Photocleavage of Water with Silver Phosphate

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Silver phosphate is found to photocatalyse decomposition of water into oxygen and hydrogen without the presence of either electron or hole transfer catalysts.

The possibility of achieving photocleavage of water with semiconductor photocatalysts has attracted much attention.[1] While most reports deal with sacrificial systems, a few indicate that the photodecomposition of water can be accomplished by using semiconductor particles loaded with electron and hole transfer supports.[1,2] The observed quantum yields are exceedingly small, the reproducibility is poor, and frequently only hydrogen is liberated while oxygen remains bound to the catalyst.[3—6]

Here we report the unusual behaviour of silver phosphate which was found to photogenerate both H_2 and O_2 simultaneously from water without electron and/or hole transfer agents.

Ag_3PO_4 was prepared by mixing aqueous solutions of K_2HPO_4 and $AgNO_3$ (0.5 M). The pale yellow precipitate of Ag_3PO_4 (washed and dried of 110 °C) was completely photostable in the absence of moisture. The diffuse reflectance spectrum of the Ag_3PO_4 powder (Figure 1) shows an absorption edge at 494 nm suggesting a band gap of *ca.* 2.5 eV. Hall and thermoelectric tests indicate that the material is p-type. Photolysis experiments were carried out in a 35 ml quartz reaction vessel provided with polarographic detector (Applied Photophysics). In all the experiments 20 mg (*ca.* 5 × 10^{-4} moles) of the catalyst was suspended in 35 ml of water by stirring. The full spectrum of a 200 W medium pressure Hg lamp was used as the light source and the intensities were

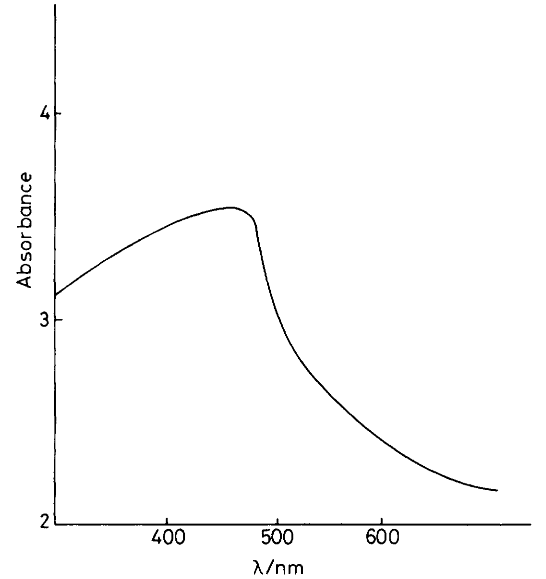

Figure 1. Diffuse reflectance spectrum of Ag_3PO_4 powder.

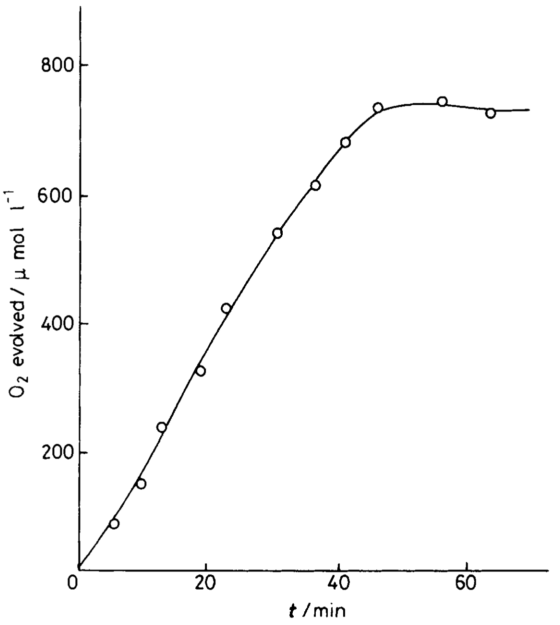

Figure 2. Photogeneration of oxygen.

measured using an International Light IL 700 Radiometer. Prior to irradiation, all solutions were degassed (99.9 Ar). Ag_3PO_4 photolysis does not poison the polarographic detector and give false signals. This was confirmed by carrying out the photolysis in a separate vessel, with the Ar slowly purging through the vessel being fed into the detector containing pure degassed water. Clear H_2 and O_2 signals were obtained.

Figures 2 and 3 show the photogeneration of H_2 and O_2 using 20 mg of of the Ag_3PO_4 catalyst. The H_2 evolution rate [$R(H_2)$] was greatest at pH *ca.* 7 (Figure 3). $R(O_2)$ was less sensitive to change of pH in the pH range possible (Ag_3PO_4 dissolves when the pH is less than *ca.* 5.3 and undergoes hydrolysis if the pH exceeds *ca.* 7.8; pH adjustments were made using K_3PO_4 and H_3PO_4). H_2 evolution ceased after 10—25 min whereas O_2 evolution continued for more than 40 min. When the solution was degassed and illuminated, H_2 liberation was again noted, but the rate was less pronounced [Figure 3(d) and (e)]. Upon prolonged irradiation (with a source containing u.v.), the catalyst turned black with the formation of metallic silver. In addition to H_2 liberation, Ag_3PO_4 is itself reduced to metallic silver while water is oxidized concomitantly. The silver thus produced can be detected by dissolving the degraded catalyst in ammonia. When the light intensity is kept constant, the amounts of H_2 and O_2 evolved initially increase with increasing catalyst concentration, then become nearly independent of the concentration of the catalyst. The catalyst concentration used in our experiments corresponds to the latter region.

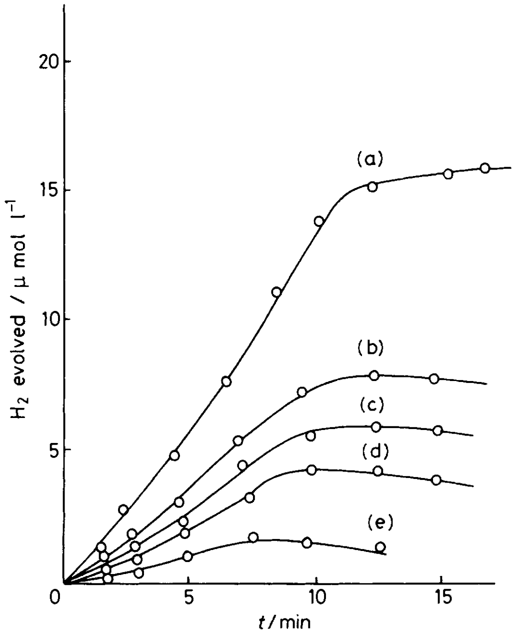

Figure 3. Photogeneration of hydrogen. *Reaction conditions*: (a) pH 7; (b) pH 6.5; (c) pH 7.5; (d) pH 7, sample degassed after 15 min; (e) pH 7, sample degassed after 10 min. Light source: full spectrum of the Hg lamp.

Table 1. H_2 and O_2 quantum yields.

λ/nm	% $\phi(H_2)$	% $\phi(O_2)$
490	0.100	0.048
470	0.152	0.068
430	0.143	0.059
366	0.114	0.128

The initial quantum efficiences $\phi(H_2)$ and $\phi(O_2)$ at different wavelengths (λ; selected using filters) are presented in Table 1. Nearly stoicheiometric amounts of H_2 and O_2 are formed [*i.e.*, $\phi(H_2) \simeq ½\phi(O_2)$] when λ is near the band gap radiation (494 nm). As the photon energy increases, in addition to H_2 production, Ag_3PO_4 is partly reduced to Ag and consequently $\phi(H_2)$ becomes smaller than $\phi(O_2)$. The anomaly between data presented in Figure 2 and Table 1 is a consequence of this effect. In the former case the full spectrum of the Hg lamp was used and $R(O_2)$ exceeds $2R(H_2)$.

The overall reactions occurring in the two cases can be represented by Schemes 1 and 2. We have not succeeded in establishing why Schemes 1 and 2 differ in the spectral response. Perhaps the reaction in Scheme 2 in which Ag_3PO_4

$$2H_2O + 2e^- (CB) \rightarrow H_2 + 2OH^-$$

$$2OH^- + 2h^+ (VB) \rightarrow H_2O + \tfrac{1}{2}O_2$$

Scheme 1

$$3H_2O + Ag_3PO_4 + 3e^- (CB) \rightarrow H_3PO_4 + 3Ag + 3OH^-$$

$$3OH^- + 3h^+ (VB) \rightarrow \tfrac{3}{2} H_2O + \tfrac{3}{4}O_2$$

Scheme 2

is degraded is caused by photogenerated carriers before they relax into the band gap energy (hot carriers). Another possibility is that an intermediate product formed in Scheme 1 interacts with shorter wavelength radiation initiating the reactions of Scheme 2. A likely process is outlined in Scheme 3.

$$H_2O + e^- (CB) \rightarrow H + OH^-$$

$$Ag_3PO_4 + H \rightarrow Ag_2HPO_4{\cdot}Ag$$

$$Ag_2HPO_4{\cdot}Ag + Ag_2HPO_4{\cdot}Ag \rightarrow 2Ag_3PO_4 + H_2$$

$$2OH^- + 2h^+ (VB) \rightarrow H_2O + \tfrac{1}{2}O_2$$

Scheme 3

Hydrogen free radicals, created when the conduction band (CB) electrons are transferred to H^+ ions, react with Ag_3PO_4 to yield an unstable intermediate $Ag_2HPO_4{\cdot}Ag$ of silver monohydrogen phosphate and silver. Two 'units' of this intermediate could combine to yield molecular hydrogen regenerating Ag_3PO_4. The intermediate (having a spectral sensitivity different from Ag_3PO_4) can accept more photogenerated hydrogen radicals leading to the reaction in Scheme 4. This scheme explains why Ag_3PO_4 can liberate molecular hydrogen without the help of an electron transfer catalyst.

$$Ag_2HPO_4{\cdot}Ag + H_2O \rightarrow H_3PO_4 + \tfrac{1}{2}O_2 + 3Ag$$

Scheme 4

The process allowing the formation of H_2 is the second step of Scheme 3. When Ag_3PO_4 is impregnated with Pt, contrary to expectation, $R(H_2)$ is markedly reduced. This observation can be understood in terms of Scheme 3. The electrons that concentrate in Pt inhibit step 1 of Scheme 3 as H free radicals now appear near Pt. Clearly this also explains the fact that the degradation of the catalyst with the accumulaton of Ag causes a decrease of $R(H_2)$, but not of $R(O_2)$. However, as we have no direct evidence for the intermediate steps in Scheme 3, other possibilities cannot be ruled out, *e.g.* hydrogen could simply be adsorbed into the surface of the silver phosphate particles and facilitate H_2 evolution.

$\phi(H_2)$ increases substantially in the presence of a sacrificial electron donor (*e.g.* sodium acetate), but the degradation of the catalyst is not suppressed. We have not succeeded in ascertaining the flat band potential of Ag_3PO_4.

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