Water Photodecomposition with Two Reversible and Separable Photosystems

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An aqueous suspension of TiO_2 and Ag_2O, at pH <7.4 photogenerates O_2 reducing Ag_2O to Ag; if the pH of the residual product is increased (12.3—12.6) H_2 is photogenerated, while Ag is oxidized to Ag_2O.

One of the most promising methods for chemical storage of solar energy seems to be photocatalytic systems based on semiconductor dispersions.[1—6] Several aqueous semiconductor suspensions readily photoreduce or photo-oxidize water in the presence of a sacrificial electron donor or an acceptor.[1—6] There is also evidence that photocleavage of water into H_2 and O_2 can be accomplished with semiconductor particles loaded with catalysts which enhance the evolution of these gases.[1,4—8] The systems of the first type that employ sacrificial agents are irreversible. Those of the second type that decompose water into its components, present a severe complication as the reaction product is explosive. Again O_2 and H_2 generated near the same microparticle are more likely to recombine, drastically reducing the decomposition efficiency. The above problems can be circumvented if reduction and oxidation processes are separated in space and time as two photosystems, PS I and PS II, linked by an intermediate redox couple. Natural photosynthesis operates in this fashion.[9] In this note we describe a reversible system for photodissociation of water based on the intermediate redox couple Ag_2O/Ag. An aqueous suspension of TiO_2 and Ag_2O powders, when irradiated, is found to evolve O_2 until all the Ag_2O is reduced to Ag, if the pH is below 7.4, *i.e.*, PS II. When the pH of the residual product is increased (12.3—12.6), H_2 evolves on illumination while the Ag is oxidized back to Ag_2O, *i.e.*, PS I. PS II operates only at the band gap radiation (BGR) of TiO_2. However, PS I which is initially sensitive only to same wavelengths, responds to BGR of Ag_2O as well when the reaction proceeds with formation of Ag_2O.

$$2Ag_2O \rightarrow 4Ag + O_2,\ \Delta G = 22.4\ \text{kJ mol}^{-1}\ \text{(PS II)}$$

$$4Ag + 2H_2O \rightarrow 2Ag_2O + 2H_2,\ \Delta G = 452.7\ \text{kJ mol}^{-1}\ \text{(PS I)}$$

Ag_2O was prepared by adding an excess of NaOH to $AgNO_3$ (AnalaR) and boiling the mixture. The precipitate was throughly washed, taking care to avoid contamination with organic materials, and dried at 110 °C. A calibrated membrane polarographic detector with a thermostatted (26 °C) 35 ml quartz cell (Applied Photophysics) irradiated with a 200 W medium pressure Hg lamp was used to detect O_2 and H_2. Light intensities were measured with an International Light IL 700 Radiometer. Quantum efficiency measurements were performed with a monochromator (Applied Photophysics) and 500 W halogen lamp. The catalyst in PS II mode was prepared by grinding Ag_2O with TiO_2 anatase (BDH and Aldrich, tested to have n-type conductivity). The cell was degassed with N_2, and the O_2 evolution rate from 0.50 mg of the catalyst was determined at different pH's (7—14 adjusted with NaOH). Oxygen production was seen to be optimum

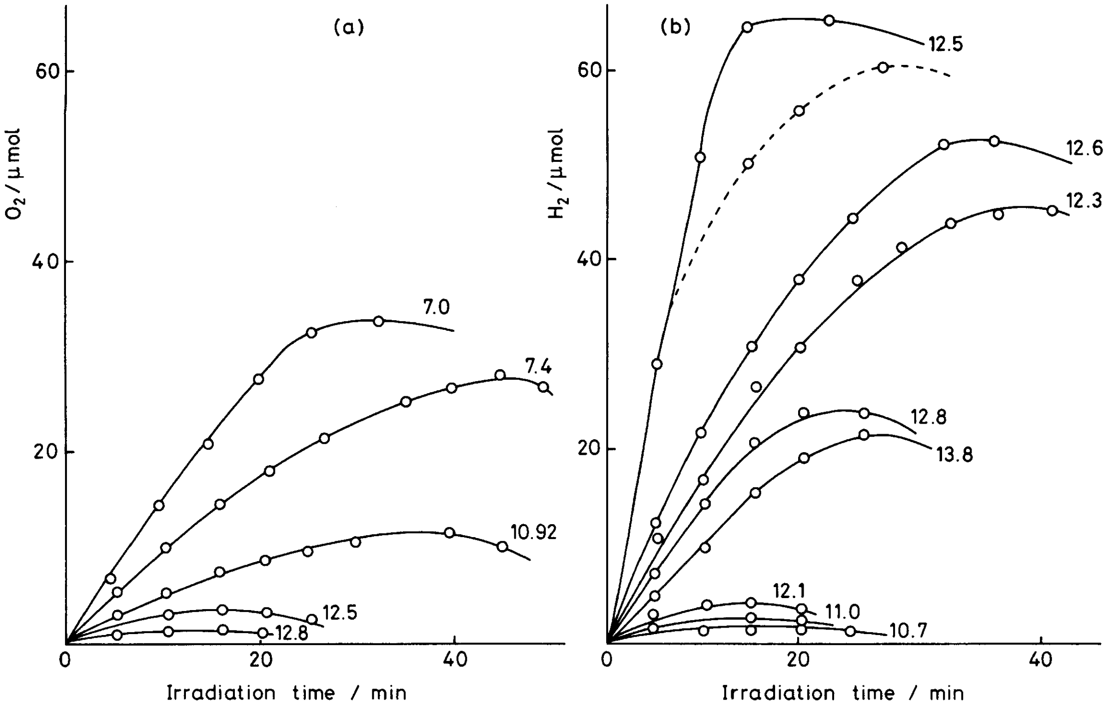

Figure 1. (a) O_2 photoproduction from 5 mg of PS II catalyst (TiO_2 : Ag_2O = 10 : 1); (b) H_2 photoproduction in PS I (TiO_2 : Ag corresponds to the PS II composition), pH values are indicated near each curve.

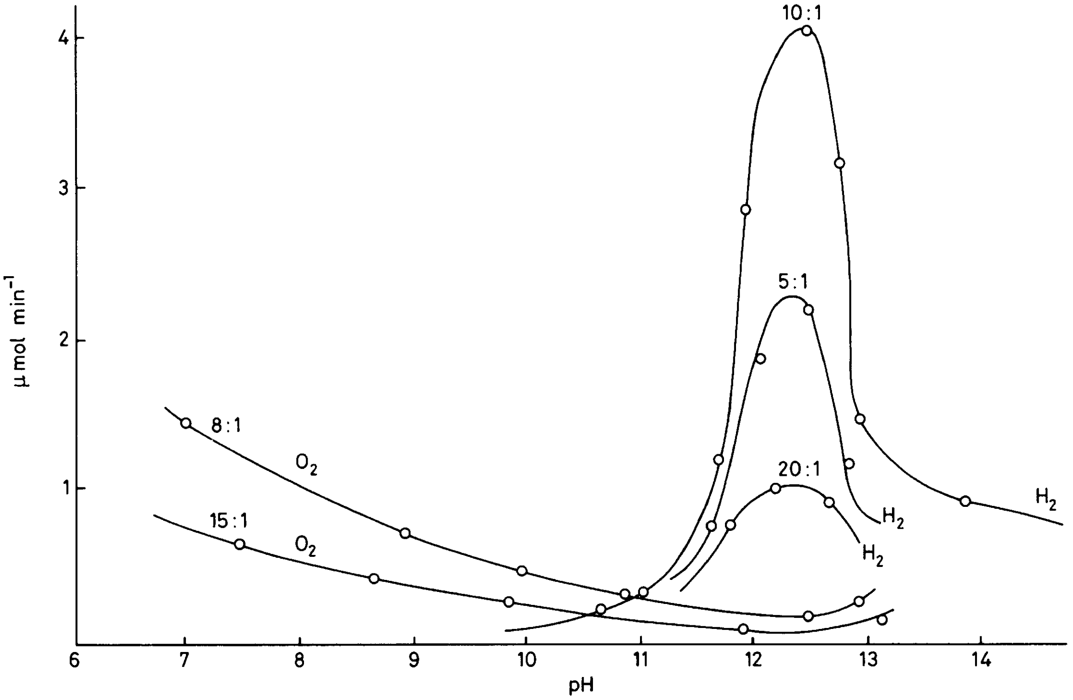

Figure 2. Variation of initial photoproduction rates of O_2 and H_2 with pH. TiO_2 : Ag_2O and TiO_2 : Ag ratios are indicated near each curve.

when TiO_2 : Ag_2O = *ca.* 10 : 1 by weight. At pH's < 7.4, the total amount of photogenerated O_2 was found to be practically the same as the stoicheiometric content in Ag_2O. This was also confirmed by the observation that residual catalyst remained free from Ag that could be extracted with ammonia.

PS I was studied by irradiating the product that has completed PS II, by adjusting the pH and determining the H_2 evolution rate after degassing. When the pH was in the range *ca.* 12.3—*ca.* 12.6, all the Ag was oxidized to Ag_2O, producing H_2. The catalyst in the PS I mode, prepared by grinding silver dust (made by reacting formaldehyde and ammoniacal $AgNO_3$) and TiO_2 was also tested and noted to behave in the same way as the PS II catalysts. The initial H_2 production rate was seen to be optimum when TiO_2 : Ag = *ca.* 8 : 1 by weight. It was also

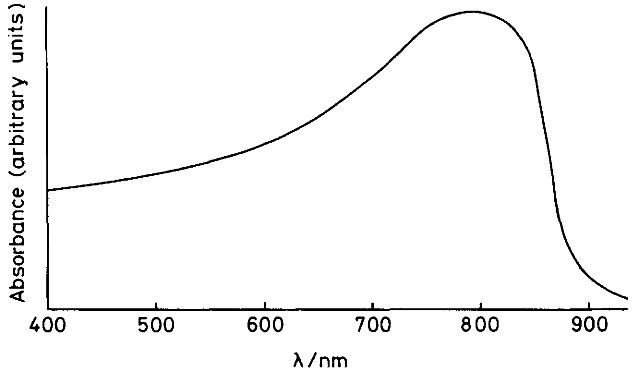

Figure 3. Diffuse reflectance spectrum of Ag_2O powder.

noted that at optimum pH's both photosystems function in the presence of dissolved H_2 and O_2 and reversibility is possible. Figure 1 gives O_2 and H_2 yields from PS II and PS I as a function of time at different pH's. The initial reaction rates (*i.e.*, in the first few minutes, when gas generation increases linearly with time) are compared in Figure 2. It is seen that H_2 evolution rate is maximum at pH *ca.* 12.5, where O_2 evolution rate is minimum.

The curve with broken lines in Figure 1 (b) indicates O_2 production from PS I irradiated with the full spectrum of a Hg lamp and the $\lambda > 630$ nm component filtered off after 5 min. As Ag_2O is formed PS I becomes sensitive to the BGR of Ag_2O, which is p-type having a band edge at *ca.* 840 nm (1.5 eV). The diffuse reflectance spectrum taken with a Unicamp SP 500 spectrophotometer is shown in Figure 3. Aqueous suspensions of Ag_2O and Ag, pH 12.0—13.5, evolve H_2 on illumination at *ca.* 800 nm, confirming the above observation. PS II was seen to be insensitive to the BGR of Ag_2O. Here light absorbed by Ag_2O is wasted; this explains why optimum O_2 evolution occurs when the fraction of TiO_2 in the catalyst is fairly high. Aqueous dispersions of Ag_2O generate H_2 in the presence of other electron donating agents, *e.g.* ethanol at *ca.* 800 nm. However, no O_2 evolution is seen in the presence of electron acceptors, *e.g.*, persulphate or dichromate, showing that band positions are favourable only for H_2 evolution.

Oxygen in PS II should come from H_2O; except for the observation that Ag_2O does not undergo photodecomposition, we have not proved this directly. The energy conversion efficiency for one cycle is *ca.* 0.6% (a 200 W medium pressure Hg lamp at 460 W m^{-2} was used as the light source). The quantum efficiencies of O_2 (pH 7) and H_2 (pH 12.5) corrected for transmission were estimated to be 2.3 and 13.6% respectively at 380 nm. The determination of this quantity at different wavelengths near the absorption peak of Ag_2O is involved because of the progressive sensitivity of PS I to the BGR of Ag_2O. A mixture of Ag_2O and Ag (10:1 by weight) generates H_2 with a quantum efficiency of *ca.* 16% at *ca.* 800 nm.

Although conversion efficiencies are low and cycling between PS I and PS II involves operations that consume some energy, the present system is useful as a model for the dual system photocleavage of water.

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