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Photochemical diodes of a TiO_2 film prepared by a sol–gel method

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Photochemical diodes were prepared using a thin film of TiO_2 made from titanium isopropoxide by a sol–gel method. A half part of a conductive SnO_2 film plated on a quartz plate was coated with the TiO_2 film, and the other parts of the SnO_2 substrate were coated with a thin Pt film. The photochemical diode thus prepared shows photocatalytic activity for hydrogen evolution from aqueous ethanol solutions containing NaOH or $HClO_4$. No other products are detected in the gas phase. Hydrogen evolution from the Pt part is definitely observed, indicating electron transfer from the TiO_2 film to the Pt film through the SnO_2 film. Another type of photochemical diode, the TiO_2 film coated on a Pt plate, is found to show higher activity than the $TiO_2/SnO_2/Pt$ device for the hydrogen photo-evolution without any support electrolyte. Hydrogen evolution on this device, however, occurs on the TiO_2 side but not on the Pt side. These results are discussed in terms of a photo-electrochemical mechanism at semiconductor surfaces.

Keywords: photochemical diode; titanium dioxide; thin film; hydrogen photo-evolution; light–energy conversion

1. Introduction

Powdered TiO_2 shows higher activity for most of photocatalytic reactions than crystalline TiO_2 [1]. For example, metallized TiO_2 powder can photodecompose water into hydrogen and oxygen without any external bias [2], while crystalline TiO_2 requires some external bias for water photosplitting in a photo-electrochemical (PEC) cell [3]. Although the activity difference between powder and crystalline TiO_2 is not understood very well, it is partly because TiO_2 powder used in photocatalysis is usually anatase in crystal form whereas available crystalline TiO_2 is only rutile, which is less active for photoreduction of water to hydrogen than anatase due to a more positive flat band potential than that of anatase [4,5]. Powder CdS also exhibits much higher photocatalytic activity than crystalline CdS [6]. Semiconductor photocatalysts, however, have a fatal disadvantage that photoproducts such as oxygen and hydrogen get mixed after their evolution though photo-oxidized and reduced products are separately formed at different sites of photocatalysts. Photochemical diodes [7] as well as PEC cells indeed produce products separately at a semiconductor and a counter electrode, but powder semiconductors cannot be used for this purpose. We have found that a transparent thin film of TiO_2 prepared from iso-$Ti(OC_3H_7)_4$ by a sol–gel method consists of small particles of anatase and exhibits photocatalytic activity for hydrogen evolution from alcoholic solutions when loaded with small Pt particles. In the present paper, we describe properties of photochemical diodes of the TiO_2 film spin-coated on a conductive SnO_2 film or a Pt plate.

2. Experimental

Titanium isopropoxide was slowly added to an aqueous solution of 1,3-butanediol containing nitric acid under continuous stirring with a magnetic stirrer, and the resulting sol was further stirred for 15 h at room temperature. The TiO_2 sol thus prepared was spin-coated on a substrate under illumination of a far-infrared lamp. The thickness of the film was increased with decreasing spin speed or increasing concentration of TiO_2 in the sol. The spin-on film was dried at 110°C for 15 min and then calcined at 500°C for 4 h. The films are transparent in the visible light region. XRD shows no pattern when the film is calcined at 400°C, while anatase peaks are definitely observed after calcining the film at 500°C. Scanning electron microscopy reveals that the film comprises small TiO_2 particles and particle size increases with increase in film thickness. The maximum film thickness obtained was 500 nm.

A Schottky-type photochemical diode [7] was prepared in two ways: The brief designs for the diode are shown in fig. 1. One (fig. 1a) is made by using a transpar-

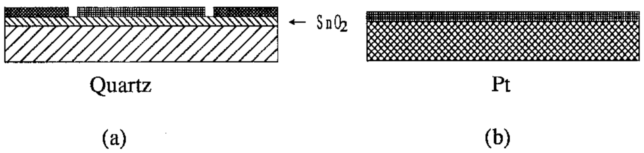

Fig. 1. Brief designs for two models of Schottky-type photochemical diodes: (a) $TiO_2/SnO_2/Pt$ (TSP) type, (b) TiO_2/Pt (TP) type.

ent, conductive SnO_2 film (ca. 300 nm thickness) coated on a quartz plate (36 × 24 mm) as a substrate. About a half part of the SnO_2 film is coated with the spin-on TiO_2 film (ca. 480 nm), and the other parts with a Pt film (ca. 60 nm) by vacuum evaporation. Care was taken to separate both parts completely to prevent direct electron transfer from TiO_2 to Pt. For this device, a photo-induced electron–hole pair could be separated at a space charge layer of the TiO_2 film, the electron being moved to the bulk and the hole being migrated to the surface. The electron could be moved to the SnO_2 film through an ohmic contact between the TiO_2 and the SnO_2 films, and then transferred to the Pt part through the SnO_2 film. Pt can catalyze water reduction with photo-induced electrons to evolve hydrogen. Hydrogen evolution is, therefore, expected at the Pt film when the device is illuminated in an aqueous alcoholic solution, which works as a sacrificial reducing reagent. Another model of the photochemical diode (fig. 1b) is prepared using a Pt plate (36 × 24 mm), one side of which is fully coated with the spin-on TiO_2 film. In this device, photo-induced electrons would be transferred from the TiO_2 film to the Pt plate, and therefore, hydrogen evolution is expected to occur at the Pt side when the TiO_2 side is irradiated in a reducing reagent solution.

Reactions were carried out in an evacuable circulating system equipped with a pyrex glass cell (50 mm in diameter) with a flat bottom. The sample can be put into the cell through a large taper joint connected to its upper side. After setting the sample in the cell, 20% ethanol solution is put into the cell until the sample is covered with the solution. Freeze-and-pumping cycle is then repeated twice for outgassing solutions as well as for evacuating gas phase. Light source is a 500 W high pressure Hg lamp that is filtered through a band pass filter (Toshiba UV-D33S, 240–400 nm), and the cell is illuminated from the bottom side using a mirror. The intensity of the incident photon flux was measured by chemical actinometry. Reaction products are sampled at intervals and, after passage through a cold trap at ca. −100°C to remove water, are analyzed with a quadrupole mass spectrometer.

3. Results and discussion

The spin-on TiO_2 films show no photocatalytic activity for hydrogen evolution from aqueous ethanol solutions. When the TiO_2 films are loaded with small Pt particles by a photodeposition method [8], the films become active for hydrogen evolution. This is because TiO_2 is inactive for electrochemical reduction of water. Photocatalytic properties of the platinized TiO_2 films will be reported in detail elsewhere.

The $TiO_2/SnO_2/Pt$ (TSP) photochemical diode shows a little activity for hydrogen evolution from the ethanol solution, and the yield of hydrogen evolution is significantly improved by addition of NaOH to the solution as shown in fig. 2. The rate of hydrogen evolution increases with increasing NaOH concentration. Since the TiO_2 film peels off from the SnO_2/quartz substrate in NaOH solution of higher

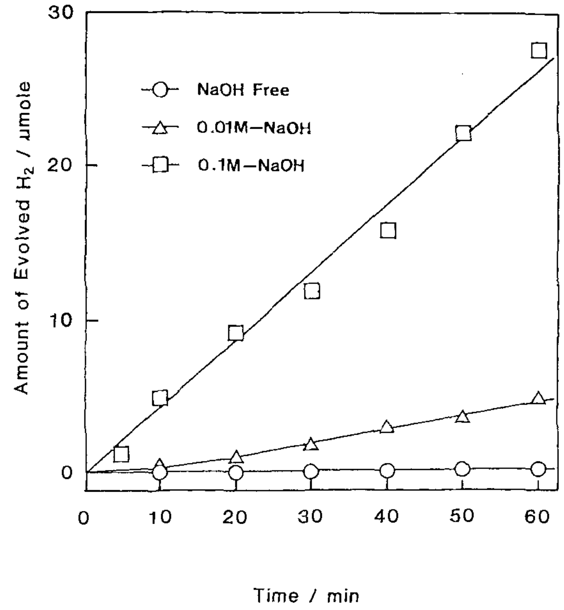

Fig. 2. Time dependence of the hydrogen photo-evolution from the TSP photodiode immersed in an aqueous ethanol solution with and without NaOH.

concentration than 0.1 M, effects of further increase in NaOH concentration were not examined. The addition of $HClO_4$ also enhances the hydrogen evolution. In a solution involving 0.1 M $HClO_4$, the rate of hydrogen evolution was similar to that observed for 0.1 M NaOH solution. These results indicate that the presence of support electrolyte is indispensable for the operation of this type of photochemical diode. This is because the semiconductor photo-anode and the metal counter electrode in this device are spatially separated so much, like in a photoelectrochemical cell, that the ion conductivity between these electrodes must be reduced by support electrolyte. Metallized, powdered semiconductor, a typical photocatalyst, on the other hand, virtually requires no support electrolyte for hydrogen photo-evolution from the aqueous solution of reducing agent [1]. This convenience of the powder photocatalysts is owing to their structure; the metal parts are so close to the semiconductor that ions can move between metal and semiconductor even if the ion conductivity is very low.

The formation of bubbles caused by gas evolution was observed mainly at the Pt side and also at the TiO_2 side to a lesser extent. As mentioned before, the gas evolved at the Pt film could be hydrogen, and the gas formed at TiO_2 the photo-oxidized products of ethanol, probably CO_2. Total analysis of the gas phase by mass spectrometry, however, indicated that hydrogen was certainly produced but no other products were present in the gas phase. Although CO_2 may react with NaOH in NaOH solution to form $NaHCO_3$ or Na_2CO_3 immediately after evolution, no CO_2 was detected when a $HClO_4$ solution was used as an electrolytic solution, indicating hydrogen evolution at the TiO_2 electrode. There is a possibility of hydrogen evolving at illuminated TiO_2 surface in alcoholic solutions. It is widely known that a photocurrent of TiO_2 PEC cell is nearly doubled by the addition of alcohol, and this phenomenon is called current doubling effect [9]. Hydrogen photo-evolution from the suspension of Pt-loaded TiO_2 powder in an aqueous alcoholic solution sometimes exceeds 100% of quantum yield [10], probably due to the same effect as the current doubling effect. In current doubling processes, the photo-oxidation of alcohol at a semiconductor surface leads to formation of intermediate species, the oxidation potential of which is more negative than the flat band potential of the semiconductor. As a result, electron transfer is thought to occur from the intermediate species to the conduction band of the semiconductor. Although a detailed feature of the intermediate species is not exactly understood, dehydrogenation of the intermediate species may occur during the current doubling processes. Another possibility is the reduction of water at the TiO_2 sites by electrons produced from the intermediate species. Fine particles of TiO_2 are easily photoreduced in the presence of alcohol to form Ti^{3+}, and reduced TiO_2 reacts with water to produce hydrogen even in the dark [10].

The illuminated TiO_2/Pt (TP) photochemical diode produces hydrogen from an ethanol solution at a higher rate than the illuminated TSP diode as shown in fig. 3. Although this arises partly from the fact that the TP diode has twice larger area of the TiO_2 film than the TSP diode as seen in fig. 1, the quantum yield of hydrogen evolution, i.e., a specific photocatalytic activity, is obviously higher for the former. The TP device also exhibits higher photocatalytic activity for the hydrogen photo-evolution than the spin-on TiO_2 film (36 x 24 mm) on which Pt particles are photodeposited. This result may indicate an advantage of TP-type

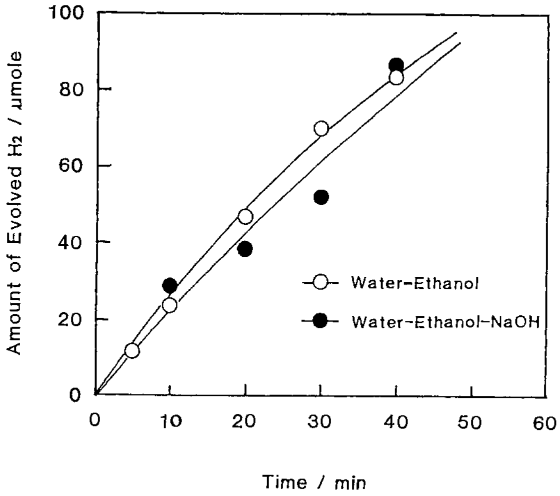

Fig. 3. Time dependence of the hydrogen photo-evolution from the TP photodiode immersed in an aqueous ethanol solution with and without NaOH.

photochemical diode to metal-loaded photocatalysts, since the metal particles on photocatalysts would reduce light absorption and sometimes become a recombination center for electron and hole. The addition of NaOH to the solution gives no effects on the yield of hydrogen evolution, indicating that this photoelectrochemical device can operate without support electrolyte. The formation of bubbles was observed at the TiO_2 side, but not at the Pt side. The reaction product in the gas phase was again hydrogen alone.

No effect of NaOH on the yield of hydrogen production is reasonable for TP device, since TiO_2 is directly contacted with Pt so that low ion conductivity between the TiO_2 film and the Pt plate is not a requisite condition for photo-electrochemical reactions in the TP diode like in metallized semiconductor photocatalysts. The reason for no hydrogen evolution at the TiO_2 side would be attributable to porous structure of the spin-on TiO_2 film. Small molecules as well as ions could migrate through the TiO_2 film that consists of small particles. If H^+ ions come at the Pt surface through the TiO_2 film, then the photo-induced electrons transferred from TiO_2 to Pt would react with H^+ at the spot without migrating to the back side of the Pt plate. In such a case, hydrogen evolution occurs at the TiO_2 side of the Pt plate. The maximum quantum yield of hydrogen evolution by the TP diode is estimated to be more than 10%. It should, however, be noted here that an uncleaned Pt plate is much less active for electrochemical hydrogen evolution from water than a Pt plate with Pt black or activated Pt plate. The yield of hydrogen evolution may be improved by use of active Pt.

In summary, the photochemical diodes made of the spin-on TiO_2 film are found to operate properly for hydrogen evolution from aqueous ethanol solutions. Electron transfer from the TiO_2 part to the Pt part through SnO_2 film is demonstrated by bubbling up of hydrogen from the Pt part of the TSP diode. Although the efficiency of hydrogen evolution by these photochemical diodes is not so high as compared to Pt-loaded TiO_2 powder photocatalysts, it may be improved by reducing ohmic resistance of the SnO_2 film or by activation of the Pt film or plate. The TP diode was found a promising type of photodevice for efficient photo-electrochemical reactions.

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