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Photodecomposition of water using Fe^{II}/Fe^{III} phosphates as an intermediate redox couple

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Abstract

The UV photolysis of an aqueous solution of iron(II) phosphate ($pH \approx 2.2$) liberates hydrogen at a rate faster than other iron(II) solutions at a similar pH, due to removal of the reaction product Fe^{3+} as insoluble iron(III) phosphate. An aqueous suspension of iron(III) phosphate ground with TiO_2 liberates molecular oxygen with reduction of iron(III) phosphate to iron(II) phosphate. The possibility of water photodecomposition using the above reactions is discussed.

1. Introduction

Practical systems for the photodecomposition of water remain a challenge [1]. The most severe constraints arise from the need for multielectron transfer and the prevention of back reactions [2]. One of the simplest methods of overcoming the above difficulties is to develop devices based on two photosystems (photosystem I (PS I) and photosystem II (PS II)). In PS I, water is reduced to hydrogen with oxidation of an intermediate compound; in PS II, water is oxidized to oxygen with reversion of the oxidized intermediate to the original state [2–6]. An additional advantage of the two-photosystem method is the possibility of spatial separation of the hydrogen and oxygen evolution sites [6]. Although several two-photosystem models have been proposed and investigated, a practical system based on this idea has yet to be developed [1]. The available model systems show poor quantum yields and are not completely reversible when the cycles are repeated. It is probable that the further search for two-photosystem processes will eventually pave the way towards the practical photodecomposition of water. We have investigated a model system for the photodecomposition of water based on the phosphates of Fe^{II} and Fe^{III} as the intermediate redox couple.

It is well known that the photolysis of Fe^{2+} in aqueous medium generates hydrogen with oxidation of Fe^{2+} to Fe^{3+} [7–10]

$$Fe^{2+} + H_2O \longrightarrow Fe^{3+} + \tfrac{1}{2}H_2 + OH^- \qquad \Delta G \approx 154 \text{ kJ} \qquad (1)$$

The initial quantum yield is high; however, when Fe^{3+} accumulates in the solution, the hydrogen yield decreases as a result of back reactions. The primary product in the photolysis of aqueous Fe^{2+} is either solvated electron or $H^\cdot$; an acidic pH favours the formation of H˙ [11]; thus we have

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \tag{2a}$$

and/or

$$Fe^{3+} + H^{\cdot} \longrightarrow Fe^{2+} + H^+ \tag{2b}$$

The rate of photogeneration of hydrogen can be maintained high, if Fe^{3+} is removed from the aqueous phase as it is formed. Furthermore, it is conceivable that, in a second step, Fe^{3+} could be reduced to Fe^{2+} with concomitant oxidation of water

$$Fe^{3+} + \tfrac{1}{2}H_2O \longrightarrow Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \qquad \Delta G \approx 44 \text{ kJ} \tag{3}$$

The sum of the PS I and PS II reactions (eqns. (1) and (3) respectively) is equivalent to the decomposition of water (values of ΔG are at the optimum pH). We have observed that in the UV photolysis of a solution of iron(II) phosphate ($pH \approx 2.2$, $[PO_4^{3-}] \approx 0.03$ M, $[Fe^{2+}] \approx 0.03$ M) hydrogen is liberated with the precipitation of iron(III) phosphate. Iron(III) phosphate mixed with TiO_2 in aqueous medium generates oxygen during photolysis.

2. Experimental details

Iron(II) phosphate solution was prepared by mixing iron(II) sulphate (0.03 M, made free of Fe^{3+} by digestion with iron filings) with a solution of sodium dihydrogen phosphate (0.03 M). The pH was adjusted using NaOH and H_2SO_4. Photolysis experiments were carried out in a 500 ml photochemical reactor (Applied Photophysics) using a 400 W medium pressure mercury lamp housed in a double-walled water-cooled (26 °C) quartz cylinder. The solution (300 ml) was contained in the annular region (thickness, approximately 0.75 cm) between the quartz cylinder and the borosilicate outer jacket. The contents of the reactor were kept continuously purged with argon (99.99%) at a rate of 11.0 ml min^{-1}. Hydrogen in the outgoing gas was estimated volumetrically at atmopsheric pressure by gas chromatography (Shimadzu GC-9AM gas chromatograph; carrier gas, argon; molecular sieve 5 Å column; thermal conductivity detector). After a period of 3 h, the precipitate formed during photolysis was separated, avoiding air contamination, and tested for Fe^{2+} and Fe^{3+} spectrophotometrically using *o*-phenanthroline and thiocyanate respectively.

Iron(III) phosphate was prepared by double decomposition of aqueous solutions of iron(III) chloride (0.3 M) and sodium dihydrogen phosphate (0.3 M). The precipitate was separated by filtration, dried in a desiccator and ground with TiO_2 ($FePO_4$:TiO_2 mixing ratio, 3:1 by mass). An aqueous suspension of the mixture (0.8 g) was kept continuously purged with argon and photolysed using a 400 W medium pressure mercury lamp. Aliquots (4.0 ml) of solution drawn from the reactor at different intervals of time were acidified with HCl to dissolve the suspension or iron phosphates, centrifuged to remove TiO_2 and estimated for Fe^{2+} spectrophotometrically using *o*-phenanthroline. Gas chromatography revealed oxygen evolution during photolysis. However, due to the gradual leakage of oxygen into the reactor from the atmosphere, the quantitative estimation of oxygen by gas chromatography was not possible. Oxygen evolution during the photolysis of an aqueous suspension of $FePO_4$ and TiO_2 was also confirmed using a photochemical reactor provided with a polarographic detector (Applied Photophysics). For measurements of the quantum yields, a 16 W low pressure mercury lamp was used and the photon flux was counted by ferrioxalate actinometry. Instead of the freshly prepared iron(III) phosphate, the precipitate from the photolysis of the iron(II) phosphate solution was also mixed with TiO_2 and tested for oxygen evolution and Fe^{2+} generation in the same manner. The diffuse reflectance spectrum or iron(III) phosphate powder and the absorption spectrum of the iron(III) phosphate aqueous suspension were obtained using a Shimadzu UV-3000 spectrophotometer. Pellets of iron(III) phosphate (diameter, 13.0 mm; thickness, 1.80 mm) compacted to a pressure of 40 MPa were used to measure the electrical conductivity. The Mott–Schottky plots at frequencies of 500 Hz and 1 kHz were obtained using pellets of $FePO_4$ prepared in the same manner. A Hewlett Packard LCR meter 4192 A and a Kenwood DL-707 digital multimeter were used to obtain the plot.

3. Results and discussion

Figure 1 illustrates the rate of hydrogen evolution ($R[H_2]$) as a function of time from solutions containing 0.03 M Fe^{2+} and 0.03 M PO_4^{3-} at different pH values. $R[H_2]$ increases with decreasing pH (from 3.1 to 2.2) and reaches an optimum at pH 2.2. For comparison, $R[H_2]$ is plotted as a function of time for an $FeSO_4$ solution of the same Fe^{2+} concentration at pH 2.5. In this case the rate is much slower than that in the presence of PO_4^{3-}. Thermodynamically, $R[H_2]$ via eqn. (1) is favoured at low pH values. However, iron(III) phosphate precipitation (under the above conditions), which removes Fe^{3+} ions from the solution and suppresses the back reactions (2a) and (2b), increases with increasing pH. Under the conditions used in our experiment, significant precipitation does not occur until $pH \approx 1.9$ (*i.e.* at the optimum pH, reactions (1) and (3) move in the desired direction). It is known that in the photolysis of aqueous iron(II) sulphate a high hydrogen yield is obtained at nearly neutral pH values where iron(III) hydroxide is precipitated [9, 10]. Although different explanations have been proposed [9] (*e.g.* the formation of $Fe(OH)(aq)^{2+}$), we believe that the removal of Fe^{3+} by precipitation is the principal reason for the enhanced hydrogen yield.

Figure 2 (curve 1) shows the development of Fe^{2+} concentration (*i.e.* total Fe^{2+} (dissolved plus solid particles in the suspension)) in an irradiated aqueous suspension of iron(III) phosphate ground with TiO_2. As oxygen evolution is confirmed qualitatively, the increase in Fe^{2+} results from the progress of reaction (3). Curve 2 of Fig. 2 shows the photogeneration of Fe^{2+} from an aqueous suspension of iron(III) phosphate in the absence of TiO_2. Although the rate is much slower, iron(III) phosphate alone also has the ability to oxidize water. A decrease in the rate of hydrogen photogeneration from aqueous iron(II) phosphate is observed during the build-up of iron(III) phosphate (Fig. 1). Although light cut-off by the precipitate is one of the reasons, the occurrence of eqn. (3) in the absence of TiO_2 may also be a contributing factor.

Solid iron(III) phosphate (compacted pellet) has a room temperature (26 °C) conductivity of $6.8 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$. The conductivity increases with increasing temperature, suggesting semiconductor properties for $FePO_4$. The diffuse reflectance spectrum of iron(III) phosphate powder and the absorption spectrum of iron(III) phosphate aqueous suspension are shown in Fig. 3. Both curves show an absorption edge in the region of approximately 400 nm, indicating that the band gap of the material is approximately 3.1 eV. The Mott–Schottky plots for a pellet of iron(III) phosphate in aqueous medium (sodium sulphate, $pH \approx 7$) at frequencies of 500 Hz and 1 kHz are presented in Fig. 4. The negative slope of the plot indicates photocathodic

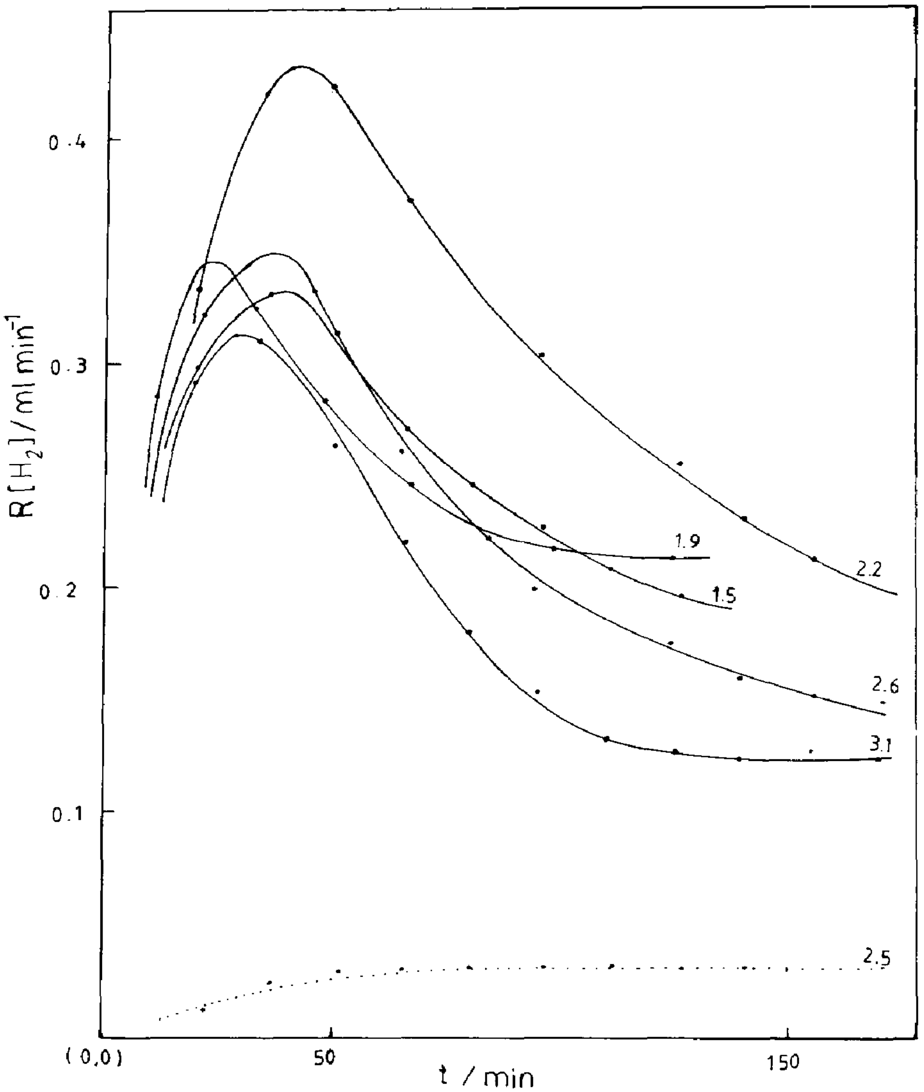


Fig. 1. Plots of $R[H_2]$ *vs.* time for the photolysis of iron(II) phosphate solutions ($[Fe^{2+}]=0.03$ M, $[PO_4^{3-}]=0.03$ M) at different pH values (given on curves). The bottom curve represents $R[H_2]$ for 0.03 M $FeSO_4$ in the absence of phosphate.

behaviour and the flat band potential of iron(III) phosphate derived from the plot is approximately 0.5 V *vs.* the saturated calomel electrode (SCE) at pH 7.

Oxygen evolution from an aqueous suspension of iron(III) phosphate ground with TiO_2 can be explained as follows. The ground mixture contains composite particles (*i.e.* miniature photochemical n–p junction cells) where TiO_2 and $FePO_4$ are in contact (Fig. 5(a)). Since the flat band potentials of $FePO_4$ and TiO_2 (pH7) are approximately 0.5 V and approximately 0.7 V *vs.* SCE respectively, the relative band positions (charge band (CB); valence band (VB)) of the TiO_2–$FePO_4$ interface are as depicted in Fig. 5(b) [12]. Consequently, electrons photogenerated in TiO_2 are transferred to iron(III) phosphate, causing its reduction. Holes accumulating in TiO_2 are used in the oxidation of water

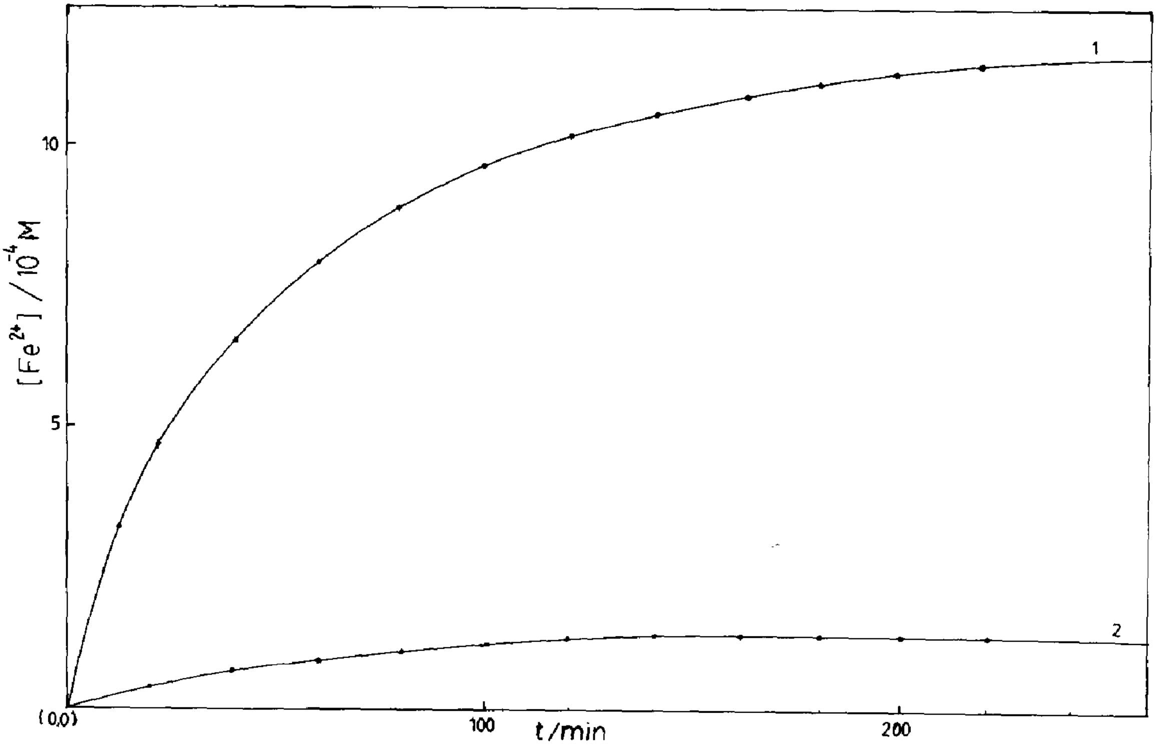
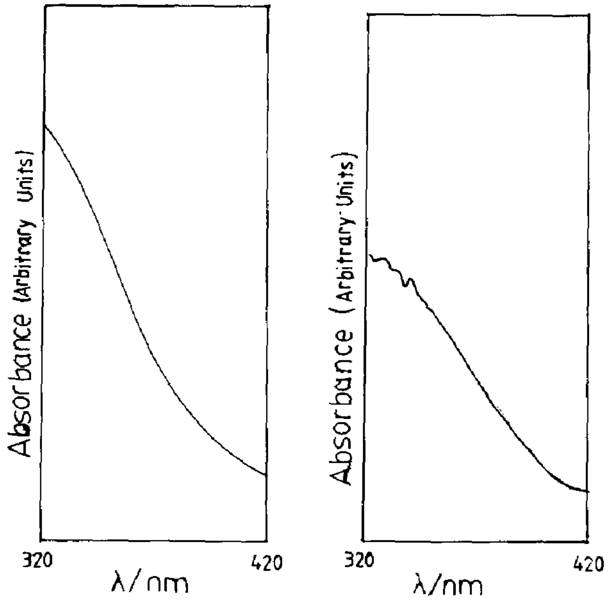


Fig. 2. Development of $[Fe^{2+}]$ as a function of time in the photolysis of 0.8 g of $FePO_4$–TiO_2 ($FePO_4$:TiO_2=3:1 by mass) (1) and 0.6 g of $FePO_4$ (2) (pH≈2.0).



(a)
(b)

Fig. 3. (a) Diffuse reflectance spectrum of iron(III) phosphate powder. (b) Absorption spectrum of an aqueous suspension of $FePO_4$.

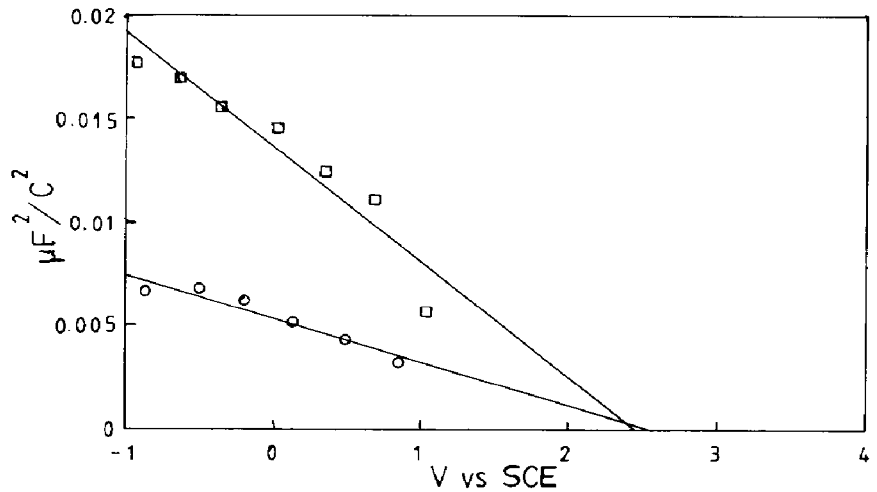


Fig. 4. Mott–Schottky plots (C = capacitance) for $FePO_4$: ○, 500 Hz; □, 1 kHz.

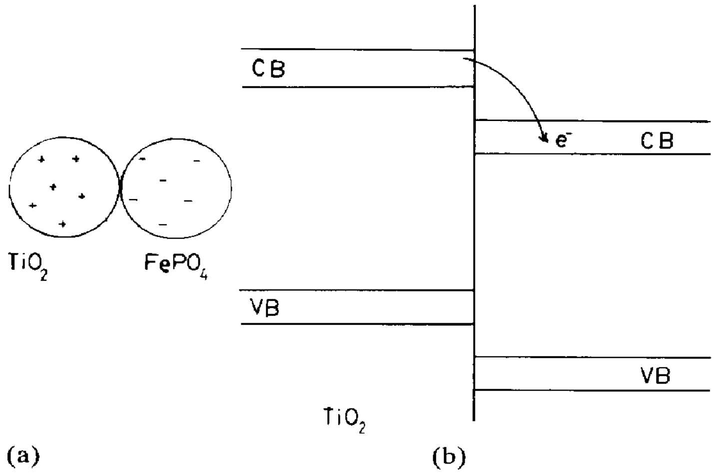


Fig. 5. (a) Schematic diagram showing a composite TiO_2–$FePO_4$ particle and charge separation. (b) Relative band positions of TiO_2 and $FePO_4$.

$$\begin{array}{l} TiO_2 \xrightarrow{h\nu} e^- \ (CB\ TiO_2) + h^+ (VB\ TiO_2) \\ \qquad\qquad \downarrow \\ \qquad\quad\ \ e^- \ (CB\ FePO_4) \end{array} \tag{4}$$

$$e^-(CB\ FePO_4) + Fe^{3+} \longrightarrow Fe^{2+} \tag{5}$$

$$h^+(VB\ TiO_2) + \tfrac{1}{2}H_2O \longrightarrow \tfrac{1}{4}O_2 + H^+ \tag{6}$$

Because of the semiconductor properties of $FePO_4$, the same reaction can occur in the absence of TiO_2. In TiO_2–$FePO_4$ there is enhanced charge separation.

The initial (in the first 30 min) quantum yield of hydrogen evolution from the PS I system at 254 nm is found to be approximately 0.20. The initial quantum yield of oxygen from PS II at the same wavelength is approximately 0.03. Thus $\Phi[O_2] < \frac{1}{2}\Phi[H_2]$

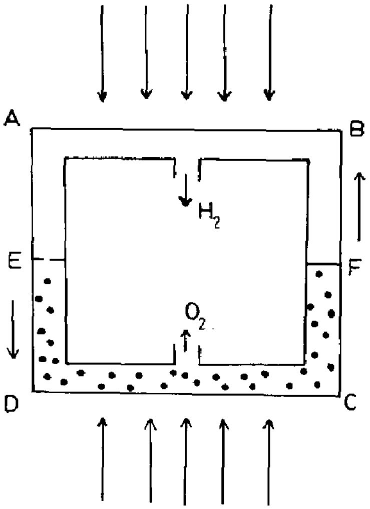


Fig. 6. Schematic diagram showing a device for the photodecomposition of water using a precipitation reaction.

and completely reversible cycles are not possible in the present form. The lower quantum efficiency of PS II could originate from chemisorption of oxygen on TiO_2 and consumption of dissolved oxygen by Fe^{2+} ions. The lack of complete reversibility, the low quantum yields and the sensitivity of the reaction to only UV light makes the system unsuitable for practical applications. However, in principle, precipitation reactions of the above form can be adopted as practical devices in the manner illustrated in Fig. 6. The solution is circulated in a circuit ABCD; E is one-way valve and F is a filter impermeable to the precipitate. The precipitate accumulates in the region CD containing a substrate coated with the catalyst (*e.g.* TiO_2). Irradiation of the regions AB and CD liberates hydrogen and oxygen.

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