

Sol-Hydrothermal Synthesis and Hydrothermally Structural Evolution of Nanocrystal Titanium Dioxide

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Received March 29, 2001. Revised Manuscript Received October 17, 2001

A sol-hydrothermal method has been proposed to prepare uniform and unaggregated nanocrystals of pure anatase and rutile from various acidic mediums. The phase formation, particle sizes, and morphologies varying with different acids and their concentrations at different reaction temperatures and times have been investigated using X-ray diffraction and transmission electron microscopy. The use of HCl and the effect of its concentrations on the formation of rutile phase at different temperatures for various reaction times have been described in detail. The effect of the addition of NaCl salt on particle sizes and rutile fractions has also been studied. In this work, the phase transformation from anatase to rutile in the presence of and the absence of NaCl salt has been considered both in neutral and in acidic mediums. The presence of a trace rutile in starting materials of anatase can show obvious effects on the phase transformation under hydrothermal conditions.

Introduction

Various properties of TiO_2 nanoparticles are definitely dependent on their crystal sizes, morphologies, and crystallographic structures.^{1–5} Controlled preparation of nanoparticles is of great interest and importance in preparative chemistry and material sciences.⁶ Several methods, such as hydrolysis (chemical precipitation),⁷ reverse micelles (microemulsion),^{8,9} sol–gel,^{10,11} and hydrothermal crystallization,^{11–19} have been used to prepare TiO_2 nanocrystallites.

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- (1) (a) Karch, J.; Birringer, R.; Gleiter, H. *Nature* **1987**, *330*, 556. (b) Wang, H.-Z.; Zhao, F.-L.; He, Y.-J.; Zheng, X.-G.; Huang, X.-G.; Wu, M.-M. *Opt. Lett.* **1998**, *23*, 777. (c) Kumar, K.; Keizer, K.; Burggraaf, A.; Okubo, T.; Nagamoto, H.; Morooka, S. *Nature* **1992**, *358*, 48. (d) Zhang, Z.; Wang, C.; Zakaria, R.; Ying, J. Y. *J. Phys. Chem. B* **1998**, *102*, 10871. (e) O'Regan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.
- (2) Zhang, H.; Banfield, J. F. *J. Mater. Chem.* **1998**, *8*, 2073.
- (3) Gribb, A. A.; Banfield, J. F. *Am. Mineral.* **1997**, *82*, 717.
- (4) (a) Penn, R. L.; Banfield, J. F. *Am. Mineral.* **1998**, *83*, 1077. (b) Zhang, H.; Banfield, J. F. *Am. Mineral.* **1999**, *84*, 528.
- (5) Penn, R. L.; Banfield, J. F. *Am. Mineral.* **1999**, *84*, 871.
- (6) (a) Dutta, P. K.; Jakupca, M.; Reddy, K. S. N.; Salvati, L. *Nature* **1995**, *374*, 44. (b) Reetz, M. T.; Maase, M. *Adv. Mater.* **1999**, *11*, 773. (c) Hopwood, J. D.; Mann, S. *Chem. Mater.* **1997**, *9*, 1819. (d) Peng, X.-G.; Manna, L.; Yang, W.-D.; Wickham, J.; Scher, E.; Kadavanich, A.; Allisatos, A. P. *Nature* **2000**, *404*, 59.
- (7) (a) Scolan, A.; Sanchez, C. *Chem. Mater.* **1998**, *10*, 3217. (b) Edelson, L. H.; Glaeser, A. M. *J. Am. Ceram. Soc.* **1988**, *71*, 225.
- (8) (a) Stathatos, E.; Lianos, P.; Monte, F. D.; Levy, D.; Tsiorvas, D. *Langmuir* **1997**, *13*, 4295. (b) Lal, M.; Chhabra, V.; Ayyub, P.; Maitra, A. *J. Mater. Res.* **1998**, *13*, 1249.
- (9) Chhabra, V.; Pillai, V.; Mishra, B.; Morrone, A.; Shah, D. *Langmuir* **1995**, *11*, 3307.
- (10) Selvaraj, U.; Prasad Rao, A. V.; Komarneni, S.; Roy, R. *J. Am. Ceram. Soc.* **1992**, *75*, 1167.
- (11) Wang, C.-C.; Ying, J. Y. *Chem. Mater.* **1999**, *11*, 3113.

The sol–gel method is one of the approaches to prepare dispersed nanoparticles by tailoring the structure of a primary precursor in which metal atoms distribute uniformly.^{10,11} This method is mainly based on the hydrolysis and polycondensation of a metal alkoxide, which ultimately yields hydroxide or oxide under certain conditions.^{20–22} To obtain homogeneous macromolecular oxide networks for qualified nanomaterials in sol–gel processing, control of hydrolysis is essentially important.

Titanium alkoxides have been widely used as titanium sources to prepare uniform TiO_2 by using alcohol or some other chelating agents such as dihydric alcohol, carboxylic acid, and β -diketonates to control hydrolysis.^{10,11,20–22} In normal sol–gel processing, gelization and calcination are necessary. If the calcination temperature for crystallization is not high enough, some

- (12) Qian, Y.-T.; Chen, Q.-W.; Chen, Z.-Y.; Fan, C.-G.; Zhou, G.-E. *J. Mater. Chem.* **1993**, *3*, 203.
- (13) Cheng, H.-M.; Ma, J.-M.; Zhao, Z.-G.; Qi, L.-M. *Chem. Mater.* **1995**, *7*, 663.
- (14) Yanagisawa, K.; Yamamoto, Y.; Feng, Q.; Yamasaki, N. *J. Mater. Res.* **1998**, *13*, 825.
- (15) Yanagisawa, K.; Ovenstone, J. *J. Phys. Chem. B* **1999**, *103*, 7781.
- (16) Wu, M.-M.; Long, J.-M.; Huang, A.-H.; Luo, Y.-J.; Feng, S.-H.; Xu, R.-R. *Langmuir* **1999**, *15*, 8822.
- (17) Adschari, T.; Kanazawa, K.; Arai, K. *J. Am. Ceram. Soc.* **1992**, *75*, 1019.
- (18) Bacs, R. R.; Gratzel, M. *J. Am. Ceram. Soc.* **1996**, *79*, 2185.
- (19) Kutty, T. R. N.; Vivekanandan, R.; Murugaraj, P. *Mater. Chem. Phys.* **1988**, *19*, 533.
- (20) Kumazawa, H.; Otsuki, H.; Sada, E. *J. Mater. Sci. Lett.* **1993**, *12*, 839.
- (21) (a) Kumar, K. P.; Kumar, J.; Keizer, K. *J. Am. Ceram. Soc.* **1994**, *77*, 1396. (b) Yoldas, B. *J. Mater. Sci.* **1986**, *21*, 1087. (c) Harris, M. T.; Byers, C. H. *J. Non-Cryst. Solids* **1988**, *103*, 49.
- (22) Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. *J. Non-Cryst. Solids* **1988**, *100*, 65.

organic molecules will remain in the product, which will lead to the incomplete crystallization of titania. However, if the temperature is too high, aggregation and/or phase transformation will occur, especially as the metastable phase consists of nanosized particles, resulting in phase-impure product. During all the procedures, the evaporation of organic molecules will lead to the environmental pollution and the process is normally time-consuming.

Hydrothermal synthesis provides an easy route to prepare a well-crystalline and phase-pure oxide in one step in a tightly closed vessel.^{23,24} The hydrothermal preparation of TiO_2 has been investigated for several decades. Under various hydrothermal conditions, products of TiO_2 with different morphologies and structural forms, such as rutile, anatase, or even brookite, have been yielded.^{11-19,24-31} The influence of temperature, pH value, and additives on crystallization of TiO_2 was reported in several publications in the 1970s.²⁷⁻³¹ Kutty et al. described the precipitation of rutile and anatase from titanium oxychloride solution and the effect of SO_4^{2-} anions as impurity on the formation of anatase in 1988.¹⁹ The results implied that SO_4^{2-} anions could retard the formation of rutile, which were consistent with other studies.^{29,30} Later, in Cheng et al.'s work, rodlike nanoparticles of rutile were prepared by using $TiCl_4$ as the titanium source, and the formation of rutile was ascribed to a growth unit with negative charge and consisting of Cl^- anions.¹³ However, this assumption cannot rationally explain the higher fraction of rutile at increased temperatures and for extended reaction times. In fact, Cl^- anions show much weaker affinity to titanium atoms than oxygen in aqueous solution, and titanium atoms should not exist as octahedral complex anions, but cations in a strongly acidic medium. Thus, the formation of rutile should be further elucidated. Furthermore, it is known that the hydrolysis of $TiCl_4$ is usually vigorous and not easy to be controlled, even at 0 °C. The evolution of white HCl fog from hydrolysis of $TiCl_4$ will also cause environmental pollution. Therefore, other titanium sources, such as titanium alkoxides, will be used instead to prepare uniform and unaggregated nanocrystals of anatase and rutile, respectively, through a hydrothermal method.¹¹

A titanium alkoxide is usually dissolved in an organic solvent to control the hydrolysis to prepare uniform TiO_2 colloids.^{21,22,26} Hydrothermal treatment of a titanium alkoxide in an organic solvent generally leads to the

(23) (a) Rabenau, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1026. (b) Riman, R. E. *Proceedings of the 11th Risø International Symposium on Metallurgy and Materials Science: Structural Ceramics-Processing, Microstructure and Properties*; Bentzen, J. J., Bilde-Sørensen, J. B., Christiansen, N., Horsewell, A., Ralph, B., Eds.; Risø National Laboratory: Roskilde, Denmark, 1990; p 111.

(24) (a) Kominami, H.; Takada, Y.; Yamagawa, H.; Kera, Y.; Inoue, M.; Inui, T. *J. Mater. Sci. Lett.* **1996**, *15*, 197. (b) Grey, I. E.; Li, C.; Watts, J. A. *Am. Mineral.* **1983**, *68*, 981. (c) Nishizawa, H.; Aoki, Y. *J. Solid State Chem.* **1985**, *56*, 158.

(25) Oguri, Y.; Riman, R. E.; Bowen, H. K. *J. Mater. Sci.* **1988**, *23*, 2897.

(26) Sugimoto, T.; Okada, K.; Itoh, H. *J. Colloid Interface Sci.* **1997**, *193*, 140.

(27) Dachille, F.; Simons, P.; Roy, R. *Am. Mineral.* **1968**, *53*, 1929.

(28) Matthews, A. *Am. Mineral.* **1976**, *61*, 419.

(29) Izumi, F.; Fujiki, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 709.

(30) Izumi, F. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1771.

(31) (a) Matijevic, E. *J. Colloid Interface Sci.* **1977**, *58*, 374. (b) Matijevic, E.; Budnik, M.; Meites, L. *J. Colloid Interface Sci.* **1977**, *61*, 302.

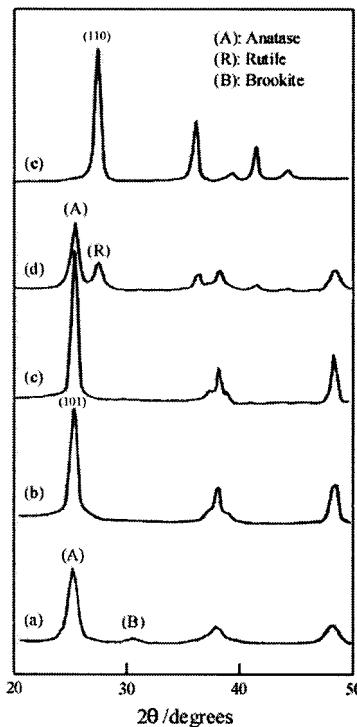


Figure 1. XRD patterns of nanocrystal titania samples prepared from various mediums: (a) H_2O , (b) CH_3COOH , (c) H_2SO_4 , (d) HNO_3 , and (e) HCl .

formation of pure anatase.^{25,26} However, the hydrothermal crystallization of a HNO_3 -peptized sol of amorphous titania, which initially precipitated from titanium alkoxides in alcohol/water, gave rise to the production of rutile. It was considered by the authors that the use of alcohol could facilitate the formation of rutile.¹⁸ Nevertheless, no rutile could be obtained under hydrothermal conditions (lower than 240 °C) unless acid was added.^{11,14,25,26} Using oxidation-hydrothermal synthesis of titanium dioxide from metallic titanium, Qian et al. obtained acicular nanocrystals of pure rutile in a HNO_3 medium.¹² It was found that larger crystals of rutile formed in more concentrated HNO_3 solution, which was similar to that in HCl .^{12,13} Conversely, a recent report exactly showed that HCl reduced the crystal sizes of TiO_2 , which were obtained from a sol by calcination, because of the adsorption of Cl^- anions on the particle surface at pH lower than the isoelectric point.¹¹

Because the isoelectric point of TiO_2 is around pH 6.7,²⁰ surface modification of colloids in an acidic medium will certainly avoid aggregation and a homogeneous colloidal solution will be formed.³¹ Thus, an inorganic acid could be used as a dispersing reagent of a titanium alkoxide to prepare dispersed nanosized TiO_2 . In this work, some inorganic acids have been used to control the hydrolysis of titanium alkoxide to form clear sols that serve as precursors to hydrothermal processing. The influence of the use of inorganic acids, acid concentrations, $NaCl$ additive, and reaction conditions on particle sizes, morphologies, and phases of TiO_2 will be discussed.

Anatase can be transformed irreversibly to rutile at elevated temperatures ranging from 400 to 1200 °C. The phase transition temperatures are definitely dependent on particle sizes, morphologies of crystals, and the addition of additives.^{2-5,11,32,33} However, the studies of

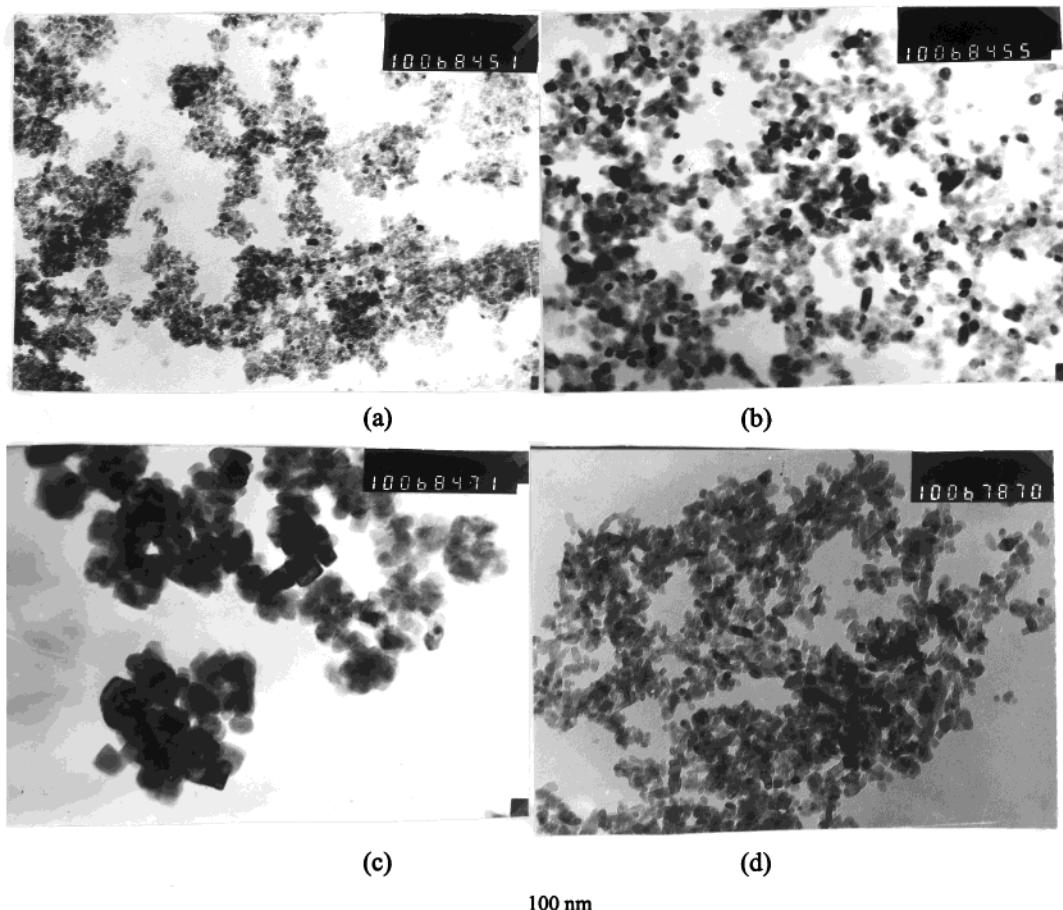


Figure 2. TEM images of nanocrystal titania samples prepared from various mediums: (a) H_2O , (b) CH_3COOH , (c) H_2SO_4 , and (d) HNO_3 .

phase evolution between anatase and rutile under hydrothermal conditions has been paid less attention so far.^{19,27–30} It was pointed out previously that anatase could not change to rutile under hydrothermal conditions in HCl .¹⁹ Herein, we believe that the phase transformation can occur and be promoted in the presence of some additives under certain hydrothermal conditions even below 240 °C.

Experimental Section

Preparation. Titanium *n*-butoxide (TNB) was added dropwise to a concentrated acid solution under magnetic stirring. A clear sol was formed first. Then, distilled water was added dropwise into the sol to prepare reactive agent with a known concentration of titanium in it. The mixture was finally loaded into a Teflon-lined vessel 80% filled and tightly closed for hydrothermal reaction. The vessel was taken out from an oven after a certain time of heating and allowed to cool to ambient temperature by being quickly rinsed in running water. The white product was filtered, washed by distilled water, and dried in a desiccator at ambient temperature. A comparable experiment was done without adding any acid to investigate the effect of an acid and its concentrations on the crystallization of TiO_2 .

To study the structural evolution of TiO_2 from anatase to rutile under specific hydrothermal conditions, commercial anatase (Guangzhou Chemicals), freshly hydrothermally prepared anatase, or a mixture of anatase and rutile was loaded into a vessel. After washing and filtering, the product was kept in a desiccator for drying.

Characterization. Products were characterized by powder X-ray diffraction using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15045 \text{ nm}$) at

30 kV and 20 mA on a Shimadzu XD-3A diffractometer. Average crystallite sizes of TiO_2 particles were calculated from the fwhm (full-width at half-maximum) of anatase (101) and rutile (110) diffraction using Scherrer's equation. The morphologies of TiO_2 particles were observed under a JEM-100CX transmission electron microscope (TEM). The samples for TEM examination were prepared by depositing an ultrasonically dispersed suspension of TiO_2 powder from a water/alcohol mixture on a carbon-coated copper grid.

Results

The Use of Acids. Using different acids in a hydrothermal reaction has been proved to play a substantial role in the formation, structure, and crystal morphologies of TiO_2 .^{11,16,29,30} Here, HCl , HNO_3 , H_2SO_4 , and CH_3COOH (HOAc) were used as acidic mediums, respectively. Their effects on the crystallization of anatase and rutile nanoparticles were investigated. The concentration of titanium and acid in each feedstock was fixed at 0.5 and 1.5 M, respectively, if not otherwise described.

The product was pure rutile from a HCl medium, while it was a mixture of rutile and anatase from a HNO_3 medium. Pure anatase was generated from aqueous solution of either 1.5 M H_2SO_4 or HOAc (Figure 1). However, if the concentration of titanium was reduced to 0.25 M, the use of H_2SO_4 yielded quite different results than that of HOAc . Pure anatase was still prepared in a HOAc medium, while, besides anatase, rutile phase was generated as the side product in a H_2SO_4 medium. This implied that the formation of rutile in a HOAc medium was more difficult than that

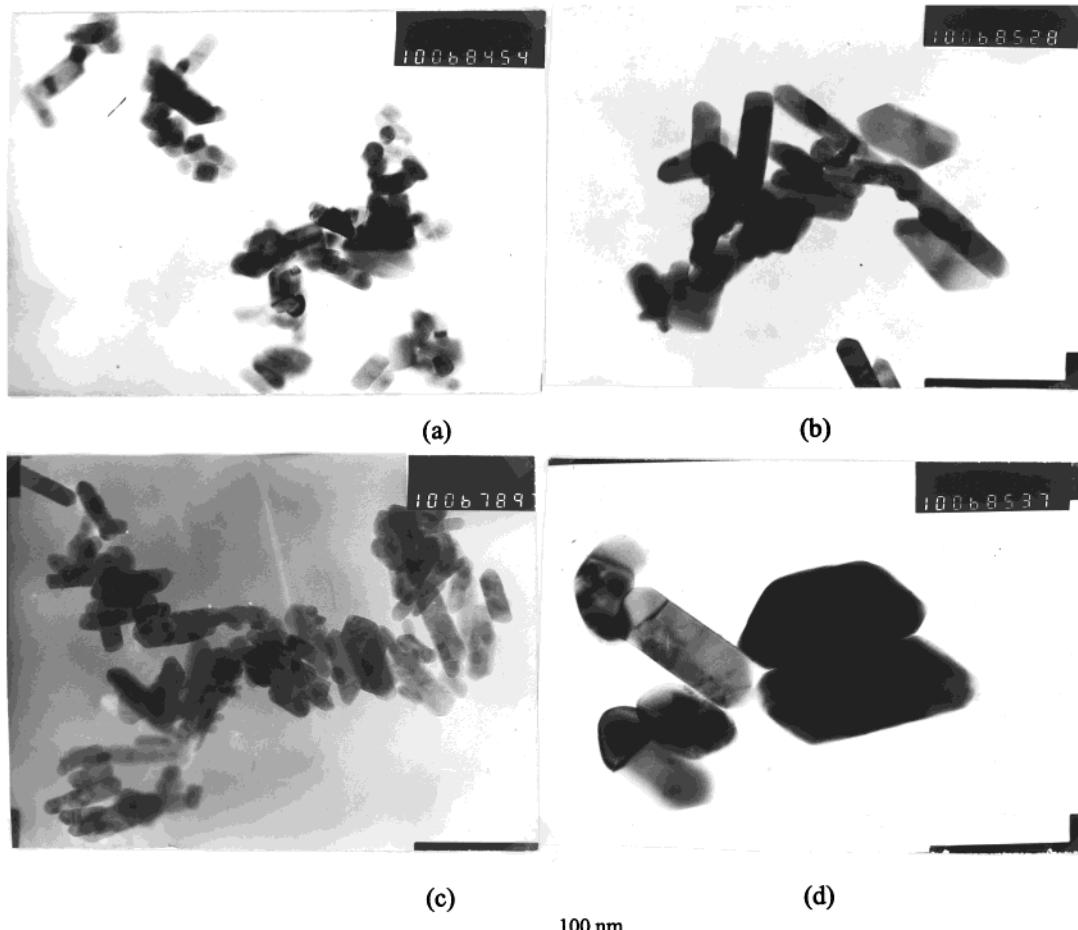


Figure 3. TEM images of titania powders prepared from acidified titanium sources under various hydrothermal conditions: (a) 0.50 M TNB and 1.5 M HCl, at 220 °C for 10 h; (b) 0.50 M TNB and 3.0 M HCl, at 220 °C for 10 h; (c) 0.25 M TNB and 1.5 M HCl, at 220 °C for 10 h; (d) 0.50 M TNB and 1.5 M HCl, at 220 °C for 72 h.

in a H_2SO_4 medium. Pure anatase could be obtained more easily from a HOAc medium than from others. A mixture of anatase as the major product and brookite as the minor product was yielded from a reaction medium without addition of any inorganic acids (Figure 1a). The results were remarkably different from Cheng et al.'s work in which the optimum conditions for preparing anatase were $pH > 7$ at 200 °C.¹³ Here, pure anatase could be prepared in an acidic medium.

The XRD peaks (Figure 1b or 1c) corresponding to anatase from either a HOAc or a H_2SO_4 medium are much sharper than those (Figure 1a) to anatase from an acid-free medium. This indicates that anatase from either HOAc or a H_2SO_4 -acidified titanium source crystallized more completely and particle sizes were larger, which is consistent with TEM results (Figure 2).

The TEM shows rutile particles from a HCl medium (Figure 3a) were longer and larger than those from a HNO_3 medium (Figure 2d). The above results indicate HCl can facilitate the formation and growth of rutile most obviously.

Concentrations of HCl. It has been reported that concentrations of $TiCl_4$ significantly influence the crystallization of rutile under hydrothermal conditions.¹³ HCl can control hydrolysis and, subsequently, polycondensation of TNB. The aqueous solution of TNB becomes more transparent with an increase of HCl concentration. At a titanium concentration below 0.5 M

and a HCl concentration over 0.5 M, the reaction mixture was a clear sol at ambient temperature. Homogeneous nucleation is fundamentally important for preparing uniform and dispersed nanoparticles. Here, the titanium concentration was fixed at 0.5 M and the HCl concentration was varied, and hydrothermal reaction was carried out at 220 °C for 10 h.

A mixture of anatase and brookite was formed from TNB without addition of any acids (Figure 1a). At a HCl concentration < 1.0 M, anatase, brookite, and rutile coexisted in the product (Figure 4a,b). The intensity of correlative XRD peaks of brookite becomes stronger with increasing HCl concentrations from 0.0 to 0.5 M. However, at a HCl concentration of 1.0 M, brookite disappeared, and a mixture of rutile and anatase was obtained in which the rutile was presented as the major product (Figure 4c). Brookite was yielded only in a certain range of acidity, which is similar to the results from others.¹³ Brookite disappeared prior to anatase with increasing acidity. Furthermore, the coexistence of only both rutile and brookite could not be observed in any HCl concentrations. The intensity of those peaks attributed to rutile in Figure 4 becomes more obvious, as the HCl concentrations increase, indicating that higher HCl concentrations favor rutile crystallization. The fraction of rutile in a product was calculated from the equation of $F_r = 1.26I_r/(I_a + 1.26I_r)$, where I_r and I_a were the strongest intensities of rutile (110) and anatase

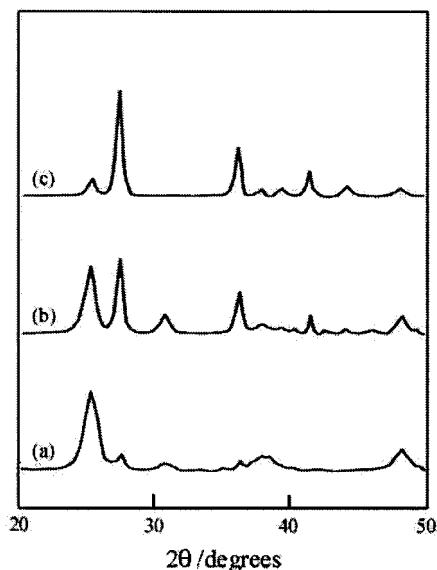


Figure 4. XRD patterns of titanium dioxide prepared hydrothermally from 0.5 M TNB at 220 °C for 10 h in a HCl medium with various HCl concentrations: (a) 0.1 M, (b) 0.5 M, and (c) 1.0 M.

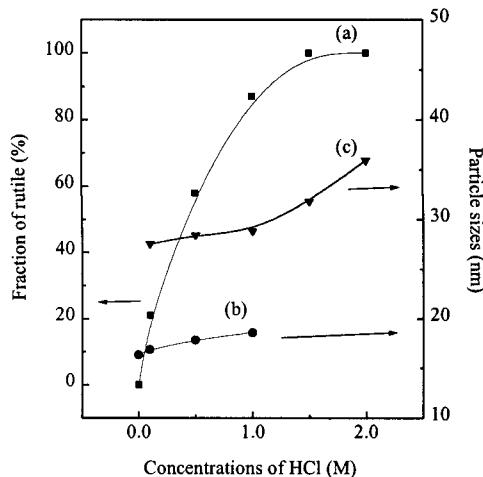


Figure 5. Influence of HCl concentrations on (a) the fractions of rutile, (b) crystalline sizes of anatase, and (c) crystalline sizes of rutile under hydrothermal conditions at 220 °C for 10 h.

(101) peaks, respectively.¹⁹ The fractions of rutile tended to be greater at higher HCl concentrations (Figure 5a). Pure rutile phase could be ultimately obtained at a HCl concentration of 1.5 M or higher (Figures 1e and 5a). The tendency of polymorphic change with increasing HCl concentrations is summarized in the following scheme, where anatase, brookite, and rutile are designated by A, B, and R, respectively:



The concentration of HCl affects not only the fraction of rutile but also the nanocrystal size in a product (Figure 5). Larger crystalline sizes of anatase can be obtained at higher HCl concentrations, and the size can be increased up to about 16 nm in a 1.0 M HCl medium (Figure 5b). It seemed there was a critical size for anatase before its disappearance. This trend could also be found in other related studies.¹¹ On the other hand, the crystalline size of rutile in the mixed phase only increased slightly as the HCl concentration increased

Table 1. Increasing NaCl Concentrations on TiO₂ Products^a

Concentrations of reagents (M)	Reaction conditions	TiO ₂ Products		
		Components	D _a	D _r
TNB	HCl	Temperature / time		
0.5	0.0	220°C / 10 h	A (main) + B (trace)	↗↘
0.5	0.5	140°C / 5 h	R + A	↘↗
0.5	0.5	220°C / 5 h	R + A	↘↗
0.5	2.0	140°C / 10 h	R	↗↘
0.5	2.0	220°C / 10 h	R	↗

^a R, rutile; A, anatase; B, brookite; D_a, crystalline size of anatase; D_r, crystalline size of rutile; F_r, fraction of rutile in a product; upward right diagonal arrows, increase; downward right diagonal arrows, decrease.

up to 1.0 M. However, the crystal size in the pure rutile phase increased significantly after the HCl concentration was over 1.5 M. Larger rodlike rutile particles with greater aspect ratios were formed in a higher concentration of HCl (Figure 3b).

Concentrations of Titanium. Besides the concentration of acid, the concentration of titanium is another factor to be studied. A product was obtained with a greater fraction of rutile at a lower titanium concentration. For instance, pure rutile was yielded from a mixture of 0.25 M TNB and 1.0 M HCl at 220 °C for 10 h. Furthermore, the result as shown in Figure 3c indicates that longer rodlike rutile was formed at a lower titanium concentration in comparison with that in Figure 3a.

Mineralizer. It has been extensively reported that mineralizers can affect not only structures and sizes but also morphologies of TiO₂ particles.^{13,15,28,29} Here, NaCl was used as the mineralizer. With a fixed TNB concentration at 0.5 M, several experiments were carried out to investigate the change of crystalline sizes and fractions of rutile in products by changing NaCl concentrations from 0.0 to 3.0 M (Table 1).

Anatase was the major product and brookite was the minor product from acid-free mediums. The crystalline sizes of anatase increased first and then decreased slightly with increasing NaCl concentrations. This implied that NaCl favored anatase growth to some extent and then confined anatase growth at its higher concentrations. Rutile phase could not be found in these products from nearly neutral reaction mediums even in the presence of NaCl salt.

The effect of NaCl concentrations on anatase and rutile crystallite sizes in a HCl medium is summarized in Table 1. The growth of both anatase and rutile nanocrystals from the mixture of 0.5 M TNB and 0.5 M HCl was confined due to the addition of NaCl salt at either 140 or 220 °C for 5 h. At 220 °C for 5 h, fractions of rutile became greater first and then less as the NaCl concentrations increased. In contrast, at 140 °C for 5 h, it decreased obviously first and then increased slightly with the increase of NaCl concentrations.

The effect of NaCl concentrations on crystallite sizes of rutile as a phase-pure product was also investigated. Pure rutile could be successfully prepared from starting materials with a higher HCl concentration for a longer aging time, such as from a mixture of 0.5 M TNB and 2.0 M HCl at 140–220 °C for 10 h. The crystal size of rutile tended to be larger with an increase of NaCl concentration at a higher temperature (220 °C), while it tended to be smaller with an increase of NaCl

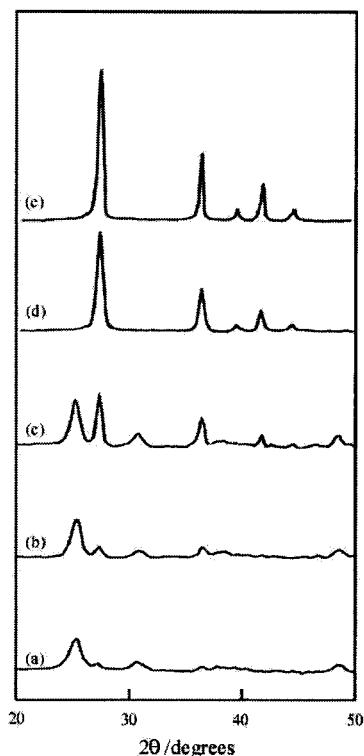


Figure 6. Influence of reaction temperatures and times on the hydrothermal synthesis of titanium dioxide from mixtures of 0.5 M TNB and 0.5 M HCl (a) at 100 °C for 10 h, (b) at 220 °C for 5 h, (c) at 220 °C for 10 h, (d) at 220 °C for 20 h, and (e) at 220 °C for 72 h.

concentration at a lower temperature (140 °C). The nanocrystals of phase-pure rutile with sizes smaller than 10 nm could be achieved at 140 °C.

Reaction Temperatures and Times. Reaction temperature and time are two important thermodynamic and kinetic factors for a hydrothermal reaction.^{16,23} The influence of reaction temperature and time on phase formation and evolution was investigated as shown in Figure 6 in which TNB and HCl concentrations were both kept at 0.5 M. The product prepared at 100 °C for 10 h was predominantly anatase with trace rutile and brookite (Figure 6a). Rutile fractions in products increased with higher reaction temperature and/or longer time. As hydrothermal aging prolonged, brookite and anatase gradually disappeared and eventually phase-pure rutile was yielded (Figure 6).

The rodlike particles attributed to rutile became larger with increasing aging temperature and/or time (Figure 3a and 3d), and the (110) diffraction intensity of rutile tended to be stronger (Figure 6). This indicated that the crystal face of {110} became more and more significant as rutile crystals grew (Figure 3).

Phase Evolution. Hydrothermal treatment on phase transformation was first investigated by using starting material composed of anatase with trace brookite. This starting material was prepared hydrothermally from 0.5 M TNB in pure water at 220 °C for 10 h (Figure 1a). The titania concentration for phase evolution was fixed at 0.2 M and the aging was performed at 220 °C for 5 days unless otherwise pointed out.

The minor brookite disappeared and the major anatase phase remained after hydrothermal treatment either in pure water or in 4.0 M NaCl aqueous solution,

and the anatase XRD peaks became sharper and stronger. If it was treated with 1.0 M HCl solution, it changed into a mixture of anatase and rutile with a rutile fraction of about 74%. If the concentration of the titania precursor reduced to 0.1 M, phase-pure rutile was yielded after being treated in 1.0 M HCl aqueous solution. These results mean that the phase transformation occurred more easily at low concentration of titania in a HCl-acidified medium. If commercial anatase was used as a precursor for phase transformation under hydrothermal conditions, it was found that anatase was more difficult to convert to rutile even in a 1.0 M HCl medium. This indicates that fresh anatase is more active and easier to change to rutile, which is similar to the solid-state phase transformations.^{3,32}

If the sample as shown in Figure 4b was used as the starting material, the fraction of rutile increased more obviously (from 58% to 96%) after being treated in 4.0 M NaCl, and the original trace of brookite disappeared, indicating the presence of rutile enhanced the phase transformation to rutile. However, if the mixture was treated in pure water, the rutile fraction remained almost the same while its peaks in XRD patterns became sharper and stronger. It is sure that phase-pure rutile could be obtained from the mixed phases in Figure 4b after hydrothermal treatment in a 1.0 M HCl medium.

In summary, the efficiency of phase transformation in mediums follows the trend HCl > NaCl > H_2O .

Discussion

General Phenomena. Although anatase, brookite, and rutile are all constructed by octahedral TiO_6 units, their densities are different from each other, at 3.90, 4.14, and 4.29 g cm^{-3} , respectively.³⁴ As initial kinetic product, anatase nucleates and grows first according to Ostwald's law. Even though the titania source was obtained from the redissolution of rutile in the presence of phosphate or fluoride anions^{29,30} or by contacting with some strongly negatively charged colloid particles such as $V_2O_5 \cdot nH_2O$, MoO_3 , and $H_2WO_4 \cdot nH_2O$,³⁵ it still led to the formation of anatase. This indicated that the growth unit could not be used to elucidate the nucleation of rutile reasonably.¹³ With relatively shorter reaction time, anatase is the dominant product. Since rutile is the thermodynamically most stable phase, rutile nuclei will appear eventually when the successive reaction is taking place. As rutile nuclei are yielded along the anatase {112} twin interface, which has structural similarity to rutile, rutile quickly grows epitaxially at the expense of mother anatase crystallites.⁵ This is why there is a critical size of anatase before its disappearance and there is an induction period for phase transformation.³² Although the nucleation of rutile is much

(32) Yoganarasimhan, S. R.; Rao, C. R. N. *Trans. Faraday Soc.* **1962**, *58*, 1579.

(33) (a) Iida, Y.; Ozaki, S. *J. Am. Ceram. Soc.* **1961**, *44*, 120. (b) Shannon, R. D.; Pask, J. A. *Am. Miner.* **1964**, *49*, 1707. (c) Heald, E. F. *Am. Miner.* **1972**, *57*, 10. (d) Ohtsuka, Y.; Fujiki, Y.; Suzuki, Y. *J. Jpn. Assoc. Mineral. Pet. Econ. Geol.* **1982**, *77*, 117. (e) Gennari, F. C.; Pasquevich, D. M. *J. Mater. Sci.* **1998**, *33*, 1571.

(34) Howard, W. J. *Crystal Chemistry and Refractivity*; Cambridge University Press: Cambridge, 1988; p 276.

(35) Kittaka, S.; Matsuno, K.; Takahara, S. *J. Solid State Chem.* **1997**, *132*, 447.

slower than its growth, it can be initiated by the original presence of rutile crystallites.⁵ It is reasonable that the addition of rutile could enhance the phase transformation. Upon the consumption of anatase as a titania source, rutile continues growing via a dissolution and precipitation process. This is why the crystalline sizes of rutile are always greater than anatase and grow obviously larger upon the disappearance of anatase, as shown in Figure 5. Increasing reaction temperature generally accelerates phase transformation from thermodynamically metastable to stable phase and condenser phase formation. The fraction of rutile becomes greater with increasing reaction temperature and/or time (Figure 6).

There are 4_2 screw axes along the crystallographic *c*-axis in the rutile structure.³⁴ The screw structure will promote crystal growth along this direction and the crystal morphology will be dominated by the {110} faces according to the Donnay–Harker rule.³⁶ This is why rutile nanoparticles prepared hydrothermally are usually acicular or rodlike (Figure 3).^{12,13}

The difference in characteristics between rutile and anatase is much more significant than that between rutile and brookite.³⁴ Brookite is an intermediate phase, which can enhance the transition from anatase to rutile.³⁷ It is much easier for brookite to change to rutile than anatase to rutile. Upon the initial kinetic product, anatase, being exhausted and rutile initiated, brookite will also disappear exhaustedly. This is why the coexistence of only two polymorphs of rutile and brookite has rarely been observed so far.

The Effect of Acids. It has also been widely reported that anatase can be stabilized in a medium with pH around IEP, and rutile formation can be accelerated in a strong acidic medium under hydrothermal conditions.^{13,37} However, both anatase and rutile could be successfully obtained in acidic mediums in this work.

The structural rearrangement of octahedral TiO_6 units is necessary during phase transformation. It has been well-documented that NO_3^- and Cl^- anions show weaker affinity to a titanium atom in an aqueous solution than CH_3COO^- and SO_4^{2-} anions do.^{22,30,31} The strong affinity to titanium inhibits the structural rearrangement and, subsequently, the phase transformation. The strong chemical coordinating anions such as SO_4^{2-} and MoO_6^{6-} to titanium in aqueous solution seems to alleviate rutile generation. Phase-pure rutile could be obtained in either HCl or HNO_3 aqueous solution. Cl^- anions show weaker affinity to a titanium atom than NO_3^- anions do, so that pure rutile could be obtained more easily in HCl than in a HNO_3 medium as described above and in our previous work.¹⁶

Acid can accelerate not only phase transformation but also crystal growth. It works like a chemical catalyst. Strong acidity (the H_3O^+ cation) accelerates crystal growth. Thus, either anatase or rutile nanocrystals tend to be larger from stronger acidic solution. The anatase crystallites from H_2SO_4 aqueous solution are larger than those from HOAc.

The Effect of NaCl Additive. Table 1 demonstrates something different from a previous work in which it was indicated NaCl reduced rutile sizes and favored

rutile formation.¹³ Here, it is proposed that NaCl can play dual roles in rutile formation and growth, namely, chemical catalysis and physical confinment. As a chemical catalyst, NaCl can promote rutile formation and crystal growth, although not so significantly as acid. In contrast, it serves as an electrolyte to confine rutile formation and crystal growth physically through electrostatic adsorption. Especially at its higher concentrations, its physical adsorption predominates. This is why rutile particle sizes were reduced markedly, and particle agglomeration was not found in the presence of SnCl_4 .¹³ However, the physical adsorption of Na^+ cations on rutile surfaces becomes weaker in aqueous solution with higher concentrations of H_3O^+ especially at a higher temperature. The crystalline sizes of rutile kept no reducing with increasing NaCl concentrations up to some extent in 2.0 M HCl at 220 °C. In fact, all the physical adsorption on particle surfaces will limit crystal growth of either anatase or rutile, as described by Wang and Ying.¹¹

Conclusions

The sol-hydrothermal method provides an alternative approach for preparing uniform, dispersed nanocrystalline anatase and rutile respectively with various sizes and morphologies. During hydrothermal processing, anatase is formed first because of its higher molar volume than its related polymorphs. Rutile nucleates slowly and epitaxially grows quickly. The crystallization of rutile can be promoted in the presence of trace rutile sources, particularly in acidified mediums, and at higher reaction temperatures.

Crystal growth of both anatase and rutile particles can be facilitated in acidified mediums, respectively. It is difficult for rutile to be formed in either acetic or sulfuric acid as either SO_4^{2-} or CH_3COO^- anions show stronger chemical coordination to titanium, while it is easy for rutile to be formed in a HCl medium as Cl^- anions show weaker coordination ability to titanium. Thus, nanocrystals of pure rutile with sizes < 10 nm can be obtained at higher HCl concentrations under much milder hydrothermal conditions, such as 140 °C. The ability of an acidic medium favoring the formation of rutile is shown as follows: $\text{HCl} > \text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HAc}$.

The presence of NaCl salt not only influences phase formation but also particle size of titanium dioxide. The physical adsorption of NaCl on titania surfaces confines the growth of crystals, especially at a lower temperature (such as 140 °C) and a higher NaCl concentration; in contrast, the chemical catalysis of NaCl additive can promote the crystallization of nanocrystals especially at a higher temperature (such as 220 °C). These opposite functions of NaCl are competing with each other in a certain reaction medium.

Acknowledgment. This work is supported by the National Natural Science Foundation of China for Youth, Provincial Natural Science Foundation of Guangdong, Government of Guangzhou City, and the Key Laboratory of ISPC. The authors show great appreciation to Samuel M.-F. Lo, Fanny L.-Y. Shek, Herman H.-Y. Sung, and Teresa S.-C. Law in the Department of Chemistry, HKUST, for helpful discussions.

(36) Donnay, J. D.; Harker, D. *Am. Miner.* **1937**, *22*, 446.

(37) Ovenstone, J.; Yanagisawa K. *Chem. Mater.* **1999**, *11*, 2770.