35. Visible Light Induced Water Cleavage in CdS Dispersions Loaded with Pt and RuO_2, Hole Scavenging by RuO_2

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Summary

Illumination of aqueous CdS dispersions loaded with Pt and RuO_2 by visible light produces hydrogen and oxygen in stoichiometric proportion. No degradation of the photocatalyst is noted after 60 h of irradiation time. The RuO_2 deposit on the particle surface greatly accelerates the transfer of holes from the semiconductor valence band to the aqueous solution thus inhibiting photocorrosion.

Cadmium sulfide is a semiconductor¹) characterized by a band gap of 2.4 eV and a position of the valence and conduction band edge around + 1.5 and − 0.9 V respectively (*vs.* NHE at pH 7). These properties would make it ideally suited as a photocatalyst for the cleavage of water by visible light (2.4 eV = 517 nm). However, a serious problem associated with the use of this material in light energy conversion devices is its inherent instability under illumination. Holes produced in the valence band migrate to the surface where rapid oxidation of sulfide ions to sulfur occurs:

$$S^{2-} + 2\,h^+ \rightarrow S. \qquad (1)$$

This photocorrosion process may be prevented [2] by the addition to the solution of a reducing agent such as $Fe(CN)_6^{4-}$ or polysulfide ions, acting as a hole scavenger in competition to reaction (1). Unfortunately, in order to be effective the hole ejection from the semiconductor into the solution requires a large driving force and hence uses up a significant fraction of the absorbed photon energy.

Previously [3–5] we reported on the light induced water cleavage in colloidal TiO_2 dispersions where the semiconductor particles were loaded with ultrafine deposits of both Pt and RuO_2. It was shown that the presence of RuO_2 drastically increases the quantum yield of H_2- and O_2-formation under band gap irradiation²). These results indicate that holes in the valence band of TiO_2 can be trapped efficiently by the RuO_2-catalyst which subsequently intervenes as a mediator in

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¹) The literature of photoelectrochemical processes on single-crystal semiconductors has been reviewed, *e.g.* see [1].

²) *Kawai & Sakata* have found a similar catalytic effect of RuO_2 in the light induced oxidation of organic compounds in mechanically mixed TiO_2/RuO_2 dispersions, *e.g.* see [6].

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the water oxidation process. We reasoned therefore that ultrafine RuO_2-deposits may function as hole scavengers also on other semiconductor materials such as CdS. Such a process would inhibit the photocorrosion (equ. 1) and instead afford oxygen evolution from water. Experimental evidence supporting this concept is given in the present paper which illustrates for the first time water cleavage through illumination of low band gap semiconductors.

The photocatalyst employed consists of CdS particles loaded with both Pt and RuO_2 and was prepared in the following way: a dispersion of 25 mg of CdS (*Fluka*, 99.999%) in 25 ml water was achieved by sonication. An aqueous solution of RuO_4 was added and the mixture stirred for *ca.* 30 min in day light. Spontaneous RuO_4 decomposition takes place3) yielding an ultrafine RuO_2

$$RuO_4 \rightarrow RuO_2 + O_2 \qquad (2)$$

deposit on the CdS particles. The final concentration of RuO_2 was 8 mg/l. The loading with Pt was carried out by photoplatinization: 3 mg of H_2PtCl_6 were added to a solution containing 25 mg of CdS/RuO_2 and 0.5 ml formaldehyde (0.5 M stock solution in methanol/water 2:3). The concentration of formaldehyde was 10^{-2} M. After deaeration with N_2 the dispersion was illuminated for 30 min by a 450-W Xe-lamp through a 320 nm cut-off-filter. This time suffices for quantitative reduction of the Pt-ions by conduction band electrons (the holes created in the valence band are used to oxidize formaldehyde). The excess formaldehyde, methanol and water were then removed under vacuum at 30°. The dried powder had a loading of 40 mg Pt and 8 mg RuO_2/g CdS. Samples of 25 ml solution containing 25 mg catalyst were illuminated in a 35 ml flask through a 400 nm cut-off-filter and a 15 cm water cell to eliminate UV. and IR. radiation. A 450-W Xe-lamp was used as the light source. The gas evolved under illumination was analyzed by gas chromatography. A *Gow Mac* system,

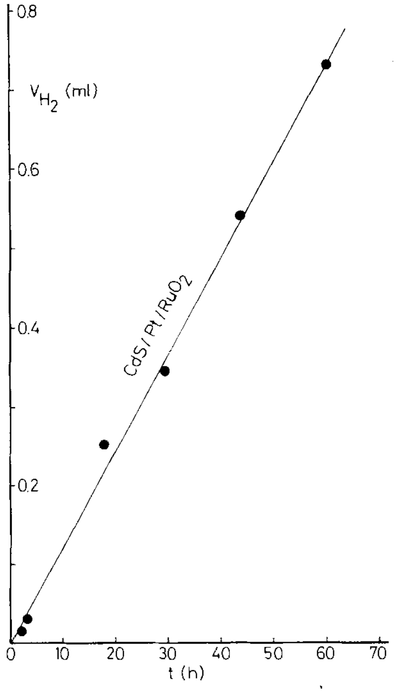

Fig. 1. *H_2- and O_2-production from illumination of CdS* (25 mg/25 ml) *loaded with 1 mg Pt and 0.2 mg RuO_2* (XBO-450 Watt lamp with 400 nm cut-off filter)

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3) The preparation of colloidal RuO_2 has been described in [7].

carbosieve column (35°) and N_2 (for H_2) or He (for O_2) carrier gas was employed. All samples were deaerated prior to illumination by flushing with nitrogen. When oxygen production had to be examined the solutions were saturated with helium.

Results are presented in *Figure 1* where the volume of hydrogen evolved is plotted as a function of irradiation time. After a short induction period the H_2-evolution rate establishes itself at 1.4×10^{-2} ml/h over at least 60 h of irradiation. No rate decrease was observed. A total of 0.8 ml of H_2 was produced after 60 h of irradiation. Oxygen is formed in stoichiometric proportion. The initial pH of the solution was 6.2 and did not change during the photoreaction in buffer free solution. Any significant contribution of photocorrosion (equ. 1) to the overall process would lead to an increase in pH since proton consumption associated with hydrogen formation would not be compensated by H^+-production resulting from water oxidation[4]).

A series of blank experiments established that the CdS particles are only photoactive in the presence of both the Pt and RuO_2 catalyst. If Pt is omitted no water cleavage is observed. Similarly the system fails to operate if CdS loaded alone with Pt is illuminated. Here rapid photodegradation of the particles and concommitant formation of sulfur is observed. Undoped CdS particles exhibit no photoactivity.

Furthermore, it was noted that the amount of RuO_2 deposited on the CdS particle strongly influenced the H_2 evolution rate. Thus if the concentration of the former is 16 instead of 8 mg/l the quantum yield is increased by a factor of 1.5.

A plausible mechanism for the intervention of the CdS particles in the water cleavage process is illustrated in *Figure 2*. Electrons and holes are initially produced through band gap excitation. The former migrate to Pt-sites where H_2-production from water occurs. The holes on the other hand are trapped by RuO_2 on the surface and subsequently used to produce oxygen from water. As a driving force of *ca.* 600 mV is available, the water oxidation on RuO_2 will be extremely

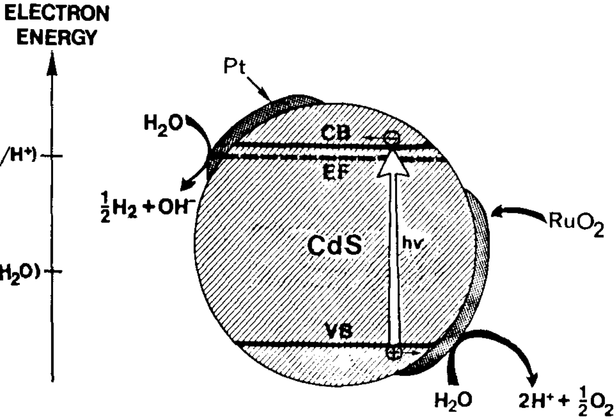

Fig. 2. *Schematic illustration of photoinduced water splitting on CdS particles loaded with Pt and RuO_2*

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[4]) Inhibition of photocorrosion by RuO_2 was also established by polarographic analysis which showed no increase in Cd^{2+}-concentration after 60 h irradiation time.

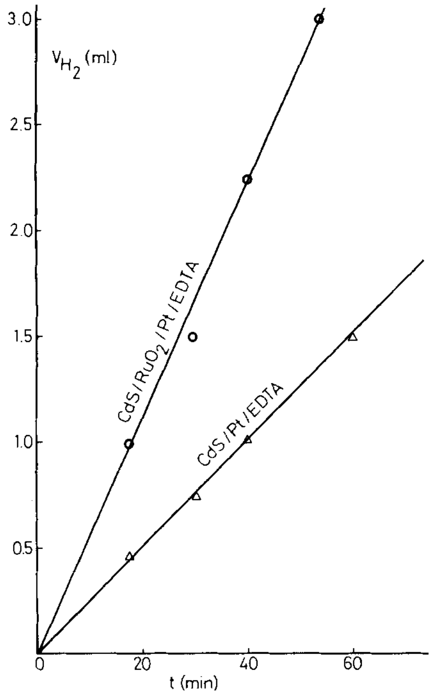

Fig. 3. *H_2-evolution from illumination of CdS particles in the presence of 0.1* M *EDTA.* Effect of RuO_2-loading on the H_2-yields. Catalyst concentration: 25 mg CdS loaded with 1 mg Pt per 25 ml solution. Upper curve 0.2 mg RuO_2 added.

fast [8] and hence can compete with surface corrosion *via* reaction 1. Thus the ultrafine RuO_2 deposit on the CdS surface promotes the transfer of holes from the valence band across the interface to the aqueous solution.

This model was further tested by performing experiments with EDTA-containing solutions; EDTA serves as a sacrificial donor which is irreversibly oxidized during the photoreaction. Results are displayed in *Figure 3.* At first we irradiated CdS particles which were loaded only by Pt. In agreement with the results obtained by *Darwent & Porter*[5]) we find efficient H_2-production. The rate is about 100 times greater than that observed in the absence of EDTA. A striking increase of the H_2-output is observed if RuO_2 is co-deposited with Pt on the CdS particle. The rate is more than doubled and amounts here to 3.6 ml/h. Apparently the role of RuO_2 in this system is to enhance the transfer of holes from the CdS to the EDTA in the electrolyte. This increases the quantum yield of H_2-production at the expense of photocorrosion.

In conclusion we have illustrated the decisive influence of RuO_2 on valence band processes in illuminated CdS particles. This catalyst, when deposited in ultrafine form, promotes oxidation of water or other electron donors at the CdS-electrolyte interface and thus diminishes the rate of photocorrosion. The quantum efficiency of the water cleavage process obtained so far is about 60 times smaller than that achieved with colloidal TiO_2 dispersions [3-5] loaded with RuO_2 and Pt.

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[5]) We thank these authors for communicating us their results prior to publication. Photochemical reactions on CdS powders have been widely investigated, *e.g.* see [9].

However the system may be improved significantly by further optimization. More importantly, the hole stabilizing ability of RuO_2 may be exploited in a photoelectrochemical device consisting of n-type single crystal CdS connected to a Pt counter electrode. Oxygen would be produced at the illuminated CdS surface covered with an ultra-thin layer of RuO_2 while H_2 would be evolved at the Pt counter electrode. Work in this direction is now in progress.

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REFERENCES

[1] a) *A.J. Nozik*, Ann. Rev. Phys. Chem. *21*, 189 (1978); b) *R. Memming*, Philips Techm. Rev. *38*, 160 (1978/79); Electrochim. Acta *25*, 77 (1980); c) *H. Gerischer*, in 'Topics in Applied Physics', *31*, 115 (1979); d) *A. Heller & B. Miller*, Electrochim. Acta *25*, 29 (1980).

[2] a) *A.B. Ellis, S.W. Kaiser & M.S. Wrighton*, J. Am. Chem. Soc. *98*, 1635 (1976); b) *G. Hodes, J. Manassen & D. Cohen*, Nature *261*, 403 (1976); c) *B. Miller & A. Heller*, Nature *262*, 680 (1976).

[3] a) *K. Kalyanasundaram & M. Grätzel*, Angew. Chem. Int. Ed. Engl. *18*, 701 (1979); b) *J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca & M. Grätzel*, Angew. Chem. Int. Ed. Engl. *19*, 646 (1980).

[4] *E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca & M. Grätzel*, Nature *289*, 158 (1981).

[5] *E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca & M. Grätzel*, J. Am. Chem. Soc., in press.

[6] *T. Kawai & T. Sakata*, J. Chem. Soc. Chem. Commun. *1979*, 1048; Chem. Phys. Lett. *72*, 87 (1980); Nature *286*, 474 (1980).

[7] a) *J. Kiwi & M. Grätzel*, Angew. Chem. Int. Ed. *18*, 624 (1979); b) *K. Kalyanasundaram, O. Micic, E. Promauro & M. Grätzel*, Helv. *62*, 247 (1979).

[8] *S. Trasatti & G. Buzzanca*, Electroanal. Chem. *29*, App. 1 (1971); *D. Galizzioli, F. Tantardini & S. Trasatti*, J. Appl. Electrochem. *4*, 57 (1974); *D. Galizzioli, F. Tantardini & S. Trasatti*, J. Appl. Electrochem. *5*, 203 (1975); *G. Lodi, G. Zucchini, A. de Battisti, E. Sivieri & S. Trasatti*, Mater. Chem. *3*, 179 (1978).

[9] *F.D. Saeva, G.R. Olin & J.R. Harbour*, J. Chem. Soc. Chem. Commun. *1980*, 401, and references cited therein.