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Electrochemical Evidence for the Mechanism of the Primary Stage of Photosynthesis⁽¹⁾

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A phenomenon analogous to photosynthesis was observed by using an electrochemical system involving semiconductor electrodes, such as *n*-type titanium dioxide (rutile) single crystals. The results help greatly to establish the nature of the initial stage of photosynthesis, especially the oxygen evolution reaction, from the electrochemical point of view. One of the most important processes in the photosynthesis is a hole injection into a water molecule, though it is not clear whether the hole exists before injection in a localized level or in an excess hole band of chlorophylls. Since van Niel[2] proposed that the photolysis of water was the basic reaction for converting light into chemical energy, Arnon and others[3] have developed this idea, especially the relation between the excitation of chlorophylls and oxygen evolution. According to the results of Arnon's primary photochemical reaction, an absorbed light quantum excites a chlorophyll molecule and expels an

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[1] Studies on Photosensitive Electrode Reactions. III.

[2] C. B. van Niel, "Photosynthesis in Plants," Iowa State College Press (1949), p. 437.

[3] D. I. Arnon, *Nature*, **184**, 10 (1959).

electron. This electron naturally has a higher potential energy at the expense of the energy of the absorbed light quantum. The chlorophyll molecule, as it expels an electron, becomes ready to accept another from water with oxygen evolution and, in this way, returns to a normal state. However, the mechanism of the oxygen evolution reaction has not yet been sufficiently explained.

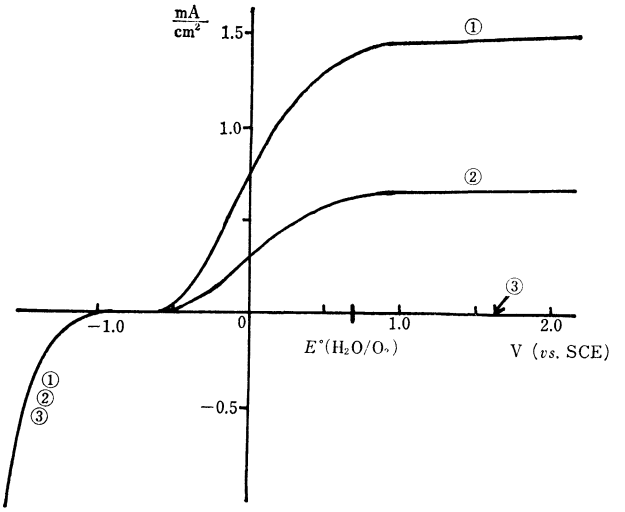

Fig. 1. Current-voltage curves of TiO_2 electrode with and without irradiation of light in the buffered solution of pH 4.7.
Curve ①: under irradiation (relative intensity of light, 100%).
Curve ②: under irradiation (relative intensity of light, 50%).
Curve ③: without irradiation.

Photosensitized Electrolytic Oxidation. The present authors[4] have previously studied the electrochemical behavior of semiconductor electrodes under the irradiation with light. In the present experiment, *n*-type titanium dioxide (TiO_2) single crystals were used after reduction treatment in order to increase the electric conductivity. The current voltage data were obtained potentiostatically. Figure 1 shows typical current-voltage curves with and without irradiation. Without irradiation, hydrogen evolution occurred in the cathodic polarization region, but the anodic current was extremely small. Under irradiation, the cathodic branch of the current-voltage curve was not influenced, but a large anodic current flowed at a potential more positive than −0.5 V (*vs.* SCE) in a neutral electrolyte solution. The magnitude of the anodic current was proportional to the light intensity and depended on the wavelength of the light. A large anodic current flowed when the semiconductor electrode was irradiated with light with an energy higher than the band gap of TiO_2, 3.0 eV.

This anodic reaction may be related to the holes, the minority carriers, which are produced in the valence band of TiO_2 by light. When an anodic current flowed, gas evolution was observed at the TiO_2 electrode surface. It was observed by gas chromatography that the gas was oxygen. As TiO_2 is very stable, it seems unlikely that the TiO_2 electrode was decomposed under irradiation. Even after the anodic current had flowed for a long time with a strong light, the TiO_2 electrode surface was not at all changed and no titanium ions could be detected in the electrolyte solution. In a 0.1 N Na_2SO_4 electrolyte solution, the relation between the change in the pH and the amount of current at 0.0 V in the case of the TiO_2 electrode was the same as that when the Pt electrode was used at 1.0 V. Therefore, the anodic reaction may be attributed to the electrolytic oxidation of water to oxygen gas.

Though the reversible oxidation potential of water to oxygen is 0.7 V (*vs.* SCE) at pH 4.7, the anodic current flowed, in fact, at potentials more positive than −0.5 V under irradiation. This fact indicates that the oxidation potential of water shifts by about 1.2 V towards the more negative region at pH 4.7. From the results described above, a mechanistic model of the electrochemical reaction at the *n*-type TiO_2 electrode is proposed; it is illustrated in Fig. 2. We call the above-mentioned phenomenon "photosensitized electrolytic oxidation." The origin of the photosensitized electrolytic oxidation is, of course, the absorption of the energy of light by the semiconductor electrode.

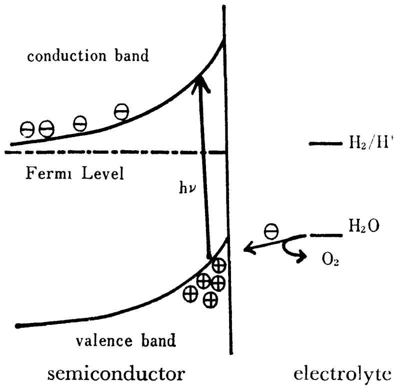

Fig. 2. A mechanistic model of photosensitized electrolytic oxidation.

If the electrolyte solution involved halogen ions, such as iodide or bromide ions, they are also oxidized in competition with the oxygen evolution reaction in relation to the concentration of halogen ions. Recently, we have investigated the photo-electrochemical reactions of *n*-type semiconductor electrodes of the zinc oxide single crystal and the cadmium sulfide single crystal;[5] under anodic polarization these crystals are dissolved because of the positive holes formed in the valence band by the irradiation with light. In the electrolyte solution involving halogen ions, the electrochemical oxidation of these anions occurs instead of the dissolution reaction on both ZnO and CdS electrodes. The oxidation potentials of halogen ions on TiO_2, ZnO, and CdS electrodes are more negative than the standard oxidation potential. Therefore, the photosensitized electrolytic oxidation of halogen ions seems to occur even with ZnO and CdS electrodes.

Photo-electrochemical Cell and Its Relation to the Primary

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[4] A. Fujishima, K. Honda, and S. Kikuchi, *Kogyo Kagaku Zasshi*, **72**, 108 (1969).

[5] A. Fujishima, M, Matsukura, K.Honda, and S.Kikuchi, Preprint of the Annual Meeting of the Electrochemical Society of Japan, 1969, P.c-45, A.Fujishima, E.Sugiyama and K.Honda, This Bulletin, **44**, 304 (1971).

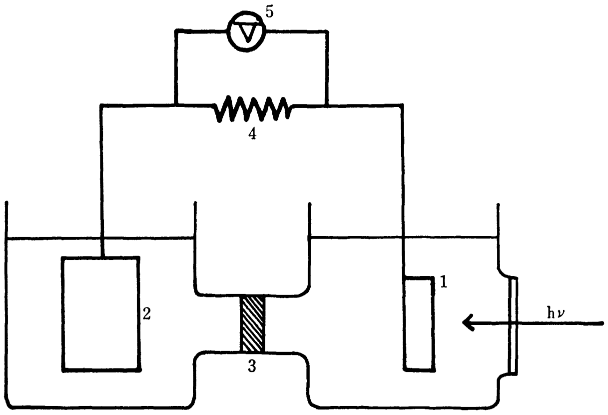

Fig. 3. An electrochemical cell with TiO_2 electrode under irradiation.
1: TiO_2 electrode, 2: Pt electrode, 3: sinter-glass diaphragm, 4: an outer load, 5: a voltmeter

Stage of Photosynthesis. The function of the TiO_2 semiconductor electrode in relation to the primary stage of photosynthesis can be better understood by constructing an electrochemical cell with a semiconductor electrode under irradiation, as is shown in Fig. 3. When the surface of the TiO_2 electrode was irradiated, the current which passed through the load was proportional to the light intensity. It was seen from the direction of the current that an oxidation reaction occurred at the TiO_2 electrode and a reduction, at the Pt electrode. The oxidation reaction was oxygen evolution resulting from water electrolysis. This fact indicates that the TiO_2 electrode absorbed the energy of light and caused the electrolysis of water to oxygen gas without any applied electric power and that, at the same time, a reduction occurred at the Pt counter electrode and electric energy was supplied to the outer load.

There has previously been presented a model(6) which regarded aggregated chlorophylls as a kind of semiconductor. This opinion has been supported in part by experimental results with regard to the photoconductivity(7) and the delayed light emission(8) of chloroplasts and other phenomenon. It may be considered that the reaction at the TiO_2 electrode and the Pt counter electrode, and the work done by electric energy to the outer load, approximately correspond to those which occur in chlorophylls, carbon assimilation, and photophosphorylation respectively. In a model of photosynthesis(9,10) where oxidation-reduction potentials were introduced with a view of placing great emphasis on the electron transfer in plants, the stages of the photoexcitation of chlorophylls and oxygen evolution are similar to the mechanism of photosensitized electrolysis at the TiO_2 electrode. This kind of work with an electrochemical system containing a semiconductor or insulator electrode will be of great help in studying the primary processes involved in photosynthesis.

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6) E. Katz, "Photosynthesis in Plants," Iowa State College Press, (1949), p. 291.
7) R. C. Nelson, *J. Chem. Phys.*, **27**, 864 (1957).
8) B. L. Strehler and W. Arnold, *J. Gen. Physiol.*, **34**, 809 (1951).
9) J. A. Bassham, *Advan. Enz.*, **25**, 39 (1963).
10) M. Calvan and G. M. Androes, Proc. Photosynthesis Conf., Paris (1962).