A COMPARISON OF THE PHOTOCHEMICAL REACTIVITY OF POLYCRYSTALLINE (ANATASE), AMORPHOUS AND COLLOIDAL FORMS OF TITANIUM DIOXIDE

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Summary

Freshly precipitated amorphous titanium dioxide and colloidal titanium dioxide are inefficient photocatalysts for hydrogen production from water and propan-2-ol and for methane and hydrogen production from acetic acid. Their reactivity, which is increased by platinization (but is less than that of platinized anatase), is attributed to the formation of titanium(III) species rather than electron–hole pairs.

1. Introduction

The photochemistry of semiconductors is an area of intense activity owing to their potential for harvesting solar energy. Of particular interest is the photochemistry of titanium dioxide. Whilst much of the earlier work on this material was concerned with the photoelectrochemistry of single crystals [1], more recently increasing attention has been paid to the chemistry of particulate suspensions [2]. In many cases these particulates have been well characterized (*e.g.* by X-ray diffraction, electron microscopy and electrophoretic properties).

In an attempt to obtain materials with reproducible catalytic efficiency the oxide has been prepared by the hydrolysis of titanium(IV) alkoxides and chlorides [3, 4]. The preparation and photocatalytic properties of colloidal titanium dioxide have been of particular interest [3, 4]. However, characterization of this material has not been particularly rigorous.

In all cases the photochemistry of the oxide samples has been interpreted in terms of the classical band model which was originally developed for highly ordered crystalline materials [5]. This treatment does not account for semiconductor–electrolyte interactions [6, 7] and should therefore be applied with caution when discussing the behaviour of particles etc. in aqueous or solvent suspensions containing additives such as salts [8]. A further problem associated with explaining the photochemistry of particulates and

colloids is that the diameter of the particles may well be less than that of the field-free region.

We now present evidence which suggests that the photocatalytic properties of amorphous and colloidal titanium dioxide is not appropriately explained by assuming them to have semiconductor character and offer an alternative model.

2. Experimental details

A variety of methods are available for the preparation of colloidal titanium dioxide [3, 4]. Titanium(IV) chloride can be hydrolysed in aqueous solution and the resultant mixture dialysed to pH 3. Alternatively, titanium(IV) alkoxides can be hydrolysed by aqueous hydrochloric (or hydrobromic acids [9]) followed by dialysis. Each of these procedures was utilized. An alternative route to the colloid which was utilized involved hydrolysis of titanium tetra isopropoxide in neutral aqueous solution. Removal of water and propan-2-ol by evaporation under reduced pressure at temperatures below 50 °C produced amorphous titanium dioxide (characterized by X-ray diffraction; elemental analysis indicates less than 0.001% C). The amorphous material can be dissolved in hydrochloric acid and dialysed to give the colloid [9]. A colloid is also obtained when the amorphous material is dissolved in sulphuric acid although care has to be taken during dialysis (to pH 1.7) to avoid precipitation of the oxide.

Polycrystalline titanium dioxide (Degussa P-25; 80% anatase and 20% rutile determined by X-ray diffraction studies) was used as received. The colloidal, amorphous and polycrystalline samples were platinized using previously described methods [3, 4] and a loading of 0.2 wt.% was utilized.

Irradiation of the colloidal solutions and of vigorously stirred suspensions was conducted under an atmosphere of argon at 35 - 40 °C. Light from an 1800 W xenon lamp was passed through a cell containing water (path length, 11 cm) to remove IR radiation and was focused on the front surface of the irradiation cell. The light intensity on the front surface of the cell was found to be $10\,000$ W cm^{-2}. The cell, of volume 27 cm^3, was filled with 20 cm^3 of reactant solution. Gas samples (200 μl) were removed from the cell at regular intervals and were analysed at 100 °C using a Pye 104 gas chromatograph with a column of internal diameter 1/8 in (packed with 5A molecular sieve) equipped with a hot-wire detector.

The photoacoustic spectra were recorded using an EDT model OAS 400 spectrometer.

3. Results

3.1. Absorption spectra of samples

All the dialysed solutions showed an absorption edge at 365 nm (for a titanium dioxide concentration of 5 g l^{-1}). This is blue shifted from that of

anatase (388 nm; 3.2 eV) and rutile (414 nm; 3.0 eV) [10]. The absorption edge of the amorphous material was found by photoacoustic and diffuse reflectance spectroscopy to be at 365 nm.

3.2. Photocatalytic activity of samples in aqueous solution

Irradiation of colloidal titanium dioxide (pH 3) (Fig. 1) produced hydrogen, but oxygen evolution could not be detected. This result is at variance with those obtained by other workers [3, 4]. Hydrogen evolution only occurred after an induction period (about 1.5 h). During this period the solution became turbid and eventually a flocculent precipitate with a blue colouration was observed. We attribute the blue colouration to the formation of a titanium(III) species, although this has not been proved unambiguously. (Attempts were made to detect formation of titanium(III) ions by electron spin resonance. No signals could be detected. This could be due to the lines being very broad as a result of the titanium(III) ions being part of a particle surface and to their low concentration.) The colour is rapidly dissipated on admission of oxygen to the reaction cell:

$$Ti^{III} + O_2 \longrightarrow Ti^{IV} + O_2^{-}$$
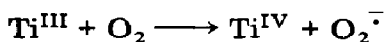
Irradiation of an aqueous suspension of the amorphous material did not lead to hydrogen production. Neither the solution nor the solvent became coloured upon irradiation. The polycrystalline material behaved in a similar manner to the amorphous material.

Platinization of the colloid led to a marked improvement in its catalytic efficiency for hydrogen production and furthermore there was no evidence of an induction period (Fig. 1). Oxygen evolution could not be detected. What is more surprising is that injection of oxygen into the reaction mixture during irradiation leads to its consumption together with a decrease in the concentration of hydrogen. The presence of platinum decreases the tendency
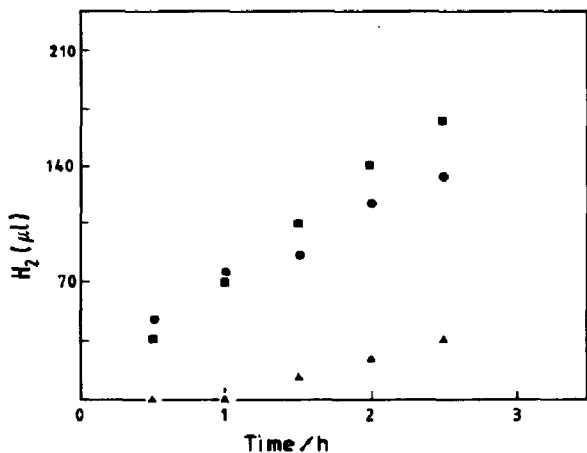

Fig. 1. Hydrogen produced upon irradiation of titanium dioxide samples in water: ▲, colloid; ●, platinized Degussa anatase; ■, platinized colloid.

for precipitation and a blue colouration in the irradiated solution did not develop. The colloid is stable in the pH range 1.7 - 3.0 and hydrogen evolution occurs over this range. The platinized amorphous material showed no marked catalytic activity and underwent no noticeable colour change upon irradiation. The platinized polycrystalline material gave yields of hydrogen comparable with those obtained from the colloid although, because of the different light-absorbing characteristics of the two systems, relative quantum yields for hydrogen production cannot be obtained.

Use of the colloid prepared by dissolution of amorphous titanium dioxide in sulphuric acid produced no hydrogen when irradiated in the presence or absence of platinum. To check that this lack of reactivity is not due to inhibition of reaction by adsorption of sulphate ions on the surface of the colloidal particles, the colloid prepared using hydrochloric acid was irradiated in aqueous solution containing sodium sulphate (0.3 M) and colloidal platinum. The sulphate ions did not inhibit hydrogen production.

3.3. Photocatalytic activity of samples in aqueous acetic acid (pH 2.5)

Irradiation of all three types of sample in aqueous acetic acid solution produced little methane and hydrogen (Fig. 2(a)). Irradiation of the colloid led to the development of a blue colouration which persisted throughout. Admission of oxygen to the cell led to dissipation of the colour, the solution remaining transparent. Irradiation of the amorphous and polycrystalline materials led to no perceptible colour changes.

Irradiation of the platinized colloidal and amorphous material led to little hydrogen and methane production (Figs. 2(b) and 2(c)). During the irradiation colour changes were not observed. In accord with previous work [11] irradiation of the platinized polycrystalline material led to substantial methane and hydrogen evolution and the catalyst had a light blue colour throughout the irradiation.

3.4. Photocatalytic activity of samples in aqueous propan-2-ol

Irradiation of the colloid led to hydrogen evolution. There was an induction period (Fig. 3(a)) although this was considerably shorter than that observed when aqueous solutions of the colloid were irradiated (Fig. 1). Irradiation of the colloid caused the production of a blue colour and the appearance of this colour coincided with measurable hydrogen evolution. The amorphous titanium dioxide underwent no perceptible colour change upon irradiation and after a long induction period produced a little hydrogen. The polycrystalline sample produced hydrogen upon irradiation and no colour changes were observed.

Platinization of the colloid increased its catalytic activity leading to a doubling in the rate of hydrogen production and eliminating the induction period. Platinization of the amorphous material also led to an increased rate of hydrogen production. The most marked effect of platinization was obtained with the polycrystalline sample in which a high rate of hydrogen production was observed (Fig. 3(b)).
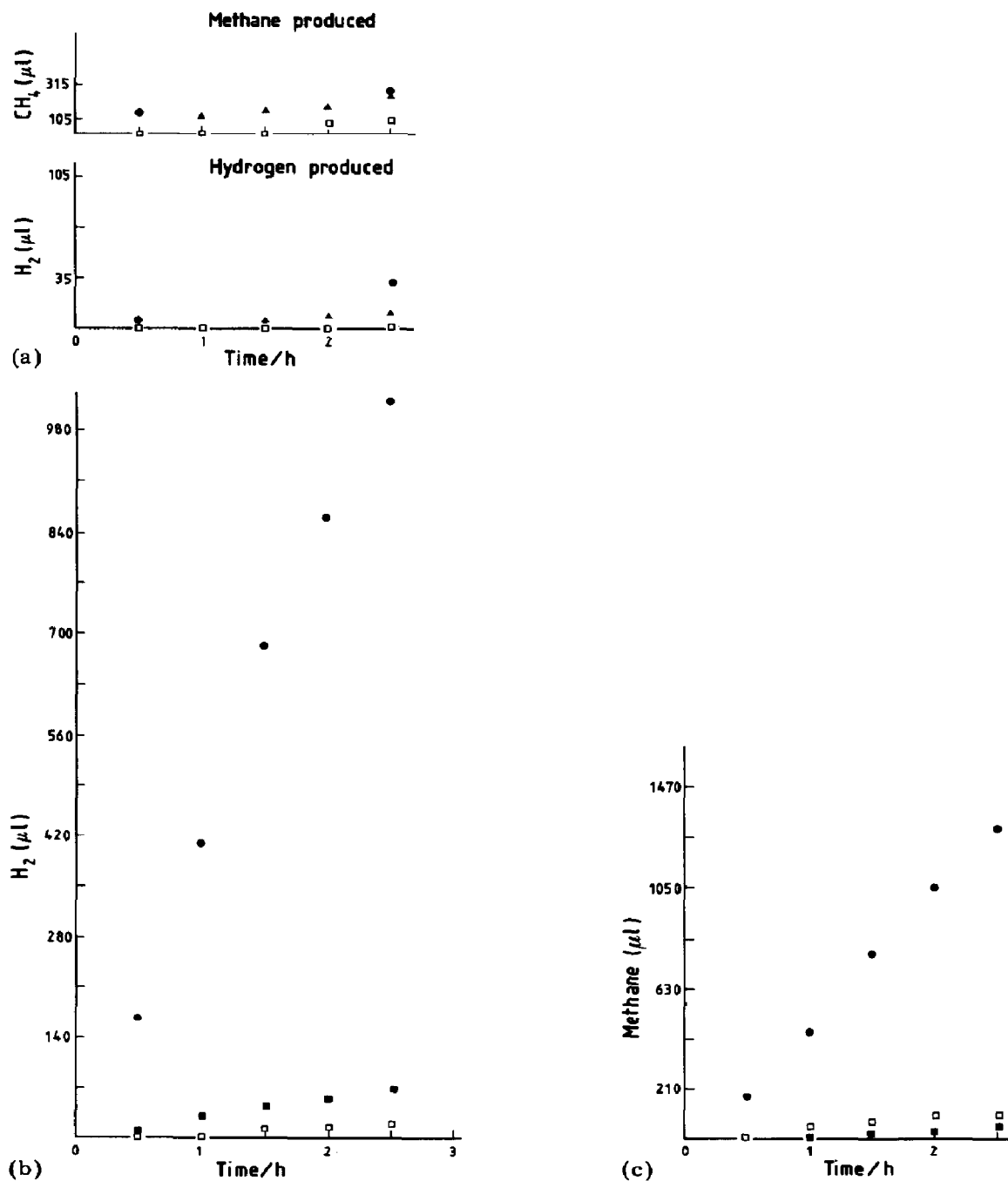
Fig. 2. (a) Methane and hydrogen formation produced by irradiating non-platinized titanium dioxide samples in aqueous acetic acid solution (□, amorphous, ▲, colloid; ●, Degussa anatase); (b) hydrogen formation produced by irradiating platinized titanium dioxide samples in aqueous acetic acid (□, amorphous; ■, platinized colloid; ●, platinized Degussa anatase); (c) methane formation produced by irradiating platinized titanium dioxide samples in aqueous acetic acid (□, platinized amorphous; ■, platinized colloid; ●, platinized Degussa anatase).
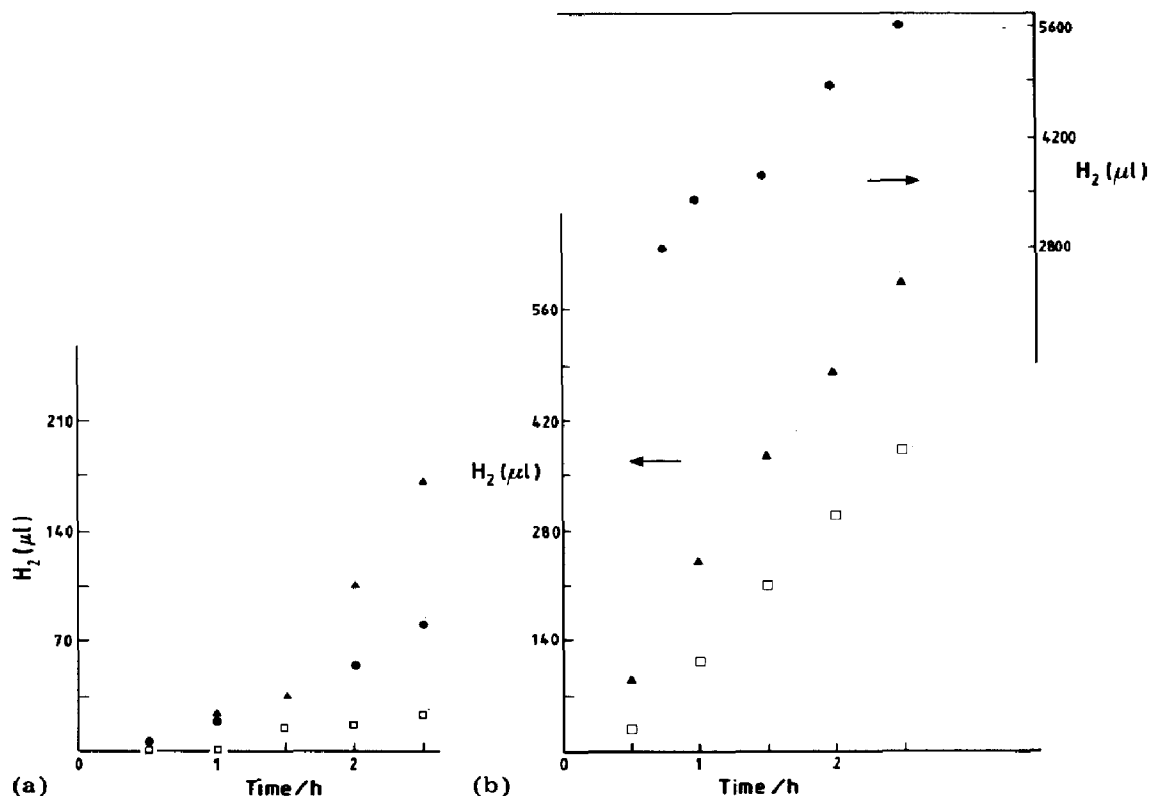
Fig. 3. Hydrogen produced upon (a) irradiation of non-platinized titanium dioxide samples in aqueous propan-2-ol and (b) platinized titanium dioxide samples in aqueous propan-2-ol: □, amorphous; ▲, platinized colloid; ●, Degussa anatase.

4. Discussion

The catalytic properties of the colloid appear to be dependent upon its mode of preparation. When it is prepared from halo acids reactivity is observed, but when sulphuric acid is used no activity is found. If the colloids are really semiconductor-type titanium dioxide then the difference in activity could be attributed to the fact that strongly adsorbed halide ions do not impair reactivity whereas strongly adsorbed sulphate ions have the opposite effect. However, the finding that the presence of sodium sulphate does not impair the reactivity of the colloid prepared from hydrochloric acid shows that adsorption of sulphate ions is not responsible for the lack of reactivity displayed by the colloid prepared from sulphuric acid. Thus the difference in the reactivities of the colloids produced from halo acids and sulphuric acids must be in the chemical constituents of the colloids. The fact that the colloids show an absorption edge at 365 nm and not at wavelengths above 388 nm must also lead to serious questioning of the assumption that the colloid is titanium dioxide with electronic properties similar to those of the crystalline dioxide. It has been argued that if the particle size of a semi-conductor is less than that of the field-free region the band structure of the

semiconductor will be seriously disturbed and this would cause a shift in the band edge. To date there is no experimental evidence to support this claim. Gratzel and coworkers, on the basis of light-scattering experiments, have concluded that the colloidal solutions contain particles with hydrodynamic radii of 200 Å [3] and 25 Å [12]. Interestingly, these materials were described on the basis of X-ray studies as having a crystalline structure which in one case was significantly amorphous [3] and in the other case was mainly anatase [12].

Our optical spectra suggest that little, if any, of the colloid has the anatase structure. Furthermore, if the colloid really is titanium dioxide, why is the role of the acid in the preparation of the colloid so crucial? We suggest that the colloid contains a polymeric titanium species, and when it is prepared using a halo acid it contains some titanium—halogen bonds. The latter can undergo homolysis upon irradiation to generate titanium(III) species, *e.g.*

$$Ti-Cl \xrightarrow{h\nu} Ti^{III} + Cl^{\cdot} \xrightarrow{Cl} Cl_2^{-}$$

$$\downarrow H_2O$$
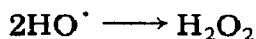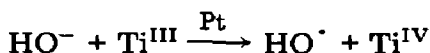
$$Ti^{IV} + \tfrac{1}{2}H_2 + OH^{-}$$
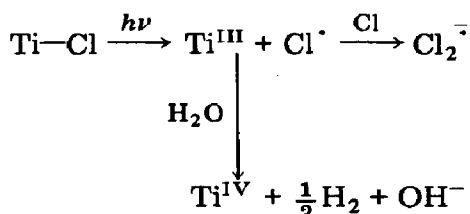
The formation of titanium(III) ions is consistent with the observation that irradiation generates a blue colouration and the known reducing capability of these ions explains hydrogen production in aqueous solution. In addition, the formation of Cl_2^{-} ions has been previously observed in these systems [13]. Clearly these reaction pathways are not available when sulphuric acid is used in place of halo acids for preparation of the colloids.

That platinization of the colloid leads to enhanced reactivity can be adduced as evidence for the semiconductor character of the colloid. However, on the basis of the foregoing mechanism, the colloid should be capable, upon irradiation, of reducing chloroplatinate ions to platinum:

$$PtCl_6^{2-} + 4Ti^{III} \longrightarrow Pt^0 + 6Cl^{-} + 4Ti^{IV}$$
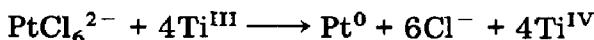
Furthermore, the presence of platinum will, from known work [13], aid the reduction of protons by titanium(III) ions to produce hydrogen, thereby enhancing the rate of production of hydrogen. The presence of platinum will also lead to a much lower steady state concentration of titanium(III) ions which would account for the non-appearance of the blue colour upon irradiation of the platinized samples. The lack of oxygen production under conditions where hydrogen formation is quite vigorous is unusual:

$$HO^{-} + Ti^{III} \xrightarrow{Pt} HO^{\cdot} + Ti^{IV}$$

$$2HO^{\cdot} \longrightarrow H_2O_2$$

$$HO^{\cdot} \text{ or } H_2O_2 + \text{colloid} \longrightarrow Ti^{IV} \text{ peroxo complex}$$

Irradiation of the platinized colloid gives rise to a yellow colouration and this may be due to the formation of a titanium peroxo complex [12, 14]. As yet there is no experimental evidence to support this view.

The lack of reactivity of the platinized colloid in aqueous acetic acid is quite remarkable. Even if acetic acid is a non-reactive component of the mixture, we would have expected the water to have reacted to produce hydrogen. The result is also curious in that it is known [11], and we have also shown, that semiconductor-type titanium dioxide is an effective agent for the photodecarboxylation of acetic acid. We ascribe the lack of reactivity of the colloid as being due to exchange of the chlorine of the Ti—Cl bond present in the colloid (prepared from hydrochloric acid) by acetate.

The platinized colloid is more reactive in aqueous propan-2-ol than in aqueous solution although the difference in reactivity is quite small. By way of contrast, the platinized semiconductor material is extremely effective in producing hydrogen from aqueous propan-2-ol solutions. The lower oxidation potential of propan-2-ol compared with water would be expected to favour the reaction. Furthermore propan-2-ol has hydrogen atoms readily available for hydrogen production.

The greater reactivity of propan-2-ol compared with acetic acid and water probably accounts for the fact that in this system the platinized amorphous titanium dioxide shows some measurable reactivity. The question also arises as to the reason for the reactivity of the amorphous material. X-ray data and the absorption spectrum of this material clearly show that it is neither anatase nor rutile. Furthermore, since the particle size of this material is greater than that of the Degussa anatase, the position of the absorption edge of this material cannot be ascribed to an effect of particle size upon the degree of band bending. What little reactivity this material does display can be ascribed to the photoinduced cleavage of Ti—OH bonds to produce titanium(III) ions which act as oxidizing agents [2]. Further work is in progress to characterize this material. The performance of this material is in marked contrast with that of the polycrystalline material which, as expected [15], gives rise to substantial hydrogen evolution.

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