

WATER PHOTOLYSIS VIA REVERSIBLE OXIDATION AND REDUCTION BETWEEN MnO_2 AND MnO_4^{2-}

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Summary

TiO_2 ground with MnO_2 and suspended in an aqueous alkaline medium is found to photogenerate hydrogen with concomitant oxidation of MnO_2 to MnO_4^{2-} . TiO_2 suspended in a solution of MnO_4^{2-} liberates oxygen on irradiation. Thus, in principle, reversible oxidation and reduction between MnO_2 and MnO_4^{2-} can be used to photodecompose water.

1. Introduction

Reversible redox reactions between two photosystems are perhaps the most promising way of achieving photocleavage of water [1]. In photosystem I (PS I) water is reduced to hydrogen by extracting electrons from a donor D which is then oxidized to an acceptor A. In photosystem II (PS II) A is reduced back to D releasing oxygen. The redox couple A/D serves as the electron pool linking PS I and PS II. Light energy is absorbed by a sensitizer or by the redox molecules themselves. A two photosystem process has several advantages.

(1) The utilization of two photons for each electron transfer. Consequently, photons of lesser energy (compared with a single step process) are required for splitting one molecule of water.

(2) The highly reactive primary oxidation and reduction products of water are generated at sites separated spatially and thus the back reactions are suppressed.

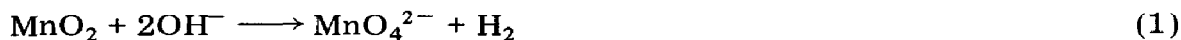
(3) Hydrogen and oxygen produced in spatially separated sites can be fed into different compartments.

(4) Each photosystem can function independently of the other for a limited duration of time.

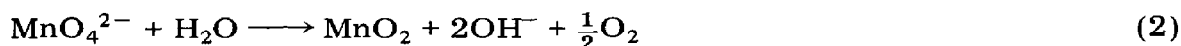
Although examples of irreversible individual photosystems, *i.e.* sacrificial photochemical reduction and oxidation of water [2 - 7], are well known, reversible cyclic models are quite rare [8 - 10]. In this paper, we describe a

system for the cyclic photocleavage of water based on the reversible oxidation–reduction between manganese dioxide and the manganate ion. The photosystems are described below.

(i) PS I: TiO_2 ground with MnO_2 and suspended in an aqueous alkaline medium liberates hydrogen with oxidation of MnO_2 to MnO_4^{2-} on irradiation



(ii) PS II: irradiation of an aqueous solution of MnO_4^{2-} in the presence of TiO_2 generates oxygen



2. Experimental details

Photolysis experiments were carried out in a thermostatically controlled (26 °C) quartz reaction vessel (35 ml) provided with a polarographic detector (Applied Photophysics) for monitoring the hydrogen and oxygen concentrations. To carry out the PS I reaction, TiO_2 powder (Aldrich; purity, 99.99%) ground with MnO_2 ($\text{MnO}_2:\text{TiO}_2 = 1:10$ (w/w); amount of mixture used, 20 mg) and suspended in 30 ml of water was irradiated with a 90 W medium pressure mercury lamp. Adjustments of pH were made using NaOH. Hydrogen photogeneration from the system is illustrated in Fig. 1.

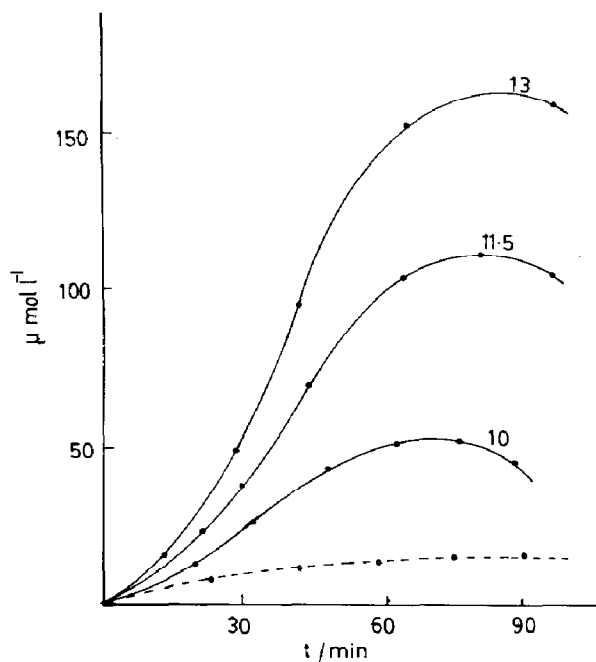


Fig. 1. Hydrogen generation during photolysis of H_2O using $\text{TiO}_2\text{--MnO}_2$ (full lines; pH values indicated) and oxygen photogeneration from the same system at pH 13 (broken line).

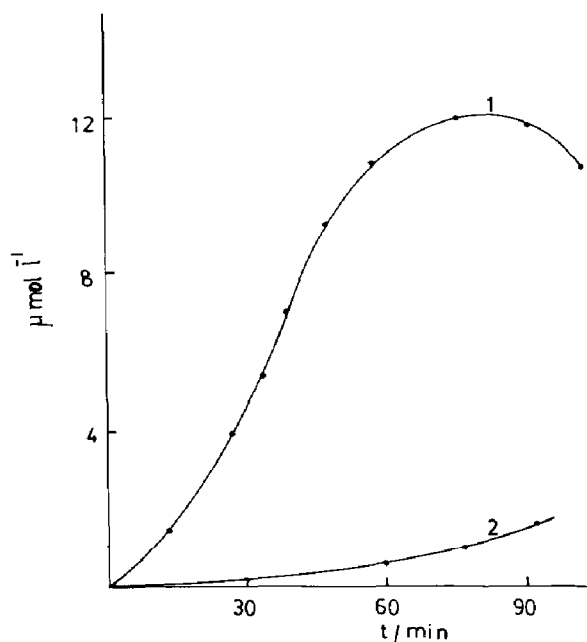
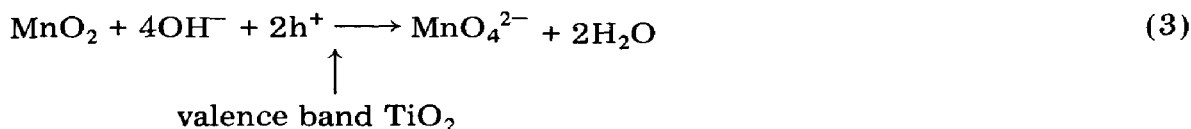


Fig. 2. Oxygen photogeneration during photolysis of a solution of Na_2MnO_4 (0.01 M) at pH 13 (1) and hydrogen photogeneration from the same system (2).

Spectrophotometric examination of centrifuged samples of the photolysis solution indicated the formation of the manganate ion. The PS II reaction was performed by irradiating an argon-purged suspension of TiO_2 (20 mg in 30 ml) in 0.01 M Na_2MnO_4 at pH 13. Oxygen generation from PS II is shown in Fig. 2. The gases evolved in the two cases were confirmed to be hydrogen and oxygen by gas chromatography (Shimadzu gas chromatograph GC-9AM).

3. Discussion

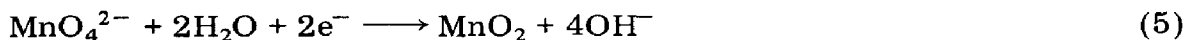
When TiO_2 is ground with MnO_2 , composite particles are produced where MnO_2 and TiO_2 grains are in intimate contact. As MnO_2 is an efficient hole transfer catalyst [11] (*cf.* RuO_2), the holes photogenerated in TiO_2 are transferred to MnO_2 and participate in the reaction



The electrons remaining in TiO_2 reduce water to hydrogen



The sum of reactions (3) and (4) is equivalent to reaction (1) of PS I. In the PS II reaction, where TiO_2 is suspended in an aqueous solution of MnO_4^{2-} , the following electron transfer reactions take place



\uparrow
 conduction band TiO_2



\uparrow
 valence band TiO_2

Steps (5) and (6) are equivalent to reaction (2) of PS II. As hole transfer from TiO_2 to MnO_2 is very efficient, the composite particles are unable to initiate the PS II reaction via eqns. (5) and (6). However, the ground powder always contains free TiO_2 particles and, consequently, the photolysis of the TiO_2 - MnO_2 mixture is found to generate small quantities of oxygen simultaneously with hydrogen (Fig. 1). In addition, during the photolysis of MnO_4^{2-} in the presence of TiO_2 , the MnO_2 deposition on TiO_2 generates detectable quantities of hydrogen via the PS I reaction (Fig. 2). The rate of the PS I reaction is found to increase with an increase in pH (Fig. 1) as expected from its overall equilibrium. Also the flat band potential of TiO_2 shifts in the negative direction with an increase in pH favouring hydrogen liberation [12]. The PS II reaction is largely unaffected by pH changes in the alkaline region (manganate ion transforms to permanganate ion when the pH is acidic). The yield of hydrogen obtained using TiO_2 ground with RuO_2 is much smaller than that obtained with MnO_2 . Although RuO_2 is a better hole transfer agent, hole sacrifice (*e.g.* via formation of ruthenates) does not appear to occur at an RuO_2 -coated catalyst.

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