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ScienceDirect
Applied Catalysis A: General 314 (2006) 179–183
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Decomposition of water in the separate evolution of hydrogen and oxygen using visible light-responsive TiO_2 thin film photocatalysts: Effect of the work function of the substrates on the yield of the reaction

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Received 7 August 2006; accepted 11 August 2006
Available online 18 September 2006

Abstract

The development of visible light-responsive TiO_2 thin films (vis-TiO_2) was successfully carried out by applying a radio-frequency magnetron sputtering (RF-MS) deposition method. The Pt-loaded vis-TiO_2 thin films clearly showed high potential for the decomposition of water into H_2 and O_2 by the evolution of H_2 from methanol/water as well as O_2 from a silver nitrate/water system under both UV and visible light irradiation ($\lambda \geq 420$ nm). These thin films were found to decompose pure water into H_2 and O_2 stoichiometrically under light irradiation of wavelengths longer than 390 nm. Next, a novel TiO_2 thin film photocatalyst was prepared on various metal substrates such as Al, Fe, Pd, Pt, Ti and Zr, while nanoparticles of Pt were deposited on the other side of these substrates. The reaction rate was revealed to increase with a decrease in the work function (ϕ) of the substrate. Moreover, the separate evolution of H_2 and O_2 could be successfully achieved under solar light irradiation by applying these thin film photocatalysts in an H-type glass container consisting of two water phases separated by a TiO_2 thin film and proton-exchange membrane.
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Keywords: Photocatalytic decomposition of water; Hydrogen production; Titanium oxide photocatalyst; Separate evolution of hydrogen and oxygen; Visible light; Solar light

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1. Introduction

In the pioneering work of Fujishima and Honda [1], UV light irradiation of a TiO_2 photoelectrode in aqueous solution led to the production of H_2 and O_2 on a Pt electrode and TiO_2 photoelectrode, respectively, onto which a small electric voltage was applied. It was observed that TiO_2 semiconducting nano-powdered photocatalysts loaded with small amounts of Pt worked to decompose H_2O into H_2 and O_2 as a mixture gas under UV light of wavelengths shorter than 400 nm [2–6]. The reaction yields were, however, rather low, due in part to the recombination of the liberated gases at the surface of the Pt particles [3]. Since then, much work on TiO_2 photocatalysts has been carried out since they are readily available, thermally and photostable, non-toxic, environmentally ideal materials. However, to prove viable under natural conditions on a large global scale, TiO_2 photocatalysts must be so fashioned as to absorb and operate with high efficiency even under visible light [7–9].

Numerous attempts have been made to develop an appropriate system whereby, in the absence of an external applied field, irradiation with visible light may separately and efficiently generate H_2 and O_2. Towards this end, an advanced method of metal ion-implantation, in which transition metal ions of V and Cr were incorporated within TiO_2, was successfully implemented to produce photocatalysts that exhibited significant activity under visible light [10,11]. The ion-implantation method is, however, discouragingly expensive and, therefore, not conducive for mass production of photocatalysts for practical applications. Addressing this problem, we have devised another method of producing visible light-responsive TiO_2 photocatalysts, circumventing ion-implantation by high velocity bombardment.

In the present work, an RF-MS method has been applied to develop visible light-responsive TiO_2 thin film photocatalysts and their efficiency for the photocatalytic splitting of water has

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doi:10.1016/j.apcata.2006.08.017

been investigated. The separate evolution of H_2 and O_2 from H_2O was investigated under visible or solar light irradiation by applying these photocatalysts in an H-type glass container consisting of two water phases separated by a TiO_2 thin film and proton-exchange membrane.

2. Experimental

The TiO_2 thin films were prepared by an RF-MS method using a TiO_2 plate (High Purity Chemicals Lab. Corp., Grade: 99.990%) as the source material and Ar gas (99.995%) as the sputtering gas. As reference samples, depositions were also carried out in a mixture of Ar and O_2 (99.995%). The base pressure in the chamber was less than 6×10^{-4} Pa and the working pressure was kept at 2.0 Pa. The thin films were deposited on metal substrates such as Al, Fe, Ti, Zr, Pd, Pt (15 mm × 25 mm × 0.1 mm) and quartz (10 mm × 10 mm × 1 mm) by inducing an RF power of 300 W with the substrate temperature (T_S) held at a fixed value between a range of 473–873 K. During the deposition of TiO_2 and Pt, the substrate holder was kept rotating to keep the deposition uniform. Pt was then deposited on the thin films or metal substrate (TiO_2/M/Pt; M = Al, Fe, Pd, Pt, Ti and Zr) at an RF power of 70 W at $T_S = 298$ K.

Photocatalytic reactions were carried out using a quartz cell connected to a conventional vacuum system. The TiO_2 thin film photocatalyst was introduced into distilled water or an aqueous solution including a sacrificial reagent (50% methanol or 0.05 M silver nitrate solution) in the reaction cell. Light irradiation was carried out with a 500 W high pressure Hg lamp through the quartz window of the reaction cell. The separate evolution of H_2 and O_2 from water was investigated by an H-type Pyrex glass container. The container consisted of two water phases separated by a TiO_2/Ti/Pt photocatalyst and a proton-exchange membrane. Visible light irradiation was carried out with a 500 W Xe arc lamp through a color glass filter (L-42, Asahi Techno Glass) and sunlight irradiation was carried out using a sunlight-gathering system (Laforet Engineering, XD-50D). The evolved gases were analyzed by gas chromatography (G2800-T, Yanaco).

Optical transmittance measurements were carried out with a UV–vis spectrophotometer (Shimadzu, UV-2200A). The crystal structures of the TiO_2 thin films were investigated by X-ray diffraction (XRD, XRD-6100, Shimadzu) using a Cu Kα line (λ = 1.5406 Å). Secondary ion mass spectrometry (SIMS, Physical Electronics, ADEPT1010) was carried out to obtain the depth profiles of ^{18}O and ^{48}Ti for the thin films.

The AC-impedance of the TiO_2 films prepared on ITO (TiO_2/ITO) was measured with a potentiostat (HZ3000, Hokuto Denko) where the TiO_2/ITO electrode, Pt electrode and a saturated calomel electrode (SCE) were set as the working, counter and reference electrodes, respectively. The AC amplitude and frequency of the AC signals were 10 mV and 1 kHz, respectively. A 0.05 M NaOH (pH 12.3) solution was used as an electrolyte and degassed by purging with 99.99% pure Ar gas before the experiments. The working electrode area was about 1.0 cm^2.

3. Results and discussions

3.1. Effect of the substrate temperature on the optical properties of the TiO_2 thin films

The effect of the substrate temperature (T_S) on the UV–vis transmission spectra of the TiO_2 thin films prepared on a quartz substrate is shown in Fig. 1. The thickness for all the films was around 1.20 ± 0.05 μm. The transmission spectra were characterized by well-known oscillations appearing when a transparent thin film of a material having a high refractive index was deposited on a substrate with a lower refractive index. The thin films prepared at low substrate temperatures ($T_S = 473$ K) were observed to be colorless and transparent to visible light, thus enabling the absorption of UV light having wavelengths shorter than 380 nm (hereafter, designated UV-TiO_2). On the other hand, TiO_2 thin films prepared on substrates at higher temperatures ($T_S > 673$ K) were observed to be yellow-colored, enabling the absorption of visible light [12–14]. The TiO_2 thin films formed at $T_S = 873$ K exhibited an absorption edge at the longest wavelength regions among the three types of films (hereafter, designated vis-TiO_2). Interestingly, the coexistence of O_2 with Ar in the sputtering chamber led to the formation of UV light-responsive TiO_2 thin films (Fig. 1), regardless of the substrate temperature during the sputtering process ($T_S > 673$ K). These results suggest that TiO_2 deposition under pure Ar gas without any trace of O_2 is also a major factor in the preparation of vis-TiO_2 thin film photocatalysts. Moreover, XRD investigations revealed that UV-TiO_2 has an anatase crystalline structure while vis-TiO_2 mainly consists of rutile crystalline phases. AC-impedance measurements of vis-TiO_2 and UV-TiO_2 were performed to determine their donor density at an AC frequency of 1000 Hz which were calculated to be 2.86×10^{17} and 1.74×10^{16}, respectively. These results suggest that the conductivity of vis-TiO_2 is higher than that of UV-TiO_2 since the donor density is an important parameter to gauge the semiconductivity and higher donor densities can lower the bulk resistance [15].

The photocatalytic decomposition of water including sacrificial reagents such as CH_3OH or $AgNO_3$ was carried out. It is known that photocatalytic water splitting reaction is an

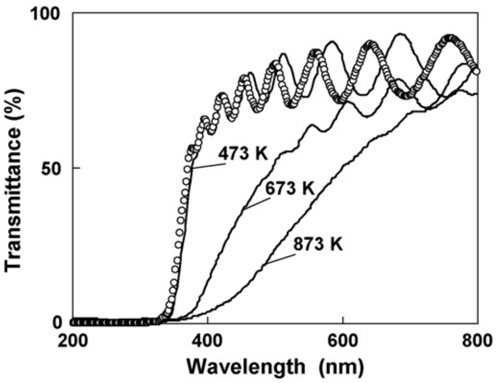

Fig. 1. UV–vis transmission spectra of TiO_2 thin films prepared in pure Ar atmosphere (solid line) under various substrate temperatures and the TiO_2 thin film prepared in Ar + O_2 atmosphere (open circle) at 873 K.

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