

The photo-oxidation of water by sodium persulfate, and other electron acceptors, sensitised by TiO₂

Andrew Mills^{a,*}, Miguel A. Valenzuela^b

^a Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK

^b Laboratorio de Catálisis y Materiales, ESIQIE-Instituto Politécnico Nacional, Edificio 8, tercer piso, Zacatenco 07738, Mexico, D.F., Mexico

Received 16 January 2004; accepted 20 February 2004

Abstract

A number of different electron acceptors are tested for efficacy in the oxidation of water to oxygen, photocatalysed by titanium dioxide. The highly UV-absorbing metal ion electron acceptors, Ce⁴⁺ and Fe³⁺, appear ineffective at high concentration (10⁻² M), due to UV-screening, but more effective at lower concentrations (10⁻³ M). The metal-depositing electron acceptor, Ag⁺, is initially effective, but loses activity upon prolonged irradiation due to metal deposition which promotes electron-hole recombination as well as UV-screening the titania particles. Most striking of the electron acceptors tested is persulfate, particularly in alkaline solution (0.1 M NaOH). The kinetics of the photo-oxidation of water by persulfate, photocatalysed by titania are studied as a function of pH, [S₂O₈²⁻] and incident light intensity (*I*). The initial rate of water oxidation increases with pH, is directly proportional to the concentration of persulfate present and depends upon *I*^{0.6}. The TiO₂/alkaline persulfate photosystem is robust and shows very little evidence of photochemical wear upon repeated irradiation. The results of this work are discussed with regard to previous work in this area and current mechanistic thinking. The formal quantum efficiency of the TiO₂/alkaline persulfate photosystem was estimated as ca. 2%.

© 2004 Elsevier B.V. All rights reserved.

Keywords: TiO₂; Water oxidation; Persulfate; Photocatalysis

1. Introduction

The efficient photocleavage of water into hydrogen and oxygen has, for many, long been the Holy Grail of photochemistry [1]. Such a system, coupled to solar irradiation, offers the possibility of almost limitless energy for the rest of humankind's existence. Many photosystems capable of water-splitting have been reported but none appear to meet the demands of high efficiency, long-term stability and low cost per m² required for a commercially viable product [2,3].

Initially, work on water-splitting systems focussed on dye-sensitised systems such as the notoriously irreproducible Ru(bpy)₃³⁺/MV²⁺/Pt(TiO₂)RuO₂ photosystem [4]. In this system a bifunctional catalyst, comprising particles of TiO₂ with deposits of Pt and RuO₂, was reported to be most effective in ensuring the oxidation of water to oxygen by Ru(bpy)₃³⁺ and concomitant reduction of water to hydrogen by MV⁺, where Ru(bpy)₃³⁺ and

MV^{+•} were the products of photo-oxidative quenching of excited Ru(bpy)₃²⁺ by MV²⁺. The poor reproducibility, very low efficiency and poor long-term stabilities of such dye-sensitised systems prompted interest in other types of photosensitisers, including heterogeneous, inorganic semiconductors [5]. However, most semiconductor sensitisers capable of promoting the cleavage of water, such as CdS, were found to be prone to efficiency-lowering processes, such as photoanodic corrosion and/or dissolution. Only UV-absorbing metal oxides, such as TiO₂, appeared sufficiently stable, both chemically and photochemically, and active to be able to sensitise the photocleavage of water [1]. Recently there has been a sudden upsurge in work on semiconductor-sensitised water-splitting photo-systems [6]. However, despite a variety of new and fairly esoteric photocatalysts, and many striking claims, there appears to be as yet no easily reproduced system that is capable of the sustained, efficient photocleavage of water. The discovery of the Holy Grail of photochemistry appears as elusive as ever.

So difficult is the water-splitting reaction, many researchers have contented themselves with studying the individual redox reactions associated with water-splitting [2–5]. Thus, there are many reports in the literature of the

* Corresponding author. Tel.: +44-141-548-2458;

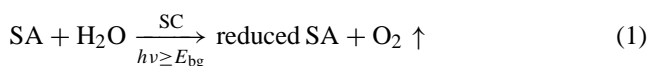
fax: +44-141-548-4822.

E-mail addresses: a.mills@strath.ac.uk (A. Mills), mavalenz@ipn.mx (M.A. Valenzuela).

photoreduction of water to hydrogen by a sacrificial electron donor, such as methanol, ethanol, sugar, starch and biomass, sensitised by a semiconductor, such as TiO₂. In such systems, the rate of hydrogen evolution is usually negligible, due to a high overpotential, unless a hydrogen catalyst, such as Pt or Au, is present, usually as many small island deposits, or polka-dots, on the semiconductor particles.

Curiously, studies of the photo-oxidation of water by a sacrificial electron acceptor, sensitised by a semiconductor are much less common [2,3,7]. This is not too surprising as the photo-oxidation of water is considered to be a much more demanding process than the reduction of water. For example, in the photo-oxidation of water the semiconductor sensitiser is required to operate under highly oxidising conditions and, given that $E^0(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$ and that the overpotential for water oxidation is on many of these materials $>1 \text{ V}$, then potentials as high as, or greater than, 2.23 V are required! Only metal oxide semiconductors, such as TiO₂ appear able to operate with impunity to anodic dissolution or passivation under such conditions. Thus, it would appear a reasonable demand of any 'new' photocatalyst for water-splitting, to first demonstrate its prowess as a photocatalyst for water oxidation by sensitising the prolonged and efficient photo-oxidation of water to oxygen by a sacrificial electron acceptor. Any photocatalyst that can perform well under such chemically, and photochemically, demanding conditions may have potential as a water-splitting catalyst, whereas those that perform badly are unlikely to have any real prospect of future use in this role. Not surprisingly, very few recent heterogeneous photocatalysts for water splitting have been tested in this way.

In the photo-oxidation of water by a sacrificial electron acceptor (SA), sensitised by a semiconductor (SC), the overall process can be represented as



where E_{bg} is the bandgap energy of the semiconductor. In practice, to date the number and range of sacrificial electron acceptors employed for the above purpose has been very limited and the list is dominated by metal ions, or complexes, such as Ce⁴⁺, Fe³⁺, Ag⁺, PtCl₄²⁻, AuCl₄⁻ [8–20]. Most of the SAs are hardly 'sacrificial' since, as in the case of Ag⁺, PtCl₄²⁻, AuCl₄⁻, often the products of reduction, in the above cases: Ag, Pt and Au, respectively, can be re-oxidised. Even if the latter reaction is difficult, the photodeposition of metals as reaction (1) proceeds obviously alters the very nature of the semiconductor-sensitisers' surface. The presence of such metals can not only act as a screen to ultra-bandgap light falling on the photocatalyst's surface but also provide recombination centres for photogenerated electron-hole pairs. Given the latter effect, it is no surprise that such photodeposition-type electron acceptors do not allow the prolonged photo-oxidation of water via reaction (1) with most semiconductors appearing to lose photoactivity with irradiation time. If photodeposition-type

electron acceptors, such as Ag⁺, etc., do not deserve the title of SA, nor do metal ions such as Ce⁴⁺ and Fe³⁺, which generate reduction products, namely: Ce³⁺ and Fe²⁺, that impede the overall process by reacting with the photogenerated holes and so promote the overall undesirable process of electron-hole recombination rather than the separate reduction of the SA by the photogenerated electrons and oxidation of water to O₂ by the photogenerated holes.

There does, however, appear to be one sacrificial electron acceptor which deserves this title, namely persulfate, S₂O₈²⁻. Although a fairly common SA in dye-sensitised water photo-oxidation systems [21,22], the use of S₂O₈²⁻ in the study of the photo-oxidation of water sensitised by semiconductors has been very limited [23]. It has, however, been used with some success as a substitute for, or enhancer with, dissolved oxygen as an oxidiser of organic pollutants, sensitised by semiconductor photocatalyst materials, such as TiO₂ [25–27]. In order to redress this imbalance, in this paper, the efficacies of various established electron acceptors, such as Ce⁴⁺, Fe³⁺ and Ag⁺, and the little-studied S₂O₈²⁻, in the photo-oxidation of water, sensitised by TiO₂ are studied. In addition, the kinetics of reaction (1), with SC = TiO₂ and SA = S₂O₈²⁻ are examined in more detail.

2. Experimental

2.1. Materials

The TiO₂ used throughout this work was P25 TiO₂ supplied by Degussa. The SEAs: Fe(NO₃)₃·9H₂O, Na₂S₂O₈ and AgNO₃ were supplied by Aldrich Chemicals. Ce(SO₄)₂ was purchased as 0.25 M solutions also from Aldrich Chemicals. All materials were used as received. Solutions of Fe³⁺ or Ce⁴⁺ were prepared using 0.01 and 0.5 M H₂SO₄, respectively, as the solvent. Sodium persulfate solutions were prepared using, unless stated otherwise, an aqueous 0.1 M NaOH solution as the solvent. Solutions containing AgNO₃ were prepared using 0.01 M HNO₃ as the solvent. In all cases the water used to make up the solutions was doubly distilled. Nitrogen used to purge the solutions before each irradiation was obtained from BOC and was free of O₂.

2.2. Methods

UV-Vis absorption spectra were recorded using a Helios β UV-Vis spectrophotometer (Thermo Spectronic) and quartz 1 cm cells. Details of the photochemical reactor have been reported elsewhere [28]. In brief, the photoreactor comprised two half cylinders, each containing six 8 W black light UVA lamps set against a half-cylinder aluminium reflector. Each of the lamps (Coast Air[®]) emitted a broad range of UVA light, typically 320–390 nm, with λ_{max} (emission) = 355 nm. The photochemical reaction vessel used in this work comprised a 60 cm³ thermostated cylindrical glass vessel (i.d. 3 cm), fitted with a Perspex

plunger and with an oxygen electrode in its base. Both items, i.e. the glass vessel and oxygen electrode, were purchased from Rank Bros., Cambridge. The oxygen electrode itself comprised a Pt working electrode (1 mm diameter) polarised at -0.85 V with respect to a Ag/AgCl counter reference ring electrode. The electrolyte used was a mixture of 0.5 M KCl and 0.5 M KOH. The Pt working electrode was covered with a 25 μ m Teflon membrane which provide the required gas-permeable, ion-impermeable covering associated with an oxygen electrode. With such an oxygen electrode, after deducting the negligible residual current (typically <0.05 μ A), the measured current is dependent directly upon the rate of diffusion of oxygen across the gas-permeable membrane. Since a highly reducing polarising voltage is employed, the level of oxygen at the Pt electrode is zero and, as a result, the current is directly proportional to the level of dissolved oxygen in the solution in the reaction vessel [29]. Thus, typically a current of 6 μ A was measured using the above set-up for an air-saturated solution in which the concentration of oxygen was 2.5×10^{-4} M. Before each kinetic run the oxygen electrode was calibrated with air-saturated and nitrogen-purged solutions in order to provide the necessary proportionality constant relating observed current and dissolved oxygen concentration, and the residual current.

Before each experiment the reaction solution under test (typically comprising 25 mg of P25 TiO₂ photocatalyst dispersed in a 25 ml aqueous solution containing an 0.01 M of an SEA), was sonicated for 15 min in an ultrasonic bath to disperse the semiconductor powder. The solution was then transferred to the photochemical reaction vessel and purged with oxygen-free nitrogen prior to illumination. The reaction solution was stirred continuously before and during illumination. The oxygen electrode was used to monitor the level of dissolved oxygen in the reaction solution as a function of time, via the observed variation in current. Initial rates, R_i , of oxygen generation were calculated from the measured initial variations in current as a function of irradiation time.

3. Results and discussion

3.1. Initial testing of electron acceptors

The efficacies of different electron acceptors under identical reaction conditions appear easily tested, given the apparent simplicity of reaction (1). However, in practice, it is usually not possible to conduct such useful experiments under identical conditions. In particular, the metal ion electron acceptors, such as Ce⁴⁺ and Fe³⁺, are intolerant of high pHs; conditions under which they undergo rapid hydrolysis to form complex, highly coloured and poor-defined, hydroxylated products which, depending upon the pH, can precipitate, often as a gel, from solution. It follows that research into reaction (1) conducted using such electron acceptors outside the very low pH zone (typically pH < 2) in which these metal ions exist in some well-defined and stable

state is of questionable value. In order to avoid problems of extensive and ever-changing metal ion hydrolysis, as indicated in Section 2 in this work, solutions of Fe³⁺ ions were made up in 0.01 M HNO₃, Ag⁺ in 0.01 M H₂SO₄ and those of Ce⁴⁺ ions in 0.5 M H₂SO₄. In contrast, sodium persulfate is stable and very soluble in acidic, neutral and alkaline solution. However, preliminary work showed that the latter performs best in an alkaline medium and so, in this initial trial, 0.1 M NaOH was used as the solvent for S₂O₈²⁻.

A quick test of the efficacy of each of the SAs described above was achieved using 10^{-2} M of the SA under test, under the pH conditions described above. To 25 ml of each solution were added 25 mg of P25 TiO₂, which were then placed in the reaction vessel, after sonicating to disperse the TiO₂. The oxygen electrode in the base of the reaction vessel was used to monitor the variation in dissolved oxygen concentration, via the measured diffusion current, as a function of irradiation time. Some typical results of this work are illustrated in Fig. 1, and show that the most striking SA tested is the previously poorly studied persulfate ion.

At first it may appear very strange that Ce⁴⁺, with an oxidation potential so high that, on thermodynamic grounds at least, it is able to oxidise water to oxygen efficiently without assistance, i.e. $E^0(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.44$ V, is the poorest performing of the SAs tested, as indicated in the results in Fig. 1. Indeed, Ce⁴⁺, or more precisely a hydroxylated, undefined Ce(IV) species that was originally Ce⁴⁺, has been a very popular choice of an electron acceptor in such work, over the last decade [2,8,11,12,17]. Interestingly, like Ce⁴⁺, Fe³⁺, which also appears from the results in Fig. 1 to be a poor electron acceptor, has also proven effective in promoting reaction (1) when used by others testing different semiconductor photocatalysts, once again usually in some unrecognised, undefined, hydroxylated form [11,12,15]. The reason for the apparently poor electron-acceptor performance of these SAs, as illustrated by the results in Fig. 1, is revealed by the plots of their UV-Vis absorbance spectra illustrated in Fig. 2. Also illustrated in Fig. 2 is the emission profile of the black light blue (BLB) lamps used throughout this work. Given that Degussa P25 TiO₂ is a 70:30 mixture of anatase ($E_{\text{bg}} = 3.2$ eV \equiv 388 nm) [1], it is clear that the dispersed TiO₂ particles should absorb much of the light emitted by the BLBs (λ_{max} (emission) = 365 nm). However, from the UV-Vis spectra illustrated in Fig. 2, it is also clear that at the high SA concentration of 10^{-2} M, the Ce⁴⁺ and Fe³⁺ solutions are so strongly absorbing in the wavelength range spanned by the BLB lamps that little of the UV light emitted by the lamp is likely to reach and be absorbed by the dispersed TiO₂ particles. Thus, UV-screening by the SA is responsible for the poor performances of the Ce⁴⁺ and Fe³⁺ electron acceptors. This UV-screening action is rather nicely revealed by reducing the concentration of these SAs by a factor of 10, before studying, once again, their effectiveness as SAs in reaction (1) using the O₂-electrode system. The results of this latter work reveals oxygen generation rates similar to those

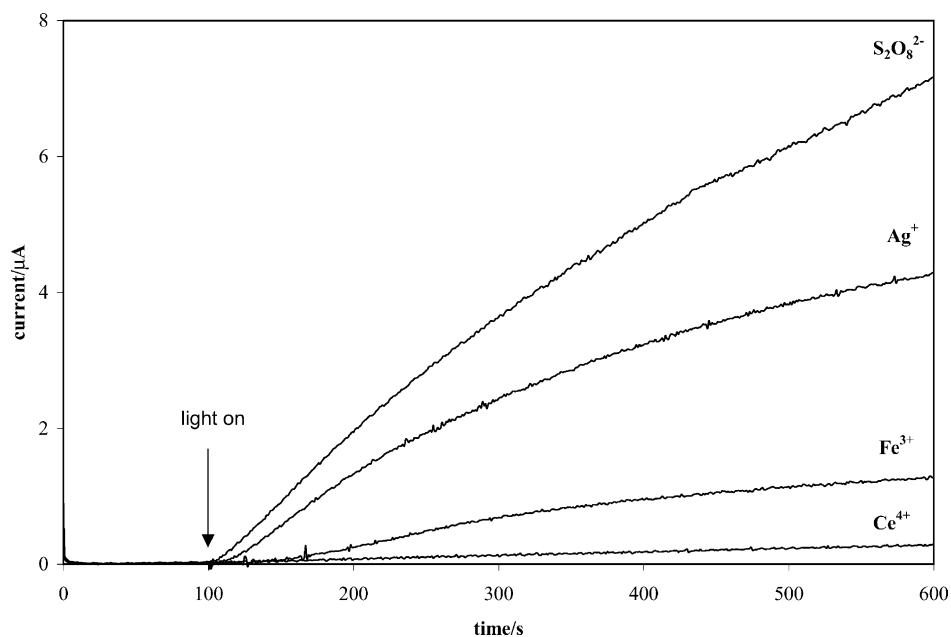


Fig. 1. Observed variation in the current from the oxygen electrode (which is directly proportional to the concentration of dissolved oxygen) as a function of reaction time. At $t = 100$ s, the UV photoreactor, surrounding the photochemical cell, was switched on. The reaction solution in the photochemical cell comprised 25 mg of P25 TiO_2 dispersed in 25 ml of an aqueous solution containing the electron acceptor (0.01 M) under test.

observed for 10^{-2} M $\text{Na}_2\text{S}_2\text{O}_8$ in 0.1 M NaOH, i.e. much faster despite the lowering in concentration. Thus, Ce^{3+} and Fe^{2+} ions are effective electron acceptors in reaction (1) when used in dilute ($<10^{-2}$ M) solution. However, as noted earlier, these electron acceptors cannot be really classified as 'sacrificial' since the products of their electron-accepting action, namely Ce^{3+} and Fe^{2+} , are effective electron acceptors which compete, with water in reaction (1), for the photogenerated holes and so bring about an overall loss in efficiency. Silver ions, in contrast to Ce^{4+} and Fe^{3+} ions,

are much less UV-screening and so more effective in their role as electron acceptor ($E^0(\text{Ag}^+/\text{Ag}) = +0.80$ V). However, as noted earlier, for this type of electron acceptor, the product is a metal, rather than a metal ion, and upon UV irradiation of the semiconductor the surfaces of the TiO_2 particles gain a covering of metal island deposits as the photoreaction proceeds. With such a metal island covering comes a loss of efficiency, due to UV-screening of the surface and/or an increased probability of electron-hole recombination, both effects being enhanced with the increased

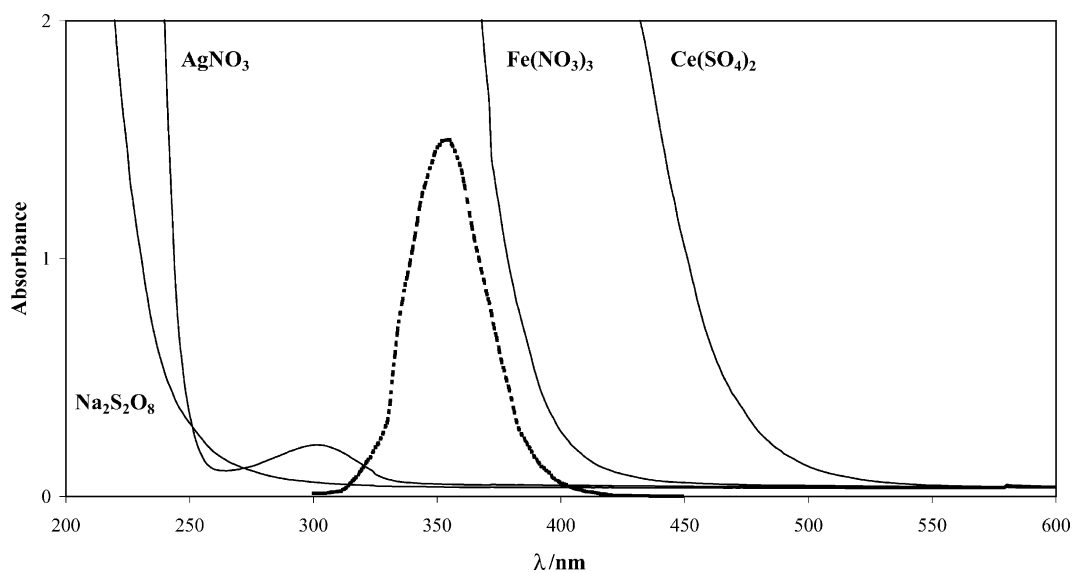
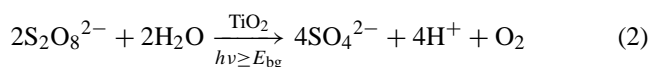


Fig. 2. UV-Vis absorption spectra of the 10^{-2} M electron donor aqueous solutions used in Fig. 1, in the absence of the TiO_2 . All spectra were recorded in a 1 cm quartz cuvette. The broken line is the relative emission profile of a typical black light blue fluorescent tube used in the photoreactor in this work.

density of metal island deposits that accompanies prolonged irradiation. Certainly in our work, at an initial AgNO_3 concentration of 10^{-2} M, the initially milk-white dispersion of TiO_2 in AgNO_3 solution, rapidly (i.e. within 5 min) develops a dark brown colouration upon UV irradiation. Other work carried out here showed that Hg^{2+} and Cu^{2+} ions failed to act as electron acceptors in reaction (1) and this is probably due to the high reactivities of the initial Hg^+ , Hg and Cu^+ and Cu products of reduction by the photogenerated electrons. Thus, of all the electron acceptors tested, persulfate appeared the most suitable, not only because of its effectiveness, due in some part to their high oxidation potential ($E^0(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}) = 2.1$ eV) and its negligible UV-screening ability (see Fig. 2), but also because it is inexpensive, readily soluble and stable over a wide pH range.

3.2. Persulfate as a sacrificial electron acceptor: an investigation into the kinetics of the process

Using persulfate ions as a sacrificial electron acceptor in the photo-oxidation of water sensitised by TiO_2 , the overall photocatalytic process can be summarised as follows:



The change in Gibbs free energy, ΔG , for reaction (2) is given by the expression:

$$\Delta G = -4F\Delta E \quad (3)$$

where

$$\Delta E = E^0 \left(\frac{\text{S}_2\text{O}_8^{2-}}{\text{SO}_4^{2-}} \right) - E^0 \left(\frac{\text{O}_2}{\text{H}_2\text{O}} \right) - \left(\frac{RT}{4F} \right) \ln \left\{ \frac{[\text{SO}_4^{2-}]^4 [\text{H}^+]^4 [\text{O}_2]}{[\text{S}_2\text{O}_8^{2-}]^2 [\text{H}_2\text{O}]} \right\} \quad (4)$$

where $E^0(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-})$ and $E^0(\text{O}_2/\text{H}_2\text{O})$ are 1.96 and 1.23 V, respectively.

Thus, under standard conditions, i.e. at pH 0, the Gibbs free energy for this process is large and negative ($\Delta G_{298}^\circ = -282$ kJ/mol) and it is a highly irreversible process. The driving force for reaction is also very pH sensitive, with ΔG increasing with pH according to the following equation:

$$\Delta G_{298}^\circ \text{ (kJ/mol)} = -282 - (5.7 \times \text{pH}) \quad (5)$$

Thus, at pH 0, 7 and 13, ΔG for reaction (2) is -282 , -322 , and -355 kJ/mol. Given reaction (2) and Eq. (5), it is possibly not surprising, therefore, based on energetic considerations, that in a series of experiments in which the pH of the reaction solution was varied from 1 to 13 that the initial rate of reaction (2) was found to increase markedly, as illustrated by the results in Fig. 3. In this work the usual, standard reaction conditions were employed (i.e. 10^{-2} M $\text{Na}_2\text{S}_2\text{O}_8$, 25 mg of P25 TiO_2 dispersed in 25 ml of reaction solution placed in the photoreactor, with $T = 25^\circ\text{C}$). The initial rate of photoproduction of oxygen via reaction (2) was measured using the O_2 -electrode in the base of the reaction vessel and twelve 8 W BLBs to irradiate the photoreactor. Despite the

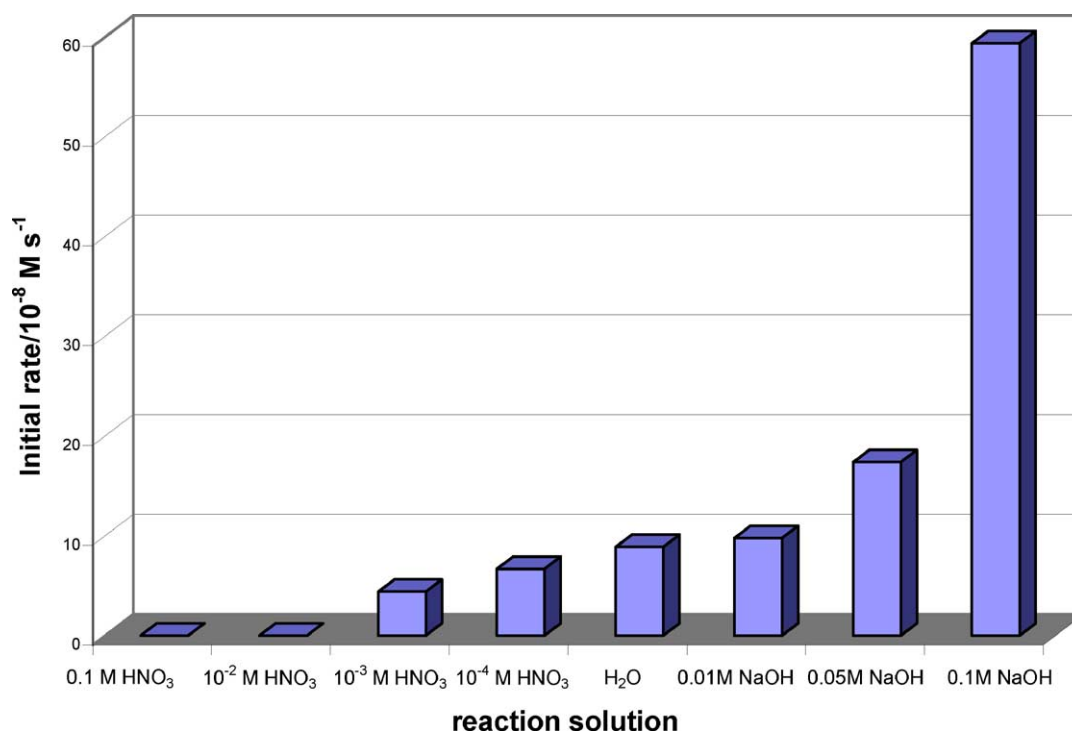


Fig. 3. Histogram of the measured initial rate of O_2 photogeneration via the photocatalytic reaction (2) as a function of reaction solution pH. As in Fig. 1, the reaction solution comprised 25 mg of P25 TiO_2 dispersed in 25 ml of an aqueous solution containing 0.01 M $\text{K}_2\text{S}_2\text{O}_8$.

fact that reaction (2) is pH sensitive, it is slightly surprising to note, from the results illustrated in Fig. 3, that the reaction proceeds at a negligible rate under acidic (i.e. $\text{pH} \leq 2$) conditions, despite the fact that the thermodynamic driving force, i.e. ΔG , for this reaction is still large and negative at this low pH. It is not clear at present why persulfate fails to act as a good sacrificial electron acceptor under very acidic conditions, although it may be associated with a $\text{p}K_{\text{a}}$ transition of one, or more, of the reaction intermediates, such as the sulfate radical $\text{SO}_4^{\bullet-}$, involved in reaction (2). In addition, nitrate is a strong UV absorber, thus, UV-screening may be responsible for the observed low rate at high $[\text{HNO}_3]$. From the results illustrated in Fig. 3 it appears for maximal rates the best pH conditions to study the sacrificial electron acceptor action of persulfate using TiO_2 as a photocatalyst, is at a high pH. Thus, in all subsequent work investigating the kinetics of reaction (2), the reaction solution contained 0.1 M NaOH, i.e. pH 13.

The kinetics of water oxidation via reaction (2) was measured as a function of the concentration of persulfate, $[\text{S}_2\text{O}_8^{2-}]$. In this work the usual experimental system, i.e. photoreactor, oxygen electrode and twelve 8 W black light bulbs, was used. The reaction solution comprised 25 mg of P25 TiO_2 dispersed in 25 ml of 0.1 M NaOH and different concentrations of persulfate spanning the range 0.01–0.004 M. Fig. 4 illustrates the typical outputs of the O_2 oxygen electrode observed in this study for a variety of different persulfate concentrations. From these results the plot of initial rate versus $[\text{S}_2\text{O}_8^{2-}]$ illustrated in Fig. 5 was generated, from which it appears that the initial rate is simply proportional to the initial concentration of per-

sulfate. Similar results have been reported by others using $\text{S}_2\text{O}_8^{2-}$ as an SA in the photo-oxidation of trichloroethylene, sensitised by TiO_2 [24]. These workers also found that at higher concentrations, i.e. $[\text{S}_2\text{O}_8^{2-}] > 10^{-2}$ M, the initial rate was independent of $[\text{S}_2\text{O}_8^{2-}]$ [24]. The latter observations, and those reported here, are consistent with the kinetics of the oxidative photocatalytic process fitting a Langmuir–Hinshelwood-type format, i.e.

$$R_i = \frac{kK_{\text{SA}}[\text{SA}]}{(1 + K_{\text{SA}}[\text{SA}])} \frac{K_{\text{X}}[\text{X}]}{(1 + K_{\text{X}}[\text{X}])} \quad (6)$$

where k is a constant, that depends upon the absorbed light intensity, I_{abs} , $[\text{SA}]$, and $[\text{X}]$ are, respectively, the concentrations of the sacrificial electron acceptor and species, X (that is being oxidised), and K_{SA} and K_{X} are constants associated with the adsorption of SA and X on the surface of the photocatalyst [1]. Eq. (6) is the general empirical form of the kinetic equation found to relate the initial rate of photocatalytic oxidation of X by SA, sensitised by TiO_2 , R_i , to $[\text{SA}]$ and $[\text{X}]$. A more careful analysis of this general kinetic equation for a number of different, actual systems has revealed that invariably K_{SA} and K_{X} are *not* the Langmuir dark adsorption coefficients for SA and X, but rather are some function of them and I_{abs} [30,31]. In most studies of the photocatalytic destruction of organic pollutants (such as: X = trichloroethylene, phenol and 4-chlorophenol), the sacrificial electron acceptor is oxygen, usually dissolved in solution [1]. In contrast, in this work X = water and SA = $[\text{S}_2\text{O}_8^{2-}]$. It follows that the parameter, $K_{\text{X}}[\text{X}]/(1 + K_{\text{X}}[\text{X}])$, is a constant in our experiments and, given $R_i \propto [\text{SA}]$ (see Fig. 5), $K_{\text{SA}}[\text{SA}]$ must be $\ll 1$. Under such conditions Eq. (6)

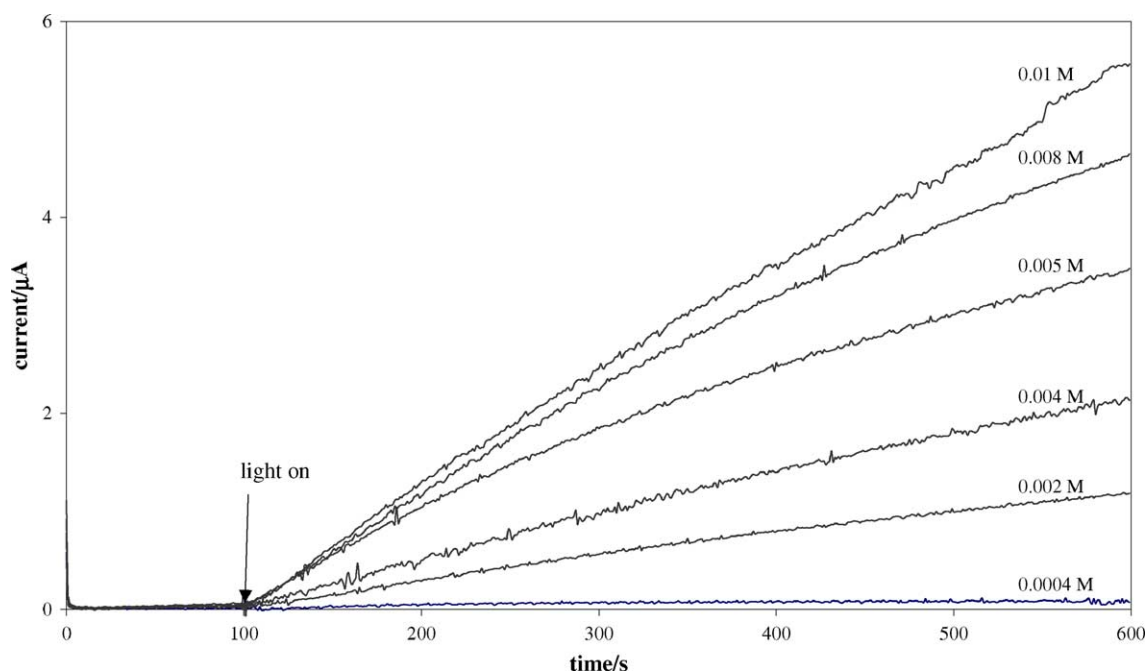


Fig. 4. Observed variation in the oxygen electrode current, set in the base of the photoreaction vessel, as a function of reaction time. The different current–time profiles were generated by varying the initial concentration of persulfate present in the reaction solution. All other conditions were as in Fig. 1.

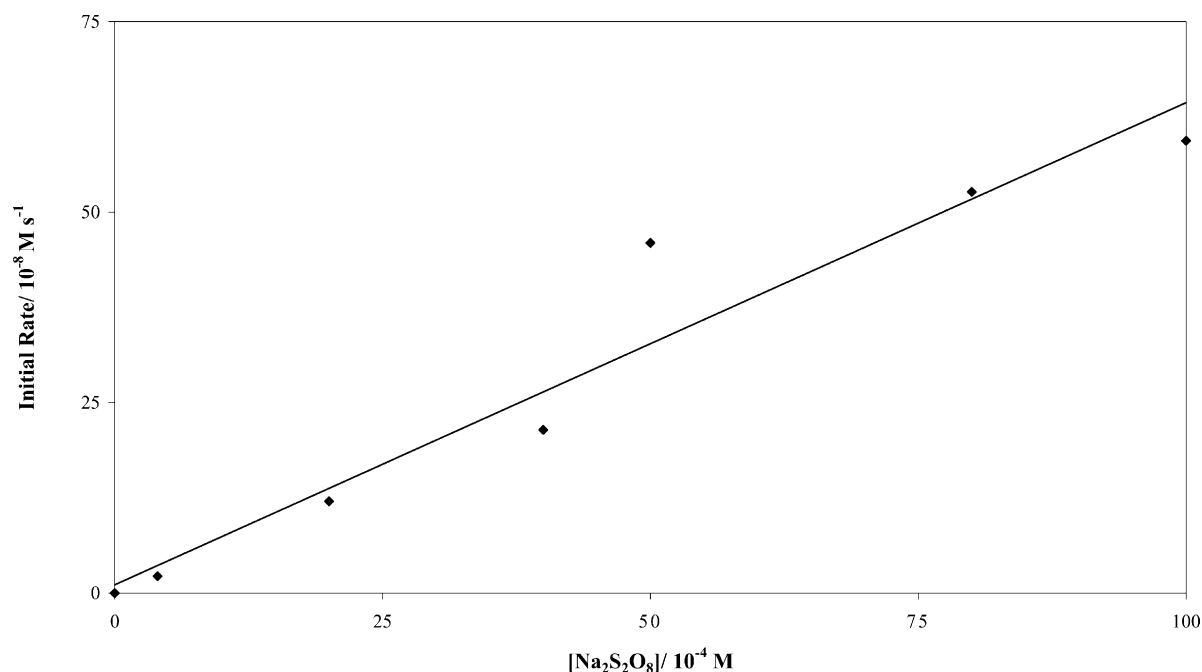


Fig. 5. Plot of the initial rates of oxygen photogeneration as a function of initial persulfate concentration. The initial rates were calculated using the data in Fig. 4.

reduces to

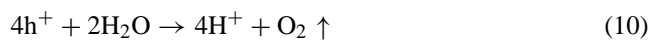
$$R_i = k'[\text{S}_2\text{O}_8^{2-}] \quad (7)$$

where k' is a constant which depends upon I_{abs} , amongst other things. Eq. (7) is, of course, consistent with the observed linear relationship between R_i and $[\text{S}_2\text{O}_8^{2-}]$ illustrated by the results in Fig. 5.

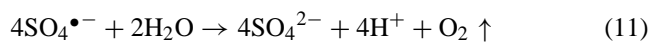
In reaction (2) the role of the persulfate ions is to react with the conduction band electrons photogenerated on the TiO_2 particles and so suppress the efficiency lowering process of electron–hole recombination, i.e.



As a result, the photogenerated holes, h^+ , are allowed to accumulate and subsequently oxidise water, i.e.



In fact, it needs to be recognised that the $\text{SO}_4^{\bullet-}$ radical is also a very strong oxidising agent, capable of oxidising water to oxygen [21], i.e.



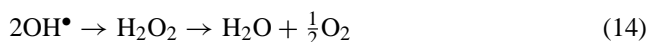
The overall oxidation of water either by h^+ or $\text{SO}_4^{\bullet-}$ is unlikely to be achieved by a concerted four-electron transfer process, such as summarised by Eqs. (10) and (11), but rather via hydroxyl radical formation, i.e.



or



Hydroxyl radicals can then oxidise water via a myriad of radical reactions including peroxide formation, i.e.



As noted earlier, from the empirical kinetic equation for semiconductor photocatalysis, summarised by Eq. (6), it is generally found that the constant, k , is a function of the intensity of ultra-bandgap light absorbed, I_{abs} [1]. Thus, if all other reaction conditions are kept the same (such as $[\text{X}]$, $[\text{SA}]$, T , etc.), typically it is found that R_i is proportional to the incident light intensity, I , at low light intensities and proportional to $I^{0.5}$ at high light intensities [32]. The former situation is generally assumed to arise because the steady-state concentrations of photogenerated electrons and holes are proportional to I_{abs} at low absorbed light levels since, under such conditions, the efficiency-lowering process of electron–hole recombination is not significant. At high I values, the latter process dominates and, as a consequence, the steady-state concentrations of h^+ and e^- are proportional to $I^{0.5}$ [32]. In a simple set of experiments, involving a standard reaction system (i.e. 25 ml of reaction solution containing 25 mg of TiO_2 dispersed in an aqueous solution 0.1 M in NaOH and 0.01 $\text{Na}_2\text{S}_2\text{O}_8$), the incident light intensity falling on the photoreactor was varied using a series of fine cylindrical metal gauzes placed between the lamps and the photoreactor vessel. The initial rate of oxygen evolution, R_i , was measured as a function of the relative incident light

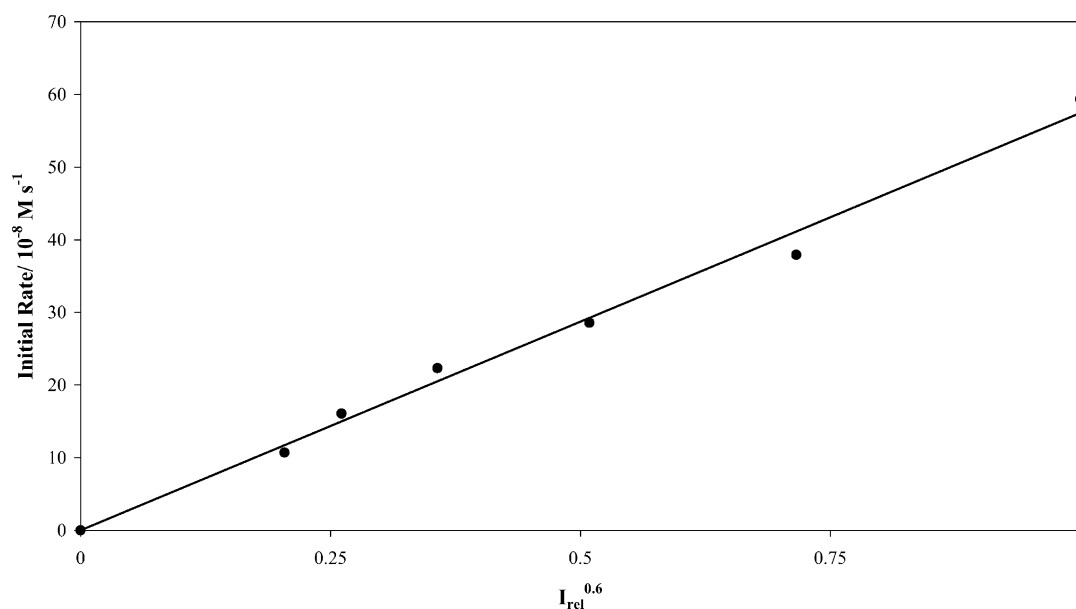


Fig. 6. Plot of the measured initial rate of oxygen photogeneration via reaction (2) as a function of $I^{0.6}$, where I is the incident light intensity. The reaction conditions were as in Fig. 3, with the solution pH 13.

intensity, I_{rel} , and *not* found to be related directly. Instead, a plot of this data in the form of R_i versus $I_{rel}^{0.6}$ was found to give a good straight line, as illustrated by the results in Fig. 6. In this work an I_{rel} value of 1.00 is equivalent to 7.6×10^{17} photons $\text{cm}^{-2} \text{min}^{-1}$ (ca. 6.9 mW cm^{-2}), as measured by chemical actinometry. In the classic semiconductor photocatalysis experiment conducted by Egerton and King into the kinetics of oxidation of isopropyl alcohol by rutile TiO_2 , the changeover from a first- to half-order dependence upon I occurs at ca. 3.6×10^{16} photons $\text{cm}^{-2} \text{s}^{-1}$ [33]. Pichat and co-workers have reported R_i is proportional to $I^{0.5}$ for the photo-oxidation of 4-chlorophenol by P25 TiO_2 over the range $(0.4\text{--}9.2) \times 10^{16}$ photons $\text{cm}^{-2} \text{min}^{-1}$ [34]. Thus, in our work, the observation that R_i is proportional to $I_{rel}^{0.6}$ over the intensity range $(0.25\text{--}1.3) \times 10^{16}$ photons $\text{cm}^{-2} \text{s}^{-1}$ appears consistent with the work of others working on similar systems and indicates that in our work the kinetics fall in the transition range between the first-order (low intensities) and half-order (high intensities) dependence upon incident intensity expected from such systems.

In heterogeneous photocatalysis it is often very difficult to measure accurately the intensity of absorbed light and so obtain a value for the quantum yield (ϕ) of the photosystem under test [1]. Instead, many researchers are content in quoting the formal quantum efficiency, δ , for their photosystem, where

$$\delta = \frac{\text{rate of photoreaction}}{\text{intensity of incident photons}} \quad (15)$$

Given Eq. (15), it is not surprising to note that the quantum yield for most heterogeneous photosystems is usually much greater than δ , since a substantial amount of incident light is often lost to reflection and scattering, rather than absorbed.

Despite the clear deficiency in quoting δ , compared to ϕ data for such systems, formal quantum efficiency data does provide a very quick and easy measure of the very general efficacy of the photosystem, with a δ value of 0.01 indicating a very promising photosystem. Thus, given in this work $I = 7.6 \times 10^{17}$ photons $\text{cm}^{-2} \text{min}^{-1}$, $R_i = 59.4 \times 10^{-8} \text{ M s}^{-1}$, $V = 25 \text{ ml}$ and the surface area of the reactor was: $A \text{ (cm}^2\text{)}$. It follows that

$$\begin{aligned} \delta &= \frac{59.4 \times 10^{-8} \times N_A \times 25/1000 \times 60}{7.6 \times 10^{17} \times 33} \\ &= 0.021 \text{ molecules per photon} \end{aligned} \quad (16)$$

Thus, despite the fact that persulfate was the (1 mg/ml) best SA tested and that the conditions of high: $[\text{TiO}_2]$ (21 mg/ml), pH (13) and $[\text{SA}]$ (10^{-2} M) were used, the photo-oxidation of water appears to be quite an inefficient process. However, this value for δ is significantly greater than that reported [20] by this group for the photo-oxidation of water by Fe^{3+} ions, sensitised by WO_3 ($\delta = 3.1 \times 10^{-3}$) and is greater than the many values of δ reported by others studying the photo-oxidation of organic pollutants by oxygen or persulfate sensitised by TiO_2 (typically $\delta \cong 0.01$) [1]. Given that others [35] have estimated the reflection and scattering losses associated with such heterogeneous photocatalytic systems to be as high as 70% in some cases, it appears likely that for this, as well as many photocatalytic systems, $\phi \gg \delta$.

Finally, in an effort to establish the photochemical robustness of the $\text{S}_2\text{O}_8^{2-}/\text{TiO}_2$ photosystem, the standard system (i.e. 25 mg TiO_2 dispersed in 25 ml of solution containing 0.1 M NaOH and $10^{-2} \text{ M Na}_2\text{S}_2\text{O}_8$) was irradiated for ca. 25 min, the light turned off and the solution nitrogen purged. This process of irradiation and nitrogen purging

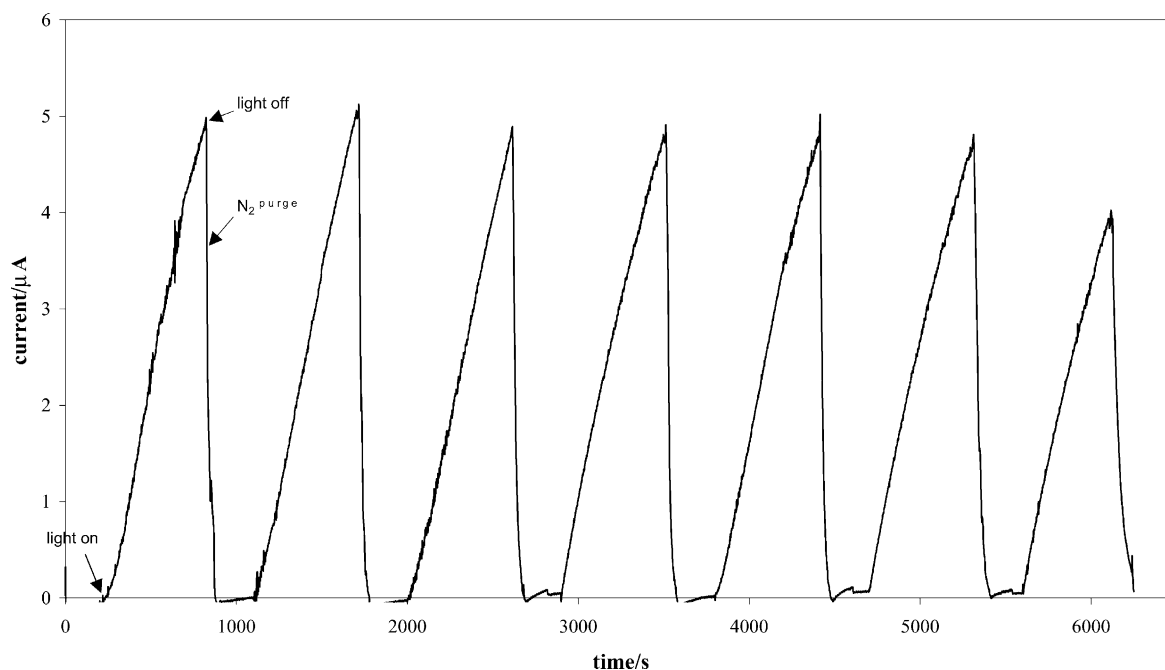


Fig. 7. Oxygen electrode current vs. reaction time, recorded for a standard $\text{TiO}_2/\text{S}_2\text{O}_8^{2-}/\text{pH } 13$ reaction solution (see Fig. 6 for details) when subjected to a series of irradiation and N_2 -purge cycles.

was repeated on the same solution a further six times. The level of dissolved oxygen in the above system was measured continuously and the results of this work are illustrated in Fig. 7. From these results it can be seen that little deterioration in the performance of the TiO_2 photocatalyst occurs in this photosystem despite its repeated use. The photochemical robustness of TiO_2 is well established in organic photomineralisation studies [1,34] and is responsible for a good part of the appeal of this semiconductor as a photocatalyst for commercial systems, such as self-cleaning glass or tiles [36]. The results illustrated in Fig. 7 show that TiO_2 is not only a good, robust photocatalyst for organic oxidation reactions, but also for inorganic oxidation reactions, such as the extremely difficult and chemically demanding oxidation of water. There are few semiconducting materials, other than TiO_2 , which are able to withstand the highly oxidising conditions required for the oxidation of water to oxygen. Any new or current photocatalyst which is proposed as being sufficiently stable, reliable, robust, reproducible materials for water splitting, or simply water oxidation, would do well to be tested using the alkaline $\text{S}_2\text{O}_8^{2-}/\text{photocatalyst}$ system for water oxidation used in this work, since a cycle experiment, such as used to generate the results in Fig. 7 for TiO_2 , will readily expose the weakness of most supposedly 'new', improved photocatalytic materials for water oxidation or splitting to oxidative corrosion and/or inhibition. Such a weakness would rule out the proposed new photocatalyst as a future water-splitting photocatalyst and consign it to the already overflowing novelty bin of 'tried, failed and soon to be forgotten' photocatalysts. It is important that the major objective of finding a better photocatalyst than TiO_2 ,

in terms of activity and/or solar absorption cross-section, is not lost. The $\text{S}_2\text{O}_8^{2-}/\text{photocatalyst}$ water oxidation system provides a simple means to help prove new photocatalysts for such work.

4. Conclusion

Of a number of sacrificial electron acceptors tested, including: Ce^{4+} , Ag^+ , Fe^{3+} and $\text{S}_2\text{O}_8^{2-}$, persulfate, at pH 13, appeared the best for oxidising water using a TiO_2 powder photocatalyst. The initial rate of oxygen photo-production by this $\text{S}_2\text{O}_8^{2-}/\text{TiO}_2$ system depends directly upon $[\text{S}_2\text{O}_8^{2-}]$ and $I^{0.6}$; observations that are consistent with current understanding of semiconductor photocatalytic systems. Repeated use of the same photosystem shows no evidence of loss of activity, once again championing the photostability and activity of TiO_2 above all other photocatalysts. Such a system, i.e. $\text{S}_2\text{O}_8^{2-}$ (10^{-2} M, pH 13)/photocatalyst would provide a useful screening method for new water-splitting, or water oxidation, photocatalyst hopefuls that seek to depose TiO_2 from its almost total domination of semiconductor photocatalysis for water and air purification as well as water splitting.

Acknowledgements

MAV and AM thank IPN and CONACYT for funding a sabbatical year for MAV at Strathclyde University in order to study semiconductor-photocatalysed reactions.

References

- [1] A. Mills, S. LeHunte, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 1, and references therein.
- [2] A. Mills, in: D. Thompson (Ed.), *Insights into Speciality Inorganic Chemicals*, Royal Society of London, 1995 (Chapter 18).
- [3] A. Mills, S.K. Lee, *Platinum Met. Rev.* 47 (2003) 2.
- [4] M. Graetzel, in: M. Graetzel (Ed.), *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, 1983 (Chapter 3).
- [5] N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis: Fundamentals and Applications*, Wiley/Interscience, New York, 1989.
- [6] T. Takata, A. Tanaka, N. Harara, J.N. Kondo, K. Domen, *Catal. Today* 44 (1998) 17, and references therein.
- [7] M. Yagi, M. Kaneko, *Chem. Rev.* 101 (2001) 21.
- [8] G.R. Bamwenda, H. Arakawa, *Solar Energy Mater. Solar Cells* 70 (2001) 1.
- [9] G.R. Bamwenda, K. Sayama, H. Arakawa, *J. Photochem. Photobiol. A: Chem.* 122 (1999) 175.
- [10] T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi, M. Matsumura, *J. Photochem. Photobiol. A: Chem.* 118 (1998) 41.
- [11] G.R. Bamwenda, H. Arakawa, *J. Mol. Catal. A: Chem.* 161 (2000) 105.
- [12] G.R. Bamwenda, T. Uesigi, Y. Abe, K. Sayama, H. Arakawa, *Appl. Catal. A: Gen.* 205 (2001) 117.
- [13] K. Hara, K. Sayama, H. Arakawa, *Appl. Catal. A: Gen.* 189 (1999) 127.
- [14] K.H. Chung, D.C. Park, *Catal. Today* 30 (1996) 157.
- [15] T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi, M. Matsumura, *J. Photochem. Photobiol. A: Chem.* 127 (1999) 107.
- [16] M.I. Litter, *Appl. Catal. B: Environ.* 23 (1999) 89, and references therein.
- [17] G.R. Bamwenda, H. Arakawa, *Appl. Catal. A: Gen.* 210 (2001) 181.
- [18] T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi, M. Matsumura, *J. Photochem. Photobiol. A: Chem.* 127 (1999) 107.
- [19] A. Mills, G. Porter, *J. Chem. Soc., Faraday Trans. 1* 78 (1982) 3659.
- [20] J.R. Darwent, A. Mills, *J. Chem. Soc., Faraday Trans. 2* 78 (1982) 359.
- [21] F. Bolletta, A. Juris, M. Maestri, D. Sandrini, *Inorg. Chim. Acta* 44 (1980) L175.
- [22] A. Mills, in: F.R. Hartley (Ed.), *Chemistry of the Platinum Group Metals: Recent Developments*, Academic Press, New York, 1983 (Chapter 3).
- [23] D.H.W.M. Thewissen, M. Eeuwhorst-Reinten, K. Timmer, A.H.A. Tinnemans, A. Mackor, in: D.O. Hall, W. Palz (Eds.), *Photochemical, Photoelectrochemical and Photobiological Processes*, Series D, vol. 1, Reidel, Dordrecht, 1981, p. 56.
- [24] S. Yamazaki, S. Matsunaga, K. Hori, *Water Res.* 35 (2001) 1022.
- [25] B. Neppolian, H.C. Choy, S. Sakthival, B. Arabindoo, B. Murugesan, *Chemosphere* 46 (2002) 1173.
- [26] Y. Wang, C.S. Hong, *Water Res.* 33 (1999) 2031.
- [27] T. Zhang, T. Oyama, S. Horikoshi, J. Zhao, N. Serpone, H. Hidaka, *Appl. Catal. B: Environ.* 1278 (2002) 1.
- [28] A. Mills, S. Morris, R. Davis, *J. Photochem. Photobiol. A: Chem.* 70 (1993) 183.
- [29] M.L. Hitchman, *Measurement of Dissolved Oxygen*, Wiley, Geneva, 1978.
- [30] A. Mills, J. Wang, *Z. fur Physik.* 213 (1999) 49.
- [31] A.V. Emeline, V. Ryabchuk, N. Serpone, *J. Photochem. Photobiol. A: Chem.* 133 (2000) 89.
- [32] C.S. Turchi, D.F. Ollis, *J. Catal.* 122 (1990) 178.
- [33] T.A. Egerton, C.J. King, *J. Oil Col. Chem. Assoc.* 62 (1979) 386.
- [34] G. Al-Sayyed, J.C. D'Oliveira, P. Pichat, *J. Photochem. Photobiol. A: Chem.* 58 (1991) 99.
- [35] A. Salinaro, A. Emeline, J. Zhao, H. Hidaka, V. Ryabchuk, N. Serpone, *Pure Appl. Chem.* 71 (1999) 321.
- [36] A. Mills, S.K. Lee, *J. Photochem. Photobiol. A: Chem.* 152 (2002) 233.