 10 mg of the

TABLE I. Initial Rates of H_2 Production with CdS Semiconductor Dispersions in 25-ml Alkaline Aqueous Solution Containing 0.1 *M* Na_2S and 1 *M* NaOH.[a]

Dispersion[b]	$r(H_2)^c$, ml/hr
CdS (puratronic grade)	0.002
CdS (Fluka-1)	0.24
CdS (Fluka-2)	0.13
CdS (Fluka-3)	0.41
CdS (prepared from $CdSO_4$)	0.12
CdS (prepared from $CdCl_2$)	0.27
CdS (prepared from $Cd(NO_3)_2$)	0.50
CdS (prepared from $Cd(NO_3)_2$ salt with excess Cd_2^+ ions)	0.59[d]
CdS (prepared from $Cd(NO_3)_2$ salt with excess S^{2-} ions)	0.015[d]

[a] Irradiation wavelength >400 nm; 450-Watt Xe lamp. [b] 50 mg in 25-ml solution. [c] Estimated error ~±15–20%. [d] Irradiance of the lamp ~140 mW/cm². These samples were contained in round-walled pyrex vials closed with a septum.

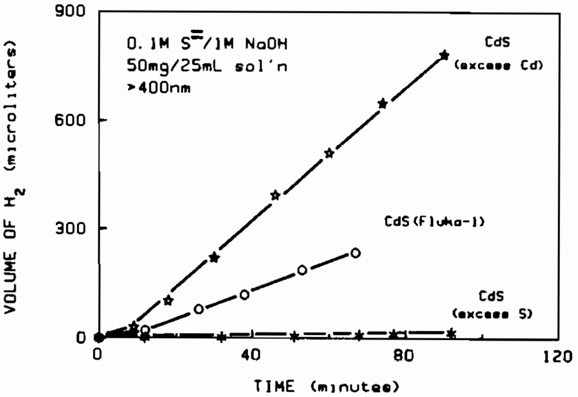

Fig. 3. Volume of hydrogen generated against irradiation time in CdS microdispersions prepared in the presence of excess cadmium ions and sodium sulfide. The behavior of commercially available CdS sample is also shown for comparison. Conditions same as for Fig. 1.

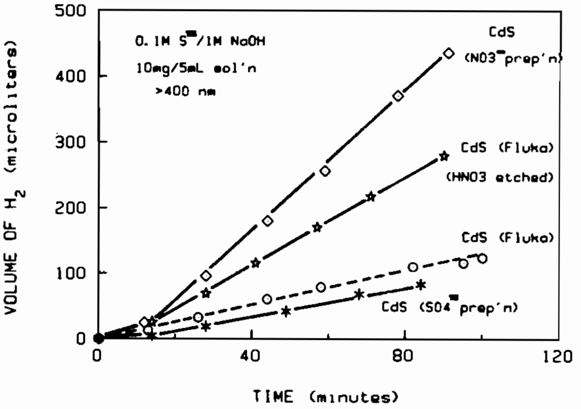

Fig. 4. Volume of hydrogen (STP) produced by visible light irradiation of various CdS dispersions as a function of irradiation time. One of the CdS samples was chemically etched with HNO_3; conditions: temperature ~40 °C, 0.1 *M* Na_2S/1 *M* NaOH, weight of CdS was in every case 10 mg/5-ml solution.

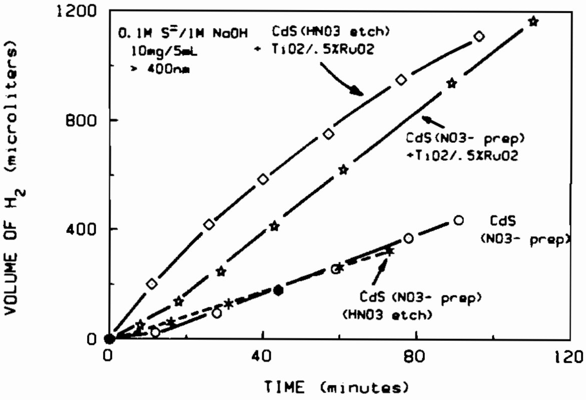

Fig. 5. Volume of hydrogen (STP) produced by visible light illumination of various catalytic CdS dispersions as a function of irradiation time. The RuO_2-loaded TiO_2 particles are present as 10 mg/5-ml solution; other conditions same as in Fig. 4.

semiconductor CdS material, 0.1 *M* Na_2S and 1 *M* NaOH, we compare the behavior of naked CdS precipitated from sulfate and nitrate solutions with a sample of CdS (Fluka) and an identical sample of CdS (Fluka) but chemically etched with nitric acid. This etching with HNO_3 was carried out to test whether H^+ or NO_3^- ions play the significant role in surface modification of the CdS dispersions. Etching with other acids (*e.g.* HCl, H_2SO_4, or AcOH) proved less effective in producing hydrogen from the S^{2-}/OH^- solutions (pH 14) [9]. Within experimental error, $r(H_2)$ for CdS (SO_4^{2-} preparation) and CdS (Fluka) is nearly the same, 0.069 ml/hr and 0.084 ml/hr respectively. Etching of the CdS (Fluka) sample with nitric acid increases $r(H_2)$ to 0.20 ml/hr. This compares with $r(H_2)$ for the CdS (NO_3^- preparation) which is 0.33 ml/hr. Interestingly, chemical etching of this latter sample with nitric acid has no effect on $r(H_2)$ (*cf.* Fig. 5); $r(H_2)$ is 0.28 ml/hr (etched sample) against 0.33 ml/hr for the unetched sample.

Figure 5 illustrates the amount of hydrogen generated *vs.* time in 5-ml S^{2-}/OH^- solutions which contain, in addition to 10 mg naked CdS (from Fluka and from the NO_3^- preparation), 10 mg of RuO_2-loaded TiO_2 particles (0.5% w/w). The initial rates are, respectively, 0.68 ml/hr (nitrate sample) and 0.87 ml/hr (Fluka, HNO_3-etched). If the CdS (Fluka) is unetched, a two-fold increase in $r(H_2)$ results (1.6 ml/hr). It is also noteworthy that, irrespective of the source of CdS (nitrate or sulfate preparations), $r(H_2)$ is unaffected in the presence of RuO_2-loaded TiO_2 (0.68 ml/hr *vs.* 0.66 ml/hr). Moreover, $r(H_2)$

TABLE II. Initial Rates of H_2 Production with CdS Semiconductor Dispersions of Various Compositions in 5-ml Alkaline Aqueous Solutions Containing 0.1 *M* Na_2S and 1 *M* NaOH.[a]

Dispersion[b]	$r(H_2)$,[c] ml/hr
CdS (prepared from $CdSO_4$)	0.069
CdS (Fluka)	0.084
CdS (puratronic grade)	0.002
CdS (Fluka, etched with HNO_3)	0.20
CdS (puratronic, etched with HNO_3)	0.20
CdS (prepared from $Cd(NO_3)_2$)	0.33; 0.31
CdS (prepared from $Cd(NO_3)_2$ salt and etched with HNO_3)	0.28
CdS (prepared from $CdSO_4$) + TiO_2/0.5% RuO_2	0.66
CdS (prepared from $Cd(NO_3)_2$ salt) + TiO_2/0.5% RuO_2	0.68
CdS (Fluka, etched with HNO_3) + TiO_2/0.5% RuO_2	0.87
CdS (Fluka) + TiO_2/0.5% RuO_2	1.6

[a] Irradiation wavelength >400 nm; 450-Watt Xe lamp.
[b] 10 mg in 5-ml solutions. [c] Estimated error ~ ± 15–20%.

increases by one order of magnitude in the presence of TiO_2/RuO_2 for the sulfate-prepared CdS but it increases by only a factor of two when CdS is prepared from the nitrate salt (*cf.* Table II).

To the extent that the presence of NO_3^- ions in the semiconductor dispersions seem to play a significant role in the value of $r(H_2)$, we investigated the influence of added NO_3^- ions to a dispersion of CdS (Fluka). The results are depicted in Fig. 6 for the temporal course of the hydrogen evolution. Initial rates are identical, 0.14 ml/hr, whether $[NO_3^-]$ is 0.001 or 0.1 *M* and are nearly twice the value of $r(H_2)$ for NO_3^--free, naked CdS dispersions (0.084 ml/hr). A ten-fold increase in $[NO_3^-] = 1$ *M* leads to a near three-fold decrease in $r(H_2)$, 0.055 ml/hr. In the experiments noted in Fig. 6, the appropriate amount of solid $NaNO_3$ was added to the 5-ml CdS dispersion. Addition of an equal amount of a nitrate solution, such that $[NO_3^-] = 0.1$ *M*, to solid CdS followed by drying at 320 °C for 1.5 hr has no effect on the temporal course of hydrogen production; $r(H_2)$ is 0.15 ml/hr when the resulting mixture is used to make the CdS dispersion. An additional feature in Fig. 6 is the fact that in the presence of 1 *M* NO_3^- ions, hydrogen formed rapidly and reached a plateau at ~40 μL of hydrogen. In the presence of either 0.001 *M* or 0.1 *M* NO_3^-, the evolution of hydrogen from naked CdS is sustained for a longer period.

In the presence of RuO_2-loaded TiO_2 particles, cadmium sulfide (Fluka) is more effective, $r(H_2) =$ 1.6 ml/hr, than CdS precipitated from the sulfate solution (0.66 ml/hr). Addition of 1 *M* $NaNO_3$ to the CdS–TiO_2/RuO_2 combination has little or no effect on $r(H_2)$, 1.4 ml/hr, but 0.1 *M* NO_3^- slightly decreases $r(H_2)$, 1.1 ml/hr.

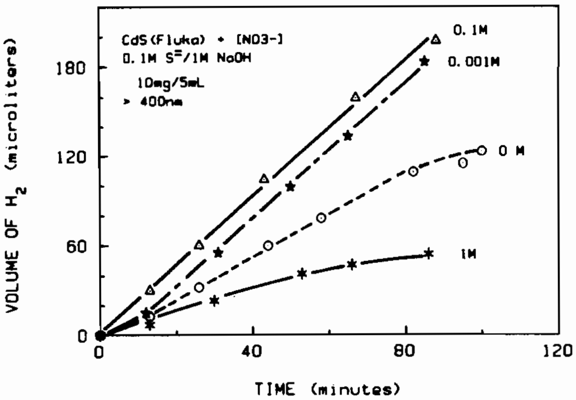

Fig. 6. Temporal course of the evolution of hydrogen (STP) produced by a commercially available CdS dispersion in the presence of various concentrations of nitrate ions; conditions as in Fig. 4.

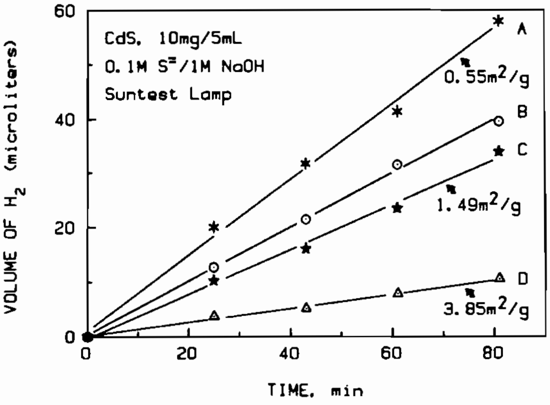

Fig. 7. Volume of hydrogen *vs.* time for four different commercially available batches of cadmium sulfide. The specific surface area of the samples used is also indicated for three of them. Other conditions, see text.

The results of an important experiment are shown in Fig. 7, in which we illustrate the temporal evolution of hydrogen for four different batches of commercially available CdS; for three of them, we indicate their specific surface area. In 5 ml suspensions, the $r(H_2)$ and surface area are: (A) 43 μl/hr, 0.55 m^2/g; (B) 30 μl/hr; (C) 24 μl/hr, 1.49 m^2/g; (D) 8 μl/hr, 3.85 m^2/g.

Discussion

Microheterogeneous dispersions, such as semiconductor particulates, combine a number of desirable properties that render them particularly attractive as light harvesting units. Among others, these are (a) high extinction coefficients, (b) fast carrier (e_{CB}^-

and h^+) diffusion to the solid–solution interface, and (c) suitable positioning of their valence and conduction bands. In addition, the possibility of modifying the surface of the semiconductor particle *via* chemisorption, chemical derivatization, chemical etching and/or catalyst deposition that can assist the light-induced charge separation and the subsequent fuel generating dark reaction is a definitive added advantage. In this regard, it is worth remarking that *two* quanta of light are required to reduce water to hydrogen and *four* quanta of light are needed to oxidize water to oxygen. Catalyst-loaded semiconductors through effective charge separation can store these quanta to induce the requisite redox reactions.

We have noted earlier [4–6, 8] that irradiation of naked CdS particles (2.4 eV band-gap) by visible light (>400 nm) leads to production of charge separated carriers (reaction 1), e_{CB}^- and h^+_{VB}l, which rapidly migrate to the particle–liquid interface. Conduction band electrons reduce water to hydrogen (reaction 2) while valence band

$$\mathrm{CdS} + h\nu \xrightarrow{>400\,\mathrm{nm}} e_{CB}^-(\mathrm{CdS}) + h_{VB}^+(\mathrm{CdS}) \qquad (1)$$

$$2e_{CB}^-(\mathrm{CdS}) + 2H_2O \longrightarrow H_2 + 2OH^- + \mathrm{CdS} \qquad (2)$$

holes oxidize HS^- or S^{2-} ions at pH 14 to produce sulfur. Concomitant formation of sulfur does not

$$2h_{VB}^+(\mathrm{CdS}) + S^{2-} \longrightarrow S + \mathrm{CdS} \qquad (3)$$

seem to affect reduction of water. Also, reduction of sulfur by conduction band electrons appears to be kinetically inhibited, though thermodynamically favored. The overall reaction thus corresponds to the photo-decomposition of hydrogen sulfide by *two* quanta of visible light to form hydrogen and sulfur (reaction 4). Sulfide oxidation is rapid enough to compete effectively with photo-corrosion of the CdS semiconductor particles [3–5].

$$H_2S + 2h\nu \xrightarrow{\mathrm{CdS}} H_2 + S \qquad (4)$$

In the presence of S^{2-}, sulfur reacts to form polysulfides, S_n^{2-}, which absorb visible light and thus compete with CdS particles for the incident photons. This leads to an apparent decrease in hydrogen formation, as evident from the curving of the plots in Figs. 5 and 6.

As illustrated in Figs. 1–3, the source and the nature of CdS preparation have a profound effect on the extent of reaction 4. Different commercial batches of CdS produce different amounts of hydrogen. We have observed that cadmium sulfide prepared from three different cadmium salts (nitrate, chloride, or sulfate) also leads to different amounts of hydrogen produced in a given period; the CdS from the nitrate salt is the most effective (Fig. 2). Electronically pure samples, such as 'puratronic' grade CdS generate very little hydrogen (0.002 ml/hr) upon band-gap excitation. Clearly, adventitious substances must be present in the particle structure or on the particle surface that affect the process of water reduction (reaction 2). Also, it is worth noting that the CdS powders precipitated in the presence of excess Cd^{2+} ions generate more hydrogen than those powders precipitated in the presence of excess sodium sulfide. Additionally, the nature of CdS proper may be affected by the nature of the anions present in its preparation. In this regard, we note that cadmium sulfide exists in two polymorphic forms [11]. The α-CdS normally obtains from preparations from chloride, bromide, or iodide solutions in the absence of acids and possesses the hexagonal crystalline structure. The other polymorph, β-CdS, is obtained by precipitation from the sulfate and nitrate solutions; it has the cubic zinc-blende structure.

The temporal course of hydrogen evolution from CdS dispersions (Fig. 2) originating from precipitates obtained from the sulfate, chloride, and nitrate solutions cannot be attributed to differences in the polymorphic forms of CdS. We note, for example, that the β-CdS polymorph from sulfate and nitrate salts produce the least (0.12 ml/hr) and the most (0.50 ml/hr) quantity of hydrogen, respectively. The α-CdS dispersion from the chloride salt produces 0.27 ml/hr. The difference must be sought elsewhere. The nature of the anion of the cadmium salt must play an important role here. In every case, we have observed the effect on $r(H_2)$ to decrease as the anion varies $NO_3^- > Cl^- > SO_4^{2-}$. This observation is confirmed by chemical etching experiments on puratronic grade CdS in which $r(H_2)$ also varies as $HNO_3 > HCl \sim H_2SO_4 > AcOH$ [9]. Moreover, Fig. 4 shows that chemical etching of CdS (Fluka) by nitric acid produces 2.4 times more hydrogen than does an unetched identical sample. However, nitric acid etching of the CdS obtained from nitrate solutions has no influence on $r(H_2)$ (*cf.* Table II). Evidently, nitrate ions have already modified CdS. The presence of nitrate ions in solutions (Fig. 5) also influences $r(H_2)$, but to a lesser extent than acid etching of the CdS particles.

These observations suggest that NO_3^- ions are chemisorbed on the surface and modify the active sites at which water reduction occurs. In the precipitates of cadmium sulfides prepared in this work, the anions may be present as intercalated 'impurities' in CdS and increase the activity by alteration of the nature and the number of active sites. It is possible, for example, that these anions increase the extent of charge separation of conduction band electrons and valence band holes and concomitantly reduce the extent of their recombination. Their ability to do so may vary as $NO_3^- > Cl^- > SO_4^{2-}$. Under our experimental conditions, the CdS samples used do not luminesce; this confirms recent results [12] that certain dissolved substances can quench, partially or completely, the CdS fluorescence. Anions decrease the fluorescence intensity of CdS [12] and the effect is rationalized by formation of CdS valence band holes/anion pairs at the particle surface inasmuch as the positive holes are attracted by the adsorbed anions, A_{ads}^- (reaction 5). This explains the NO_3^- effects observed in Fig. 6 at 0.001 *M* and 0.1 *M* in

$$h_{VB}^+(CdS) + A_{ads}^- \longrightarrow \{h_{VB}^+(CdS)\cdot A^-\}_{surface} \qquad (5)$$

nitrate. The decrease in $r(H_2)$ in the presence of 1 *M* NO_3^- ions is not clearly understood. Future work will address this.

Particularly intriguing is the behavior of the CdS particles illustrated in Fig. 3. The larger $r(H_2)$ for CdS prepared in the presence of excess cadmium is attributed to an increase of conduction band electron surface traps 0.7 ev [13] below the conduction band of CdS. These traps decrease e_{CB}^-/h_{VB}^+ recombination and allow reactions 2 and 3 to compete effectively with charge carrier annihilation. By contrast, if CdS is prepared in the presence of excess sulfide, these traps are greatly reduced with the consequence noted in Fig. 3, *viz.*, a forty-fold decrease in hydrogen produced. Support of these contentions comes from recent work [13] on the photoluminescence of colloidal CdS sols. Addition of Cd^{2+} ions to CdS sols increases the quantum yield of the red emission (ϕ_{red}) at ~700 nm, as expected since Cd^{2+} increases the number of sulfur vacant sites at the particle surface. Conversely, the presence of sulfide ions reduced ϕ_{red} inasmuch as the S^{2-} ions fill up the sulfur vacancies. In addition, Thomas and co-workers [14] have demonstrated that intercalation of cadmium and/or sulfide ions into the CdS structure produces defect sites which lead to red shifts in the band edge emission maxima and to longer-lived luminescence. Thus, it appears that both intercalated ions decrease the rate of conduction band electrons–valence band holes recombination. Our suggestion that excess sulfide in the preparation of CdS particulates reduces the number of water reduction sites is thus indirectly confirmed. Gutierrez and Henglein [15] recently made an interesting observation that a certain amount of finely divided cadmium deposited on the surface of CdS particles is required for the reduction of water to become a favorable process inasmuch as a catalytically active surface is now available on the CdS particles. That this may be the case in our experiments with chemically etched microdispersions and with microdispersions of CdS containing excess cadmium in its preparation cannot be precluded. Certainly, our observations of more efficient hydrogen production in these two cases would be consistent with Henglein's suggestion.

Finally, it must be noted that the variations in $r(H_2)$ for different batches of commercial CdS cannot be attributed to differences in the surface area of the particles (see Fig. 7). The CdS suspension with the larger surface area yields the least amount of hydrogen, under our experimental conditions. Variations in $r(H_2)$ must be due to chemically modified properties of the particles surface rather than to changes in the physical properties of these surfaces. No doubt, the often observed discrepant results from batch to batch of cadmium sulfide (commercial or prepared) and from laboratory to laboratory is understandable on the basis of the present results.

Acknowledgements

We are grateful to the Swiss National Science Foundation and to Ciba-Geigy, Basel, for financial support. M.B. and E.P. thank the Regione Piemonte of Italy for support. N.S. thanks Professor M. Grätzel for his kind hospitality during a sabbatical leave (1983–1984) and for several useful discussions on semiconductor properties.

References

1 Invited Professor, on leave (1983–84) from the Department of Chemistry, Concordia University, Montréal, Québec, Canada.
2 N. Serpone, E. Borgarello and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 342 (1984).
3 E. Borgarello, K. Kalyanasundaram, M. Grätzel and E. Pelizzetti, *Helv. Chim. Acta, 65*, 243 (1982).
4 E. Borgarello, J. Desilvestro, M. Grätzel and E. Pelizzetti, *Helv. Chim. Acta, 66*, 1827 (1983).
5 E. Borgarello, W. Erbs, M. Grätzel and E. Pelizzetti, *Nouv. J. Chim., 7*, 195 (1983).
6 E. Borgarello and M. Grätzel, in T. N. Veziroglu, W. D. Van Vorst and J. H. Kelley (eds.), 'Proc. 4th World Hydrogen Energy Conference, Hydrogen Energy Progress, Vol. 2, Pergamon, New York, 1982, p.739.
7 E. Borgarello, N. Serpone, M. Grätzel and E. Pelizzetti, in T. N. Veziroglu and J. B. Taylor (eds.), 'Proc. 5th World Hydrogen Energy Conference', Pergamon, New York, 1984, p. 1039.
8 E. Borgarello, M. Grätzel, K. Kalyanasundaram and E. Pelizzetti, *Chemtech., 13*, 118 (1983).
9 Evidence for surface modification upon chemical etching will be reported elsewhere: N. Serpone, E. Borgarello, M. Grätzel and E. Pelizzetti, to be submitted for publication.
10 The experimental conditions were: 10 mg CdS in Argon-purged 5-ml solutions of 0.1 *M* Na_2S, 1 *M* NaOH; irradiation $\lambda > 340$ nm with a Hanau Suntest Lamp equipped with a glass filter to remove wavelengths below 340 nm and the global irradiance of the lamp was ~100 mW/cm^2.
11 W. O. Milligan, *J. Phys. Chem., 38*, 797 (1934).
12 A. Henglein, *Ber. Bunsenges. Phys. Chem., 86*, 301 (1982).
13 J. J. Ramsden and M. Grätzel, *J. Chem. Soc., Faraday Trans. I*, in press (1984).
14 J. P. Kuczynski, B. H. Milosavijevic and J. K. Thomas, *J. Phys. Chem., 87*, 3368 (1983).
15 M. Gutierrez and A. Henglein, *Ber. Bunsenges. Phys. Chem., 87*, 474 (1983).