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Sol−Gel Synthesis and Hydrothermal Processing of Anatase and Rutile Titania Nanocrystals

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The alkoxide sol−gel synthesis of nanostructured TiO_2 has been studied systematically to examine the processing parameters that control crystallite size and phase. Nonagglomerated, ultrafine anatase particles have been generated by hydrothermally treating the sol−gel-derived hydrous oxides. The degree of crystallinity and purity of the synthesized materials could affect their structural evolution during heat treatment. It was found that the 10-nm anatase TiO_2 sample derived by hydrothermal processing at 180 °C underwent neither phase change nor significant grain growth up to 800 °C. Nanocrystalline rutile TiO_2 particles have also been attained via hydrothermal treatment in an acidic medium. They possessed an ultrafine rutile grain size and a high surface area, which could not be achieved via phase transformation from thermal treatment of anatase particles.

Introduction

Titania has been extensively used in a variety of applications such as gas sensors, dielectric ceramics, catalysts for thermal or photoinduced processes, photovoltaic solar cells, and pigments.[1−9] The physical and chemical characteristics of TiO_2 can be controlled by its particle size, morphology, and crystalline phase. Nanostructured materials with ultrafine crystallite sizes (<100 nm) and high surface areas have attracted substantial interests due to their unusual optical, electrical, and catalytic properties.[6,10−12] This work is focused on the synthesis and characterization of ultrafine TiO_2 particles with tailored microstructure, crystal phase, and thermal stability.

Titania can be synthesized by several different methods: (i) inert gas condensation,[13] (ii) flame synthesis by $TiCl_4$ oxidation,[14] (iii) oxidation−hydrothermal synthesis of metallic Ti,[15] and (iv) hydrolysis precipitation of titanium alkoxides or chlorides.[16−18] In this study, the processing parameters in wet-chemical synthesis of TiO_2 nanoparticles were investigated. Of particular interest is the sol−gel approach,[19,20] which allows compositional and microstructural tailoring through controlling the precursor chemistry and processing conditions. Sol−gel processing provides for excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. It involves the formation of a metal−oxo−polymer network from molecular precursors such as metal alkoxides or metal salts.[21] For example, the metal alkoxides may be hydrolyzed (eq 1) and polycondensed (eqs 2 and 3) to form a metal oxide gel as follows:

$$\mathrm{M{-}OR + H_2O \rightarrow M{-}OH + ROH} \tag{1}$$

$$\mathrm{M{-}OH + M{-}OR \rightarrow M{-}O{-}M + ROH} \tag{2}$$

$$\mathrm{M{-}OH + M{-}OH \rightarrow M{-}O{-}M + H_2O} \tag{3}$$

where M = Si, Ti, Zr, Al, etc., and R = alkyl group. The relative rates of hydrolysis and polycondensation strongly influence the structure and properties of the resulting metal oxides. Factors affecting the sol−gel process include the reactivity of metal alkoxides, pH of the reaction medium, water:alkoxide ratio, reaction temperature, and nature of solvent and additive. By varying

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these processing parameters, materials with different microstructure and surface chemistry can be obtained.

Typically, sol−gel-derived precipitates are amorphous in nature, requiring further heat treatment to induce crystallization. The calcination process frequently gives rise to particle agglomeration and grain growth and may induce phase transformation. Hydrothermal treatment represents an alternative to calcination for promoting crystallization under milder temperatures. Hydrothermal processing has been widely applied in the synthesis of zeolites,[22] and in the production of advanced ceramic powders.[23] In our study, hydrothermal processing is adopted to produce nanocrystalline oxides with ultrafine particle size. In the hydrothermal treatment, grain size, particle morphology, crystalline phase, and surface chemistry can be controlled via processing variables such as sol composition and pH, reaction temperature and pressure, aging time, and nature of solvent and additive.

In this work, nanocrystalline anatase TiO_2 particles with grain size systematically tailored in the range of 5−100 nm have been derived via sol−gel precipitation of alkoxides, followed by hydrothermal treatment or calcination. Nanoparticles with ultrahigh surface areas and negligible agglomeration were obtained with excellent thermal stability. Rutile TiO_2 particles were also created by hydrothermal aging of the hydrolysis precipitates in an acidic medium.

Experimental Section

Synthesis. TiO_2 nanocrystals were derived via sol−gel hydrolysis precipitation of titanium isopropoxide ($Ti(OC_3H_7)_4$) (Alfa Chemicals, MA), followed by calcination or hydrothermal treatment. A specific amount of titanium isopropoxide was dissolved in anhydrous ethanol, and mixed with a water−ethanol solution with a water:alkoxide molar ratio of 3−170. The isopropoxide solution was added dropwise to the aqueous solution with rigorous stirring at room temperature. White precipitates of hydrous oxides were produced instantly, and the mixture was stirred for at least 2 h. The amorphous precipitates were then subjected to either calcination or hydrothermal treatment. In the former, the precipitates were first separated from the mother liquor by centrifugation and were redispersed in ethanol to minimize particle agglomeration from hydrogen bonding. This washing process was repeated five times. The resulting materials were then dried and calcined at 450 °C in flowing oxygen for removal of volatile and organic species and for formation of crystalline oxides. In the hydrothermal route, the mother liquor containing the amorphous precipitates was transferred to a sealed pressure-safe tube (Ace Glass Inc., Vineland, NJ) or a stainless steel autoclave (Parr Instruments Inc., Moline, IL), and aged at 80−240 °C for 1−4 days. The hydrothermally treated suspension was then centrifuged; the powder recovered was washed with deionized water, and dried at room temperature.

Characterization. The titania samples were characterized by powder X-ray diffraction (XRD) with a Siemens D5000 diffractometer (45 kV, 40 mA) using Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å). XRD patterns were obtained for 20−70° (2θ) by step-scanning with a step size of 0.02°. To determine the average crystallite size, peak broadening analysis was applied to anatase (101) and rutile (110) diffractions using Scherrer's equation.

The morphology and grain size of the titania particles were examined by transmission electron microscopy (TEM) on a JEOL 200CX or 2010 microscope operating at 200 kV. Drops of a powder suspension were added to carbon-coated copper grids in TEM sample preparation.

Nitrogen adsorption−desorption isotherms were obtained with a Micromeritics ASAP 2000 or 2010 system for analysis of BET (Brunauer−Emmett−Teller) surface area and BJH (Barrett−Joyner−Halenda) pore size distribution. The samples were degassed at 110 °C under vacuum prior to adsorption studies at 77 K.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 System. TGA experiments were conducted in flowing oxygen at a ramp rate of 5 °C/min.

Results and Discussion

Alkoxide Sol−Gel Processing of Anatase Nanocrystals. The as-derived precipitates from sol−gel processing of titanium isopropoxide were amorphous in nature. A significant weight loss was noted in the TGA curves for the titania gels below 400 °C, which could be attributed to the removal of water, alcohol, and unreacted alkoxy species. The amorphous gel began to be crystallized upon heat treatment at 200 °C, as indicated by the emergence of a very broad, low-intensity XRD peak associated with anatase (101) diffraction. Calcination at this low temperature could not completely crystallize the material, giving a mixture of amorphous and nanocrystalline titania. To convert the sol−gel-derived sample fully to crystalline TiO_2, a calcination treatment of 450 °C was applied; this temperature was also necessary to eliminate water and organic species from the hydrous gel.

In sol−gel processing of early transition metal alkoxides, hydrolysis and condensation reactions occur very rapidly, so that uniform and ultrafine products are difficult to obtain. With the use of bulky, branched alkoxy groups (such as isopropoxides), the hydrolysis and condensation rates can be reduced to favor the formation of small colloidal clusters, yielding a more uniform particle size.[20] To achieve a very narrow particle size distribution in the desired range, we have examined the water:alkoxide ratio as a synthesis parameter to control the absolute and relative rates of nucleation and growth of clusters. The effect of water:alkoxide ratio on the sol−gel synthesis of titania is illustrated in Figure 1. Upon calcination at 450 °C, distinct anatase peaks were noted in the XRD patterns of the various samples. Anatase is the metastable phase of titania, typically associated with high surface areas; it undergoes a transformation to the rutile phase upon thermal treatment typically at 400−1200 °C.[24] It was noted in Figure 1a−c that increasing the water:alkoxide molar ratio led to reduced crystallite size in the calcined material. Anatase nanocrystals of 20 nm could be obtained by calcining titania gel synthesized with a water:alkoxide ratio of 165. The water:alkoxide ratio determines the sol−gel chemistry and the structural characteristics of the hydrolyzed gel. High water:alkoxide ratios in the reaction medium ensure a more complete hydrolysis of alkoxides, favoring nucleation versus particle growth.

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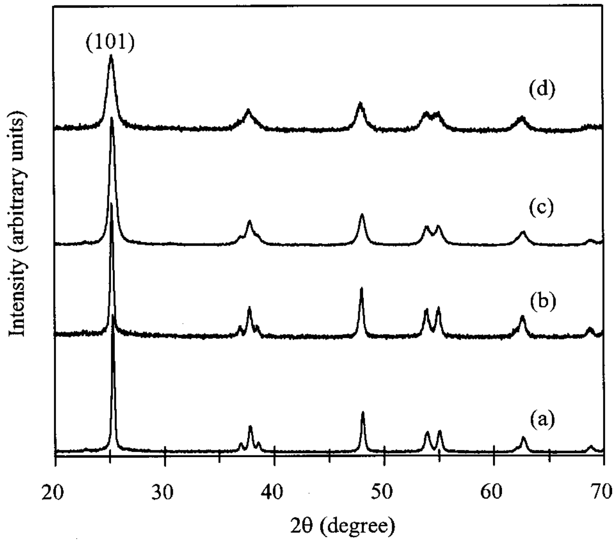

Figure 1. XRD patterns of nanocrystalline anatase titania samples prepared with a water:alkoxide ratio of (a) 3.3 (without acid) (82 nm), (b) 10 (without acid) (57 nm), (c) 165 (without acid) (20 nm), and (d) 165 (with HCl) (14 nm). The samples were characterized after calcination at 450 °C for 2 h. All peaks noted corresponded to the anatase phase. The crystallite sizes indicated in parentheses were calculated from peak broadening of the anatase (101) diffraction.

Even at a very high water:alkoxide ratio, precipitates appeared shortly after the alkoxide solution has been introduced to the aqueous solution. Additives such as electrolytes,[25] polymers,[26]and cellulose,[27] or complexing ligands[28] have been employed to modify the reactivity of the metal alkoxide precursors to inhibit the condensation reactions so that monodispersed particles of well-controlled sizes could be obtained. An alternative approach to controlling the sol−gel reaction rates involves the use of acid or base catalysts.[29,30] In some of our experiments, hydrochloric acid was added to the water−ethanol solution, so that the HCl:alkoxide molar ratio was 0.25 in the reaction medium. For the system with a water:alkoxide ratio of 165, the addition of HCl resulted in the reduction of crystallite size from 20 to 14 nm for materials calcined at 450 °C (Figure 1c,d). Besides a finer grain size, a narrower pore size distribution with a smaller average pore diameter was also attained for the sample synthesized with HCl. The amount of acid added, or pH of the system, affects the state of the hydrolyzed products in the form of sol, gel, and precipitates. The presence of acid catalysts promotes the hydrolysis reaction versus the condensation reaction. The gelation process was delayed in the synthesis with HCl addition, so that a turbid gel was formed instead of white precipitates. HCl serves not only as an acid catalyst, but also as an electrolyte to prevent particle growth or agglomeration through electrostatic repulsion. Since the isoelectric point of TiO_2 lies at a pH of 5−7,[31] surface charges on the particles in an acidic medium help to keep discrete particles in the dispersed state.

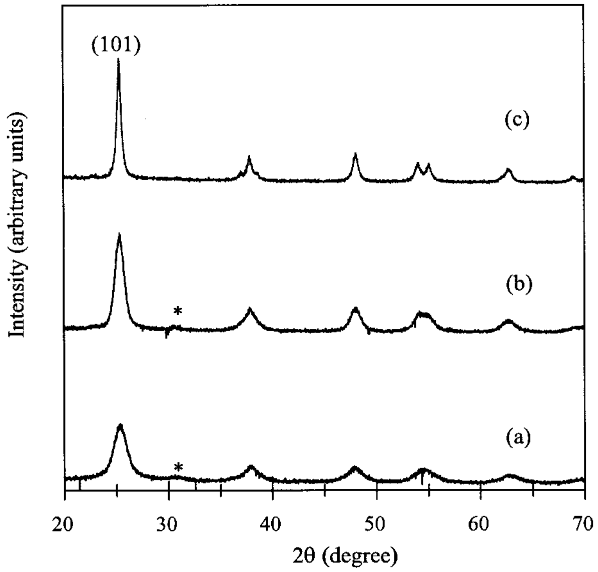

Figure 2. XRD patterns of nanocrystalline titania samples prepared by hydrolysis precipitation with a water:alkoxide ratio of 92, followed by hydrothermal aging for 1 day at (a) 80 °C (6 nm), (b) 180 °C (10 nm), and (c) 240 °C (28 nm). All peaks noted corresponded to the anatase phase, except for those denoted with an asterisk (*), which corresponded to the brookite phase. The crystallite sizes indicated in parentheses were calculated from peak broadening of the anatase (101) diffraction.

Figure 2 shows the XRD patterns of titania derived from alkoxide hydrolysis precipitation, followed by hydrothermal treatment. The samples were synthesized with a water:alkoxide ratio of 92, and subjected to hydrothermal treatment at 80−240 °C for 1 day. The titania gels were successfully crystallized to the anatase phase at relatively low temperatures through hydrothermal aging. Nanocrystalline anatase materials with grain sizes of 6, 10, and 28 nm were obtained from hydrothermal treatment at 80, 180, and 240 °C, respectively. A minor brookite peak at 31° (2θ) was noted for samples prepared at 80 and 180 °C (Figure 2a,b). Compared to the calcination approach, titania with much finer crystallite sizes can be produced via hydrothermal treatment, especially at low aging temperatures. These nanocrystalline anatase TiO_2 powders are associated with ultrahigh surface areas attractive for catalytic and photocatalytic applications.[32,33] The well-defined nanometer-sized particles could also be compacted to give greenbodies with an ultrafine microstructure that would facilitate sintering of TiO_2 for advanced ceramics applications.

Figure 3 illustrates the effects of water:alkoxide ratio, and aging temperature and time on the anatase XRD crystallite size of hydrothermally prepared TiO_2. Water:alkoxide ratios of ≤10 and ≤3.3 produced amorphous titania materials after aging at 80 °C for 1 day and 4 days, respectively. This showed that the water content in the mother liquor was crucial to creating crystalline

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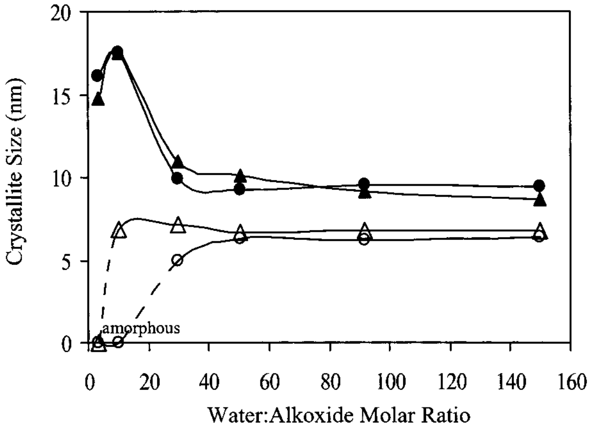

Figure 3. Crystallite sizes of titania samples prepared by hydrolysis precipitation with the water:alkoxide ratios indicated, followed by hydrothermal aging at (○) 80 °C for 1 day, (△) 80 °C for 4 days, (●) 180 °C for 1 day, and (▲) 180 °C for 4 days. The crystallite sizes were calculated from the broadening of the anatase (101) XRD peak.

structures at the low hydrothermal treatment temperature. Yin et al.[34] also indicated that the amount of water determined the degree of crystallization. We found that if the mother liquor consisted of a low water content (water:alkoxide ratio $\leq$ 10), crystallization would require hydrothermal aging for periods longer than 1 day and/or at a temperature higher than 80 °C. Aging period did not have significant effects on the anatase crystallite size for systems with a high water content (water:alkoxide ratio $>$ 30) or for systems hydrothermally treated at a temperature of 180 °C. Anatase crystallite sizes of 6–7 nm and 9–10 nm were obtained for systems hydrothermally synthesized with a water:alkoxide ratio of $\geq$50 at 80 and 180 °C, respectively. A high water content in the mother liquor ensured proper hydrothermal treatment of the amorphous gel to promote nucleation of nanocrystals. Such conditions allowed an ultrafine crystallite size to be achieved, especially at a low hydrothermal aging temperature whereby particle growth was minimal. For the systems with a low water:alkoxide ratio of $<$30, the nucleation process was very slow. If these systems were subjected to hydrothermal treatment at 180 °C, the few nuclei generated would undergo relatively rapid grain growth, yielding coarser crystals of 15–18 nm.

Transmission electron micrographs of nanocrystalline anatase TiO_2 samples are shown in Figure 4. Samples with 6, 10, and 28 nm grain sizes were synthesized via hydrothermal treatment at 80, 180, and 240 °C, respectively (Figure 4a,b,d). The sample with 20 nm grain size was obtained via calcination at 450 °C (Figure 4c). The titania grains in Figure 4a–c were quite uniform in morphology, and their TEM grain sizes were consistent with those calculated from XRD peak broadening. According to the surface areas of these samples, the calculated equivalent particle sizes would be 6.1 nm (253 m^2/g), 10.2 nm (151 m^2/g), and 22.0 nm (70 m^2/g), respectively, assuming a spherical particle morphology. These calculated values matched well with the grain sizes observed by TEM and XRD, indicating that particle agglomeration was negligible for these three samples. Compared to the samples obtained from hydrothermal treatment at 80 and 180 °C, the sample synthesized from hydrothermal aging at 240 °C (Figure 4d) was less uniform in particle morphology and larger in grain size. At the high aging temperature of the latter, the nucleation and growth processes might not have proceeded slowly and uniformly enough, so that a mixture of uniaxed and elongated grains were produced.

Structural Evolution of Alkoxide-Derived Anatase Nanocrystals. The four as-synthesized nanocrystalline titania samples illustrated in Figure 4 were subjected to a series of heat treatments in flowing oxygen for structural evolution studies. Their phase composition and average anatase/rutile grain sizes were analyzed by XRD after heat treatments at 300–800 °C (Figure 5). The phase composition of the samples were obtained from the following equation:[35]

$$x_A = [1 + 1.26\,(I_R/I_A)]^{-1} \tag{4}$$

where x_A is the weight fraction of anatase in the mixture. I_A and I_R were obtained from the peak areas of the anatase (101) and rutile (110) diffractions, respectively.

The samples obtained from hydrothermal treatment at 80 °C (Figure 5a) and from calcination at 450 °C (Figure 5c) underwent partial anatase → rutile phase transformation at 600 °C, which was accompanied by a significant grain growth. The sample that was hydrothermally synthesized at 240 °C underwent partial phase transformation at a higher temperature of 800 °C (Figure 5d). It experienced minor grain growth from 28 to 49 nm at 700 °C; its anatase grains remained unchanged in size at 800 °C despite the formation of a substantial number of 68 nm rutile grains. Interestingly, the sample produced from hydrothermal aging at 180 °C demonstrated a remarkable thermal stability (Figure 5b). It retained a pure anatase phase even after a 2-h heat treatment at 800 °C. TEM studies (not shown) indicate that this 800 °C calcined titania sample still retained a spherical particle morphology, although the particles became more agglomerated. Usually at such a high temperature, phase transformation to rutile would have occurred with significant grain growth to $>$100 nm. This sample, however, underwent only minor grain growth from 10 to 17 nm and 35 nm at 700 and 800 °C, respectively.

It is presently not clear why the materials obtained from hydrothermal aging at 180 °C reproducibly exhibited such unusual stability against phase transformation and grain growth, but several factors might have contributed to it. Parameters such as particle size,[36–38] impurity,[39,40] and reaction atmosphere[41,42] have been known to affect the phase transformation phenomenon. The crystallinity and surface chemistry of the ultrafine

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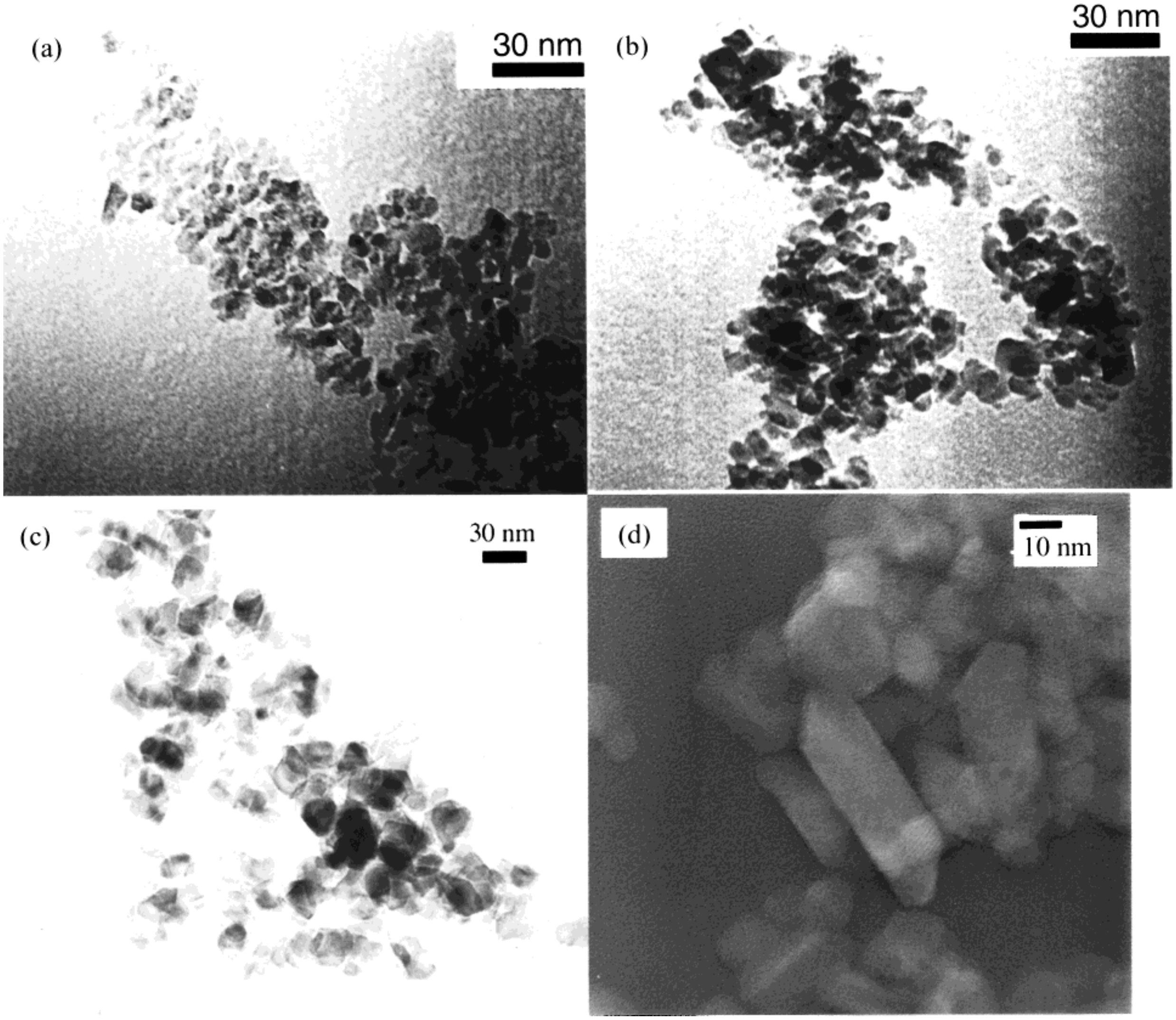

Figure 4. TEM micrographs of titania samples prepared by hydrolysis precipitation with a water:alkoxide ratio of (a) 92, followed by hydrothermal aging at 80 °C for 1 day (6 nm), (b) 92, followed by hydrothermal aging at 180 °C for 1 day (10 nm), (c) 165, followed by calcination at 450 °C for 2 h (20 nm), and (d) 92, followed by hydrothermal aging at 240 °C for 1 day (28 nm). The crystallite sizes indicated in parentheses were calculated from the broadening of the anatase (101) XRD peak.

grains obtained from the wet-chemical synthesis might have a strong influence on the subsequent structural evolution of these materials. During the hydrothermal aging process, the amorphous hydrous gels gradually developed into crystalline titania grains with further hydrolysis/polycondensation reactions and structural rearrangements. This was a very different process from crystallization via calcination, which involved rapid purification and thermal transformation of hydrous gels that had not yet fully reacted. The mild hydrothermal synthesis would be capable of yielding a more well-defined structure with less surface impurities/defects if appropriate aging temperature and period were employed to ensure complete sol−gel reaction and crystallization in an appropriate medium. This might explain the excellent thermal stability associated with 10-nm anatase grains synthesized via hydrothermal aging at 180 °C. A lower aging temperature could produce a finer as-synthesized average grain size, but might be inadequate at inducing complete reactions of the residual alkoxy and hydroxy groups. The impurities in the samples synthesized via hydrothermal treatment at 80 °C and via calcination at 450 °C might have promoted the nucleation of rutile,[43] so that phase transformation was initiated at a lower heat treatment temperature of 600 °C for these materials. Elemental analysis and TGA characterization results supported the fact that these two samples have substantially greater amounts of organic residues than the samples synthesized from hydrothermal treatment at 180 and at 240 °C.

Besides purity and crystallinity,[24] particle arrangement and packing would also influence the thermal stability and phase transformation of materials.[44−47] Banfield and co-workers[48,49] reported that the anatase → rutile transformation could be initiated from the rutile-like elements created at the oriented contacts

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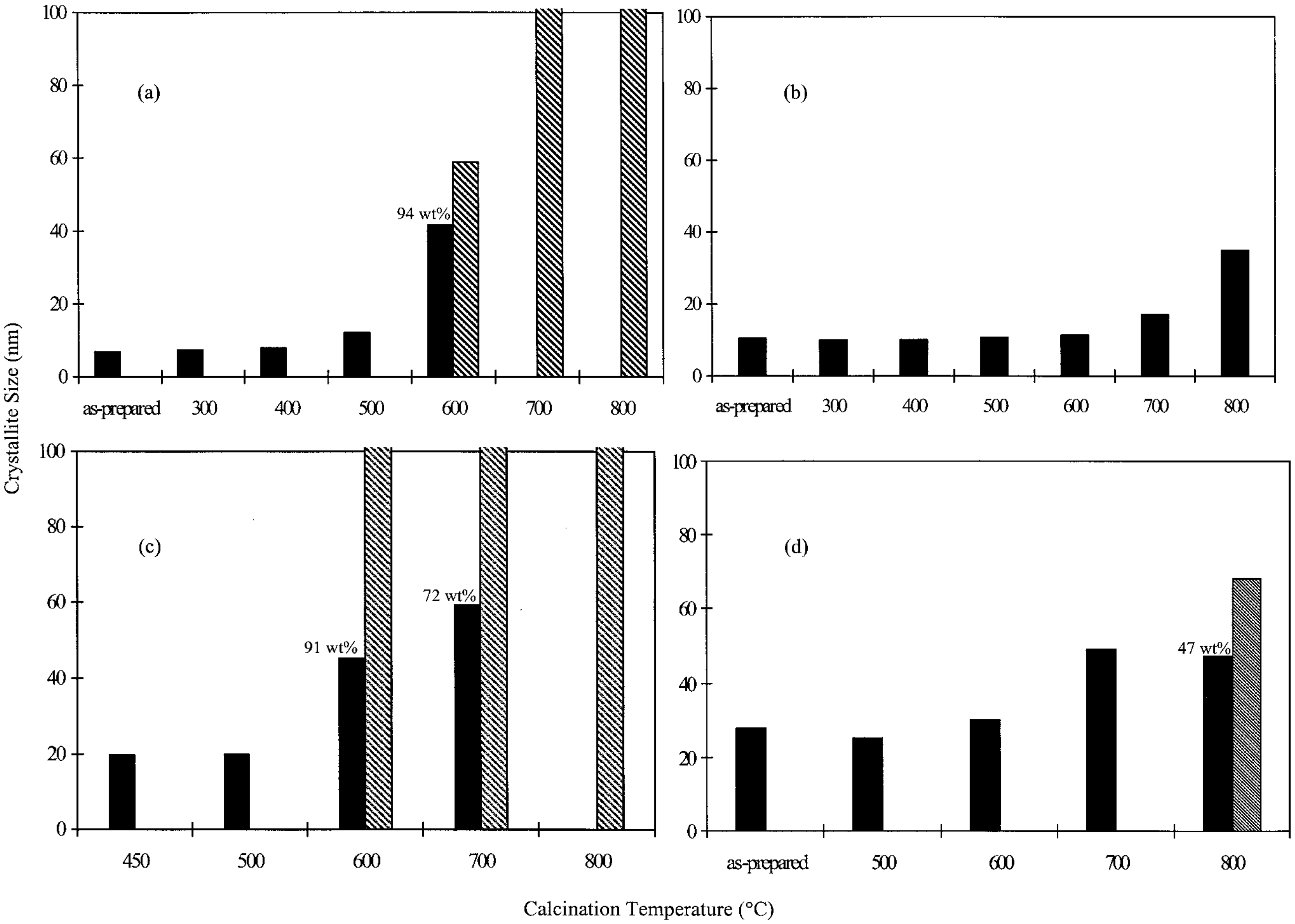

Figure 5. XRD crystallite sizes corresponding to the anatase (101) peak (solid bars) and the rutile (110) peak (shaded bars) for titania samples described in Figure 4 after heat treatments at the temperatures indicated. The wt % of anatase in the mixed-phase systems are denoted.

between anatase particles. The lack of proper particle attachment or particle coordination would decrease the possibility of rutile nucleation. Generally, calcination causes particles to form hard agglomerates while the hydrothermal treatment creates a softer agglomeration of particles. The hard agglomerates formed in the calcined sample might have an increased degree of packing, which facilitated the phase transformation. The looser packing of particles generated in the hydrothermal treatment might be one of the factors responsible for their relatively high thermal stability.

Figure 5 illustrates that the phase transformation to rutile was initiated after the anatase grains have grown to a certain size. The samples prepared by hydrothermal treatment at 80 °C and by calcination at 450 °C consisted of anatase grains of 42−46 nm when <10 wt % of the titania material was transformed to the rutile phase at 600 °C. The sample hydrothermally treated at 240 °C consisted of 47 nm anatase grains when 53 wt % of transformation to rutile took place at 800 °C. For the sample hydrothermally treated at 180 °C, phase transformation was initiated at 840 °C, when 96 wt % of the titania consisted of 51 nm anatase grains. Although these anatase grain sizes might be larger than that needed to initiate the anatase → rutile transformation, it appeared that the critical nuclei size for rutile formation could be estimated to be in the range of 40−50 nm from this study. Once the critical nuclei size has been attained from anatase grain growth during heat treatment, rapid rutile formation and grain growth were observed, so that the resulting rutile grains were larger than the coexisting anatase grains.

The critical nuclei size for phase transformation is governed by the volume free energy, surface energy, and strain energy, which would vary with different materials synthesis and processing. In previous studies,[50−52] the rutile crystallites began to form after the anatase grains grew to certain sizes (~13−50 nm), and the resulting rutile grains were always larger than the anatase grains. The critical nuclei size is achieved through particle densification and/or particle growth.[53] These two mechanisms resulted in different critical nuclei sizes and microstructures. The delayed phase transformation shown by samples hydrothermally treated at 180 and 240 °C could be attributed to their slow grain growth in reaching the critical nuclei size. Their grain growth might have been suppressed due to their high crystallinity and purity attained in the high-temperature hydrothermal aging. The sample hydrothermally treated at 240 °C underwent phase transformation at

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a lower temperature than the sample hydrothermally treated at 180 °C. The former was shown by TEM (Figure 4d) to possess larger grains of less uniform morphologies compared to the latter (Figure 4b). The presence of nonequiaxed grains might have contributed to grain growth at a lower temperature to the critical nuclei size for the former. The larger grain size and elongated morphology of titania particles attained from hydrothermal treatment at 240 °C might have also facilitated the phase transformation process.

This study illustrates the flexibility of hydrothermal processing at attaining titania samples of controlled grain size and stability. The nanocrystalline anatase grain size (35 nm) and high surface area (43.1 m^2/g) retained at 800 °C by the system derived via hydrothermal treatment at 180 °C present unique opportunities for high-temperature catalytic applications. The 47−53% mixture of ultrafine anatase−rutile grains obtained from 800 °C calcination of the sample derived via hydrothermal aging at 240 °C might also be of interest to special applications that would benefit from designed mixed titania phases.

Alkoxide Sol−Gel Processing of Rutile Nanocrystals. As illustrated by this study and other reports, rutile titania particles can be obtained via thermal treatments. However, the elevated temperatures that were typically applied to produce rutile crystals frequently led to significant grain growth and loss of surface area. It is desired in some applications to obtain ultrafine rutile crystals with a high surface area and a controlled morphology. We are interested in investigating hydrothermal processing as a novel means to directly generate rutile nanocrystals with unique microstructures. Our approach utilized sol−gel hydrolysis precipitation of titanium isopropoxide with a water: alkoxide ratio of 165. After recovery of the amorphous gel via centrifugation, the sample was dried at room temperature before it was introduced to 30 mL of an aqueous HNO_3 solution for hydrothermal treatment at 180 °C. Figure 6 shows the XRD patterns of these acid-treated materials and a sample produced in a HNO_3-free aqueous solution. The latter was composed of 10 nm anatase grains (Figure 6a). A mixture of anatase grains (of 10−11 nm) and rutile grains were produced from hydrothermal aging in 1 and 1.5 N of HNO_3 for 1 day (Figure 6b,c). The weaker acidic solution produced finer rutile grains (35 nm vs 77 nm) and a smaller weight fraction of rutile (30% vs 64%) in the resulting titania sample. A longer aging time of 7 days in 1 N HNO_3 created a pure rutile phase with an average grain size of 49 nm (Figure 6d).

With a short hydrothermal aging period (i.e., 1 day) in the HNO_3 medium, a mixture of anatase and rutile was obtained. Both of these titania phases belong to the tetragonal crystal system, consisting of $[TiO_6]$ octahedra as a basic structural unit. Their crystalline structures differ in the assembly of the octahedral chains. The complexation between the anatase grains and HNO_3 might have contributed to the reorientation of the less dense structure of anatase to produce more rigid, linear-like chains that favored the nucleation of rutile crystals.

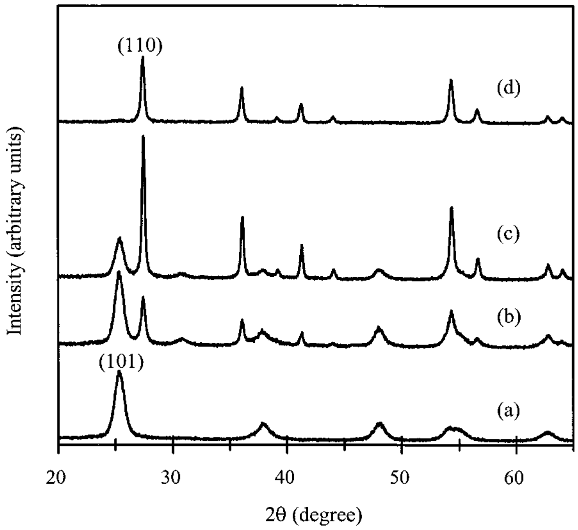

Figure 6. XRD patterns of nanocrystalline titania samples prepared by hydrolysis precipitation with a water:alkoxide ratio of 165. After recovery and drying, these samples were hydrothermally aged at 180 °C in (a) an acid-free solution for 1 day, (b) 1 N HNO_3 solution for 1 day, (c) 1.5 N HNO_3 solution for 1 day, and (d) 1 N HNO_3 solution for 7 days. All diffraction peaks noted in part a corresponded to the anatase phase; all diffraction peaks noted in part d corresponded to the rutile phase.

It was noted in parts b and d of Figure 6 that the formation and growth of rutile crystals proceeded at the expense of anatase crystals with increasing hydrothermal aging period, possibly via a dissolution−precipitation mechanism.[23,54] As with HCl,[17,55] HNO_3 of increased acid concentration accelerated this transformation process during hydrothermal aging (part b vs part c of Figure 6). However, not every inorganic acid would facilitate the formation of rutile with increasing acid concentration. H_2SO_4 and HF have been observed to transform anatase to rutile at moderate levels of acidity, with phase reversion to anatase at high acidity.[17,55] This study shows that hydrothermal aging in an acidic medium presents a unique and flexible means of obtaining ultrafine rutile grains or mixed-phase titania materials under a milder temperature than that required by the conventional calcination approach.

Conclusions

Nanocrystalline TiO_2 materials have been successfully synthesized via sol−gel hydrolysis precipitation, followed by calcination or hydrothermal treatment. High water:alkoxide ratios were found to favor the formation of ultrafine titania particles. Anatase grains as small as 6 nm were obtained via hydrothermal treatment at 80 °C, without the grain growth or particle agglomeration commonly induced by the calcination process. Ten-nanometer-sized anatase nanocrystals derived via hydrothermal aging at 180 °C were shown to possess unusual thermal stability against grain growth and the anatase → rutile phase transformation. Rutile grains have been generated with ultrafine grain size via

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hydrothermal treatment in an acidic medium. This study illustrates the successful tailoring of TiO_2 grain size, crystalline phase(s), and thermal stability via wet-chemical synthesis. Hydrothermal treatment was shown to be an effective means to crystallize titania at mild temperatures. The processing chemistry highly depended on the composition and pH of the mother liquor, as well as the aging temperature and duration. The nanocrystalline titania of ultrahigh surface area and thermal stability presents unique characteristics useful toward chemical and advanced materials applications.

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