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Photolysis of Water on Illuminated Strontium Titanium Trioxide

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Synopsis. The photolysis of water was demonstrated in an illuminated strontium titanium trioxide suspension. Electrochemical mechanism takes place in the decomposition reaction.

The photolysis of water by the use of light from a xenon lamp was accomplished by Fujishima and Honda in a photoelectrochemical cell using a semiconducting titanium dioxide photoanode.[1)] It was found that the photolysis occurs at illuminated titanium dioxide suspended in an aqueous solutions.[2)] Schrauser and Guth[3)] reported the quantitative photodecomposition of chemisorbed water on titanium dioxide.

It has been revealed from electrochemical studies on photocatalysis of n-type semiconductors[4–11)] that electrochemical mechanisms are occasionally involved in heterogeneous photocatalytic reactions using semiconductor catalysts. In these cases, the photocatalytic reaction consists of a photosensitized oxidation process coupled with a reduction process thermodynamically regulated, the onset potential of the photosensitized oxidation being more negative than that of the reduction process. The coupled processes proceed spontaneously on an illuminated n-type semiconductor accompanied by local cell action. This principle is basically the same as that for construction of photoelectrochemical cells.[12)]

If such a mechanism prevail in photolysis of water at illuminated n-type semiconductor catalysts, the following reaction schemes are established for pure water.

photosensitized oxidation

$$H_2O + 2p^+ \longrightarrow 1/2O_2 + 2H^+ \qquad (1)$$

reduction

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad (2)$$

overall

$$H_2O \longrightarrow H_2 + 1/2O_2 \qquad (3)$$

where p^+ and e^- represent a positive hole in the valence band and an electron in the conduction band, respectively. The oxidation of water (Reaction 1) should then occur at potentials negative to the reversible hydrogen electrode potential (RHE).

It is well known in semiconductor electrochemistry[12–14)] that photosensitized oxidation on a semiconductor electrode sets on at its flat-band potential. Thus, photodecomposition of water is expected if a semiconductor having a flat-band potential more negative than RHE is used as a photocatalyst. Strontium titanium trioxide (Strontium titanate) satisfies this prerequisite for the flat-band potential.[14–16)]

Experimental

The decomposition experiments were carried out in an air-tight cell made of pyrex glass, with gas inlet and outlet, a flat window (dia. 30 mm) and a mouth in a tubular form for sampling the gas. The mouth was sealed in the lower portion with silicone rubber packing (dia. 5 mm, height 8 mm), water being filled on the packing (height 10 mm) in order to make a perfect seal during the course of gas sampling.

Strontium titanium trioxide powder, purity 99.9%, was reduced by hydrogen at 900 °C for 3 h, giving the surface area 0.67 m^2/g, and stored in a desiccator under humid nitrogen for a week. 1 g was suspended in 20 cm^3 of distilled water and the suspension was magnetically stirred overnight in the cell into which prepurified nitrogen was continuously bubbled. Stop cocks of the gas inlet and outlet were then closed, and the light from an 1 kW xenon lamp was illuminated on the suspension. The light was so focused as to fit with the cell window, its intensity being *ca.* 3 W as measured by a laser power meter (Coherent Radiation, model 201). The gas was analyzed at intervals with a gas chromatograph using a molecular sieve 5A coloum.

A strontium titanium trioxide single crystal (Nakazumi Crystal Co., Ltd.) was used as an electrode in order to confirm govering of photodecomposition by the electrochemical processes given by Eqs. 1 and 2. The electrode was prepared in the same way as reported by Watanabe *et al.*[15)] The effective area of the electrode was 0.3 cm^2.

Results and Discussion

Figure 1 shows the evolution of gases as a function of illumination time. With no illumination, no gas evolution took place. Illumination without strontium titanium trioxide caused no decomposition. The results (Fig. 1) satisfy the stoichiometry of the decomposition reaction. However, the rate of the decomposition showed a tendency to diminish with illumination time.

The cause of the decline in the evolution rate is not clear. This may reflect some change in the surface condition of the catalyst. However, judging from the volume ratio of the evolved gases, the reduction of the catalyst surface does not seem probable. It might

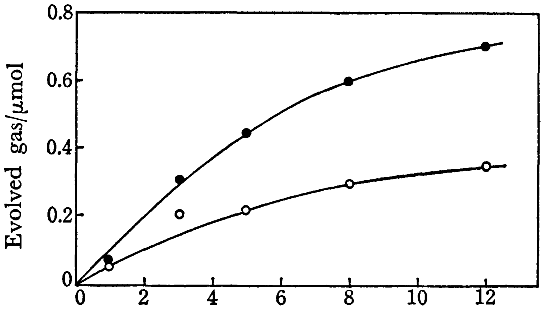

Fig. 1. Amount of oxygen and hydrogen evolved as a function of illumination time. —●—: H_2, —○—: O_2.

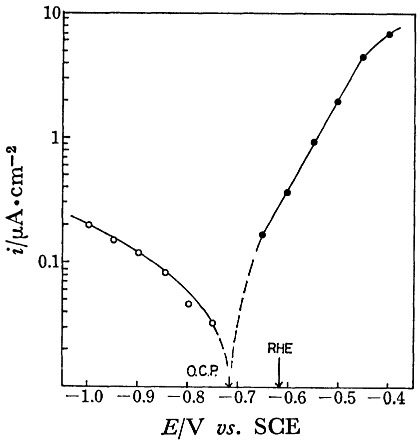

Fig. 2. Polarization curves of a single crystal $SrTiO_3$ electrode in 0.5 $mol \cdot dm^{-3}$ Na_2SO_4 (pH=6.4). —●—: Anodic curve under illumination, —○—: cathodic curve in the dark, O.C.P.: open circuit potential under illumination. Illumination: 1 kW xenon lamp.

be postulated that the mode of reaction changed from water decomposition to a cycled reaction of oxygen evolution and reduction of the evolved oxygen. However, this does not seem to be the case. From Henry's law, the amount of evolved oxygen seems to be too small to dissolve into water in an appreciable amount.

Figure 2 shows polarization curves of the single crystal electrode in 0.5 $mol \cdot dm^{-3}$ Na_2SO_4. The anodic curve obtained under illumination (a) is related to the oxygen evolution reaction.[14,15] On the other hand, the cathodic curve in the dark (b) seems to be due to the hydrogen evolution reaction, since small bubbles were observed to stick on the electrode surface when a relatively high cathodic polarization was made. The open circuit potential of the illuminated strontium titanium trioxide electrode shown by arrow was in the potential region where the hydrogen evolution is thermodynamically feasible. Although these polarization curves were obtained in the solution of pH=6.3 and not in the pure water, almost the same situation should take place in pure water. The flat-band potential at which the oxidation of water sets on has the same pH dependency as RHE.

The decomposition rate is 0.03—0.05 $\mu A/cm^2$ (Fig. 2), corresponding to the water photolysis of 0.001 μmol/h per unit surface area of the catalyst at most. Since light was concentrated into a cell window of *ca.* 7 cm^2, the decomposition rate of 0.007 μmol/h can be expected for a single crystal having an area equal to that of the cell window. However, the rate estimated is low, suggesting that the quantum yield of water photolysis is too low to be significant. The potential at which the photolysis proceeds is near the flat-band potential, resulting in a weak field strength to anihilate photo-generated carriers.[13]

The surface area can be increased greatly with use of powder catalyst. However, attempts to increase the surface area do not always bring about a proportional increase in the photodecomposition rate. The decomposition rate of 0.1 μmol/h was observed in the initial stage of the experiment (Fig. 1). This gives only fourteen times the value estimated above for the single crystal catalyst having the area of the cell window. The increase in the surface area can in principle enhances the cathodic process, but the anodic process is usually controlled by the number of incident photons rather than by the surface area. Thus, the result seems to be reasonable.

This suggests that the photolysis of water can be carried out on illuminated n-type semiconductors having flat-band potentials more negative than RHE, if they are stable against both anodic and cathodic decomposition.

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