

# Preparation of Thin Films of a Layered Titanate by the Exfoliation of $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$

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Thin films composed of a layered titanate were prepared by a so-called soft-chemical method that took advantage of exfoliation of the layered material  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ . The exfoliated titanate sheets were easily oriented on a substrate by means of spin-coating. The prepared thin films had a layered structure, and the modification of them was possible by utilizing its ion-exchange and photocatalytic abilities.

## Introduction

Thin films of inorganic materials, especially those made of metals and semiconductors, have been used for various purposes in many fields. With the spread of the applications of such thin films, various methods of preparation such as sputtering, molecular beam epitaxy (MBE), laser ablation, and chemical vapor deposition (CVD) have been developed. However, these methods require high technologies and elaborate conditions, e.g., high temperature, ultrahigh vacuum, and so on. In addition, the methods usually require long preparation time to obtain films with thicknesses on the order of micrometers.

A series of methods that do not require high temperature or ultrahigh vacuum of preparation by the so-called soft chemical technique has been contrived and explored. For example, a method that took advantage of the exfoliation of layered compounds was developed. Some layered materials, such as layered titanates and niobates, have been reported to be exfoliated in aqueous solutions containing amine surfactants,<sup>1–4</sup> and some ultrathin films based on the exfoliated layers originated from  $\alpha\text{-Zr}(\text{HPO}_4)_2$  and  $\text{K}_4\text{Nb}_6\text{O}_{17}$  were successfully synthesized.<sup>3,4</sup> The exfoliation method seems to be promising because there exist a large number of the layered inorganic solids whose layers would be exfoliated.

The method of spin-coating is widely used for the preparation of thin films by spreading solutions uniformly and is expectedly applicable to the construction of thin films having exfoliated layers from layered materials.

We are especially interested in thin films composed of layered photofunctional semiconductors such as titanates (e.g.,  $\text{K}_{0.8}\text{Fe}_{0.8}\text{Ti}_{1.2}\text{O}_{10}$ <sup>5</sup>) and niobates (e.g.,  $\text{K}_4\text{Nb}_6\text{O}_{17}$ <sup>6–9</sup>), because some optical studies of the photofunctionality should be more successfully carried out in the form of films rather than in heterogeneous powders. In addition, the preparation of thin films based on such materials is significant with respect to their applicability to many fields. For example, they may be useful in the electronics field as electrodes taking advantage of their layered structure and ion-exchange properties.

$\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ , where  $\square$  represents vacancy, is one of the alkali metal titanates that has a layered structure related to that of lepidocrocite,  $\text{FeOOH}$ .<sup>10</sup> The structure of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  ( $x \sim 0.7$ ) is shown in Figure 1. The ion-exchange properties of this material were reported,<sup>11,12</sup> and the exfoliation of titanate layers of  $\text{H}^+/\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  was performed by using tetrabutylammonium hydroxide ( $\text{TBA}^+\text{OH}^-$ ).<sup>13</sup>

In this paper we report the preparation of the layered thin films of  $\text{H}^+/\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  by utilizing spin coating, and the characterization and modification of the thin films are described.

## Experimental Section

**Materials.** The layered alkali-metal titanate  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  ( $x \sim 0.7$ ) was prepared by a conventional solid-state reaction.

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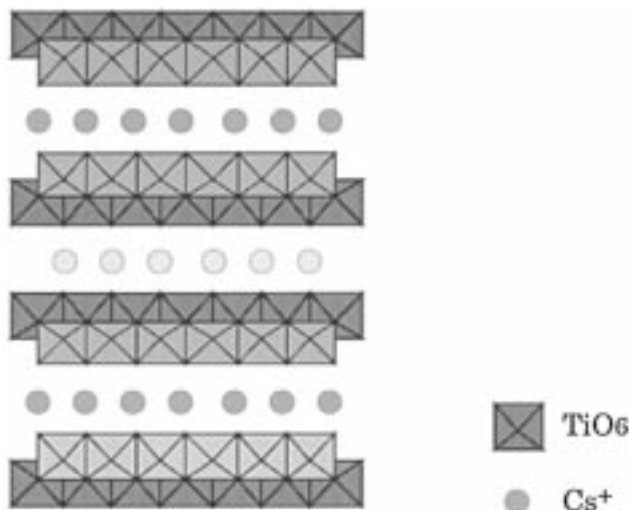
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**Figure 1.** Crystal structure of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ .

A stoichiometric mixture of  $\text{CsCO}_3$  and  $\text{TiO}_2$  was calcined at 1027 K for 20 h. Then the obtained material  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  was converted into its proton-exchanged form by stirring the powder of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  (5 g) in 100 mL of HCl aqueous solution ( $1.0 \text{ mol L}^{-1}$ ) at room temperature for 24 h. After several times repetition of this acid-treatment, the product was filtered, washed by distilled water, and dried in air. The almost 100% degree of  $\text{H}^+$  exchange was confirmed by energy-dispersive X-ray spectrometry (EDX). Therefore, the  $\text{H}^+$ -exchanged form of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  is referred to as  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  hereafter.

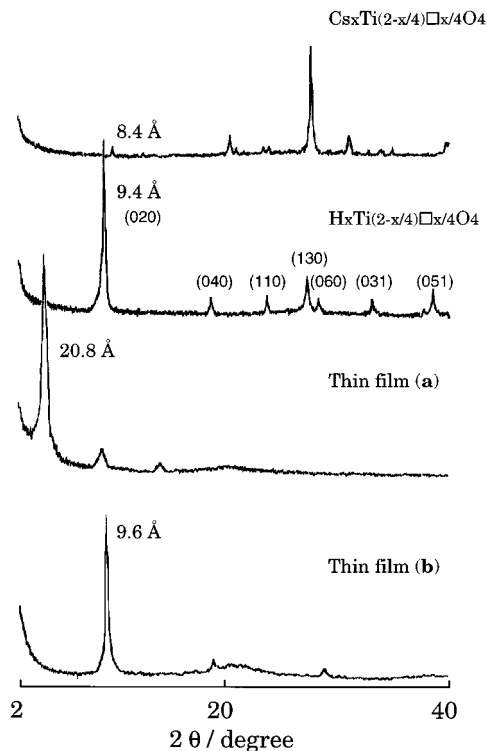
**Exfoliation of Titanate Sheets.** The exfoliation of titanate sheets was carried out in aqueous tetrabutylammonium hydroxide ( $\text{TBA}^+\text{OH}^-$ ) solution or in aqueous ethylamine solution at room temperature for 24 h.  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  (0.5 g) was added to the aqueous solution (100 mL) which contained 8 times more of the  $\text{TBA}^+\text{OH}^-$  or ethylamine in molar quantity than that of  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$ , and it was stirred for 24 h at room temperature. The obtained suspension was centrifuged at 2000 rpm for 30 min, and then the precipitate was removed from the suspension. The suspension was used as the "original" suspension for preparation of thin films. The 1.0 mL of the "original" suspension was diluted to 100 mL by distilled water, and it was used as the "diluted" suspension.

**Preparations of Thin Films.** A glass plate ( $2 \times 2 \text{ cm}$ ) was fixed on the spin-coater and rotated at 2000 rpm, and then the suspension (0.1 mL) was added dropwise to the plate. The plate was rotated until the suspension spread homogeneously onto the plate. This process of spin-coating was repeated several times.

A series of the thin films that were obtained from aqueous  $\text{TBA}^+\text{OH}^-$  solution are referred to as thin films **a**, and those obtained from aqueous ethylamine solution are referred to as thin films **b**, respectively.

Some thin films **b** were prepared with different times of spin-coating and with the "original" or the "diluted" suspension: the thin films **b-1**, **b-2**, and **b-3** were obtained from one, two, and three, spin-coatings of the "original" suspension, respectively, while thin film **b-4** was prepared from two spin-coatings of the "diluted" suspension.

**Characterization of the Thin Films.** The structural characterizations were carried out by X-ray diffraction (XRD, Geigerflex RAD-B system  $\text{Cu K}\alpha$  15 mA, Rigaku) and scanning electron microscopy (SEM, Akashi ISI DS130S). For SEM photographs, thin films prepared on Pt-coated Si wafers were used. Infrared spectroscopy was used to check the existence of amine in the interlayers. Sixty-four scans were collected for each spectrum at a resolution of  $4 \text{ cm}^{-1}$  with a Fourier transform FT-IR (JASCO FT-IR 7300) spectrometer with an MCT detector. An IR cell was directly connected to a closed-gas circulating system. For the IR measurement, thin films



**Figure 2.** XRD patterns of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ ,  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$ , thin films **a** and **b**.

were prepared on a  $\text{CaF}_2$  plate instead of a glass plate. The surface morphology of the thin films was studied in ambient air by atomic force microscopy (AFM, TopoMetrix TMX-2100) of the constant-force mode.

**Modification of the Thin Films.** Modification of thin films was attempted in two different ways. One is replacing amines at the interlayer with other cations to synthesize thermally stable thin films. The other is the photooxidation of amines utilizing the photocatalytic ability of the titanate sheets to remove amines at the interlayer. The modification of the thin films was successfully carried out only for the thin films **b**, which were obtained from ethylamine suspensions, because the thin films **a** were dissolved in water again, in contrast to the thin films **b**, which were stable in water. Therefore, the thin film **b-2** was used for the study of modification.

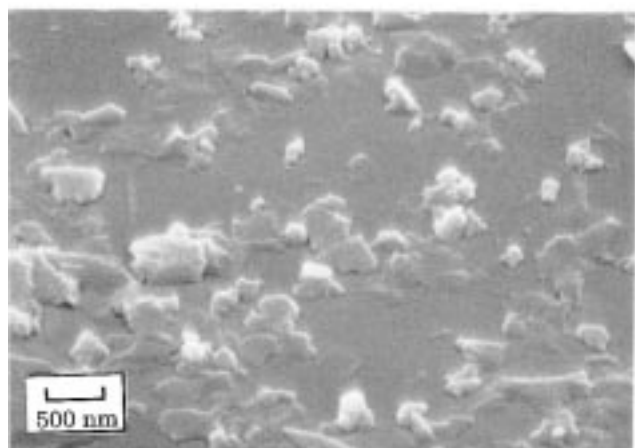
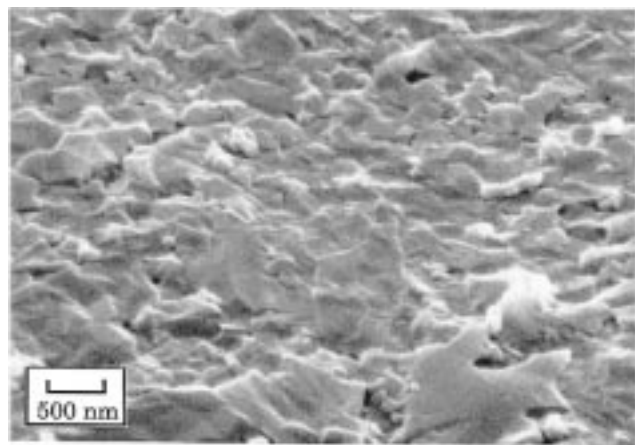
Replacing of amines with other cations was carried out in various aqueous solutions such as  $\text{CsOH}$ ,  $\text{KOH}$ ,  $\text{CsNO}_3$ ,  $\text{KNO}_3$ , and  $\text{Ni}(\text{NO}_3)_2$  ( $0.1 \text{ mol L}^{-1}$ ) at room temperature. The thin film **b-2** was placed in the bottom of a beaker containing an aqueous solution and was left for a certain period, from several hours to a few weeks. Then the thin film was washed with distilled water.

Photooxidation of amine was carried out in distilled water by irradiation with a Xe lamp (500 W). The thin film was placed in a Pyrex beaker, and the light was irradiated from the side of the beaker for 24 h without stirring.

## Results and Discussion

**XRD.** The XRD patterns of the thin films are shown in Figure 2. Those of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  and  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  powders are also shown in Figure 2 for comparison. A strong (020) diffraction peak was observed in the XRD pattern of the  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  powder. The  $d$  value of the (020) diffraction of  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  and  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  are 8.3 and 9.4 Å, respectively.

Only peaks due to the (0 $k$ 0) diffraction peaks were observed for the thin film **a**, and the  $d$  value of the (020)

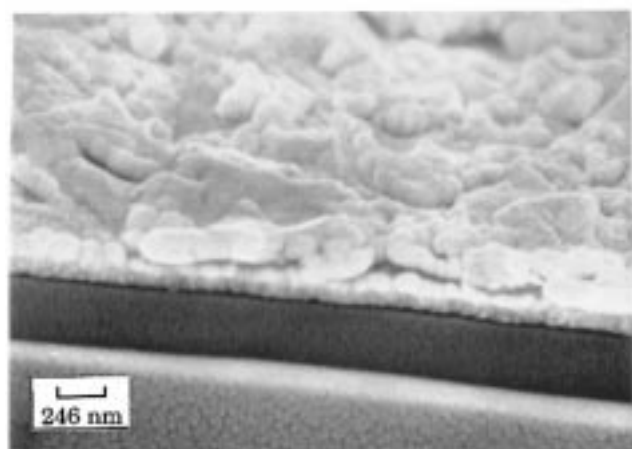
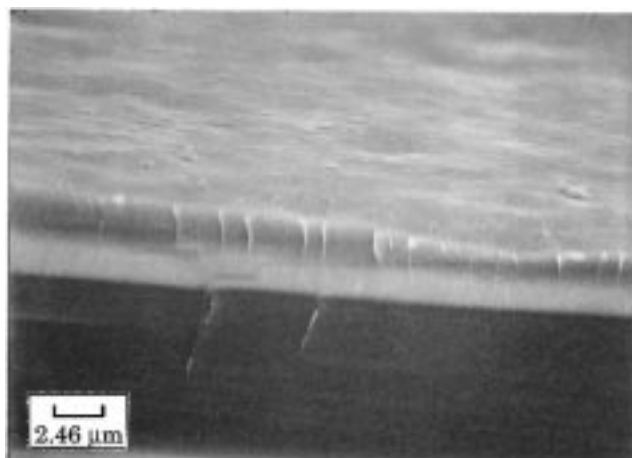


**Figure 3.** SEM photographs (20 000 $\times$ ) of the thin films **b-1** (top) and **b-3** (bottom).

diffraction was estimated to be 20.8 Å. The appearance of an intense peak indicates that the titanate sheets of  $H_xTi_{(2-x/4)}\square_{x/4}O_4 \cdot H_2O$  are well oriented parallel to the glass plate and that the thin film has a layered structure. The increment of the  $d$  value of the (020) diffraction from the original  $H_xTi_{(2-x/4)}\square_{x/4}O_4 \cdot H_2O$  powder was 11.6 Å which is attributable to the intercalation of  $TBA^+$  cations to the titanate sheets.

A strong peak was also observed in the XRD pattern of the thin film **b**, and only peaks due to (0 $k$ 0) diffraction were observed. The  $d$  value of the (020) diffraction was 9.6 Å. It is reasonably supposed that the titanate sheets are oriented parallel to the glass plate. But in the case of thin film **b** the increase of the  $d$  value from the original  $H_xTi_{(2-x/4)}\square_{x/4}O_4 \cdot H_2O$  powder was only 0.2 Å, and it is difficult to conclude from the XRD patterns whether ethylamine (or ethylammonium ion) exists or not in the interlayer space of the titanate sheets. If they exist in the interlayer space, they should exist in the form of ethylammonium ions to compensate for the negative charge of the titanate layers. This is discussed in the IR section.

**SEM.** SEM photographs of the thin films **b** are shown in Figure 3. Very similar morphologies were also observed for the thin films **a**. Figure 3a is a photograph of the thin film **b-1** which was obtained from one spin-coating of the "original" suspension, and Figure 3b is that of the thin film **b-3** from three spin-coatings of the "original" suspension. As shown in Figure 3a, two-dimensional titanate sheets parallel to the glass plate



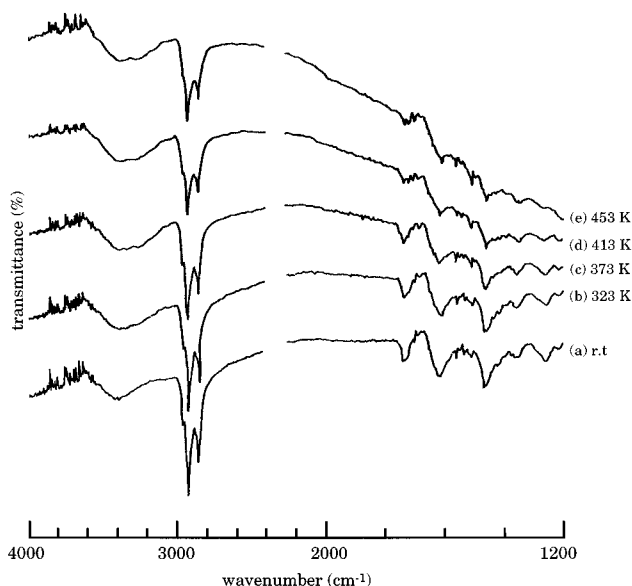
**Figure 4.** SEM photographs of vertical sectional views of the thin films **b-2** (top, 4070 $\times$ ) and **b-4** (bottom, 40 700 $\times$ ).

are observed. The size of titanate sheets are approximately 0.5–1  $\mu$ m. The surface of the thin film **b-1** is rather rough (Figure 3a), while that of the thin film **b-3** is more flat and homogeneous as a whole (Figure 3b). The difference between the two photographs indicates that a thin film having a flat surface can be obtained by repetition of spin-coating.

Figure 4a,b shows vertical sectional views of thin films **b-2** and **b-4**, respectively (Figure 4a,  $\times$ 4070; Figure 4b,  $\times$ 40700). In Figure 4a, the light and dark parts correspond to titanate sheets and the Si wafer, respectively. In Figure 4b three parts were observed; they corresponded to titanate sheets, the Pt coating, and the Si wafer, successively from the top. The thicknesses of the thin films **b-2** and **b-4** are estimated to be about 4000–5000 and 150–200 nm, respectively. It is clear that the difference in thickness between thin films **b-2** and **b-4** is derived from the difference of the concentration of the suspensions, because the other preparation conditions such as the times of spin-coating and the rotation speed were the same for both films. It is thus suggested that the thickness of the thin film can be controlled by changing the concentration of the suspension.

**IR Measurement.** An IR measurement was carried out to determine where the ethylamine (or ethylammonium ion) located in the thin films **b**.

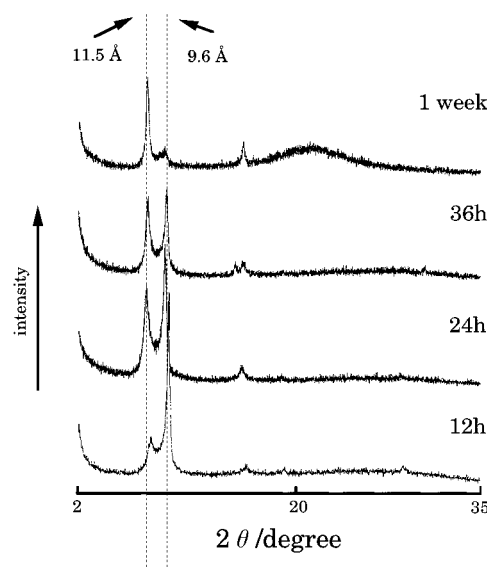
Figure 5 shows IR spectra of the thin film **b-2** on a  $CaF_2$  plate obtained by the same procedure on a glass



**Figure 5.** IR spectra of the thin film **b-2** which were evacuated for 5 min at room temperature (a) and 323 (b), 373 (c), 413 (d), and 453 K (e), respectively.

plate after 5 min evacuation under the temperature of 300, 323, 373, 413, and 453 K. For the film evacuated at room temperature (spectrum a), several absorption bands at around 2800–3000 and 1200–1800  $\text{cm}^{-1}$  were observed. The bands in the former range are assigned to C–H stretching vibrations of  $\text{CH}_2$  and  $\text{CH}_3$ . The bands at 1460 and 1610  $\text{cm}^{-1}$  are mainly assigned to bending vibrations of  $-\text{NH}_3^+$  and  $-\text{NH}_2$ , respectively, while those at around 1200–1400  $\text{cm}^{-1}$  and a part of 1460  $\text{cm}^{-1}$  band are assigned to the bending vibrations of the ethyl group. These absorption bands indicate the presence of ethylamine and ethylammonium ion in the thin film **b**. All the bands remained even after the film was heated to 453 K under evacuation, although they gradually decreased in intensity by increasing temperature. The appearance of strong absorption bands cannot be explained by the ethylamine adsorption on only the external surface and confirmed the ethylamine and ethylammonium ion being at the interlayer space of the thin films **b**.

**Modifications of Thin Films.** Although the layered titanate thin film was obtained, the thin film had some problems for further modification. One was thermal stability of the thin film. In general, the  $\text{H}^+$  exchanged form of the layered compounds are not thermally stable, because of the shrinkage of the interlayer space (destruction of layered structure) at around 473–573 K due to the desorption of  $\text{H}_2\text{O}$  from two hydroxyls at the interlayer space.<sup>14,15</sup> The layered structure of  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$  powder was destroyed at 473 K and resulted in formation of amorphous titanate. For the thin films, the layered structures of the thin films **a** and **b** were also lost when they were calcined above 473 K. If insertion of other cations instead of  $\text{H}^+$  into the interlayer space is possible, the destruction of the layered structure would be prevented. So, replacement



**Figure 6.** Time course of XRD patterns of the thin film **b-2** during treatment with  $\text{Ni}(\text{NO}_3)_2$  aqueous solution.

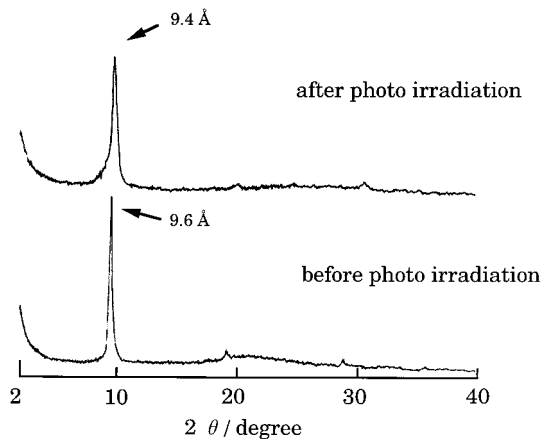
of ammonium ions with other cations was attempted. Another problem was the presence of amines. Some optical studies of the photofunctionality would be inhibited by the amines. Therefore, the removal of amines was also attempted by several ways.

Although aqueous solutions of metal cations such as  $\text{K}^+$ ,  $\text{Cs}^+$ , and  $\text{Ni}^{2+}$  were used, only  $\text{Ni}^{2+}$  cations were successfully inserted into the interlayers without destroying the layered structure of the thin film **b-2**. The insertion of  $\text{K}^+$  and  $\text{Cs}^+$  ions was not successful. The change of the XRD pattern during the exchange reaction in  $\text{Ni}(\text{NO}_3)_2$  aqueous solution is shown in Figure 6. The  $d$  value of (020) increased from 9.6 to 11.5 Å. The increase of the  $d$  value is attributable to the intercalation of  $\text{Ni}^{2+}$  cations. The presence of  $\text{Ni}^{2+}$  was confirmed by EDX. The layered structure of the  $\text{Ni}^{2+}$  exchanged thin film was stable up to 673 K, in contrast to the original thin film which lost the layered structure at 473 K.

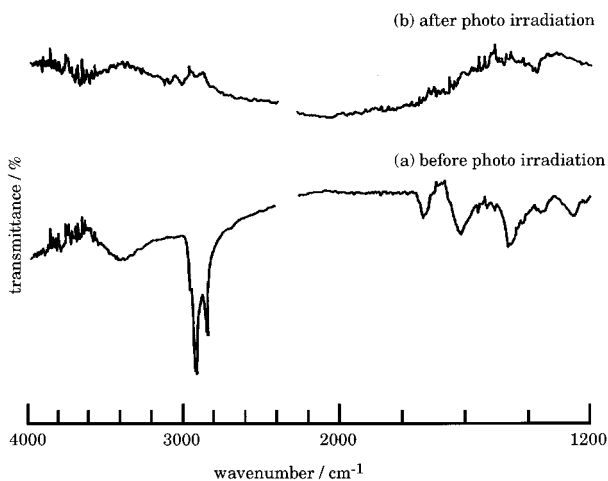
The removal of the amines and ammonium ions existing in the interlayer was attempted by various acids, but all attempts resulted in the destruction of the layered structure of the thin films. The layered titanate  $\text{Cs}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4$  has the photocatalytic ability for the oxidation of organic materials. Then the removal of amines from the interlayer space was attempted by the photooxidation. The XRD patterns of the thin film **b-2** before and after photoirradiation are shown in Figure 7. Even after photoirradiation the layered structure remained, although the peak intensity was a little weakened. The  $d$  value of (020) diffraction decreased from 9.6 to 9.4 Å; the latter value agreed with that of the powder of  $\text{H}_x\text{Ti}_{(2-x/4)}\square_{x/4}\text{O}_4 \cdot \text{H}_2\text{O}$ . The IR spectra of the thin film **b-2** before and after the photo irradiation are shown in Figure 8. The absorption bands that indicated the presence of ethylamine and ethylammonium were found to disappear after photoirradiation. It is mentioned here that the amine and ammonium ion were confirmed to remain in the thin film which was left in water for 24 h without photoirradiation. That is to say, they were removed by photoirradiation and not by dissolution by water. These results obtained from

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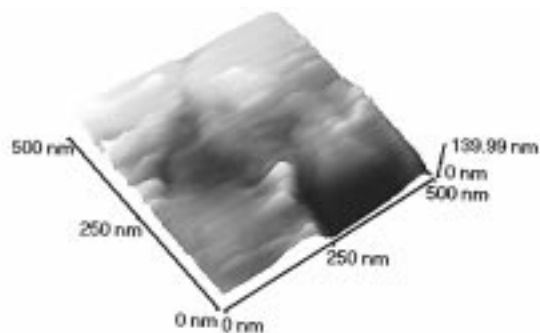
**Figure 7.** XRD pattern of the thin film **b-2** before and after photoirradiation.



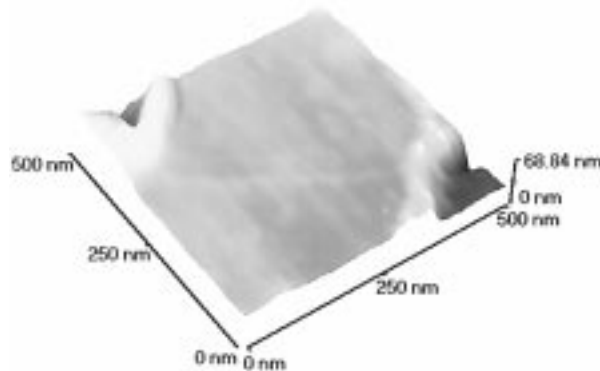
**Figure 8.** IR spectra of the thin film **b-2** before and after photoirradiation.

XRD and IR indicate that ethylamine and ethylammonium ion existing at the interlayer were removed by photoirradiation. Another cation, probably  $H^+$ , would replace the ammonium cations to compensate the negative charge of the layer, because the layered structure of the thin film remained even after photoirradiation and the  $d$  value agreed with that of the  $H_xTi_{(2-x/4)}□_{x/4}O_4 \cdot H_2O$  powder.

In addition to the results above, the surface features of the thin film **b-2** before and after photoirradiation was examined by AFM. Figure 9 (top) shows the AFM image of the surface of the thin film before photoirradiation. The surface exhibits some corrugation. The roughness is probably attributable to the ethylamine molecules that exist at the external surface of the thin film. On the other hand, the appearance of the thin film after photoirradiation is rather smooth, and flat planes of the titanate sheets are clearly observed as shown in Figure 9 (bottom). This result indicates the presence



Before photo irradiation



After photo irradiation

**Figure 9.** AFM height images of the thin film **b-2** before and after photoirradiation.

of a considerable amount of amine at the external surface before photoirradiation, and the disappearance of them from the surface also after photoirradiation.

## Conclusions

Layered thin films of titanate were obtained by spin-coating of suspensions containing exfoliated titanate sheets. The thin films obtained from the ethylamine suspension were stable in water, and modification of them was possible by taking advantage of the ion-exchange property and photocatalytic ability. Synthesis of a thermally stable thin film was achieved by  $Ni^{2+}$  exchange, and the removal of the amine in the thin films was attained by photooxidation of the amine.

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