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HYDROGEN EVOLUTION ON SURFACE-MODIFIED SILICON POWDER PHOTOCATALYSTS IN AQUEOUS ETHANOL SOLUTIONS

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Illumination of n-type Si powder photocatalysts whose anodic surfaces and cathodic surfaces were coated with polypyrrole and platinized Ag, respectively, caused hydrogen evolution from aqueous ethanol for longer than 150 h with a quantum efficiency of 2.1 % at 550 nm.

Light-induced heterogeneous reactions on semiconductor powders in solution have been studied from the viewpoint of solar energy utilization mainly with the use of stable semiconductor photocatalysts such as TiO_2 and $SrTiO_3$,[1)] but these semiconductors have too large bandgaps to utilize visible light with a high conversion efficiency,[2)] imposing us a severe limitation to the development of solar energy utilization systems of practical significance. Recently, the use of CdS powders have been reported,[3-5)] but this material is still insufficient for solar energy utilization; the theoretically predicted maximum conversion efficiency of solar energy is ca. 15 %. Silicon is known to be one of the best materials for this purpose, but its applicability to photocatalysts is severely limited by the high instability in aqueous solutions. Thereby, no successuful result has been published with the use of Si powder photocatalysts.

In this communication, we report the first success in evolving hydrogen from aqueous ethanol on surface-modified Si powder photocatalysts. One of the most interesting heterogeneous reactions on semiconductor powders will be the decomposition of water, but this reaction is possible to occur in principle on semiconductors whose bandgaps are larger than 1.23 eV, which exceeds that of Si (1.1 eV). The reaction system chosen here requires a lesser energy and was previously reported for platinized TiO_2 photocatalysts.[6)] The success of the present study was due to the employment of the method of the simultaneous photodeposition of polypyrrole and Ag as a means for modifying Si powder surfaces. The simultaneous photodeposition was previously discovered by the present authors in the course of another study using semiconductor single crystals on characterization of effective surfaces of semiconductor photocatalysts for light-induced heterogeneous reactions, as will be reported in a separate paper.[7)] The important points of the simultaneous photodeposition are that polypyrrole and Ag deposit selectively on the "anodic surfaces" and the "cathodic surfaces", respectively, and that the former surfaces consist of defect-free sites of the powder surfaces whereas flaws or defects on surfaces serve as the latter surfaces.

n-Type Si powder was prepared by doping a commercially available powder (Mitsuwa Pure Chemicals Co., 99.999 % purity) with phosphorus in vacuo at 800 °C for 1 h. About one half of this powder consisted of particles of 2.8 ∿ 4.7 μm diameter, while the other half consisted of particles of 12 ∿ 19 μm and of a small number of larger particles of about hundred μm diameter.

Illumination with a 300 W tungsten halogen lamp of the Si powder suspended in an acetonitrile solution containing 0.1 mol dm^{-3} pyrrole and $AgClO_4$ caused the simultaneous photodeposition of polypyrrole and Ag. With illumination for 30 min, 16 ∿ 18 μg of Ag deposited on 1 g of the Si powder, as determined by the colorimetric analysis with dithizone of a solution obtained by dissolving the deposited Ag with HNO_3. By taking into consideration of the charge balance between the anodic and cathodic reaction and by assuming the number of electrons consumed in the polymerization reaction to be 2.25,[8] 4.5 ∿ 5.6 μg of polypyrrole is believed to have been deposited on 1 g of the Si powder. The platinum loading of the Si powder previously coated with polypyrrole and Ag was carried out by illuminating the powder for 1 h in a 2 mmol dm^{-3} H_2PtCl_6 ethanolic solution. The anodic reaction as a counterpart of the Pt deposition in this case was oxidation of ethanol. After dissolution with aqua regia, Pt was determined by the colorimetric analysis using $SnCl_2$; ca. 1 mg Pt was loaded per 1 g of the Si powder. The simultaneous photodeposition of polypyrrole and Pt was attempted for preparation of the photocatalysts coated with these substances, but it was unsuccessful owing to a direct chemical reaction of pyrrole with H_2PtCl_6 in the solution. Besides these photocatalysts, platinized Si was prepared with the same manner as employed in platinization of the Ag/Si/polypyrrole powder. Figure 1 shows a SEM photograph of one of the largest Si particles coated with polypyrrole, Ag and Pt. The metallic deposits, shown as white areas of irregular shape, are distributed randomly on the surface. X-ray microanalysis revealed that Pt coexisted with Ag, suggesting that the Pt deposition took place selectively on the previously deposited Ag.

The experiments of hydrogen evolution were carried out in a cell of ca. 15 cm^3 capacity in which 0.2 g of the photocatalysts was suspended in 7 cm^3 of aqueous ethanol (50 vol %). After the solution was de-aerated with N_2 for more than 1 h, the cell was closed, and illumination was started. The amount of hydrogen was determined intermittently as a function of the illumination time by using a gas chromatograph. The gas was sampled with a microsyringe through a septum tightley fitted in a port installed in the upper portion of the cell.

Figure 2 shows the results obtained with illumination up to 80 h. The photocatalytic activities are in the following order; Pt(Ag)/Si/polypyrrole > Ag/Si/polypyrrole > Pt/Si > bare Si. After 80 h, the pressure of gases inside the cell became so high for the case of Pt(Ag)/Si/polypyrrole catalyst that some leakage began to occur. The lifetime of the photocatalysts was then tested in another cell of large capacity. Both Pt(Ag)/Si/polypyrrole and Ag/Si/poly-

Fig. 1. SEM photograph of an Si particle coated with polypyrrole, Ag and Pt. Metallic deposits are seen as small white areas randomly distributed on the surface.

pyrrole worked effectively for 150 ∿ 200 h. In cases of Pt/Si and the bare Si, the activities were lost within 100 h.

The evolved gas contained several oxidation products of ethanol: inspection of the chromatograms showed the evolution of a large amount of carbon dioxide, a smaller amount of acetaldehyde,and traces of methane and acetic acid. Trace amounts of methane, ethane and acetic acid were found in the liquid phase. It is inferred that the major photocatalytic reaction in this system is the hydrogen evolution from water accompanied by oxidative decomposition of ethanol to carbon dioxide.

$$12H^+ + 12e^- \longrightarrow 6H_2 \qquad E^0 = 0\ V \qquad (1)$$

$$C_2H_5OH + 3H_2O + 12p^+ \longrightarrow 2CO_2 + 12H^+ \qquad E^0 = 0.083\ V \qquad (2)$$

$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2 \qquad (3)$$

The ratio of the amount of hydrogen to that of carbon dioxide accumulated in the gas phase in the reaction cell was ca. 7 for the Pt(Ag)/Si/polypyrrole catalyst at the time when it lost the photocatalytic activity. Since carbon dioxide has higher solubility, it must have been retained in the solution more than hydrogen, and the obtained result will not conflict with the proposed reaction schemes.

The acetaldehyde and acetic acid detected must be oxidation intermediates of ethanol, and methane and ethane must have been produced by the photocatalytic decomposition of acetic acid.[9)] The standard electrode potentials for the corresponding reactions are $E^0(CH_3CHO/C_2H_5OH) = 0.19$ V, $E^0(CH_3COOH/CH_3CHO) = -0.12$ V, and $E^0(C_2H_6/CH_3COOH) = 0.12$ V. It is known from these values together with the electrode potentials of reactions 1 and 2 that the theoretical energies required for the photocatalytic reactions to give the detected products are much smaller than the bandgap of Si.

It is seen in Fig. 2 that some induction periods were needed for appreciable evolution of hydrogen to occur. Preferential reduction of oxygen adsorbed on the catalyst surfaces may be responsible for the appearence of this phenomenon. Another noticeable thing is that hydrogen evolution continuously occurred even at the bare Si catalyst. This is not strange, because hydrogen evolution can take place as a counterpart reaction of the anodic passivation of Si. Judging from the very low rate of hydrogen evolution observed on the bare Si photocatalyst, the passivation progressed too slowly to cover the entire surfaces.

The Pt loading of the bare Si improved

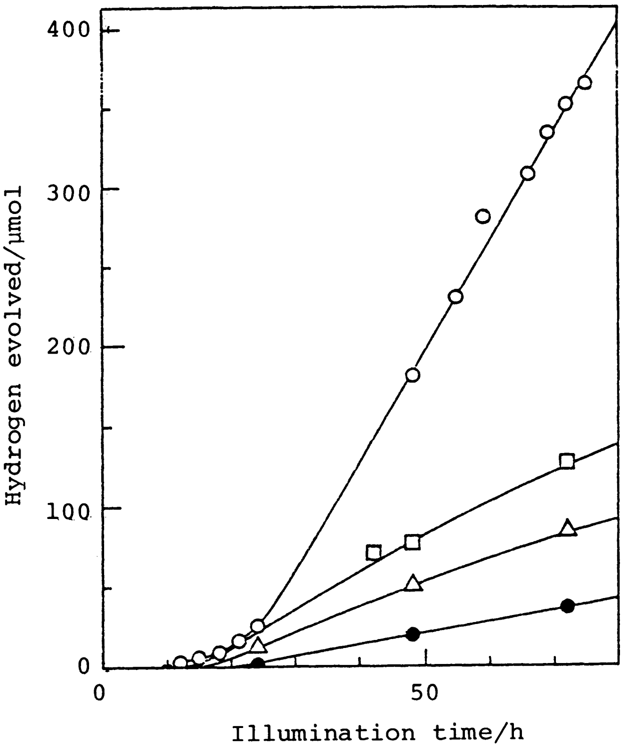

Fig. 2. The amount of hydrogen evolved from aqueous ethanol (50 vol %) as a function of illumination time.
(○) Pt(Ag)/Si/polypyrrole, (△) Pt/Si, (□) Ag/Si/polypyrrole, (●) Bare Si.

a little the activity of the photocatalysts. The hydrogen evolution should be enhanced by platinization; but the passivated surfaces cannot contribute to the photocatalytic reaction, and remarkable enhancement of the rate of hydrogen evolution would not arise. The photocatalysts whose anodic surfaces were coated with polypyrrole showed longer lifetime than the uncoated ones. It has already been shown for polypyrrole-coated n-type Si photoelectrodes[10-12)] that photoanodic reactions can occur on the coated surfaces with retardation of the passivation.

The quantum efficiency of hydrogen evolution at Pt(Ag)/Si/polypyrrole, which showed the highest activity for the hydrogen evolution among the photocatalysts examined here, was determined at 550 nm. The monochromatic light was obtained by using an interference filter, and the number of incident photons was measured with the use of an Eppley thermopile. The result was 2.1 %, and better results are expected by more appropriate choice of preparation conditions of the surface coating.

The procedures of the coating employed in this study is quite simple; it is enough just to illuminate Si powders in the solutions suitable for simultaneous photodeposition. Therefore, application of the present method of the surface modification to other semiconductor powders which are unstable in the presence of water will also be of significance.

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