

Preparation of a transparent and flexible self-standing film of layered titania/isostearate nanocomposite

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A titania-based self-standing film with high transparency and flexibility was successfully prepared via a sol-gel process, in which a titanium tetraisopropoxide/isostearate complex (precursor), *n*-hexylammonium isostearate (catalyst), and *o*-xylene (solvent) were used. The sol obtained by the sol-gel reaction was floated on a water surface to form an unsupported film. This film was composed of a titania/isostearate nanocomposite with ordered layer structure. The basal spacings of the nanocomposites depended on the chain length of the carboxylate modifier.

I. INTRODUCTION

Recently, the preparation of inorganic/organic nanocomposites by the sol-gel process has been intensively investigated.¹⁻³ Of the various inorganic/organic nanocomposites, layered nanocomposites consisting of stacked oxide sheets belong to one of the most important material systems because these materials have potential applicability as adsorbents, catalysts, and hosts for various guest molecules. So far, a large number of papers have been published on the synthesis of silica-based layered nanocomposites obtained by the sol-gel reaction of silicon alkoxide in the presence of surfactants forming micelle templates.⁴⁻⁷

Processing these materials into thin films is another important subject, especially from a technological point of view. A large number of papers have reported the synthesis of supported films of nanocomposites,⁵⁻⁸ however, the films required for practical application are unsupported ones. Self-standing films would find wide application, such as catalyst supports and separation membranes, for which supported films are not suitable. The preparation of transparent self-standing films of silica-based nanostructured materials was already reported by Ogawa and his co-workers.^{9,10} They prepared transparent films of layered silica/surfactant nanocomposites from tetramethoxysilane and obtained self-standing films by peeling the dried films off a polyethylene substrate.⁹

They also prepared thin films of the silica/surfactant mesostructured materials by removing the films from PMMA-coated glass substrates by dissolving the intervening [poly(methyl methacrylate)] (PMMA).¹⁰ In these works on the synthesis of silica-based nanocomposite films, silica/alkyltrimethylammonium complexes were assembled by the hydrophobic interaction between the long alkyl chains in aqueous solution, and an ordered structure was constructed on the substrate by condensation due to the evaporation of the solvent.^{7,8}

The preparation and characterization of titania (TiO₂) is one of the subjects of current research because of its excellent photo-semiconducting property, and in particular, highly transparent titania are strongly desired.¹¹ If the titania-based oxide materials can be obtained in a layered form, they could be used as the precursor for new types of photofunctional materials due to their highly ordered structure and to a large interlayer area suitable for the incorporation of other photofunctional guests. However, transparent self-standing films of layered titania/organic nanocomposites have not been obtained by similar methods for preparing silica/organic nanocomposite films. These difficulties come from the reactivity of titanium alkoxide, which is much higher than that of silicon alkoxide.^{3,12,13} The hydrolysis rate of titanium alkoxide is much faster than that of silicon alkoxide. With the coexistence of surfactants such as alkyltrimethylammonium ion, layered silica is obtained by two-dimensional growth in aqueous solution; in contrast, spherical particles of titanium oxide are usually obtained from titanium alkoxide in the same aqueous environment.¹⁴ Ogawa et al.¹⁵ reported the synthesis of a transparent self-standing film of nanoporous silica containing titanium oxide; however,

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it was basically composed of silica because the Ti/Si ratio was quite low (Ti/Si = 1/50). Xu and Anderson¹⁶ prepared unsupported titania membranes via the sol-gel reaction of titanium tetra-*tert*-amyloxide. These membranes were obtained by firing a xerogel consisting of small colloidal particles (less than 3 nm in diameter) and cannot be classified as inorganic/organic nanocomposites. These membranes did not have an ordered layer structure, but instead they had a microporous structure formed by the packing of fine particles. Moriguchi et al.^{17,18} obtained a TiO₂ nanoparticulate film on various substrates such as a quartz plate and a Si wafer by the Langmuir-Blodgett method, though the material thus obtained was not self-standing.

Deceleration of the hydrolysis of titanium alkoxide is necessary for the synthesis of layered titanium oxide because the dimension of polymerization in the sol-gel process depends on the rate of hydrolysis.¹⁹ Without the deceleration of the hydrolysis, three-dimensional polymerization takes place due to very rapid hydrolysis of the titanium alkoxides. For the formation of layered materials, two-dimensional polymerization is required.

Only decelerated hydrolysis leads to the formation of small colloidal particles with the development of a titanium oxide network.¹⁶ Appropriate two-dimensional growth does not occur because the polycondensation rate of titanium alkoxide is significantly slow.²⁰ The reactive sites for polycondensation are hydroxy groups formed by the hydrolysis of titanium alkoxide, so polycondensation would be decelerated by slow hydrolysis. Therefore, not only the deceleration of the hydrolysis but also the acceleration of the polycondensation is indispensable for forming an ordered layer structure.

In this paper, we report the synthesis of a layered titania/isostearate nanocomposite with the simultaneous controlling of the hydrolysis and polycondensation. For decelerating hydrolysis, a hydrophobic organic solvent, *o*-xylene, was used. The hydrolysis of metal alkoxides is retarded in hydrophobic solvents.²¹ On the other hand, for accelerating polycondensation, *n*-hexylammonium isostearate salt was used as a catalyst. We have already found that the salt catalyst effectively accelerates the polycondensation of titanium alkoxide.^{19,20,22,23} We also report the unique procedure for making a self-standing film of layered titania/isostearate nanocomposite by floating the sol on the water surface, which yields self-standing films with good transparency and flexibility.

II. EXPERIMENTAL

A. Materials and sample preparations

Titanium tetraisopropoxide (>97%, Kanto Chemical Co., Inc., Tokyo, Japan), isostearic acid (>95%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), *n*-octanoic acid (>98%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan),

n-hexanoic acid (>98%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), *n*-butyric acid (>99%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), *n*-hexylamine (>98%, Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), and *o*-xylene (>99%, Kanto Chemical Co., Inc., Tokyo, Japan) were used without further purification.

The typical experimental procedure is as follows.

Two *o*-xylene solutions were prepared under nitrogen atmosphere. One contained 12.5 mmol titanium tetraisopropoxide Ti[OCH(CH₃)₂]₄ and 6.25 mmol isostearic acid {CH₃(CH₂)₈-CH[(CH₂)₆CH₃]-COOH} in 15 ml *o*-xylene, and the other contained 1.25 mmol isostearic acid and 1.25 mmol *n*-hexylamine in 10 ml *o*-xylene. The sol-gel reaction was started by mixing both solutions together. Hydrous nitrogen gas (300 ppm in moisture content) was used to add the water required for the sol-gel reaction. The reactor was kept under the bubbling hydrous nitrogen gas with a 2.5 ml min⁻¹ flow rate to gradually absorb moisture from the gas for 180 h. The reaction temperature was 25 °C. The sol obtained by this reaction was floated on the water. After floating the sol on the water surface for 2 h, the floating film was pulled up and dried at 80 °C.

B. Characterization techniques

Infrared absorption spectra of solutions were obtained with a Perkin-Elmer 1650FTIR (Boston, MA) spectrometer by the transmission method. The reaction process was monitored by measuring the solution viscosity (Viscomate VM-1A-L, Yamaichi Electronic Co. Ltd., Tokyo, Japan). The obtained sols and precipitates were diluted with a solvent and dropped on smooth plates of a cleaved, highly oriented pyrolytic graphite and dried under vacuum for 5 h. Their morphology was observed with a scanning electron microscope (SEM, S-500, Hitachi, Ltd., Tokyo, Japan). Samples (sol or film) for x-ray diffraction (XRD; RINT2550H, Rigaku Co. Ltd., Tokyo, Japan) were cast on a glass plate and dried at 80 °C. The ultraviolet-visible (UV-vis) absorption spectrum of the resultant film was obtained using a spectrometer (UV-2400PC, Shimadzu Corporation, Kyoto, Japan). The dried film was ground to powder and dispersed with methanol for the observation with a transmission electron microscope (TEM; JEM1010, JEOL Ltd., Tokyo, Japan).

III. RESULTS AND DISCUSSION

A. Formation of isostearate-modified titanium alkoxide and a salt catalyst

In the solution containing a mixture of Ti[OCH(CH₃)₂]₄ and isostearic acid, isostearate-modified titanium alkoxide was readily formed. The infrared (IR) spectra of the mixture [Fig. 1(B)] showed characteristic absorption bands at 1427, 1460, and 1542 cm⁻¹, which were attributed to the COO⁻ stretching for bidentate coordination of

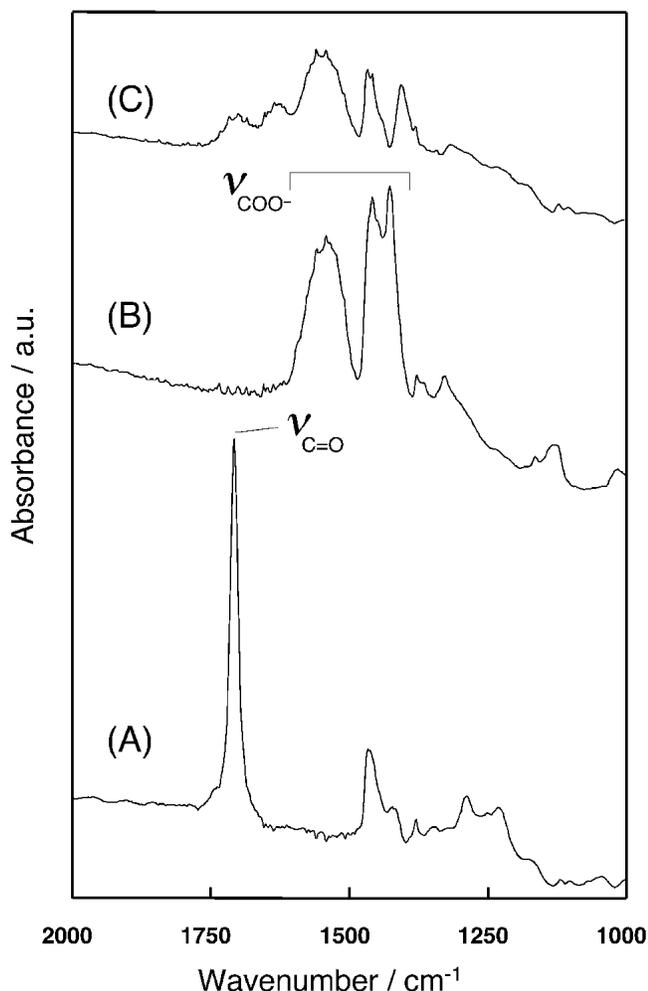


FIG. 1. IR absorption spectra of *o*-xylene solution containing (A) isostearic acid, (B) a mixture of isostearic acid and titanium alkoxide, and (C) a mixture of isostearic acid and *n*-hexylamine.

the Ti(IV)-carboxylate complex.¹⁹ An absorption band at 1707 cm^{-1} assigned to the C=O stretching for isostearic acid [Fig. 1(A)] was not observed. Isostearate-modified titanium alkoxide could be easily dispersed in *o*-xylene because isostearate has an organophilic long alkyl chain.²²

In the *o*-xylene solution of a mixture of isostearic acid and *n*-hexylamine, *n*-hexylammonium isostearate salt formed. As shown in Fig. 1(C), the absorption band at 1707 cm^{-1} attributable to isostearic acid [Fig. 1(A)] disappeared due to the neutralization of isostearic acid by *n*-hexylamine.

B. Formation of titania/isostearate nanocomposite in a hydrophobic solvent with a salt catalyst

Titania/isostearate nanocomposites were prepared via a sol-gel process from isostearate-modified titanium alkoxide in a hydrophobic solvent (*o*-xylene). The water required for the hydrolysis of the sol-gel reaction was

successively added by continuous bubbling of the hydrous nitrogen gas. Because of the hydrophobicity of the solvent and the gradual water addition procedure, the water content of the reaction system was kept very low. Although such a condition is suitable for the control of the hydrolysis reaction, slow reaction rate caused by the low-water content can be a problem. To overcome this problem, hexylammonium isostearate was used as a salt catalyst to accelerate polycondensation.

Viscous clear sol was formed by the sol-gel reaction with an increase in the solution viscosity, as shown in Fig. 2(A). This indicates that the well-grown titania product would be formed in the solution. Characteristic IR absorption bands at 1428 and 1533 cm^{-1} were observed for the sol after drying at $120\text{ }^{\circ}\text{C}$. These bands were attributed to the COO^- stretching of the titania/carboxylate complex.¹⁹ Isostearate modifiers still remained and were bonded to the final titania product; that is, the titania/isostearate composite was formed. Sanchez and Ribot³ indicated that for low water content ($[\text{H}_2\text{O}]/[\text{Ti}] \ll 1$) acetylacetonate (acac) modified titanium alkoxide led to modified oxo-alkoxide clusters. Here acac-modifiers coordinate onto these molecular clusters. Also in our process, isostearate-modified oxo-alkoxide clusters may have formed during the initial stage because the water content is very low. Further continuous addition of water from the hydrous nitrogen atmosphere causes the oxide growth to proceed. Complex formation between the isostearate modifiers and oxide products probably continued to occur during the oxide growth process because of the gradual water addition. This would be a reason for the formation of the titania-based nanocomposite with organic modifiers.

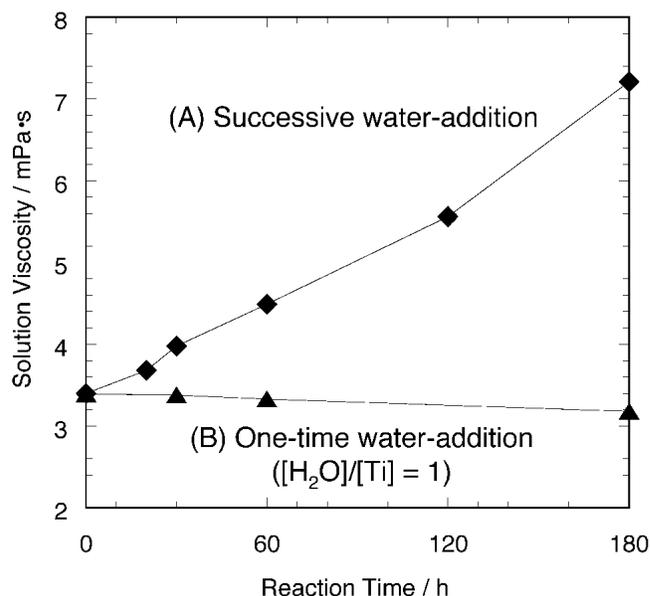


FIG. 2. Time-course of the solution viscosity and its dependence on the method of adding water.

C. Effect of the method of adding water on oxide growth

In the sol-gel reaction, water addition is required to start the hydrolysis of the alkoxide. We tried two ways of adding water, and the reaction was monitored by measuring solution viscosity because oxide growth in the sol-gel reaction can be monitored by the change in solution viscosity.^{19,20}

When the water was successively added by continuous bubbling of the hydrous nitrogen gas, the solution viscosity increased as the reaction time advanced [Fig. 2(A)] to form a clear sol. The oxide growth probably proceeded as the reaction time progressed without causing any phase separation. However, when water was added to the solution at all at once at the beginning, a homogeneous viscous sol was not formed regardless of the amount of added water. In the case of high water content, the ratio $[\text{H}_2\text{O}]/[\text{Ti}] \geq 1.5$, a turbid gel was rapidly formed and separated from the solution phase. Sanchez and Ribot³ indicated that the hydrolysis and condensation reactions of acac-modified titanium alkoxide were governed by the hydrolysis ratio ($[\text{H}_2\text{O}]/[\text{Ti}]$) and more “condensed species” were obtained as it increased. Similar condensed products may have formed also in our case by the large amount of water, leading to phase separation. In contrast, an obvious change was not observed in the case of less water addition. For example, no increase in solution viscosity was observed [Fig. 2(B)] for the case of low water ratio ($[\text{H}_2\text{O}]/[\text{Ti}] = 1$). The results suggest that oxide growth scarcely proceeded

with the reaction time. The same holds for the case with less water addition, $[\text{H}_2\text{O}]/[\text{Ti}] < 1$. Viscous sol was not obtained by one-time water addition even if the amount of added water was varied. The results suggest that the oxide growth proceeded with the reaction time in the case of the successive water-addition process with the hydrous nitrogen gas, while it hardly progressed in the case of the one-time water-addition process. Thus, successive water addition is required for sufficient oxide growth without phase separation in this system.

D. Effect of the salt catalyst on the dimensionality of the resultant products

A transparent viscous sol was obtained using *n*-hexylammonium isostearate as a salt catalyst. SEM observation was conducted to reveal whether two-dimensional polymerization took place. After drying a diluted solution of the sol, SEM observation was conducted to reveal the morphology of the products in solutions. Two-dimensional sheets were clearly observed [Fig. 3(a)], indicating the successful two-dimensional polymerization. The sheets were very thin, on the order of a nanometer. As will be mentioned in the next section, the x-ray diffraction profile for the titania/isostearate nanocomposite [Fig. 4(A)] showed a diffraction peak with $d = 1.83$ nm. All these observations support the formation of a two-dimensional sheet. Characteristic IR absorption bands at 1428 and 1533 cm^{-1} due to the COO^- stretching of the titania/carboxylate complex¹⁹ were observed for the sol after drying at 120 °C. Isostearate ions

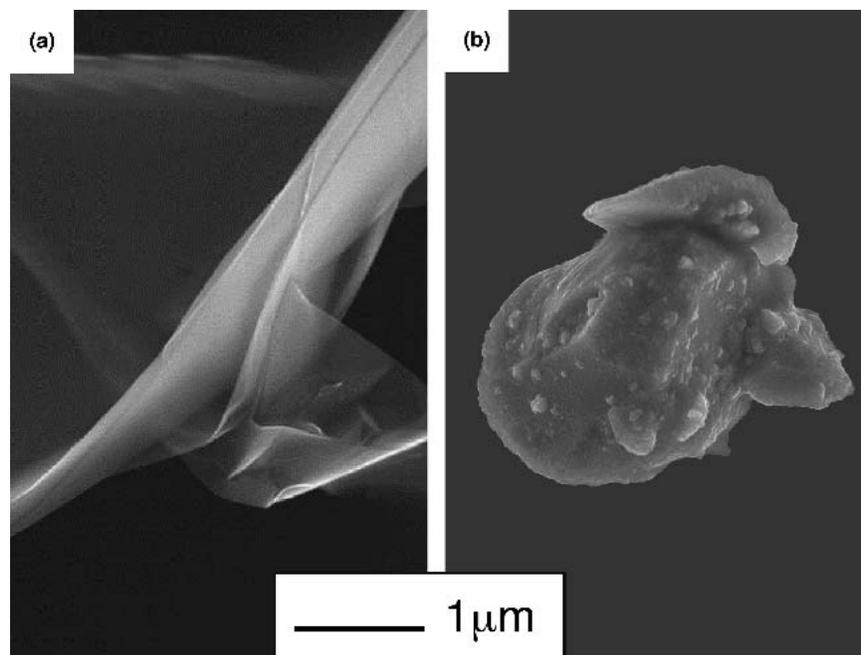


FIG. 3. Scanning electron micrographs of the products in the sol prepared (a) with and (b) without *n*-hexylammonium isostearate used as a salt catalyst. Samples were dried under vacuum at room temperature.

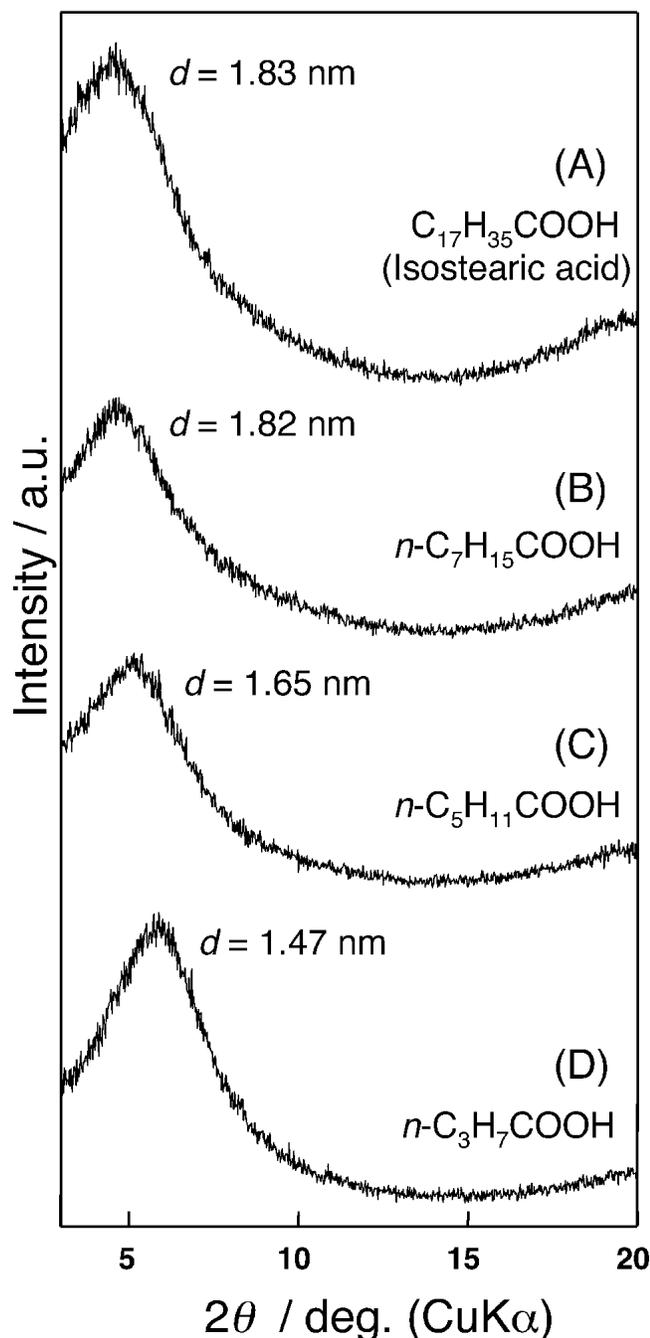


FIG. 4. XRD profiles of titania/carboxylate nanocomposites obtained by casting the sol on glass substrates. Samples were dried at 80 °C. The incorporated carboxylic acids and the d values for the diffraction peaks are indicated in the figure.

would coordinate on the surface of the two-dimensional titania sheets. Because an isostearate ion has a long alkyl chain, the sheets would be stabilized in a hydrophobic solvent solution by the coordination with such carboxylates.²²

Without using a salt catalyst, the solution became turbid with precipitation. Only bulky particles of about 2- μm diameter were obtained [Fig. 3(b)]. Although the hydrolysis was decelerated by the hydrophobic solvent

and gradual water-addition procedure, three-dimensional growth would take place. This indicates that the polycondensation was slower than the hydrolysis because of the absence of the salt catalyst; namely, the hydrolysis proceeded to a large degree before polycondensation occurred, which makes the three-dimensional growth dominant. Thus, not only the deceleration of the hydrolysis but also acceleration of polycondensation by the addition of a salt catalyst is required in this system to obtain titania sheets formed by two-dimensional growth.

E. Formation of layer structure and its dependence on the length of carboxylic acids

The x-ray diffraction pattern for the titania/isostearate nanocomposite was obtained by casting and drying the sol on a glass [Fig. 4(A)]. A diffraction peak with $d = 1.83$ nm was observed. This pattern was ascribed to a layer structure with the basal spacing of the d value. When titanium alkoxide was modified with other carboxylic acids (n -octanoic acid, n -hexanoic acid, and n -butyric acid) instead of isostearic acid, the basal spacing changed with the variety of the carboxylic acids [Figs. 4(B)–4(D)]. To estimate the long-axis length of used carboxylic acids, these were calculated using a semiempirical molecular dynamics program (MM2 in Chem3D, Cambridge Soft, MA), taking van der Waals radii into consideration (Fig. 5). The basal spacing of the layer structure depended on the length of the carboxylic acid, and almost the same basal spacing was observed for each case using isostearic acid and n -octanoic acid, the long-axis lengths of which are similar. The layer structure was probably constructed by the self-assembly of carboxylates coordinating on the titania sheet surfaces.

The diffraction peaks were not observed for the sol before drying. This is because the sol contained a substantial amount of solvents before drying, and ordering of the layers was not attained. Only after solvent evaporation were the layers stacked in an orderly manner to form the layered nanocomposite. To assemble titania/organic nanocomposites, solvent removal and hydrophobic interaction between the organic species would be necessary. The stacking of layers is usually hampered in the presence of a hydrophobic solvent. The long alkyl chains in a hydrophobic solvent cannot interact well because of the high affinity of the hydrophobic solvent for the long alkyl chains.

F. Preparation of self-standing film of layered titania/isostearate nanocomposite

Using the viscous clear sol obtained with the isostearate-modified titanium alkoxide and a salt catalyst (n -hexylammonium isostearate), a flexible and transparent self-standing film was formed on a water surface. The floating sol gradually coagulated on the water with slight

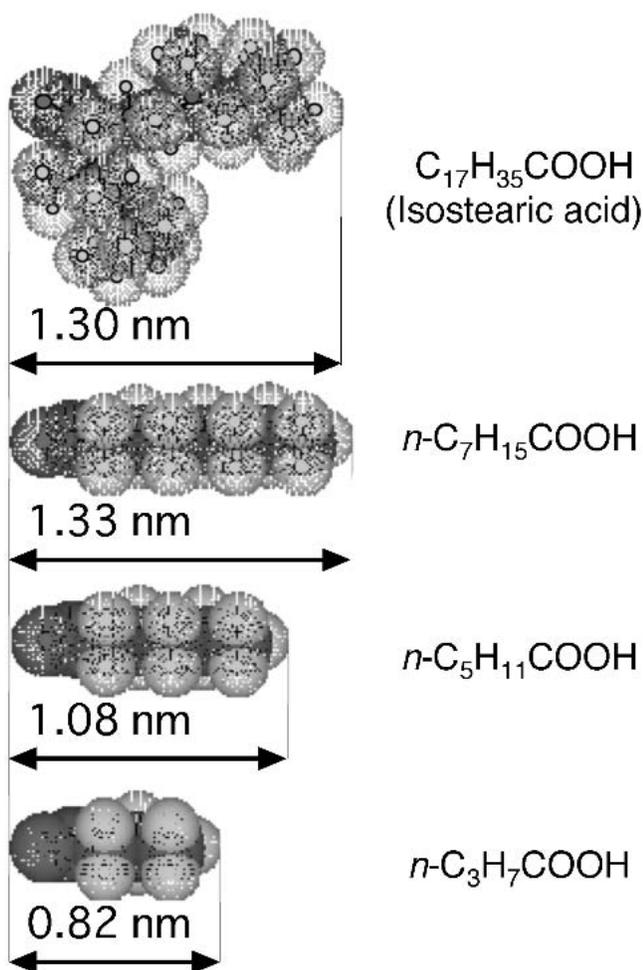


FIG. 5. Long-axis lengths for carboxylic acid molecules calculated by a semiempirical molecular dynamics program.

shrinkage and oozing of the solvent to form a film. The formed film was pulled up from the water surface and dried to evaporate the remaining solvent. The thickness of the obtained film was estimated at dozens of μm . Figure 6 shows the UV-vis transmission curve for the self-standing film. The film was transparent (about 75%) in the visible-light region ($>350\text{ nm}$). Figure 7 shows the TEM image for the powder obtained by grinding the film. The stacking of the sheets, and their edges, are observed. This indicates that the obtained film was constructed by the aggregation of titania sheets. These sheets were so thin that a sheet can be seen through the sheet in front of it. The thickness of the sheet is possibly on the order of a nanometer. Since the thickness was smaller than the wavelength of the visible light, the film was highly transparent, and it allows the light to pass through without scattering.¹⁴ On the other hand, this film cut the UV light off sharply in the range below about 350 nm, as shown Fig. 6. Titanium oxide is a kind of photo-semiconducting oxide material, and the value of the absorption edge for the obtained film is assignable to

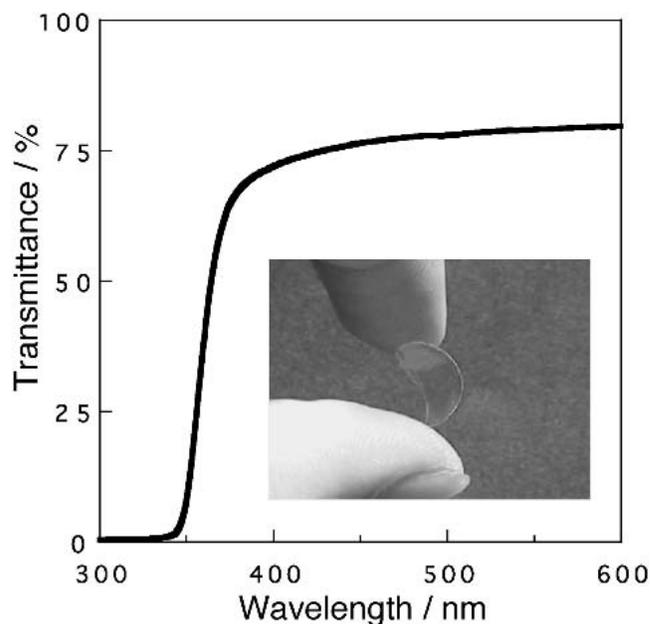


FIG. 6. Transmission spectrum for the self-standing film prepared from the sol containing titania/isostearate nanocomposites. (Inset) A photograph of the obtained self-standing film.

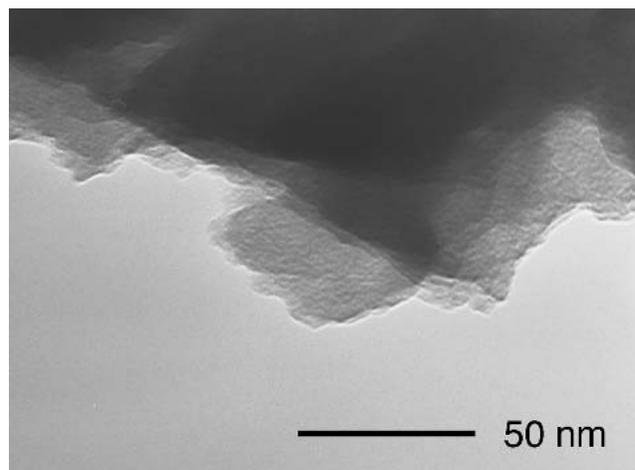


FIG. 7. Transmission electron micrograph of the self-standing film prepared from the sol containing titania/isostearate nanocomposites. The sample was ground to powder and dispersed with methanol for the observation.

a charge-transfer band of titanium oxide. Most of the UV light would be absorbed by the titania sheets, which constitute the obtained film.

A diffraction peak with $d = 2.20\text{ nm}$ was observed for this film (Fig. 8). The self-standing film also has an ordered layer structure constructed by the stacking of titania sheets. The d value was slightly larger, and the peak width was narrower than that for the dried sol formed on a glass plate subjected to x-ray diffraction. The reason for the larger basal spacing and better peak shape for the self-standing film is not clear; however,

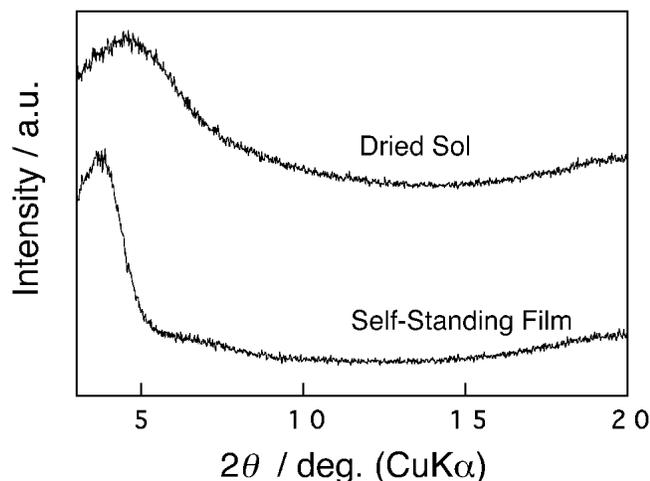


FIG. 8. XRD profiles of the sol containing titania/isostearate nanocomposites and the self-standing film obtained from the same sol. Both samples were dried at 80 °C.

they probably occur because the titania/organic nanocomposites formed on water were much more ordered due to hydrophobic interaction between the alkyl chains in the carboxylates at the interface of the sol and water.

G. Dependence of film-formability on the amount of added isostearic acid

Table I summarizes the state of the obtained sol and the formation of self-standing films for different amounts of isostearic acid in the titanium tetraisopropoxide solution. For the low content of isostearic acid ([isostearic acid]/[Ti] = 0, 0.25), the resulting solution became turbid with precipitation. A self-standing film could not be obtained from these turbid solutions. Three-dimensional growth caused by rapid hydrolysis would have occurred because of an insufficient amount of isostearic acid. The control of the reactivity of titanium alkoxide has been achieved through the addition of complexing ligands,^{3,13,24,25} and the coordination of carboxylic acid is also known to restrict the hydrolysis of the titanium alkoxide and the dimension of oxide growth.¹⁹ The added isostearic acid would act not only as a structural director but also as a hydrolysis inhibitor.

Film-formable clear sol was obtained when the ratio

TABLE I. Dependence of the amount of added isostearic acid on the state of the resultant solution and the film-formability.

| [Isostearic acid]/[Ti] | State of the resultant solution | Film-formability |
|------------------------|---------------------------------|------------------|
| 0 | Precipitation | No |
| 0.25 | Precipitation | No |
| 0.50 | Clear Sol | Yes |
| 0.75 | Clear Sol | No |
| 1.0 | Clear Sol | No |

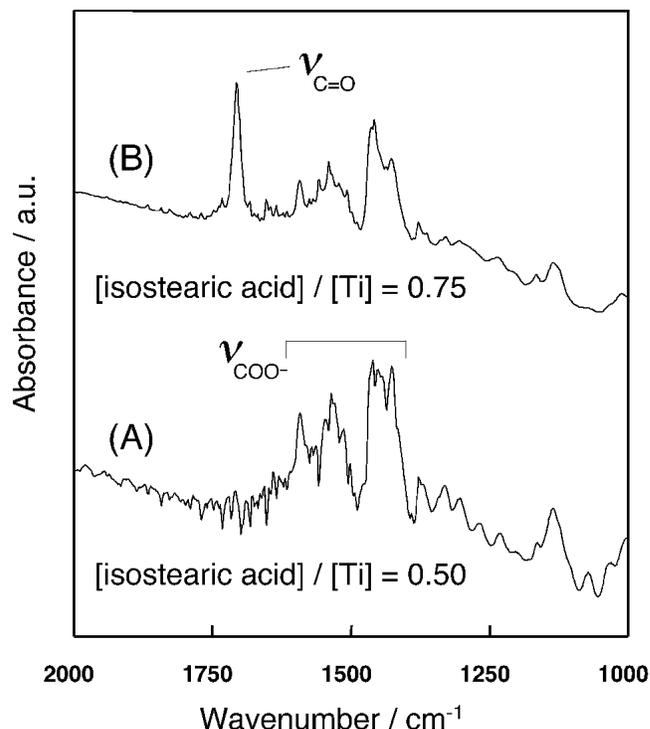


FIG. 9. IR absorption spectra of the resulting sol containing titania/isostearate nanocomposites and its dependence on the amount of added isostearic acid. The ratios [isostearic acid]/[Ti] are shown in the figure.

[isostearic acid]/[Ti] was 0.5. The IR spectra of the solution containing both isostearic acid and titanium tetraisopropoxide showed characteristic adsorption bands at 1426, 1458, and 1540 cm^{-1} , which were attributable to COO^- stretching bands for the bidentate coordination of the Ti(IV)-carboxylate complex¹⁹ [Fig. 9(A)]. The coordination of isostearate should have restricted the hydrolysis reaction so that a sheetlike structure was formed by the lower dimensional growth.

In the case of more isostearic acid content, the ratio [isostearic acid]/[Ti] ≥ 0.75 , floated sol was not concentrated on the water surface, and a self-standing film was not formed in spite of the formation of the clear sol. The IR spectra of this sol ([isostearic acid]/[Ti] = 0.75) exhibited an additional absorption peak at 1707 cm^{-1} [Fig. 9(B)]. This peak is due to the carbonyl band (C=O stretching), which was observed for the solution containing only isostearic acid [Fig. 1(A)]. This indicates that the non-coordinating isostearic acid exists in this sol. Such excess isostearic acid in sol would block the concentration of the sol on the water surface and inhibit the formation of a self-standing film.

IV. CONCLUSIONS

In summary, a flexible and transparent self-standing film of titania/isostearate nanocomposite was obtained by floating a sol on water. The sol was prepared by a

hydrophobic sol-gel process, in which a titanium tetra-isopropoxide/isostearate complex (a precursor), *n*-hexylammonium isostearate (catalyst), and *o*-xylene (solvent) were used. The sol thus obtained was poured onto water, and after the removal of the solvent, the ordered layer structure was constructed, yielding a self-standing film.

Because the obtained film was optically clear, a new application may be expected in the field of optics and optoelectronics. There is a possibility that a new type of photoconducting material will be obtained by intercalating photofunctional guests into the titania interlayer. It may be used as a precursor of novel photocatalysts, although both processes for the removal of organic modifiers and for the crystallization of titania sheets would be necessary. The development of such a synthetic approach would pave the way for a new application field for titania.

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