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Preparation of Visible Light-responsive TiO_2 Thin Film Photocatalysts by an RF Magnetron Sputtering Deposition Method and Their Photocatalytic Reactivity

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Visible light-responsive TiO_2 (Vis-TiO_2) thin films were successfully developed by a radio-frequency (RF) magnetron sputtering deposition method. These Vis-TiO_2 thin films exhibited a declined composition of the O/Ti ratio from the surface (O/Ti = 2.00) to bottom (O/Ti = 1.93), enabling the absorption of visible light. Pt-loaded Vis-TiO_2 was, thus, found to decompose water involving methanol or a 0.05 M silver nitrate solution under visible light irradiation.

Intensive studies of photocatalysis on semiconducting materials have been carried out since the pioneering work of Honda and Fujishima[1] 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. Recently, the production of H_2 and O_2 by water splitting using various types of powdered photocatalysts has also been reported.[2–4] In some cases, the photocatalytic splitting of water could be achieved even under visible light irradiation.[5] However, powdered photocatalytic systems yield a mixture of H_2 and O_2 since the redox sites to produce H_2 and O_2 are close to each other. The separate evolution of H_2 and O_2 from water is strongly desired to obtain pure H_2 gas that can be easily and safely utilized as fuel on a large, global scale. To address such concerns, thin film photocatalysts able to initiate efficient reactions using solar energy are vital.[6]

TiO_2 thin films have been investigated for such significant applications as the purification of toxic compounds in polluted water and air, for photochemical solar cells and in systems using their photoinduced superhydrophilicity.[7] However, these TiO_2 were only reactive under UV light of wavelengths shorter than 400 nm and could not absorb or utilize visible light. However, in recent years, there have been some developments in TiO_2 photocatalysts which can absorb and operate not only under UV but also visible light irradiation.[8–13]

In the present work, an RF magnetron sputtering method was applied for the design of visible light-responsive Pt-loaded TiO_2 thin films on a quartz substrate and their efficiency for the photocatalytic splitting of water involving sacrificial reagents was then investigated.

The thin films prepared by RF magnetron sputtering deposition involved 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 in parallel just above the source material (TiO_2 target), with a target-to-substrate distance ($D_{T\text{-}S}$) set at 70 or 80 mm. The films were then prepared on a quartz substrate (10 × 20 mm) with an RF power of 300 W with the substrate temperature (T_S) held at a fixed value between the range of 473–873 K. The Pt was deposited on the thin films by magnetron sputtering deposition with an RF power of 70 W at $T_S = 298$ K. The photocatalytic reactions were carried out using a quartz cell connected to a conventional vacuum system. The evolved gases from the aqueous solutions including the sacrificial reagent (50% methanol solution or 0.05 M silver nitrate solution: 2 mL) were analyzed by gas chromatography.

Figure 1 shows the UV–vis transmission spectra of the TiO_2 thin films prepared on quartz substrates with a thickness of 1.2 μm under differing T_S. The films prepared at $T_S = 473$ K were colorless and transparent to visible light, thus enabling the absorption of only UV light of wavelengths shorter than 380 nm (hereafter, designated UV-TiO_2). The films prepared at $T_S >$ 673 K were yellow in color, thereby enabling the absorption of visible light (Vis-TiO_2-T_S of $T_S = 673, 873$). In fact, the absorption band at visible light regions shifted toward longer wavelength regions at around 600 nm with an increase in T_S. Among the three types of TiO_2 thin films, Vis-TiO_2-873 exhibited an absorption edge at the longest wavelength regions. Thus, the control of the T_S during the simple one-step TiO_2 deposition process was found to be the major factor in controlling the efficiency of visible light absorption. Moreover, XRD analysis revealed that both the UV-TiO_2 and Vis-TiO_2-673 have an anatase crystalline structure while the Vis-TiO_2-873 mainly consisted of a rutile phase. From surface SEM observations, the particle size was found to increase with an increase in T_S. The surface areas of UV-TiO_2, Vis-TiO_2-673 and Vis-TiO_2-873 were 50.9, 36.1, and 22.7 m^2/g, respectively.

The photocatalytic activity of the three types of TiO_2 thin film photocatalysts was investigated for H_2 evolution from water

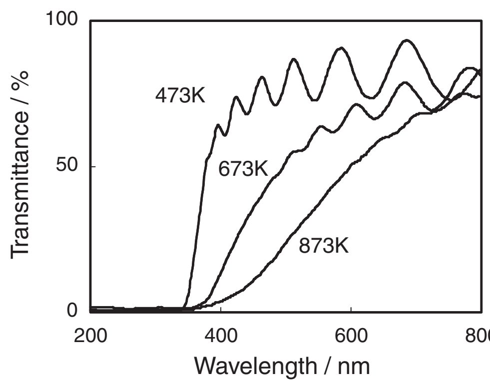

Figure 1. UV–vis spectra of TiO_2 thin films prepared on quartz substrates by an RF magnetron sputtering deposition method at various substrate temperatures.

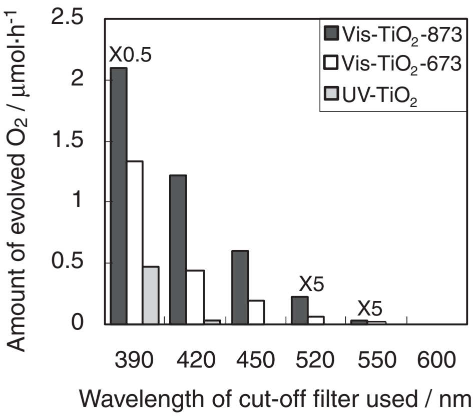

Figure 2. The effect of the wavelengths of the irradiated light on the yields of the photocatalytic evolution of O_2 from an aqueous silver nitrate solution on Pt-loaded UV-TiO_2, Vis-TiO_2-673, and Vis-TiO_2-873 thin film photocatalysts. (Film thickness: 3.0 µm) "×0.5" and "×5" indicate that the values are shown as 0.5 or 5 times greater than the actual values so that the comparisons are clearer.

involving methanol as the sacrificial reagent. The film thickness was about 3.0 µm. Light irradiation was carried out using a 500-W Xe arc lamp with an interference filter ($\lambda_{max} = 360$ nm, half width: 22.9 nm; $\lambda_{max} = 420$ nm, half width: 11.7 nm). H_2 could be evolved when the Pt-loaded UV-TiO_2 was irradiated under UV light but not under visible light. However, with the Pt-loaded Vis-TiO_2-673 and Vis-TiO_2-873 thin films, H_2 could be evolved under visible light irradiation. Moreover, gas evolution immediately ceased when light irradiation was terminated, clearly indicating that the reaction proceeded in response to visible light. The quantum yields are determined to be: 26.2% (UV-TiO_2), 27.2% (Vis-TiO_2-673), and 34.2% (Vis-TiO_2-873) at 360 nm; and 0 % (UV-TiO_2), 0.13% (Vis-TiO_2-673), and 1.25% (Vis-TiO_2-873) at 420 nm.

Figure 2 shows the wavelength dependency for O_2 evolution from a 0.05 M $AgNO_3$ solution on Pt-loaded UV-TiO_2, Vis-TiO_2-673 and Vis-TiO_2-873. The wavelength was controlled with cut-off filters. No reaction took place before light irradiation. Pt-loaded Vis-TiO_2-673 and Vis-TiO_2-873 evolved O_2 efficiently under visible light of wavelengths up to 550 nm, showing a good parallel relationship between the photocatalytic activity and absorption spectrum (Figure 1). These results clearly show that the Vis-TiO_2-673 and Vis-TiO_2-873 photocatalysts could utilize a wide range of light even in visible light regions of wavelengths as long as 550 nm.

To clarify the origin and cause of visible light absorption up to 600 nm by the Vis-TiO_2, SIMS measurements were carried out and the depth profiles are shown in Figure 3. The secondary ion intensity of ^{18}O for Vis-TiO_2-873 gradually decreases from the top surface (O/Ti ratio of 2.00 ± 0.01) to the 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). Moreover, the effect of $D_{T\text{-}S}$ on the photocatalytic activity of Vis-TiO_2-873 for O_2 evolution under visible light irradiation ($\lambda = 420$ nm) was investigated. The quantum yield of Vis-TiO_2-873 prepared at $D_{T\text{-}S} = 80$ mm was 2.43% and higher than 0.48% determined for Vis-TiO_2-873 prepared at $D_{T\text{-}S} = 70$ mm (O/Ti ≤ 1.7). These results clearly show that a slight de-

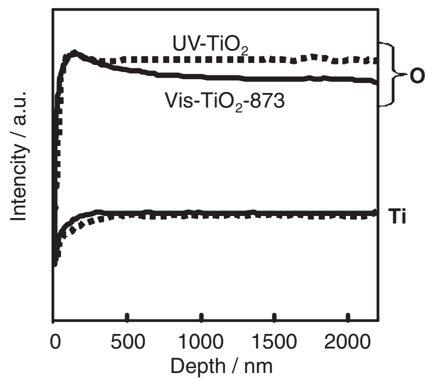

Figure 3. SIMS depth profiles of UV-TiO_2 and Vis-TiO_2-873 thin film photocatalysts. (Film thickness: 3.0 µm)

crease in the O/Ti ratio of the TiO_2 thin films plays an important role for the reactivity to the visible light. Such a declined structure could modify the electronic properties of the thin films leading to the changes in the band gap energy. Furthermore, the sample was stable for the photooxidation of water. The unique declined composition of the O/Ti ratio indicated that the surface of Vis-TiO_2 is covered with a stoichiometric and stable TiO_2 phase. No noticeable differences were obtained in the UV–vis spectra and XRD patterns of Vis-TiO_2 before and after the reactions. Moreover, changes in the UV–vis spectrum for Vis-TiO_2 could not be observed even after calcination at 723 K in oxygen atmosphere, indicating that Vis-TiO_2 remained stable even under heat treatment.

In conclusion, visible light-responsive TiO_2 thin films which consists of anatase or rutile phases were successfully developed by an RF magnetron sputtering deposition method. Vis-TiO_2-873 showed the highest photocatalytic activity for H_2 or O_2 evolution from water involving sacrificial reagents under both UV and visible light irradiation. The unique declined O/Ti composition could be seen to enable absorption and high photocatalytic performance under visible light irradiation.

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