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The effect of the hydrothermal treatment with aqueous NaOH solution on the photocatalytic and photoelectrochemical properties of visible light-responsive TiO_2 thin films

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Abstract

The effect of the hydrothermal treatment with aqueous NaOH solution on the photoelectrochemical and photocatalytic properties of visible light-responsive TiO_2 thin films prepared on Ti foil substrate (Vis-TiO_2/Ti) by a radio-frequency magnetron sputtering (RF-MS) deposition method has been investigated. The hydrothermally treated Vis-TiO_2/Ti electrodes exhibited a significant increase in their photocurrent under UV and visible light irradiation as compared to untreated Vis-TiO_2/Ti electrode. SEM investigations revealed that the surface morphology of Vis-TiO_2/Ti are drastically changed from the assembly of the TiO_2 crystallites to the stacking of nanowires with diameters of 30–50 nm with increasing hydrothermal treatment time (3–24 h), accompanying the increase in their surface area. The separate evolution of H_2 and O_2 from water under solar light irradiation was successfully achieved using the Vis-TiO_2/Ti/Pt which is hydrothermally treated for 5 h, while the H_2 evolution ratio was 15 μmol h^{-1} in the early initial stage, corresponding to a solar energy conversion efficiency of 0.23%.

Keywords: Vis-TiO_2 thin film; Hydrothermal treatment; Photocatalyst; Visible and solar light; Water splitting reaction

1. Introduction

Recently, the water splitting reaction using photocatalysts under visible or solar light irradiation has been regarded as an ideal method of converting solar energy directly into clean fuel, namely, hydrogen energy [1–12]. So far, several powdered semiconducting oxides [2,3] or oxynitrides [4] have been found to exhibit high activity for the water splitting reaction under visible light irradiation. It has been also reported that TiO_2 catalysts deposited with Pt (Pt/TiO_2) can decompose gaseous or liquid water into H_2 and O_2 stoichiometrically under UV light irradiation [5–7]. However, these TiO_2 catalysts can operate only under UV light irradiation. Strongly desired is the development of simple preparation method for visible light-responsive TiO_2 photocatalysts. Previously, we have reported the successful preparation of visible light-responsive TiO_2 (Vis-TiO_2) thin films by a radio-frequency magnetron sputtering (RF-MS) deposition method at high substrate temperature and their applications for the separate evolution reaction of H_2 and O_2 from water under visible light irradiation [8–12]. However, since the high substrate temperature (873 K) during deposition leads to a small surface area of Vis-TiO_2 thin film, surface modification processes are desired to enlarge its surface area. Recently, Kasuga et al. have found that TiO_2 nanotubes can be prepared by the simple one-step hydrothermal treatment of TiO_2 crystals with NaOH aqueous solution [13,14]. Furthermore, it has been reported that nanowire TiO_2 thin films [15] as well as rutile nanotube-like TiO_2 electrode [16] can be prepared by hydrothermal treatment of calcined Ti foil in NaOH aqueous solution and the films exhibited a remarkable enhancement in the efficiency of photoelectrochemical oxidation of water [15] or organic compounds [16] under UV light irradiation.

In the present work, Vis-TiO_2 thin films prepared on Ti foil substrate were hydrothermally treated with NaOH aqueous solution in order to improve their photoelectrochemical and

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photocatalytic performances through the chemical surface modification. Special attentions will be focused on the effect of the hydrothermal treatment of Vis-TiO_2 thin films on their characteristics, photoelectrochemical properties, and photocatalytic activities for the separate evolution of H_2 and O_2 from water under solar light irradiation.

2. Experimental

Vis-TiO_2 thin films were prepared on Ti foil substrate by an RF-MS deposition method using a TiO_2 target (High Purity Chemicals Lab., Corp., Grade: 99.99%) as the source material and Ar gas (99.995%) as the sputtering gas. Before the deposition of Vis-TiO_2 thin film, Ti foil substrate was calcined at 723 K for 5 h in air. The calcined Ti foil substrate was positioned within the camber of the RF-MS deposition apparatus in the center parallel above the TiO_2 target as source material at a target-to-substrate distance of 80 mm in accordance with previous works [8–12]. The chamber was evacuated to less than 6.0×10^{-4} Pa followed by the introduction of Ar at 2.0 Pa. Vis-TiO_2 and UV-TiO_2 thin films deposited on the Ti foil substrate (Vis-TiO_2/Ti, UV-TiO_2/Ti) were then prepared by inducing an RF power of 300 W with the substrate temperature at 873 K and 473 K, respectively. According to our previous works [8–12], Vis-TiO_2 thin film deposited on quartz substrate prepared in the same condition exhibited considerable absorption in visible light regions, while UV-TiO_2 thin films exhibited absorption only in the UV region ($\lambda < 380$ nm). Vis-TiO_2/Ti were then reacted with 10 M NaOH aqueous solution in a Teflon-lined stainless autoclave and kept for 5–24 h at 393 K. After cooling down to room temperature, the films were washed with 0.1 M HCl solution. These hydrothermally treated Vis-TiO_2/Ti were referred to as NaOH(*X*)-Vis-TiO_2/Ti, where *X* is the time (h) of hydrothermal treatment.

The surface morphologies of the films were examined by scanning electron microscopy (SEM, S-4500, Hitachi) and the crystal structures were investigated by X-ray diffractometer analysis (XRD, XRD-6100, Shimadzu). The chemical composition of the thin films were investigated by X-ray photoelectron spectroscopy (XPS, ESCA-3200, Shimadzu). The photoelectrochemical properties of the film electrodes (Vis-TiO_2/Ti and NaOH(*X*)-Vis-TiO_2/Ti) were evaluated using a potentiostat (HZ3000, Hokuto Denko) with a three-electrode cell that consists of the film electrode, a Pt electrode and a saturated calomel electrode (SCE) as the working, counter and reference electrodes, respectively. The working electrode was irradiated from the front side (light incident on the electrolyte/electrode interface) by a 500 W Xe lamp through a color glass filter in 0.25 M K_2SO_4 aqueous solution which was mechanically stirred and degassed by purging with 99.99% pure Ar gas before and during the experiment. The working electrode area was about 0.2 cm^2. The separate evolution of H_2 and O_2 from water was investigated by using an H-type Pyrex glass container connected to a conventional vacuum system (10^{-3} Pa). The detailed experimental procedures have been described in previously reported works [8–12]. The back side of Vis-TiO_2/Ti or NaOH(*X*)-Vis-TiO_2/Ti, where the Ti metal surface is exposed, was deposited with Pt by an RF-MS deposition method with an RF power of 70 W under a substrate temperature at 298 K. These Pt-loaded TiO_2 thin films were referred to as Vis-TiO_2/Ti/Pt and NaOH(*X*)-Vis-TiO_2/Ti/Pt. The container consists of two water phases separated by a TiO_2 thin film and proton-exchange membrane (Nafion film). Prior to the reaction, the reaction cell was de-aerated by purging with 99.99% pure Ar gas for 3 h. Light irradiation was carried out with a sunlight-gathering system (Laforet Engineering, XD-50D) and the evolved H_2 and O_2 were analyzed by a gas chromatograph (GC, G2800-T, Yanaco) with a thermal conductivity detector (TCD).

3. Results and discussion

Photoelectrochemical measurements were performed using a standard three-electrode system. Fig. 1 shows the current–potential curves of Vis-TiO_2/Ti and NaOH(5)-Vis-TiO_2/Ti electrodes. For both electrodes, anodic photocurrent increased with an increase in anodic bias, while the dark current was negligible under scanning potentials of −0.5 to +1.5 V versus SCE. These results suggest the anodic oxidation of water to oxygen by photogenerated holes occurs on these electrodes under UV ($\lambda \geq 300$ nm) and visible light ($\lambda \geq 420$ nm) irradiation. Furthermore, significant increase in the anodic photocurrent under UV and visible light irradiation was observed after hydrothermal treatment. As reported in previous works, the Vis-TiO_2 thin film has a unique declined O/Ti composition from the surface (2.00 ± 0.01) to the deep inside bulk (1.93 ± 0.01) [8–12]. Such a unique anisotropic structure

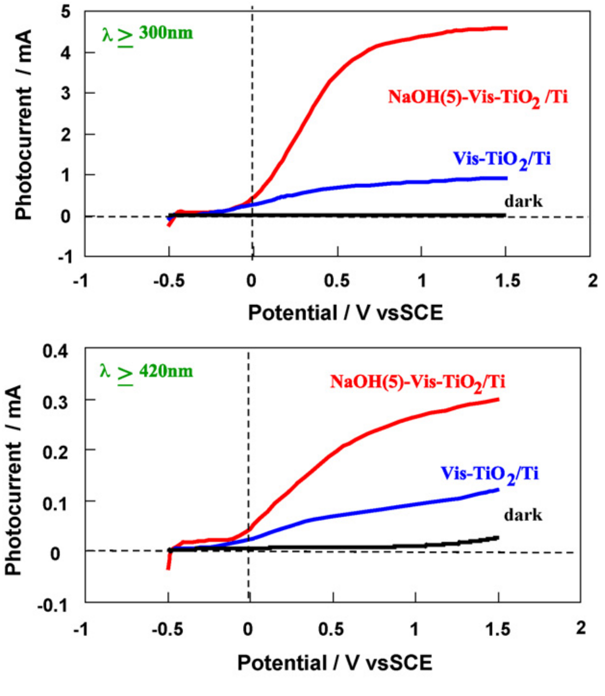

Fig. 1. Current–potential curves of Vis-TiO_2/Ti and NaOH(5)-Vis-TiO_2/Ti electrodes under UV ($\lambda \geq 300$ nm) and visible light ($\lambda \geq 420$ nm) irradiation. Light source: 500 W Xe lamp.

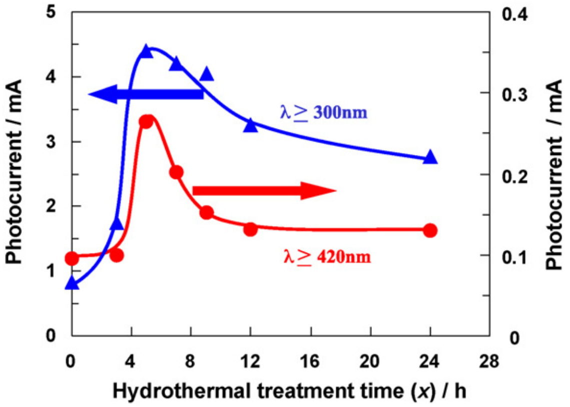

Fig. 2. Anodic photocurrent of NaOH(X)-Vis-TiO_2/Ti electrodes as a function of the hydrothermal treatment time with NaOH aqueous solution under UV ($\lambda \geq 300$ nm) and visible light irradiation ($\lambda \geq 420$ nm). Measurements were performed under a bias of +1.0 V vs. SCE.

was considered to play an important role in the modification of the electronic properties, thus, enabling the absorption of visible light.

Fig. 2 shows the anodic photocurrent of the NaOH(X)-Vis-TiO_2/Ti electrode as a function of the hydrothermal treatment time with NaOH aqueous solution. These measurements were carried out with a bias of +1.0 V versus SCE in 0.25 M K_2SO_4 aqueous solution. The observed photocurrents correspond to the oxidation of H_2O by the photoformed holes. Under UV ($\lambda \geq 300$ nm) and visible light ($\lambda \geq 420$ nm) irradiation, the anodic photocurrent increased with an increase in the hydrothermal treatment time, reaching a maximum at 5 h and then decreased above 7 h hydrothermal treatment. It should be noted that the anodic photocurrent is increased by hydrothermal treatment regardless of the hydrothermal treatment time (3–24 h) as compared to that of the Vis-TiO_2/Ti electrode. Thus, it was clearly shown that hydrothermal treatment with NaOH aqueous solution is effective for the improvement of the photoelectrochemical performance of the Vis-TiO_2/Ti electrode.

Fig. 3 shows the SEM images of Vis-TiO_2/Ti and NaOH(X)-Vis-TiO_2/Ti. Surface morphology of Vis-TiO_2/Ti was drastically changed by the hydrothermal treatment. After 5 h hydrothermal treatment, small sheet-like structures are started to be observed on the surface of the large TiO_2 crystallites, while these are completely covered with the accumulation of sheet-like structures after hydrothermal treatment for 12 h. After hydrothermal treatment for 24 h, complicated surface structures consisting of the numerous stacking of nanowires with diameters of 30–50 nm can be observed, showing a remarkable contrast to the Vis-TiO_2/Ti without hydrothermal treatment. In addition, an increase in the surface areas was

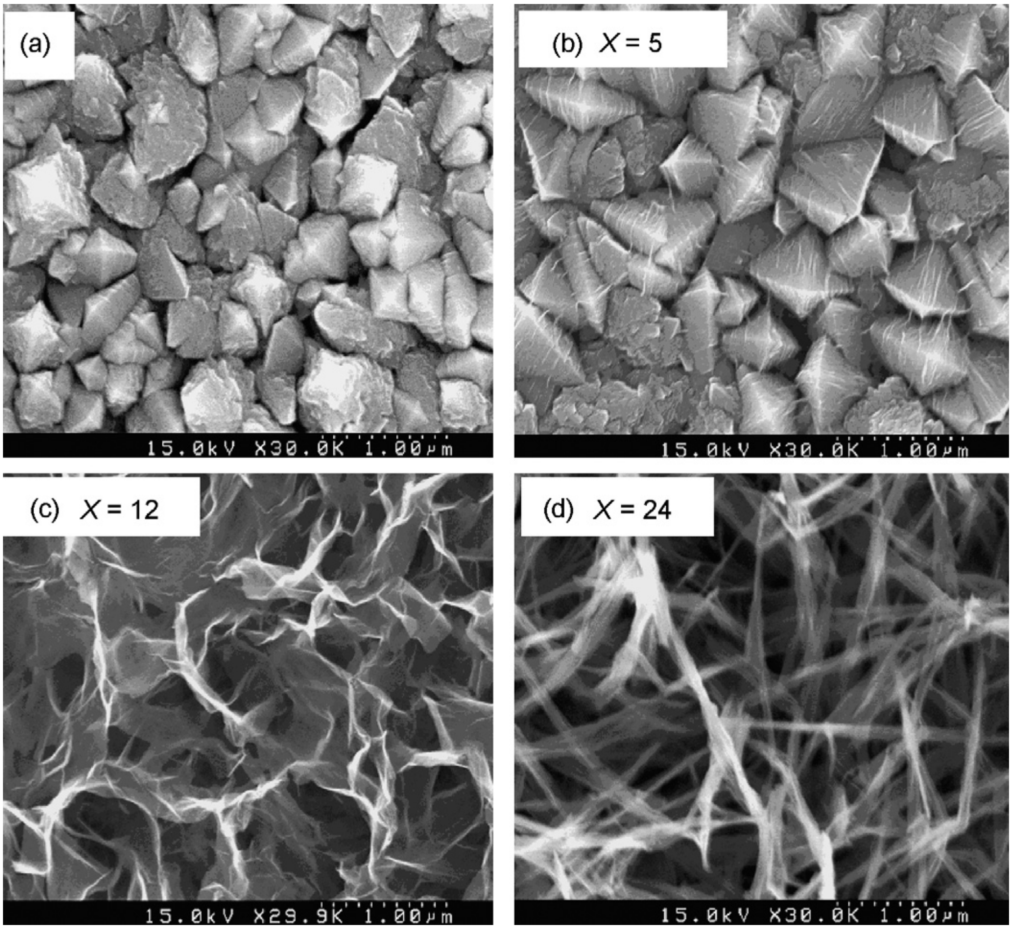

Fig. 3. SEM images of (a) Vis-TiO_2/Ti and (b–d) NaOH(X)-Vis-TiO_2/Ti.

Table 1
Surface areas of Vis-TiO_2/Ti and NaOH(*X*)-Vis-TiO_2/Ti

Sample	A_{bet}[a] (cm^2)
Vis-TiO_2/Ti	467
NaOH(5)-Vis-TiO_2/Ti	716
NaOH(12)-Vis-TiO_2/Ti	1328
NaOH(24)-Vis-TiO_2/Ti	3040

[a] Sample size: 5 mm × 20 mm.

observed with increasing hydrothermal treatment by BET surface measurements as shown in Table 1. The hydrothermal treatment of Vis-TiO_2 thin film can be divided into two stages. At the first stage (hydrothermal treatment time <5 h), the surface morphology changes of Vis-TiO_2 thin films are not significant, while the drastic increase in the surface areas as well as the anodic photocurrents can be observed. At the second stage (hydrothermal treatment time >5 h), the nanowire structures start to be formed on Vis-TiO_2 thin film accompanying the increase in the surface area, while the anodic photocurrent gradually decreases with the increase in the hydrothermal treatment time. From these results, it can be considered that the drastic increase in the anodic photocurrent is ascribed to the moderate surface modification by hydrothermal treatment within 5 h which increases the surface area of Vis-TiO_2 thin film, while further hydrothermal treatment decreases the anodic photocurrent through the structural transformation of Vis-TiO_2 thin film into the inactive TiO_2 nanowires having high surface areas.

Fig. 4 shows the effect of the hydrothermal treatment on the XRD patterns of Vis-TiO_2/Ti. The intensity of the peaks due to the rutile phase decreased with an increase in the hydrothermal treatment time, and at the same time, the peaks due to titanates at 2θ of around 10° start to be observed [17]. The decrease in the photocurrent after prolonged hydrothermal treatment can, therefore, be ascribed to the formation of titanates such as $A_2Ti_3O_7$ or $A_2Ti_2O_5$ H_2O, where A represents Na and/or H [17]. Fig. 5 shows the Ti 2p and Na 1s XPS spectra of the Vis-TiO_2/Ti before and after hydrothermal treatment. The intensity of the Ti 2p peaks due to Ti^{4+} (Ti $2p_{3/2}$: 459 eV, Ti $2p_{1/2}$: 465 eV) [18] scarcely changed after hydrothermal treatment,

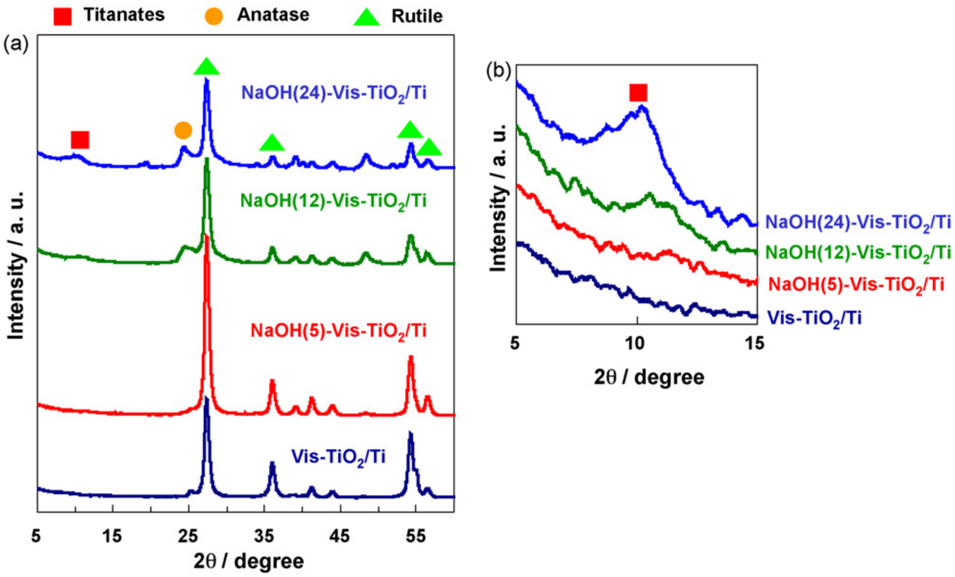

Fig. 4. (a) XRD patterns of Vis-TiO_2/Ti and NaOH(*X*)-Vis-TiO_2/Ti and (b) the expanded XRD patterns of (a) ($2\theta = 5$–15°).

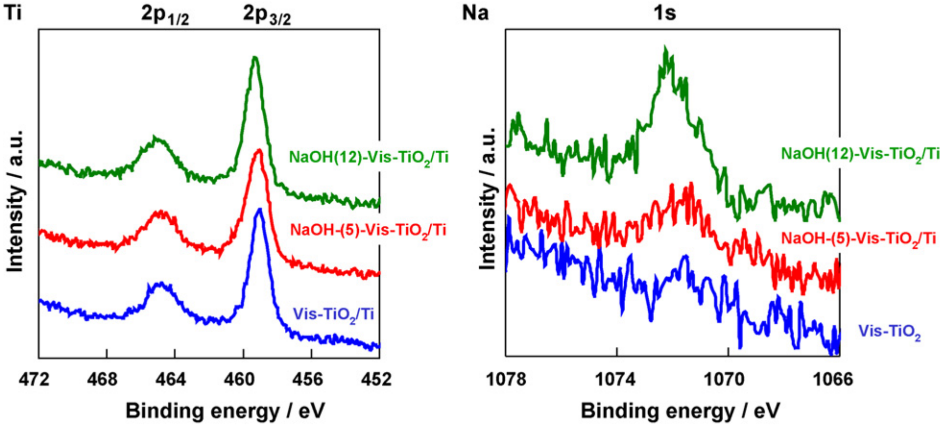

Fig. 5. XPS spectra of the Ti 2p (right) and Na 1s (left) peaks of the Vis-TiO_2/Ti and NaOH(*X*)-Vis-TiO_2/Ti.

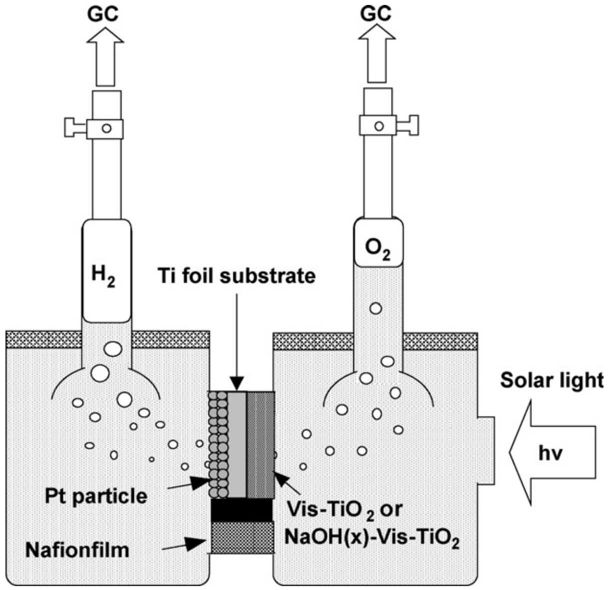

Fig. 6. H-type glass container for the separate evolution of H_2 and O_2 using Vis-TiO_2/Ti/Pt or NaOH(*X*)-Vis-TiO_2/Ti/Pt (TiO_2 side: 1.0 M NaOH aq; Pt side: 0.5 M H_2SO_4 aq).

while the intensity of the Na 1s peak around 1072 eV increased at the same time [19]. These results suggest that the decrease in the photocurrent after prolonged hydrothermal treatment can also be ascribed to the existence of small amounts of Na^+ which enhances the recombination rate of the photoformed electrons and holes.

The photocatalytic activities of Vis-TiO_2/Ti/Pt or NaOH(5)-Vis-TiO_2/Ti/Pt were investigated by the separate evolution of H_2 and O_2 from water under solar light irradiation. Vis-TiO_2/Ti/Pt or NaOH(5)-Vis-TiO_2/Ti/Pt are mounted at the center of an H-type glass container, separating two aqueous solutions, as shown in Fig. 6. A Nafion film is also mounted on the H-type glass container to provide the electrical connections which allow the electron transfer 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 into 1.0 M NaOH and the Pt side was immersed into 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 into the Pt side through the metal substrate. Fig. 7 shows the separate evolution reaction of H_2 and O_2 under solar light irradiation using sunlight-gathering system that removes almost all the UV rays found in sunlight. Water was decomposed into H_2 and O_2 separately with a good linearity against the irradiation time and NaOH(5)-Vis-TiO_2/Ti/Pt exhibited much higher activity than Vis-TiO_2/Ti/Pt. From the initial slope of the plot, the evolution rate of H_2 on NaOH(5)-Vis-TiO_2/Ti/Pt was estimated at about 15 μmol h^{-1}, showing that the total solar energy conversion efficiency (η) in the presence of an external applied potential was 0.23% determined by the following equation [20]:

$$\eta\ (\%) = \frac{100j(1.23 - E_{app})}{I_0} \tag{1}$$

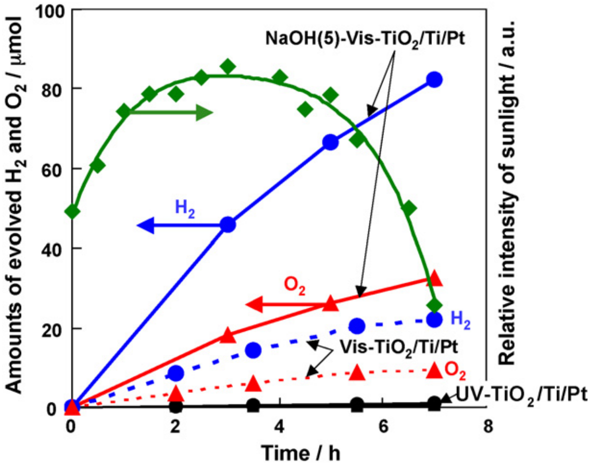

Fig. 7. Reaction time profiles of the separate evolution of (●) H_2 and (▲) O_2 under solar light irradiation on NaOH(5)-Vis-TiO_2/Ti/Pt, Vis-TiO_2/Ti/Pt and UV-TiO_2/Ti/Pt in an H-type glass container and the time profile of the relative intensity of sunlight. Irradiation area: 10 mm × 20 mm.

where j is the current density (mA/cm^2) estimated from the H_2 evolution rate, E_{app} is the applied chemical bias (0.826 V) and I_0 is the intensity of the incident light (mW/cm^2).

It should be noted that UV-TiO_2/Ti/Pt does not exhibit any activity for the separate evolution of H_2 and O_2 from water under solar light irradiation. Thus, the hydrothermally treated Vis-TiO_2 thin films were found to act as efficient photocatalysts for the separate evolution of H_2 and O_2 from water under solar light irradiation.

4. Conclusions

Vis-TiO_2 thin films were prepared on Ti foil substrate by RF-MS deposition method at high substrate temperature (873 K). It was found that the hydrothermal treatment of the Vis-TiO_2/Ti with NaOH aqueous solution led to the drastic increase in the surface area of Vis-TiO_2/Ti as well as an enhancement of the anodic photocurrent under UV and visible light irradiation. The highest anodic photocurrent was obtained after 5 h hydrothermal treatment. The separate evolution of H_2 and O_2 from water under small chemical bias were investigated under solar light irradiation and it was elucidated that the hydrothermally treated Vis-TiO_2/Ti/Pt thin films act as efficient photocatalysts for the separate evolution of H_2 and O_2 from water with a solar energy conversion efficiency of 0.23%. The hydrothermally treated Vis-TiO_2/Ti/Pt could, thus, be considered a unique photofunctional material for applications in clean and safe H_2 production systems from water using abundant and pollution-free resource, solar energy.

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