NANO LETTERS

2001
Vol. 1, No. 2
81−85

Preparing Single-Phase Nanocrystalline Anatase from Amorphous Titania with Particle Sizes Tailored by Temperature

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Received November 3, 2000

ABSTRACT

Series of samples of nanoparticles with discrete sizes are needed for studies of the particle size dependence of materials properties. In this study, phase relations during heat treatment of initially amorphous titania were determined. Heating amorphous titania in air at specific temperatures for specific lengths of time resulted in single-phase nanocrystalline anatase powders with average particle sizes between 7 and 50 nm. An important pathway for anatase growth involved nanocrystal reorientation within particle aggregates. Large quantities of single phase solids can be produced via this method.

In addition to its traditional applications in white pigments, new applications are being developed for nanocrystalline titania (TiO_2). For example, dye-sensitized nanocrystalline titania can be used as an energy converter in solar cells,[1−3] doped or undoped nanocrystalline titania can be used to photochemically degrade toxic chemicals,[4] and nanocrystalline anatase is a very promising electrode material in lithium batteries.[5] The particle size of nanocrystalline titania plays an import role in the physical and chemical behavior of the material because the specific surface area, the chemical stability, and the chemical reactivity of the material are all highly correlated with the particle size. It has been shown that the adsorption of organics onto surfaces of nanocrystalline anatase is size-dependent[6] and that the particle size is a crucial factor in photocatalytic decomposition of choroform by nanocrystalline anatase.[4] It is evident that preparing single-phase nanocrystalline titania with a wide range of particle sizes is essential to the study of the size-dependent properties of nanocrystalline titania.

Normally, the anatase phase of titania is the main product in hydrolytic sol−gel synthesis of nanocrystalline titania. However, brookite (a polytype of anatase) is also typically present in synthesis products. Brookite can be detected by the appearance of its (121) peak in powder X-ray diffraction (XRD) patterns at $2\theta = 30.8°$ (Cu Kα radiation; e.g., in ref 4). In some previous studies, the existence of significant brookite phase was overlooked (e.g., in refs 7−8). Even if the intensity of the brookite (121) peak is very low compared to the anatase (101) peak, the amount of brookite may be considerable. The amount of brookite can be quantified by XRD.[9] For instance, although the area of the brookite (121) peak is only 2% of that of the anatase (101) peak, the weight percent of brookite may be ∼6%.[9]

Improved synthesis routes for producing single-phase nanocrystalline titania are required. Single-phase titania can be synthesized by applying specific hydrolysis catalysts,[10,11] using a non-hydrolytic sol−gel method,[12] and by hydrothermal processing of hydrolytic sol−gel products.[13−15] Conversion of a primary reaction product (usually in amorphous state) into crystalline titania is common to these methods. However, these authors did not determine quantitatively whether an amorphous titania fully crystallizes to anatase under a certain condition. This issue requires resolution, because single-phase anatase samples are needed for some investigations (i.e., samples free of amorphous titania, brookite, and rutile). Anatase nanoparticles with special morphologies were prepared by Chemseddine and Moritz by means of wet chemistry.[16] These nanocrystals were suspended in a solution with extremely dilute titanium concentration (1−12 μmol Ti per liter solution). However, an alternative method is needed to produce large enough quantities of titania for most experimental studies.

Fine nanocrystalline anatase samples (∼5 nm) can be prepared using the method of Scolan and Sanchez.[11] In addition to producing very fine crystalline anatase powders, more coarse crystalline pure phases are also required for a variety of experiments designed to measure size-dependent properties of titania. A simple approach is to coarsen anatase particles at elevated temperatures.[17,18] However, anatase is

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10.1021/nl0055198 CCC: $20.00

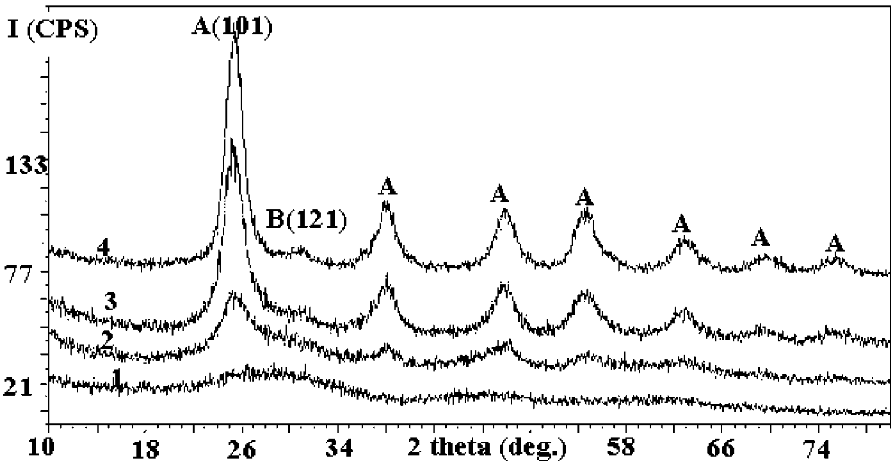

Figure 1. XRD patterns of raw materials (Cu Kα radiation, 0.4°/min): (1) No. 1, synthesized at 0 °C; (2) No. 2, large amount batch, synthesized at 0 °C; (3) No. 3, synthesized at 50 °C; and (4) No. 4, synthesized at 70 °C. A = anatase, B = brookite.

Table 1. Phase Composition and Average Particle Size of Samples Heated at Various Temperatures (time = 3 h)

T (°C)	No. 1	No. 2	No. 3	No. 4
375	100% A[a] (10 nm)	100% A (8 nm)	81% A(8 nm) + 19% B[b](6 nm)	81% A (8 nm) + 19% B (7 nm)
400	100% A (12 nm)	100% A (8 nm)	84% A(9 nm) + 16%B(8 nm)	81% A (9 nm) + 19% B (7 nm)
450	100% A (17 nm)	100% A (12 nm)	87% A (12 nm) + 13% B (9 nm)	83% A (11 nm) + 17% B (8 nm)
500	100% A (27 nm)	100% A (31 nm)	93% A (18 nm) + 7% B (11 nm)	89% A (17 nm) + 11% B (9 nm)
550	100% A (50 nm)	87% A (56 nm) + 14%R[c] (>100 nm)[d]	98% A (35 nm) + 2% R (>100 nm)	97% A (40 nm) + 3% R (>100 nm)

[a] A= anatase, [b] B = brookite, [c] R = rutile, [d] time = 2 h.

metastable with respect to rutile at larger particle sizes (approximately >16 nm[9,19]), and it transforms to rutile during the coarsening (see refs 17−18). To obtain pure anatase samples with particle sizes >16 nm, the formation of anatase from its precursor must be faster than formation of rutile at the temperature of the experiment. For this reason, solid amorphous titania may serve as an appropriate precursor for preparing single-phase anatase. In this work, we controlled the temperature of the hydrolysis of titanium ethoxide to synthesize nanocrystalline and amorphous titania. By heating the amorphous titania in air (rather than under hydrothermal conditions used in previous studies) at temperatures from 375 to 550 °C for 3 h, single-phase anatase powders with discrete average particle sizes ranging from 7 to 50 nm were prepared. It is possible to rapidly produce many grams of material by this method.

It has been reported that single-phase anatase can be synthesized by hydrolysis of titanium ethoxide [$Ti(OCH_3CH_2)_4$] in water at 70 °C, in the presence of ethanol, and using acetic acid as the catalyst.[10] In accordance with this method, we mixed 0.1 mol (21 mL) titanium ethoxide (ACROS Organics, New Jersey) with 25 mL ethanol (AAPER Alcohol and Chemical Co., Kentucky). The mixture was stirred and refluxed at 70 °C for 2 h. Then, a 1.6 mol portion of water (29 mL) with 4 drops of acetic acid (EM Science, New Jersey) was dripped into the mixture. The solution was stirred and refluxed for 20 h. The reaction product was removed from the reactor and centrifuged 3 times at 8 rpm for 15 min after washing with water. The pH value of the final filtrate was about 5. The white titania product was dried at 70 °C for 40 h. XRD examination of the final product showed that the brookite phase was present in addition to anatase (Figure 1). A careful inspection of Figures 8 and 10 of ref 10 reveals that their synthesis product was a mixture of brookite and anatase, rather than pure anatase, as reported previously.[10]

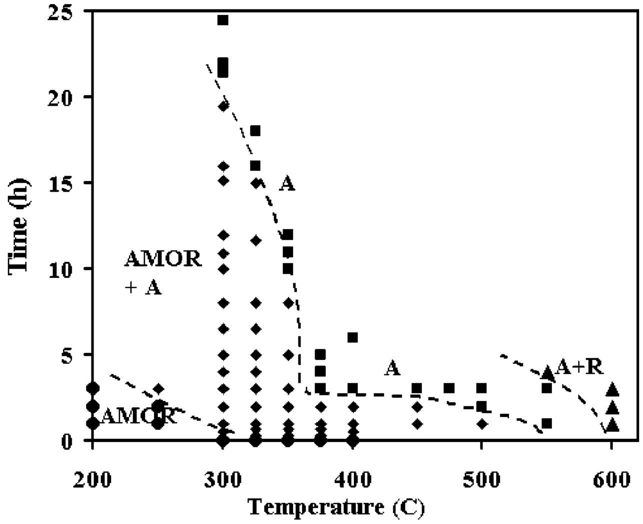

Figure 2. Temperature−time-phase relation diagram for samples of raw material No. 1. A = anatase, AMOR = amorphous titania, R = rutile.

In a second synthesis experiment using the above method, we decreased the reaction temperature to 50 °C**.** The final product consisted of 60% amorphous titania + 40% (anatase + minor brookite) (Figure 1).

Synthesis was also carried out at 0 °C (cooled using a mixture of water and ice) without refluxing. Before being

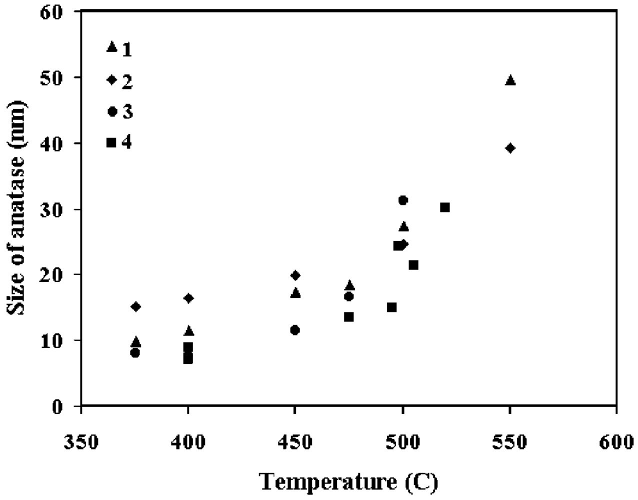

Figure 3. Variation of the average particle size of single-phase anatase prepared by heating various starting materials at different temperatures for 3 h. Starting materials: (1) No. 1 amorphous titania; (2) No. 1 amorphous titania, with 3 additional centrifuge and washing steps; (3) No. 2, 89% amorphous titania + 11% anatase; (4) No. 2, 89% amorphous titania + 11% anatase, each sample weighed ~2 g.

centrifuged, the product was aged for 30 min. The final product consisted of amorphous titania (Figure 1). Interestingly, when quadruplicate quantities of all chemicals were used, the final product synthesized at 0 °C was a mixture of 89% amorphous titania + 11% anatase (Figure 1). The reason for this is unclear, but it may relate to incomplete stirring of the larger volume of solution during the fast hydrolysis process. The final products synthesized at 0 °C (small batch), 0 °C (large batch), 50 °C, and at 70 °C, as described above, were denoted as raw materials No. 1−4, respectively.

Forty mg samples of raw materials No. 1−4 were heated at 375, 400, 450, 500 and 550 °C for 3 h in order to characterize their phase transformation behavior. The phase composition and the average particle size (Table 1) of each sample were analyzed by XRD using the analytical method described in the Supporting Information (for mixtures of amorphous titania and anatase) as well as the analytical method described in ref 9 (for mixtures of anatase, brookite, and rutile). Table 1 illustrates that only raw materials No.1 and No.2 are suitable for preparing single-phase anatase. A complete determination of phases present in samples (of No.1 raw material) heated at different temperatures and time is shown in Figure 2. Figure 2 shows that in order to produce single-phase anatase by heating amorphous titania at $T <$ 375 °C, the reaction time must be $>$10 h. The average particle size of single-phase anatase formed by complete transformation of amorphous titania is $\leq$ 13 nm. However, at $T \geq$ 375 °C, single-phase anatase can be generated from amorphous titania after heating for only 3 h or less. The average particle size of the single-phase anatase can be as high as 50 nm at temperatures up to 550 °C (Table 1). Higher

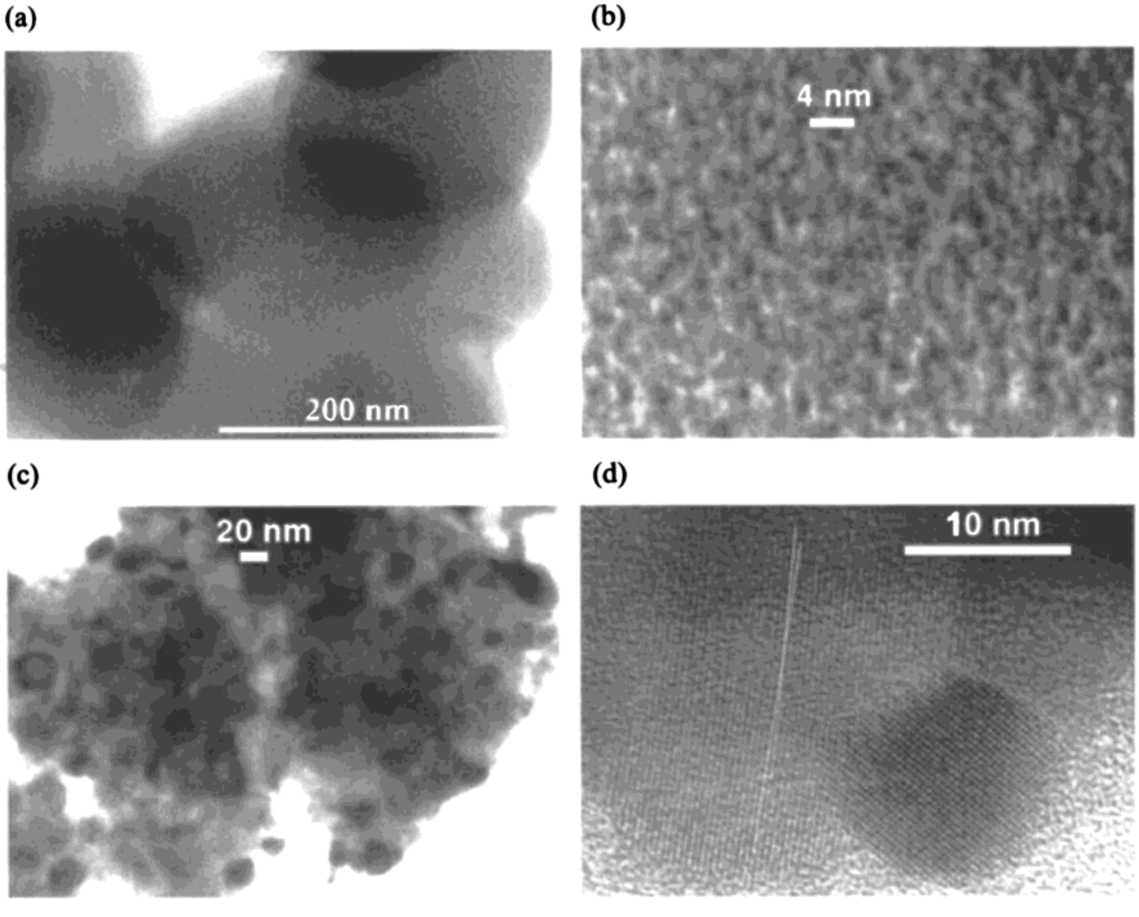

Figure 4. TEM images of No. 1 amorphous titania (a, b) and a sample of No. 1 heated at 500 °C for 3 h (c, d).

temperatures and/or too long a reaction time may result in the formation of rutile (Figure 2).

Many experiments yielded pure anatase materials (Figure 2). Because our intention was to prepare single-phase nanocrystalline anatase with a fairly wide range of particle sizes, appropriate temperatures are 375−550 °C (Table 1). Thus, we examined the products when raw materials No.1 and No. 2 were heated at 375−550 °C for 3 h (Figure 3). In all experiments, samples of ∼40 mg each were used, except for data points # 4 (squares), where samples of ∼2 g each were used. For the # 2 data points (diamonds), raw materials from No.1 were centrifuged three additional times after water washing and before drying in order to further purify the raw material by removal of remaining volatiles (see Supporting Information). All products associated with data points in Figure 3 were confirmed to be single-phase nanocrystalline anatase by the analyses of the corresponding XRD data. Figure 3 shows that the average particle size of anatase depends on the history of the starting material. This is reasonable because the material history can affect the transformation kinetics and thus the average particle size. Nevertheless, the average particle size of anatase increases exponentially with the increase in temperature.

Figure 4 shows transmission electron microscope (TEM) images of raw amorphous material No.1 and a heated No.1 sample. At low magnification, amorphous titania is present as micron-scale spherical balls (Figure 4a). However, higher magnification reveals fine structure within these balls (Figure 4b). The micron-sized titania balls consist of tightly packed 2−3 nm amorphous titania particles. Anatase particles formed by heating of this amorphous titania are almost spherical (Figure 4c and 4d). Large anatase particles may have grown by one of three pathways. First, they may form directly from aggregates of smaller amorphous titania particles. Second, they may grow by atom-by-atom recrystallization of smaller anatase particles. Third, large anatase crystals may form by solid-state aggregation of adjacent small anatase particles as they adopt appropriate crystallographic orientations.[20] For example, the ∼13 nm anatase particle on the right side of Figure 4d is spherical, suggesting that it may have formed directly from an amorphous region or by complete recrystallization of smaller anatase particles. In contrast, the much bigger anatase particle (∼20 nm) on the left side of Figure 4d consists of two slightly misoriented domains (see white lines, which trace lattice fringes across the crystal). This suggests that it formed by reorientation of a pair of particles. Imperfect attachment, as seen here, leads to the incorporation of dislocations in the resulting single crystal.[21] The average particle size derived from XRD is 27 nm, consistent with the diameter of this particle and many others in the TEM image (Figure 5).

The particle size of a nanocrystalline anatase sample can also be estimated from its specific surface area, as determined from adsorption of nitrogen onto the sample at 77.1 K. The specific surface area is derived from the adsorption data using the Brunauer−Emmett−Teller (BET) equation. The BET surface area of one nanocrystalline anatase sample whose XRD average particle size is 24 nm (data set 4 in Figure 3, 498 °C) was 45.9 m^2/g (see Supporting Information). This value corresponds to a particle size of 34 nm assuming all particles are spherical. There is always particle aggregation in an anatase sample, so it is not unexpected that the measured BET size is greater than the corresponding XRD size.

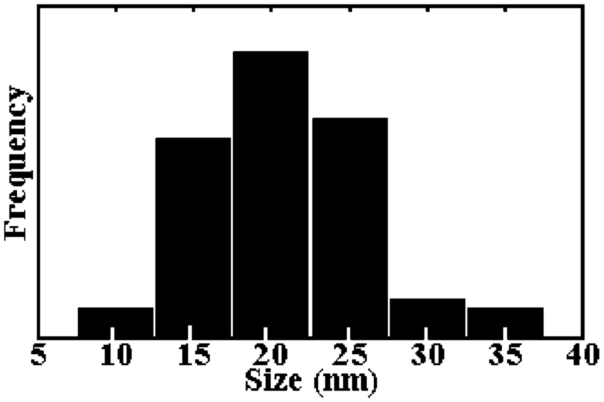

Figure 5. Particle size distribution of anatase derived from TEM images (for the sample of No. 1 heated at 500 °C for 3 h).

Acknowledgment. Financial support for this study was provided by National Science Foundation Grant EAR-9814333. We thank Yohey Suzuki for assistance with some of the TEM work and Prof. Marc Anderson of Water Chemistry Program for providing access to the BET instrument.

Supporting Information Available: XRD patterns of samples heated at different temperatures, analytical method used to determine the amount of anatase in a mixture of amorphous titania and anatase, and a diagram showing the BET isotherm. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL0055198