21. Visible Light Induced Generation of Hydrogen from H_2S in CdS-Dispersions, Hole Transfer Catalysis by RuO_2

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Summary

Illumination of CdS-dispersions by visible light in solutions containing H_2S or sulfide ions leads to efficient generation of hydrogen and sulfur. Very small quantities of RuO_2 deposited on the CdS-particles improve markedly the quantum yield of H_2-formation for which the optimum value obtained so far is $\phi = 0.35 \pm 0.1$. The effect of RuO_2 is attributed to catalysis of hole transfer from the valence band of CdS to H_2S or sulfide in solution.

Introduction. - The generation of hydrogen by visible light illumination from cheap and readily available sources is a subject of high priority in solar energy related research. Recently, we have reported that macrodisperse [1] or colloidal [2] CdS-particles when loaded with RuO_2 and Pt are capable of splitting water into hydrogen and oxygen under band-gap illumination. While Pt served as a catalyst for water reduction by conduction band electrons, RuO_2-promoted transfer of holes from the valence band to water, thus producing oxygen at the expense of photocorrosion[2]).

Apart from water, other agents such as H_2S have the potential to play an important role as an alternative source for hydrogen production from sunlight. Sulfides occur widely in nature and H_2S is produced in large quantities as an undesirable by-product in coal- and petrol-related industries. The present report deals with the design and operation of a catalytic system in which the cleavage of H_2S into hydrogen and sulfur is driven by visible light:

$$H_2S \xrightarrow{h\nu} H_2 + S \qquad (1)$$

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[2]) Holes (h^+) produced in the valence band under illumination migrate to the surface where decomposition occurs, *i.e.*

$$CdS + 2h^+ \rightarrow Cd^{2+} + S$$

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As the standard enthalpy of reaction 1 is +9.4 kcal/mol, this provides a method for energy conversion and storage.

Experimental Part. - CdS (*Fluka*, 99.99%) and $RuCl_3$ (*Fluka, purum*, 10% H_2O) were used as supplied. All other compounds employed were at least reagent grade. Water was distilled from permanganate and subsequently twice from a quartz still.

CdS-particles loaded with an ultrafine deposit of RuO_2 were employed as a catalyst. The loading was carried out in the following manner: 200 mg CdS (*Fluka*, 99.99%) were brought in contact with 50 µl of a solution containing 60 mg $RuCl_3 \cdot aq.$ (*Fluka, purum*, 10% H_2O) and mixed thoroughly. After drying in air for 15 min the powder was heated at 300° for 30 min under a stream of Ar and subsequently under air to afford oxidation of Ru^{3+} to RuO_2. This treatment may also lead to some substitution of S^{2-} in the CdS-lattice by Cl^-, which would result in *n*-type conduction. The amount of RuO_2 deposited on CdS corresponds to 0.1% weight. When higher loading was required, the amount of $RuCl_3$ solution was increased accordingly.

Illuminations were carried out with a 250 Watt halogen lamp (*Oriel*) equipped with a 15 cm water jacket and a 400 nm cut-off filter to remove IR.- and UV.-radiation, respectively. H_2 was analyzed by gas chromatography using a *Gow Mac* detector, carbosieve column (35°) and N_2 as a carrier gas.

Results and discussion. - When RuO_2-loaded CdS-particles are dispersed in aqueous sulfide solutions and illuminated with visible light, H_2 is generated at an astonishingly high rate. Results obtained from irradiating a 25 ml solution containing 25 mg CdS loaded with 0.025 mg RuO_2 in the presence of 0.1 M Na_2S (pH = 3) are displayed in *Figure 1*. After a brief induction period the H_2-generation rate established itself at 3.2 ml/h until almost all the H_2S has been consumed. In *Figure 1* the total amount of H_2 is 54 ml, *i.e.* $2.25 \cdot 10^{-3}$ mol. As $2.5 \cdot 10^{-3}$ mol of sulfide were present initially, this corresponds to a 90% conversion of H_2S into H_2. The process is catalytic with respect to CdS and RuO_2 turnover numbers being 11 and $1.2 \cdot 10^4$, respectively.

The pH has a pronounced effect on the yield of H_2-formation. *Figure 2* shows that rates of H_2-formation ($r(H_2)$) increases from 1.5 to 7 ml H_2/h upon increasing the pH from 0 to 14. The change occurs gradually, a somewhat abrupt augmentation being noted between pH 0 and 3 as well as 13 and 14. Increasing the Na_2S-concentration at the latter pH from 0.1 to 1 M has no significant influence on $r(H_2)$.

The effect of RuO_2-loading of CdS on the rate of light induced hydrogen generation is displayed in *Figure 3*. In these experiments the pH and CdS concentration was maintained at 14 and 25 mg/l, respectively. In the absence of RuO_2 $r(H_2)$ is only 2.5 ml/h. It increases steeply with RuO_2 loading until a plateau is attained at 0.5% from whereon no further changes are noted. In this region the H_2-generation proceeds at a rate of 10 ml/h which, by comparison with a standard system[3]), corresponds to a quantum yield of $\phi(H_2) = 0.35 \pm 0.1$.

A similar effect of RuO_2 was also noted at other pH values. Thus, at pH 13 the H_2-generation rate is 9 ml/h when CdS-particles loaded with 0.3% RuO_2 are used as catalysts, while in the absence of RuO_2 only 2.5 ml H_2/h are obtained. Interestingly, when Pt is deposited onto CdS instead of RuO_2, no catalytic effect is noted. The value of $r(H_2)$ remains unchanged upto 4% Pt-loading which was

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[3]) This model system uses EDTA instead of H_2O as on electron source [1] [2].

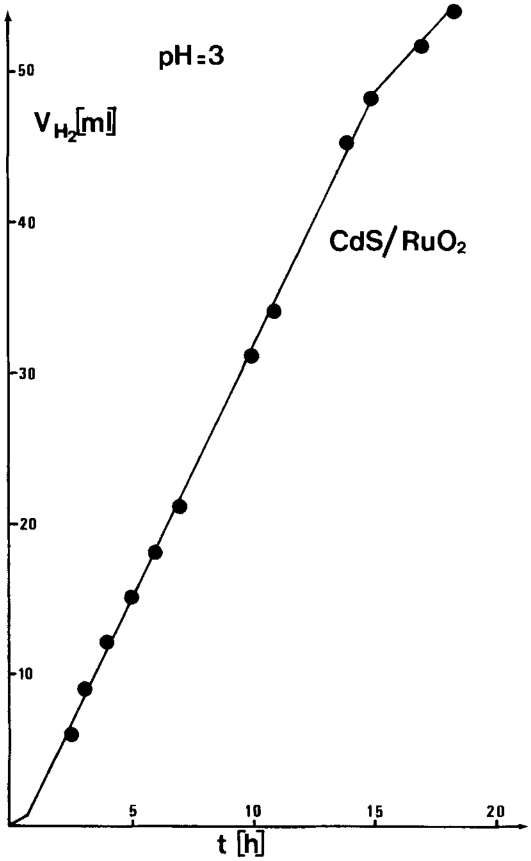

Fig. 1. *Volume of H_2 evolved from irradiating a 25 ml solution containing 0.1 M Na_2S (pH=3) and 25 mg CdS loaded with 0.025 mg RuO_2 by visible light* (Solution was briefly deaerated prior to illumination by flushing with Ar)

carried out by photoplatinization[4]). Also, when Pt is deposited onto CdS in addition to RuO_2 the H_2-output of the system does not change.

These observations may be rationalized in terms of band-gap excitation of the CdS-particles producing electrons in the conduction and holes in the valence band[5]). The former migrate to the interface where reduction of water to H_2 occurs:

$$2\,e^-_{cb} + 2\,H^+ \rightarrow H_2 \qquad (2)$$

while the holes react with H_2S (or HS^- depending on pH)[6]) under sulfur formation

$$H_2S + 2\,h^+ \rightarrow 2\,H^+ + S \qquad (3)$$

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[4]) Pt-deposition was carried out by photoplatinization as described in [1] [2].

[5]) For literature on other photoprocesses on CdS-powders, see [3].

[6]) The dissociation constants for H_2S are $1.02 \cdot 10^{-7}$ and $1.3 \cdot 10^{-15}$ (25°) for the first and second step, respectively.

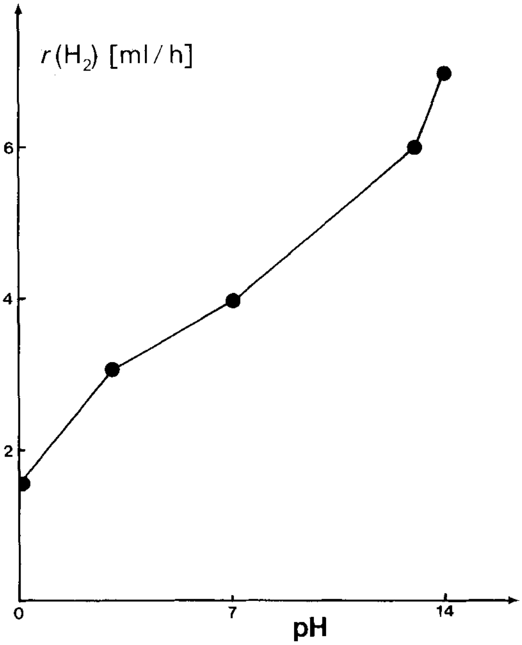

Fig. 2. *Effect of pH on the H_2-evolution rates* (solution conditions otherwise as in *Fig. 1*)

The overall reaction corresponds to splitting of H_2S into hydrogen and sulfur by four quanta of visible light.

Several important conclusions concerning the mechanism of this reaction can be drawn from the present investigation. The first concerns H_2-formation from conduction band electrons. Despite the fact that CdS is not a good electrode for water reduction[7]), this process occurs rapidly and efficiently making the intervention of an electrocatalyst such as Pt superfluous. The presence of such a catalyst was indispensable in earlier CdS-based systems for the photoproduction of H_2 from water [1] [2] [4][8]). The reason for this surprising behaviour may be sought in the effect of sulfide on the flat-band potential of the CdS-particles. For crystalline CdS-electrodes V_{fb} shifts cathodically [6] with increasing SH^- concentration according to the relation

$$V_{fb} = \text{const.} - 0.060 \log[SH^-] \qquad (4)$$

Thus, at neutral pH, $V_{fb} = -0.66$ V (NHE.) in the absence of sulfide while at 10^{-5} M and 10^{-1} M Na_2S-concentrations the values are -0.87 and -1.06 V, respectively [6c]. This cathodic shift in V_{fb} induced by adsorption of SH^- ions increases

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[7]) Electrochemical measurements on polycrystalline electrodes carried out by Drs. *Neumann-Spallart, Kalyanasundaram* and *Desilvestro* in our laboratory show that the overvoltage for H_2-evolution on CdS is approximately 300 mV higher than that on Pt.

[8]) The photochemical transformation

$$S^{2-} + H_2O \xrightarrow{h\nu} S + H_2 + OH^-$$

was investigated also by *Nozik*, who used a photochemical diode consisting of a single crystal platelet of *n*-CdS covered on one side with a Pt-layer [5].

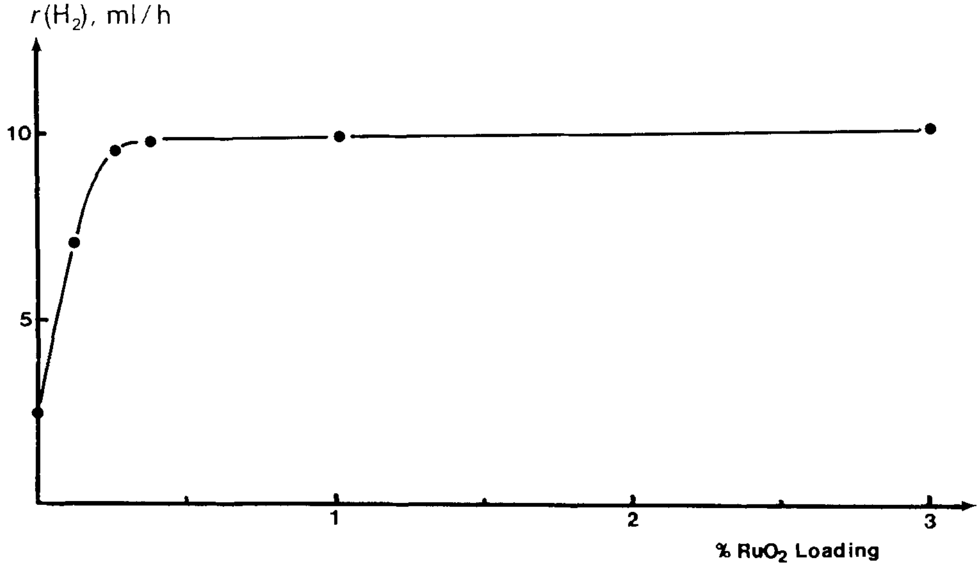

Fig. 3. *Effect of RuO_2-loading on the H_2-evolution rates* (pH 14, 25 mg CdS, 0.1M Na_2S)

greatly the driving force for reduction of water to H_2 which can occur here at a high rate even in the absence of Pt-catalyst.

Sulfur formed concomitantly with H_2 in the photoreaction does not seem to interfere with water reduction. It appears therefore that the reduction of sulfur by conduction-band electrons of CdS, though thermodynamically favoured, is strongly inhibited for kinetic reasons. This explains why the H_2S-photocleavage can proceed almost to completion without decrease in the reaction rate.

Oxygen, on the other hand, can compete with water reduction by conduction-band electrons. Thus, at pH 13 and 0.3% CdS loading with RuO_2, $r(H_2)$ is decreased from 9 ml/h to 8 ml/h when air-saturated instead of deaerated suspensions are illuminated. Still, this competition of oxygen is surprisingly inefficient.

In order to explain the effect of pH on $r(H_2)$, we note that V_{fb} of CdS-electrodes decreases by -40 mV per pH unit [7][9]. This may be a consequence of decreasing negative surface charge determined by adsorbed SH^--ions. The commercial CdS-powder employed in our experiments had a point of zero zeta potential of 3.5. If one assumes that the flat-band potential of the particle has the same pH dependence as that of a crystalline electrode, than H_2-generation should be favoured at lower pH, since the change in the reduction potential of water is -59 mV/pH. Apparently, this effect is overcompensated by the decrease in SH^--concentration due to protonation in acidic medium[6]. This, according to *Equation 4*, displaces V_{fb} anodically, thus reducing the driving force for H_2-generation.

With regards to the valence band process, it was already recognized earlier during attempts to stabilize crystalline CdS-electrodes [9] that sulfide oxidation by holes is fast enough to compete efficiently with photocorrosion. The important

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[9] The pH-dependence of V_{fb} for CdS has been a point of contention (see [8]).

discovery made here is that this process can be remarkably accelerated by the ultrafine RuO_2-deposit on the CdS-particle. The role of RuO_2 is to enhance the rate of hole transfer from the valence band of CdS across the interface to H_2S. (The concentration of H_2S is high enough that this process occurs in preference over water oxidation.) Electron-hole separation is thus very efficient leading to high quantum yields for H_2-production from visible light.

In conclusion, the present paper illustrates how electrochemical concepts can be applied successfully to microheterogeneous systems in which conversion and storage of visible light energy is to be achieved.

The principal effects discovered during this study may be summarized as follows: i) RuO_2 is shown unambiguously to accelerate the transfer of holes from the valence band of CdS to redox species in solution. This effect complements earlier observations [10] in which the catalysis of water oxidation by colloidal RuO_2 was illustrated; ii) Water reduction to H_2 can occur on CdS-particles efficiently even in the absence of a noble metal catalyst such as Pt. This shows that the CdS-particle itself operates as an efficient microelectrode for H_2-generation; iii) During the photolysis an oxidation product, *i.e.* sulfur, is formed that does not interfere with water reduction. Thus, quantitative conversion of H_2S into H_2 and S is possible. Also, the competition of oxygen reduction with H_2-generation is surprisingly inefficient.

Apart from its importance for solar energy research, the process may find application in industrial procedures where H_2S or sulfides are formed as polluting waste products whose rapid removal and conversion into a fuel, *i.e.* H_2, is desirable. Also, in an intriguing fashion, these systems mimic the function of photosynthetic bacteria which frequently use sulfides as electron donors for the reduction of water to $H_2$¹⁰).

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¹⁰) Nitrogen-fixing bacteria can be directed in their photosynthesis activity to achieve water reduction.