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Photocatalytic water splitting using Pt-loaded visible light-responsive TiO_2 thin film photocatalysts

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Abstract

Visible light-responsive TiO_2 (Vis-TiO_2) thin films which exhibit a unique declined O/Ti composition from the surface to the deep inside bulk have been successfully developed under a substrate temperature of 873 K by applying a radio-frequency magnetron sputtering deposition (RF-MS) method. By controlling the Ar gas pressure during the deposition procedure, it was possible to control the optical properties of the TiO_2 thin films. These Pt-loaded Vis-TiO_2 thin films were found to decompose water involving methanol (H_2 production reaction from H_2O) or 0.05 M silver nitrate solution (O_2 production reaction from H_2O) under visible light ($\lambda \geq 420$ nm) irradiation. In particular, the photo-oxidation of water to produce O_2 proceeds under visible light of wavelengths longer than 550 nm. The conduction and valence bands of Vis-TiO_2 thin film photocatalysts were, thus, seen to have enough potential for the decomposition of water into H_2 and O_2 under visible light irradiation. These thin films were found to be stable and the declined composition could be retained even after the reaction and calcination treatment at 723 K in O_2 atmosphere. Moreover, the stoichiometric and separate evolution of H_2 and O_2 from H_2O could be successfully achieved using an H-type glass container even under visible light.

Keywords: Water decomposition; Evolution of H_2 and O_2; Photocatalysis; Visible light-responsive TiO_2 photocatalyst; Thin film photocatalyst

1. Introduction

Photocatalysis on semiconducting materials has been an intensive area of research since the pioneering work of Fujishima and Honda [1], which deals with the photoassisted production of H_2 and O_2 from water with a photoelectrochemical cell consisting of a Pt and TiO_2 electrodes under a small electric bias. TiO_2 photocatalytic materials are especially attractive for their non-toxic, clean and safe properties as well as their thermal stability and the abundance of the necessary raw materials [2]. In fact, many studies have attempted the production of H_2 and O_2 from water splitting with the use of various types of powdered photocatalysts [3–7]. And in some cases, the splitting of water has been achieved under visible light [8–10], although powdered photocatalytic systems yield a mixture of H_2 and O_2 since the redox sites to produce H_2 and O_2 are in close proximity. In order to obtain pure H_2 gas that can be easily and safely utilized as fuel on a large, global scale, the separate evolution of H_2 and O_2 from water using TiO_2 thin film photocatalysts able to initiate reactions with solar energy is strongly desired [11–14].

TiO_2 thin films have been widely investigated for such environmental and energy needs, such as the purification of toxic compounds in polluted water and air [15], the development of photochemical solar cells [16] and applications utilizing properties, such as photo-induced super-hydrophilicity [17,18]. TiO_2 thin films synthesized by a wet process, such as sol–gel have also been examined [19] and although they have shown high photocatalytic reactivity, their mechanical durability is less stable. In this regard, sputtering deposition has shown promise for uniform, high density coatings of large surface areas with a strong adhesion. Although sputtering

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deposition of TiO_2 thin films have been previously reported [20,21], the development of TiO_2 photocatalysts that can initiate reactions even under visible light is necessary for the conversion of solar energy into useful chemical energy [22–24].

In our present work, a radio-frequency magnetron sputtering (RF-MS) method was applied to synthesize such visible light-responsive TiO_2 thin films (Vis-TiO_2). Optimization of the preparation conditions was performed by varying the substrate temperatures and Ar gas pressures. The efficiency of these Pt-loaded Vis-TiO_2 thin films for the photocatalytic splitting of water was then investigated.

2. Experimental

TiO_2 thin films were prepared by an RF-MS method using a calcined TiO_2 plate (High Purity Chemicals Lab., Corp., grade: 99.99%) as the source material and Ar gas (99.995%) as the sputtering gas. The system was equipped with a substrate center positioned parallel just above the source material with a target-to-substrate distance set at 80 mm. The base vacuum pressure was set at 5.0×10^{-4} Pa in each sputtering operation. The films were then prepared on a quartz substrate (10 mm × 20 mm) by inducing an RF power of 300 W with the substrate temperature held at a fixed value of 873 K and the Ar gas pressure (P_{Ar}) was varied from 1.0 to 3.0 Pa during the deposition process. Pt was deposited on the thin films by RF-MS with an RF power of 70 W under a substrate temperature of 298 K. XPS measurements revealed two specific peaks with binding energies of around 70 and 74 eV as the $4f_{7/2}$ and $4f_{5/2}$ electrons of the Pt metal, respectively. Moreover, it is found that these peaks have small shoulder peaks with binding energies of around 73 and 76 eV due to the $4f_{7/2}$ and $4f_{5/2}$ electrons of the oxidized Pt, respectively. These results show that only a small part of the Pt loaded on the thin film is slightly oxidized into PtO while most of the Pt exists as Pt metal. In order to clean the target surface and stabilize the sputtering process, pre-sputtering with Ar gas was carried out for 20 min. During the deposition of TiO_2, the substrate holder was kept rotating in order to obtain a uniform finish.

Photocatalytic reactions were carried out using a quartz cell connected to a conventional vacuum system (10^{-3} Pa). The reaction cell was placed in a cooling water bath to keep its temperature constant at 288 K. The TiO_2 thin film photocatalyst was then introduced into the aqueous solution in the reaction cell. Prior to the reaction, the mixture was de-aerated by evacuation and then flushed with Ar gas (100 kPa) repeatedly to remove the air dissolved in water. Finally, Ar gas (40 kPa) was introduced into the reaction cell and light irradiation was carried out with a 500 W high pressure Hg lamp or a 500 W Xe arc lamp using various color glass filters through the quartz window of the reaction cell. The apparent quantum yields were measured using a 500 W Xe arc lamp with an interference filter attachment ($\lambda_{max} = 360$ nm, half width: 22.9 nm; $\lambda_{max} = 420$ nm, half width: 11.7 nm). The number of incident photons to the cell was determined by a potassium ferrioxalate actinometer (photon numbers: 6.25×10^{14} photons/cm^2 s at $\lambda = 360$ nm and 5.07×10^{14} photons/cm^2 s at $\lambda = 420$ nm). The photocatalytic evolution of gases from aqueous solutions including a sacrificial reagent (50% methanol solution or 0.05 M silver nitrate solution: 2 ml) were analyzed by gas chromatography. The crystal structures of these films were then investigated by X-ray diffractometer (XRD, XRD-6100, Shimadzu) using a Cu Kα line ($\lambda = 1.5406$ Å). Optical transmittance measurements were carried out with a UV–vis spectrophotometer (UV–vis, UV-2200A, Shimadzu). Secondary ion mass spectrometry (SIMS, ADEPT1010, Physical Electronics) analysis was also carried out to obtain detailed information on the in-depth distribution of the ^{18}O and ^{48}Ti in these TiO_2 thin films.

The photoelectrochemical properties of the TiO_2 thin films prepared on Ti foil (TiO_2/Ti) were investigated using a potentiostat (HZ3000, Hokuto Denko) where the TiO_2/Ti electrode, Pt electrode and a saturated calomel electrode (SCE) were set as the working, counter and reference electrodes, respectively. The working electrode was irradiated by a 500 W Xe arc lamp in 0.05 M NaOH (pH 12.3) solution which was mechanically stirred and degassed by purging with 99.99% pure Ar gas during the experiments.

3. Results and discussion

The UV–vis transmission spectra of TiO_2 thin films prepared on quartz substrates with a TiO_2 thickness of 1.5 μm under differing Ar gas pressures (P_{Ar}) are shown in Fig. 1. The substrate temperature was kept constant at 873 K. The UV–vis spectrum of the film prepared at 473 K is also shown as reference. The films prepared at 473 K were colorless and transparent to visible light, thus, enabling the absorption of only UV light of wavelengths shorter than 380 nm regardless of the Ar gas pressure (hereafter, designated UV-TiO_2). On the other hand, the films prepared at 873 K under various P_{Ar} exhibited considerable absorption in visible light regions (hereafter, Vis-TiO_2-P_{Ar}, P_{Ar} = 1.0, 2.0, 3.0). In fact, the absorption band at visible light regions shifted toward longer wavelength regions with a decrease in the P_{Ar}. A broad absorption in the range 600–800 nm was observed for Vis-TiO_2-

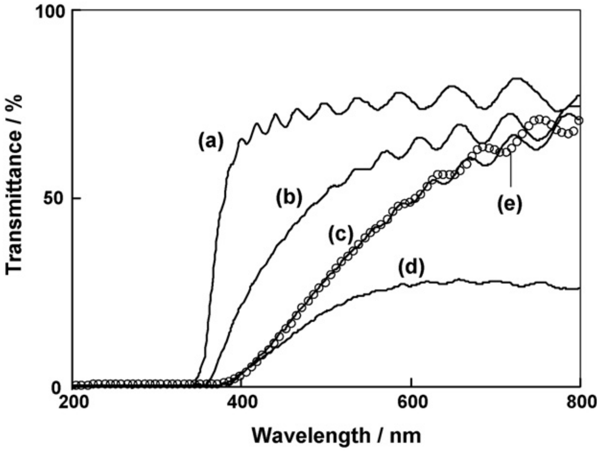

Fig. 1. The UV–vis transmission spectra of the TiO_2 thin films prepared on quartz substrates under various Ar gas pressures (P_{Ar}) and substrate temperatures. Substrate temperatuer (K): (a) 473 and (b–e) 873; P_{Ar} (Pa): (b) 3.0, (c) 2.0, (d) 1.0 and (e) after calcination of (c) at 723 K in O_2 atmosphere.

1.0, indicating that Ti^{3+} species are formed in the film [25]. In fact, an ESR signal due to the Ti^{3+} centers ($g_{\perp} = 1.975$ and $g_{||} = 1.940$) [26] was observed for Vis-TiO_2-1.0. The control of the Ar gas pressure during the simple one-step TiO_2 deposition process was, thus, found to be one of the major contributing factors in synthesizing visible light-responsive TiO_2 thin films. When Vis-TiO_2-2.0 was calcined at 723 K in O_2 atmosphere, no noticeable changes in the UV–vis spectrum could be observed (Fig. 1.), indicating that Vis-TiO_2-2.0 was thermally stable. Moreover, characterization of these TiO_2 thin films by XRD investigations showed that UV-TiO_2 consists only of an anatase phase, while the crystal structure of Vis-TiO_2-P_{Ar} varied depending on the P_{Ar}. The concentration of rutile phases was observed, as follows: 100% (Vis-TiO_2-1.0), 90% (Vis-TiO_2-2.0) and 60% (Vis-TiO_2-3.0).

The photocatalytic activity of these thin films for the water splitting reaction was investigated and a small amount of Pt (21 μg/cm^2) was loaded onto the TiO_2 surface. The effect of the Ar gas pressure on the reactivity of Pt-loaded Vis-TiO_2 for the splitting of pure water under irradiation with the full arc of a 500 W high pressure Hg lamp is shown in Fig. 2. Pt-loaded Vis-TiO_2-1.0 exhibited rather low activity for the reaction and the evolution of O_2 could not be observed at all. The Ti^{3+} species observed in Fig. 1 may act as the recombination center for the photo-formed electrons and holes, suppressing photocatalytic activity [27]. On the other hand, UV irradiation of Pt-loaded Vis-TiO_2-2.0 and Vis-TiO_2-3.0 led to the stoichiometric evolution of H_2 and O_2 (H_2:O_2 = 2:1) from pure water. In particular, Pt-loaded Vis-TiO_2-2.0 exhibited higher activity than Pt-loaded UV-TiO_2. The optimization of the Ar gas pressure was, thus, found to be crucial in synthesizing highly active TiO_2 thin film photocatalysts for the water splitting reaction.

The photocatalytic activity of the TiO_2 thin film photocatalysts under visible light was investigated for H_2 and O_2 evolution from water involving sacrificial reagents. H_2 evolution from methanol aqueous solution was observed for Pt-loaded Vis-TiO_2-P_{Ar} thin films under visible light, while no reaction proceeded on UV-TiO_2, as shown in Table 1. Moreover, Pt-loaded Vis-TiO_2-P_{Ar} exhibited high photocatalytic activity for O_2 evolution from aqueous silver nitrate solution under visible light, while no O_2 evolution could be observed for the Pt-loaded UV-TiO_2. These results show that the optimum P_{Ar} can be determined at 2.0 Pa since Pt-loaded Vis-TiO_2-2.0 exhibited the highest activity for both H_2 and O_2 evolution under visible light (Table 1). The quantum yields of Pt-loaded Vis-TiO_2-2.0 for H_2 and O_2 evolution under visible light irradiation ($\lambda = 420$ nm) were determined to be 1.25 and 2.43%, respectively. Control of the Ar gas pressure was, thus, seen to play an important role in the absorption of visible light and high photocatalytic reactivity. It is known that sputtered atoms from the target material experience many collisions with the sputtering gas molecules before they reach the substrate. The number and kinetic energy of the sputtered atoms which reach the substrate, thus, increase with a decrease in the sputtering gas pressure. Under low sputtering gas pressure conditions, the TiO_2 thin film is easily reduced by bombardment with the large number of sputtered atoms with high energy in the deposition process. In fact, SIMS investigations revealed that Vis-TiO_2-2.0 exhibited a unique declined O/Ti composition from the surface (2.00 ± 0.01) to the deep inside bulk (1.93 ± 0.01), although no significant changes were observed for UV-TiO_2 which is composed of stoichiometric TiO_2 (2.00 ± 0.01). It was observed that the lower the sputtering gas pressure, the lower the O/Ti ratio of TiO_2 thin films, accompanied by a large shift in their absorption band toward visible light regions. Such a unique anisotropic structure was seen to play an important role in the modification of the electronic properties, thus, enabling the absorption of visible light. However, despite its large absorption of visible light, Vis-TiO_2-1.0 exhibited the lowest activity since it contains large amount of Ti^{3+} species which enhance the recombination processes between the photo-formed electrons and holes.

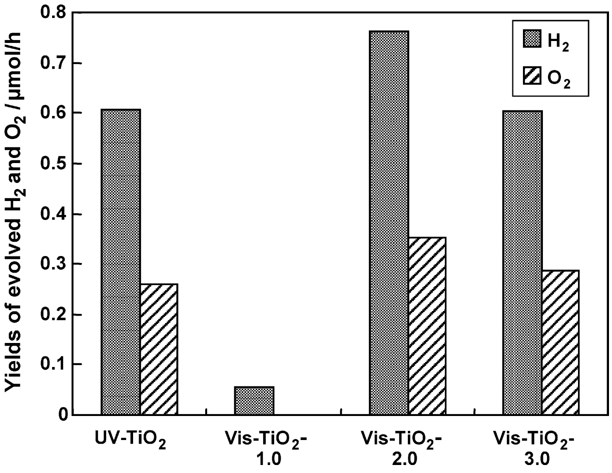

Fig. 2. Yields of evolved H_2 and O_2 for the water splitting reaction on Pt-loaded UV-TiO_2 and Vis-TiO_2-P_{Ar} (P_{Ar} = 1.0, 2.0, 3.0) under irradiation with the full arc of a 500 W high pressure Hg lamp.

Table 1
Photocatalytic activities for H_2 and O_2 evolution from aqueous solutions involving sacrificial reagents on Pt-loaded TiO_2 thin films under visible light irradiation

Photocatalyst	Activity (μmol)	
	H_2[a]	O_2[b]
UV-TiO_2	0.00	0.00
Vis-TiO_2-1.0	0.14	2.05
Vis-TiO_2-2.0	0.87	5.02
Vis-TiO_2-3.0	0.46	2.77

Film thickness, 1.5 μm; light source, 500 W Xe arc lamp with cut-off filter ($\lambda \geq 420$ nm); irradiation time, 10 h.

[a] From 50 vol% methanol aqueous solutions.

[b] From 0.05 M silver nitrate aqueous solutions.

The wavelength dependence of the O_2 evolution rate from aqueous silver nitrate solutions on Pt-loaded UV-TiO_2 and Pt-loaded Vis-TiO_2-2.0 is shown in Fig. 3. The wavelength of the irradiated light was controlled with cut-off filters and no reaction was seen to proceed before light irradiation. Pt-loaded Vis-TiO_2-2.0 evolved O_2 efficiently under visible light of wavelengths up to 550 nm, showing a good parallel relationship

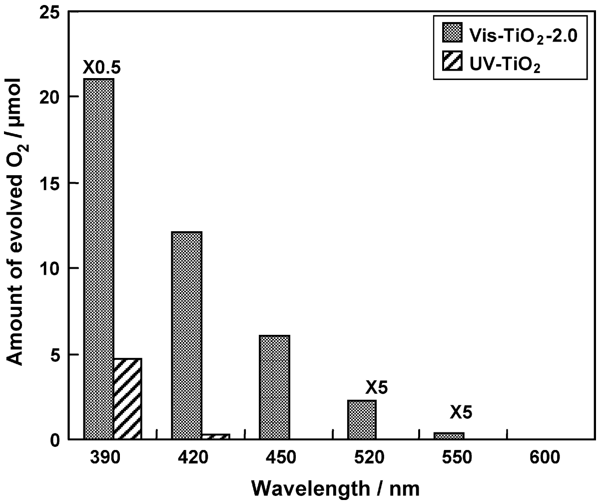

Fig. 3. Effect of the wavelengths of irradiated light on the yields of the photocatalytic evolution of O_2 from a 0.05 M $AgNO_3$ aqueous solution on Pt-loaded UV-TiO_2 and Vis-TiO_2-2.0 (film thickness, 3.0 μm; irradiation time, 10 h).

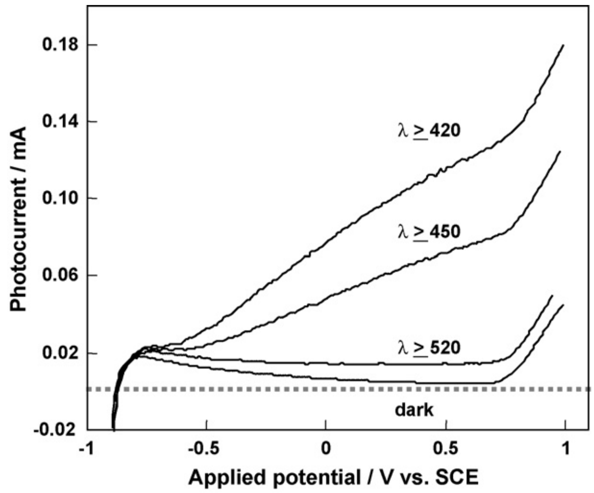

Fig. 4. Current–potential curves of the Vis-TiO_2-2.0/Ti electrode under visible light irradiation (electrolyte: 0.05 M NaOH).

between the photocatalytic activity and absorption spectrum (Fig. 1). Vis-TiO_2-2.0 photocatalyst could, thus, be seen to utilize a wide range of light even in visible regions as long as 550 nm. Pt-loaded Vis-TiO_2-2.0 was also shown to exhibit higher activity than Pt-loaded UV-TiO_2 under UV light irradiation ($\lambda < 390$ nm). The quantum yields for O_2 evolution from an aqueous silver nitrate solution were as follows: 12.6% (UV-TiO_2) and 60.0% (Vis-TiO_2-2.0) at 360 nm; 0% (UV-TiO_2) and 2.43% (Vis-TiO_2-2.0) at 420 nm. The high photocatalytic reactivity of Vis-TiO_2-2.0 could, thus, be attributed to its efficient absorption of visible light and the low concentration of the Ti^{3+} species which act as the recombination center of the photo-formed electrons and holes. The band gap energy of Vis-TiO_2 was also observed to be smaller than that of UV-TiO_2 while the bottom of the conduction band (E_{CB}) and top of the valence band (E_{VB}) had enough potentials for the reduction of H^+ and the oxidation of water, respectively. Indeed, Pt-loaded Vis-TiO_2 decomposed water into H_2 and O_2 stoichometrically under light irradiation of wavelengths longer than 390 nm with a good linearity against irradiation time.

The photoelectrochemical properties of the Vis-TiO_2-2.0 films prepared on a Ti foil substrate (Vis-TiO_2-2.0/Ti) under visible light were also investigated. The current–potential curves were then measured in dark and under visible light for Vis-TiO_2-2.0/Ti in 0.05 M NaOH aqueous solution. An anodic photocurrent was observed even under visible light of wavelengths longer than 520 nm, as shown in Fig. 4. This photocurrent could be attributed to the photo-oxidation of water into O_2 since O_2 evolution was also confirmed by photocatalytic reactions (Fig. 3). The anodic photocurrent was also observed under scanning potentials of −0.8 to +1.0 V versus SCE, indicating a flat band potential (E_{FB}) for Vis-TiO_2-2.0 at ca. −0.8 V versus SCE at pH 12.3. Moreover, the E_{CB} of Vis-TiO_2-2.0 was estimated to be ca. −1.0 V versus SCE at pH 12.3, since, in general, the energy difference between E_{CB} and E_{FB} has been assumed to be 0.2 eV for n-type semiconductors [28]. Current–voltage characteristics as well as the results of the H_2 evolution reaction support the findings that the E_{CB} of Vis-TiO_2-2.0 is more negative than the redox potential of H^+/H_2 (−0.97 V versus SCE at pH 12.3). In addition, the photocurrent was observed to be constant during the approximately 20 h consecutive measurements under visible light longer than 450 nm (Fig. 5). These results suggest the photocurrent is not ascribed to the oxidation of Vis-TiO_2-2.0 itself but to the oxidation of water into O_2. According to the previous work [22,23], it has already been clarified that Vis-TiO_2 thin films are covered with a stable TiO_2 layer of stoichiometric composition. In fact, no noticeable changes in the UV–vis spectrum could be observed, even after Vis-TiO_2-2.0 was subjected to calcination at 723 K in oxygen atmosphere, as shown in Fig. 1. Such a stable surface layer was seen to play an important role as a passive state in preventing the oxidation of the inside bulk, thus, enabling the stable absorption of visible light and high photocatalytic reactivity.

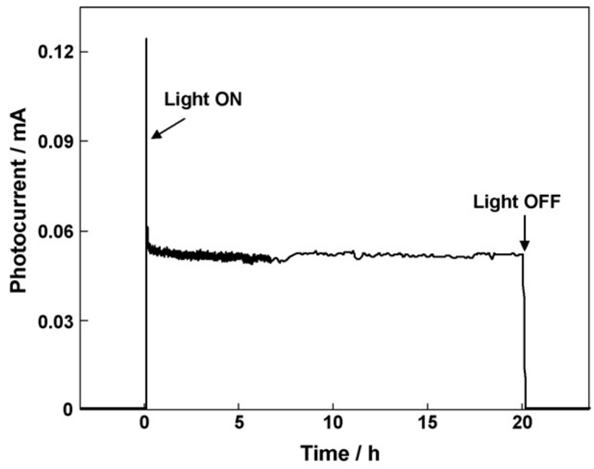

Fig. 5. Current–time curve of the Vis-TiO_2-2.0/Ti electrode measured in 0.05 M NaOH aqueous solution at +0.5 V vs. SCE under visible light irradiation ($\lambda \geq 450$ nm).

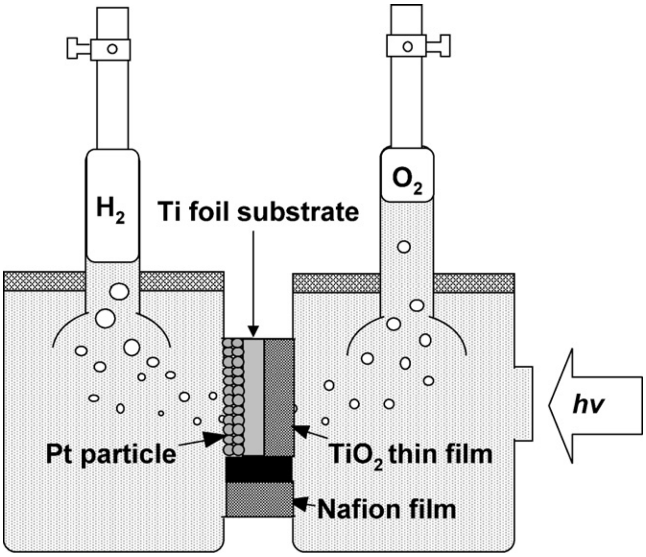

Fig. 6. H-type glass container for the separate evolution of H_2 and O_2 using a TiO_2 thin film photocatalyst device (TiO_2 side, 1.0 M NaOH aq.; Pt side, 0.5 M H_2SO_4 aq.).

The separate evolution of H_2 and O_2 from water was also investigated using a thin film photocatalytic device consisting of a Ti foil substrate deposited with a TiO_2 thin film on one side and Pt particles (0.68 mg/cm^2) on the other side. This photocatalyst and a Nafion film were mounted at the center of an H-type glass container, separating two aqueous solutions, as shown in Fig. 6. The Nafion film provided the electrical connection between the two reaction vessels while keeping the two reactions separate. It also allowed the electron transfer between the two vessels and was seen to play the same role as a salt bridge. The TiO_2 side of the photocatalyst was immersed in 1.0 M NaOH and the Pt side in 0.5 M H_2SO_4 aqueous solution in order to add a small chemical bias to assist the electron transfer from the TiO_2 side to the Pt side through the metal substrate. When this device is irradiated, O_2 is produced on the TiO_2 thin film side, while at the same time, H_2 is evolved at the Pt metal sites on the other side. H_2 and O_2 could, thus, be separately produced on such a Vis-TiO_2-2.0 thin film device with good linearity against the visible light ($\lambda \geq 450$ nm) irradiation time, while no reaction was seen to proceed on a UV-TiO_2 thin film device, as shown in Fig. 7. Moreover, sunlight irradiation of this device successfully led to the stoichiometric separate evolution of H_2 and O_2 from the Pt side and Vis-TiO_2-2.0, respectively. These results have clearly demonstrated that Vis-TiO_2 thin film photocatalyst can be applied for an H_2 evolution system from water under sunlight, showing that the conversion of the abundant sunlight energy into chemical energy is possible.

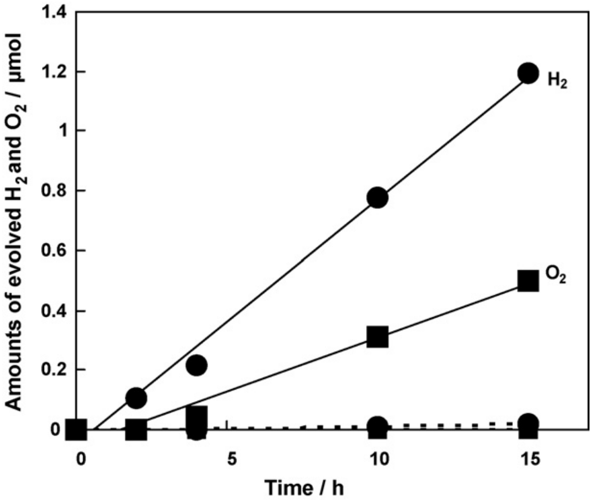

Fig. 7. Time profiles of the photocatalytic decomposition of H_2O with the separate evolution of H_2 and O_2 under visible light ($\lambda \geq 450$ nm) on the UV-TiO_2 (broken line) and Vis-TiO_2-2.0 (solid line) thin film device in an H-type glass container of two aqueous phases of different pH values (TiO_2 side, 1.0 M NaOH aq.; Pt side, 0.5 M H_2SO_4 aq.).

4. Conclusions

Visible light-responsive TiO_2 thin films were successfully developed by a radio-frequency magnetron sputtering deposition method in which the substrate temperatures and Ar gas pressures (P_{Ar}) were carefully controlled. The absorption bands of the films were seen to shift toward longer wavelength regions with a decrease in the Ar gas pressure when the substrate temperature was fixed at 873 K. Vis-TiO_2 prepared at $P_{Ar} = 2.0$ Pa showed the highest photocatalytic activity under both UV and visible light irradiation, enabling O_2 evolution even under visible light of wavelengths longer than 550 nm. Based on the results of their photoelectrochemical properties and the photocatalytic evolution of H_2 and O_2 from aqueous solution involving sacrificial reagents, the bottom of the conduction and top of the valence band were found to have enough potentials for the decomposition of water under visible light. SIMS measurements revealed that the O/Ti ratio of Vis-TiO_2 decreases from the top surface (2.00 ± 0.01) to the inside bulk (1.93 ± 0.01). This unique declined O/Ti composition or anisotropic structure is assumed to cause a significant perturbation in the electronic structure of the TiO_2, enabling the absorption of visible light and high photocatalytic reactivity. Moreover, Vis-TiO_2 was found to be stable even under photocatalytic reactions or calcination treatment at 723 K in air, indicating that the surface of Vis-TiO_2 is covered with a stoichiometric and stable TiO_2 phase which prevents the complete oxidation of the bulk TiO_2. The Vis-TiO_2 thin film photocatalyst was, thus, seen to enable the separate evolution of H_2 and O_2 from H_2O under visible or sunlight irradiation, thus, paving the way for applications in clean and sustainable H_2 evolution systems utilizing ideal energy resources, sunlight and water.

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