

Controlling Size, Shape and Polymorph of TiO₂ Nanoparticles by Temperature-Controlled Hydrothermal Treatment

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ABSTRACT. The crystallization and morphology change of amorphous titanias by hydrothermal treatment have been investigated. The amorphous titanias were prepared by pure water hydrolysis of two different precursors, titanium tetraisopropoxide (TTIP) and TTIP modified with acetic acid (HOAc) and characterized prior to hydrothermal treatment. In order to avoid complicate situation, the hydrothermal treatment was performed in a single solvent water with and without strong acids at various temperatures. The effects of strong acid, temperature and time were systematically investigated on the transformation of amorphous titania to crystalline TiO₂ under simple hydrothermal condition. Without strong acid the titanias were transformed into only anatase phase nanoparticle regardless of precursor type, temperature and time herein used (up to 250 °C and 48 hours). The treatment temperature and time effected only on the crystalline size, not on the crystal phase et al. However, it was clearly revealed that the strong acids such as HNO₃ and HCl catalyzed the formation of rutile phase depending on temperature. HCl was slightly better than HNO₃ in this catalytic activity. The morphology of rutile TiO₂ formed was also a little affected by the type of acid. The precursor modifier, HOAc slightly reduced the catalytic activity of the strong acids in rutile phase formation.

Key words: TiO₂, Anatase, Rutile, Hydrothermal treatment, Nanoparticle, Nanorod

INTRODUCTION

Titanium dioxide (TiO₂) has been one of the most extensively investigated metal oxide semiconductors in the field of solar energy conversion because of its outstanding photochemical activities.¹ Especially, it has been a core material in the field of photoelectrochemistry since Fujishima and Honda's work² and Grätzel's dye-sensitized solar cells.³ Recent researches have been focused on the nanostructural aspects and surface modifications of TiO₂ aiming at the practical applications such as sensors,⁴ smart windows,⁵ and waste treatments,⁶ etc. The critical parameters that determine the physicochemical properties of TiO₂ are crystal phase, size and morphology. Many synthetic methods and titanium precursors have been utilized to prepare the nanostructured TiO₂ that had controlled size, morphology and crystal structure.⁷ Among the various synthetic techniques, the hydrothermal method provides a simple and easy way to get controlled TiO₂ nanoparticles.⁸ Especially, the method provides a low-temperature route of phase transformation from anatase to rutile crystal structure of TiO₂ which normally occurs at the temperature higher than 600–700 °C.

In hydrothermal method there are many control factors to govern the final structural result of TiO₂. The kind of titanium precursor, modifier and acid/base, co-solvent with water, solution pH, and reaction temperature are known to be

critical factors. Titanium tetraisopropoxide (TTIP) is one of the most popular precursors for the hydrothermal synthesis of TiO₂. There were many studies of the synthesis of TiO₂ nanoparticles using TTIP or similar other titanium alkoxide as precursor under different hydrothermal reaction conditions as indicated in ref. 7 and 8. However, the results are sometimes confusing and controversial because of small variations in the treatment methods. For examples, some articles reported that an amorphous titania was first isolated from hydrolysis solution of titanium precursors and it was redispersed in aqueous solution and then hydrothermally treated.^{8c,d} On the other hand, the clear titania sols prepared in aqueous media were directly hydrothermally treated in other articles.^{8g,i} Some authors also reported that the isolated titania was peptized in acidic or basic condition at an elevated temperature before hydrothermal treatment.^{8e,f} The preparation methods of titania precursors as a form of sol or powder were diverse too from article to article. Therefore, it is hard to compare the reported results in various articles and to tell the effect of control parameters explicitly.

The reactions in hydrothermal synthesis of TiO₂ from titanium alkoxide precursors always proceed in the two steps: the hydrolysis/condensation, first and the crystallization/phase transformation, second. The first step always occurs before hydrothermal treatment because the precursors react vigorously with water and result in *titania* that is

in the complex form depending on reaction conditions such as amount of water, the existence of catalysts, electrolytes and temperature. And the subsequent hydrothermal treatment transforms the titania precursor to the final TiO₂ that has a certain crystallinity, particle size and morphology. Therefore, whenever we mention the effect of control parameters in hydrothermal method for the synthesis of TiO₂, the titania precursor that is first prepared must be characterized. Most of literatures for the hydrothermal synthesis of TiO₂ did not clarify this point. In this context, here we report how the size and polymorphs of TiO₂ nanoparticle could be controlled by certain conditions of hydrothermal treatment of the amorphous *titanias* which were prepared from pure TTIP and TTIP modified with acetic acid (HOAc) in pure water where any catalyst or co-solvent was not included. We have studied especially the effect of acids, temperature and time on the transformation of the amorphous *titanias* to the crystalline TiO₂ during hydrothermal treatment.

EXPERIMENTAL

Preparation

6.0 mL of TTIP (98%, Junsei, 2.0×10^{-2} mol) only or TTIP mixed with 1.2 mL of anhydrous acetic acid (HOAc, 98%, Yakuri Pure Chemicals, 2.0×10^{-2} mol) was slowly dropped to 30.0 mL of deionized water and stirred vigorously for 60 min. The white suspension of the reaction mixture was transferred to a hydrothermal reactor that was made of stainless steel with Teflon liner. In the case of using strong acid, 2 mL of 65% nitric acid (3.0×10^{-2} mol) or 2.5 mL of 35% HCl (3.0×10^{-2} mol) was added to the reaction mixture before the hydrothermal reaction. The reactor was kept in oven for 12 or 24 hours at various temperatures (90–250 °C). After the reaction the products were separated by centrifugation for 15 minutes at 8,000 rpm. The washing was repeated four times with pure ethanol and the final products were dried in vacuum oven at room temperature.

Characterization

X-ray diffraction patterns (XRD) were measured by Philips PW3040 X'Pert-MPD X-ray diffractometer with CuK α source and 0.02°/s scan rate. Thermal gravimetric analyses (TGA) were done with Perkin Elmer Pyris 1 and 10 °C/min scan rate under N₂. Transmission electron microscopic (TEM) images were taken by Jeol JEM-2010 with carbon-coated copper grid. Fourier-transform Infrared (FT-IR) spectra were measured by Perkin-Elmer Spectrum 2000 in KBr pellet method.

RESULTS AND DISCUSSION

When pure TTIP or the TTIP modified with HOAc was mixed with pure water, the hydrolysis and condensation reactions occurred very rapidly and gave a white precipitate. We used pure water without co-solvent for the hydrolysis to eliminate the effect of co-solvent and water content.⁹ Prior to hydrothermal treatment the hydrolysis and condensation products of pure TTIP and TTIP modified with HOAc were isolated and analyzed. These products will be called the precursor *titanias* hereafter. The XRD data of the precursor *titanias* did not show any recognizable peak. It means that both samples were amorphous. The IR absorption spectra of the *titanias* were shown in Fig. 1. There is a distinct difference between two spectra of the *titanias* from pure TTIP and the TTIP modified with HOAc. The doublet of 1536 and 1446 cm⁻¹ appeared in the spectrum of the product from the TTIP modified with HOAc, while it was absent in the spectrum from pure TTIP. It was known to be due to the asymmetric and symmetric stretching vibration of the carboxylic group coordinated to Ti as a bidentate ligand.¹⁰ The common broad bands of 3300–2500 and 1000–400 cm⁻¹ in the both spectra can be assigned to the vibrations of -OH and Ti-O-Ti, respectively.¹¹ And the sharp peak of 1629 cm⁻² can be associated with the vibration of hydrated H₂O. The thermogravimetric data of both the *titanias* were shown in Fig. 2. The total weight losses of the *titanias* from pure TTIP and TTIP modified with HOAc were slightly less than 20% and about 27%, respectively. The weight loss of the product from pure TTIP occurred by two steps: about 10 % loss below 250 °C and another 10% between 250–350 °C. The first loss can be easily thought

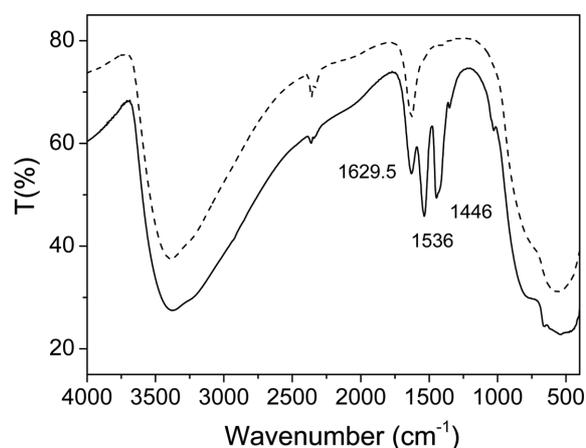


Figure 1. Infrared absorption spectra of the amorphous titanias prepared from pure TTIP (dotted line) and TTIP modified with HOAc (solid line).

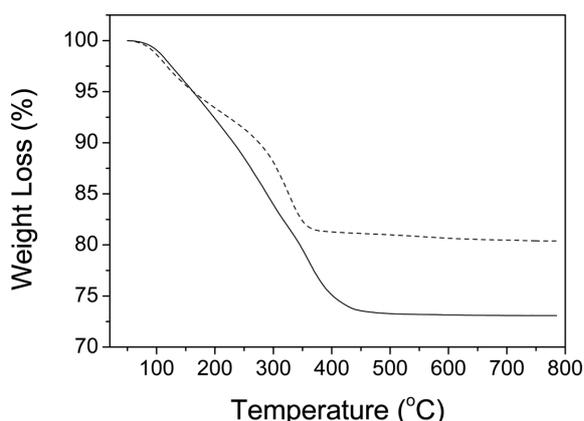


Figure 2. Thermogravimetric curves of the amorphous *titania*s prepared from pure TTIP (dotted line) and TTIP modified with HOAc (real line).

to be due to the adsorbed and hydrated water. The second loss at the higher temperature might be due to the transformation from the hydroxide to the oxide since this kind of transformation was known to be usually occurred at this temperature.¹² Whereas, the product from TTIP modified with HOAc lost more weight at higher temperature than that from pure TTIP. The loss below 350 °C might be caused by the same reason with the product from pure TTIP and the loss above 350 °C might be due to the loss of acetate ligand remained from hydrolysis. The TTIP modified with HOAc was prepared by direct mixing of TTIP and HOAc in an equivalent molar ratio without solvent. When HOAc was added to TTIP in the molar ratio, $\text{Ti}(\text{OCOCH}_3)(\text{OCH}(\text{CH}_3)_2)_2$ (TADIP) complex was known to be formed and it was known to be less reactive to the hydrolysis and condensation in aqueous solution.¹³ Therefore, both the hydrolysis products of pure TTIP and TTIP modified with HOAc were mainly consisted of amorphous hydrated *titania* that has a mixed composition of oxide and hydroxide but two products were different in the aspect that the *titania* from TTIP modified with HOAc, i.e. TADIP has some remained acetate ligand that was not completely hydrolyzed and removed.

The transformation of these *titania*s into crystalline TiO_2 by hydrothermal treatment was investigated under the variations of temperature and types of acids added as catalyst. When the *titania*s from pure TTIP and TTIP modified with HOAc were hydrothermally treated in water without any additional acid or base at the temperatures of 90–250 °C, all the *titania*s were transformed to particulate crystalline TiO_2 with only anatase phase regardless of temperature and time. *Fig. 3* shows the XRD patterns of the products that were prepared from TTIP and TTIP modified with HOAc

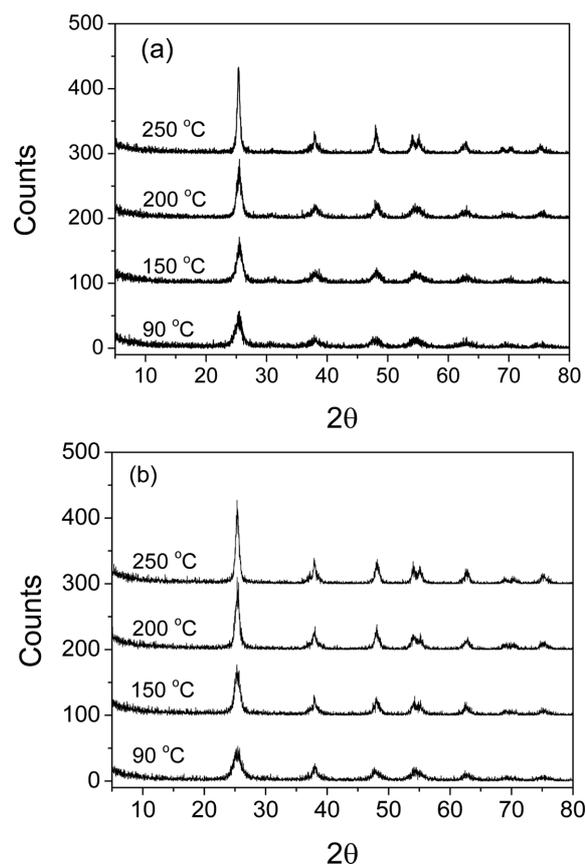


Figure 3. XRD patterns of TiO_2 nanoparticles that were synthesized by the hydrothermal treatment of two precursors at various temperatures without additional acid for 12 hours: (a) Pure TTIP and (b) TTIP modified with HOAc.

and hydrothermally treated for 12 hours at various temperatures without any additional acid. The patterns of all the samples correspond to well-known pure anatase¹⁴ regardless of reaction temperature and the kind of precursors. However, the particle size increased systematically as the reaction temperature increased for the constant reaction time. The estimated particle sizes by applying Debye-Scherrer equation to (101) peaks in XRD were listed in *Table 1*. They varied in the range of ca. 5–16 nm in the tempera-

Table 1. The estimated particle sizes of TiO_2 nanoparticles that were prepared by the hydrothermal reactions of pure TTIP and TTIP modified with HOAc at various temperatures without additional acid for 12 hours

Reaction Temperature (°C)	XRD Particle Size (nm)	
	TTIP only	TTIP+HOAc
90	5.9	4.8
150	7.1	7.7
200	8.8	10.3
250	16.6	12.6

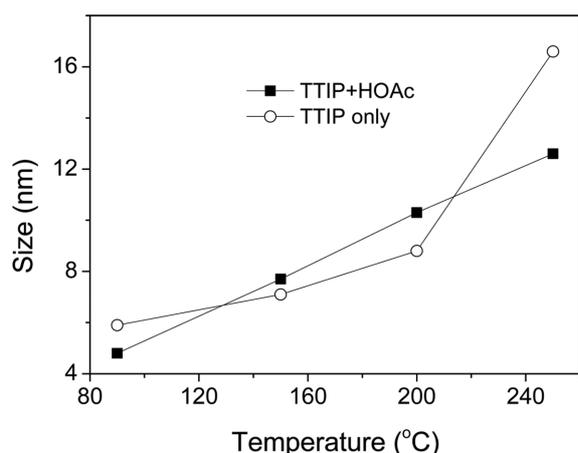


Figure 4. The size dependence on the reaction temperature for TiO₂ nanoparticles synthesized by the hydrothermal treatment of two precursors without additional acid for 12 hours.

ture range of 90–250 °C. The temperature dependence of the particle size was shown in Fig. 4. In the experimental temperature range the particle size increased as the temperature increased. While the particle sizes increased pretty linearly for the samples that were prepared from TTIP modified with HOAc, the size increment for the samples that were prepared from pure TTIP was very small below 200 °C but became suddenly large at 250 °C. Fig. 5 shows the TEM pictures of TiO₂ nanoparticles prepared from TTIP modified with HOAc at the various temperatures. The images show clearly the systematic size increment depending on the reaction temperature. The reaction time for these hydrothermal treatments did not affect much on the crystallization of TiO₂ as shown in Fig. 6. The crystallinity of TiO₂ that was prepared from TTIP modified with

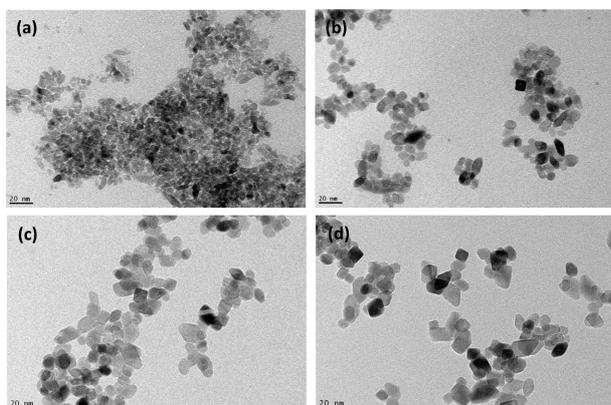


Figure 5. TEM images of TiO₂ nanoparticles that were prepared by the hydrothermal treatment of the *titania* from TTIP modified with HOAc without additional acid at various temperatures for 12 hours: (a) 90 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C.

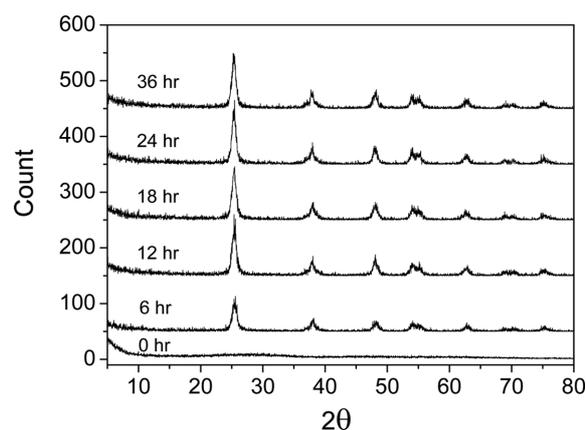


Figure 6. XRD patterns of TiO₂ nanoparticles that were prepared by the hydrothermal treatment of the titania from TTIP modified with HOAc at 200 °C without additional acid for various times.

HOAc at 200 °C increased noticeably until about 12 hours and then the change became very small after 12 hours. This tendency was similar to the cases of other reaction temperatures, regardless of the precursors.

Therefore the hydrothermal treatment of the amorphous titanias prepared from TTIP crystallized them preferentially to anatase phase regardless of temperature up to 250 °C and time, whether the precursor TTIP was modified with HOAc or not. In this hydrothermal treatment the reaction condition not only depends on temperature but also on pressure because the reaction proceeded in a closed system and the pressure also increased as the temperature increased. As the temperature increased from 90 to 250 °C, the pressure increased nonlinearly from about 1.9 to 53 atm because of mostly the increase of water vapor pressure.¹⁵ The pressure increases steeply as temperature increases by following the Clausius-Clapeyron equation for water vapor pressure. The size increasing tendency of TiO₂ prepared from pure TTIP is similar to that of pressure. So the crystallization of TiO₂ prepared from pure TTIP was more sensitive to pressure rather than temperature, whereas TiO₂ prepared from TTIP modified with HOAc was less sensitive to pressure. According to the study of Parra *et al.*¹³ TTIP modified with HOAc was preferentially crystallized to anatase phase by the control of hydrolysis and oligomerization degrees although they did not perform the control experiment with TTIP unmodified with HOAc. However, our study showed that the hydrothermal treatment of the *titanias* from TTIP without additional strong acid always gave anatase phase up to 250 °C that was maximum temperature available to normal autoclave, whether TTIP was modified with HOAc or not. This means that TTIP modified with HOAc does not have

relative preference to pure TTIP for the crystallization to specific phase, i.e. anatase in the hydrothermal treatment with maximum temperature of 250 °C. However, TTIP modified with HOAc gave the better control of size by the control of temperature than pure TTIP.

When the *titania*s from pure TTIP and TTIP modified with HOAc were treated hydrothermally under strong acid at various temperatures, the results were significantly different from those without strong acid, previously discussed. The amount of strong acids was used as much as 1.5 times of titanium in molar ratio in all the cases. This is high enough the result not to be varied by the amount of acid.¹⁶ Fig. 7(a) shows the XRD patterns of TiO₂ prepared by hydrothermal treatment of the *titania* from pure TTIP with nitric acid at various temperatures for 12 hours. TiO₂ that was prepared at 90 °C showed mostly anatase phase with poor crystallinity and a trace of rutile phase. The rutile phase grew significantly with very small portion of remained anatase at the higher temperature, 150 °C. When the temperature increased further to 200 and 250 °C, only rutile phase was

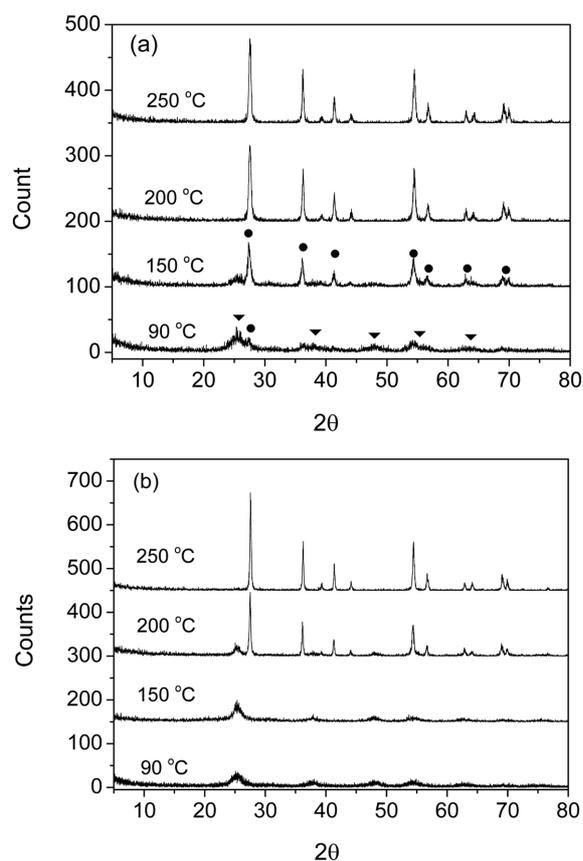


Figure 7. XRD patterns of TiO₂ prepared by hydrothermal treatment of titania from (a) pure TTIP and (b) TTIP modified with HOAc under nitric acid at various temperatures for 12 hours (● and ▼ indicate rutile and anatase peaks, respectively).

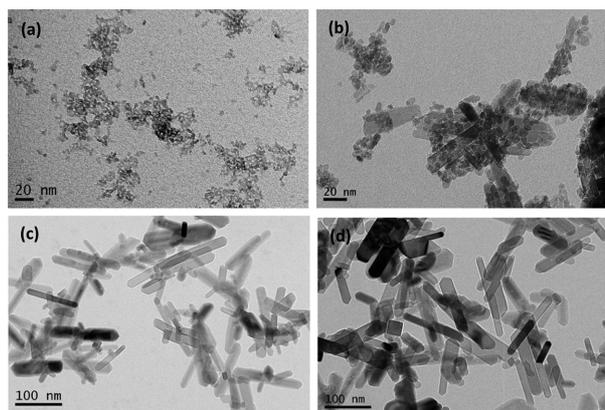


Figure 8. TEM images of TiO₂ nanoparticles prepared by hydrothermal treatment of the titania from pure TTIP under nitric acid at various temperatures for 12 hours: (a) 90 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C.

shown with increased intensity. The TEM images of those TiO₂ nanoparticles are shown in Fig. 8. The rutile TiO₂ prepared at 200 and 250 °C were mostly nanorods with aspect ratios of ca. 7-10, while anatase TiO₂ prepared at 90 °C were mostly nanoparticles of ca. 3-4 nm in diameter. TiO₂ prepared at 150 °C were both nanoparticles larger than those at 90 °C and nanorods smaller than those at 200 and 250 °C. In the case of *titania* from TTIP modified with HOAc the result from the hydrothermal treatment was a little different as shown in Fig. 7(b). Only anatase phase was shown up to 150 °C. Rutile phase was mostly shown at 200 °C but some anatase phase was still remained. And only rutile phase was shown at 250 °C. The morphologies of these TiO₂ nanoparticles are shown in Fig. 9 as TEM images. The samples prepared at 90 and 150 °C were all nanoparticles of 3-5 nm in diameter as shown in anatase TiO₂ nanoparticles that were

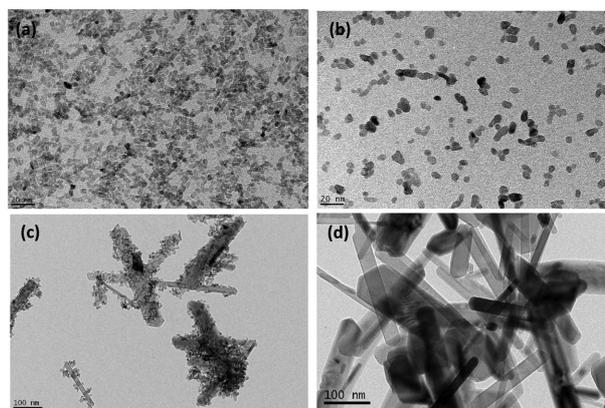


Figure 9. TEM images of TiO₂ nanoparticles prepared by hydrothermal treatment of the titania from TTIP modified with HOAc under nitric acid at various temperatures for 12 hours: (a) 90 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C.

prepared without strong acid. The sample prepared at 200 °C, which was in mostly rutile and some anatase phases, had shapes of both nanoparticle and nanorod as shown in Fig. 9(c). The pure rutile TiO₂ prepared at 250 °C was only rod-shaped. Apparently the TiO₂ samples that showed both anatase and rutile phases were composed of both nanoparticle and nanorod, while the sample that showed either anatase or rutile only was composed of either nanoparticle or nanorod only, respectively. This does not necessarily mean that anatase and rutile TiO₂ that were prepared here were in shape of nanoparticle and nanorod only, respectively. The comparison of the results between pure TTIP and TTIP modified with HOAc tells that the formation of rutile phase was slightly easier in the case of pure TTIP than TTIP modified with HOAc at the temperature below 200 °C.

When nitric acid was replaced with hydrochloric acid in these hydrothermal treatments, the results were slightly different as shown in XRD patterns of Fig. 10. The titania from pure TTIP was transformed into mostly rutile phase at 90 °C though the crystallinity was poor, whereas only

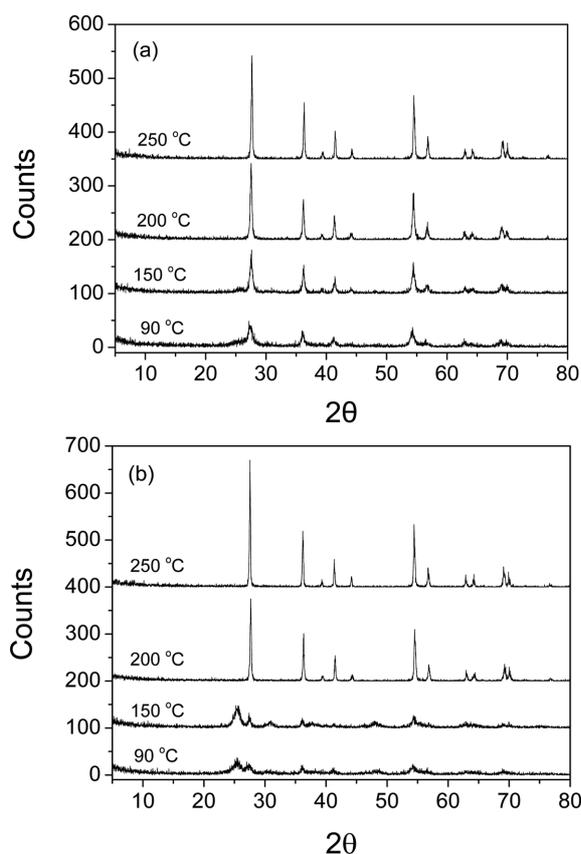


Figure 10. XRD patterns of TiO₂ prepared by hydrothermal treatment of the titanias from (a) pure TTIP and (b) TTIP modified with HOAc under hydrochloric acid at various temperatures for 12 hours.

trace of rutile phase was shown in the case of nitric acid. At 150 °C only the intensity of rutile peak was increased with a trace of anatase still remained and only pure rutile phase was shown at 200 and 250 °C. The results at 200 and 250 °C were same as those of nitric acid but the crystallinity seemed better considering peak intensity. In the case of the titania from TTIP modified with HOAc, the results at 90 °C and 150 °C were significantly different from that of pure TTIP. Both anatase and rutile phases appeared but anatase seemed to be major component. At the temperatures of 200 and 250 °C only pure rutile phase was shown as same as pure TTIP but the peak intensity seemed stronger. Thus, the hydrothermal treatment at the temperature higher than 200 °C under HCl gave pure rutile phase whether the precursor was pure TTIP or TTIP modified with HOAc. This means that the formation of rutile phase by hydro-

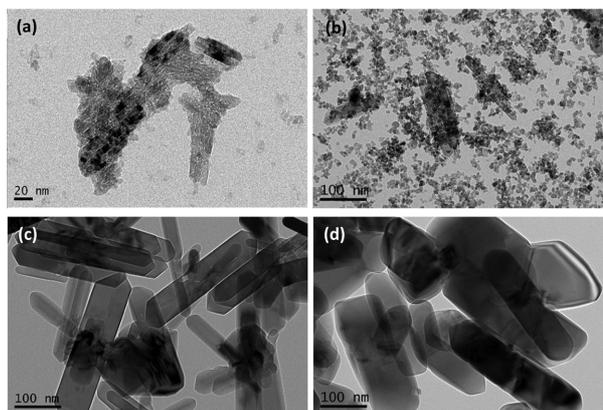


Figure 11. TEM images of TiO₂ nanoparticles prepared by hydrothermal treatment of the titania from pure TTIP under hydrochloric acid at various temperatures for 12 hours: (a) 90 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C.

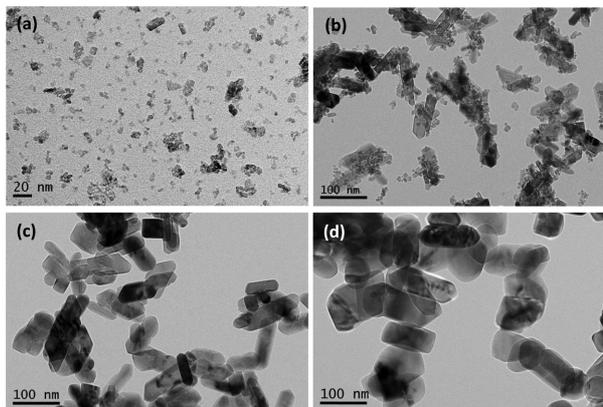


Figure 12. TEM images of TiO₂ nanoparticles prepared by hydrothermal treatment of the titania from TTIP modified with HOAc under hydrochloric acid at various temperatures for 12 hours: (a) 90 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C.

thermal treatment under strong acid proceeds slightly better with HCl than HNO₃. Fig. 11 and 12 show TEM images of TiO₂ particles prepared under hydrochloric acid from pure TTIP and TTIP modified with HOAc, respectively. The morphologies of TiO₂ prepared from pure TTIP at 90 and 150 °C are both spherical and rod-shaped while all TiO₂ prepared at 200 and 250 °C have a rod-shaped morphology. In the case of TTIP modified with HOAc the sample at 90 °C is mostly spherical nanoparticle while that at 150 °C has both spherical and rod shapes. The samples at 200 and 250 °C are all rod-shaped. The sizes of rod-shaped rutile TiO₂ prepared from pure TTIP was much bigger than those from TTIP modified with HOAc. Here we can again confirm that the titania from pure TTIP can be crystallized into rutile phase under strong acid more easily than that from TTIP modified with HOAc.

Considering both the results with HNO₃ and HCl, the formation of rutile phase by hydrothermal treatment of amorphous titania proceeded slightly better with HCl than with HNO₃. There is also some morphology difference between rutile TiO₂ nanorods from HNO₃ and HCl. The higher aspect ratio of rutile nanorod could be obtained with HNO₃ than with HCl. This difference must be due to the anionic effect. The affinities of nitrate and chloride ions to titania surface might be slightly different and the catalytic activity of hydrogen ion might be slightly affected. The amorphous titania that was prepared from TTIP modified HOAc had some unhydrolyzed acetate ligand as discussed above and this acetate seemed to reduce the catalytic activity of hydrogen ion for the formation of rutile phase.

CONCLUSION

We have studied the structural evolution of the amorphous titanias that were prepared from two precursors, TTIP and TTIP modified with HOAc by hydrothermal treatment at various temperatures (max. 250 °C). Without strong acid only anatase phase was developed regardless of temperature and time, whether they were prepared from pure TTIP or TTIP modified with HOAc. The temperature and time affected only the crystallinity and particle size of the phase. The strong acids such as HNO₃ and HCl catalyzed the formation of rutile phase depending on temperature. The pure rutile phase was obtained at the temperature of above 200 °C with both the acids in the case of the titania from pure TTIP. HCl showed slightly the better catalytic activity for rutile phase formation than HNO₃. The titania from TTIP modified with HOAc had acetate ligand remained after hydrolysis and this remained acetate reduced the catalytic activity of

hydrogen ion toward rutile phase formation. The precursor modifier, HOAc which has been considered to be a phase control agent preferentially leading to anatase, seems to be merely an obstructor in formation of rutile phase.

The morphologies of the crystalline TiO₂ prepared here by hydrothermal treatment had apparently only two types depending on crystal phase: spherical nanoparticle for anatase and nanorod for rutile. Nitric acid gave nanorod rutile that has higher aspect ratio than hydrochloric acid.

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- Our study excludes the effect of alcoholic solvents for the precursor TTIP. Some studies showed that the content of water relative to the alcoholic solvent for Ti alcoxide was one of important factors to determining the size of synthesized TiO₂ nanoparticles.
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 15. The pressure was calculated as the sum of air and vapor pressure which depend on temperature, linearly and by Clausius-Clapeyron equation, respectively.
 16. In order to eliminate pH dependence of structural evolution we used the acid amount enough to maintain pH nearly 0 before and after hydrothermal treatment.
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