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Photosensitised Oxidation of Water by CdS-based Suspensions

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Dispersions of CdS powder with or without metal or metal oxide deposits, such as Pt, Au, Ag, Rh, Rh_2O_3 and RuO_2, have been used to sensitise the oxidation of water by $PtCl_6^{2-}$. The most active of the CdS-based photosensitisers was found to be one in which Pt was deposited by precipitation of a Pt colloid onto the surface of a CdS sample which had been annealed in air for 3 h prior to platinisation. A study was made to determine the optimum conditions for O_2 evolution. The initial rate of O_2 evolution was found to depend upon a number of factors including: pH, [CdS/Pt], $[PtCl_6^{2-}]$, $[O_2]$, Pt loading and CdS annealing temperature and environment. Although a number of different electron acceptors were tried, including $PtCl_6^{2-}$, $PtCl_4^{2-}$, $Pt(OH)_6^{2-}$, $H_2AuO_3^-$, $S_2O_8^{2-}$, $Co(NH_3)_5Cl^{2+}$ and $Fe(CN)_6^{3-}$, O_2 photogeneration was observed with only $PtCl_6^{2-}$ and $Fe(CN)_6^{3-}$. A number of other materials were tested as photocatalysts for the oxidation of water by $PtCl_6^{2-}$, including TiO_2, TiO_2/Pt, TiO_2/Rh_2O_3, CdO, CdO/Pt, HgS/Pt, SiO_2/Rh_2O_3 and Al_2O_3/Pt; however, only the TiO_2-based materials showed any activity. The results of this work are discussed with respect to the current controversy over the mechanism for O_2 evolution.

1. Introduction

Cadmium sulphide (CdS) is an n-type semiconductor which has attracted a great deal of attention from workers in the field of solar-energy conversion.[1] One reason for this attention is its low band gap (2.4 eV), which allows it to absorb an appreciable fraction of the solar spectrum (*i.e.* $\lambda \leqslant 526$ nm).[2] Another reason is the strongly reducing nature of its conductance band electrons, e^-, (-0.9 V *vs.* standard calomel electrode, SCE) and the strongly oxidising nature of its valence-band holes, h^+ (1.5 V *vs.* SCE), both of which are generated simultaneously[3] on absorption of a photon of light, $\lambda \leqslant 526$ nm, by CdS. This combination of properties has encouraged many to attempt the photocleavage of water with visible light, using CdS as the photosensitiser, *i.e.*

$$2H_2O \xrightarrow[h\nu \geqslant 2.4\ \text{eV}]{\text{CdS}} 2H_2 + O_2\uparrow. \tag{1}$$

Although some groups have claimed success[4–6] in their attempts, others have failed.[7,8] The problem does not appear to be associated with the reduction side of the reaction, *i.e.*

$$2e^- + 2H^+ \rightarrow H_2\uparrow \tag{2}$$

since many groups[9–14] have used CdS, coupled to a H_2 catalyst, to efficiently sensitise this reaction in the presence of a sacrificial electron donor, such as EDTA,[9–11] TEOA,[12] cysteine,[10] sulphide[13] or formic acid.[14] The role of the sacrificial electron donor (D) is to react irreversibly with the photogenerated holes to prevent electron–hole recombination, *i.e.*

$$h^+ + e^- \rightarrow \text{heat} \tag{3}$$

and encourage the reduction of water by the remaining photogenerated electrons, *i.e.* reaction (2). Essential to the overall efficiency of the photosystem is the inclusion of an active, stable H_2 catalyst, such as Pt or Cd metal or RuO_2, to mediate reaction (2).[9-14]

In contrast to the photoreduction of water, the photo-oxidation of water, *i.e.*

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

when sensitised by CdS, is much more difficult and is generally considered to be the major obstacle preventing the efficient photocleavage of water sensitised by CdS.[4-8] At the heart of the problem is that the photogenerated holes tend to react with the semiconductor, *i.e.*

$$2h^+ + CdS \rightarrow Cd^{2+} + S \qquad (5)$$

or, in air-saturated water,

$$CdS + 2O_2 \xrightarrow{h\nu \geqslant 2.4\ \text{eV}} Cd^{2+} + SO_4^{2-} \qquad (6)$$

rather than with water, *via* reaction (4). In order to prevent this it is necessary to have present an O_2 catalyst to promote reaction (4) over reactions (5) and (6). Much of the current controversy which surrounds the research into CdS as a photocatalyst for the oxidation or dissociation of water centres on the existence of such an O_2 catalyst.[15]

It has been demonstrated for both photoelectrochemical[1,9] and photochemical systems[16,17] that sacrificial electron acceptors (A), such as hexachloroplatinate ($PtCl_6^{2-}$) or persulphate, allow systems capable of photosensitising the oxidation of water to O_2 to be studied and optimised. Ideally, the role of the sacrificial electron acceptor is to react irreversibly with the photogenerated electrons to prevent the electron–hole back reaction, reaction (3), and encourage the oxidation of water by the remaining photogenerated holes, reaction (4). The use of such 'sacrificial' electron acceptors in this way has become a popular method for testing the effectiveness of both new sensitisers and catalysts for the oxidation of water.

In this paper we describe the results of a detailed study of the oxidation of water by $PtCl_6^{2-}$ and other sacrificial electron acceptors, sensitised by CdS with and without a number of different metal or metal oxide deposits which have been proved capable of mediating the oxidation of water.

2. Experimental

2.1. Materials

The main source of cadmium sulphide (purity > 99.99 %) used throughout this work was Koch–Light Laboratories. However, samples of CdS from other sources were also tested, including those from Fluka (99.99 %), Johnson Matthey (99.99 %) and B.D.H. (98 %). Chloroplatinic acid (H_2PtCl_6), rhodium trichloride ($RhCl_3$), chloroauric acid ($HAuCl_4$) and ruthenium trichloride ($RuCl_3 \cdot xH_2O$) were obtained from Johnson Matthey. Chloroauric acid undergoes rapid hydrolysis to $H_2AuO_3^-$ under the highly alkaline conditions (pH 13) used throughout this work; thus we refer to the Au^{III} used in this work as $H_2AuO_3^-$. The cobalt(III) pentammine dichloride was synthesised as described elsewhere;[18] all other materials were obtained from B.D.H. in their purest available forms. The water used to make up solutions was always doubly distilled and deionised.

2.1.1. *Photocatalyst Preparation*

Unless stated otherwise, platinisation of the CdS was carried out using the following procedure. Initially a very stable Pt/citrate colloid, black in colour, was prepared by refluxing for 4 h a solution containing 30 mg of chloroplatinic acid, 30 cm^3 of a 1% sodium citrate solution and 120 cm^3 of water. Transmission electron micrographs of the Pt colloid showed that the Pt particles formed clusters, with an average diameter of 29 ± 4 nm. The average diameter of the Pt particles which made up these clusters appeared to be *ca.* 4 nm. Two thirds of the resultant Pt colloid (100 cm^3) were stirred with 1 g of the CdS as 11.6 g of NaCl were added. Although destabilisation of the Pt sol followed by Pt precipitation appeared to be complete within seconds, the solution was left stirring for *ca.* 1 h before being filtered and washed thoroughly with distilled water to remove the NaCl and citrate from the CdS/Pt. A variation in the amount of Pt deposited on the 1 g of CdS was achieved by using different volumes of the Pt/citrate colloid.

The method of depositing Pt onto CdS described above can also be used for depositing other materials provided they can be prepared in colloidal form,[19] Thus it proved possible to prepare both Au and Ag deposited CdS samples by using a Au/citrate and a Ag/citrate colloid, respectively. In addition, using the method of platinisation described above, it proved possible to platinise supports other than CdS, including TiO_2, Al_2O_3, CdO and HgS.

Samples of CdS/Rh_2O_3,[17] CdS/RuO_2[17] and photoplatinised CdS (CdS/Pt^*)[9] were prepared as described in the literature.

2.2. Methods

A dispersion (5 mg cm^{-3}) of the photocatalyst under test (30 cm^3) was placed in a thermostatted (25 °C) quartz cell with an O_2-membrane polarographic detector (O_2-MPD) in its base and stirred continuously. The details of the O_2-MPD have been given in a previous paper.[20] Unless stated otherwise, prior to illumination the dispersion was saturated with nitrogen (B.O.C., white spot) for at least 15 min. Illumination of the dispersion in the cell was carried out using a 250 W xenon lamp (Applied Photophysics) whose u.v. output was removed by means of a 400 nm cut-off filter.

In some of the prolonged irradiations, *i.e.* $t > 1$ h, the photogeneration of O_2 was monitored *via* the headscape (volume = 17 cm^3) using gas chromatography. The gas chromatograph used (Perkin-Elmer, model F33) was fitted with two 2 m stainless-steel columns (3 mm o.d. and packed with 5A molecular sieve) and a thermistor-type thermal-conductivity detector. The carrier gas used was argon (B.O.C.).

In some of the experiments atomic absorption spectroscopy (a.a.s.) was carried out, using a Perkin-Elmer Alpha 2 instrument, to monitor the levels of Cd^{2+} ions in solution before and after irradiation of a CdS/Pt dispersion. In this work an irradiated dispersion was acidified to pH 5 using 10^{-2} mol dm^{-3} acetic acid and stirred for 2 h to dissolve any $Cd(OH)_2$ generated. The particles were removed using a 0.2 μm membrane filter (Schleicher and Schüell) incorporated into the syringe used to sample the dispersion. The level of Cd^{2+} ions in the filtrate was then determined using a.a.s. A blank experiment was carried out in which $Cd(NO_3)$ (5.1×10^{-5} mol dm^{-3}) was added to a solution (20 cm^3) containing CdS/Pt (5 mg cm^{-3}) and 0.1 mol dm^{-3} NaOH. This solution was stirred in the dark for 2 h and then analysed for Cd^{2+} ions as described above. After subtracting for the blank (*i.e.* [Cd^{2+}] when no $Cd(NO_3)_2$ was added) the concentration of Cd^{2+} was determined as 4.1×10^{-5} mol dm^{-3}; thus *ca.* 82% of the Cd^{2+} added was detected by a.a.s.

In addition, a.a.s. was used to monitor the amount of Pt deposited onto the surface of a CdS/Pt dispersion before and after irradiation. This was achieved by first filtering off, washing and drying in air the CdS/Pt sample under test. A part of this sample (typically 0.11 g) was then dissolved in 10 cm^3 of a boiling *aqua regia* solution and the solution made up to 50 cm^3. The amount of Pt dissolved in solution, and therefore contained in the original CdS/Pt sample, was then determined by a.a.s.

Electron microscopy coupled with energy-dispersive analysis (e.d.a.) was carried out

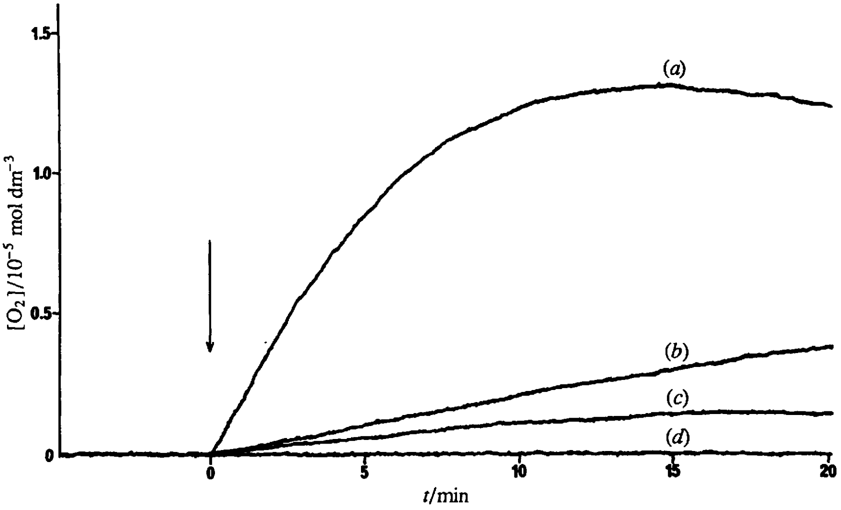

Fig. 1. Typical dissolved O_2 concentration *vs.* irradiation time observed for dispersions of the following CdS-based photosensitisers: (*a*) CdS/Pt (0.8 % Pt), (*b*) CdS/Pt (photoplatinised sample, 0.6 % Pt), (*c*) CdS and (*d*) no photosensitiser. The irradiations were carried out using light of $\lambda > 400$ nm with a solution (30 cm^{-3}) containing 150 mg of the photosensitiser under test, $PtCl_6^{2-}$ (10^{-2} mol dm^{-3}) and NaOH (0.1 mol dm^{-3}).

Table 1. Initial rates of O_2 evolution for a variety of CdS-based photocatalysts[a]

photocatalyst	metal/metal oxide deposited (% w/w)	initial rate of O_2 evolution /μmol dm^{-3}
CdS/RuO_2	1.2	0.2
CdS/Rh_2O_3	1.0	2.2
CdS (Fluka)/Pt	0.6	3.3
CdS (BDH, GPR grade)/Pt	0.8	0.5
CdS (Johnson Matthey)/Pt	0.4	0.2
CdS/Pt	0.8	2.3
CdS/Pt	0.6	1.9
CdS/Pt	0.4	1.7
CdS/Rh	0.3	0.5
CdS/Au	0.5	0.4
CdS/Ag	0.4	0.1
CdS/Pt*[b]	0.6	0.3
CdS	0	0.1
none	0	0

[a] Unless stated otherwise the CdS used was supplied by Koch–Light (puriss, > 99.999 %). [b] In this case the platinum was photodeposited onto the CdS.

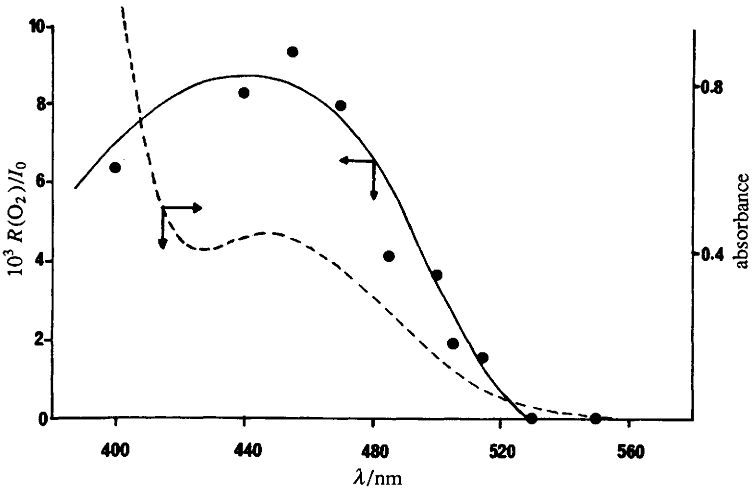

Fig. 2. Initial rate of O_2 evolution *vs.* wavelength of irradiation ($\lambda \pm 20$ nm); all other reaction conditions were as described for fig. 1. The broken line is the absorption spectrum of a $PtCl_6^{2-}$ solution (10^{-2} mol dm^{-3}) recorded in a 1 cm cell.

using a 120C TEM-SCAN instrument (JEOL Ltd) and was used to examine the CdS/Pt samples before and after irradiation. The electron micrographs recorded at 100000 magnification showed that the CdS/Pt powder comprised CdS microcrystals (diameter *ca.* 1.2 μm) with a sparse but uniform covering of Pt particle clusters (average diameter *ca.* 29 ± 4 nm). Calculations show that the Pt clusters cover typically only 1.8% of the surface area of any one CdS particle. Energy-dispersive analysis for Pt carried out on the CdS/Pt particles confirmed these observations. CdS/Pt particles from samples taken both before and after prolonged irradiation showed no evidence in their transmission micrographs of corrosion.

X-Ray powder diffraction patterns recorded for the CdS before and after heat treatment (up to 400 °C) showed no other lines except those due to CdS.

3. Results

3.1. Different CdS-based Photocatalysts

In a study of the photocatalytic activities of a number of different CdS-based powders, 150 mg of the photocatalyst under test were dispersed in 30 cm^3 of a solution containing $PtCl_6^{2-}$ (10^{-2} mol dm^{-3}) and NaOH (0.1 mol dm^{-3}). The solution was then purged with nitrogen and subsequently irradiated. Fig. 1 illustrates the variation in O_2 concentration *vs.* time observed for several of the samples, and table 1 lists the measured initial rates of O_2 generation.

3.2. Evolution sensitised by CdS/Pt

Using the most active of the CdS-based photocatalysts, *i.e.* CdS/Pt; 0.8% w/w, the initial rate of O_2 evolution was determined as a function of irradiation wavelength ($\lambda \pm 20$ nm). The irradiations were performed using a 250 W xenon arc lamp coupled to a high-radiance monochromator, and the results are illustrated in fig. 2.

In another set of experiments the concentrations of Cd^{2+} ions were determined before and after a typical irradiation. The dissolved oxygen generated during this irradiation was determined as 2×10^{-5} mol dm^{-3} and the concentration of Cd^{2+} ions was found to

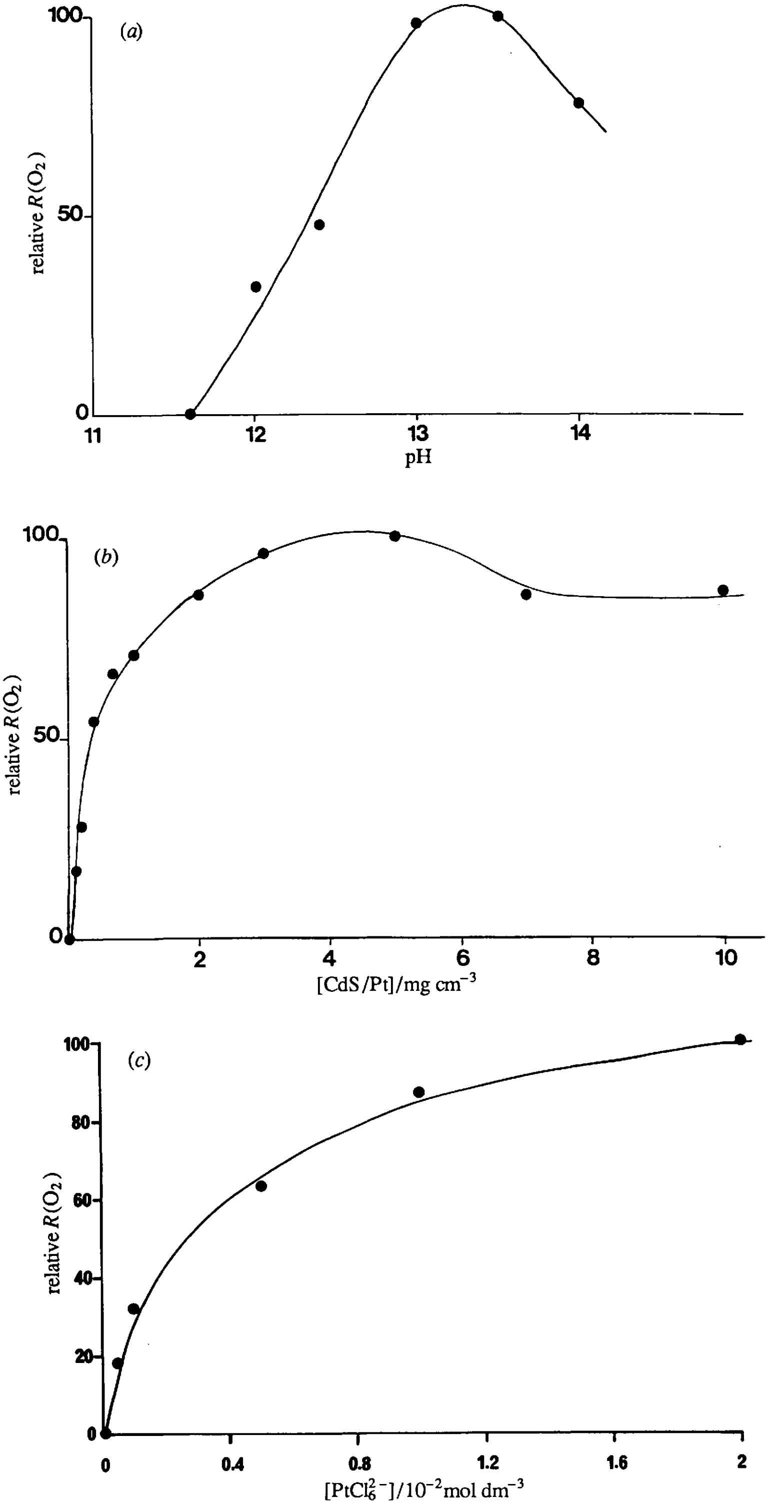

Fig. 3(*a*–*c*). For legend see facing page.

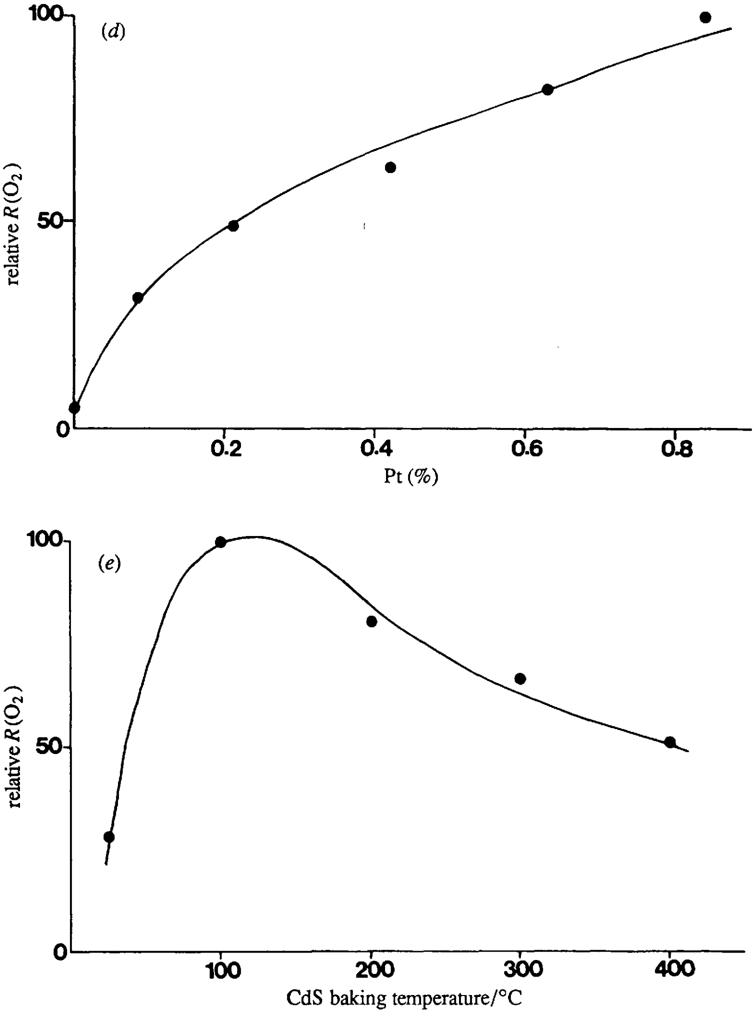

Fig. 3. Relative rate of O_2 evolution as a function of the following different reaction parameters: (*a*) solution pH (b) [CdS/Pt] (in mg cm^{-3}), (*c*) [$PtCl_6^{2-}$] (in mol dm^{-3}), (*d*) Pt loading on the CdS/Pt photocatalyst (in %) and (*e*) temperature used to bake the CdS powder, in air for 3 h, prior to platinisation. All other reaction conditions were as described for fig. 1.

be 7.8×10^{-5} mol dm^{-3} before and after irradiation. The high background [Cd^{2+}] (7.8×10^{-5} mol dm^{-3}) was most likely due to the CdS/Pt particles with diameters < 0.2 μm which were able to pass through the membrane filter employed to remove the CdS/Pt particles when sampling the liquid phase of the dispersion (see section 2.2).

In addition to the [Cd^{2+}] measurements, the Pt loadings on the CdS/Pt photocatalyst were determined before and after an irradiation in which 69 mm^3 of O_2 were generated in the head-space. The Pt loading before irradiation was determined as 0.81 %, which compares well with the value of 0.84% predicted from the known concentration and volume of the original Pt colloid used in the platinisation procedure. After irradiation the Pt loading on the CdS/Pt sensitiser had increased to 1.2%. Thus, from these results it appears that 3.0×10^{-6} mol Pt were deposited onto the surface of the CdS/Pt photocatalyst during the generation of at least 2.8×10^{-6} mol O_2.

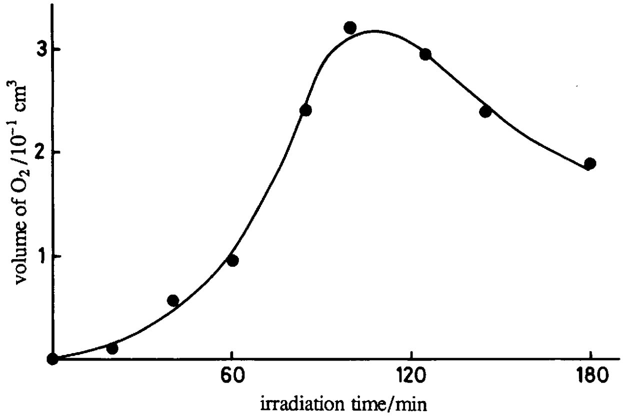

Fig. 4. Volume of O_2 photogenerated and detected by gas chromatography in the head-space (17 cm^3) of the irradiation cell *vs.* irradiation time. The illumination of a CdS/Pt dispersion was carried out under optimum reaction conditions, *i.e.* pH 13, [CdS/Pt] = 5 mg cm^{-3}, [$PtCl_6^{2-}$] = 10^{-2} mol dm^{-3}, Pt = 0.8 % and a CdS powder which was annealed in air for 3 h at 100 °C prior to platinisation.

3.2.1. *Determination of the Optimum Reaction Conditions*

The most active of the CdS-based photocatalysts tested was the sample with a high platinum content (0.8 % w/w) (see section 3.1). Using this sample as the photocatalyst, a series of experiments was carried out in which the reaction conditions were systematically varied and the effect on the initial rate of O_2 evolution [$R(O_2)$] monitored. The observed variation in $R(O_2)$ as a function of pH, [CdS/Pt] and [$PtCl_6^{2-}$] is illustrated in fig. 3(*a*), (*b*) and (*c*), respectively. $R(O_2)$ was also found to vary with the amount of Pt deposited onto the CdS, as illustrated in fig. 3(*d*). In addition, $R(O_2)$ was found to vary in a surprising manner when the CdS starting material was annealed in air at various temperatures above ambient, prior to platinisation; the observed variation is illustrated in fig. 3(*e*). In contrast to these latter findings, the photocatalytic activity of a CdS/Pt sample was reduced appreciably if it was annealed in air at $T > 100$ °C, after the CdS has been platinised.

3.2.2. *Prolonged and Repeated Irradiations*

From the results of the work described in the above section the optimum conditions for O_2 evolution were taken as [$PtCl_6^{2-}$] = 10^{-2} mol dm^{-3}, pH 13 and [CdS/Pt] = 5 mg cm^{-3}. These conditions were used in a series of experiments involving prolonged irradiation of the CdS/Pt sensitiser in the presence of $PtCl_6^{2-}$. The CdS/Pt sensitiser itself was prepared by platinisation of a CdS sample pre-baked in air for 3 h. The O_2 generated during the long-term irradiation of the optimised photosystem was monitored *via* the head-space using gas chromatography. The observed variation in the volume of O_2 photogenerated *vs.* irradiation time is illustrated in fig. 4. Prolonged irradiation of the photosystem did not, however, alter significantly [$PtCl_6^{2-}$], as determined by u.v.–visible absorption spectroscopy. From the gas chromatograms there was clear evidence that a small amount of H_2 was generated along with the O_2 after prolonged irradiation (> 60 min) of the CdS/Pt photosystem, although work with an H_2-MPD indicated that no H_2 was photogenerated by the system in the first 30 min of irradiation.

In another set of experiments the optimised CdS/Pt system was irradiated for 20 min, purged with nitrogen and then re-irradiated for another 20 min. This cycle was repeated

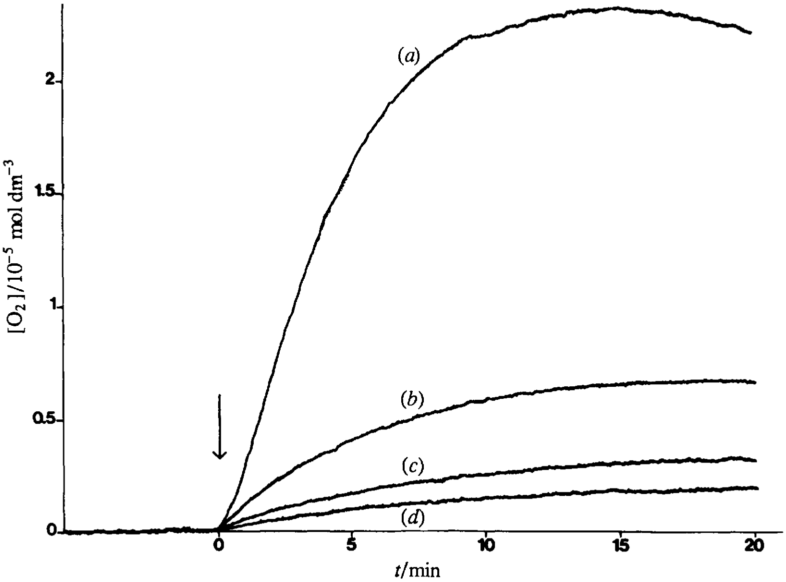

Fig. 5. Typical $[O_2]$ *vs.* irradiation time profiles for the same dispersion of CdS/Pt irradiated for four 20 min periods with only N_2 purging in between each irradiation, resulting in curves (*a*)–(*d*), respectively. The initial reaction conditions were as described for fig. 4.

another two times. The $[O_2]$ *vs.* irradiation time profiles for all of these irradiations are illustrated in fig. 5. In this work $[PtCl_6^{2-}]$ did not vary appreciably from the first to the last of the irradiations. In addition, when the used CdS/Pt photocatalyst was filtered, washed thoroughly with water and then placed in a fresh $PtCl_6^{2-}$ solution, no recovery in photocatalytic activity was observed. In attempt to regenerate the CdS/Pt photocatalyst, other experiments were carried out in which, after washing with water, the used CdS/Pt powder was stirred for 1 h in the presence of acetate, citrate or EDTA (typically 10^{-2} mol dm^{-3}) and then washed again with water before being placed in a fresh $PtCl_6^{2-}$ solution. Upon irradiation all of these dispersions showed a partial recovery in photocatalytic activity, typically 50%.

3.2.3. *Sensitised Oxygen Reduction* vs. *Generation*

Experiments carried out using the optimised photosystem described in section 3.2.1, in the absence of $PtCl_6^{2-}$ but in the presence of oxygen (air-saturated solution), showed that the rate of O_2 photoreduction sensitised by CdS/Pt was six times that for CdS. However, in the presence of $PtCl_6^{2-}$ (10^{-2} mol dm^{-3}) the rate of oxygen photoreduction in air-saturated solution by either CdS/Pt or CdS was greatly diminished (see fig. 6).

A more rigorous study was carried out on the effect of the initial $PtCl_6^{2-}$ concentration on the rate of O_2 photoreduction and photogeneration using a fixed concentration of CdS/Pt (5 mg cm^{-3}) and O_2 (12% air-saturated). The results of this work are illustrated in fig. 7.

3.2.4. *Alternative 'Sacrificial' Electron Acceptors*

A number of sacrificial electron acceptors other than $PtCl_6^{2-}$ were tested, using the optimised reaction conditions described in section 3.2.1., and the observed initial rates of O_2 evolution for $PtCl_6^{2-}$ and these other sacrificial electron acceptors are given in table

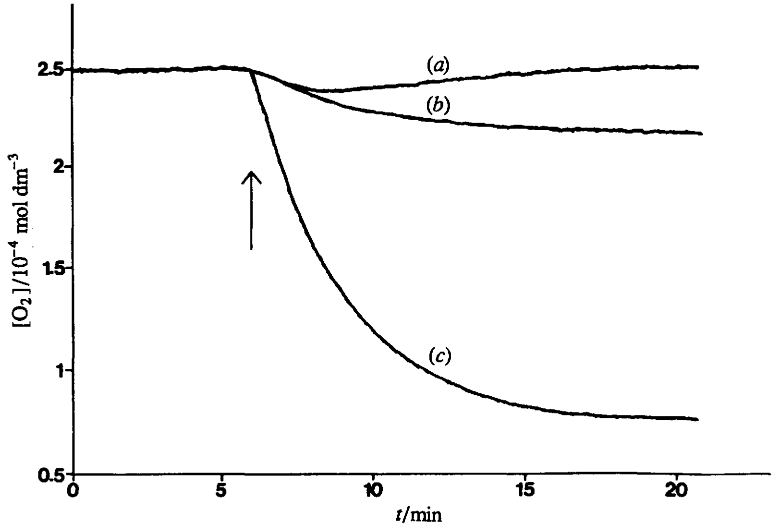

Fig. 6. $[O_2]$ *vs.* irradiation time profiles observed for dispersions of CdS/Pt [(*a*) and (*c*)] and CdS (*b*) in air-saturated solution. In this work, for curves (*b*) and (*c*) $PtCl_6^{2-}$ was absent. Unless stated otherwise all other reaction conditions were as described for fig. 4.

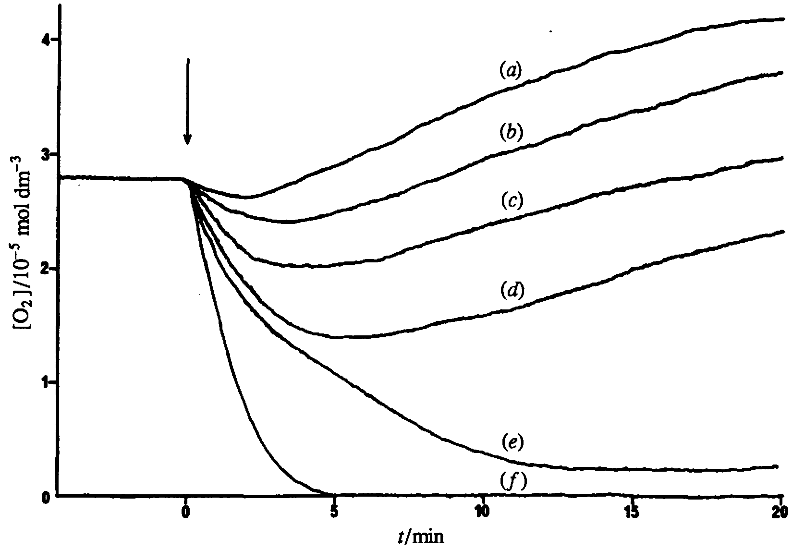

Fig. 7. $[O_2]$ *vs.* irradiation time profiles recorded for a dispersion of CdS/Pt in *ca.* 12% air-saturated solution containing different concentrations of $PtCl_6^{2-}$. The $PtCl_6^{2-}$ concentrations used were: (*a*) 5×10^{-3}, (*b*) 2×10^{-3}, (*c*) 10^{-3}, (*d*) 5×10^{-4}, (*e*) 10^{-4} and (*f*) 0 mol dm^{-3}. All other reaction conditions were as described for fig. 4.

2, along with some relevant redox information.[21, 22] Interestingly, when $H_2AuO_3^-$ and, to some extent, $PtCl_4^{2-}$ were used as electron acceptors, the CdS/Pt photocatalyst darkened considerably within a short time of irradiation (20 min), even though no O_2 evolution was observed.

Table 2. Initial rate of O_2 generation observed using different sacrificial electron acceptors

acceptor	initial rate of O_2 generation $/10^{-6}$ mol dm^{-3} min^{-1}
$PtCl_6^{2-}$	2.7
$PtCl_4^{2-}$	0
$Pt(OH)_6^{2-}$	0
$H_2AuO_3^-$	0
$S_2O_8^{2-}$	0
$Co(NH_3)_5Cl^{2+}$	0
$Fe(CN)_6^{3-}$	0.3

relevant redox couples[21, 22]

$$PtCl_6^{2-} + 2e \rightarrow PtCl_4^{2-} + 2Cl^- \qquad \text{(i)}$$
$$E^\circ = 0.68 \text{ V } \textit{vs.} \text{ NHE}$$
$$PtCl_6^{2-} + 4e \rightarrow Pt + 4Cl^- \qquad \text{(ii)}$$
$$E^\circ = 0.72 \text{ V } \textit{vs.} \text{ NHE}$$
$$PtCl_4^{2-} + 2e \rightarrow Pt + 4Cl^- \qquad \text{(iii)}$$
$$E^\circ = 0.76 \text{ V } \textit{vs.} \text{ NHE}$$
$$H_2AuO_3^- + H^+ + 3e \rightarrow Au + 3OH^- \qquad \text{(iv)}$$
$$E^\circ = (1.8 - 0.079 \times \text{pH}) \text{ V } \textit{vs.} \text{ NHE}$$
$$S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-} \qquad \text{(v)}$$
$$E^\circ = 2.01 \text{ V } \textit{vs.} \text{ NHE}$$
$$Fe(CN)_6^{3-} + 1e \rightarrow Fe(CN)_6^{4-} \qquad \text{(vi)}$$
$$E^\circ = 0.36 \text{ V } \textit{vs.} \text{ NHE}$$

Table 3. Initial rates of O_2 evolution for a variety of different photocatalysts

photocatalyst	metal/metal oxide deposited (% w/w)	initial rate of O_2 evolution $/\mu$mol dm^{-3}
TiO_2	0	3.9[a]
TiO_2/Rh_2O_3	1.0	3.7[a]
TiO_2/Pt	0.8	1.3[a]
CdO	0	0
CdO/Pt	0.8	0
HgS/Pt	0.4	0
SiO_2/Rh_2O_3	5.0	0
Al_2O_3	0.8	0

[a] Irradiations were performed using the full output of the 250 W Xe lamp. In the absence of the photocatalyst no O_2 evolution was observed upon illumination of the $PtCl_6^{2-}$ solution.

3.3. Other Photocatalysts

In addition to CdS and CdS/Pt other materials, such as TiO_2, TiO_2/Pt, CdO, CdO/Pt, HgS/Pt, SiO_2/Pt and Al_2O_3/Pt, were tested for photocatalytic activity. The reaction conditions were similar to those used in the CdS/Pt optimised system, *i.e.* $[PtCl_6^{2-}] = 10^{-2}$ mol dm^{-3}, [photocatalyst] = 5 mg cm^{-3} and solution pH 13. The initial rates of O_2 evolution recorded for the other photocatalysts are given in table 3.

4. Discussion

From the work described in section 3.1. it appears that a number of different CdS based materials are able to photosensitise the oxidation of water by chloroplatinic acid ($PtCl_6^{2-}$). It is usually believed[17, 23] that $PtCl_6^{2-}$ is reduced to Pt metal by the photogenerated electrons, and, in the presence of an ideal O_2 catalyst, the photogenerated holes oxidise water. Thus the overall reaction may be expressed as

$$PtCl_6^{2-} + 2H_2O \rightarrow Pt + 6Cl^- + 4H^+ + O_2 \qquad (7)$$

$$\Delta G = -4F[(0.72-1.23)-0.0591 \times pH].$$

In support of this we found that the amount of Pt deposited onto the CdS/Pt sensitiser was approximately equal to that of the O_2 photogenerated (see section 3.2). In addition, it was found that the concentration of Cd^{2+} ions before and after a typical irradiation remained unchanged, indicating that the CdS sensitiser does not undergo extensive photocorrosion [reactions (5) and (6)] during the irradiation.

The initial rate of O_2 generation was found to vary with the wavelength of irradiation under conditions of constant light flux (I) (see fig. 2). The observed variation of $R(O_2)$ with λ (± 20 nm) is similar to the expected absorption spectrum of a direct band-gap semiconductor such as CdS.[9] As the band-gap of CdS is 2.4 eV, then only light of $\lambda < 516$ nm should be effective in driving reaction (7) forward if CdS is acting as the sensitiser. This prediction is confirmed by the results illustrated in fig. 2. In the absence of CdS/Pt or in the presence of a large-band-gap semiconductor, such as Al_2O_3/Pt or SiO_2/Rh_2O_3, no O_2 evolution was observed (see tables 1 and 3). These results indicate that CdS/Pt is responsible for photosensitising the oxidation of water by $PtCl_6^{2-}$ when irradiated with ultraband-gap light (*i.e.* $\lambda < 516$ nm).

The work of Rajeshwar and Kaneko[24] and others[25, 26] has demonstrated that the interface between n-CdS and a metal or metal oxide deposited onto its surface is difficult to predict and can vary from an ohmic to a Schottky barrier. For example, Gissler *et al*,[26] have reported that RuO_2 forms a Schottky barrier of 0.5 V with CdS, whereas Rajeshwar and Kaneko[24] have found that it forms an ohmic barrier. Work carried out by Aspnes and Heller[25] has shown that Pt forms a high Schottky barrier (> 1 V) with CdS; however, they also suggest that if the surface of the CdS is damaged then an ohmic contact might be formed. As a consequence it may be possible to have two or more types of contact for only one material deposited onto the CdS surface.

The results of table 1 show that deposits of RuO_2, often used as an O_2 catalyst,[27, 28] do not enhance significantly the photocatalytic activity of CdS. This would not be surprising if the majority of the contacts formed between the two materials were ohmic, since the RuO_2 would then reflect the potential of the conductance-band electrons and thus be more likely to mediate the transfer of the photogenerated electrons to the $PtCl_6^{2-}$ than to mediate raction (4). The low rate of O_2 evolution observed for photoplatinised CdS may indicate that Pt deposited in this manner occurs mainly on damaged surfaces of the semiconductor and, like RuO_2, forms mainly ohmic contacts with the CdS particles. However, enhanced rates of O_2 generation were observed for CdS samples platinised by the standard method employed in this work (see section 2.1.1.); this may be due to the formation of a larger number Schottky barriers on the CdS particles. A Schottky barrier between CdS and a Pt site would channel photogenerated holes to the Pt site owing to the directing influence of the electric field associated with the barrier. Once at the Pt site the holes could oxidise water *via* reaction (4).

Since it is generally considered unlikely that the oxidation of water could be made to occur on the bare surface of CdS,[1] it is surprising that CdS alone was able to photosensitise reaction (7) (see table 1). From the $[O_2]$ *vs.* irradiation time profile [fig. 1(*c*)] for CdS alone, it appears that O_2 generation is prompt, indicating that O_2

generation is possible even if there is initially little or no O_2 catalyst (such as photodeposited Pt) on the surface of the CdS. In the mechanism for the photocatalysis of reaction (7) discussed above, O_2 evolution is most likely to occur at a Pt site which forms a Schottky junction with the CdS. Thus when CdS alone is used to sensitise reaction (7), it is necessary to propose that the oxidation of water occurs on some of the freshly deposited Pt sites produced by the initial photoreduction of $PtCl_6^{2-}$. However, the low rate of O_2 generation for both CdS, after prolonged irradiation (see fig. 1), and photoplatinised CdS/Pt (see table 1) indicates that the photodeposition of Pt does little to enhance the ability of CdS to sensitise reaction (7), possibly due to the predominant formation of ohmic, rather than Schottky, CdS–Pt contacts.

From the variation of the initial rate of O_2 generation [$R(O_2)$] as a function of pH [see fig. 3(*a*)] it would appear that reaction (7) cannot be made to proceed at a measurable rate if the solution pH is < 12 although, at this low pH, ΔG for reaction (7) is still very negative (-77 kJ mol^{-1}). At the optimum pH (13) the driving force for reaction (7) is increased ($\Delta G = -100$ kJ mol^{-1}), and therefore it is not surprising that the rate of O_2 evolution is also increased. The decrease in $R(O_2)$ at pH > 13, despite a further increase in ΔG, may be due to an ionic-strength effect.

The observed variation of $R(O_2)$ with [CdS/Pt] illustrated in fig. 3(*b*) is typical of semiconductor dispersions.[9, 29] Initially, by increasing [CdS/Pt] the amount of light absorbed increases, and therefore so does $R(O_2)$. Eventually a semiconductor dispersion concentration is reached at which the amount of incident light which is absorbed reaches a maximum. A further increase in the concentration of the dispersion serves only to reduce the penetration depth of the incident light and thereby increase the likelihood of losing to the surroundings any scattered light which could be absorbed. At high [CdS/Pt] the penetration depth is reduced to such a level that the light lost to the surroundings due to scattering is significant, but constant.

The observed variation of $R(O_2)$ with [$PtCl_6^{2-}$] is illustrated in fig. 3(*c*) and is the product of at least two effects. As [$PtCl_6^{2-}$] is increased it is expected that the probability of reaction between $PtCl_6^{2-}$ and any photogenerated reducing species, such as conduction-band electrons or S^- radicals, will increase. In addition, as illustrated by the broken line in fig. 2, an increase in the [$PtCl_6^{2-}$] will increase the amount of light absorbed by the electron acceptor, and therefore decrease the amount of light absorbed by the CdS/Pt. However, this latter effect is not expected to be large, since the [CdS/Pt] employed in this work was high (5 mg cm^{-3}) and the $PtCl_6^{2-}$ does not absorb very strongly light of $\lambda > 400$ nm (see fig. 2). Under the experimental conditions employed in this work most of the irradiation light ($\lambda > 400$ nm) will be absorbed by the CdS/Pt particles close (1–2 mm) to the front cell wall and not by the $PtCl_6^{2-}$, even at concentrations of 10^{-2} mol dm^{-3}.

The rise in $R(O_2)$ with increasing Pt deposited onto the surface of the CdS is illustrated in fig. 3(*d*) and may be taken as a reflection of the increasing probability of electron transfer to the $PtCl_6^{2-}$, rather than electron–hole recombination [(reaction (3)], with increasing Pt present. This trend in $R(O_2)$ with Pt indicates that the role of some of the Pt sites may be that of a 'sink' for electrons and a catalyst for electron transfer to the $PtCl_6^{2-}$ from the reducing species (e^- and/or S^- radicals). In support of this, several studies[9, 30] on the photoreduction of water sensitised by other semiconductors have demonstrated that the rate of H_2 evolution varies with the Pt deposited in a manner similar to that illustrated in fig. 3(*d*). In this latter work the majority of the Pt sites functioned as H_2 catalysts.

The effect on $R(O_2)$ of baking the CdS in air, prior to platinisation is illustrated in fig. 3(*e*). We refer to this process as 'thermal activation', since it leads to an increase in photocatalytic activity of the CdS/Pt. Separate experiments showed that the CdS could not be 'thermally activated' in the absence of O_2. This latter finding suggests that the process of 'thermal activation' is most likely due to the oxidation of at least some of the surface of the CdS powder, probably to CdO. Since increasing the baking temperature above 100 °C leads to a gradual decline in activity, it would appear that increasing the thickness of the oxidised CdS surface layer above an optimum level is detrimental to the activity of the CdS/Pt sensitiser. How the CdO film enhances the activity of the CdS is not clear. It may be that the CdO film produces an improvement in the electrical contact between the CdS and the Pt deposits and so increases the efficiency of electron transfer from the CdS to the $PtCl_6^{2-}$ *via* the Pt sites. A second possibility is that the CdO film removes recombination centres, such as surface SH^- groups, and so increases the lifetime of the photogenerated reducing and oxidising species, such as e^- and h^+. Supporting evidence for the latter suggestion comes from the work of Henglein and co-workers.[31] This group has demonstrated recently that a precipitate of cadmium hydroxide onto the surface of colloidal CdS particles not only increases their luminescence lifetimes and intensities but also stabilises them against anodic corrosion. The most likely surface product formed on placing CdO in solution at pH 13 is $Cd(OH)_2$. However, in contrast to the observations made by Henglein *et al.*,[31] in our work 'thermal activation', which presumably produces a surface layer of CdO, does not produce any detectable enhancement in the very weak, if any, luminesence of the CdS powders and increased the activity of the original CdS. However, it was found that a precipitate of $Cd(OH)_2$ [0.73% w/w $Cd(OH)_2$/CdS/Pt] onto the surface of a CdS/Pt powder did lower (by *ca.* 2 fold) its photocatalytic activity.

The results illustrated in fig. 4 and 5 indicate that both prolonged and repeated irradiation of the CdS/Pt leads to a deterioration in $R(O_2)$, even under optimum reaction conditions and with no significant decrease in $[PtCl_6^{2-}]$. Washing the used CdS/Pt with water does not regenerate the photocatalytic activity of th CdS/Pt. However, stirring with acetate, citrate or EDTA does produce a partial recovery in the photocatalytic activity of the CdS/Pt, and it is relevant to note that $Cd(OH)_2$ is known to dissolve in these washing solutions. These results suggest that during the photocatalysis of reaction (7) by CdS/Pt some anodic corrosion of the CdS occurs, thereby generating $Cd(OH)_2$ on its surface which, with time, accumulates and eventually destroys the photocatalytic action of the CdS/Pt, possibly in a manner similar to that described by Hengelein *et al.*[31] and outlined above. Although our a.a.s. studies of the CdS/Pt systems indicated no significant generation of Cd^{2+} ions, the irradiation time employed was short (20 min) and the background concentration of Cd^{2+} ions was high (7.8×10^{-5} mol dm^{-3}), see section 3.2. It seems quite possible, therefore, that some photocorrosion of the CdS/Pt does occur during illumination but not to an extent sufficient for detection by our method of analysis.

Experiments carried out in the presence of O_2, but in the absence of $PtCl_6^{2-}$ (see section 3.2.3 and fig. 6) demonstrate that CdS/Pt is *ca.* six times more active than CdS at sensitising the photoreduction of O_2; similar findings have been reported by others.[11] Work carried out by Memming and his co-workers and others on CdS single crystals[7, 15, 32] and colloids[33-35] has shown that O_2 is reduced by the photogenerated electrons (e^-) to OH^-, *i.e.*

$$O_2 + 2H^+ + 4e^- \rightarrow 2OH^-. \quad (8)$$

In addition, these workers found that O_2 can also be reduced *via* a photoelectrochemical oxidation process, *i.e.*

$$S^{2-} + 2H_2O + O_2 + 4h^+ \rightarrow SO_4^{2-} + 4H^+ \quad (9)$$

in which the initial step is believed[32] to be

$$S^{2-} + h^+ \rightarrow S^- \quad (10)$$

followed by

$$S^- + O_2 \rightarrow SO_2^-. \quad (11)$$

In an air-saturated solution, with $[PtCl_6^{2-}] = 10^{-2}$ mol dm^{-3}, no overall O_2 evolution or reduction was observed (see fig. 6). Thus it seems likely that under these conditions the rates of O_2 evolution and reduction were similar. At a lower $[O_2]$ (12% air-saturated) and a high $[PtCl_6^{2-}]$ (1×10^{-3} mol dm^{-3}) it was possible to observe O_2 evolution (see fig. 7) and at the same rate as observed in the absence of O_2. Thus from the results of the latter set of experiments it would appear that $PtCl_6^{2-}$, at concentrations $> 10^{-2}$ mol dm^{-3}, is more efficient at scavenging the photogenerated electrons and S^- radicals than O_2, at concentrations < 12% air-saturated. Since most of the work reported in this paper was carried out under N_2-purged conditions and in the presence of a high $[PtCl_6^{2-}]$, it was assumed that under such conditions the rate of O_2 evolution was not affected by the generation of O_2 until the concentration of dissolved O_2 reached *ca.* $\geqslant 12\%$ air saturation. As a result, at very low concentrations of $[O_2]$, as found in the initial part of any irradiation, the likely major processes are

$$e^- + PtCl_6^{2-} \rightarrow PtCl_6^{3-} \tag{12}$$

and possibly

$$S^- + PtCl_6^{2-} \rightarrow PtCl_6^{3-} + S. \tag{13}$$

The likelihood of reaction (13) taking place will depend upon whether reaction (10) predominates over reaction (4) even in the presence of a suitable O_2 catalyst, such as some, or all, of the Pt sites on the CdS.

In a recent paper Memming and co-workers[15] have suggested that O_2 evolution photosensitised by CdS does not occur *via* reaction (4) but rather that an unstable Pt^{III} species ($PtCl_6^{3-}$ or some other Pt^{III} species) which is generated *via* steps (12) and/or (13), is responsible, *i.e.*

$$4PtCl_6^{3-} + 6H_2O \rightarrow 4Pt + 12H^+ + 24Cl^- + 3O_2. \tag{14}$$

It has yet to be proved whether reaction (14) occurs, if at all, in bulk solution and/or on the surface of a CdS/Pt powder particle. However, if the latter were the case it would be more likely to occur at a Pt site than on the easily oxidised CdS surface.

Some evidence for and against the Pt^{III} intermediate mechanism comes from our work with sacrificial electron acceptors other than $PtCl_6^{2-}$ (section 3.2.4). As can be seen from table 2, the use of sacrificial agents, such as $PtCl_4^{2-}$, $Pt(OH)_6^{2-}$, $Co(NH_3)_5Cl^{2+}$, $H_2AuO_3^-$ and $S_2O_8^{2-}$, did not lead to the photogeneration of O_2. However, most of the sacrificial electron acceptors [$PtCl_4^{2-}$, $Pt(OH)_6^{2-}$ and $H_2AuO_3^-$] did reduce to a large extent the ability of CdS/Pt to photoreduce O_2 under air-saturated conditions. This indicates that these electron acceptors are efficient at scavenging the photogenerated electrons and S^- radicals. The observed rapid darkening of the CdS/Pt upon illumination in the presence of $H_2AuO_3^-$ or $PtCl_4^{2-}$, presumably owing to their reduction to the metal, provided further evidence of the effective scavenging action of these two electron acceptors.

Given that several of the electron acceptors, other than $PtCl_6^{2-}$, appear to act as efficient scavengers of any photogenerated reducing species, it is difficult to explain using the conventional mechanism, proposed by Grätzel and co-workers and summarised by reaction (7), why the photogenerated holes do not bring about the oxidation of water *via* reaction (4). Such difficulties are not encountered using the Pt^{III} mechanism, since the intermediate species $PtCl_6^{3-}$ will only be generated when $PtCl_6^{2-}$ is used as the sacrificial electron acceptor.

Interestingly, the Pt^{III} mechanism provides an alternative, and slightly simpler explanation for the observed photogeneration of O_2 by CdS alone, *i.e.* some photoreduction of the $PtCl_6^{2-}$ to Pt^{III} occurs and water oxidation then occurs *via* reaction (14). The enhancement in $R(O_2)$ observed for CdS/Pt over CdS may be interpreted in terms of the Pt^{III} mechanism as evidence that some Pt sites serve to mediate the reduction of $PtCl_6^{2-}$ *via* reactions (12) and (13), and that other Pt sites possibly catalyse reaction (14).

The Pt^{III} mechanism does not offer a ready explanation as to why the CdS/RuO_2 sample was little better than CdS in sensitising the oxidation of water, despite the likely formation of ohmic or low-Schottky-barrier CdS–RuO_2 junctions and the established[27, 28] O_2 catalytic activity of RuO_2. In addition, the Pt^{III} mechanism does not provide an adequate explanation for the observed photogeneration of O_2 when $Fe(CN)_6^{3-}$ was used as a sacrificial electron acceptor (see table 2). In the absence of CdS/Pt, and in the presence or absence of Al_2O_3/Pt, illumination of the $Fe(CN)_6^{3-}$ does not lead to O_2 generation. These findings suggest that the oxidation of water photosensitised by CdS/Pt is possible in the absence of $PtCl_6^{2-}$ and this, in turn, lends support to the idea that at least some oxidation of water can occur, *via* reaction (4), on the surface of a CdS/Pt particle. It may be, however, that the reduction of $Fe(CN)_6^{3-}$ at pH 13 can produce an intermediate species capable of oxidising water; this would represent a similar route for O_2 evolution, as suggested by the Pt^{III} mechanism.

The variations in $R(O_2)$ observed using different photocatalysts are summarised in table 3. Although TiO_2 was able to photocatalyse reaction (7) readily,[23, 36] the presence of Pt or Rh_2O_3 on the TiO_2 reduced, if anything, its photocatalytic activity. Similar observations[9] have been made for TiO_2 when used to sensitise the photo-oxidation of water to O_2 by Fe^{3+} ions at a concentration of 10^{-3} mol dm^{-3} in 5×10^{-3} mol dm^{-3} H_2SO_4. Although this effect may be simply due to the deposited material 'screening' the TiO_2 from the incident light,[37] it may also be that the deposited material enhances electron-hole recombination.[38]

Like CdS, both CdO[39] and HgS[40] are n-type semiconductors which, upon absorption of ultra-band-gap irradiation, generate conductance-band electrons capable of reducing $PtCl_6^{2-}$ and holes capable of oxidising water. However, neither CdO or CdO/Pt photosensitised the photogeneration of O_2 in the presence of $PtCl_6^{2-}$. In addition, these two materials failed to photoreduce O_2 in the absence of $PtCl_6^{2-}$. The lack of any photoactivity for either of the two materials is disappointing, given the reported ability of CdO to sensitise the photo-oxidation of water by $Fe(CN)_6^{3-}$ under the same conditions of pH.[39] The lack of photocatalytic activity by SiO_2/Rh_2O_3 and Al_2O_3/Pt was not unexpected, since both these materials possess band gaps too large to absorb the incident irradiation ($\lambda > 400$ nm).

5. Conclusions

Cadmium sulphide, with or without metal or metal oxide deposits such as Pt, Au, Ag, Rh, RuO_2 and Rh_2O_3, is able to photocatalyse the oxidation of water by $PtCl_6^{2-}$ at pH 13. A CdS-based photocatalyst with a high activity is produced by depositing Pt onto the CdS (0.8% w/w) using a method involving precipitation of a Pt colloid onto CdS which had been annealed at 100 °C for 3 h prior to platinisation (see section 2.1.1.). Using this photocatalyst the optimum conditions for the photogeneration of O_2 are as follows: pH 13, [CdS/Pt] = 5 mg cm^{-3}, Pt content $\approx 0.8\%$ and $[PtCl_6^{2-}] = 10^{-2}$ mol dm^{-3}. The majority of the experimental evidence described in this paper supports the original findings of Grätzel and co-workers[17] and favours their suggested mechanism in which the CdS/Pt truely acts as a photocatalyst for reaction (7), *i.e.* corrosion of the CdS is not a major reaction. The lack of O_2 evolution observed when electron acceptors other than $PtCl_6^{2-}$ were used, such as $PtCl_4^{2-}$, $Pt(OH)_6^{2-}$, $H_2AuO_3^-$, $Co(NH_3)_5Cl^{2+}$ and $S_2O_8^{2-}$, is difficult to explain using this mechanism. Results such as these have led other workers[15] to propose an alternative mechanism in which the water is oxidised by a Pt^{III} species, generated by the reduction of $PtCl_6^{2-}$ by a photogenerated reducing species, such as e^- or S^-. However, the Pt^{III} mechanism fails to explain many of the results reported here, including the photo-oxidation of water by $Fe(CN)_6^{3-}$, sensitised by CdS/Pt. In order to resolve these differences, further work is now in progress to elucidate the mechanism for O_2 evolution when CdS/Pt is used as the photosensitiser.

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