

## EFFICIENT PHOTOCHEMICAL CONVERSION OF AQUEOUS SULPHIDES AND SULPHITES TO HYDROGEN USING A RHODIUM-LOADED CdS PHOTOCATALYST

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### Summary

An efficient photocatalytic dispersion has been developed from CdS and a 0.2 wt.% rhodium(III) salt via photodeposition. The catalyst is presumed to contain rhodium species on the surface of the CdS particles and has been exploited in the photocleavage of hydrogen sulphide in the absence and presence of SO<sub>2</sub> in alkaline media (pH 14) to produce hydrogen and sulphur or hydrogen and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> respectively. The thermodynamic energy conversion efficiency is 0.17% or more and the quantum efficiency measured at 436 nm (bandpass, about 22 nm) is 0.45 ± 0.05 or more for hydrogen atom formation; the engineering energy conversion efficiency (energy in compared with energy out) is 2.6% or more. The turnover number is 2200 for rhodium and 15 for the CdS particles. One interesting aspect of this photocatalyst is that oxygen seems not to affect the hydrogen evolution rate.

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### 1. Introduction

The generation of fuels and chemicals from wastes through photochemical reactions is a subject under intensive investigation [1]. The light-driven cleavage of hydrogen sulphide to hydrogen and sulphur on colloidal semiconductors (*e.g.* CdS) is a very interesting process, and its use as an alternative to the present Claus process affords the recovery of hydrogen and sulphur [2, 3]. Several improvements have been reported regarding the devices and the efficiency of this photocatalytic process [4 - 15], including the use of two appropriately chosen semiconductor particles (CdS and TiO<sub>2</sub>) [16, 17].

An engineering energy conversion efficiency of 2% was recently reported [17] for hydrogen evolution from the cleavage of hydrogen sulphide using the combination of CdS and  $\text{TiO}_2\text{-RuO}_2$  in alkaline media with  $\text{SO}_3^{2-}$  present. Addition of an  $\text{RhCl}_3\cdot\text{H}_2\text{O}$  solution to irradiated naked CdS particles in  $\text{S}^{2-}\text{-SO}_3^{2-}$  aqueous media forms a slurry which exhibits a remarkable hydrogen evolution rate  $r(\text{H}_2)$ ; the engineering energy conversion efficiency under experimental conditions identical with those used earlier is 2.6% or more. The quantum efficiency of  $0.45 \pm 0.05$  or more in the present work shows the potential utility of the system when the importance of hydrogen as a fuel and the concomitant removal of hydrogen sulphide and sulphur dioxide from the environment are considered. Following the recent report of Tricot and Fendler [18], we believe rhodium(0) to be photochemically formed on the surface of CdS. (Studies are continuing [19] to define the precise nature of the supported redox catalyst using the techniques of surface science (Auger, electron spectroscopy for chemical analysis etc.). Spectroscopic evidence by Tricot and Fendler [18] indicates rhodium to be rhodium(0).)

Herein, we report the facile preparation of this photocatalyst and demonstrate the dramatic improvement in the yields of hydrogen generated from irradiating 5 ml aqueous alkaline solutions of  $\text{S}^{2-}$  and  $\text{SO}_3^{2-}$  containing 10 mg CdS "loaded" with an appropriate amount of rhodium.

## 2. Experimental details

CdS (Fluka) was used as received. Three batches of CdS (puriss., 99.999%) were tested to verify the reproducibility [20] of the reaction under the experimental conditions used. The samples are denoted Fluka-1, Fluka-2 and Fluka-3. A CdS luminescent-grade batch (Strem Chemicals) was also tested. In addition we tested a CdS sample synthesized by precipitation from a  $\text{Cd}(\text{NO}_3)_2$  aqueous solution and stoichiometric amounts of  $\text{Na}_2\text{S}$ , as well as CdS prepared similarly but with the cadmium salt present in a fivefold excess (molar) following the procedure described elsewhere [20]. A very photo-active but short-lived catalyst was obtained by addition of  $\text{Cd}(\text{NO}_3)_2$  to an  $\text{Na}_2\text{S}\text{-Na}_2\text{SO}_3$  alkaline solution in the presence of  $\text{RhCl}_3$ . Irradiation under argon, without further treatment, led to hydrogen evolution. After a brief period, the powder turned green and the photo-activity fell sharply.

A stock solution of  $\text{RhCl}_3\cdot\text{H}_2\text{O}$  (Fisher Scientific) in water ( $1 \text{ mg ml}^{-1}$ ) was freshly prepared because of the decrease in the catalytic activity when an aged rhodium(III) solution was employed. Solid  $\text{RhCl}_3\cdot\text{H}_2\text{O}$  dissolved in water shows a negligibly small concentration of free  $\text{Cl}^-$  ( $\text{AgNO}_3$  titration); on standing, however, the solution turns yellow and the concentration of free chloride ions increases significantly [21]. A similar chloride-water exchange occurs in  $\text{H}_2\text{PtCl}_6$  aqueous solutions [22]. Once the rhodium(III) is photodeposited on CdS particles, the problem of aging is no longer determinant in the photo-activity of the catalyst.

$\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  were AnalaR grade materials. Doubly distilled water was used throughout.  $\text{RuO}_2$  loading on  $\text{CdS}$  was done as described earlier [2, 3]; loading of  $\text{RuO}_2$  on  $\text{TiO}_2$  Degussa P25 was carried out as detailed in ref. 17. Etching of naked  $\text{CdS}$  (Fluka-1) powder with  $\text{HCl}$  or  $\text{HNO}_3$  acids did not improve  $r(\text{H}_2)$  [20]. All the experiments were performed in 14 ml flasks that were sealed with rubber septa and aluminium seals. The slurry was either argon purged (about 15 min) prior to illumination or was left air equilibrated. In each case a 5 ml sample was irradiated. Because of the pressure build-up of hydrogen in these small flasks when the experiments generated much hydrogen, the reported volumes of hydrogen represent the sum of three to five runs for the same slurry after degassing between runs.

Irradiation was carried out with a 1000 W Hg-Xe lamp fitted with a 10 cm water jacket and a 405 nm cut-off filter to remove both IR and UV radiation respectively. The output of the lamp was about  $243 \text{ mW cm}^{-2}$ , measured with a Scientech 362 energy power meter. Quantum efficiencies were measured using a 0.25 m monochromator set at 436 nm (bandpass, 22 nm). Hydrogen was measured using gas chromatographic methods on a GowMac gas chromatograph equipped with a molecular sieve 5A column and a thermoconductivity detector; argon was the carrier gas. Thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ), sulphide and sulphite ions were analysed using pulse polarographic techniques on a Metrohm 626 Polarecord that was coupled to an E505 polarograph stand and BM505 inverse polarography equipment. The sulphide half-wave potential was determined with a dropping mercury electrode in 0.1 M  $\text{NaOH}$  and is 0.75 V (measured with respect to a normal hydrogen electrode (NHE));  $E_{1/2}$  for  $\text{SO}_3^{2-}$  and  $E_{1/2}$  for  $\text{S}_2\text{O}_3^{2-}$  in an acetic acid-acetate solution (0.1 M) are 0.47 V(NHE) and  $-0.10 \text{ V(NHE)}$  respectively.

The rhodium(III) content in solution was monitored using atomic absorption techniques employing a Perkin-Elmer 503 atomic absorption spectrometer. The monitoring light source was a rhodium hollow cathode lamp (Spectrex Ltd.) and the measurements were carried out at 343.5 nm.

The catalytic slurry was prepared by adding the calculated amount of  $\text{RhCl}_3 \cdot \text{H}_2\text{O}$  solution to a  $\text{CdS}$  suspension followed by irradiation with visible light (wavelength, 405 nm or longer). Irradiation with UV light during the photodeposition had no effect on  $r(\text{H}_2)$ . It is worth noting that degassing was not necessary to ensure good catalytic activity. However, it was important to limit to less than 15 min the time at which rhodium(III) was kept in the dark in an  $\text{Na}_2\text{S}$ - $\text{NaOH}$  solution; if left for longer times, formation of  $\text{Rh}_x\text{S}_y$  took place. This does not occur during irradiation in the presence of  $\text{CdS}$ ; only when polysulphides ( $\text{S}_n^{2-}$ ) start to be produced can interference with rhodium(III) occur.

### 3. Results

#### 3.1. Hydrogen evolution in the absence of $\text{SO}_3^{2-}$ ions

Addition of rhodium(III) to a  $\text{CdS}$  (Fluka-1) dispersion in 0.1 M  $\text{Na}_2\text{S}$  and 1 M  $\text{NaOH}$  leads to an efficient catalytic evolution of hydrogen when

TABLE 1

Rates of hydrogen evolution for various semiconductor dispersions

<i>Dispersion</i>	$r(\text{H}_2)$ (ml h <sup>-1</sup> )
CdS	0.13 ± 0.01
CdS-1 wt.% RuO <sub>2</sub>	1.93 ± 0.20
CdS plus TiO <sub>2</sub> -0.5 wt.% RuO <sub>2</sub>	2.77 ± 0.25
CdS plus 0.04 wt.% Rh <sup>3+</sup>	1.85 ± 0.18
CdS plus 0.2 wt.% Rh <sup>3+</sup>	1.92 ± 0.20
CdS plus 0.4 wt.% Rh <sup>3+</sup>	2.76 ± 0.25
CdS plus 2 wt.% Rh <sup>3+</sup>	2.55 ± 0.25
CdS plus 0.4 wt.% Rh <sup>3+</sup> <sup>a</sup>	3.22 ± 0.30
CdS plus 0.4 wt.% Rh <sup>3+</sup> <sup>b</sup>	1.40 ± 0.15

10 mg CdS Fluka-1; 0.1 M Na<sub>2</sub>S in 1 M NaOH; 5 ml samples; Hg-Xe lamp operated at 900 W; irradiation wavelength, 405 nm or longer with a cut-off filter; samples argon purged for about 15 min.

<sup>a</sup>Etched with concentrated HCl after addition of RhCl<sub>3</sub>.

<sup>b</sup>Etched with concentrated HCl after addition of RhCl<sub>3</sub> and subsequently calcined in an oven at 320 °C for 30 min in the presence of air.

the sample is irradiated with light of wavelength 405 nm or longer. The catalyst so formed is more photo-active than CdS-1wt.%RuO<sub>2</sub> [2, 3] and is comparable with the CdS plus TiO<sub>2</sub>-0.5wt.%RuO<sub>2</sub> combination [16, 17] under identical conditions. The rates of hydrogen evolution for different catalytic dispersions are collected in Table 1. The initial  $r(\text{H}_2)$  from dispersions containing rhodium(III) was measured for the first hour of illumination; for longer irradiation periods,  $r(\text{H}_2)$  decreases owing to the formation of a complex between rhodium(III) and the generated S<sub>2</sub><sup>2-</sup> [21], a product of the photoreaction together with hydrogen. The colour of this Rh<sub>x</sub>S<sub>y</sub> complex is brownish yellow and strongly depends on the rhodium(III) concentration; the nature of the complex was not investigated. However, because of its optical properties, the complex acts as an inner filter and interferes with light absorption by CdS and can also compete with H<sup>+</sup> for the conduction band electrons (e<sub>cb</sub><sup>-</sup>) of CdS. A similar interference occurs in the absence of rhodium(III) when yellow S<sub>n</sub><sup>2-</sup> are formed in alkaline solution [2, 3, 7].

Naked CdS generates hydrogen (Table 1) at an average rate of 0.13 ml h<sup>-1</sup>. When the same batch of CdS [20] is loaded with 1 wt.% RuO<sub>2</sub>,  $r(\text{H}_2)$  increases to 1.93 ml h<sup>-1</sup>. This near 15-fold increase in  $r(\text{H}_2)$  depends exclusively on the characteristics of the batch and on the effect of etching during RuO<sub>2</sub> loading [20]. In contrast, addition of TiO<sub>2</sub>-0.5wt.%RuO<sub>2</sub> to naked CdS yields 2.77 ml h<sup>-1</sup>, resulting from the partial suppression of e<sup>-</sup>-h<sup>+</sup> recombination through interparticle electron transfer from CdS to TiO<sub>2</sub> [16]. Further chemical and electrochemical evidence for this pathway is forthcoming [23].

Surprisingly, simple addition of rhodium(III) to naked CdS particles affords a catalyst as efficient as the CdS plus TiO<sub>2</sub>-0.5wt.%RuO<sub>2</sub> combination in solutions of 0.1 M S<sup>2-</sup> and 1 M OH<sup>-</sup>. However, in long-time irradiation experiments, this coupling of two semiconductor catalysts gave higher hydrogen yields than CdS plus 0.4 wt.% rhodium(III), as a result of the vectorial displacement of charges between the two semiconductors [16, 23]. The results of Table 1 also show that the 0.4 wt.% rhodium(III) addition yields the higher  $r(\text{H}_2)$  (2.76 ml h<sup>-1</sup>). The catalytic activity increases ( $r(\text{H}_2) = 3.22 \text{ ml h}^{-1}$ ) if the powder is etched with concentrated HCl after rhodium(III) is added to the CdS suspension. This increase in  $r(\text{H}_2)$  on etching is the result of chemically modified properties of the particle surface rather than changes in the physical properties of these surfaces [20]. (Etching with acids has been shown to change the surface morphology of the CdS particles drastically as revealed by scanning electron microscopy [24].) However, the catalytic activity decreases [19, 20] if the same sample, which was acid etched and was active in generating hydrogen, is calcined at 320 °C for 30 min [2, 3].

### 3.2. Hydrogen evolution in the presence of SO<sub>3</sub><sup>2-</sup> ions

We [4] and others [5, 7] have noted previously that addition of SO<sub>2</sub> to an alkaline Na<sub>2</sub>S solution leads to the formation of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions on irradiation in the presence of CdS particles. The reaction removes the polysulphide ions as they immediately react with SO<sub>3</sub><sup>2-</sup> to form the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> species [4, 5, 7], which is transparent to visible light and does not interfere with protons in the reduction process. Under such conditions, the CdS-Rh catalyst shows no decrease in  $r(\text{H}_2)$  during several hours of irradiation. This suggests that no strong complex forms between rhodium and thiosulphate ions [21]. Figure 1 illustrates the temporal evolution of hydrogen (at standard temperature and pressure (STP)) as a function of illumination time for CdS-Rh in the presence (curve a) and absence (curve b) of SO<sub>3</sub><sup>2-</sup> ions. The maximum  $r(\text{H}_2)$  (2.76 ml h<sup>-1</sup> at 0.2 wt.% rhodium(III) in the absence of sulphite ions) reaches 7.0 ml h<sup>-1</sup> at 0.2 wt.% rhodium(III) in the presence of sulphite ions (0.1 M). Table 2 reports  $r(\text{H}_2)$  obtained for CdS, CdS plus TiO<sub>2</sub>-0.5wt.%RuO<sub>2</sub> and CdS slurries with different weight percentages of rhodium(III) in alkaline Na<sub>2</sub>S and in the presence of SO<sub>3</sub><sup>2-</sup>. Interestingly, in the presence of sulphite, the CdS plus TiO<sub>2</sub>-RuO<sub>2</sub> suspensions do not prove to be the most active combination (2.84 ml h<sup>-1</sup>) when compared with CdS-0.2wt.%Rh(III) which is 2.5 times more photo-active ( $r(\text{H}_2) = 7.0 \text{ ml h}^{-1}$ ).

In order to follow the action of rhodium in this active catalytic slurry, we monitored the changes in [Rh(III)] in solution using atomic absorption techniques. In a typical experiment, 0.3 wt.% rhodium(III) was added to a CdS suspension in the presence of an alkaline Na<sub>2</sub>S-Na<sub>2</sub>SO<sub>3</sub> (0.1 M) solution and then irradiated for 1 h until a considerable amount of hydrogen (about 7 ml) was produced. The sample was subsequently centrifuged and the supernatant was analysed for rhodium. More than 90% of the initial rhodium(III)

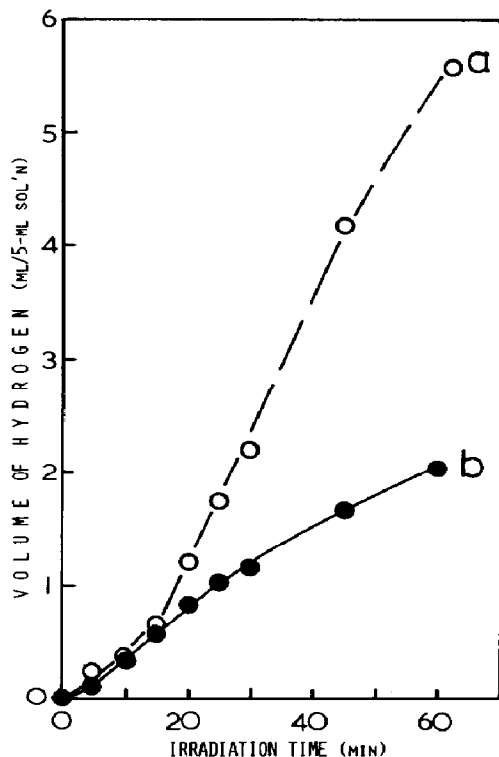


Fig. 1. Volume of hydrogen generated (STP) as a function of irradiation time in the presence of 0.1 M  $\text{Na}_2\text{SO}_3$  for CdS dispersions containing 0.2 wt.% rhodium (curve a) or 0.4 wt.% rhodium (curve b) (10 mg CdS; 5 ml suspensions; 0.1 M  $\text{Na}_2\text{S}$ ; 1 M NaOH; argon purged for about 15 min; Hg-Xe lamp as the light source; cut-off filter, 405 nm; temperature, about 35 °C).

TABLE 2

Rates of hydrogen evolution for various semiconductor dispersions

Dispersion	$r(\text{H}_2)$ (ml h <sup>-1</sup> )
CdS	0.27 ± 0.03
CdS plus $\text{TiO}_2$ -0.5wt.% $\text{RuO}_2$	2.84 ± 0.30
CdS plus 0.04 wt.% $\text{Rh}^{3+}$	3.34 ± 0.35
CdS plus 0.2 wt.% $\text{Rh}^{3+}$	7.30 ± 0.70
CdS plus 0.4 wt.% $\text{Rh}^{3+}$	5.30 ± 0.50
CdS plus 2 wt.% $\text{Rh}^{3+}$	5.13 ± 0.55

10 mg CdS Fluka-1; 0.1 M  $\text{S}^{2-}$ - $\text{SO}_3^{2-}$  in 1 M NaOH; 5 ml samples; Hg-Xe lamp operated at 900 W; 405 nm cut-off filter; samples argon purged for about 15 min.

is on the surface of the CdS particles, and the remainder (less than 10%) stays in solution bound to the colloidal particles that had not been fractionated by centrifugation. This suggests that rhodium is "active" only when on the particle surface. To demonstrate this notion further, we subjected a

given catalytic powder to several cycles: 10 mg CdS-0.2wt.%Rh(III) were added to a 5 ml solution of 0.06 M  $S^{2-}$  and 0.1 M  $SO_3^{2-}$  at pH 14. The concentration of  $S^{2-}$  and  $SO_3^{2-}$  was monitored using pulse polarography before irradiation. Following argon purging, the flask was illuminated for 3 h until no more hydrogen was produced and no more  $S^{2-}$  was detectable in solution;  $3.1 \times 10^{-4}$  mol hydrogen formed together with  $3.0 \times 10^{-4}$  mol  $S_2O_3^{2-}$ , in accord with the reaction stoichiometry of 1:1 [4, 5, 7]. The suspension was subsequently centrifuged, the supernatant solution removed and the powder washed with water. After a second centrifugation, a fresh  $Na_2S$ - $Na_2SO_3$  solution was added to the powder and the irradiation experiment repeated. Several such cycles were carried out with this powder. The rate of hydrogen formation drops by 10% - 20% after each cycle:  $r(H_2) = 4.30 \text{ ml h}^{-1}$  for the first run, decreasing to  $3.5 \text{ ml h}^{-1}$  and to about  $2.7 \text{ ml h}^{-1}$  in the next few cycles.

### 3.3. Hydrogen evolution in the presence of oxygen

Much of the work on hydrogen generation with semiconductor dispersions is carried out in an oxygen-free atmosphere to avoid the back recombination processes and oxygen interference with the catalyst that occurs on formation of superoxides and/or peroxides [25]. Previously, [2, 3] we remarked that in the photocleavage of hydrogen sulphide to hydrogen and sulphur on colloidal CdS the presence of oxygen caused a slight decrease in  $r(H_2)$  in comparison with the  $r(H_2)$  from argon-purged systems because of the competition of oxygen and  $H^+$  for the reduction sites.

The results of an experiment in which a 10 mg CdS-0.2wt.%Rh(III) slurry was irradiated in a 0.06 M  $Na_2S$ -0.1 M  $Na_2SO_3$  alkaline argon-purged solution are depicted in Fig. 2. After 30 min illumination, 200  $\mu$ l oxygen were injected into the flask (during the irradiation). No changes were observed in  $r(H_2)$  (about  $3.65 \text{ ml h}^{-1}$ ), suggesting that for this photocatalyst

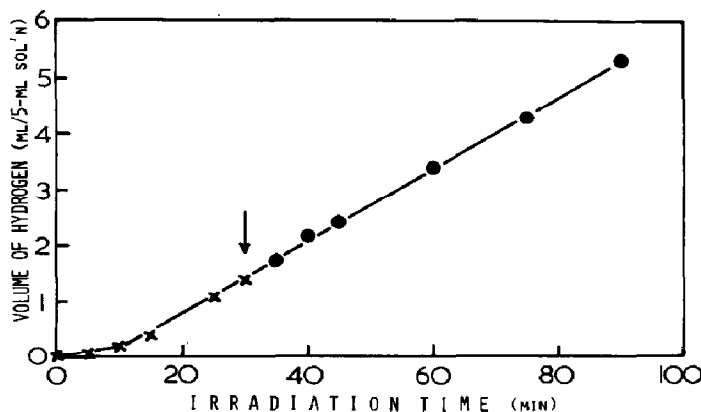


Fig. 2. Volume of hydrogen evolved (STP) as a function of irradiation time for a CdS-0.2wt.%Rh suspension. The slurry was argon purged for 15 min prior to illumination; after 30 min, 200  $\mu$ l oxygen was added to the suspension (as indicated by an arrow) and irradiation was continued. Other conditions are as in Fig. 1.

the efficiency of the cathodic process is not affected by oxygen. We further verified this observation by running two parallel experiments in which an air-equilibrated CdS-0.2wt.%Rh(III) suspension in an  $S^{2-}$ - $SO_3^{2-}$  (0.1 M) alkaline solution was compared with an identical argon-purged suspension under identical conditions. Oxygen had no effect on  $r(H_2)$  with both runs giving about  $6.7 \text{ ml h}^{-1}$  hydrogen. In the air-equilibrated slurry, oxygen was consumed and the molar ratio of hydrogen to  $S_2O_3^{2-}$  was 1:2; the ratio was 1:1 for the argon-purged dispersion [4, 5, 7].

### 3.4. Completeness of the reaction

We indicated above that the stoichiometric amount of hydrogen is produced on the total consumption of  $S^{2-}$  ions with  $SO_3^{2-}$  present in solution. In an experiment designed to test the completeness of the reaction, 10 mg CdS-0.2wt.%Rh(III) in a 0.14 M argon-purged solution of  $Na_2S$ - $Na_2SO_3$  in 1 M NaOH produced 15 ml hydrogen ( $6.7 \times 10^{-4}$  mol; also see Section 2) after 2 h irradiation with visible light; also produced were  $7.00 \times 10^{-4}$  mol  $S_2O_3^{2-}$ . Analogous experiments were undertaken for lower  $Na_2S$  concentrations. Using the same catalyst preparation, a 0.01 M  $Na_2S$ - $Na_2SO_3$  argon-flushed slurry was photolysed for 12 h, generating 1.2 ml hydrogen. A third experiment was also carried out using a 5 ml sample in a 56 ml flask; this was to avoid pressure build-up arising from the formation of hydrogen gas. With 0.11 M  $Na_2S$ , 13.5 ml hydrogen were produced. These experiments demonstrate that it is feasible to achieve 100% conversion of a sulphide solution to hydrogen. This is an important parameter in designing scale-up of processes towards practical applications.

### 3.5. Effect of CdS preparation on $r(H_2)$

In our efforts at understanding the often discrepant results from catalysts prepared from different batches of CdS and to achieve reproducible results, we tested the rhodium-loaded CdS photocatalyst using different CdS preparations [20]. Figure 3 shows the volume of hydrogen evolved (STP) as a function of irradiation time for different CdS slurries subjected to identical conditions (10 mg powder; 0.2 wt.%  $RhCl_3 \cdot H_2O$ ; 0.1 M  $Na_2S$ - $Na_2SO_3$ ; 1 M NaOH; 5 ml sample; temperature, about  $35^\circ C$ ; argon-purged solutions). Our previous findings [20], among various batches of CdS purchased from the same vendor, indicated different  $r(H_2)$ . CdS Fluka-1 showed the highest rate ( $r(H_2) \approx 7.0 \text{ ml h}^{-1}$ ), while the rate is  $4.75 \text{ ml h}^{-1}$  and  $4.25 \text{ ml h}^{-1}$  for Fluka-2 and Fluka-3 respectively. Reber and coworkers [7] have shown that differences in  $r(H_2)$  from different samples are due to the presence of surface impurities (e.g. CdO) and etching the powder with acetic acid was necessary to remove these impurities prior to irradiation. On treating our catalytic powders with acid, we found (under our conditions) no improvement in  $r(H_2)$ . An example is illustrated in Fig. 3 where we report CdS Fluka-3 etched with concentrated HCl. (In the present instance we did not use acetic acid to etch our powder. Previously [20] we had found that etching with HCl or with  $HNO_3$  acids was more effective.) For the untreated



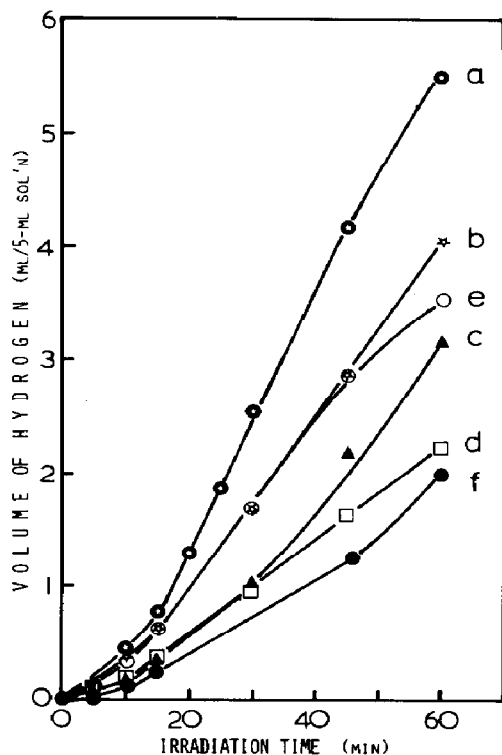


Fig. 3. Volume of hydrogen produced (STP) as a function of irradiation time for CdS-0.2wt.%Rh in  $S^{2-}$ - $SO_3^{2-}$  (0.1 M) suspensions in which CdS was from different batches or from different preparations (other conditions are identical with those of Fig. 1): curve a, CdS Fluka-1; curve b, CdS Fluka-2; curve c, CdS Fluka-3; curve d, CdS Fluka-3 etched with concentrated HCl acid; curve e, luminescent grade CdS; curve f, CdS containing five times excess  $Cd^{2+}$ .

sample,  $r(H_2) = 4.2 \text{ ml h}^{-1}$ , and  $r(H_2) = 2.5 \text{ ml h}^{-1}$  for the etched sample. No doubt other processes occur on the surface on etching. It is also interesting to note that luminescent grade CdS is as active as CdS Fluka-2, producing  $4.75 \text{ ml h}^{-1}$  hydrogen; CdS prepared by precipitation using  $Cd(NO_3)_2$  and  $Na_2S$  (5 M excess in cadmium) was the least efficient under these conditions.

### 3.6. Blank experiment

In a typical experiment, CdS-0.2wt.%Rh(III) was irradiated in the presence of  $Na_2S$  (0.06 M) and  $Na_2SO_3$  (0.1 M) at pH 14, and the slurry was argon purged. After 1 h illumination, the light source was turned off for 90 min and subsequently turned on again. No hydrogen was produced in the dark; hydrogen evolution is a light-driven process. Moreover, deletion of CdS from the solution was deleterious in as much as no hydrogen was produced in the absence of the light harvesting unit.

### 3.7. Turnover number, quantum efficiency and energy conversion efficiency

Irradiation of a 50 mg CdS-0.2wt.%Rh(III) ( $3.5 \times 10^{-4}$  mol CdS and  $10^{-6}$  mol rhodium(III)) argon-purged suspension for 20 h produced 123 ml

hydrogen (0.1 M Na<sub>2</sub>S–Na<sub>2</sub>SO<sub>3</sub>–1 M NaOH) and an equivalent quantity of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions. To the extent that 5.5 × 10<sup>-3</sup> mol hydrogen and 5.4 × 10<sup>-3</sup> mol S<sub>2</sub>O<sub>3</sub><sup>2-</sup> are formed, the turnover number for rhodium is 2200 and it is 15 for CdS.

The energy conversion efficiencies were determined for a 5 ml sample containing 10 mg catalyst in 0.1 M S<sup>2-</sup>–SO<sub>3</sub><sup>2-</sup> solution (argon purged). The output of the light source (wavelength, 405 nm or longer) was 243 mW cm<sup>-2</sup> and  $r(\text{H}_2) = 7.3 \text{ ml h}^{-1}$ . With an irradiated surface of area 4.8 cm<sup>2</sup>, the engineering energy conversion efficiency is 2.6%, based on the heat of combustion of hydrogen (68.3 kcal mol<sup>-1</sup>); the thermodynamic energy conversion efficiency is 0.17%, based on the reaction  $\text{H}_2\text{S} + \text{SO}_3^{2-} \rightarrow \text{H}_2 + \text{S}_2\text{O}_3^{2-}$  and on 0.11 eV storable energy per absorbed photon [4]. These values must be regarded as lower limits in as much as not all the photons have been absorbed and optimization of the photoreactor should improve  $r(\text{H}_2)$ . Irradiation of the same catalytic slurry as above with monochromatic light at 436 nm yields a quantum efficiency of atomic hydrogen produced of 0.45 ± 0.05 with respect to the number of incident photons. By far, this is the best quantum efficiency yet reported for the photocleavage of hydrogen sulphide with CdS as the light harvester.

#### 4. Discussion

Irradiation of CdS particles with visible light generates electron–hole pairs:



While conduction band electrons afford water reduction



holes normally undergo photocorrosion in water



a process which is suppressed by the presence of suitable electron donors [26 - 35]. In the experiments reported here, CdS holes oxidize S<sup>2-</sup> ions to sulphur



thereby achieving the photocleavage of hydrogen sulphide to hydrogen and sulphur (in alkaline media) [2 - 15].

Sulphur atoms do not compete with water for the reduction sites, but in alkaline media they combine with S<sup>2-</sup> to form the water-soluble polysulphides S<sub>n</sub><sup>2-</sup>. These compete with CdS particles in the light absorption act and with protons for the e<sub>cb</sub><sup>-</sup> [2 - 15].

We have noted that addition of a rhodium(III) salt to naked CdS suspensions enhances the rate of hydrogen generation in the hydrogen sulphide cleavage process, no doubt the result of the formation of very active rhodium species on the CdS particle surface [18, 19]. The data reveal that this catalyst is not promising for the simple hydrogen sulphide cleavage process, since a complex forms between  $\text{Rh}^{3+}$  and  $\text{S}_n^{2-}$  [21], preventing long-term catalyst stability. However, in an  $\text{SO}_3^{2-}$ -alkaline solution of hydrogen sulphide, the CdS-Rh catalyst becomes very efficient in the hydrogen generation reaction with concomitant longer stability.

The presence of  $\text{SO}_3^{2-}$  suppresses formation of polysulphides



and thiosulphate results from the anodic reaction [4, 5, 7].  $\text{S}_2\text{O}_3^{2-}$  is not easily reduced and forms no complex with the rhodium species [21] that might detract from the activity of the catalyst under our experimental conditions. Of importance, regarding this CdS-Rh catalyst, oxygen seems not to interfere in the reduction process. This is significant since oxygen generally competes with the reduction of protons and is thereby consumed during irradiation [2, 3, 7]. Of course, an induction period is often observed in the hydrogen evolution, particularly when hydrogen is formed at small rates. (It should be noted that in the present work an induction period is observed in the absence as well as in the presence of oxygen. This would suggest that the induction period in our case may arise from such sources as surface reconstruction during the initial stages of hydrogen evolution [1] and/or formation of good ohmic contact [36] between rhodium and CdS initially on formation of atomic hydrogen.) This is in keeping with similar work on CdS-Pt [7], CdS-RuO<sub>2</sub> [2, 3] and CdS-RhO<sub>x</sub> [9] suspensions.

The photouptake of oxygen in CdS suspensions is an efficient process even in the absence of  $\text{S}^{2-}$  ions [37 - 42]. The primary step is reduction of oxygen to superoxide by conduction band electrons [37 - 42]:



For CdS-Rh<sub>2</sub>O<sub>3</sub>, oxygen consumption appears too rapid at pH 9, but the rate decreases with increasing pH [43].

The presently available data (see Fig. 2) show that CdS-Rh is equally efficient for hydrogen evolution both in oxygen-free and air-equilibrated samples; the anodic process, however, is different. In the latter samples, the molar ratio of hydrogen to  $\text{S}_2\text{O}_3^{2-}$  is 1:2 instead of the 1:1 found in argon-purged suspensions [4, 5, 7]. The oxygen consumption (see Section 3) and the above ratio may be rationalized by a process which considers that, at pH 14, oxidation of  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  is kinetically inhibited, at least within the time scale of our experiments. We suggest the formation of a sulphide radical as the first oxidation product between  $\text{S}^{2-}$  and  $h_{vb}^+$



following which  $\text{S}^-$  can be trapped by oxygen to form  $\text{O}_2^-$ :



subsequently, polysulphides and thiosulphate form. Although this mechanism appears to be reasonable, we note that evidence for the existence of  $S^{\cdot -}$  radical is lacking; evidence for the existence of the analogous  $Se^{\cdot -}$  radical has been reported [44].

Further support that oxygen consumption in the case of the CdS–Rh catalyst is not due to the reaction of oxygen with  $e_{cb}^-(CdS)$  originates from the following experiment. A CdS–Rh(III) aqueous suspension was irradiated in the presence of ethylenediaminetetraacetic acid (0.1 M) as a hole scavenger.  $r(H_2)$  was the same for both argon-purged and air-equilibrated systems; for the latter, oxygen consumption does occur [45]. No attempts were made to analyse the oxidation products.

## 5. Conclusions

Disposal of hydrogen sulphide and sulphur dioxide by photochemical means in the presence of CdS is an attractive route; hydrogen and thiosulphate are produced. In this paper we have dealt with a new catalytic dispersion for the degradation process; the catalyst formed is very efficient and easy to prepare. It should prove to be suitable for practical exploitation and its efficiency seems not to be affected by air. Experiments are under way to fix CdS–Rh on some solid support in order to separate the reaction products from the catalyst [14]. Moreover, to the extent that oxygen is consumed during the reaction to form thiosulphate, the hydrogen generated will be relatively free of oxygen. The amount of hydrogen evolved for the same amount of  $Na_2S$  will be less in air-equilibrated devices than in those that are oxygen free. The process noted here is already valuable for pollution abatement since two waste toxic gases are removed in one single operation. For the production of hydrogen, the long-term stability of the catalyst needs to be addressed. Several suggestions have been advanced on the feasibility of a large-scale plant for hydrogen sulphide photocleavage [1, 46]. The possibility of using sunlight coupled to an artificial source renders the process attractive.

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