

# Pt-TiO<sub>2</sub> thin films on glass substrates as efficient photocatalysts

MASANARI TAKAHASHI, KEISUKE MITA, HIROSHI TOYUKI

*Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536, Japan*

MAKOTO KUME

*Nihon Sheet Glass, 1 Kounoike, Azakaidou, Itami, Hyogo 664, Japan*

Photocatalytic Pt-TiO<sub>2</sub> thin films of various thicknesses (ca. 20 to 100 nm) were prepared on Vycor glass substrates by spray-coating. The photocatalytic activity of the films was examined through the dehydrogenation of methanol in aqueous solution. The plot of the activity against the thickness of the film gave a sigmoidal curve. A drastic increase in activity was observed at about 50 nm thickness. From thin-film X-ray diffraction measurements of the films it was revealed that anatase was formed at a thickness of more than 50 nm, whereas amorphous TiO<sub>2</sub> was formed at thicknesses of less than 50 nm. The increase of activity was, therefore, attributed to the formation of anatase. Compared with powder catalysts, the thin films showed a remarkable improvement in specific photocatalytic activity due to the high dispersion of the catalyst.

## 1. Introduction

Through a lot of investigations related to solar energy conversion and storage [1-12] it has been proved that TiO<sub>2</sub> containing platinum (Pt-TiO<sub>2</sub>) is one of the most active catalysts [2-4, 7]. However, the use of conventional powder catalysts results in disadvantages for stirring during the reaction and for separation after the reaction. Preparation of the catalysts coated as thin films will make it possible to overcome these disadvantages and to extend the industrial applications, but photocatalytic Pt-TiO<sub>2</sub> thin films have not been studied in detail so far.

In the present paper, Pt-TiO<sub>2</sub> catalysts coated as thin films are prepared on Vycor glass substrates. The photocatalytic activity of the films is examined through the dehydrogenation reaction of methanol in aqueous solution. The relation between the photocatalytic activity and the form of titanium oxide in the films is discussed.

## 2. Experimental procedure

Thin films of TiO<sub>2</sub> containing platinum were prepared on Vycor glasses by spray-coating [13], in which dimethyl formamide (DMF) solutions containing titanil-acetyl acetate (TiO(acac)<sub>2</sub>) and dichloro-bis(benzonitronil)platinum(II) (PtCl<sub>2</sub>(PhCN)<sub>2</sub>) were used. Table I shows the compositions of the solutions, where the mole ratio of TiO(acac)<sub>2</sub> and PtCl<sub>2</sub>(PhCN)<sub>2</sub> was kept constant. Solutions of 2 ml were sprayed on to Vycor glass substrates (30 mm × 25 mm × 3 mm in size) which were previously heated to 700°C. Thus, eight pieces (denoted by A1 to A8 in Table I) of the thin films were prepared. Another four pieces (denoted by

TABLE I Composition of the DMF solutions

Run no.	TiO (acac) <sub>2</sub> (mmol dm <sup>-3</sup> )	PtCl <sub>2</sub> (PhCN) <sub>2</sub> (mmol dm <sup>-3</sup> )	Thin film	
			Series A	Series B
1	4.88	0.329	A1	B1
2	7.53	0.493	A2	B2
3	10.1	0.658	A3	
4	12.5	0.822	A4	
5	17.4	1.15	A5	
6	22.5	1.48	A6	B3
7	25.3	1.65	A7	
8	27.7	1.81	A8	B4

B1 to B4 in Table I) were prepared with the use of partially masked glass substrates. The thicknesses of these films (B1 to B4) were measured by a surfcoorder (Kosaka Institute SE-3).

Thin-film X-ray diffraction for the films was measured by a Rigakudenki TFD with an incident beam angle of 2° using a copper target under 50 kV and 200 mA.

The electronic spectra of the films were measured by a Hitachi 340 spectrophotometer with a reference of Vycor glass substrate.

The dehydrogenation reaction of methanol was carried out in an aqueous methanol solution (CH<sub>3</sub>OH:H<sub>2</sub>O = 2:1 vol %) by photo-irradiation with a 500 W high-pressure mercury lamp at room temperature under an N<sub>2</sub> atmosphere. The amounts of H<sub>2</sub> gas produced were measured by gas chromatography.

The content of titanium in the films was determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES), in which the solutions used

were prepared by treatment of the thin films with sulphuric acid at 200°C for 3 h.

### 3. Results

The thin-film X-ray diffraction patterns observed for some films (A2, A4, A6 and A8) and the Vycor glass substrate (A0) are shown in Fig. 1. The films A6 and A8 show a peak at  $2\theta = 25.3^\circ$  which is assigned to diffraction from the (101) plane of anatase. On the other hand, the films A2 and A4 show only a halo at about  $2\theta = 25.3^\circ$ . The halo could result from an insufficient content of titanium oxide or the formation of amorphous  $\text{TiO}_2$ . In order to clarify this point, additional heat treatment for A2 and A4 was carried out at 900°C for 2 h (denoted by A2\* and A4\* in Fig. 2). An intense peak assigned to diffraction from the (110) plane of rutile was observed at  $2\theta = 27.5^\circ$  in A2\* and A4\*. This result shows that the titanium oxide in A2 and A4 is amorphous  $\text{TiO}_2$ .

Electronic absorption spectra for the thin films A1 to A8 are shown in Fig. 3. An intense band derived from  $\text{TiO}_2$  is observed at around 250 nm for each film. The absorbance at 250 nm for the films is given in Table II. The content of  $\text{TiO}_2$  calculated from the content of titanium determined by ICP-AES is also given in Table II. The absorbance increases with an increase of the  $\text{TiO}_2$  content. The thicknesses of films B1 to B4 determined by surfcoorder are listed in Table II. All the thin films in Series A show the production of  $\text{H}_2$  gas by the photocatalytic reaction. The reaction rate is followed by the amount of  $\text{H}_2$  gas produced. The rate is almost constant after an induction period of ca. 30 min. The photocatalytic activity for the films is represented by the average  $\text{H}_2$  gas evolution rate for the first few hours after the induction period, and the specific photocatalytic activity is determined as the photocatalytic activity per unit of  $\text{TiO}_2$ . A summary of these results is given in Table II. The thickness and the photocatalytic activity of the films are increased with an increase of  $\text{TiO}_2$  content in the films.

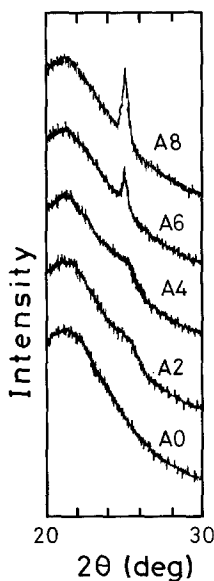


Figure 1 Thin film X-ray diffraction patterns for Pt- $\text{TiO}_2$  thin films (A0 = substrate glass).

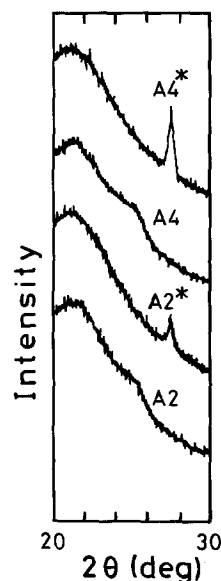


Figure 2 Changes of thin-film X-ray diffraction patterns of some Pt- $\text{TiO}_2$  thin films by additional heating at 900°C for 2 h (before A2 and A4; after: A2\* and A4\*).

### 4. Discussion

It is well known that the titanium atoms in  $\text{TiO}_2$  are coordinated octahedrally with the six ligand oxygen atoms. It may therefore be reasonable to consider that the assignments for the electronic spectra of  $\text{TiO}_2$  thin films can be discussed by using the molecular-orbital energy-level scheme of the octahedral  $\text{TiO}_6^{8-}$  ion (Fig. 4).

According to the energy-level scheme for an octahedral transition-metal complex [14], the highest occupied orbital and the lowest unoccupied orbital of  $\text{TiO}_6^{8-}$  ion belong to  $T_{1u}$  and  $T_{2g}$  species, respectively. The  $T_{1u}$  orbital is mainly constructed with the 2p atomic orbitals of ligand oxygens and the  $T_{2g}$  orbital is mainly constructed with the 3d orbitals of Ti(IV). Moreover, the transition of an electron from  $T_{1u}$  to  $T_{2g}$  is allowed theoretically. It is, therefore, considered that the intense band at around 250 nm observed for the  $\text{TiO}_2$  thin films is assigned to the  $T_{1u}$ - $T_{2g}$  charge transfer band.

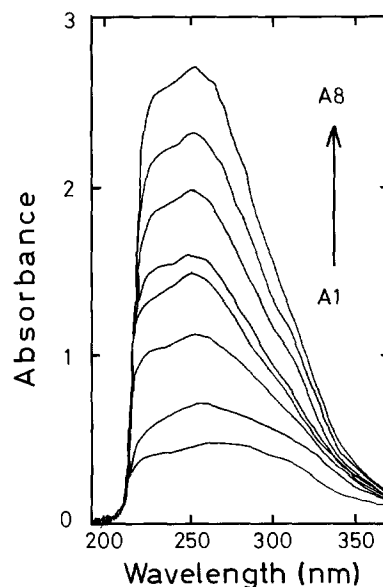


Figure 3 Electronic absorption spectra for Pt- $\text{TiO}_2$  thin films.

TABLE II Characteristics of the Pt-TiO<sub>2</sub> thin films

Thin film	Absorbance at 250 nm	TiO <sub>2</sub> content* (g m <sup>-2</sup> )	Thickness (nm)	Photocatalytic activity† (μmol h <sup>-1</sup> )	Specific photocatalytic activity‡ (10 <sup>3</sup> μmol h <sup>-1</sup> g <sup>-1</sup> )
A1	0.52	0.057	14.8 <sup>§</sup>	2.28	53.3
A2	0.72	0.079	20.5 <sup>§</sup>	7.33	124
A3	1.16	0.128	33.9 <sup>§</sup>	5.78	60.2
A4	1.48	0.163	42.2 <sup>§</sup>	12.1	98.6
A5	1.60	0.176	45.6 <sup>§</sup>	13.5	102
A6	1.96	0.216	55.7 <sup>§</sup>	55.6	343
A7	2.32	0.255	66.1 <sup>§</sup>	59.0	309
A8	2.72	0.300	77.3 <sup>§</sup>	63.5	282
B1	0.45		10.0 ± 3 <sup>¶</sup>		
B2	0.91		27.0 ± 3 <sup>¶</sup>		
B3	2.12		64.0 ± 3 <sup>¶</sup>		
B4	3.15		88.0 ± 3 <sup>¶</sup>		

\*Calculated from the content of titanium determined by ICP-AES.

† Represented by the average H<sub>2</sub> gas production rate after the induction period.

‡ Determined by photocatalytic activity per unit of TiO<sub>2</sub>.

§ Estimated from the absorbance at 250 nm using Equation 2.

¶ Determined by surfcoorder.

A relation between the absorbance at 250 nm,  $A_{250}$ , and the amount of TiO<sub>2</sub>,  $M$ , for the films in Series A is shown in Fig. 5. The relation can be represented empirically by the equation

$$M = 0.11 A_{250} \quad (1)$$

in which  $M$  is given in g m<sup>-2</sup> units. A similar relation between the absorbance and the thickness,  $L$ , is also found for the films in Series B, as also shown in Fig. 5. The linear relationship in this figure is represented by the empirical equation

$$L = 28.4 A_{250} \quad (2)$$

in which  $L$  is given in nanometres. It is therefore concluded that the amount of TiO<sub>2</sub> and the thickness of a Pt-TiO<sub>2</sub> thin film can be estimated from the intensity of the electronic spectrum. The thicknesses of the films in Series A are calculated from Equation 2 and the estimated values are also given in Table II.

The relation between the photocatalytic activity and the thickness of TiO<sub>2</sub> thin films containing platinum is shown in Fig. 6. The curve in the figure shows a drastic increase of the activity at a thickness of about 50 nm. If the photocatalytic activity is simply proportional to the absorbance at 250 nm, the relation between the activity and the thickness of the films will be given by the equation

$$P = k_1 \cdot I_0 [1 - \exp(-k_2 \cdot A_{250})] \quad (3)$$

where  $P$ ,  $k_1$ ,  $I_0$ ,  $k_2$  and  $A_{250}$  are the photocatalytic activity, a constant, the initial intensity of radiation, a

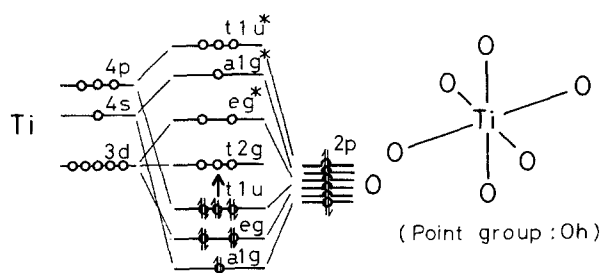


Figure 4 Molecular-orbital energy-level scheme for an octahedral complex. Small arrows represent electrons with spin and the bold arrow represents the transition of an electron.

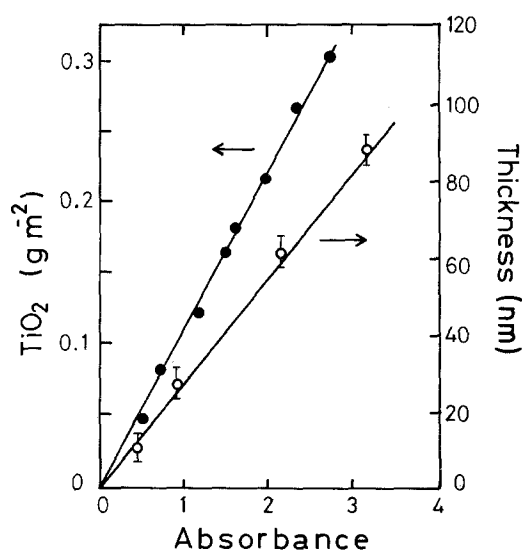


Figure 5 The relation between absorbance at 250 nm and (●) TiO<sub>2</sub> content or (○) thickness for Pt-TiO<sub>2</sub> thin films.

constant, and the absorbance at 250 nm, respectively. However, the experimental plot of photocatalytic activity against the thickness of the thin film does not obey the theoretical Equation 3, but gives a sigmoidal

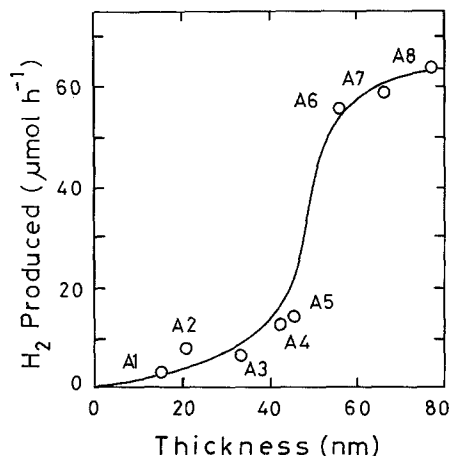


Figure 6 The relation between the thickness of a Pt-TiO<sub>2</sub> thin film and the rate of H<sub>2</sub> evolution during the photocatalytic reaction.

curve as shown in Fig. 6. A drastic increase of activity is found at about 50 nm.

According to the results for thin-film X-ray diffraction and film thickness, the TiO<sub>2</sub> in the films is anatase for a thickness of more than 50 nm, and is amorphous TiO<sub>2</sub> for a thickness of less than about 50 nm. In general, the photocatalytic activity of anatase is higher than that of amorphous TiO<sub>2</sub> [12]. The drastic increase in the photocatalytic activity of the films at a thickness of about 50 nm is thought to be due to the formation of anatase. As for the reason for the formation of various kinds of TiO<sub>2</sub> depending on the film thickness, it is considered that at the beginning of the deposition the process of depositing TiO<sub>2</sub> is influenced by the surface condition of the substrate; amorphous Pt-TiO<sub>2</sub> is formed on the amorphous substrate at the initial stage, as in the epitaxial growth of a crystal.

The thin film A6 gives a specific photocatalytic activity of  $343 \times 10^3 \mu\text{mol h}^{-1} \text{g}^{-1}$ . Compared with the usual Pt-TiO<sub>2</sub> powder catalyst that gives an activity of  $2.22 \times 10^3 \mu\text{mol h}^{-1} \text{g}^{-1}$  [8], the activity of the film is higher than that of the powder by about two orders of magnitude. Such a high activity of the TiO<sub>2</sub> can result from the effective use of the catalyst due to its high degree of dispersion on the surface.

## 5. Conclusion

Pt-TiO<sub>2</sub> thin films were prepared on a Vycor glass substrate as efficient photocatalysts. A drastic increase of the photocatalytic activity for Pt-TiO<sub>2</sub> thin films was observed above a thickness of about 50 nm, and it was caused by the formation of anatase. The specific photocatalytic activity of the thin film A6 was higher than that of Pt-TiO<sub>2</sub> powder by about two orders of

magnitude. The improvement in the activity was due to the high dispersion of the catalyst. As a result, it was concluded that the preparation of photocatalysts in the form of thin films more than 50 nm thick was an effective method of using the catalyst economically and efficiently.

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