Photo-oxidation of Water sensitised by Cadmium Sulphide Dispersions

Andrew Mills* and **Geraint Williams**

University College of Swansea, Department of Chemistry, Singleton Park, Swansea SA2 8PP, U.K.

A dispersion of CdS in alkali (pH >12) was employed to sensitise the photo-oxidation of water to O_2 by a sacrificial electron acceptor, $PtCl_6{}^{2-}$; heat treatment and platinisation of the CdS particles prior to irradiation markedly improved (20—40 times) their sensitising power.

The semiconductor CdS has a band gap (2.4 eV) which enables it to absorb an appreciable fraction of the solar spectrum (*i.e.* $\lambda \leqslant 526$ nm)[1]. In addition its conductance and valence band positions [−0.9 and +1.5 V *vs.* standard calomel electrode (S.C.E.)][2] are such that CdS should be capable of sensitising the photo-cleavage of water into H_2 and O_2. In recent years many groups[3—7] have been successful in employing CdS as a sensitiser for the photoreduction of water, using a 'sacrifical' electron donor (D) and H_2 catalyst (such as Pt, Cd, or RuO_2), *i.e.* reaction (1). In contrast, only a few groups[8—10] have been successful in photo-oxidising water to O_2 using CdS as a sensitiser and a 'sacrificial electron acceptor' (A), *i.e* reaction (2). This lack of success by others[11] is generally believed to be due to a preferred reaction of the photogenerated holes (h^+) with the semiconductor [reaction (3)] rather than with the water [reaction (4)].

$$2H_2O + 2D \xrightarrow[H_2 \text{ catalyst}]{\text{CdS}, h\nu \geqslant 2.4 \text{ eV}} H_2 + 2OH^- + \underset{\substack{\text{decomposes}\downarrow \\ \text{irreversibly}}}{2D^+} \quad (1)$$

$$2H_2O + 4A \xrightarrow[O_2 \text{ catalyst}]{\text{CdS}, h\nu \geqslant 2.4 \text{ eV}} O_2 + 4H^+ + \underset{\substack{\text{decomposes}\downarrow \\ \text{irreversibly}}}{4A^-} \quad (2)$$

$$2h^+ + CdS \rightarrow Cd^{2+} + S \quad (3)$$

$$4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \quad (4)$$

The work of Rajeshwar and Kaneko[12] and others[8] has demonstrated that the interface between n-CdS and deposited RuO_2 is an Ohmic barrier and thus will reflect the redox potential of solution and the potential of conductance band electrons in the bulk crystal. As a result, RuO_2, often used as an O_2 catalyst, is more likely to mediate the transfer of the photogenerated electrons (e^-) to the sacrifical electron acceptor than to mediate reaction (4). Indeed work by Grätzel and his co-workers[10] using CdS suspensions and $PtCl_6{}^{2-}$ as the sacrificial acceptor suggests that RuO_2 deposits are ineffective at mediating reaction (4). This group has achieved some success, however, using Rh_2O_3 deposits instead. Aspnes and Heller have suggested[13] that because of the high (>1 V) Schottky barrier formed between CdS and Pt, it is likely that any photogenerated holes would be channelled to the Pt sites where water oxidation could occur. The movement of the photogenerated holes and electrons towards and away from the Pt sites, respectively, is due to the directing influence of the electric field associated with the Schottky barrier. Evidence for this process occurring is provided in this communication in which we report on a dramatic improvement in the ability of CdS to mediate the oxidation of water upon platinisation.

Platinisation of the CdS (Fluka or Koch Light) was achieved using the method developed by Mills and Porter[14] which involved the precipitation of a Pt colloid in the presence of the CdS by addition of an electrolyte (NaCl) at a high concentration (2 M). Unlike photoplatinisation, this method does not lead to substantial damage of the semiconductor's surface which can produce an Ohmic contact, and, as a result, the CdS/Pt interface formed is most likely to be a high Schottky barrier.[13]

In a typical experiment, an aqueous solution (30 ml; pH 13) containing a CdS sample (5 mg/ml) (naked, platinised, or with another type of deposit) and 10^{-2} M H_2PtCl_6 was placed in a thermostated (25 °C) quartz reaction cell with an O_2-membrane polarographic detector (O_2-MPD) in its base. The details of the O_2-MPD have been described in a previous

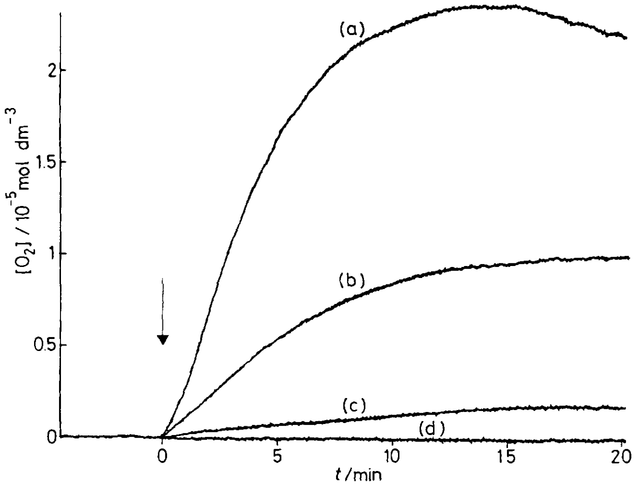

Figure 1. Typical dissolved O_2 concentration *vs.* time profiles observed upon the irradiation (λ >400 nm) of different semiconductors (5 mg ml^{-1}) dispersed in 30 ml of a chloroplatinic acid solution (10^{-2} M) containing 0.1 M NaOH. The semiconductors were (a) platinised CdS (0.8% Pt) in which the CdS had been baked at 100 °C for 3 h in air prior to platinisation, (b) platinised CdS (0.8% Pt), in which the CdS was unbaked, (c) CdS (unbaked), and (d) platinised Al_2O_3 (0.8% Pt). The arrow denotes the start of illumination.

Table 1.

Photocatalyst[a]		Initial rate of O_2 evolution/ (μmol dm^{-3} min^{-1})
CdS/Rh_2O_3	(1%)	2.2
CdS/RuO_2	(1.2%)	0.2
CdS		0.1
CdS/Pt	(0.8%)	2.3
CdS/Pt[b]	(0.8%)	4.1
Al_2O_3/Pt	(0.8%)	0
None		0

[a] The photocatalyst (5 mg ml^{-1}) was dispersed in 30 ml of solution containing $PtCl_6^{2-}$ (10^{-2} M) and NaOH (0.1 M). The irradiation source was a 250 W Xe arc lamp with a 400 nm cut-off filter. The CdS used in these experiments was obtained from Fluka or Koch Light, and its purity was typically >99.99%. [b] In this sample, the CdS was baked in air for 3 h at 100 °C prior to platinisation.

paper.[14] The reaction cell was irradiated using the light from a 250 W Xe arc lamp with a 400 nm cut-off filter. Figure 1 illustrates the observed variation of O_2 concentration as a function of time of illumination for several of the samples and Table 1 lists the measured initial rates of O_2 generation. In the absence of CdS or in the presence of a large band gap semiconductor (*e.g.*, Al_2O_3/Pt) no O_2 evolution was observed. In addition, no O_2 evolution was observed using any of the CdS samples if light λ >516 nm was employed. These results indicate that CdS, when irradiated with ultraband-gap light (*i.e.* $\lambda \leqslant 516$ nm), is responsible for photosensitizing the oxidation of water by the sacrifical electron acceptor $PtCl_6^{2-}$. From Table 1 it is apparent that an initial deposit of Pt greatly enhances the ability of CdS to photo-oxidise water. The photo-oxidation of water using *naked* CdS particles, therefore, most probably occurs on the fresh deposits of Pt produced by the initial photoreduction of $PtCl_6^{2-}$. Prolonged irradiation of platinised CdS (*ca.* 2 h) produced 300 μl of O_2 (as determined by g.c.) in the head space above the dispersion and traces of H_2 were also observed.

The rate of oxygen evolution [$R(O_2)$] was found to be a function of pH. At pH <12, no O_2 evolution was observed, presumably because the driving force for the reaction [*i.e.*, $\Delta E = E_{VB}(CdS) - E(O_2/H_2O)$; VB = valence band] is less than the overpotential (η) for water oxidation on the Pt sites by the photogenerated holes. At or above pH 12, O_2 evolution does occur and increases steadily with increasing pH to reach a maximum at *ca.* pH 13. From this work it would appear that η is *ca.* 1.04 V.

Interestingly, an initial heat treatment of the CdS (100 °C for 3 h in air) almost doubled the initial rate of water photo-oxidation in the irradiation system for the naked *and* platinised (after baking) CdS samples although the reasons for this remain, as yet, unclear.

Atomic absorption spectroscopy was used as the analytical technique to check whether O_2 generated from platinised CdS was accompanied by anodic corrosion, indicated by an increase in Cd^{2+} ion concentration. A suspension of the platinised CdS (5 mg ml^{-1}; 20 ml) containing 0.1 M NaOH and 10^{-2} M $PtCl_6^{2-}$ was irradiated until the dissolved oxygen concentration was at least 2.3×10^{-5} M. The dispersion was then acidified to pH 5 with acetic acid and stirred for at least 2 hours in order to dissolve any $Cd(OH)_2$ formed during irradiation. The particles were removed using a 0.2 μm membrane filter (Scheicher and Schüell), incorporated into the syringe used to sample the dispersion. The concentration of Cd^{2+} ions in the supernatant was determined as 7.8×10^{-5} M. A blank experiment was also performed using an identical suspension of Pt/CdS which was not irradiated and the level of Cd^{2+} ions was found to be the same. These data indicate that photocorrosion [reaction (3)] is not the major valence band process which occurs upon illumination of the Pt/CdS suspensions in the presence of $PtCl_6^{2-}$.

The procedure used for the qualitative analysis of Cd^{2+} was checked by adding $Cd(NO_3)_2$ (5.1×10^{-5} M) to a solution (20 ml) containing Pt/CdS (5 mg ml^{-1}) and 0.1 M NaOH. This solution was stirred in the dark for *ca.* 2 h and then analysed using the procedure described above. The detected amount of Cd^{2+} (after subtracting for the blank) was determined to be 4.2×10^{-5} M; thus *ca.* 82% of the Cd^{2+} added was detected using this method.

Evidence of the very effective nature of $PtCl_6^{2-}$ as an electron scavenger in this system was provided by monitoring the photo-uptake of O_2 in air-saturated solution containing platinised CdS in the absence and presence (10^{-2} M) of $PtCl_6^{2+}$. In the former case, the photo-uptake of O_2, which involves an initial reduction step (5), was readily observed ($-d[O_2]/dt$ = *ca.* 3.3×10^{-5} mol dm^{-3} min^{-1}) and was significantly greater (*ca.* 6 times) than when no Pt was present on the CdS. In the presence of $PtCl_6^{2-}$, however, little or no photo-uptake was observed even after a long irradiation (2 h) period. This result implies that in the presence of 10^{-2} M $PtCl_6^{2-}$, the rate of photoreduction of O_2 [reaction (5)] was reduced to that of water photo-oxidation (*ca.* 4×10^{-6} mol dm^{-3} min^{-1}), sensitised by the platinised CdS particles. Sacrifical electron acceptors other than $PtCl_6^{2-}$ were also tried [*e.g.*, $S_2O_8^{2-}$, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_6^{3-}$]; however O_2 evolution sensitised by the platinised CdS was only observed with $Fe(CN)_6^{3-}$, and in this case the rate of O_2 generation was low (*ca.* 5×10^{-7} mol dm^{-3} min^{-1}).

$$e^- + (O_2)_{ads} \rightarrow (O_2^{\cdot -})_{ads} \qquad (5)$$

Prolonged irradiation of the platinised CdS suspensions containing 0.1 M NaOH and 10^{-2} M $PtCl_6^{2-}$ resulted eventually in a gradual decrease in the rate of O_2 evolution. Subsequently N_2-purging of the system did not lead to the system fully recovering its ability to photo-oxidise water. Repeated irradiation of the CdS/Pt suspension following N_2-purging led to the eventual failure of the system to photo-generate detectable amounts of O_2. Possible reasons for this failure include: (i) coverage of the CdS particles with a thin layer of Pt originating from the $PtCl_6^{2-}$ which would encourage e^-h^+ recombination as well as reduce the light absorbed by the CdS particles,[10] and (ii) generation of a steady-state concentration of $(O_2^{\bullet-})_{ads.}$ sufficient to react with any holes produced [reaction (6)], thus preventing water oxidation *via* reaction (4), as has been found for dispersion of TiO_2/Pt.[3,15]

$$(O_2^{\bullet-})_{ads.} + h^+ \rightarrow (O_2)_{ads.} \qquad (6)$$

In conclusion, platinisation of CdS particles previously subjected to a mild (100 °C for 3 in air) heat treatment produced a marked improvement in the ability of CdS to sensitise the photo-oxidation of water by an electron acceptor such as $PtCl_6^{2-}$ or, to a lesser extent, $Fe(CN)_6^{3-}$, at pH >12. However, after prolonged use at pH 13 the Pt/CdS particles appear to lose their capacity for water photo-oxidation.

We thank the S.E.R.C. for their financial support of this work.

Received, 24th October 1986; Com. 1520

References

1 K. Rajeshwar, P. Singh, and J. DuBow, *Electrochim. Acta*, 1978, **23**, 1117.
2 T. Watanabe, A. Fujishima, and K. Honda, *Chem. Lett.*, 1974, 897.
3 A. Mills and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3659.
4 J. R. Darwent, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1703.
5 J. R. Harbour, R. Wolkow, and M. L. Hair, *J. Phys. Chem.*, 1981, **85**, 4026.
6 I. Willner and Z. Goren, *J. Chem. Soc., Chem. Commun.*, 1986, 172.
7 D. H. M. W. Thewissen, K. Timmer, E. A. Zouwen-Assink, A. H. A. Tinnemans, and A. Mackor, *J. Chem. Soc., Chem. Commun.*, 1985, 1485.
8 K. Kalyanasundaram, E. Borgarello, and M. Grätzel, *Helv. Chim. Acta*, 1981, **64**, 362.
9 A. J. Frank and K. Honda, *J. Phys. Chem.*, 1982, **86**, 1933.
10 N. M. Dimitrijevic, S. Li, and M. Grätzel, *J. Am. Chem. Soc.*, 1984, **106**, 6565.
11 D. Meissner, R. Memming, B. Kastening, and D. Barhnermann, *Chem. Phys. Lett.*, 1986, **127**, 419 and references therein.
12 K. Rajeshwar and M. Kanenko, *J. Phys. Chem.*, 1985, **89**, 3587.
13 D. E. Aspnes and A. Heller, *J. Phys. Chem.*, 1983, **87**, 4919.
14 A. Mills, A. Harriman, and G. Porter, *Anal. Chem.*, 1981, **53**, 1254.
15 D. Duonghong and M. Grätzel, *J. Chem. Soc., Chem. Commun.*, 1984, 1597.