The Synthesis of Nanocrystalline Anatase and Rutile Titania in Mixed Organic Media

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The synthesis of anatase and rutile titania could be achieved in mixed organic media with the variation of alcohols in the media under mild conditions. Although a nonhydrolytic process cannot be excluded, it is suggested that the formation of titania in these systems is based mainly on the hydrolytic process initiated by the water generated as a result of an esterification reaction between the alcohols and acetic acid. It has been found that the phase of the TiO_2 produced depends on the choice of alcohols and temperature. Partial morphology and size are also affected by these factors. It is proposed that the viscosity and pressure of the reaction media influence the particle size. X-ray diffraction, transmission electron microscopy, Raman spectroscopy, and UV−visible adsorption spectroscopy were employed to characterize the final products.

Introduction

Nanocrystalline titanium dioxide, as one of the most important oxide semiconductor materials, has been extensively researched during recent years for its superior physical and chemical properties, such as catalytic activity,[1] photocatalysis,[2] good stability toward adverse environment,[3] sensitivity to humidity and gas,[4,5] dielectric character ,[6] photo-electrochemical conversion,[7] nonlinear optics,[8] photoluminescence[9] and so on. These properties are dictated to a large extent by crystal structure and morphology as well as by grain size. There are three crystalline phases of titania: rutile, anatase, and brookite. Rutile is the thermodynamically stable polymorph and can be used as a white pigment in making paints, while anatase, as one of the other two kinetic products, has been documented in the literature as having a far higher photocatalytic activity than the rutile phase. Amorphous, microporous titania, modified with transition metal salts, has now been demonstrated to be able to induce a photocurrent and photocatalyze the degradation of 4-chlorophenol with visible light.[10] So, it is practically and scientifically significant to explore new synthetic methods to control the crystal structure, morphology, and size of titania and, therefore, optimize the properties of desired material.

Among the large number of preparation methods for TiO_2, the hydrolysis of titanium compounds such as titanium alkoxides and halides has been extensively studied, in which water acts as an oxygen donor. The hydrolysis can be initiated at low temperature and fulfilled in either aqueous or organic media. However, the traditional method of hydrolysis is based mainly on the physical introduction of water into the reaction system. This might introduce some negative effects on the control of reaction rates and homogeneity. Recently, the hydrolysis method to synthesize titania has been no longer limited to this scope. When exposed to atmosphere, titanium alkoxides containing templates absorb moisture and subsequently hydrolyze to form porous titania materials.[11,12] The reactions took place at the interface between liquid and atmosphere, and the rates could be controlled to some extent depending on the atmospheric moisture. Control over particle size and size distribution for anatase TiO_2 has been achieved by Chemseddine and Moritz[13] through a wet chemically controlled hydrolysis method. By the adjustment of the relative concentrations of titanium alkoxide [$Ti(OR)_4$] and Me_4NOH, temperature, and pressure, nanocrystalline TiO_2 could be obtained in different sizes and shapes (triangular, rodlike). The crystal structure was always confined to the anatase form of TiO_2. Colvin and co-workers[14] proposed a nonhydrolytic method to obtain nanocrystalline TiO_2 to modify the surface structure. With the use of titanium alkoxide and halides as precursors, the anatase phase of nanocrystalline TiO_2 with the size smaller than 10 nm and irregular shapes was obtained at 300 °C under dry nitrogen. The absence of surface hydroxyl has permitted the exploration of new types of surface derivation, which might find application in catalytic reaction. With increase in the nucleophilicity (or size) of the halide, we also noticed that the mean size of the anatase crystals decreased and larger rutile particles could be obtained in the case of TiI_4.

Traditionally, the rutile phase of TiO_2 is obtained at an elevated temperature in sol−gel procedure. But this is accompanied by sintering, grain growth, and loss of surface area[15−17] which makes it unsuitable in some applications that

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(1) Coulter, L. E.; Sault, A. G. *J. Catal.* **1995**, *154*, 56.
(2) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
(3) Tonejc, A. M.; Goti, M.; Grozetu, B.; Music, S.; Popoui, S.; Trojko, R.; Turkovi, A.; Musevic, I. *Mater. Sci. Eng.* **1996**, *1340*, 177.
(4) Yeh, Y. C.; Tseng, T. T.; Chang, D. A. *J. Am. Ceram. Soc.* **1989**, *72*, 1472
(5) Ketrom, L. *Am. Ceram. Soc. Bull.* **1989**, *68*, 860.
(6) Fukushima, K.; Yamada, I. *J. Appl. Phys.* **1989**, *65*, 619.
(7) Bard, A. J. *Science* **1980**, *207*, 139.
(8) Gratzel, M. *Nature* **1992**, *353*, 737.
(9) Liu, Y.; Claus, R. O. *J. Am. Chem. Soc.* **1997**, *119*, 5273.
(10) Kisch, H.; Zang, L.; Lange, C.; Maier, W. F.; Antonius, C.; Meissner, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3034.
(11) Feng, S.-H.; Xu, R.-R.; Judith, C. G.; Wijnhoven, J.; Vos, W. L. *Science* **1998**, *281*, 802.
(12) Imhot, A.; Pine, D. J. *Adv. Mater. (Weinheim, Ger.)* **1999**, *11*, 311.
(13) Chemseddine, A.; Moritz, T. *Eur. J. Inorg. Chem.* **1999**, 235.
(14) Trentler, T. J.; Denler, T. E.; Bertone, J. F.; Agrawal, A.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 1613.
(15) Lopez, T.; Sanchez, E.; Bosch, P.; Meas, Y.; Gomez, R. *Mater. Chem. Phys.* **1992**, *32*, 141.

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Table 1. Experimental Conditions and Crystal Structure, Morphology, and Size of the Products

	absolute ethanol + acetic acid		ethylene glycol + acetic acid		glycerol + acetic acid	
	100 °C	150 °C	100 °C	150 °C	100 °C	150 °C
crystal phase	rutile	rutile	anatase	anatase	amorphous	rutile
morphology	tenuous fiber	rodlike	spherical	spherical		spherical
crystal size	6 nm × 1μm	10 nm × 70 nm	4.5 nm	5.2 nm		6.5 nm

require ultrafine rutile crystallites with a high surface area and a controlled morphology. An alternative approach is the hydrothermal treatment of amorphous gel or anatase crystals in inorganic acid media via a possible dissolution−precipitation mechanism.[18−22] Recently, TiO_2 nanoparticles have been synthesized by the homogeneous hydrolysis of titanium alkoxides involving a high-temperature processing to obtain well-crystallized products.[23,24]

In this paper, we describe a chemical solution method to synthesize nanocrystal rutile and anatase TiO_2 in mixed organic solvents composed of alcohols and acetic acid. This process differs from that of Gotic[25] in that control of some properties of the final products is achievable.

Experimental Section

Since titanium chloride is highly sensitive to moisture, the alcohol and acetic acid were distilled before use. The pipets and autoclaves were dried under vacuum before use. All manipulations were carefully performed in a glovebox with the protection of flowing dry nitrogen.

After adding 3 mL of $TiCl_4$ (about 27 mol) into each of the three liquid phases (30 mL of absolute ethanol and 15 mL of acetic acid for liquid phase 1, 20 mL of ethylene glycol or glycerol and 20 mL of acetic acid for liquid phases 2 and 3), the mixtures were transferred to Teflon-lined stainless steel autoclaves. Then the autoclaves were heated at 100 or 150 °C for 18 h. After being naturally cooled to room temperature, the products were filtered in air. The reaction was believed to be complete for liquid phases 1 and 2 after 18 h at 100 °C and liquid phase 3 after 18 h at 150 °C, since the yield of each system was larger than 97%. The filtered solutions were collected and analyzed by gas chromatography−mass spectrometry (GC-MS). (Special attention should be paid to the 100 °C reaction mixture from liquid phase 3. It should be diluted with 100 mL or more of absolute ethanol to decrease the viscosity and satisfy the requirements for filtration.) The white products were washed three times with 50 mL of distilled water, washed with 30 mL of absolute ethanol, and dried at 60 °C for several hours.

The products were subjected to the characterization of X-ray diffraction (XRD), transmission electron microscopy (TEM), and IR, UV−visible (UV−vis), and Raman spectroscopy. X-ray diffraction was carried out with a Regaku D/max γA X-ray diffractometer with Cu Kα (λ = 1.5418 Å) incident radiation at room temperature over the 2θ range of 10−70°. The morphology and particle sizes were investigated with TEM (Hitachi-800). GC-MS spectra were recorded on a Perkin-Elmer Autosystem XL (GC) and a Perkin-Elmer TurboMass (MS). The UV−vis absorption was investigated on a Shimadzu UV-2100S. The Raman absorption was obtained on a Perkin-Elmer spectrometer (GX/FT-Ramanspectrometer).

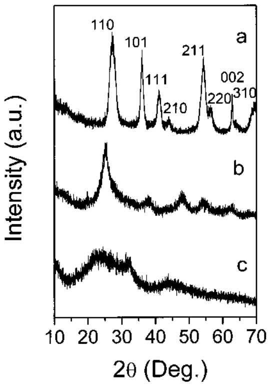

Figure 1. X-ray diffraction pattern: (a) rutile phase obtained in absolute ethanol and acetic acid, (b) anatase phase obtained in ethylene glycol and acetic acid, and (c) amorphous phase obtained in glycerol and acetic acid after being heated at 100 °C for 18 h.

Results and Discussion

The products from the three systems, after being heated at 100 °C for 18 h, were rutile, anatase, and amorphous TiO_2, respectively, for liquid phase systems 1, 2, and 3, as judged by powder XRD. No brookite phase was detected. The experimental conditions and some results are summarized in Table 1.

The analysis of the diffraction line widths of the pure rutile phase of nanocrystalline TiO_2 produced in liquid phase 1 showed a variation among them (Figure 1a). (101) and (002) are lesser in width than the others indicating that epitaxial growth might have occurred on each of these two lattice planes. TEM showed that the product consisted of tenuous fibers of rutile TiO_2 with diameters less than 10 nm and lengths up to 1 μm (Figure 2a). The dark areas in Figure 2a were the result of aggregations of the fibers as shown by higher magnification (Figure 2b). As further proof of this morphology, diffraction circles and dots were apparent in the electron diffraction (ED) pattern (Figure 2c). Nanocrystalline spherical particles of anatase phase of TiO_2 (Figure 1b) could be obtained in liquid phase 2. The grain size was estimated to be 4.8 nm using the well-known Scherrer equation. A slightly larger size could be observed with TEM (Figure 2d). Under the same conditions, the product obtained in liquid phase 3 was amorphous as shown in XRD (Figure 1c). IR spectra of this product in the range from 400 to 3600 cm^{-1} showed that the amorphous product contained organic components.

Optical Raman spectroscopy (Figure 3) of the rutile phase of TiO_2, obtained in liquid phase 1 at 100 °C, reveals two Raman bands at 608 and 446 cm^{-1} ranging between 200 and 800 cm^{-1}.[26] The Raman bands at 214, 409, 503, and 626 cm^{-1} of the product obtained in liquid phase 2 can also be indexed as that of the anatase phase of TiO_2.[27] We did not find Raman active peaks for any impurities such as chemical reaction products. This means that the rutile and anatase phases of TiO_2 thus obtained are of good quality. The UV absorption spectra

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(16) Nagpal, V. J.; Davis, R. M.; Desu, S. B. *J. Mater. Res.* **1995**, *10*, 3068.

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

(18) Wang, C. C.; Ying, J. Y. *Chem. Mater.* **1999**, *11*, 3113.

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

(20) Matoijevic, E.; Budnik, M.; Meites, L. *J. Colloid Interface Sci.* **1977**, *61*, 302.

(21) Dawson, W. J. *Am. Ceram. Soc. Bull.* **1988**, *67*, 1673.

(22) Kondo, M.; Shinozaki, K.; Ooki, R.; Mizutani, N. *J. Ceram. Soc. Jpn.* **1994**, *102*, 742.

(23) Wu, J. C. S.; Yeh, C.-Y. *J. Mater. Res.* 2001, *16* (2), 615.

(24) Kominami, H.; Kato, J.; Murakami, S.; Kera, Y.; Inoue, M.; Inui, T.; Ohtani, B. *J. Mol. Catal.* **1999**, *144*, 165.

(25) Ivanda, M.; Music, S.; Popovic, S.; Gotic, M. *J. Mol. Struct.* **1999**, 480−481, 645.

(26) Melendres, C. A.; Narayanasamy, A.; Maroni, V. A.; Siegel, R. W. *J. Mater. Res.* **1989**, *4*, 1246.

(27) Mammone, J. F.; Sharma, S. K.; Nichol, M. *Solid State Commun.* **1980**, *34*, 799.

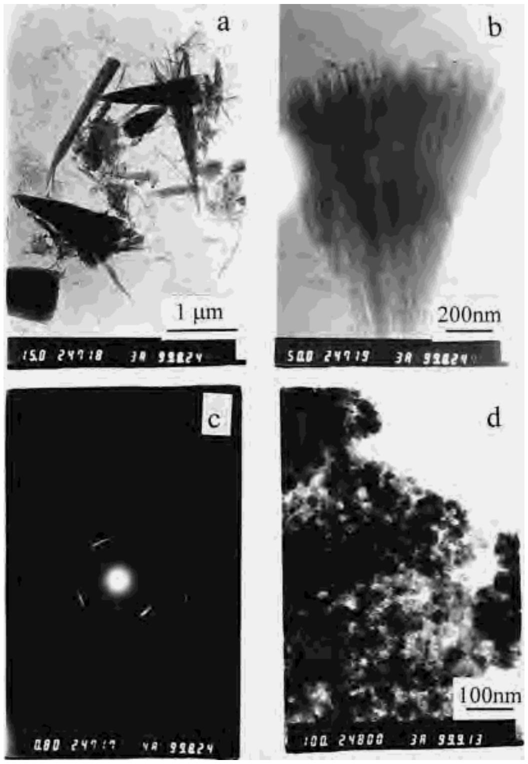

Figure 2. Transmission electron microscopy: (a) tenuous fiber of rutile phase (scale bar 1 μm) prepared in absolute ethanol and acetic acid, (b) higher magnification of the dark area in (a) (scale bar 200 nm), (c) electron diffraction pattern in selected area of (a), and (d) spherical particles of anatase phase (scale bar 100 nm) prepared in ethylene glycol and acetic acid after being heated at 100 °C for 18 h.

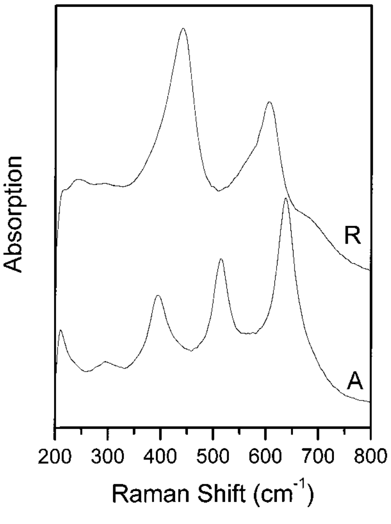

Figure 3. The Raman spectra of titania: R, rutile phase obtained in absolute ethanol and acetic acid; A, anatase phase obtained in ethylene glycol and acetic acid after being heated at 100 °C for 18 h.

Table 2. GC-MS Results of Filtrates of Liquid Phases 1, 2, and 3

reaction system	retention time (min)	compositions
ethanol + acetic acid	2.694	$CH_3COOCH_2CH_3$
ethylene glycol + acetic acid	2.969	$ClCH_2CH_2OH$
	5.169	$CH_3COOCH_2CH_2Cl$
	6.214	$CH_3COOCH_2CH_2OH$
	10.265	$CH_3COOCH_2CH_2OOCCH_3$
glycerol + acetic acid	6.049	$CH_2ClCH_2OHCH_2Cl$
	7.314	$CH_2ClCH_2OHCH_2OH$
	10.595	$CH_2OHCH_2OHCH_2OOCCH_3$

of the samples show that the rutile and anatase phases have absorption maxima at 272 and 242 nm, respectively. The absorption band edge for them can be estimated to be around 350 nm by extrapolating the steep slopes in the curve to the long-wavelength side. This observation is consistent with its reported band gap (3.2 eV).[28,29] No absorption maximum and band edge could be observed for the amorphous phase obtained in liquid phase 3.

When $TiCl_4$ was added to alcohols at room temperature, it reacted with the alcohols to produce $Ti(OR)_xCl_{4-x}$ with the liberation of HCl. After stirring these solutions for several hours and allowing the evolution of HCl, Vioux et al. had fulfilled nonhydrolytic processes to some metal oxides including titania.[30−32] Although we could not exclude the nonhydrolytic process, we believe that the formation of TiO_2 in our systems is mainly a hydrolytic process based on our experimental results. GC-MS results of the filtrates of the three liquid phases after being heated at 100 °C for 18 h are shown in Table 2. (The source alcohols and acetic acid are not listed.) Given that only ethanol, acetic acid, and ethyl acetate were present in the filtrate from liquid phase 1, it was suggested that TiO_2 was formed as a result of the hydrolysis of $Ti(OR)_xCl_{4-x}$ by the water released from the esterification of ethanol and acetic acid. *Even though we could not exclude the nonhydrolytic process for the expected* CH_3CH_2Cl*, as an indication of nonhydrolytic byproducts, might evolve from the filtrate after opening the autoclave.* If ethanol is used as the only solvent, we can obtain nanocrystalline spherical anatase titania (this will be reported elsewhere). The GC-MS results showed more complex pictures for the systems from liquid phases 2 and 3. Chlorine-substituted alkyls and esters are detected to a level of less than 4%. The chlorine-substituted alkyls could be attributed to either the nonhydrolytic process or the reactions between the alcohols and HCl. Since the total replacement is very low, the nonhydrolytic process could not have been the major route. The treatment of $TiCl_4$ in ethylene glycol or glycerol at 100 °C without acetic acid did not produce crystalline TiO_2; a mixture of rutile and anatase TiO_2 could be obtained in ethylene glycol at a higher temperature such as 150 °C but no crystalline product could be formed in glycerol either. This further confirms that esterification might be an essential requirement.

In our systems, after we added the $TiCl_4$ to the mixed solvents, the autoclaves were immediately sealed. Thus, the evolution of HCl produced by the reaction between ethanols and acetic acid is prevented, which differs from the manipulations of Vioux et al.[32] The HCl that is retained in the reaction systems can play a catalytic role, to initiate the esterifications of the alcohols and acetic acid at an elevated temperature such as 100 °C, and makes the hydrolytic process a feasible and major route to TiO_2.

With an increase in the hydroxyl content of the alcohol, there is a decrease in the crystallinity of TiO_2 as shown in Figure 1. Likewise, an increase in the viscosity of the three liquid phases was observed ($1 < 2 < 3$); we suggest that the higher viscosity

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(28) Turkovic, A.; Radic, N.; Sokcevic, D. *Mater. Sci. Eng.* **1994**, *B23*, 41.

(29) Crocker, M.; Herold, R. H. M.; Wilson, A. E.; Mackay, M.; Emeris, C. A.; Hoogendoorn, A. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2791.

(30) Corriu, R. J. P.; Leclercq, D.; Lefévre, P.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1992**, *2*, 673.

(31) Corriu, R. J. P.; Leclercq, D.; Lefévre, P.; Mutin, P. H.; Vioux, A. *J. Non-Cryst. Solids* **1992**, *146*, 301.

(32) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Mutin P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1925.

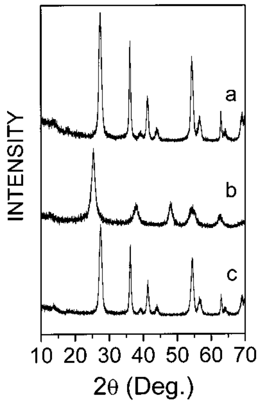

Figure 4. X-ray diffraction pattern: (a) rutile phase obtained in absolute ethanol and acetic acid, (b) anatase phase obtained in ethylene glycol and acetic acid, and (c) rutile phase obtained in glycerol and acetic acid after being heated at 150 °C for 18 h.

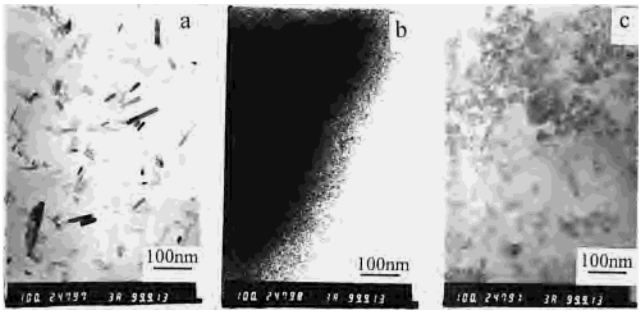

Figure 5. Transmission electron microscopy: (a) short rods of rutile phase (scale bar 100 nm) obtained in absolute ethanol and acetic acid, (b) spherical particles of anatase phase (scale bar 100 nm) obtained in ethylene glycol and acetic acid, and (c) spherical particles of rutile phase (scale bar 100 nm) obtained in glycerol and acetic acid after being heated at 150 °C for 18 h.

can inhibit nucleation of the product and keep the particles from growing larger. This makes the control of particle size feasible. In addition, since our synthesis was conducted under autoclaving conditions, the higher viscosity might reduce the reaction pressure and thus lead to smaller crystallites. A direct comparison between the XRD results given in Figures 1 and 4 reveals that the influence of the reaction pressure on the resulting crystallinity might be not critical at higher reaction temperatures. Generally, this is the way by which typical crystallization proceeds and thus is easy to be understood. Surprisingly, besides particle size, dramatic variations of crystal morphologies and structures are observed by a simple change of alcohol in our experiments. As explained by other researchers,[33] the dramatic change in crystal morphology could be rationalized on the basis of selective interaction of the solvents with surface ions, slowing the growth of specific lattice planes and thus resulting in the expression of these lattice planes in the final crystal form. In our process, we suggest that strong, selective surface interactions involving ethanol and acetic acid will lead to surface roughening and enhanced growth on the (101) and (002) lattice planes.[34] Although a glimpse of the change in the crystal morphology could be understood, the changes in crystal structure still remain elusive to us. Here, we attributed this change to the variations in titanium precursors, which might be the result of reactions between $TiCl_4$ and alcohol or acetic acid before the hydrolysis took place. The influence of pressure on the crystal morphology in the reaction system, dependent upon temperature and viscosity of the reaction media, might also be involved.

As pointed out and evidenced in the literature in sol−gel synthesis of TiO_2,[23] acetic acid (HAc), especially in the anionic form, which usually has a strong coordination capacity on metal centers, might form an intermediate complex with titanium chloride. The chelation between acetic acid and Ti(IV), if existing in our reaction system, might have somewhat of a stabilizing effect and thus moderates the reaction between titanium chloride and water produced through the esterification between alcohols and acetic acid. In addition, as mentioned above, the formation of this kind of chelate might also have a possible relationship with the morphologies of the resulting products. However, as a large amount of HCl is released as a product of the reaction between $TiCl_4$ and H_2O in our system, which is obviously different from the literature system that employs titanium alkoxides as Ti(IV) reagents, the resultant solutions should be strongly acidic. The resultant acidic environment is especially favorable for the acid-catalyzed esterification reaction but not for the coordination between Ac^- and Ti(IV), since the main existing form of acetic acid would now be the neutral HAc molecule with much less coordination activity. Therefore, the chelation between Ti(IV) and HAc as well as the existence of titanium acetate should not be predominant.

The chelation of glycol and glycerol on Ti(IV) might also exist in the reaction systems involving glycol and glycerol. The impact of this kind of a stabilization effect on the nucleation of TiO_2 is not very clear; lowered nucleation speed and improved crystallinity might be a possible result. Unfortunately, it would be rather difficult to distinguish this kind of influence based on our experimental results due to counteraction. On the other hand, the resultant morphologies of the TiO_2 products might have some inherent affiliation with these chelate precursors between $TiCl_4$ and alcohols.

Reaction temperature plays another important role in our process. The initiation of the reaction and nucleation depends on the temperature. For liquid phase 1, with the elevation of temperature from 100 to 150 °C, the tenuous fibers of the rutile phase of TiO_2 turned out to be shorter and wider (Figure 4). Meanwhile, the crystallinity was improved. However, this change has little effect on the synthesis of the anatase phase of TiO_2 in liquid phase 2. The most interesting phenomenon was observed for liquid phase 3 when the reaction temperature was increased to 150 °C. This resulted in the formation of spherical particles (5.5 nm mean diameter) of rutile TiO_2 (Figures 4 and 5). This is ascribed to complete esterification and a lowering of the viscosity of the system. The spherical particles deposited themselves at the bottom of the autoclave while the amorphous product produced at 100 °C remained as a stable dispersion.

Conclusion

In summary, titanium dioxide with different crystal structures, morphology, and grain sizes could be obtained in mixed organic solvents. Although a nonhydrolytic process could not be excluded, it is supposed that a hydrolytic process is a main route to titania based on the water released from the esterifications between alcohols and acetic acid. Since the release of water could be governed in some manner by the rate of esterification, the hydrolytic process can be controlled homogeneously in the reaction system. It has been found that the phase of TiO_2 produced, particle morphology, and particle size depend on the choice of alcohols and temperature. This process provides a good example toward connecting organic and inorganic reactions for the preparation of inorganic materials.

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(33) Doxsee, K. M.; Cheng, R. C.; Chen, E.; Myerson, A. S.; Huang, D. P. *J. Am. Chem. Soc.* **1999**, *120*, 585.

(34) Bennema, P. *J. Cryst. Growth* **1992**, *122*, 110.

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