Hydrothermal Preparation of Uniform Nanosize Rutile and Anatase Particles

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Uniform nanosize rutile and anatase particles were prepared by a hydrothermal method using $TiCl_4$ as starting material. The influences of various hydrothermal conditions on the formation, phase, morphology, and grain size of products were investigated and tentatively discussed from coordination chemistry. Increasing the acidity in reaction medium and the concentration of $TiCl_4$ aqueous solution favored of the formation of rutile type TiO_2. Raising the temperature (>200 °C) can decrease the agglomeration among TiO_2 grains. The mineralizers $SnCl_4$ and NaCl reduce markedly the grain size and favor the formation of rutile type TiO_2. The mineralizer NH_4Cl will increase greatly agglomeration among grains. The optimum conditions for preparing rutile-type TiO_2 were that $[TiCl_4] > 0.5$ mol dm^{-3}, 220 °C for 2 h and using $SnCl_4$ or NaCl as mineralizer. The average particle size of rutile TiO_2 was 20 nm by 8 nm. The optimum conditions for preparing anatase type TiO_2 were that pH > 7, 200 °C for 2 h. The average particle size of anatase TiO_2 was ca. 10 nm. The Raman spectra of nanosize rutile and anatase were studied. With decreasing grain size of rutile, the all peaks broadened and their wavenumber decreased, while a new broad band near 112 cm^{-1} appeared gradually.

Introduction

Titanium dioxide is commercially very important as a white pigment because of its maximum light scattering with virtually no absorption and because it is nontoxic, chemically inert, and a dielectric ceramic material for its higher dielectric constant. There are a lot of methods for preparing TiO_2.[1-5] Titanium dioxide is industrially produced generally by the so-called sulfate process and the so-called chloride process. In the former, the processing is very complicated. In the latter, the requirements for equipment and materials are very harsh because of high reaction temperature (>1400 °C) and strong corrosiveness of Cl_2 at high temperature. Comparing with other methods, the hydrothermal method has many advantages: (1) A crystalline product can be obtained directly at relatively lower reaction temperature (in general < 250 °C). Hence the sintering process, which results in a transformation from the amorphous phase to the crystal phase, can be avoided. It favors a decrease in agglomeration between particles. (2) From a change in hydrothermal conditions (such as temperature, pH, reactant concentration and molar ratio, additive, etc.), crystalline products with different composition, structure, and morphology could be formed. For example, perovskite-type (tabular), pyrochlore-type (starlike) and tetragonal body-centered type (acicular) $PbTiO_3$,[6,7] $PbTi_3O_7$,[8] and $PbO-TiO_2$ solid solution ($PbTi_xO_{1+2x}$, $x = 0.8$) (tabular)[9] have been obtained under different hydrothermal conditions. In this work, rutile-type TiO_2 (rodlike) and anatase-type TiO_2 (granulous) have also been prepared under different hydrothermal conditions. (3) The purity of product prepared in appropriate conditions could be high owing to recrystallization in hydrothermal solution. (4) The equipment and processing required are simpler, and the control of reaction conditions is easier, etc. So the hydrothermal synthesis is a good method for the preparation of oxide ceramic fine powders. But research on the mechanism of hydrothermal reaction has seldom been reported. The main reason could be that the related thermodynamic data under hydrothermal conditions are much more scarce and usually limited to the Gibbs energies at 298.15 K. Lencka and Riman[10] made a beneficial attempt; they studied "Thermodynamic modeling of hydrothermal synthesis of ceramic powders" and obtained some interesting results. But on the other hand, they also indicated that the thermodynamic data used were most accurate at low and moderate temperatures

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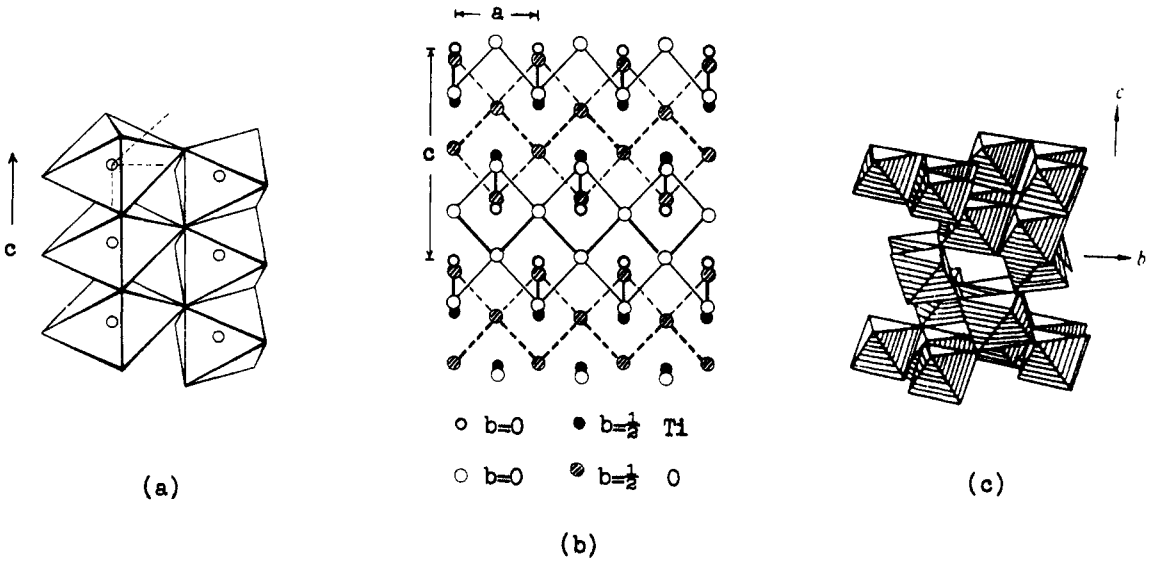

Figure 1. Modes of link among $[TiO_6]$ octahedrons in (a) rutile, (b) anatase, the projection along the *b* axis (the thick line shows the edge-shared link), and (c) brookite.

and lose accuracy above ca. 473 K. So far the knowledge and experimental data for ions in hydrothermal systems, especially more complex ions such as Ti^{4+}, $TiOH^{3+}$, $Ti(OH)_2^{2+}$, $Ti(OH)_3^{+}$, etc., are less well known. These caused difficulty for the research on the mechanisms of hydrothermal reaction.

Recently, ultrafine nanophase ceramics are attracting attention. Karch et al.[11] tested the low-temperature plastic deformation of nanocrystalline TiO_2 and CaF_2 ceramics and observed that conventinally brittle ceramics became ductile, permitting large (100%) plastic deformations at low temperature if a polycrystalline ceramic was generated with a crystal size of a few nanometers. This nanocrystalline TiO_2 was obtained by oxidizing the small Ti crystals accumulated on the surface of the coldfinger. X-ray diffraction revealed this TiO_2 to be pure rutile and its average crystal size of all specimens to be about 8 nm. The report about the hydrothermal preparation of nanosize TiO_2 particles has been limited. The aim of the present work is to research the preparation of uniform nanosize rutile and anatase particles by the hydrothermal method and to make an attempt to discuss the influences of preparation conditions on the formation, morphology, phase, and particle size of the TiO_2 products from coordination chemistry. In this paper, a grain is a small single crystal, and its size is determined by XRD. A particle is an identical one observed by TEM, which could be single crystal or polycrystal, and its size is measured with electromicrograph.

Experimental Procedure

Titanium tetrachloride ($TiCl_4$) was used as starting material. It was added slowly (ca. 1 mL min^{-1}) into ice water (ca. 0 °C) under stirring to prepare a $TiCl_4$ aqueous solution. The $TiCl_4$ solution was filtered to removel insoluble species. The concentrations of three $TiCl_4$ solutions determined by the gravimetrical analysis were 1.40, 0.88, and 0.53 mol dm^{-3}, respectively. The pH in the medium was adjusted using KOH. The feedstock of 60 mL was charged into a 100 mL Teflon-lined stainless steel autoclave apparatus with an electromagnetic stirrer (Peking University Instrument Factory). The hydrothermal preparations were conducted in the temperature range 85–220 °C for 1–4 h (heating rate 3 °C/min). The influences of concentration of $TiCl_4$ solution, pH in reaction medium, temperature, time, and mineralizer on the formation, phase, morphology, and particle size of TiO_2 were examined. After the autoclave apparatus was cooled to room temperature in ca. 2 h, the product (suspension) was allowed to stand for 24 h and was filtered after removing the supernatant, washed with acetic acid–ammonium acetate buffer solution and alcohol in order to prevent peptization, and dried at 80 °C. The chemical agents used were all analytical reagent grade.

The prepared TiO_2 powders were analyzed by X-ray diffraction (XRD) using Cu Kα radiation at 40 kV and 100 mA and a graphite monochromator and by scanning at 2° 2θ min^{-1} with a diffractometer (Model Dmax-2000, Rigaku Co., Tokyo, Japan) to determine the phase of the crystalline products. The morphology of products was observed using transmission electron microscopy (TEM, Model JEM-200 CX, JEOL Ltd., Tokyo, Japan). Differential thermal analysis (DTA) was conducted using DuPont 1090B thermal analysis systems (DuPont Co.). Raman spectra were detected with a Bruker FRA 106 FT-Raman accessory using a Nd:YAG laser (λ = 1064 nm, 200 mW, Bruker Instrument Inc.). The surfacial components of sample were analyzed with an electron spectrometer (Model VG ESCA LAB 5, VG Instrument Inc.) using Al Kα, *HV* = 50 eV (FAT), 10 kV, 20 mA.

Results and Discussions

The crystalline titanium dioxide has three crystalline forms: rutile, anatase, and brookite. Brookite and anatase are metastable and transform exothermally and irreversibly to the rutile over a range of temperatures but usually at 750 and 1000 °C, respectively.[12] The fundamental structure unit in three TiO_2 crystals are all $[TiO_6]$ octahedron, but their modes of arrangement and link are different. In rutile, $[TiO_6]$ octahedrons link by sharing an edge along the *c* axis to form chains and then corner-shared bonding among chains leads to a three-dimensional framework.[13] In anatase, the formation of a three-dimensional framework is all with edge-shared bonding among $[TiO_6]$ octahedrons.[13] The struc-

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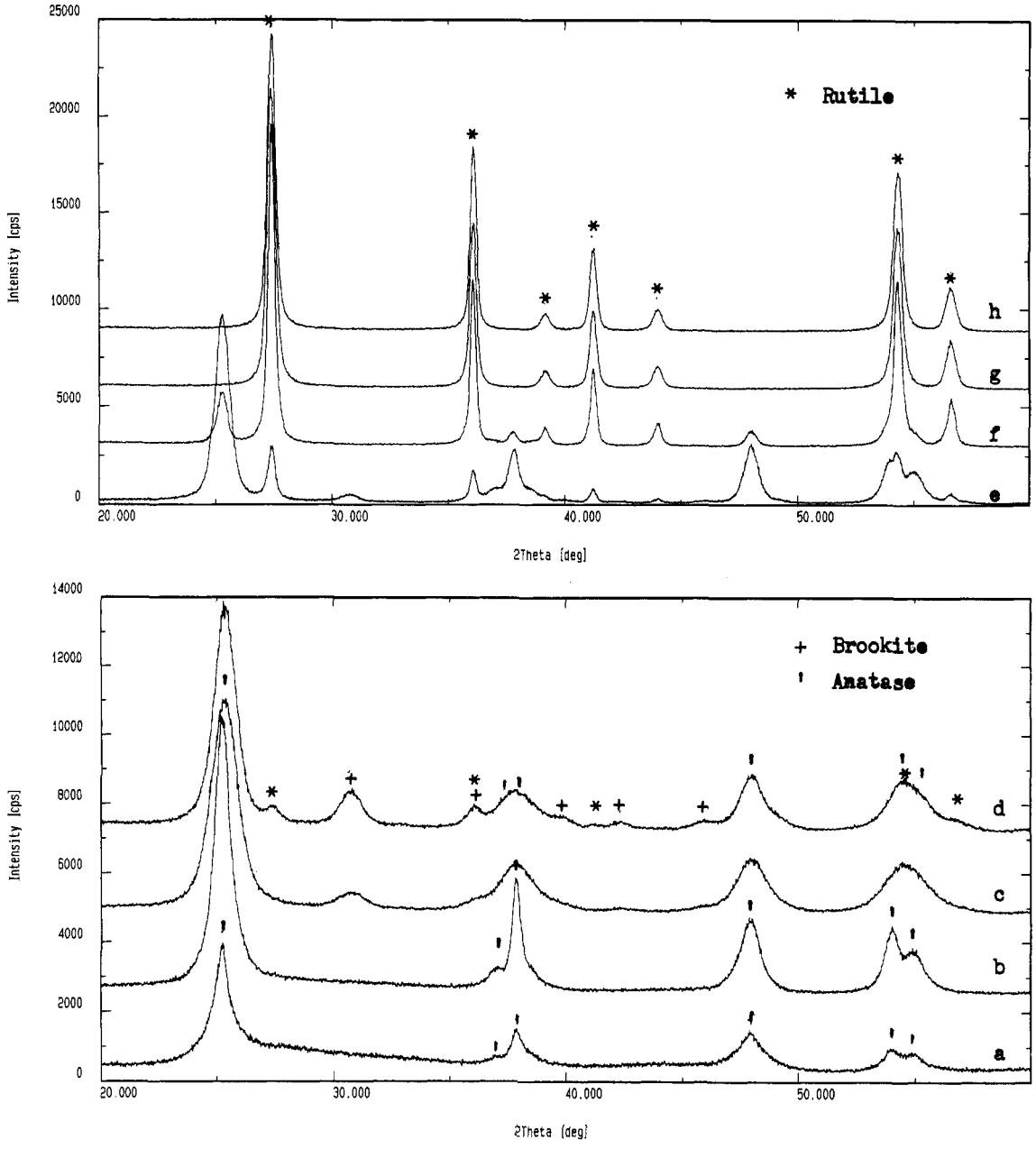

Figure 2. XRD patterns of the products prepared at different pH: (a–e) and [$TiCl_4$]: (f–h): (a) 8.2, (b) 7.1, (c) 3.4, (d) 1.0, (e) 0.0, (f) 0.44 mol dm^{-3}, (g) 0.53 mol dm^{-3}, (h) 1.40 mol dm^{-3}

ture of brookite is slightly complicated and contains edge-shared and corner-shared bonding.[14] The modes of link among [TiO_6] octahedrons in three TiO_2 crystals are shown in Figure 1.

Titanium dioxide prepared by the hydrothermal method can have different crystal structures and various morphologies, depending on the hydrothermal conditions. It could be concerned with the composition and structure of Ti(IV) complex ion in hydrothermal solution.

(I) Influence of Hydrothermal Conditions. *pH and Concentration in the Reaction Medium.* The pH in the reaction medium had a significant effect on the phase of TiO_2 products. The feedstocks were prepared as follows: taking 30 mL of $TiCl_4$ solution of 0.88 mol dm^{-3}, using KOH solution to adjust the pH to the required value and concentration of titanium species in samples a–f (Figure 2) was kept to be 0.44 mol dm^{-3}. The reactions were conducted at 220 °C for 2 h. The XRD patterns of the products prepared at different pH are given in Figure 2. The relevant TEM micrographs of products are shown in Figure 3. Figure 2 shows that high acidity is in favor of the formation of rutile phase. When the concentration of [Ti^{4+}] was 0.44 mol dm^{-3} (at this moment, the pH in the medium was negative and cannot be measured), the product was a mixture of rutile (majority) and anatase (minor) (Figure 2f) and had rodlike (rutile) and granulous (anatase) morphologies (Figure 3d). With increasing pH, the anatase phase in the products increased. As pH = 1.0, the product was mainly anatase and contained some brookite and a little rutile. When pH = 3.4, the rutile phase disappeared and the brookite phase in the product reduced. As pH = 7.1, the pure anatase phase with granulous morphol-

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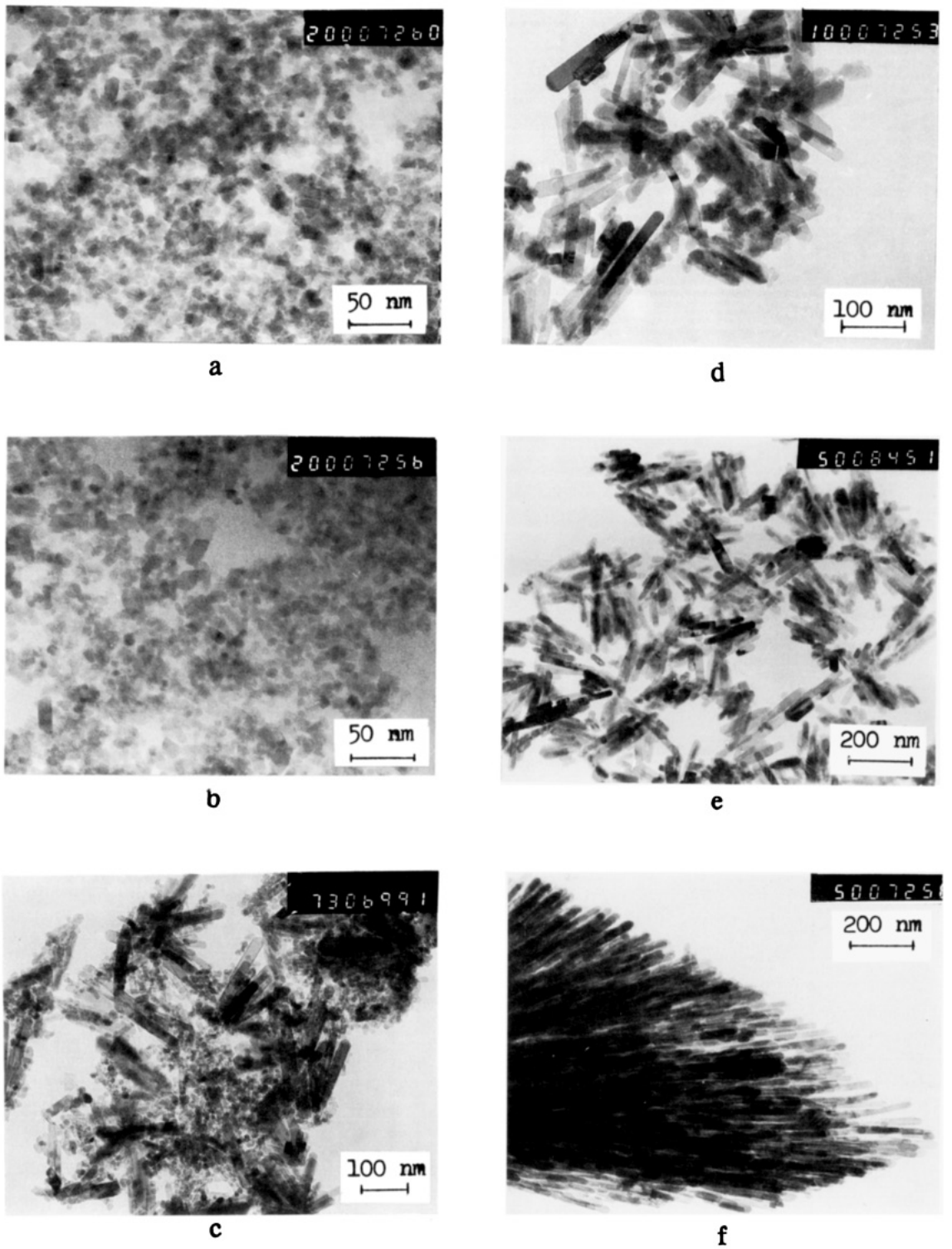

Figure 3. TEM micrographs of the products prepared at different pH: (a–c) and [$TiCl_4$]: (d–f): (a) 7.1, (b) 3.4, (c) 0.0, (d) 0.44 mol dm^{-3}, (e) 0.53 mol dm^{-3}, (f) 1.40 mol dm^{-3}.

ogy and grain size of ca. 10 nm was obtained (Figure 3a). If pH > 8, an amorphous phase began to appear, and when pH = 13, the product was quite amorphous. To obtain a pure rutile phase, it is necessary to further increase the acidity in the medium or the concentration of the $TiCl_4$ solution.

The concentration of $TiCl_4$ solution is increased while the acidity in reaction medium is also increased. The effect of concentration can be attributed mainly to the effect of acidity. Increasing the concentration of $TiCl_4$ solution on one hand favors the formation of the rutile type TiO_2 (Figure 2g and 2h) and, on the other hand, will lead to agglomeration among TiO_2 particles. For example, when the concentration of $TiCl_4$ solution is 0.53 mol dm^{-3}, the agglomeration phenomenon is seldom observed and the particle size is quite uniform (about 100 nm by 10 nm) (Figure 3e), but as the concentration is increased to 1.40 mol dm^{-3}, rodlike rutile TiO_2 grains agglomerated orientationally to form a broomlike aggregate, although every grain is still very small (Figure 3f).

From Figure 2, it can be seen that TiO_2 formed at different acidity could have a different structure, which could be concerned with the coordination group of Ti-

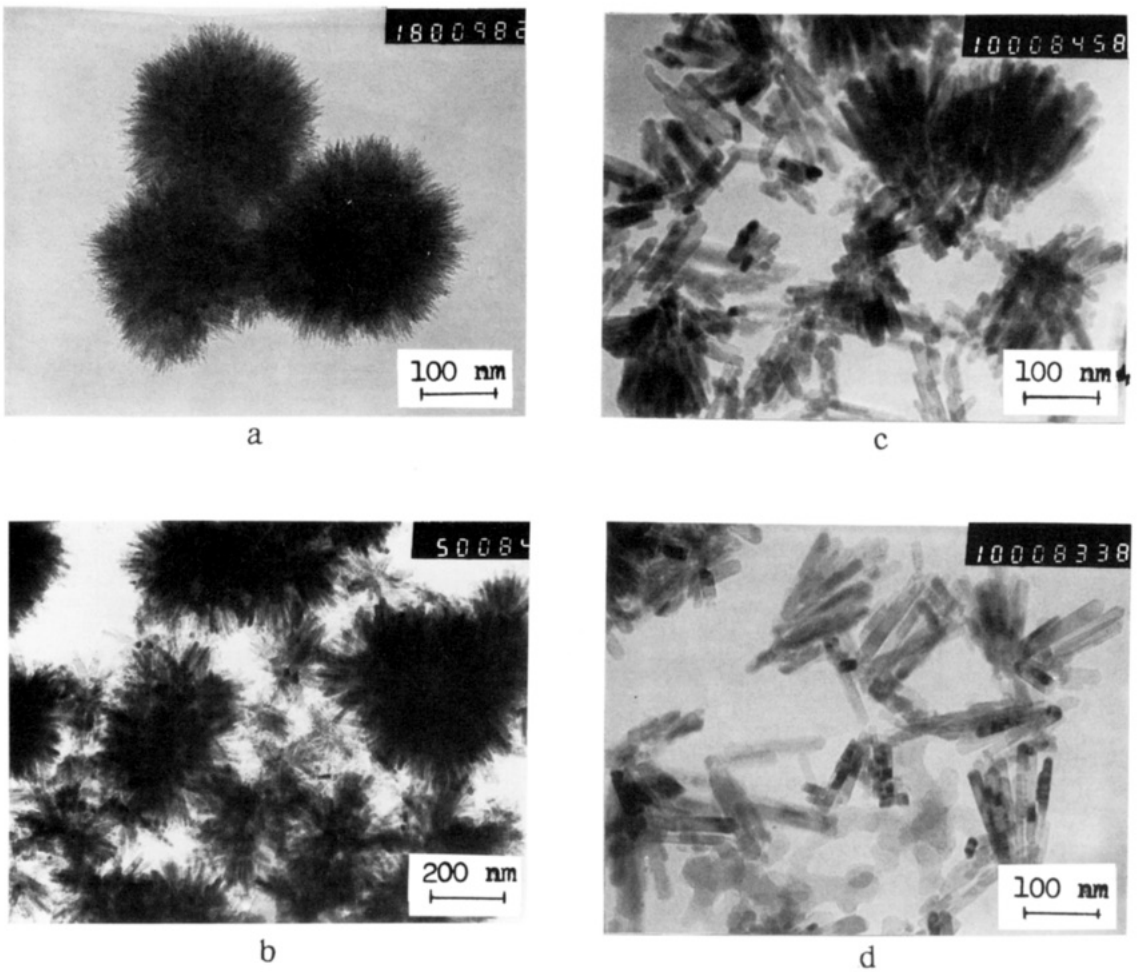

Figure 4. Effect of temperature on the agglomeration among grains: (a) 85 °C, (b) 180 °C, (c) 200 °C, (d) 220 °C ([$TiCl_4$] of 0.44 mol dm^{-3}, for 2 h).

(IV) complex ion. According to ligand field theory, Ti(IV) ($3d^0$) complex ions are all octahedrally coordinated in solution and crystal. The ligand field strength of OH group is larger than that of Cl^- ion. Nicholls[15] considered that in acids containing anions capable of coordinating to the titanium, the titanium(IV) was kept in solution as anionic complexes of type $[Ti(OH)Cl_5]^{2-}$ and $[TiCl_6]^{2-}$, because salts of this hexachlorotitanate(IV) anion can be precipitated from solutions of $TiCl_4$ in saturated hydrochloric acid. Zhong et al.[14] investigated the electrophoretic experiment of a $BaTiO_3$ solution (Ba/Ti = 1) under hydrothermal conditions (250 °C, pH 7–8, 6 V, for 8 h) and found that brookite formed on the anode. It showed that titanium(IV) existed as an anionic coordinate polyhedron $[Ti(OH)_6]^{2-}$ in the abovementioned solution. Hence the exact nature of titanium(IV) complexes depended on the acidity and ligand in solution. In the present work, it could be reasonable to assume that the Ti(IV) complex ion has the formula $[Ti(OH)_nCl_m]^{2-}$ (H_2O could be a ligand too), where $n + m = 6$, and n and m are concerned with the acidity and concentration of Cl^- ion in feedstock, i.e., the higher the acidity and [Cl^-], the bigger is m. The linking between [TiO_6] units is carried out by dehydration reactions (i.e., oxolation) between OH ligands in $[Ti(OH)_nCl_m]^{2-}$ complex ions. When the acidity in feedstock is lower, the number of OH ligand in $[Ti(OH)_nCl_m]^{2-}$ is more. In this case, the probability of edge-shared bonding is larger, which could favor the formation of the anatase phase. As the acidity in feedstock is higher, the number of OH ligands in $[Ti(OH)_nCl_m]^{2-}$ is less. Because the edge-shared bonding requires that two dehydration reactions between a pair of $[Ti(OH)_nCl_m]^{2-}$ take place simultaneously, and therefore the edge-shared bonding could be suppressed and the corner-shared bonding may easily occur in higher acidity. Thus higher acidity and concentration of [$TiCl_4$] could be beneficial for the formation of rutile phase.

Reaction Temperature and Time. The temperature had a great effect on the grain size of the products and the agglomeration among grains. Lowering temperature will give rise to decreasing grain size and increasing agglomeration among grains. The concentrated aqueous $TiCl_4$ solution (>0.5 mol dm^{-3}) was more steady at room temperature. As it was heated to about 85 °C, a white precipitate began to appear. After this, a vast amount of precipitate formed rapidly in ca. 10 min. The precipitate was filtered, washed, and dried at 80 °C. X-ray phase analysis and TEM observation indicated that the precipitate was a mixture of rutile (majority) and anatase (minor) with remarkable agglomeration although its average grain size was very small (ca. 5 nm from Debye–Scherrer formula). We further examined the effect of temperature in the range 180–220 °C. A group of samples with the major phase being rutile were used as examples. At 180 °C, the

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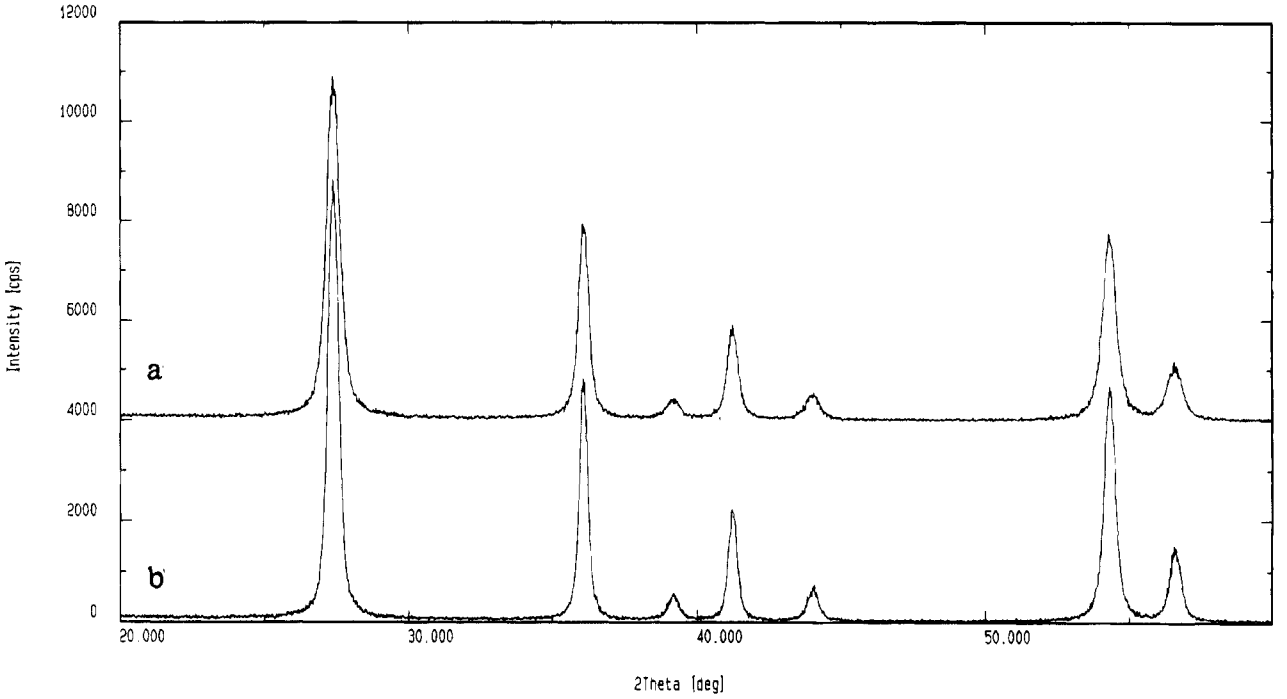

Figure 5. XRD patterns of the rutile samples prepared for different reaction time: (a) 1 h, (b) 2 h ([$TiCl_4$] of 0.53 mol dm^{-3}, 220 °C).

Table 1. Effect of Temperature on Grain Size[a]

temp, °C	HHB, deg	*D*, nm
180	1.00	8
200	0.76	10
220	0.59	14

[a] HHB, half-height breadth of (101) XRD peak for anatase. D, average grain size. Hydrothermal conditions: [$TiCl_4$] of 0.27 mol dm^{-3} for 2 h.

agglomeration phenomenon was still serious and did not disappear until the temperature rose to 220 °C. The relevant TEM micrographs were shown in Figure 4. Decreasing temperature will give rise to the broadening of XRD peaks of the products, and it meant that the grain size of the products reduced. A group of samples with the major phase being anatase were used as examples. The effect of temperature on the grain size of the products was listed in Table 1. Prolonging the reaction time will make the grains grow, and the relevant XRD peaks were getting higher and sharper (Figure 5). It showed that the average grain size of products increased with prologing reaction time. Their morphology essentially uncharged as Figure 3e.

The reasons for the agglomeration at lower temperature could be concerned with the large surface area of newly formed titanium dioxide particles. In strong acid medium, because the formation of Ti(IV) complex ions, the hydrolysis of titanium tetrachloride in water did not lead to the precipitation of much aqueous TiO_2 at room temperature. Raising the temperature enhanced the hydrolysis of $[Ti(OH)_nCl_m]^{2-}$ complex ions, i.e., the Cl^- ligand in it was substituted gradually by OH^- ligand, while the dehydration reactions between $[Ti(OH)_nCl_m]^{2-}$ complex ions gradually took place to form crystalline TiO_2. This crystallite TiO_2 easily formed an aggregate because of its large surface area. In the hydrothermal conditions, the recrystallization of small TiO_2 particles enhanced to form regular TiO_2 crystallite over 200 °C, and the agglomeration phenomenon decreased relevantly.

Mineralizer. We examined the effects of three mineralizers, NH_4Cl, NaCl, and $SnCl_4$, on the titanium dioxide formed in hydrothermal reactions. Mineralizer solution (20 mL) was added to 50 mL of $TiCl_4$ solution (0.44 mol dm^{-3}). The total volume of the feedstock was kept at 70 mL. The concentration of mineralizers NH_4Cl, NaCl, and $SnCl_4$ were 4, 4, and 1 mol dm^{-3}, respectively, to keep the total concentration of Cl^- in the reaction medium was constant. The other hydrothermal reaction conditions were temperature 220 °C and reaction time 2 h. The results showed that these mineralizers had marked effects on the phase, morphology, and particle size of products. First, the three mineralizers were all in favor of the formation of rutile phase. The product was a mixture of rutile and anatase phase in the absence of mineralizer (Figure 2f) and a pure rutile phase in the presence of mineralizer. The XRD patterns of the relevant products were given in Figure 6. Second, the three mineralizers had different effects on the morphology and grain size of product. Ammonium chloride (NH_4Cl) reduced grain size (XRD peaks broadened remarkably) but increased greatly agglomeration to form a hairy spheroid of particles. Sodium chloride (NaCl) decreased particle size (from 100–150 nm by 20 nm to 40 nm by 15 nm) and the agglomeration did not take place essentially. Tin tetrachloride ($SnCl_4$) reduced markedly the particle size (to ca. 20 nm by 8 nm), and the agglomeration phenomenon was not found, while the distribution of the particle size was uniform. Their electromicrographs were shown in Figure 7.

From Figure 6, it can be seen that the background was lower in the samples (b) and (c) but the background near $2\theta = 26°$, 34°, and 51° was higher in the sample (a). It indicated that very small crystallite SnO_2 (tetragonal) was formed. (SnO_2: JCPDS-21-1250, the 2θ

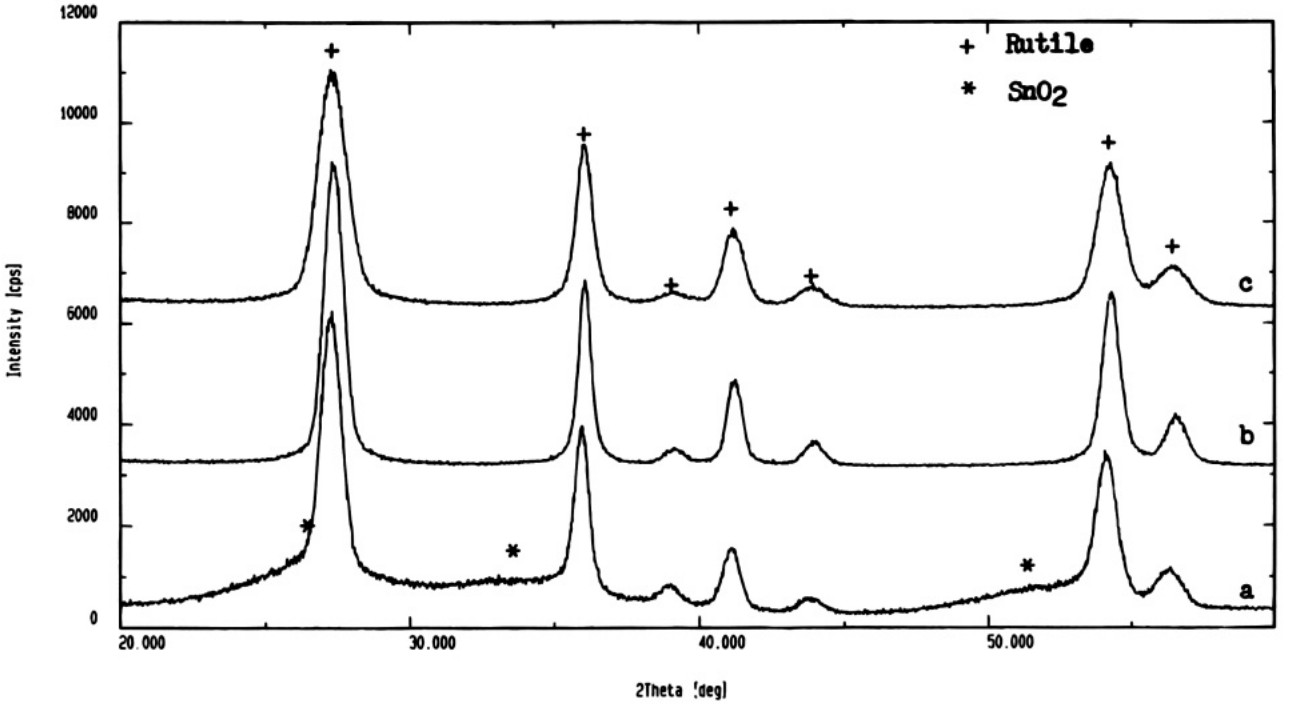

Figure 6. XRD patterns of products with different mineralizer: (a) $SnCl_4$, (b) NaCl, (c) NH_4Cl ([$TiCl_4$] of 0.44 mol dm^{-3}, 200 °C for 2 h).

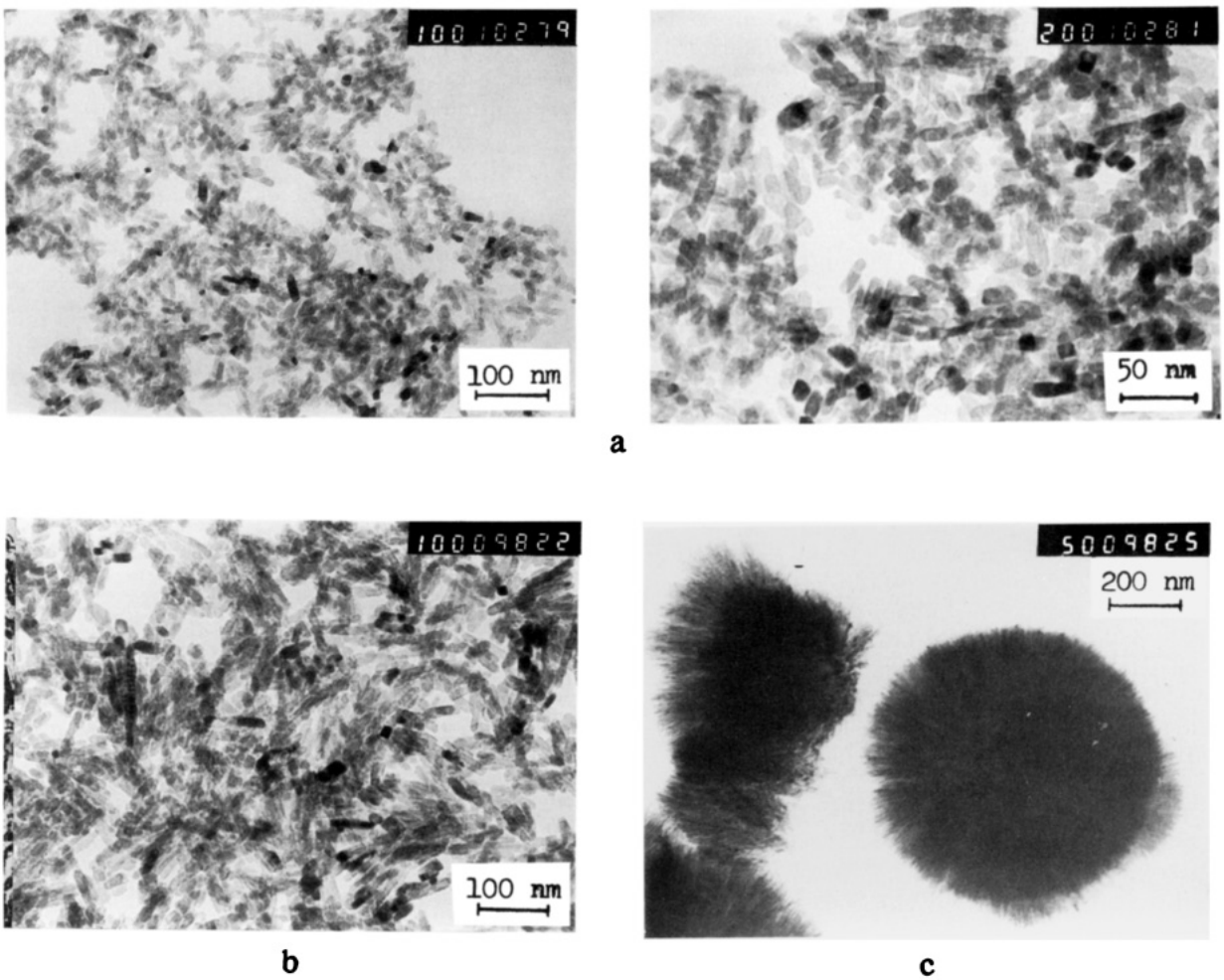

Figure 7. TEM micrographs of the products with different mineralizer: (a) $SnCl_4$, (b) NaCl, (c) NH_4Cl ([$TiCl_4$] of 0.44 mol dm^{-3}, 200 °C for 2 h).

of its three strongest XRD peaks are at 26.6°, 33.9°, and 51.7°, respectively). Because the tetragonal SnO_2 has the rutile-type structure, these crystallite SnO_2 could grow on the surface of rutile TiO_2 grains. Surfacial

component analysis of the sample (6a) with the X-ray photoelectron spectrum (XPS) showed that before and after Ar^+ ions etching (2 kV, 30 μA, 1 min), the Sn/Ti atomic ratios on the surface of the sample were 1.30 and 0.51, respectively. It could be considered as evidence that TiO_2 particles were coated by SnO_2.

Suyama et al.[16] and Akhtar et al.[17] investigated the effects of additives on the formation, phase, and particle size of TiO_2 powders in vapor-phase synthesis. They considered that the additives could act as nucleating agents and changed the surface state of TiO_2 particles to decrease the growth rate and inhibited the anatase-to-rutile transformation. The mechanism on effect of additives (or mineralizer) in hydrothermal reactions were seldom reported. Pyda et al.[18] studied the hydrothermal crystallization of zirconia and zirconia solid solutions. They found that sodium, potassium, and lithium hydroxides greatly influence both the morphology of the crystallites and their sizes and suggested that sticking of the elementary units in an ordered manner was the plausible mechanism of the elongated particle growth in the basic environments. Our experimental conditions were different from theirs. According to our investigations, the effects of additives in hydrothermal reactions could have two aspects: (1) The additive was adsorbed on the surface of crystallites. If the adsorption had selectivity to lead to a decrease in vertical growth rate of adsorbed crystal plane, which should result in the change of morphology of crystallite.[6,7] If the adsorption had not selectivity, the adsorbed additives on the surface may retard the deposition of the product component to decrease the growth rate, resulting in the reduction of the particle size. SnO_2 has same crystal structure with TiO_2 (rutile), therefore it was easily adsorbed on the surface of TiO_2 to retard the growth of TiO_2 particles and enhance new nucleation. The additive $SnCl_4$ could play this role in hydrothermal synthesis of TiO_2. (2) The additive could affect the composition or coordination structure of the growth unit. The OH^- in KOH and the Cl^- in NaCl and NH_4Cl could act as this effect, while the larger Na^+ and NH_4^+ ions could be adsorbed on the negatively charged surface of TiO_2 particles to prevent the growth of TiO_2 particles. Thus the grain size of the product TiO_2 was very small (XRD peaks broadened, Figure 6b,c) in the case of using NaCl and NH_4Cl as additives.

(II) Differential Thermal Analysis (DTA). The DTA curve of a typical nanosize rutile TiO_2 sample ($[TiCl_4]$ of 0.53 mol dm^{-3}, 220 °C, for 2 h) is shown in Figure 8. In the range of room temperature to 1000 °C, except for a small endothermic peak near 100 °C there are no considerable thermal effects. The endothermic peak near 100 °C is attributed to the desorption of the adsorption water on the surface of the sample. This result can be considered as collateral evidence to confirm this sample to be a pure rutile TiO_2.

(III) Raman Spectrum. The Raman spectrum of TiO_2 has been studied extensively, but the investigation

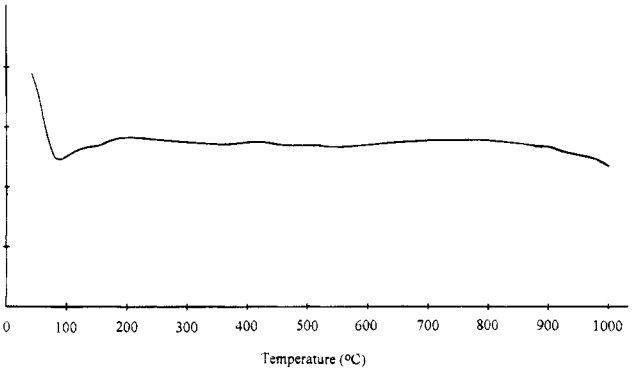

Figure 8. DTA curve of a nanocrystalline rutile TiO_2.

of the Raman spectrum of nanocrystalline TiO_2 is limited. From previous work, in the Raman spectrum of rutile TiO_2, the band near 608 cm^{-1} is identified as the A_{1g} mode, the band near 446 cm^{-1} as the E_g mode, and the weak sharp band at 142 cm^{-1} as the B_{1g} mode. The broad band near 240 cm^{-1} is a second-order phonon as identified by Porto et al.[19] and confirmed by its disappearance in the 4.2 K spectrum.[20] Betsch et al.[20] researched the Raman spectra of stoichiometric and nonstoichiometric rutile crystals with prismatic morphology about 1 mm in cross section and 5–10 mm long in the range 4.2 K to room temperature. They discovered that the peak wavenumber of A_{1g} and B_{1g} modes in rutile crystal remained essentially constant with increasing temperature and changing stoichiometry but the E_g mode decreased by about 15 cm^{-1} between 4.2 and 480 K in stoichiometric rutile and by about 6 cm^{-1} between 80 and 300 K in nonstoichiometric rutile. They considered that the Raman line widths of rutile were an anomalous line broadening caused by a dynamic disorder phenomenon of the TiO_6 octahedra. Melendres et al.[21] investigated the Raman spectroscopy of nanophase TiO_2. Their results seemed to rule out the influence of grain size on the line sharpness of the rutile phonons at 600 and 418 cm^{-1} (here, the peak wavenumber of A_{1g} and E_g modes were different from that in refs 19 and 20 and our work) and considered that intragrain defects dominated the shaping of the spectral features.

We measured the Raman spectra of four TiO_2 samples (rutile: 3, anatase: 1) with different grain sizes. Three rutiles are referred to as R_1, R_2, and R_3, respectively and the anatase is referred to as A_1. R_1, R_2, and A_1 are prepared by the hydrothermal method and have grain sizes of 20 nm by 8 nm (Figure 7a), 100–150 nm by 20 nm (Figure 3e) and 10 nm by 10 nm (Figure 3a), respectively. R_1 is the rutile TiO_2 coated by SnO_2, but no other bands were observed besides the characteristic bands of rutile TiO_2 in the Raman spectrum of R_1. R_3 is a chemical agent in analytical grade and with grain size of ca. 200 nm. The Raman spectra of TiO_2 samples at room temperature are shown in Figure 9. From Figure 9, it can be seen that the Raman spectrum of R_3 sample coincided essentially with that of stoichiometric

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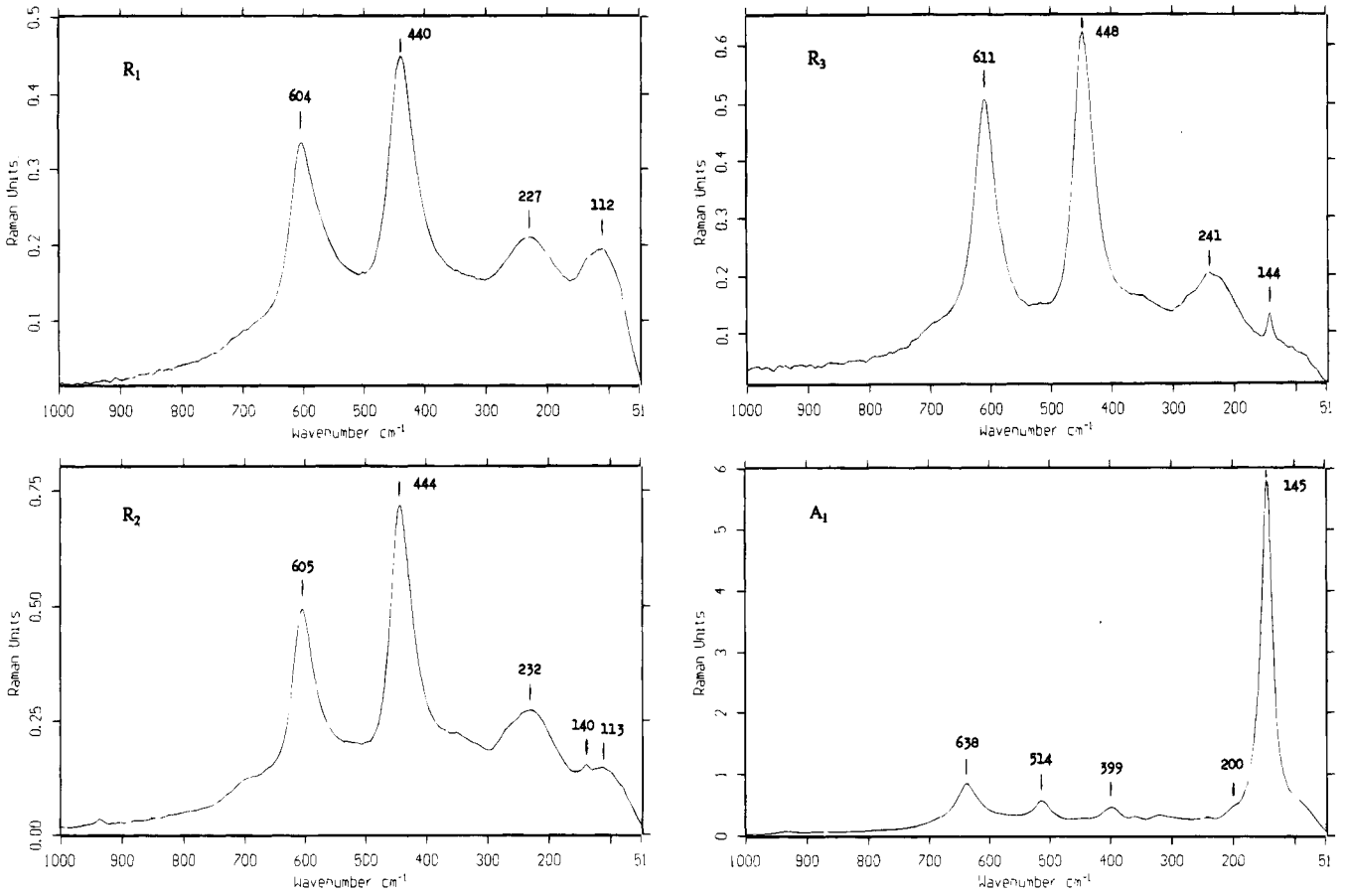

Figure 9. Raman spectra of several TiO_2 samples: R_1, rutile, 20 nm by 8 nm; R_2, rutile, 100–150 nm by 20 nm; R_3, rutile, ca. 200 nm; A_1, anatase, ca. 10 nm.

rutile crystal at 280 °C in ref 20. With decreasing grain size from R_3 to R_1, the wavenumber of all peaks decreased relevantly; in particular, the E_g mode decreased by about 8 cm^{-1}, while a new broad band near 112 cm^{-1} appeared gradually and the band near 144 cm^{-1} could be covered. Besides, with decreasing grain size, the peak height to half-width ratio also lowered. The rutile TiO_2 particles prepared by hydrothermal method have regular morphology and less intragrain defects because of the recrystallization of TiO_2 particles in the reaction medium. Therefore, the above-mentioned results could be considered an effect of grain size for nanocrystalline rutile TiO_2. The Raman spectrum of A_1 sample consisted essentially with the result for anatase powders reported by Pawlewicz,[22] but all the peaks in A_1 became more broad.

Conclusions

Uniform nanosize rutile and anatase particles have been prepared by a hydrothermal method using $TiCl_4$ aqueous solution as starting material. The hydrothermal conditions have significant effects on the formation, phase component, morphology, and particle size of titania products. High acidity and concentration of $TiCl_4$ solution are in favor of the formation of rutile phase. Lowering temperature and increasing concentration could lead to agglomeration among grains. Mineralizers ($SnCl_4$, NaCl, NH_4Cl, etc.) are advantageous to forming rutile phase and decreasing grain size, but NH_4Cl will promote agglomeration among grains. Selecting appropriate hydrothermal conditions, uniform nanosize TiO_2 (rutile or anatase) particles could be obtained. The effects of acidity and concentration in feedstock, temperature, and mineralizers on growth unit and crystal structure of products were tentatively discussed from coordination chemistry. The hydrothermal method is a good method for preparing uniform nanosize rutile and anatase particles.

The differences between the Raman spectra of nanosize and normal rutile TiO_2 were mainly that peaks broadened, the peak wavenumber decreased, and a new band near 112 cm^{-1} appeared in the former. It could be considered as an effect of grain size for nanosize rutile TiO_2.

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