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Photodecomposition of H_2S in Aqueous Alkaline Media Catalyzed by RuO_2-loaded Alumina in the Presence of Cadmium Sulfide. Application of the Inter-particle Electron Transfer Mechanism

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Abstract

The photodecomposition of hydrogen sulfide by visible light (>400 nm) has been investigated in alkaline aqueous media (0.1 m Na_2S and 1 M NaOH) in the presence of naked CdS dispersions and in mixtures composed of the combination CdS + Al_2O_3/RuO_2. A 5-fold increase in the hydrogen evolution rate is obtained through the coupling of the excited semiconductor and the redox catalyst. The data are interpreted in terms of the inter-particle electron transfer pathway in which the conduction band electrons of the excited CdS (bandgap 2.4 eV; threshold wavelength 520 nm) are transferred to the redox catalyst via the alumina support or directly, in competition with electron/hole pair recombination. The engineering energy efficiency is estimated at 1.2% from the total incident light energy and the heat of combustion of hydrogen.

Introduction

Interest has accrued [1–3] in recent years since the first reports of photochemical cleavage of hydrogen sulphide [4] over semiconductor dispersions of CdS in aqueous alkaline media [5, 6]. This is as a result of the search for a viable system to collect and store solar energy in the form of a useful fuel, hydrogen. Of additional importance has been the research dedicated to the removal of sulfur from petroleum, coal, and natural gas; in the latter case, the sulfur content is more than 90% H_2S [7]. In seeking alternative energy sources, combustion of sulfur (to SO_2, SO_3, etc.) must be avoided to prevent serious damage to the environment and to works of art through the formation of acid rain and smog [8].

The mechanism of the cleavage of hydrogen sulfide involves oxidation of S^{2-} ions (or HS^-; pH 14) by the valence band holes of CdS, h_{vb}^+, produced by bandgap excitation of a microheterogeneous dispersion of CdS (bandgap 2.4 eV; threshold wavelength 520 nm), with the concomitant reduction of protons to hydrogen by the conduction band electrons of CdS, e_{cb}^-. Several other catalysts have been studied [2, 3, 9–12] and different devices are presently under active investigation in many laboratories [13–16].

One recent interesting finding from our laboratories is the coupling of two semiconductor catalysts to improve charge separation on irradiated CdS particles [9, 17, 18]. This new strategy accomplishes vectorial displacement of charges on the semiconductor and reduces electron-hole recombination on the excited particles [19a]*. This inter-particle electron transfer mechanism was first applied successfully to the visible light-induced decomposition of H_2S into H_2 and S [17], and recently to the photo-dehydrogenation of alcohols [18]. Coupling of CdS with TiO_2 followed by irradiating CdS with visible light ($\lambda > 400$ nm) induces the formation of e_{cb}^-(CdS) and h_{vb}^+(CdS) which subsequently recombine in competition with a transfer of e_{cb}^-(CdS) onto the conduction band of TiO_2. Charge separation is even more efficient when the latter is loaded with a noble metal (e.g. Pt) or metal oxide (e.g. RuO_2) redox catalyst. This leads to greatly improved efficiencies in the light driven photo-processes [9, 17, 18], with oxidation occurring on CdS and reduction taking place on TiO_2/RuO_2 particles.

The present paper reports on the substitution of TiO_2 with Al_2O_3 as the support for the redox catalyst

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*For CdS colloidal particles (<100 Å diameter), the electron/hole pair recombination occurs in $\leq 30 \times 10^{-12}$ s.

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in the decomposition of hydrogen sulfide. Though alumina may have semiconducting properties, its bandgap is much too large (>7 eV) and its conduction band is probably at a much higher energy level than that of CdS, thereby precluding the identical pathway for the electron transfer as occurs with the CdS + TiO_2 couples. Evidence is presented that also suggests the transfer of e_{cb}^-(CdS) to the redox catalyst supported on Al_2O_3.

Experimental

All chemicals were reagent purissimum grade; Fluka CdS (99.99%, ~3 m^2/g; 10–30 μm diameter) was employed. All the reactions were carried out with the same batch of CdS [19b][*] TiO_2 (anatase, 145 m^2/g, elementary particle size ~100 Å, doped with 600 ppm Nb) was kindly provided by Dr. P. Panek, Bayer GmbH, West Germany. Degussa Al_2O_3–C was used as supplied (surface area BET 85.2 m^2/g). Loading of RuO_2 onto CdS was performed according to literature methods [19b]. For RuO_2 loading of TiO_2 and Al_2O_3, a similar procedure was employed except that no HCl etching was performed during the mixing of $RuCl_3$(aq) with the particles.

Irradiation was carried out on 25 ml samples (unless noted otherwise) invariably containing 0.1 M Na_2S, 1 M NaOH, and 50 mg of CdS. When mixtures were investigated, the slurries contained, in addition to CdS, 50 mg Al_2O_3, or Al_2O_3/x%wtRuO_2, or TiO_2/x%wtRuO_2. All suspensions were sonicated for ~15–30 s and argon-purged for ~15 min prior to irradiation. The excitation light source was a 450 W Xe lamp equipped with a water jacket and a 400 nm cutoff filter to remove both IR and UV radiation, respectively. The integral irradiance ($\lambda > 330$ nm) of this lamp was 160 mW/cm^2. Parallel experiments were undertaken using a concave mirror to concentrate the sun's radiation (at the focal point, the intensity was *ca.* 500 times that of the sun) during a period when the sun's irradiance was 80 ± 5 mW/cm^2.

Hydrogen was detected by gas chromatography with a Carbosieve 5A column and argon was the carrier gas. The light intensities were determined with a YSI Kettering Model 65A Radiometer.

Results

Figure 1 compares the time dependence of hydrogen evolution (STP) from solutions composed of 0.1 M S^{2-}, 1 M NaOH, and various semiconductor dispersions after irradiation with visible light (⩾400 nm). The puratronic (Alfa) CdS is totally inactive in producing hydrogen from the photocleavage of hydrogen sulfide with respect to other suspensions; the rate of hydrogen evolution is $r(H_2) \leq 0.002$ ml/h. However, chemical etching of this CdS with various acids yields a CdS which generates H_2 at rates comparable to those of commercial batches of CdS. More on this aspect will appear in a forthcoming publication [20].

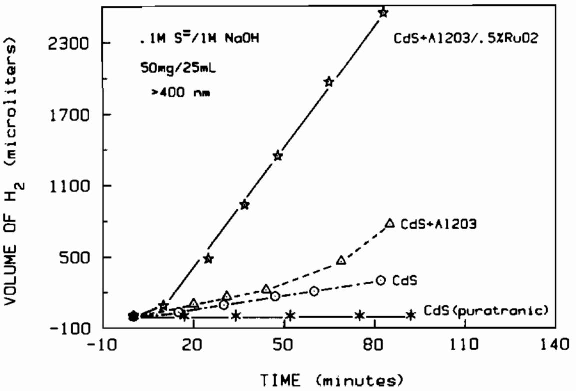

Fig. 1. Volume of hydrogen (STP) produced by visible light irradiation of various CdS dispersions containing 0.1 M Na_2S and 1 M NaOH. In one case, naked CdS is used (puratronic and a commercial sample) and in another alumina is added to the dispersion. In a third case, a redox catalyst, RuO_2, has been deposited on the alumina particles (0.5% by wt).

The CdS batch used throughout (Fluka, 99.99% purissimum) gives 0.41 ml/h; addition of 50 mg of Al_2O_3 has little effect on $r(H_2)$, 0.45 ml/h. A four-fold improvement in $r(H_2)$ is seen upon loading the alumina particles with a metal oxide (RuO_2) redox catalyst; $r(H_2) = 1.92$ ml/h. To the extent that the rate of hydrogen evolution is dependent on the concentration of redox catalyst present, we have investigated how $r(H_2)$ varies as a function of percent loading of RuO_2 on CdS, TiO_2, and Al_2O_3. Figure 2 illustrates and compares the behaviour of the three laoded supports. It is evident that $r(H_2)$ is maximized at low loading levels for CdS and TiO_2. For the photodecomposition of H_2S, the optimum conditions are 1 wt% RuO_2 on CdS and 0.5wt% RuO_2 on TiO_2. For Al_2O_3, 10 wt% RuO_2 yields the best-performing catalyst under our experimental conditions, but even at the 1 wt% level, $r(H_2)$ is still significant (2.01 ml/h *vs.* 2.55 ml/h for the 10 wt.% level).

We have also loaded Rh_2O_3 onto CdS (1 wt%) inasmuch as this redox catalyst was found superior to RuO_2 in promoting H_2O oxidation under alkaline conditions [21]. Rh_2O_3 was prepared by impregnating CdS with $RhCl_3$(aq) followed by calcination at 500 °C for 1 h. Its performance is compared to RuO_2 under the same conditions: $r(H_2)$ is 1.22 ml/h

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[*] Note that particles of CdS from commercial batches have very irregular shapes (SEM studies [20]) with sizes ranging from 10 to 30 μm. However, because of the sonication of the slurries prior to irradiation (see 'Experimental'), the actual size of these particles in the suspensions is unknown, but some may be < 10 μm.

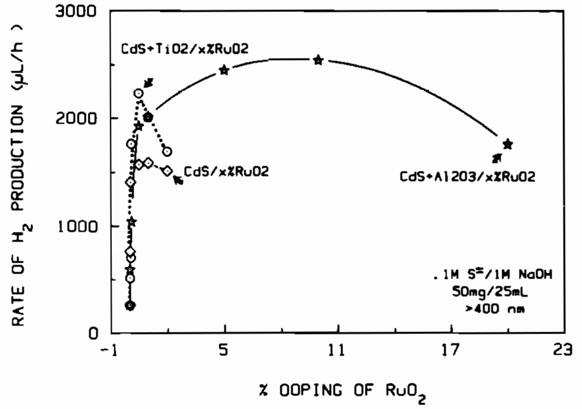

Fig. 2. Plot of the rate of H_2 production as a function of the percent loading of the redox catalyst RuO_2 on alumina paticles. Loading onto TiO_2 anatase particles and directly onto CdS is also shown for comparison.

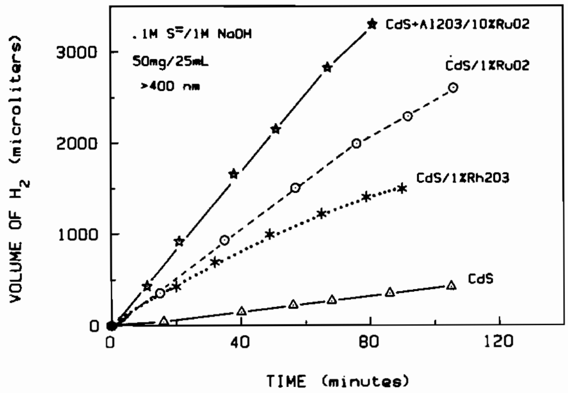

Fig. 3. Volume of hydrogen (STP) produced as a function of irradiation time for four CdS dispersions containing 0.1 M Na_2S and 1 M NaOH along with: (i) naked CdS, (ii) Rh_2O_3 deposited onto CdS (1 wt%), (iii) RuO_2 deposited onto CdS (1 wt%), and (iv) RuO_2 catalyst deposited on Al_2O_3 support (10 wt%).

for CdS/1 wt% Rh_2O_3 and 1.59 ml/h for the RuO_2 analog. Compared to these two systems, a near 2-fold increase in performance is observed when RuO_2 is loaded on Al_2O_3. The negative deviations noted in the volume of H_2 formed as a function of irradiation time (Fig. 3) are the result of the formation of polysulfides (see 'Discussion') which are known to interfere with light absorption by the CdS particles [3, 22].

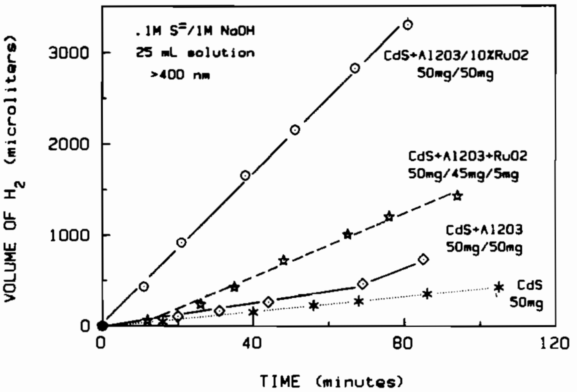

Fig. 4. Volume of hydrogen (STP) produced as a function of irradiation time in the photodecomposition of hydrogen sulfide in alkaline aqueous media. Four dispersions of CdS are shown: (i) naked CdS, (ii) alumina added to a naked CdS slurry, (iii) alumina and RuO_2 added to the naked CdS dispersion, and (iv) the redox catalyst RuO_2 is deposited on alumina (10 wt%).

The results of an important experiment are summarized in Fig. 4 where we illustrate the volume of H_2 produced by visible light irradiation of different CdS dispersions as a function of irradiation time. Of particular interest is the comparison between the dispersion containing $CdS + Al_2O_3/10$ wt% RuO_2 and the dispersion made up of $CdS + Al_2O_3 + RuO_2$, where the redox catalyst is also present in 10 wt% quantity but is not loaded on alumina. The yield of H_2 is 1.16 ml/h for the latter and is nearly double (2.55 ml/h) when the redox catalyst is supported on Al_2O_3.

The effect of the presence of SO_3^{2-} (0.1 M) on $r(H_2)$ in solutions containing 0.1 M S^{2-} and 1 M NaOH was also investigated for this new Al_2O_3/RuO_2 (0.5 wt%) catalyst: $r(H_2)$ is 2.5 ml/h compared to 2.1 ml/h in the absence of sulfite. One advantage of sulfite ions is that hydrogen evolution is sustained for longer periods since the formation of polysulfides is suppressed [3, 22–24*].

A practical aspect of the decomposition of hydrogen sulfide involves using sunlight as the irradiation source. Illuminating a 5 ml sample containing 0.1 M S^{2-}/1 M OH^- and $CdS + Al_2O_3/10$ wt% RuO_2 (10 mg of each) with concentrated sunlight (see 'Experimental') gives the equivalent of ~435 ml/h of hydrogen, and with sulfite present, ~500 ml/h (scaled-up to a 25 ml solution for comparison).

Discussion

Some of the results presented above can be rationalized in terms of the inter-particle electron transfer pathway alluded to earlier [17]. Visible light is absorbed by the CdS particles producing electron/hole pairs (reaction (1)). Holes react with S^{2-} (or HS^-) ions to give sulfur, which, on interacting with S^{2-}, dissolves as polysulfide in solution (reaction (2)).

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*The transformation of CN^- to SCN^- is also indicative of the suppression of polysulfide formation.

The concomitant reaction of conduction band electrons, competing with electron/hole pair recombination, is the reduction of water to hydrogen (eqn. (3)).

$$\mathrm{CdS} \underset{\text{Heat}}{\overset{h\nu}{\rightleftharpoons}} e_{cb}^-(\mathrm{CdS}) + h_{vb}^+(\mathrm{CdS}) \qquad (1)$$

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

$$nS + S^{2-} \longrightarrow S_n^{2-} \; (n = 2, 3, 4, \ldots) \qquad (2b)$$

$$2e_{cb}^-(\mathrm{CdS}) + 2H_2O \longrightarrow H_2 + 2OH^- \qquad (3)$$

Because of the back reaction (1), the yields of hydrogen and the extent of H_2S decomposition are low. If the charge carriers could be separated physically, thus suppressing the energy-wasting back reaction, yields would improve. This was indeed verified. Addition of Al_2O_3 to a slurry of CdS gave a slight increase in the H_2 yield. This was surprising inasmuch as we had expected the yield to decrease because of possible interference via light scattering by the 'inert' alumina particles. Equally surprising is the 4-fold increase in $r(H_2)$ obtained when a redox catalyst is present supported on the Al_2O_3 particles. An increase is also seen when the redox catalyst is deposited on the excited semiconductor CdS. We interpret these findings as follows.

Evolution of hydrogen can occur via: (i) direct reduction of water by e_{cb}^- on naked CdS (reaction (3), driving force 250 mV [17]); (ii) reduction of water assisted by a redox catalyst, whereby the conduction band electron is first trapped by the catalyst (here, RuO_2, Rh_2O_3) deposited on CdS; and (iii) inter-particle electron transfer from CdS to Al_2O_3 (reaction (4)) or Al_2O_3/RuO_2 (reaction (5)). Once trapped by the Al_2O_3 particles, the electrons can still

$$n e_{cb}^-(\mathrm{CdS}) + Al_2O_3 \longrightarrow \mathrm{CdS} + (Al_2O_3)^{n-} \qquad (4)$$

$$n e_{cb}^-(\mathrm{CdS}) + Al_2O_3/RuO_2 \longrightarrow \mathrm{CdS} + (Al_2O_3/RuO_2)^{n-} \qquad (5)$$

generate hydrogen (reaction (6)); unfortunately, the driving force for this reaction is not known. Suffice to note, however, that the alumina surface possesses

$$\begin{matrix}(Al_2O_3)^{n-}\\ \text{or}\\ (Al_2O_3/RuO_2)^{n-}\end{matrix} + 2H_2O \longrightarrow H_2 + 2OH^- \qquad (6)$$

conducting properties [25] but water reduction by $(Al_2O_3)^{n-}$ is slow*. Loading the particles with an efficient redox catalyst leads to a significant 5-fold increase in $r(H_2)$: 0.45 ml/h to 2.55 ml/h. Also, in the presence of SO_3^{2-} ions, formation of polysulfides is suppressed through reaction of sulfur with sulfite to form thiosulfate ions according to reaction (7). Not only is the thiosulfate synthesis a valuable

$$S + SO_3^{2-} \longrightarrow S_2O_3^{2-} \qquad (7)$$

process in its own right, but the removal of the light-interfering polysulfides improves the H_2 yield by sustaining hydrogen evolution for longer periods.

Based on the heat of combustion of hydrogen and the total incident light energy, we estimate the engineering energy efficiency as 1.2% for the CdS + Al_2O_3/10 wt% RuO_2 combination.

Conclusions

Alumina particles afford an excellent support for redox catalysts in the catalyst-assisted reduction of water in the photodecomposition of hydrogen sulfide in alkaline aqueous media. Through the vectorial physical displacement of the charge carriers in the excited semiconductor, the efficiency of the redox processes by the valence band holes and by the conduction band electrons is significantly increased. A full report on this inter-particle electron transfer mechanism will appear in a forthcoming publication [26].

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*A referee has suggested that the RuO_2 loaded onto TiO_2 or Al_2O_3 may possibly 'migrate onto the surface of CdS particles' thus giving enhanced hydrogen generation. While we cannot entirely preclude this possibility, we believe such an event is highly unlikely and is mitigated against by the following: First, we have noted earlier (ref. 17) that the combinations $CdS/RuO_2 + TiO_2$ and $CdS + TiO_2/RuO_2$ yield hydrogen at 1.66 ml/h and 2.23 ml/h, respectively. If any transfer of RuO_2 had occurred during the time of our experiments from TiO_2 onto CdS for the latter combination, we would have observed deviations in the plots of volume of H_2 *vs.* irradiation time (and similarly for RuO_2 on Al_2O_3). This was not the case (see e.g. Fig. 4). Second, other experiments have been carried out (refs. 18 and 26) that add evidence in favour (but is not proof) of the inter-particle electron transfer pathway (ref. 17). It should be noted that in the electron transfer step of this mechanism, the CdS particles must come into intimate contact with RuO_2-loaded Al_2O_3 or TiO_2 particles. Whether this can be taken as 'migration' of RuO_2 from one particle to another is a matter of conjecture and semantics. In the case of the system $CdS + Al_2O_3 + RuO_2$ of Fig. 4, where RuO_2 was not *a priori* loaded onto either CdS or Al_2O_3, the higher yield of hydrogen with respect to CdS alone is no doubt the result of some trapping (pseudo-physisorption) of the redox catalyst RuO_2 particles by the rather ill-defined CdS or Al_2O_3 particle surface (ref. 20) containing many irregularities (crevices, holes).

Acknowledgements

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