Preparation of TiO₂ Thin Films Using Octadecylamine Langmuir-Blodgett Films and Evaluation of Their Photocatalytic Activity

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Abstract: A study was conducted to demonstrate that nanometer-thick titanium dioxide (TiO₂) thin films could be prepared by the hydrolysis of titanium potassium oxalate using octadecylamine (ODA) Langmuir-Blodgett (LB) films as templates. The amount of TiO₂ generated in the LB film was found to be proportional to the number of deposited ODA layers, which enables precise control of the TiO₂ film thickness. After heat treatment of the LB films at 300-600°C, the photocatalytic activities of the resulting TiO₂ films were determined from the decomposition of stearic acid cast films when irradiated with UV light for different time periods. Higher photocatalytic activity was observed in TiO₂ films heat treated at lower temperatures.

Key words: TiO₂ thin film, LB technique, octadecylamine, titanium potassium oxalate, photocatalytic activity

1 INTRODUCTION

Titanium dioxide (TiO₂) is a well-known semiconductor that has widespread applications in pigments, optical coatings, UV protection shields, solar energy conversion¹⁾, photocatalysis under UV light irradiation²⁾, and other applications. In the past decade, the Langmuir-Blodgett (LB) technique, which is usually used in the preparation of highly ordered multilayer films of various long-chain amphiphiles, has been used to obtain ultrathin TiO₂ films. This technique has significant advantages, including excellent control of film thickness and film uniformity over large areas³⁻⁶⁾. For example, ultrathin TiO₂ films have been synthesized from titanium alkoxides by a two-dimensional sol-gel process⁴⁾. The use of multilayer deposition of colloidal TiO₂ nanoparticles or nanosheets to fabricate ordered organic/inorganic structures has been demonstrated⁵⁾. Further, densely packed exfoliated titania nanosheet films can be prepared by the LB technique without any amphiphilic additives⁶⁾.

In a previous study, we reported the preparation of titania nanotube LB films by direct spreading of hydrophobized particles onto the surface of an aqueous subphase⁷⁾. The structure of the LB films obtained by subsequent deposition was found to consist of piles of rod-like particulate monolayers in which nanotube bundles were arranged in a

manner resembling floating logs. TiO₂ particulate LB films were also fabricated from Langmuir monolayers on which TiO₂ particles were adsorbed two-dimensionally from a colloidal subphase^{8,9)}. In this case, the adsorption of the particles resulted from Coulombic interactions. The TiO₂ particles in the colloidal dispersion at near-neutral pH were negatively charged, therefore cationic film materials, particularly octadecylamine (ODA), were used in these experiments.

It has been shown that the use of long-chain amine monolayers and an aqueous subphase containing titanium potassium oxalate (K₂TiO(C₂O₄)₂; TPO) results in formation of a complex at the air-water interface¹⁰⁾; TiO₂ films are then obtained by LB deposition and post-heat-treatment¹¹⁾. It has also been reported that colloidal TiO₂ clusters were simultaneously generated in the subphase by slow hydrolysis of TPO upon aging¹²⁾. Thus, it is of concern that the TiO₂ clusters might be adsorbed unevenly on the floating monolayer.

To develop this process, we conducted the present study, which is based on our previous work dealing with dye adsorption on ODA LB films¹³⁾. The sequence of the preparation steps was modified to make the process applicable to an ODA LB film as a template for nucleation and crystal growth of TiO₂ from TPO. The proposed procedure

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is considered to have the advantages of reducing TPO usage, as well as preventing excess build-up of TiO_2 clusters in the multilayered film. In particular, we examined the influence of the preparation conditions on the structure of the TiO_2 films. The photocatalytic properties of the TiO_2 films following post-heat-treatment were demonstrated by decomposition of stearic acid (SA) cast films.

2 EXPERIMENTAL PROCEDURES

ODA (>99% pure, Aldrich Chemical Company, Inc., St Louis, MO, USA) and TPO (>90% pure, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as the film material and Ti source, respectively. These materials were of the highest grade and were used without further purification. Fabrication of the LB films was accomplished using a Langmuir trough (HBM AP-type LB film balance, Kyowa Interface Science, Niza-City, Japan). Subphases were made using distilled deionized water. We adjusted the pH of the subphase to be in the range of 3.0–10.5 by adding hydrochloric acid or sodium hydroxide. An ODA monolayer was spread from a chloroform solution at a concentration of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ on the aqueous subphase at 20°C . This monolayer was left for 10 min to allow the spreading solvent to evaporate. After the compression of the ODA monolayer at a barrier speed of 10 mm min^{-1} , LB deposition on the solid substrate was carried out at a surface pressure of 45 mN m^{-1} using the conventional vertical dipping method, with dipping and withdrawal speeds of 7 mm min^{-1} . A glass plate, quartz plate, calcium fluoride plate, and silicon wafer were used as the substrates for different measurements.

TiO_2 thin layers were generated by immersing as-deposited ODA LB films (1–9 layers) in an aqueous TPO solution at 20°C for the given time periods. In this process, which is analogous to a reaction with ammonia, the TPO is expected to react with ODA to produce TiO_2 in each layer of the LB film. Subsequently, the ODA- TiO_2 LB films were sintered in air for 1 h at different holding temperatures (300 , 500 , and 600°C). According to a previous report on the thermal analysis of ODA-modified single-walled carbon nanotubes, a reduction in weight, resulting from the reaction of ODA, was observed at around 300°C in thermogravimetric/differential thermal analysis (TG/DTA) studies¹⁴⁾. Hence, although the boiling point of ODA is 347°C at ambient pressure, the temperatures used in the present experiments are sufficient for eliminating ODA from the films.

Characterizations of the thin films were carried out by measuring UV-vis spectra (UV-3100PC, Shimadzu, Kyoto, Japan), Fourier-transform infrared spectra (FT/IR-8900, JASCO, Hachioji, Japan), and by obtaining tapping-mode atomic force microscopy (AFM) images (Digital Instruments Nanoscope IIIa, Veeco Instruments, NY, USA). Photocata-

lytic activity was evaluated from the photodecomposition of an SA cast on the TiO_2 films. The light source was a 500 W xenon short-arc lamp (SX-UI500XQ optical moduleX, Ushio Inc., Tokyo, Japan) equipped with a water-based IR-cut filter, and a UV transmitting-visible absorbing filter (U330, HOYA, Tokyo, Japan) was used. FT/IR spectra were recorded over different time intervals under irradiation with UV light to estimate the amount of SA decomposition from the change in the absorbance of the CH_2 antisymmetric stretching vibration band at 2918 cm^{-1} .

3 RESULTS AND DISCUSSION

3.1 Preparation of the ODA LB film

Prior to LB deposition, we measured the surface pressure-molecular area (π -A) isotherms of ODA spread on the subphase at various pH values. As shown in Fig. 1, ODA forms an expanded monolayer at pH 3.0. As the pH increases, protonation of the amino group in the ODA molecule is inhibited and the monolayer changes to a condensed state, typically at pH values above 10.1 (corresponding to the pK_a of long-chain amines). The limiting area of the monolayer was estimated to be $0.22 \text{ nm}^2 \text{ molecule}^{-1}$ at pH 10.2, indicating a close-packed arrangement of the hydrocarbon chains. This monolayer is sufficiently stable for withstanding high surface pressures, up to 60 mN m^{-1} .

ODA LB films were then fabricated as a template for the formation of TiO_2 thin films. To prevent re-spreading of the deposited layer, a drying time of at least 10 min was used between dips of the substrate. A surface pressure of 45 mN m^{-1} was applied, and multilayer deposition of a Langmuir monolayer on the solid substrate was successfully carried out at a pH in the range of 10.1–10.5 with a transfer ratio close to unity.

Fig. 1 π -A isotherms of ODA on aqueous subphases at various pH values: (a) 3.0, (b) 6.1, and (c) 10.2.

3.2 Preparation and characterization of the TiO₂ films

The ODA LB films were next treated with an aqueous TPO solution, and UV-vis spectra were measured to ensure the formation of a TiO₂ layer. After immersion in the aqueous TPO solution, a distinctive absorption band was observed below 350 nm (see Fig. 2). This indicates formation of TiO₂, because UV light absorption is caused by the excitation of electrons from the valence band to the conduction band of TiO₂. In contrast, when we used an SA LB film, no absorption band appeared in the UV-vis spectrum. It is therefore clear that the amino groups in the ODA LB film catalyze hydrolysis of the titanium oxalate ions, and nucleation and crystal growth are induced to form a TiO₂ thin film. The ODA LB film is therefore considered to play a major role as a template during the immersion process.

Since the penetration of titanium oxalate ions into the inner layer of the LB film may become a rate-determining step for TiO₂ generation, we first examined the influence of the immersion conditions on the structure of the TiO₂ films. Figure 2 shows the time course of the UV-vis spectrum for five-layer ODA LB films during immersion in a 1×10^{-3} mol dm⁻³ TPO solution. From changes in the absorbance of the TiO₂ band in the UV region, it was found that the amount of TiO₂ generated gradually increased with immersion time, and finally reached a constant value within 30 min. When we used ODA LB films with larger numbers of build-up layers, a longer immersion time was required. A higher concentration of the TPO solution could shorten the immersion time required to attain the saturation of the generated TiO₂, but the amounts of TiO₂ were almost identical for ODA LB films with the same number of layers. We determined that, based on these results, the most appropriate conditions for achieving complete TiO₂ generation in subsequent experiments were as follows: immersion in a $1.0 \times$

Fig. 2 Time course of UV-vis spectrum of five-layer ODA LB film during immersion in 1×10^{-3} mol dm⁻³ TPO solution at 20 °C.

10^{-3} mol dm⁻³ TPO solution for 1 h using LB films with one to five layers.

Figure 3 shows the UV-vis spectra of the ODA-TiO₂ LB films with different numbers of layers. As shown in the inset in the figure, the absorbance at 240 nm increased in proportion to the number of ODA layers; it is therefore clear that the TPO reaction proceeds stoichiometrically with the deposited ODA. This indicates that the amount of TiO₂ (= thickness of the TiO₂ film) could be controlled by the number of deposited layers. Such precise and facile control of the film thickness is considered to be the most important advantage of the present method.

Using AFM measurements, changes in the surface morphology were observed for monolayer and five-layer LB films on a silicon wafer. Figures 4 and 5 show AFM images at different preparation stages. For the ODA monolayer (Fig. 4), the image of the as-deposited film revealed an almost uniform layer, apart from dust projections. However, the LB monolayer underwent a characteristic change during the course of the immersion process, with the formation of irregularly shaped patches typically seen in the image. Such a change in the layer structure was probably

Fig. 3 UV-vis spectra of ODA LB films (1-9 layers) after immersion in aqueous TPO solution. The inset shows plot of absorbance at 240 nm against number of layers.

Fig. 4 AFM images of the ODA LB monolayer at various preparation stages: (a) as-deposited LB film, (b) after immersion process, and (c) after heat-treatment at 500 °C.

Fig. 5 AFM images of five-layer ODA LB film at various preparation stages: (a) as-deposited LB film, (b) after immersion process, (c) after heat-treatment at 300°C, and (d) after heat-treatment at 500°C.

induced by the lateral expansion of the monolayer. The growth of crystalline TiO_2 around the polar head-groups in the monolayer causes the area expansion and thus results in a failure to retain a planar surface because parts of the collapsed film are pushed out of the monolayer. Subsequent heat-treatment at 500°C for 1 h eliminated organic molecules from the LB film and a thin TiO_2 film was then formed on the solid substrate. Cross-sectional analysis revealed that the TiO_2 film obtained from the ODA monolayer has a uniform and almost even surface, with a roughness of less than 1.3 nm.

In the case of the five-layer LB film (Fig. 5), the as-deposited film also has a uniform flat surface, apart from defects in the form of holes in the layer structure; the surface becomes uneven after immersion in TPO solution. A comparison of the AFM images at this stage shows that the roughness of the five-layer LB film is much larger than that of the ODA monolayer as a result of the area expansion of the respective layers in the LB film. After heat-treatment at 300°C, slight cracks appeared in the resulting TiO_2 film; these cracks became more noticeable as the temperature increased to 500°C. The cracks are caused by shrinkage of the TiO_2 film during the rapid increase in temperature, at a rate of 5–8 °C min⁻¹. It was confirmed that a slower heating rate reduces the crack formation in the films. The thickness of the five-layer film was estimated to be 3–4 nm, based on the depth of the cracks. Regardless of the presence of cracks, all the TiO_2 thin films prepared in this study were transparent and tightly bonded to the substrate.

3.3 Photocatalytic activity of TiO_2 films

Figure 6 shows the photocatalytic activity in the TiO_2 films heat-treated at various temperatures. An SA cast from a chloroform solution onto the TiO_2 film surface was used as an organic decomposition material. The films were irradiated by UV light having an intensity of 35 mW cm⁻²,

Fig. 6 Photocatalytic activities in TiO_2 films heat-treated at 300°C (Δ), 500°C ($\square$), and 600°C ($\diamond$).

All TiO_2 films were prepared from five-layer ODA LB films. Change in absorbance of CH_2 antisymmetric stretching vibration band corresponds to amount of decomposed SA after irradiation with UV light having 35 mW cm⁻² intensity.

and then FT/IR measurements were carried out. The SA decomposition rate was evaluated from the CH_2 antisymmetric stretching vibration band at 2918 cm⁻¹ because the decrease in absorbance directly translates to a decrease in SA loading on the TiO_2 film. The decomposition rate for the TiO_2 film on irradiation with UV light was faster than that for a bare quartz plate. The photodecomposition of SA proceeded according to pseudo-first-order reaction kinetics, as previously observed for TiO_2 films deposited by a dip-coating technique¹⁵). Among the TiO_2 films examined, the films heat-treated at higher temperatures had lower photocatalytic activity. Although the cause of this tendency remains uncertain at present, one possible explanation is that crystal growth is promoted as the temperature rises, accompanied by a decrease in the active TiO_2 surface area. In other words, the TiO_2 film may consist of nanoparticles with sufficient crystallinity to yield high photocatalytic activity, even in the case of heat-treatment at 300°C.

4 CONCLUSIONS

Ultrathin TiO_2 films were successfully prepared using an ODA LB film as a template. After optimizing the preparation conditions, the amount of TiO_2 generated by the hydrolysis of TPO in the LB films was found to be proportional to the number of deposited ODA layers, indicating that

the thickness of the TiO₂ films can be precisely controlled by adjusting the amount of ODA. AFM images showed that thicker TiO₂ films tended to crack during heat-treatment, while lower temperatures and slower heating rates reduced the appearance of cracks. Among the TiO₂ films calcined at 300-600°C, the films heat-treated at lower temperatures showed higher photocatalytic activity in the case of the decomposition of an SA cast film.

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