

Preparation and Characterization of Hydrophilic TiO₂ Film

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A novel titania sol for the preparation of hydrophilic TiO₂ films was synthesized from TiCl₄. TiO₂ films were prepared by spraying the sol on glass substrates and the hydrophilic properties of the films were investigated with illumination of UV light. The contact angle of a water drop on the films decreased to less than 7°, which indicates the excellent hydrophilicity of the TiO₂ films.

Keywords : Hydrophilic property, TiO₂ sol, Contact angle, Photocatalyst.

Introduction

TiO₂ exhibits the outstanding decomposition ability toward organic compounds and fairly good antibacterial activity with their strong photocatalytic reaction induced by the illumination of UV light.¹⁻³ It has also been known that the TiO₂ film shows the hydrophilicity due to the photocatalytic nature of TiO₂.⁴⁻⁷ For example, the TiO₂ film coated on ordinary plastics, which is essentially hydrophobic, is so hydrophilic that the oily substances adsorbed on the surface can be easily removed.

The hydrophilicity of the TiO₂ film can be estimated by measuring the contact angle of water drop on the TiO₂ film; the contact angle, which was above 50° at first, decreases to less than 10° with UV light irradiation. As one of the applications of this phenomenon, TiO₂ film coated on the surface of window glass of automobile can prevent dewing caused by the temperature difference between the inside and outside of the automobile on a humid day. It is also possible that the films prevent adsorbing oily substances, and even those adsorbed already are easily washed out by water.

For the industrial application, it is essential to find out the suitable titania sol-gel solutions, which lead to the TiO₂ film with excellent hydrophilic ability. The optimum process techniques in preparing uniform TiO₂ films should be developed as well.

Previously, we synthesized a titania sol derived from Ti(OC₂H₅)₄ for the purpose of preparing hydrophilic TiO₂ film. The synthetic procedure of titania sol and the hydrophilic properties of the fabricated TiO₂ film with this sol were reported in the previous paper.⁸ In this work, we report the synthetic route for a novel titania sol based on TiCl₄, which induces a better hydrophilic properties for the derived TiO₂ films. TiO₂ films were prepared by spraying the sol, and the contact angle of a water drop on the films was measured to evaluate the hydrophilicity of the films.

Experimental Section

Preparation of sol and TiO₂ film. 0.5 M TiOCl₂ stock solution was made by adding the deionized distilled water to TiCl₄. Then, 0.5 M NH₄OH solution was added to the stock

solution, until the pH of the solution became neutral with rigorous stirring. As the result of above reactions, white precipitates dispersed finely in the solution. The precipitates were separated using a centrifuge, then washed by distilled water. Separation and washing of the precipitates were repeated five times. Then, H₂O₂ solution was added to the precipitates and stirred. This reaction was carried out in an ice bath because its reaction is exothermic. A transparent sol with a yellow color was obtained by the addition of H₂O₂ and stirring about 3 hours. The sol obtained was aged at 60 °C for 24 hours, then stored at room temperature.

TiO₂ film was prepared by spraying the sol on a glass substrate. A conventional slide glass for an optical microscope was used as a substrate. The glass was previously treated with 0.1 M HCl, then washed with distilled water before the film coating process. The TiO₂ films were deposited with the equipment described in Figure 1, by spraying 10 mL of titania sol to the glass substrate located in the electric furnace maintained at 500 °C. A nozzle was used for spraying the sol and the pressure of compressed air at the nozzle tip was kept constant at 20 psi. To prevent the temperature drop of the furnace caused by spraying the sol, the sol was sprayed several times at about two-second intervals. The glass substrates coated by the sol were transferred to another electric furnace maintained at 500 °C and heat treated for 1 hour in air.

Characterization of sol and film. The size and morphology of titania colloids in the prepared sol were investigated by zeta sizer (PHOTAR, ELS-800) and TEM (Carl Zeiss, EM912 Omega). The crystal phases in the film were determined by thin film X-ray diffractometer (Rigaku, D/max-

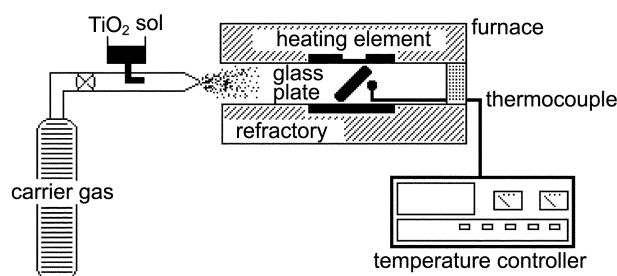


Figure 1. Spray pyrolysis apparatus.

RC). The contact angle of the water drop were measured by contact angle measuring equipment (Kyowa Interface science, CA-V150) with illumination of UV light. UV light of the He-Xe lamp with wavelength range 325 nm-390 nm and light intensity 3.2 mW/cm^2 , was used as source light. The light absorbance or transmittance of the films was also measured by UV-Vis spectrophotometer (Shimadzu, UV-2401PC).

Results and Discussion

Preparation and characterization of the sol. In general, two kinds of precursors are used for the preparation of titania sol; one is organic precursor such as titanium alkoxide or other organometallic titanium complexes, and the other is inorganic precursor such as titanium chloride or titanium sulfate. The organic precursors are so reactive, as in the case of the titanium alkoxide, that TiO_2 could be simply obtained by hydrolysis at room temperature. On the other hand, an advantage of inorganic precursors such as titanium chloride is, they are relatively less expensive than the organic precursors, but it is difficult to control the sol-gel reaction with inorganic precursors.

Aggregation of precipitates caused by the rapid hydrolysis, condensation, and polymerization of the precursor could occur in the process of sol synthesis. The addition of some acids effectively prevents the aggregation of the precipitates, because the acids lead to the electrostatic repulsion of the precipitates.⁹ The acidic sol, however, cannot be applied on the metallic substrates because of its corrosive nature. Consequently, neutral or slightly acidic TiO_2 sol is required in order to coat TiO_2 films on all kinds of materials. Recently, a method to make the neutral sol using H_2O_2 has been reported.^{10,11}

In this study, the neutral (pH=7) sol was synthesized by the addition of excess H_2O_2 to the white precipitates obtained from TiCl_4 precursor. The reactions that occurred in this process could be expressed as follows.

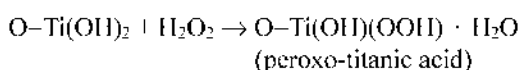
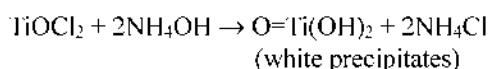
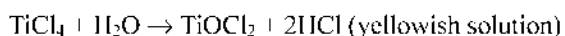


Figure 2 shows the TEM photograph of particles in the sol synthesized through the above reactions. It is indicated from Figure 2 that the needle-like particles are dispersed finely without aggregation in the solution. The particles are considered as peroxo-titanic acid formed by the addition of excess H_2O_2 to the precipitates of hydrated titanium oxide as shown in the above reaction equation.

It has been found from the result of zeta sizer analysis that the mean particle size is about 70 nm. Figure 3 shows the FT-IR spectra of the sol. The absorption band at near 900 cm^{-1} corresponds to the vibration mode for the peroxo group, -O-O-. Partial electron transfer from hydroxo, peroxo ligands to the coordination sphere Ti^{4+} ion, which has empty

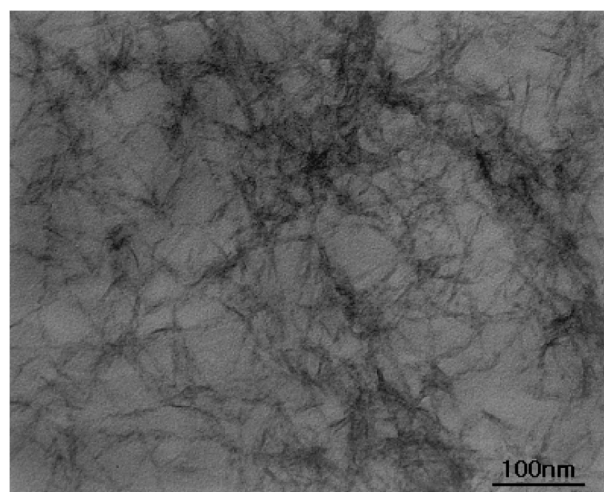


Figure 2. TEM photograph of the TiO_2 sol prepared with TiCl_4 as a precursor.

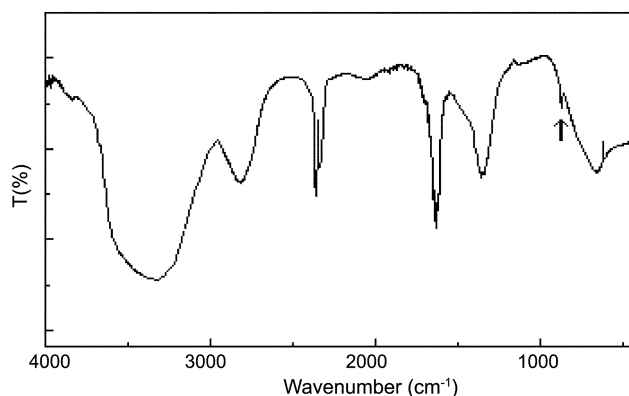


Figure 3. FT-IR curve for the prepared sol (The arrow indicates the peak position for peroxo group bond).

d-orbitals, occurs in the early stage of the sol formation. Hence, the partial positive charges are built up on the hydrogen atoms of hydroxo, peroxo ligands with the electron transfer. The positive charges on the hydrogen weaken the O-H bond, and this induces the solution acidic (pH \approx 3).¹² However, the recombination of O-H bond by the condensation of peroxo-titanic acids takes place slowly and continuously. Thus, the pH of the solution increases with the elapse of time, and finally becomes neutral (pH = 7).

Characterization of TiO_2 film. It has been known that the anatase phase of TiO_2 shows higher photocatalytic activities than rutile phase because its band gap is larger by 0.2 eV than rutile.¹³⁻¹⁵ Therefore, in this study, the films prepared by spray pyrolysis method were post-annealed at $500 \text{ }^\circ\text{C}$ to obtain anatase phase. Figure 4 shows the X-ray diffraction patterns for the TiO_2 film heated at $500 \text{ }^\circ\text{C}$. The diffraction patterns for the as-deposited film also shown in Figure 4. It can be seen from Figure 4 that the as-deposited film by spray pyrolysis method is in a noncrystalline state, but it can be converted to pure anatase phase by heating at $500 \text{ }^\circ\text{C}$.

UV-Vis absorption and transmittance spectra for the film heated at $500 \text{ }^\circ\text{C}$ are shown in Figure 5. The characteristic

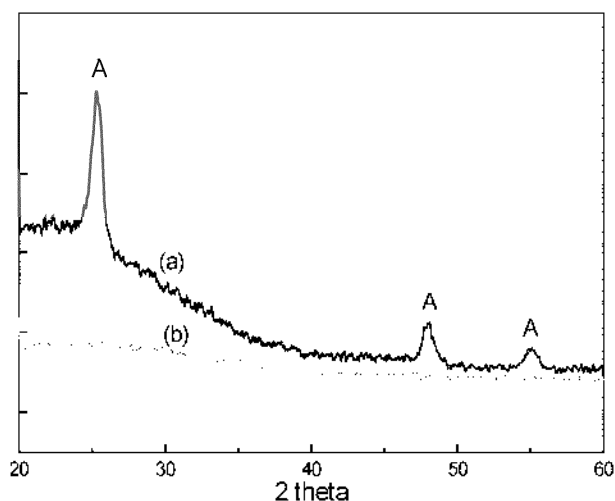


Figure 4. X-ray diffraction patterns for the prepared TiO₂ film in glancing angle mode (a: heated at 500 °C. b: as-deposited film. A: anatase)

absorption peak of anatase phase was observed at the wavelength of about 300 nm. From the transmittance curve of Figure 5, it can be seen that the film shows relatively low transmittance, below 75%, in the visible wavelength region. Heterogeneity of the film, which was formed in the process of spraying the sol, might have lowered the transmittance of the film. Haze, stripes or other ununiformities, however, were not found with the naked eye.

Fujishima *et al.*¹⁶ proposed a mechanism for the hydrophilicity of the TiO₂ film as follows. The free electrons generated in the crystal by the UV illumination reduce the valence state of Ti from +4 to +3 on the TiO₂ film surface, and the positive holes oxidize O²⁻ ion to O. Consequently, oxygen vacancies are formed in the crystal and OH groups are chemically adsorbed on the vacant site of the oxygen of the film surface.

Hydrophobic molecules, however, are adsorbed on the surface of the TiO₂ film at the first stage because the chemically adsorbed water molecules are unstable. Hence, the film shows hydrophobicity at first. With the illumination of UV

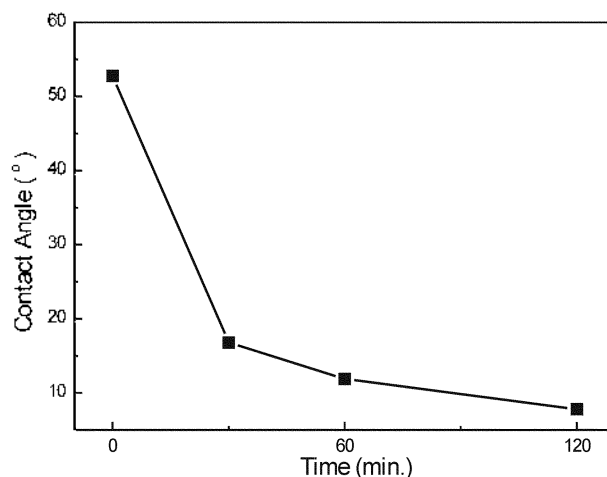


Figure 6. Change of the contact angles for the TiO₂ film with UV irradiation.

light, the hydrophobic molecules are decomposed by the photocatalytic oxidation reaction and the water molecules chemically adsorbed come out from the TiO₂ surface.¹⁷ Thus, this water can physisorb other water molecules, and the film becomes gradually hydrophilic.

The contact angle of a water drop on the surface of the film greatly decreases, as the film surface changes to hydrophilic. The change of contact angle of a water drop as a function of illumination time by UV light are shown in Figure 6. It can be seen from Figure 6 that the initial contact angles of 50° is decreased down to 7° after 120 min of UV light illumination.

We already reported the hydrophilicity of the TiO₂ film prepared from the Ti(OEt)₄-based titania sol. In this film, the contact angle of a water drop decreased to 10° after UV light illumination for 2 hr. In our present work, the TiO₂ film was prepared with the titania sol synthesized from TiCl₄, and the contact angle was decreased to 7° after UV light illumination for 1 hr, as shown in Figure 6. It can be seen from these results that the film prepared from TiCl₄-based sol in this study shows better hydrophilicity than that prepared from

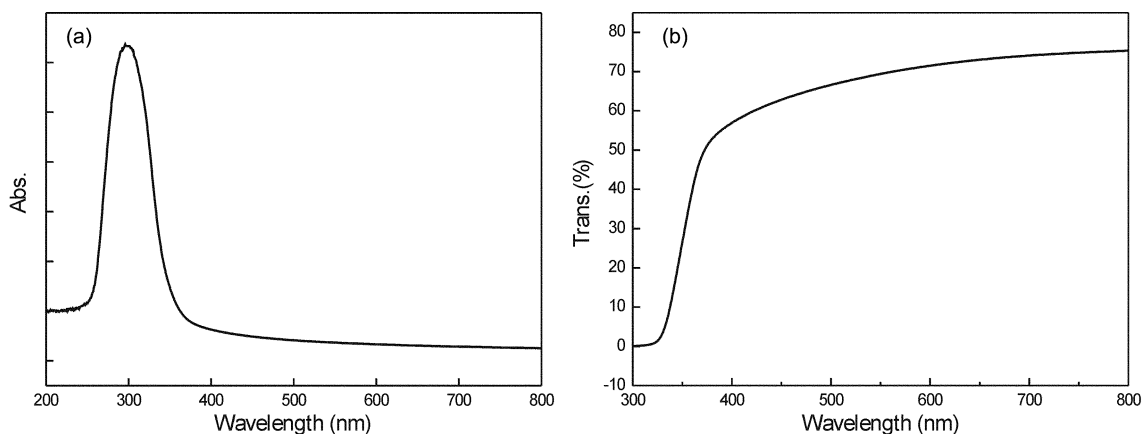


Figure 5. UV-Vis spectra of TiO₂ films.

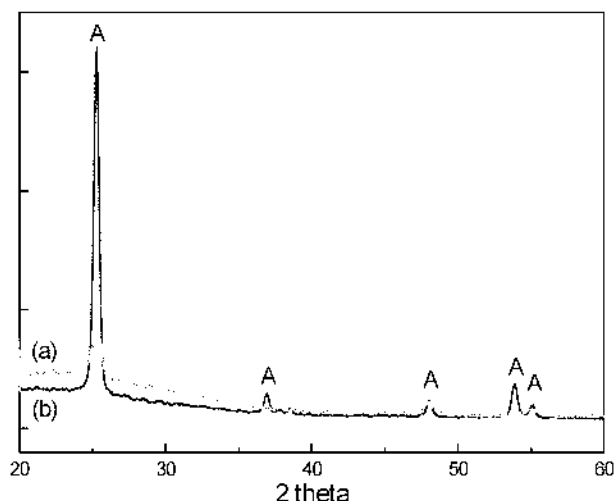


Figure 7. X-ray diffraction patterns for the prepared TiO_2 film in glancing angle mode (prepared from TiCl_4 -based sol (a), $\text{Ti}(\text{OEt})_4$ -based sol (b), A: anatase)

$\text{Ti}(\text{OEt})_4$ -based sol.

The difference of the hydrophilicity between the two films might be explained by the size effect of the crystals precipitated in the TiO_2 films. The crystal size in the films was calculated by the Debye-Scherrer formula,¹⁸ for which X-ray peak widths at half-maxima (FWHM), shown in Figure 7, were used. It can be found from Figure 7 that the FWHM in the film derived from TiCl_4 was about three times than the film from $\text{Ti}(\text{OEt})_4$. The crystal size in the film TiCl_4 was about one third of that in the film from $\text{Ti}(\text{OEt})_4$. It is suggested that the crystal size in the film is related to the hydrophilicity of the TiO_2 film.

Presumably, TiO_2 film with smaller grain size have larger specific surface area, and the increased surface area causes the crystal to adsorb more amount of water molecules.¹⁹

Conclusions

1) The titania nano-sol in needle-like shape with the size

of about 70 nm well-dispersed in aqueous solution was synthesized at pH 7, using TiCl_4 precursor.

2) TiO_2 films with anatase phase were prepared by spray pyrolysis method on a glass substrate.

3) The hydrophilicity of the TiO_2 film by this method is better than that of films derived from titanium alkoxide: The initial contact angles of 50° is decreased down to 7° by 2 hr of UV light illumination.

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