

# Ion exchanged potassium titanoniobate as photocatalyst under visible light

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**Abstract** Potassium titanoniobate ( $\text{KTiNbO}_5$ ) was synthesized by solid-state reaction. The potassium ion of  $\text{KTiNbO}_5$  was exchanged for hydrogen ion in hydrochloric acid, and the sample was heat-treated. The shrinkage of the distance between titanoniobate layers that arise from ion-exchange was observed by using X-ray diffraction. The absorption edges of the UV–Vis spectra for the ion exchanged samples which were treated at higher temperature shifted from ultraviolet region to visible region. The change of binding energy was observed by X-ray Photoelectron Spectroscopy. Photocatalytic property of the ion exchanged and subsequently heat-treated under artificial solar irradiation was less than that of the titanium dioxide. On the other hand, that of the ion-exchanged and heat-treated sample under visible irradiation was better than that of the titanium dioxide.

**Keywords** Photocatalyst · Titanoniobate · Layer structured material · Ion exchange

## 1 Introduction

Photo-catalysts [1–3] are now attracting many researchers' interest as environmentally friendly materials for reduction of organic pollutants [4],  $\text{NO}_x$ ,  $\text{SO}_x$  and so on [5, 6].  $\text{TiO}_2$  is well known as a superior photo-catalytic material [1, 2]. However the efficiency of  $\text{TiO}_2$  as a photo-catalyst is very low because of its band structure which limits usable wavelength region mainly in UV region. UV light is

absorbed by air therefore we cannot obtain enough UV light as an energy source for photo-catalysis.

In recent years, many researchers try to find new photo-catalysts which have higher efficiency and many types of materials are reported. New photo-catalysts which can utilize wider wavelength region of light should have efficiency higher than superior photo-catalyst  $\text{TiO}_2$ . The limitation of usable wavelength of  $\text{TiO}_2$  originated from wide band gap in the band structure. Narrowing band gap enlarges usable light region toward long wavelength region that is visible light. Nitrogen doped  $\text{TiO}_2$  is one of new photo-catalysts which can utilize visible light [7–10]. Nitrogen doping into  $\text{TiO}_2$  led to absorption shift toward visible light region up to 520 nm [9].

New photo-catalysts which can utilize visible light are being investigated among other inorganic materials, for example oxides [3] and oxynitrides [11]. Some oxides show photo-catalytic activity originated from redox potentials due to valence and conduction bands and band-gap energies of them. One of the materials which shows photo-catalytic activity is  $\text{SrTiO}_3$  [3], which has the perovskite structure [12]. Because  $\text{SrTiO}_3$  showed high photo-catalytic activity as much as  $\text{TiO}_2$ , other perovskite-structured oxides are expected as new photo-catalysts. Some layer structured oxides have a pseudo perovskite structure. The layer structured material has unique property. The ions existing in the space between the neighboring layers are ion-exchangeable and therefore ion-exchange process is applied to modify the layer structured material. Some ion-exchangeable layer structured material shows activity for a battery electrode such as  $\text{LiTiNbO}_5$  [13].

Ion exchange is a suitable technique to fabricate nano-scale composite materials. The layer structured composite materials containing  $\text{TiO}_2$  and CdS system [14], and doped material such as Mn, Co and Ni in  $\text{InTaO}_4$  [15] have been

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reported to show good photo-catalytic property.  $\text{KTiNbO}_5$  which is a layer-structured material was studied as a photo-catalyst [16, 17].  $\text{KTiNbO}_5$  consisted of titanium(Ti), niobium(Nb) and oxygen(O) ( $\text{TiNbO}_5$ ) octahedral sheet and potassium(K) is sited in the space between neighboring two sheets [18–20]. The structure of  $\text{KTiNbO}_5$  is shown in Fig. 1. Potassium ion is exchangeable by other ions such as  $\text{H}^+$  [18],  $\text{Li}^+$  [13],  $\text{H}_3\text{O}^+$  [16], and dye [17]. This shows that the photo-catalytic property of the layer-structured material may be improved by changing inter-layer materials and layer-materials through some sort of interaction.

$\text{HTiNbO}_5$  is synthesized from  $\text{KTiNbO}_5$  by ion exchange in acid aqueous solution. The transformation from  $\text{HTiNbO}_5$  to  $\text{TiNb}_2\text{O}_7$  by heat-treatment is reported [18, 19]. In this study, we paid attention to the intermediate products between  $\text{HTiNbO}_5$  and  $\text{TiNb}_2\text{O}_7$  and report their unique structures, optical properties and photo-catalytic properties.

## 2 Experimental procedure

### 2.1 Preparation of samples

$\text{KTiNbO}_5$  was synthesized by solid state reaction.  $\text{K}_2\text{CO}_3$  (Kanto Chemical Co., Ltd),  $\text{Nb}_2\text{O}_5$  (Kanto Chemical Co., Ltd) and  $\text{TiO}_2$  (Anatase form, Merck) were mixed. Molar ratio of starting materials was  $\text{K}_2\text{CO}_3/\text{Nb}_2\text{O}_5/\text{TiO}_2=2:2:1$ . The mixture was fired at  $1090^\circ\text{C}$  for 24 h while the heating rate was kept at  $100^\circ\text{C}/\text{h}$ .  $\text{KTiNbO}_5$  was soaked in 1 mol/L HCl aqueous solution for 12 h and ion-exchanged leading to formation of  $\text{HTiNbO}_5$ .  $\text{HTiNbO}_5$  powder was heated in an electric furnace in the temperature range of  $400^\circ\text{C}$  to  $1000^\circ\text{C}$  and the samples derived from  $\text{HTiNbO}_5$  were obtained.

### 2.2 Characterization of samples

The crystal structures of samples were characterized by X-ray diffraction (XRD, Phillips PW1710) using  $\text{CuK}\alpha$  radiation in

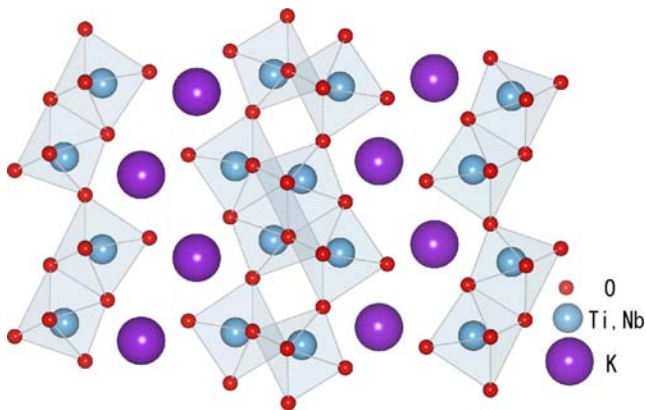


Fig. 1 Structure of  $\text{KTiNbO}_5$

the  $2\theta$  range of  $5^\circ$  to  $70^\circ$ . In order to evaluate ion-exchange rate, the amount of  $\text{K}^+$  ion in the solution used during the ion-exchange was examined by induction coupled plasma atomic emission spectrometer (ICP-AES, Seiko Instruments Inc. SPS7000A) and the thermal weight change of the product was examined by thermogravimetry and differential thermal analysis (TG-DTA, Seiko Instruments Inc. SSC5200). Optical property of the samples was examined by using UV–VIS spectrometer (JEOL V-560) in the wavelength range of 250 to 500 nm. The electronic structure was examined for the samples which were heat-treated under air or oxygen gas flow using X-ray photoemission spectroscopy (XPS, Surface Science, M-Probe Surface Spectrometer) to detect electrons from Ti, Nb and O atoms.

### 2.3 Photo-catalytic properties

Photo-catalytic property was investigated by using methylene-blue (MB: Showa Chemicals) [9]. Five milligrams of sample was soaked in 100 mL of 0.01 mM MB solution in dark for 2 h. Then, AM-1.5 light ( $100 \text{ mW cm}^{-2}$ ) was irradiated. Reduction in concentration of MB was estimated by photometric determination method measured with UV–VIS spectrometer using 693 nm adsorption ratio which was peculiar to MB. We also tested photo-catalytic property under visible light irradiation of about  $25 \text{ mW/cm}^2$  using 400 nm cut-off filter with AM-1.5 light source. P25 (commercial  $\text{TiO}_2$  photo-catalyst powder) was also examined as a reference under similar condition to the prepared samples.

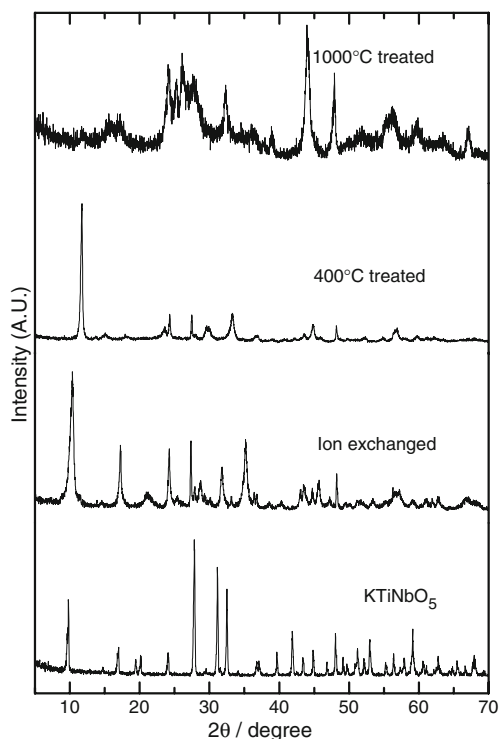
## 3 Results and discussion

### 3.1 Ion-exchange of $\text{KTiNbO}_5$

Figure 2 shows the XRD patterns of  $\text{KTiNbO}_5$ ,  $\text{HTiNbO}_5$ , the heat-treated samples at  $400^\circ\text{C}$ , and  $1000^\circ\text{C}$ .  $\text{KTiNbO}_5$  and  $\text{HTiNbO}_5$  synthesized via ion exchange from  $\text{KTiNbO}_5$  were confirmed to be single phase. Figure 3 shows the TG–DTA curves of  $\text{HTiNbO}_5$ . The amount of  $\text{K}^+$  ion in the solution after the ion exchange was 96% of the original amount of starting material measured by ICP-AES. These results mostly corresponded to the 3.6% weight loss (90% of  $\text{H}^+$ ) determined by TG–DTA results. Therefore we confirmed that the  $\text{K}^+$  ion in the  $\text{KTiNbO}_5$  sample was mostly ion-exchanged.

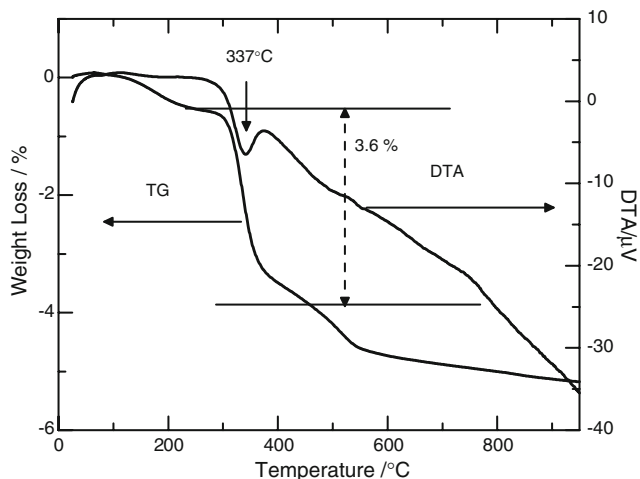
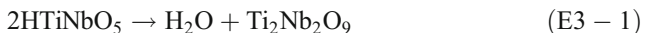
### 3.2 Thermal change of ion-exchanged samples

As we described in Section 3.1, the precursor of  $\text{HTiNbO}_5$ ,  $\text{KTiNbO}_5$  was single phase as confirmed by XRD. As shown in TG–DTA curves of  $\text{HTiNbO}_5$ , there were two



**Fig. 2** XRD patterns of as-prepared, ion-exchanged and heat-treated samples

reactions, one was endothermic reaction with weight loss at 337°C and the other gradual decrease occurred above 500°C. HTiNbO<sub>5</sub> decomposition process was reported by H. Rebbah et al. [18] as follows.

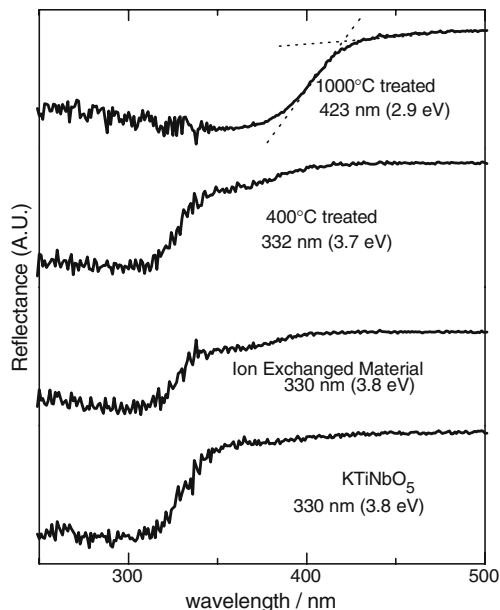


**Fig. 3** TG-DTA curve of HTiNbO<sub>5</sub> fabricated by ion-exchange in acid

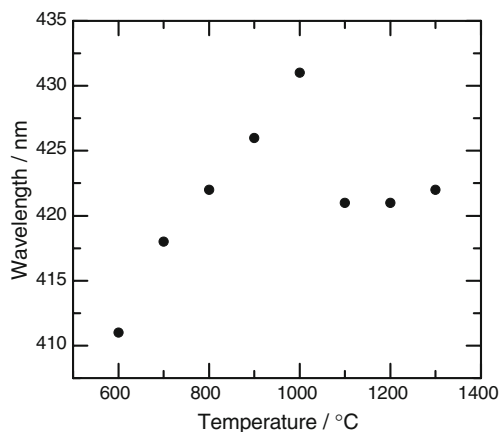
The XRD pattern of the product heated at 400°C shows Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> peak pattern reported in reference [18] and that heated at 1000°C shows a mixture pattern of TiO<sub>2</sub> and TiNb<sub>2</sub>O<sub>7</sub>. These results showed Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> was formed due to decomposition of HTiNbO<sub>5</sub> at around 400°C and Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> decomposition occurred gradually at the temperature region above 400°C.

### 3.3 Optical property of heat-treated samples

Figure 4 shows UV-VIS curves of samples. Almost the same absorption characters were observed on KTiNbO<sub>5</sub>, HTiNbO<sub>5</sub> and the heated sample at 400°C. As described above, the main phase of the sample heated at 400°C was Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> which consisted of titanium and niobium oxide octahedra. The three samples commonly had these octahedral structures, therefore similar optical absorption property was anticipated due to this octahedral structure. The absorption edge of the sample heated at 1000°C was 423 nm which was distinctively different from the other samples, which had an absorption edge at around 330 nm. The absorption edge of the sample heated at 1000°C was largely different from that of TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. The absorption edge of TiO<sub>2</sub> (anatase) is 389 nm, and that of Nb<sub>2</sub>O<sub>5</sub> is 405 nm. Therefore this absorption edge might be originated from the TiNb<sub>2</sub>O<sub>7</sub>. This difference of the absorption edge was studied by measuring absorption edges of the samples heated in the temperature range from 500°C to 1100°C. The absorption edges of these samples are shown in Fig. 5. Good linear relationship was obtained in the temperature range of 600°C to 1000°C. From these

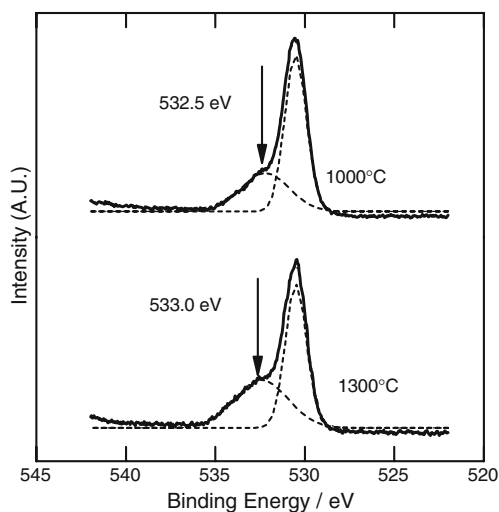


**Fig. 4** UV-VIS spectra of the samples shown in Fig. 2



**Fig. 5** The relation between the edge of adsorption wave length and the heating temperature

results, decomposition reaction which occurred above 550°C was due to a re-arrangement reaction from the layer-structure to decomposition products. The gradual change of structure which was detected by TG–DTA and XRD probably caused gradual wavelength change of the absorption edge. That means the product of this reaction was meta-stable. Two TG–DTA curves measured in air and in oxygen were shown in Fig. 3. The amount of weight loss at the temperature range of 550°C and 1000°C were around 1.2% in air and 0.6% in O<sub>2</sub>, respectively. The weight change was thought to depend on activity of oxygen at the own site. That suggests the state of the oxygen in the crystal would influence on the optical property. Figure 6 shows O<sub>1s</sub> XPS spectra of the samples heated at 1000°C and 1300°C. The main peak of O<sub>1s</sub> XPS spectrum is usually assigned to the oxygen in lattice, and the weaker peaks at high binding energy side are usually assigned to the adsorbed compounds which contain oxygen



**Fig. 6** O<sub>1s</sub> XPS spectra of samples heated at 1000°C and 1300°C

**Table 1** MB reduction rate under AM-1.5.

Progress time (min)	Blank	P-25	KTiNbO <sub>5</sub>	1000°C product
0	1.00	1.00	1.00	1.00
60	0.98	0.25	0.86	0.93
120	0.96	0.00	0.78	0.78
180	0.92	0.00	0.70	0.59

atoms [21]. Some compounds such as water are physically adsorbed on the surface of the photo-catalyst and then that are dissociated by the oxygen vacancy of the photo-catalyst. This change of the state of adsorbed compounds would generate the peak shift or splitting of the O<sub>1s</sub> XPS peak. In our samples, we could not observe splitting of the second peak in O<sub>1s</sub> XPS spectrum, however the shape of the peaks was different from each other. Especially, the positions of the peaks on the high binding energy side were different. The same difference was observed on O-defected TiO<sub>2</sub> [22]. This suggests that the states of the adsorbed compounds are different due to the different condition of the sample. Because there were no significant changes on Ti and Nb XPS spectra, the results suggests the formation of oxygen defect in the crystal would be associated with these characteristics. We presumed this reaction mechanism in the following way. According to the phase diagram between TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> [7], the excess amount of TiO<sub>2</sub> could be incorporated, solid-solution of TiO<sub>2</sub> was formed. Therefore we presume solid solution was formed, and the following reaction might occur.



It suggests that when titanium was introduced into niobium site, O-vacancy would be formed to keep electrical neutrality. The O-vacancy caused the change of the band structure and the absorption edge. Furthermore, another model could be presumed at higher temperature, assuming that O-vacancy would be formed. Once O-vacancy was formed, the following reaction would occur.



From this reaction, Ti(III) was formed which may promote the formation of more O-vacancies. That could

**Table 2** MB reduction rate under AM1.5 with UV cut-off filter.

Progress time (min)	Blank	P-25	Nb <sub>2</sub> O <sub>5</sub>	1000°C product
0	1.00	1.00	1.00	1.00
50	0.98	0.96	0.95	0.99
100	0.96	0.95	0.91	0.89
200	0.93	0.94	0.88	0.85

change the band structure. From these results, it is suggested that re-arrangement in the crystal and O-vacancy formation at higher temperature generated unique optical property.

### 3.4 Photo-catalytic property

In the report by Yan et al. [23] and Mrowetz et al. [9], there is a problem in evaluating photo-catalytic activity using MB. The problem is incorrectness of evaluating the amount of the decomposed MB by the photo-catalytic reaction, because MB is decomposed through the dye-sensitization mechanism [23]. However we considered that it was possible to evaluate relative photo-catalytic activity by using a reference material (P25). Because the action spectra of MB decomposition were almost the same between the sample and the reference reported by Yan [23] in the wavelength-range from 540 to 680 nm where the dye-sensitization mechanism is dominant, and the difference of action spectra between the sample and the reference is significant in the wavelength-range from 400 to 540 nm where both mechanisms of decomposition by photo-catalysis and dye-sensitization coexist. Therefore we think that it is possible to relatively evaluate photo-catalytic activity using MB. The results of photo-catalytic reaction measurement were exhibited in Table 1. There were not significant decomposition of MB in the tested samples, while the results of P-25 showed distinctive reduction in concentration of MB. There was no problem on the procedure to check the activity of synthesized samples. Table 2 exhibits the results of the photo-catalytic reaction measurement under light without UV region. The reduction rate of MB with the heat-treated sample was higher than P-25. The result of the test suggests the products had the potential of photo-catalytic reaction under visible-light, because no reaction occurred in TiO<sub>2</sub> system under light without UV region. Therefore these results suggest that we could modify the band structure with ion-exchange reaction and subsequent heat-treatment. One of the reasons for low activity of the modified samples might be oxygen defect which may hinder photo-catalytic reaction.

## 4 Summary

KTiNbO<sub>5</sub> was synthesized by solid-state reaction. It was easy to ion-exchange from K<sup>+</sup> to H<sup>+</sup> in HCl solutions. Heat-treatment of the ion exchanged product caused decomposition, and Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> was formed at around 400°C. Subsequently Ti<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> decomposition occurred gradually above 500°C. The sample heated above 850°C exhibited unique optical property which might be due to O-vacancy.

The heat-treated sample showed higher photo-catalytic activity under visible light than P25.

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