1 INTRODUCTION

In recent years, photocatalysts have attracted much attention as a method for degrading organic pollutant substances in air, soil and water environments1-8). In particular, it is well known that titanium dioxide (TiO2) is one of the photocatalysts that is widely used in nature 9,10). However, TiO2 photocatalysis only takes place under UV light radiation11). In order to effectively utilize solar light, many researchers in this field have focused their efforts on improving the photocatalytic performance in the visible region of the spectrum. For example, doping a semiconductor such as TiO2 with anions or cations can reduce the band gap, which enhances the absorption of visible light, leading to an improvement in photocatalytic performance12-22). Another way to promote photocatalytic activity in semiconductors is to retard the recombination of photoexcited electrons and positive holes by producing charge separation7,23-25). To achieve this, it is necessary to control the orientation of the particles or to fabricate a two-dimensional heterostructure of particles on a substrate. For this purpose, several methods have been utilized, including the Langmuir-Blodgett (LB) technique26-39), layer-by-layer self-assembly40,41), spin-coating, casting42,43), and vapor deposition44,45). Among these methods, the LB technique is the most suitable for preparing a layered structure of nanoparticles. In particular, the LB technique can effectively be used to deposit hetero-particulate, anisotropic films.

Another compound that exhibits strong photocatalytic activity is MoO3, which plays a unique role in various significant reactions, including the decomposition of NO and partial oxidation of hydrocarbons46-49). If a TiO2/MoO3 particulate film could be prepared, the electrons excited from the valence band of TiO2 should be transferred to the conduction band of MoO3, followed by charge separation of electrons and positive holes. Such a charge separation in the TiO2/MoO3 system is expected to enhance the photocatalytic effect on the decomposition of stearic acid.

In this present study, we report on the preparation of TiO2 and TiO2/MoO3 particulate films using a LB technique and also on the effectiveness of TiO2 and TiO2/MoO3 particulate films on the decomposition of stearic acid. Special attention has been paid to enhancing the photocatalytic performance of the TiO2/MoO3 particulate film.

2 EXPERIMENTAL

2.1 Materials

In the present study, the film materials of octadecylamine (ODA) and methylstearate (MeSt) were purchased from Aldrich Chemical Company and Sigma Chemical Co., respectively and used without further purification. Chloroform was employed as a spreading solvent for the monolay-
er-formation materials. The TiO$_2$ ($d = 45$ nm) sol was kindly supplied by Taki Chemical Co., Ltd. The TiO$_2$ particles were of the anatase form and their surfaces were chemically treated with organic acid. Molybdenum trioxide was purchased from Aldrich Chemical Company. The ammonium molybdate ($\text{(NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) used for synthesis of molybdenum trioxide was supplied from Wako Chemicals Co., Ltd. All other chemicals were standard, commercially available materials.

2.2 \pi-A isotherms and LB film fabrication

Measurement of surface pressure-area (\pi-A) isotherms and deposition of LB films were carried out with a Langmuir trough (PSD-100, USI System Co.). Triply distilled water, an aqueous solution containing ammonium molybdate ($1.0 \times 10^{-3}$ mg cm$^{-2}$), a colloidal solution of MoO$_3$ ($0.33 \times 10^{-3}$ mg cm$^{-2}$) and a colloidal solution of TiO$_2$ ($0.40$ mg cm$^{-2}$) were used as a subphase. The temperature of the subphase was maintained at 10-20°C and the pH was adjusted by adding hydrochloric acid or sodium hydroxide. The monolayers were produced on the surface of the subphase from ODA and ODA/MeSt mixed chloroform solutions ($1.0 \times 10^{-3}$ mol dm$^{-3}$). After spreading the solution, 15 min was allowed for the solvent to completely evaporate. The \pi-A isotherms were measured by moving hydrophobic Teflon barriers at a rate of 5 mm min$^{-1}$.

The LB film deposition was carried out by the following method. A monolayer of ODA on ODA or ODA/MeSt on the colloidal particle solution, produced using the method described above, was compressed until the surface pressure reached 10-20 mN m$^{-1}$. The monolayer was transferred onto a solid substrate at a rate of 7 mm min$^{-1}$ by the vertical dipping method under a fixed surface pressure. Microslide glass (thickness: 0.8-1.0 mm) for microscopes (Matsunami Glass Ind., Ltd) was used as the solid substrate and was first cleaned by soaking in chromic acid and rinsing several times in triply distilled water.

2.3 Characterization of the prepared LB films

The surface morphology of the as-deposited LB films was observed using atomic force microscopy (AFM) (Digital Instruments, Inc., Nanoscope IIIa). All AFM images were taken in a tapping mode using a commercially available silicon probe cantilever.

The surface composition of these films was measured with X-ray photoelectron spectroscopy (XPS) (Surface Science Instruments, SSX-100). An XP spectrometer with a non-monochromatized Mg Kα X-ray source ($h\nu=1253.6$ eV) was used. The charge-up shift correction was made by setting the C1s of the carbonized sample to 284.6 eV. The distribution of surface elements in these films was examined by an electron probe microanalyzer (EPMA) (JEOL, JXA-8200).

2.4 Evaluation of photocatalytic activity

The photocatalytic activity of the calcined thin particulate films of TiO$_2$ and TiO$_2$/MoO$_3$ was evaluated as follows. Stearic acid was deposited onto the surface of the thin particulate film or the glass substrate by the cast method. The decomposition of stearic acid was then carried out under irradiation of AM 1.5 using a solar simulator (Ushio Inc., xenon short-arc lamp (500 W), UXL-500SX) through a 365 nm bandpass filter for various durations. The light intensity was 100 mW cm$^{-2}$ at the sample surface. Changes in the light absorbance of the stearic acid monolayer as a function of irradiation time were measured by a Fourier transform infrared (FTIR) spectrophotometer (JASCO, FT/IR-8900) and the photocatalytic activity was evaluated from the change in absorbance at 2920 cm$^{-1}$.

3 RESULTS AND DISCUSSION

3.1 Fabrication of MoO$_3$ nanoparticulate films from aqueous ammonium molybdate solution

In order to investigate the deposition conditions, we measured surface pressure-area (\pi-A) isotherms on the colloidal particle subphase. Figure 1 shows the \pi-A isotherms of ODA on pure water and an aqueous ammonium molybdate solution. It can be seen that stable condensed films were formed on both subphases and collapsed at about 63 mN m$^{-1}$ for pure water and 44 mN m$^{-1}$ for aqueous ammonium molybdate solution. The limiting area of ODA on the pure water and the aqueous ammonium molybdate solution obtained by extrapolation to zero surface pressure are approximately 0.21 and 0.33 nm$^2$ molecule$^{-1}$, respectively. The value for ODA on aqueous molybdate solution is larger than that on water, implying the presence of an ionic interaction between ODA cations and molybdate anions.

Such an ODA monolayer could be maintained at a surface pressure of 30 mN m$^{-1}$ for at least 30 min and was easily transferred onto the glass substrate at a surface pressure of 30 mN m$^{-1}$ by the LB technique. This transfer means that the molybdate ions adsorb uniformly on the ODA monolayer. The results suggest that the molybdate ions were transferred as a molybdate-ODA (Mo-ODA) LB film.

To produce MoO$_3$ nanoparticles, the as-prepared Mo-ODA films were calcined in air at 400°C for 60 min. Figure 2 shows AFM images of an as-prepared five-monolayer Mo-ODA film (Fig. 2a) and calcined Mo-ODA films (Fig. 2b) three layers, Fig. 2c: five layers, Fig. 2d: seven layers), respectively. As Fig. 2a shows, a homogeneous surface, characteristic of five monolayer Mo-ODA film on glass substrate was observed before heat-treating at 400°C. In contrast, small nanoparticles on the glass substrate are visible in Figs. 2b, 2c, and 2d following heat-treating at 400°C for 60 min. This is probably due to the formation of MoO$_3$.
Fabrication and Photocatalytic Activity of TiO$_2$/MoO$_3$ Particulate Films

nanoparticles by oxidation of molybdate ions. Also, the number of small nanoparticles after calcination gradually increased with the increase of the number of Mo-ODA monolayer, indicating regular deposition of Mo-ODA monolayer.

To gain further insight into the surface composition of the Mo-ODA particles, XPS measurements were carried out. Figure 3 shows the XPS spectra for a one and three-layer Mo-ODA film before and after calcination. In Fig. 3a, c, we can see the characteristic peaks of the as-prepared one and three-layer Mo-ODA films. The peaks at 415.9, 398.9, 235.9 and 232.9 eV correspond to binding energies of Mo3p1/2, Mo3p3/2, Mo3d3/2 and Mo3d5/2 electrons, respectively. The peaks at 153.7 and 102.7 eV correspond to the binding energy of Si2s and Si2p electrons. In addition, the peaks of 532.4 and 284.7 eV represent the 1s electron of oxygen and carbon atoms, respectively. However, the peak at 376.7 eV is not clear at this moment.

In the case of the calcined Mo-ODA samples, new sharp Mo peaks were observed at 496.7 and 1066 eV and are assigned to Mo3s and Mo-MNV, respectively. Furthermore, we can observe the characteristic doublet peaks at 235.9 and 232.9 eV caused by spin-orbit splitting; these values are in good agreement with those previously reported for MoO$_3$ films.

It was found that the peak intensity of silicon in the calcined Mo-ODA samples was increased by the calcinations of the as-prepared samples. These results indicate that the surface of the glass substrate was covered with the Mo-ODA LB films before calcination and the Mo-ODA LB films were then transformed to MoO$_3$ nanoparticles by calcinations, which is due to the fact that MoO$_3$ particles form an island structure on the glass substrate.

We also prepared multilayer Mo-ODA LB films and then examined them by XPS. From the spectra, the XPS intensities of Mo and N elements increased linearly with increasing number of layers, indicating a regular deposition of Mo-ODA monolayers (not shown in the figure).

To further elucidate the presence of MoO$_3$ nanoparticles, EPMA measurements were performed. Figure 4 shows the EPMA mapping images of MoO$_3$ particles calcined at 400°C for 60 min from a nine-layer Mo-ODA LB film. Figure 4a represents the compositional image that exhibits the electron scattering coming from nanoparticles. It can be seen from the compositional image that the nanoparticles are uniformly distributed and are clumped together on the glass substrate. Figures 4b and 4c show the distribution of O and Mo atoms on the surface. From the combined EPMA images, the presence of MoO$_3$ nanoparticles on the glass substrate is confirmed. In addition, we tried to fabricate the MoO$_3$ particulate film from the colloidal MoO$_3$ solution using LB technique.

3.2 Fabrication of MoO$_3$ particulate films from aqueous MoO$_3$ suspension

We have previously studied the fabrication of TiO$_2$ and CdS-TiO$_2$ particulate films using the LB technique. It was found that the number of adsorbed particles could be
controlled by the mixing of neutrally charged MeSt to the ODA monolayer film in order to change the charge density in the film. Using this technique, both TiO₂ and CdS-TiO₂ particulate thin films were successfully deposited on a solid substrate by alternative deposition using the electrostatic interaction between the positively charged ODA monolayer and negatively charged TiO₂ or CdS particles.

Therefore, we attempted to fabricate a TiO₂/MoO₃ particulate thin film using a similar technique. At first, to determine the surface pressure on deposition, π-A isotherms were measured by changing molar fraction of ODA (XODA) for a ODA/MeSt mixed monolayer. Figure 5 shows the π-A isotherms at various XODA values for the ODA/MeSt mixed monolayer. As can be seen from the π-A isotherms in Fig. 5a, an ODA monolayer on MoO₃ colloidal solutions at XODA = 1.0 (in Fig. 6b) forms a relatively condensed film and shows an increase in molecular area compared with that on pure water. The increase is caused by adsorption of MoO₃ particles due to the presence of an interaction (mainly electrostatic) between the ODA monolayer film and MoO₃ particles. When XODA was systematically decreased by the addition of MeSt, the average molecular area was found to decrease with decreasing XODA value. This is because the density of adsorbed MoO₃ particles on the film was reduced as a result of the lower positive charge density.

Figure 6 shows surface AFM images of the single-layer MoO₃-ODA LB film obtained at various XODA values in addition to the bare film substrate. In Fig. 6a (bare substrate), no particles are visible on the surface of the glass sub-

Fig. 3 XPS Spectra of the As-prepared Mo-ODA LB Films before (a, c) and after Calcinations (b, d) at 400°C for 60 min.

Fig. 4 EPMA Mapping Images of MoO₃ Films Prepared by Calcining Mo-ODA LB Films (nine layers) at 400°C for 60 min.
strate except for pre-existing circular scratches about 50 nm in diameter. Figures 6b, 6c and 6d show AFM images of films deposited with X_{ODA} values of 1.0, 0.1 and 0.01 respectively. A MoO_3 particulate film was formed on the surface of the glass substrate. However, the surface of the LB film fabricated at X_{ODA} = 0.01 (in Fig. 6d) was sparsely covered with a monolayer of the MoO_3-ODA LB film, while that at X_{ODA} = 1.0 was partially covered with a multilayer of the MoO_3-ODA LB film. This indicates that the former and the latter films are due to the lower and higher positive charge densities of ODA/MeSt mixed monolayer films, respectively. In the case of the surface shown in Fig. 6c, MoO_3 particles were densely arranged on the surface of glass substrate; these particles had diameters of approximately 18-20 nm. Therefore, a homogeneous MoO_3 particulate film is considered to be formed on the glass substrate at X_{ODA} = 0.1. In addition, the homogeneous and uniform distribution of MoO_3 particles indicates that ODA and MeSt molecules are homogeneously mixed in the monolayer. Accordingly, the optimal X_{ODA} for preparing a closely packed MoO_3 particulate film is estimated to be about 0.1.

Next, in order to produce a tight network of MoO_3, the MoO_3-ODA LB film deposited at X_{ODA} = 1.0 was heated at 400°C for 60 min. Figure 7 shows AFM images of the surface of single-layer of the heat-treated MoO_3 particulate thin film. These AFM images confirm that the MoO_3 particulate thin film has the same structure as the as-prepared particulate film. In addition, these AFM images indicate no change in particle size except the dust of the white spots of about 200 nm.

3.3 Photocatalytic activities of MoO_3/TiO_2 particulate films

In a previous paper[37], we prepared TiO_2 and CdS/TiO_2 particulate films and evaluated their photocatalytic activities using stearic acid as decomposition substance and
H. Natori, K. Kobayashi and M. Takahashi

irradiating the films with UV radiation. The results obtained indicate that the calcined CdS/TiO₂ particulate film has a lower photodecomposition rate than the TiO₂ particulate film and thus that induced charge transfer does not occur in the CdS/TiO₂ particulate film system.

Therefore, we investigated the photocatalytic activities of TiO₂/MoO₃ particulate films prepared by the LB technique. Firstly, a MoO₃ particulate monolayer was deposited on the glass substrate by using colloidal solutions of MoO₃ as a subphase. The as-deposited particulate film was kept in a desiccator for 24 hrs. TiO₂/MoO₃ particulate films were then fabricated by depositing a TiO₂ particulate monolayer onto a MoO₃ particulate monolayer on the glass substrate.

The as-deposited particulate films were calcined in an electric furnace at 400°C for 60 min to eliminate organic compounds. AFM images of the calcined TiO₂ and TiO₂/MnO₃ particulate films indicated that the particles are sufficiently stable to maintain their size.

Next, in order to investigate the photocatalytic activity of the TiO₂ and TiO₂/MoO₃ particulate films, the surfaces of these films were covered with a stearic acid using the cast technique. The decomposition of stearic acid is estimated from the reduction in the absorbance of the CH₂ antisymmetric stretching vibration band at 2920 cm⁻¹. Figure 8 shows the photocatalytic activities for decomposition of stearic acid film deposited on TiO₂ and TiO₂/MoO₃ particulate films. In this figure, the changes in absorption (precision: ±0.003) are plotted against irradiation time. The decomposition of stearic acid on the TiO₂ and TiO₂/MoO₃ particulate films is found to proceed linearly with time and to saturate after 225 min. In particular, the decomposition rate of stearic acid on the TiO₂/MoO₃ particulate film is faster than that on the TiO₂ particulate film. As shown in Scheme 1, this is due to acceleration of the charge separation in which photogenerated electrons seem to be effectively moved to the TiO₂ surface, followed by transport to the MoO₃ particles while photogenerated holes remain within the TiO₂ particles.

These results demonstrate that photoinduced charge transfer occurs in these systems. Specifically, on irradiating with ultraviolet and visible light, excited electrons from the valency band are transferred to the conduction band and then transfer to the conduction band of MoO₃ particle. Such a charge separation system is expected to enhance the photocatalytic activity of decomposition of stearic acid.

4 CONCLUSIONS

In summary, TiO₂ and TiO₂/MoO₃ particulate films were successfully prepared by the LB technique. The TiO₂ and TiO₂/MoO₃ particulate films were found to have a layered structure. Furthermore, the calcined as-deposited particulate film exhibits higher photocatalytic activity for decomposition of stearic acid than the TiO₂ particulate film.
Fabrication and Photocatalytic Activity of TiO$_2$/MoO$_3$ Particulate Films

Scheme 1 Schematic Drawing for Charge Separation at the TiO$_2$/MoO$_3$ Particulate Film System.

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