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Photocatalytic Hydrogen Production from Aqueous Solutions of Alcohol as Model Compounds of Biomass Using Visible Light-Responsive TiO_2 Thin Films

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Abstract Visible light-responsive TiO_2 (Vis-TiO_2) thin films were prepared by a radio frequency magnetron sputtering deposition method. The photoelectrochemical performance was improved by adding various kinds and concentrations of alcohol, i.e., model compounds of biomass, to water. The separate evolution of pure H_2 was observed to proceed efficiently on these Vis-TiO_2 thin films under visible light irradiation by using an aqueous solution of methanol.

Keywords Vis-TiO_2 thin films · Decomposition of water · Separate evolution of hydrogen

1 Introduction

Since the pioneering work of Honda and Fujishima [1, 2] on the decomposition of H_2O into H_2 and O_2 with a photoelectrochemical cell consisting of Pt and TiO_2 electrodes under a small electric bias, H_2 production using photocatalysts has been considered a promising environmentally benign energy production process. And, the production of H_2 and O_2 by water splitting with various photocatalysts has been reported since the pioneering work in 1972 [3–13]. Furthermore, the promotion of the photocatalytic evolution of H_2 with aqueous solutions of alcohol has also been reported on various photocatalysts since the 1980s [14–19]. However, most of these reports involve powdered photocatalysts which yield a mixture of H_2 and O_2 since their redox reaction sites are in close proximity. The separate evolution of H_2 and O_2 is strongly desired to obtain pure H_2 and O_2 gas that can be directly utilized as fuel on a large, global scale. To address such concerns, the development of thin film photocatalysts able to evolve H_2 and O_2 separately under solar light irradiation is vital [13].

TiO_2 thin film photocatalysts have been investigated for various environmentally significant applications and there have been many efforts to improve their photocatalytic activity [20, 21]. We have also reported that visible light-responsive TiO_2 (Vis-TiO_2) thin films which evolve H_2 and O_2 separately under solar light irradiation could be prepared using an radio frequency magnetron sputtering (RF-MS) deposition method [22–24]. Various spectroscopic analyses have revealed that a decrease in the O/Ti ratio from the surface ($O/Ti = 2.00$) to the bottom ($O/Ti = 1.93$) may play a significant role in the modification of the electronic properties of these TiO_2 thin films, enabling them to absorb and operate under visible light irradiation [22]. In the present work, we have added aqueous solutions of alcohol to water in order to improve the photoelectrochemical and photocatalytic performances of Vis-TiO_2 thin films. Special attentions will be focused on the effect of the addition of various kinds of alcohols on photoelectrochemical properties and photocatalytic activities of Vis-TiO_2 thin films.

2 Experimental

2.1 Preparation of Visible-Light Responsive TiO_2 Thin Films

The Vis-TiO_2 thin films were prepared by an RF-MS deposition method using a calcined TiO_2 plate (High Purity

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Chemicals Lab., Corp., Grade: 99.99%) as the source material and Ar gas (99.995%) as the sputtering gas. The base vacuum pressure and working pressure were set at 6.0×10^{-4} and 2.0 Pa, respectively. The substrate was placed parallel to the sputtering target surface with substrate-target distances of 75 mm. The film was prepared on a Ti metal substrate at a substrate temperature (Ts) of 873 K and RF power of 300 W. The thickness of the sputtered TiO_2 thin film was about 3 µm. For comparison, the TiO_2 thin films which could absorb only UV light of wavelengths shorter than 380 nm (hereafter, designed UV-TiO_2) were prepared at $Ts = 473$ K.

2.2 Photoelectrochemical Measurements

The photoelectrochemical properties of the Vis-TiO_2 thin film prepared on Ti metal substrate (Vis-TiO_2/Ti) electrodes were investigated with a potentiostat (HZ3000, Hokuto Denko) consisting of the Vis-TiO_2/Ti and Pt electrodes as the working and counter electrodes, respectively. The working electrode was irradiated by a 500 W Xe arc lamp in 0.1 M $HClO_4$ solution that was mechanically stirred and degassed by purging with 99.99% pure Ar gas during the experiments. The unfiltered light intensity of a 500 W Xe arc lamp was measured by a power meter (OPHIR, Nova II) to be 542.5 mW/cm^2.

2.3 Photocatalytic Reactions

The photocatalytic activity of the Vis-TiO_2 thin film was investigated for the separate evolution of H_2 from an aqueous solution of methanol under visible light irradiation. The photocatalytic H_2 production reactions were carried out in an H-type glass container connected to a conventional vacuum system. Prior to the reaction, the reaction cell was de-aerated by purging with 99.99% pure Ar gas for 3 h. Visible light irradiation was carried out with a 500 W Xe arc lamp through a colored glass filter (Y-45, Asahi Techno Glass). The evolved gases from the aqueous solution of methanol were analyzed by gas chromatography.

2.4 Characterization

Ionization potential, that is, valence band maximum energy of TiO_2 thin film was analyzed by UV photo-electron spectroscopy in air (PESA, AC-2, Riken Keiki). The flat band potential (E_{FB}) was assessed by current-potential characteristics under light irradiation longer than 300 nm using a standard three-electrode system consisting of a working electrode (TiO_2/Ti), Pt counter electrode and SCE reference electrode in an Ar-purged 0.05 M NaOH aqueous solution.

3 Results and Discussion

3.1 Band Position of the Vis-TiO_2 Thin Film

In order to assess the flat band potential of the UV-TiO_2/Ti and Vis-TiO_2/Ti electrodes, the current-potential characteristics were examined under UV light irradiation ($\lambda \geq 300$ nm), as shown in Fig. 1. It can be seen that the zero-current potential is different for these two electrodes. The zero-current potential of UV-TiO_2/Ti (−0.91 V vs. SCE at pH 12.3) was more negative than that of Vis-TiO_2/Ti (−0.82 V vs. SCE at pH 12.3). This potential is equivalent to the flat band potential (E_{FB}) in polycrystalline TiO_2, from which the conduction band potential (E_{CB}) can be evaluated [25].

Moreover, in order to investigate the valence band potential (E_{VB}) of these electrodes, EPSA measurements were also carried out. If the incident photon energy is more than the ionization potential of the semiconductor, i.e., the energy required to excite an electron from the E_{VB} to vacuum level, electron emissions occur. Figure 2 shows the square root of the photoelectron emission intensity as a function of the irradiated photon energy analyzed by EPSA for Vis-TiO_2 and UV-TiO_2. The threshold energy of Vis-TiO_2 (4.6 eV) shifts to lower energy regions than that of UV-TiO_2 (5.1 eV), suggesting that the valence band edge of Vis-TiO_2 is located more negative than that of UV-TiO_2. These results suggest that these modifications in the edge positions of the conduction band as well as valence band enable visible light absorption of Vis-TiO_2.

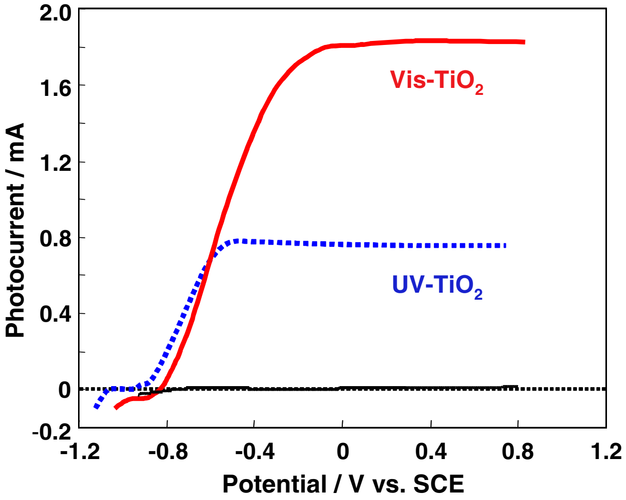

Fig. 1 Current-potential curves of Vis-TiO_2/Ti and UV-TiO_2/Ti electrodes under UV light ($\lambda > 300$ nm) irradiation. Electrolyte: Ar-purged 0.05 M NaOH aq (pH 12.3)

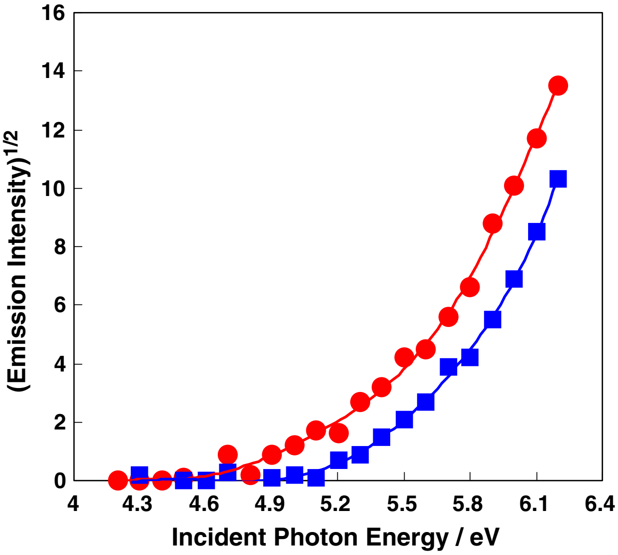

Fig. 2 The square root of the photoelectron emission intensity as a function of the irradiated photon energy analyzed by EPSA for the Vis-TiO_2 (*circle*) and UV-TiO_2 (*square*)

3.2 Photoelectrochemical Properties of the Vis-TiO_2 Thin Film

The photoelectrochemical properties of the Vis-TiO_2/Ti electrodes were examined with an aqueous solution of 0.1 M $HClO_4$ (pH = 1.0) and measured with a bias of 0 V. Figure 3 shows the photocurrent observed for the Vis-TiO_2/Ti electrode as a function of the incident light wavelength, which was controlled by cut-off filters. The photocurrents were observed under visible light up to approximately 500 nm and increased after the addition of 10 vol% methanol under UV and visible light irradiation, indicating that the photooxidation of methanol occurred in preference to that of H_2O and that the charge recombination was suppressed by the addition of methanol due to its hole scavenging effect. These tendencies corresponded with the photocatalytic activity for H_2 evolution in the presence of methanol.

The dependence of the photocurrent-wavelength was observed before and after adding various kinds and concentrations of alcohol to water. In particular, the photocurrent as a function of the concentration of methanol at the Vis-TiO_2/Ti electrode was investigated, as shown in Fig. 4. The concentration of methanol was adjusted at 5, 10, 20, and 50 vol%. The photocurrent was observed to increase with the concentrations and to saturate at 10 vol% under both UV ($\lambda \geq 300$ nm) and visible light ($\lambda \geq 450$ nm) irradiation. The IPCE value obtained at a wavelength of 360 nm was 24% with a bias of 0 V. The number of photoformed holes in the Vis-TiO_2 thin films was constant under the intensity of a 500 W Xe arc lamp (542.5 mW/cm^2). These results suggest that the concentration of the photoformed holes in the oxidation of methanol was insufficient for the oxidation of methanol in a concentration range higher than 10 vol% using the present light source. The photocurrent, as a function of the concentration of ethanol, was also investigated and the optimum concentration was found to be the same as methanol under both UV and visible light irradiation.

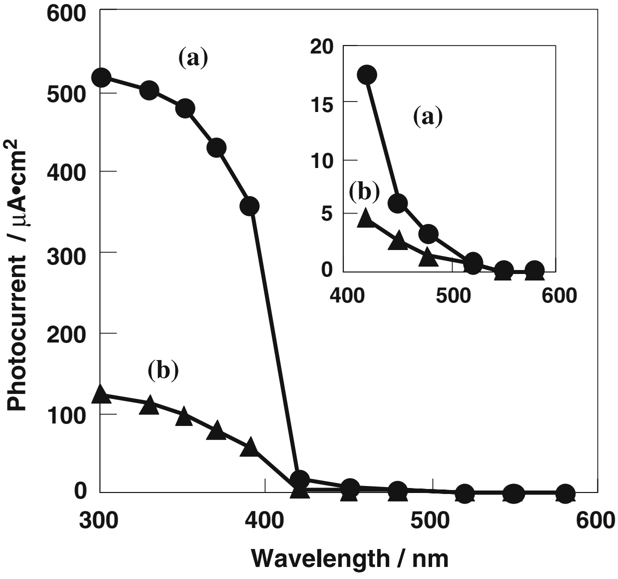

Fig. 3 Relative photocurrents as a function of the cut-off wavelength of the incident light for the Vis-TiO_2/Ti electrode measured at 0 V: (*a*) in 0.1 M $HClO_4$ + 10 vol% CH_3OH aqueous solution; and (*b*) in 0.1 M $HClO_4$ aqueous solution

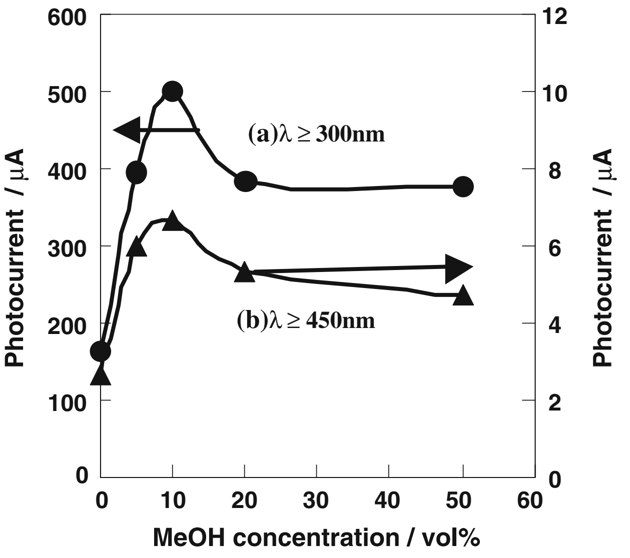

Fig. 4 Photocurrent densities as a function of the concentration of methanol for the Vis-TiO_2/Ti electrodes measured at 0 V under: (*a*) UV light ($\lambda \geq 300$ nm) irradiation; and (*b*) visible light ($\lambda \geq 450$ nm) irradiation

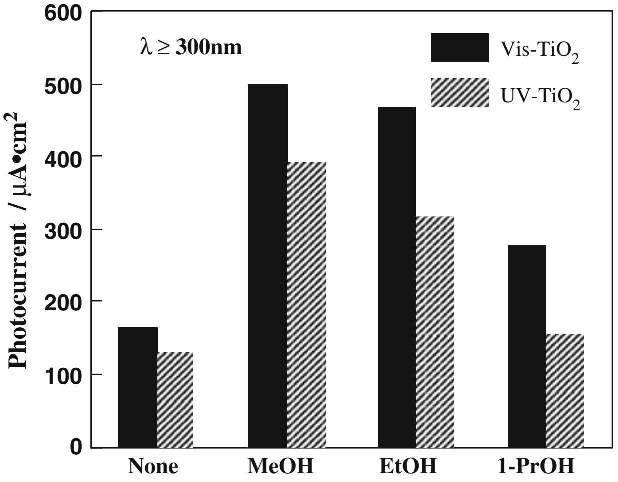

Fig. 5 Photocurrent densities of the UV-TiO_2/Ti, Vis-TiO_2/Ti electrodes measured at 0 V in various aqueous solutions of alcohol under UV light ($\lambda \geq 300$ nm) irradiation. Electrolyte: 0.1 M $HClO_4$ + 10 vol% aqueous alcohol solution

Figure 5 shows the photocurrent densities on the UV-TiO_2/Ti, Vis-TiO_2/Ti electrodes in various aqueous solutions of alcohol under UV light ($\lambda \geq 300$ nm) irradiation. The concentration of alcohol was adjusted at 10 vol%. The photocurrent was found to increase after the addition of various kinds of alcohol to water and the highest photocurrent was observed for methanol. Moreover, the photocurrent was observed to decrease with an increase in the size of the alcohol molecules, indicating that the smaller the molecule size, the more easily alcohol could adsorb to the surface of the TiO_2 thin film [17, 19]. This tendency was also observed under visible light ($\lambda \geq 450$ nm) irradiation on the Vis-TiO_2/Ti electrode, while the UV-TiO_2/Ti electrode did not exhibit any photoelectrochemical response under the same conditions.

3.3 Photocatalytic H_2 Production Reactions

The photocatalytic activities of Vis-TiO_2 or UV-TiO_2 thin films were investigated for the separate evolution of H_2 from an aqueous solution of methanol under visible light of wavelengths longer than 450 nm. The opposite sides of Vis-TiO_2/Ti or UV-TiO_2/Ti, where the Ti metal surface is exposed, was deposited with Pt by an RF-MS method using a RF power of 70 W at $Ts = 298$ K. The prepared photocatalyst was then mounted at the center of an H-type glass container, separating the two aqueous solutions. A Nafion film was also mounted on the H-type glass container to provide the electrical connections which would allow electron transfers between the two separated aqueous phases, playing the same role as a salt bridge between two aqueous phases. The TiO_2 side of the photocatalyst was immersed in 1.0 M NaOH aqueous solution and the Pt side in 0.5 M H_2SO_4 aqueous solution in order to add a small chemical bias (0.826 V) to assist the electron transfer from the TiO_2 to Pt side through the metal substrate. As shown in Fig. 6, the separate evolution of H_2 from an aqueous solution of methanol proceeded on the Vis-TiO_2 thin films under visible light irradiation, while this reaction did not proceed on the UV-TiO_2 thin films. By adding 10 vol% methanol to 1.0 M NaOH aqueous solution at the TiO_2 side, the separate evolution rate of H_2 increased from 0.08 to 0.52 μmol/h, indicating that the use of alcohol was an effective method in improving the photocatalytic activity.

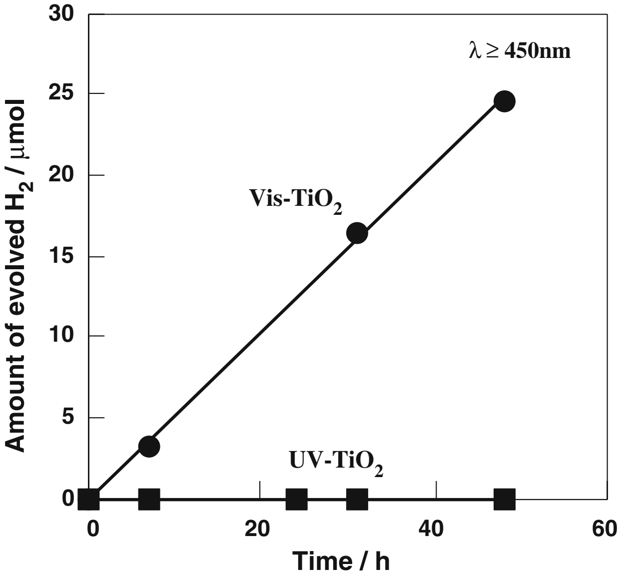

Fig. 6 Reaction time profiles of the separate evolution of H_2 from an aqueous solution of methanol on the Vis-TiO_2 and UV-TiO_2 thin film photocatalysts under visible light ($\lambda \geq 450$ nm) irradiation in an H-type glass container

It should be emphasized that in the present H-type reaction system using TiO_2 thin film photocatalysts, H_2 is produced only from water and not from alcohol since alcohol is not present on the Pt side but only on the TiO_2 side, which is in contrast to powdered TiO_2 photocatalytic systems in which H_2 is produced not only from water but also from alcohol. [14, 26]

4 Conclusions

The photoelectrochemical performance of the Vis-TiO_2 thin film was found to be improved with aqueous solutions of alcohol under both UV and visible light irradiation. The highest photocurrent was observed with methanol. The separate evolution rate of H_2 from an aqueous solution of methanol was estimated to be 0.52 μmol/h under visible light irradiation.

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