ABSTRACT: Barium titanate (BaTiO₃) nanocubes with a narrow particle size distribution were synthesized using a three-step approach. First, a water-soluble Ti complex was synthesized using a hydrolysis method. Next, the titanium dioxide (TiO₂) raw material was synthesized via a hydrothermal method using various water-soluble titanium (Ti) complexes. The TiO₂ exhibited various particle sizes and crystal structures (anatase, rutile, or brookite) depending on the water-soluble Ti complex and the hydrothermal conditions used in its synthesis. Finally, BaTiO₃ nanocubes were subsequently created through a hydrothermal method using the synthesized TiO₂ particles and barium hydroxide octahydrate [Ba(OH)₂·8H₂O] as raw materials. The present study clarifies that the particle size of the BaTiO₃ nanocubes depends on the particle size of the TiO₂ raw material. BaTiO₃ particles with a narrow size distribution were obtained when the TiO₂ particles exhibited a narrow size distribution. We found that the best conditions for the creation of BaTiO₃ nanocubes using TiO₂ involved using lactic acid as a complexing agent, which resulted in a particle size of 166 nm on average. This particle size is consistent with an average of the width of the cubes measured from corner to corner diagonally, which corresponds to a side length of 117 nm. In addition, surface reconstruction of the BaTiO₃ was clarified via electron microscopy observations, identifying the outermost surface as a Ti layer. Electron tomography using high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) confirmed the three-dimensional (3D) structure of the obtained BaTiO₃ nanocubes.

INTRODUCTION

Enhanced materials require a specific morphology design of their particles. The objective of the present study was the synthesis of highly dispersed barium titanate (BaTiO₃) nanocubes with a narrow particle size distribution leading to enhanced dielectric properties. Enhanced dielectric materials require a high relative dielectric constant. To improve the relative dielectric constant, the development of a dense ceramic is necessary. High-density ceramics facilitate greater electric conductivity than low-density ceramics. BaTiO₃ nanocubes play an important role in dense ceramics. When the BaTiO₃ nanocubes with a narrow particle size distribution are accumulated, the resulting ceramic is formed with a high density. In addition, the relative dielectric constant would increase if the interface of the BaTiO₃ nanocube that had a wide surface area was distorted and had polarization. Therefore, the BaTiO₃ nanocube has a potential to lead into an enhanced dielectric material.

Titanium dioxide (TiO₂) is a famous substance for a photocatalyst. Recently, papers concerning a TiO₂-based photocatalyst were published in 2019−2021. One of the research of the papers described highly efficient photocatalytic overall water splitting. Hydrogen and oxygen evolution with overall water splitting is the most important research in environment-harmonized materials and the clean energy demand. In this study, TiO₂ was synthesized using a hydrothermal method, and the obtained TiO₂ was used for a raw material to synthesize BaTiO₃ nanocubes.

Our synthesis of BaTiO₃ nanocubes is based on a hydrothermal method that enables control of the particle morphology. In addition, we developed a comprehensive scheme for the synthesis of BaTiO₃ nanocubes using TiO₂ synthesized in situ as a raw material. We speculated that highly dispersed BaTiO₃ nanocubes with a narrow size distribution would be obtained if TiO₂ that is also highly dispersed and exhibits a narrow size distribution was used as a raw material. The key to our approach is the use of a water-soluble titanium (Ti) complex for the synthesis of TiO₂, which leads to the
synthesis of TiO2 particles with various sizes and structures. Previous papers reported the synthesis method of water-soluble Ti complexes using various ligands such as glycolic acid, lactic acid, and citric acid. Crystal structures of (NH4)6[Ti4(C2H2O3)4(C2H3O3)2(O2)4(O2)4], (NH4)2[Ti(C2H3O3)4]3, and (NH4)6[Ti(C2H2O3)4(O2)4(O2)4]8H2O were described in detail. Moreover, TiO2 with various crystal structures such as anatase-type, rutile-type, and brookite-type was obtained using a solvothermal method. The required properties of the TiO2 nanocrystals in this study are summarized as follows:

1. Highly dispersed particles less than 25 nm in size
   Reason 1: Anatase-type TiO2 with highly dispersed particles smaller than 25 nm is difficult to source commercially because the nanoparticles tend to aggregate.
   Reason 2: BaTiO3 nanocubes with a narrow particle size distribution would be obtained if highly dispersed anatase-type TiO2 particles smaller than 25 nm were used as a raw material.

2. Crystal structure: anatase-type, rutile-type, and brookite-type
   Reason: The effect of the structure of TiO2 as a raw material on the morphology of BaTiO3 is unknown.

We can obtain anatase-type TiO2 below 25 nm from commercial sources. However, it is difficult to purchase fine TiO2 particles with dispersion. In addition, the effect of the structure of TiO2 as a raw material on the morphology of BaTiO3 is unknown. We theorized that the intermediate complex and the dissolving speed were different when anatase-type, rutile-type, and brookite-type TiO2 particles were dissolved in reaction media. Accordingly, BaTiO3 nanocubes with a narrow particle size distribution would be obtained if highly dispersed anatase-type TiO2 particles smaller than 25 nm were used as a raw material.

BaTiO3 nanocubes were hydrothermally synthesized using TiO2 nanoparticles in situ. Controlling nucleation and crystal growth of BaTiO3 nanocubes was recently published for the solvothermal synthesis of BaTiO3 nanocubes. This paper described varying the ratio of titanium tetraisopropoxide \([\text{Ti(OCH(CH3)2)}4]\) and TiO2 as raw materials, where the \([\text{Ti(OCH(CH3)2)}4]\) encouraged nucleation and the fine TiO2 nanoparticles boosted crystal growth. In this previous paper, commercial TiO2 nanoparticles were used for the synthesis of BaTiO3 nanocubes. Therefore, the present study primarily focused on the raw materials used to synthesize the TiO2 to improve the size distribution and dispersion of the BaTiO3 nanocubes. In addition, detailed observations of the surface of the BaTiO3 nanocubes were done by electron microscopy because the surface structure gave us useful information about the improved properties of the material. Our objective was to synthesize highly dispersed BaTiO3 nanocubes with a narrow particle size distribution.

## RESULTS AND DISCUSSION

BaTiO3 was synthesized in three steps. The first step was the synthesis of a water-soluble Ti complex. The second step was hydrothermal reaction of TiO2 using the water-soluble Ti complex. The third step was the hydrothermal synthesis of BaTiO3 using the synthesized TiO2.

### Synthesis of the Water-Soluble Ti Complex

One of the most important points of the present study was the synthesis of highly dispersed TiO2 nanoparticles from a water-soluble Ti complex. Various water-soluble Ti complexes were synthesized using different complexing agents, as shown in Figure S1. All of the solutions of water-soluble Ti complexes were transparent and were yellow (Figure S1a–c) or orange (Figure S1d,e), depending on the complexing agent.

Hydrothermal Synthesis of TiO2. Our aim was to synthesize highly dispersed TiO2 nanoparticles with a particle size smaller than 25 nm for subsequent use as a raw material in the synthesis of BaTiO3. The TiO2 nanoparticles were synthesized via a hydrothermal method using water-soluble Ti complexes to achieve this purpose. Various reaction media—water, an acidic solution, and an alkaline solution—were used as the reaction media in the hydrothermal synthesis. Five different ligands were used: glycolic acid, lactic acid, citric acid, d(-)-tartric acid, and L(+)-tartric acid.

TiO2 was synthesized via a hydrothermal method using water-soluble Ti complexes with glycolic acid as the ligand. X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images for the resultant products are shown in Figure S2 and Figure 1, respectively. Rutile-type TiO2 was obtained when the nitric acid solution (Figure S2a) or water (Figure S2b) was used as the medium, and brookite-type TiO2 was obtained when the ammonia solution was used (Figure S2c). The size of the rutile-type TiO2 particles was several tens of nanometers (Figure 1a,b). The brookite-type TiO2 particles (Figure 2a,b) were slightly larger than the rutile-type TiO2 particles (Figure 1c).

TiO2 was next synthesized via a hydrothermal method using a water-soluble Ti complex with lactic acid as the ligand. The corresponding XRD patterns and SEM images are shown in Figure S3 and Figure 2, respectively. Anatase-type TiO2 was obtained using the nitric acid solution (Figure S3a) or water (Figure S3b), and brookite-type TiO2 was obtained using the ammonia solution (Figure S3c). The anatase-type TiO2 particles were nanometer-scale fine particles (Figure 2a,b),

![Figure 1. BF-TEM images of obtained powders via the hydrothermal method using different water-soluble complexes of Ti and glycolic acid as the ligand dissolved in a reaction medium of (a) nitric acid solution, (b) water, or (c) ammonia solution. The reaction was performed at 200 °C for 12 h.](https://doi.org/10.1021/acsomega.1c04013)

![Figure 2. BF-TEM images of obtained powders via the hydrothermal method using different water-soluble complexes of Ti and lactic acid as the ligand dissolved in a reaction medium of (a) nitric acid solution, (b) water, or (c) ammonia solution. The reaction was performed at 200 °C for 12 h.](https://doi.org/10.1021/acsomega.1c04013)
and the size of the brookite-type TiO$_2$ particles (Figure 2a,b) was several tens of nanometers (Figure 2c).

TiO$_2$ was also synthesized via a hydrothermal method using a water-soluble Ti complex with citric acid as the ligand. The corresponding XRD patterns and SEM images are shown in Figure S4 and Figure 3, respectively. All of the synthesized powders were anatase-type TiO$_2$ irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S4a–c). Fine nanosized particles were obtained when the nitric solution or water was used (Figure 3a,b). However, the particle size became large (several tens of nanometers) when ammonia solution was used (Figure 3c).

TiO$_2$ was then synthesized via a hydrothermal method with a water-soluble Ti complex with D(−)-tartaric acid as the ligand. The corresponding XRD patterns and SEM images are shown in Figure S5 and Figure 4, respectively. All of the synthesized powders were anatase-type TiO$_2$ irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S5a–c). Fine nanosized particles were obtained when the nitric solution or water was used (Figure 4a,b). However, the particle size became large (several tens of nanometers) when ammonia solution was used (Figure 4c).

Finally, TiO$_2$ was synthesized via a hydrothermal method using a water-soluble Ti complex with D(−)-tartaric acid as the ligand. The corresponding XRD patterns and SEM images are shown in Figure S6 and Figure 5, respectively. All of the obtained powders were anatase-type TiO$_2$, irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S6a–c). Fine particles several tens of nanometers in diameter were obtained in all cases (Figure 5a–c).

Figure 6 summarizes the aforementioned results. Three types of TiO$_2$ were obtained (anatase-TiO$_2$, rutile-TiO$_2$, and brookite-TiO$_2$) from a hydrothermal synthesis with water-soluble Ti complexes that contained glycolic acid, lactic acid, citric acid, D(−)-tartaric acid, or L(+)−tartaric acid as the ligand. The complexing agents differ by their carbon number. Glycolic acid has the lowest carbon number among the investigated complexing agents, whereas D(−)-tartaric acid and L(+)−tartaric acid have the highest carbon number. In addition to the complexing agent, different reaction media of a nitric acid solution, water, and an ammonia solution were investigated for the synthesis of TiO$_2$. The pH of the nitric acid solution was low, whereas that of the ammonia solution was high. Rutile-TiO$_2$ was obtained only when glycolic acid was used in the nitric acid solution or water. Brookite-TiO$_2$ was obtained when glycolic acid or lactic acid was used in the ammonia solution. All of the other investigated conditions resulted in anatase-TiO$_2$. Increasing carbon numbers in the complexing agents tended to favor the formation of anatase-TiO$_2$.

Hydrothermal Synthesis of BaTiO$_3$ from TiO$_2$. BaTiO$_3$ was synthesized via a hydrothermal method using two types of reagent TiO$_2$ with different particle sizes. The corresponding XRD patterns and SEM images are shown in Figure S7 and Figure 7, respectively. Figure 7a,b–1 shows anatase-type TiO$_2$ with fine (<25 nm) and large particles, respectively. When the fine TiO$_2$ particles were used as the raw material, the BaTiO$_3$ particles exhibited a nanocube morphology but were small (Figure 7a–2). The BaTiO$_3$ obtained using the large-particle TiO$_2$ as the raw material exhibited a large morphology (Figure 7b–2). These results demonstrate that the morphology of the obtained BaTiO$_3$ depended on the particle size of the TiO$_2$ used as the raw material.
Our objective was to synthesize highly dispersed BaTiO3 nanocubes with a narrow particle size distribution. We speculated that using fine TiO2 nanoparticles smaller than 25 nm as a raw material would lead to the formation of BaTiO3 nanocubes with the desired properties. The fine TiO2 nanoparticles were synthesized via a hydrothermal method with water-soluble Ti complexes. That is, we synthesized BaTiO3 nanocubes with a narrow particle size distribution via a hydrothermal method with TiO2 nanoparticles synthesized in situ. Five different ligands were used for the synthesis of the water-soluble Ti complexes.

First, BaTiO3 was synthesized via a hydrothermal method using Ba(OH)2·8H2O and TiO2 synthesized from a water-soluble Ti complex with glycolic acid as the ligand (Figure 1). The XRD patterns and SEM images for the products are shown in Figure S8 and Figure 8, respectively. All the obtained powders were confirmed to be BaTiO3 irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S8a–c). Cube-like BaTiO3 with rounded edges were obtained when the nitric acid solution or water was used (Figure 8a,b). However, the particles became large when the ammonia solution was used as the reaction medium (Figure 8c).

Second, BaTiO3 was synthesized via a hydrothermal method using Ba(OH)2·8H2O and TiO2 synthesized from a water-soluble Ti complex with lactic acid as the ligand (Figure 2). The corresponding XRD patterns and SEM images are shown in Figure S9 and Figure 9, respectively. All of the obtained powders were confirmed to be BaTiO3 irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S9a–c). All of the obtained powders were confirmed to be BaTiO3 nanocubes (Figure 9). In the case of the BaTiO3 nanocubes synthesized via a hydrothermal method using water as a reaction medium (Figure 9b), bright-field transmission electron microscopy (BF-TEM) observations (Figure S10) indicate that the average size of 200 BaTiO3 nanocubes was 166 nm when measured corner to corner, corresponding to a side length of 117 nm on average. A comparison of the particle size of the BaTiO3 nanocubes in Figure 7a–2 and that of the nanocubes in Figure 9b reveals that the side length of the particles of the BaTiO3 nanocubes synthesized using TiO2 synthesized in situ was smaller by 23 nm. These results provide further evidence that the TiO2 particle size of the raw material affects the particles size of the BaTiO3 nanocubes.

Third, BaTiO3 was synthesized via a hydrothermal method using Ba(OH)2·8H2O and TiO2 synthesized from a water-soluble Ti complex with citric acid as the ligand (Figure 3). The corresponding XRD patterns and the SEM images are shown in Figure S11 and Figure 10, respectively. All of the obtained powders were confirmed to be BaTiO3 irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S11a–c). Among the investigated media, the nitric acid solution was found to result in the smallest BaTiO3 particles; however, the BaTiO3 particles were not cubic (Figure 10a). When water was used as the reaction medium, the particles of BaTiO3 were relatively small (Figure 10b), whereas the ammonia solution resulted in the growth of large particles (Figure 10c).

Fourth, BaTiO3 was synthesized via a hydrothermal method using Ba(OH)2·8H2O and TiO2 synthesized from a water-soluble Ti complex with d(-)-tartaric acid as the ligand (Figure 4). The corresponding XRD patterns and SEM images for the products are shown in Figure S12 and Figure 11, respectively. All of the obtained powders were confirmed to be BaTiO3 irrespective of whether a nitric acid solution, water, or ammonia solution was used as the medium (Figure S12a–c). When a nitric acid solution or water was used as the reaction medium, only cube-like BaTiO3 particles were obtained.

**Figure 7.** SEM images of obtained powders via the hydrothermal method using various commercially obtained TiO2 particles in water. The reaction was conducted at 200 °C for 72 h, with a reaction medium of water (40 mL). Commercial TiO2: (a-1) fine particles and (b-1) large particles. Obtained BaTiO3 using commercial TiO2: (a-2) fine particles and (b-2) large particles.

**Figure 8.** SEM images of obtained powders via the hydrothermal method using Ba(OH)2·8H2O and various TiO2 particles synthesized as shown in Figure 1. The reaction was conducted at 200 °C for 72 h. The ligand used for the synthesis of TiO2 was glycolic acid. Reaction medium: (a) nitric acid solution, (b) water, or (c) ammonia solution.

**Figure 9.** SEM images of obtained powders via the hydrothermal method using Ba(OH)2·8H2O and various TiO2 particles synthesized as shown in Figure 2. The reaction was conducted at 200 °C for 72 h. The ligand used for the synthesis of TiO2 was lactic acid. Reaction medium: (a) nitric acid solution, (b) water, or (c) ammonia solution.

**Figure 10.** SEM images of obtained powders via the hydrothermal method using Ba(OH)2·8H2O and various TiO2 particles synthesized as shown in Figure 3. The reaction was conducted at 200 °C or 72 h. The ligand used for the synthesis of TiO2 was citric acid. Reaction medium: (a) nitric acid solution, (b) water, or (c) ammonia solution.
Water-soluble Ti complex with L(+)-tartaric acid as the ligand in the synthesis medium, BaTiO3 particles were small (Figure 11c). However, during hydrothermal synthesis (Figure 13b), they also did not dissolve in the reaction medium before the hydrothermal synthesis was conducted. The ligand used for the synthesis of TiO2 was D(-)-tartaric acid. Reaction medium: (a) nitric acid solution, (b) water, or (c) ammonia solution.

(Figure 11a,b). When the ammonia solution was used as the medium, BaTiO3 particles were small (Figure 11c).

Figure 11. SEM images of obtained powders via the hydrothermal method using Ba(OH)2·8H2O and various TiO2 particles synthesized as shown in Figure 4. The reaction was conducted at 200 °C for 72 h. The ligand used for the synthesis of TiO2 was D(-)-tartaric acid. Reaction medium: (a) nitric acid solution, (b) water, or (c) ammonia solution.

(Figure 11a,b). When the ammonia solution was used as the medium, BaTiO3 particles were small (Figure 11c).

Fifth and finally, BaTiO3 was synthesized via a hydrothermal method using Ba(OH)2·8H2O and TiO2 synthesized from a water-soluble Ti complex with L(+)-tartaric acid as the ligand (Figure 5). The corresponding XRD patterns and SEM images are shown in Figure S13 and Figure 12, respectively. The obtained BaTiO3 particles were cube-like irrespective of the reaction conditions used in the synthesis of BaTiO3. Fine TiO2 was obtained; TiO2 did not fully dissolve in the reaction medium if the ammonia solution was used as the medium (Figure 12a–c).

Figure 12. SEM images of obtained powders via the hydrothermal method using Ba(OH)2·8H2O and various TiO2 particles synthesized as shown in Figure 5. The reaction was conducted at 200 °C for 72 h. The ligand used for the synthesis of TiO2 was L(+)-tartaric acid. Reaction medium: (a) nitric acid solution, (b) water, or (c) ammonia solution.

We investigated the formation mechanism of BaTiO3 nanocubes synthesized using TiO2 particles with different sizes as the raw material.22 Figure 13 shows the formation mechanism for BaTiO3 nanocubes. The raw material in Figure 13a is large TiO2 particles, and that in Figure 13b is fine TiO2 particles. The large TiO2 particles were not dissolved in the reaction medium before the hydrothermal synthesis was carried out (Figure 13a). During the hydrothermal synthesis, the large TiO2 particles became small because they dissolved in the reaction medium. As the hydrothermal reaction progressed, BaTiO3 nanocubes gradually nucleated, whereas the TiO2 particles remained in the reaction medium. Therefore, the size of the BaTiO3 nanocubes varied widely. As a result, BaTiO3 nanocubes with a broad particle size distribution were obtained; TiO2 did not fully dissolve in the reaction medium if the TiO2 particles were too large.

The behavior of fine TiO2 particles differed from that of large TiO2 particles under the hydrothermal reaction conditions used in the synthesis of BaTiO3. Fine TiO2 was also not dissolved in the reaction medium before the hydrothermal synthesis (Figure 13b). However, during the hydrothermal synthesis, fine TiO2 particles were completely dissolved in the reaction medium. As the hydrothermal reaction progressed, BaTiO3 nanocubes nucleated. Finally, BaTiO3 nanocubes were obtained with a narrow particle size distribution. The key point for the formation of BaTiO3 nanocubes with a narrow particle size distribution is a large number of nuclei that form simultaneously and grow into BaTiO3 nanocubes during the hydrothermal reaction.

XRD Analysis of the BaTiO3 Nanocubes. In the present work, we examined five ligands for the BaTiO3 synthesis. From the results in Figures 9 and 13, the best shape of the nanocube was when using lactic acid. Figure 14 shows a high-energy synchrotron XRD pattern for the BaTiO3 nanocubes. The RIETAN-FP software23 was used for a Rietveld refinement based on a P4mm model for BaTiO3 in a tetragonal crystal system. In the present work, the wavelength of an X-ray with 0.020615 nm was used for a high-energy synchrotron XRD pattern measurement, enabling us to acquire high-resolution XRD data. The same sample that is shown in Figure 9b was used for the high-energy synchrotron XRD pattern measurement. The obtained XRD data verified a single phase of BaTiO3, and the XRD results indicated that a tetragonal crystal system with a P4mm space group was assigned (Table 1).24

The pair distribution function (PDF) method was used to analyze the radial distribution from disordered materials on the basis of their powder XRD patterns and to get knowledge of the interatomic distances. A PDF analysis of the XRD pattern that was obtained using high-energy synchrotron X-rays (Figure 14) is shown in Figure 15. The results indicated Ti–O interatomic distances of 1.9 and 2.2 Å, a Ba–O interatomic distance of 2.8 Å, a Ba–Ti interatomic distance of 3.5 Å, and a Ba–Ba interatomic distance of 4.0 Å. These results suggest that there is a displacement of the Ti atom from the center of the BaTiO3 unit cell, causing spontaneous polarization of the BaTiO3 tetragonal crystal structure.24

Detailed Observation of BaTiO3 Nanocubes Using electron Microscopy. BaTiO3 nanocubes were observed in detail using electron microscopy. Secondary electron (SE) images, bright-field scanning transmission electron microscopy (BF-STEM) images, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired at an acceleration voltage of 200 kV (Figure 16). The BaTiO3 particles were clearly confirmed to exhibit sharp-edges with corners. In addition, the BaTiO3 nanocubes were highly dispersed.

Recently, the surface of perovskite structures at the atomic level has been investigated using theoretical approaches25–27 and electron microscopy.28–30 Moreover, the facets of particles have also been studied.25–30 In the present work, the surface of BaTiO3 nanocubes was examined using electron microscopy. Figure 17 shows TEM results for a BaTiO3 nanocube taken from the direction of [001] incidence. A single crystal of BaTiO3 was identified from the TEM image (Figure 17a) and the corresponding nanobeam diffraction pattern (Figure 17b).

The atomic column of BaTiO3 nanocube observed in the direction of [001] incidence is shown in Figure 18. The corresponding TEM image (Figure 17a) was used for analysis. Figure 18a-1 is a HAADF-STEM image, and Figure 18a-2 is an annular bright-field scanning transmission electron microscopy (ABF-STEM) image. Figure 18a-1,a-2 is an annular bright-field scanning transmission electron microscopy (ABF-STEM) image. Figure 18a-1,a-2 is an annular bright-field scanning transmission electron microscopy (ABF-STEM) image. Figure 18b-1,b-2,d-1,d-2,f-1,f-2,h-1,h-2 shows images of the four corners of the BaTiO3 nanocube. Figure 18c-1,c-2,c-3,c-4,e-1,e-2,g-1,g-2,j-1,j-2 shows images corresponding to the top, right, bottom, and left sides of the BaTiO3 nanocube, respectively. The arrangement of atomic column and surface reconstruction were obtained by means of Cs-corrected HAADF-STEM and ABF-STEM images of the sides of the BaTiO3 nanocube.
The contrast in HAADF-STEM images depends on the atomic number of the observed elements, where heavier elements have a higher contrast than lighter elements. This makes detecting lighter elements difficult. On the other hand, ABF-STEM allows for the detection of lighter elements such as O; accordingly, using a combination of both HAADF-STEM and ABF-STEM gives us a more complete observation that compensates for the shortcomings of both detection methods.

Figure 13. Formation mechanism for BaTiO₃ nanocubes from (a) large and (b) fine TiO₂ particles as the raw materials.

Figure 14. High-energy synchrotron XRD pattern of BaTiO₃ nanocubes and its Rietveld refinement. A wavelength of X-ray is 0.020615 nm. Concerning the Rietveld refinement, the recorded spectrum is shown as red cross marks and the light-blue solid line is a fit to the model for the BaTiO₃ phase. Red cross marks, light-blue solid lines, and blue solid lines represent observed, calculated, and differing intensities, respectively. Green ticks represent positions of the calculated Bragg reflections of the BaTiO₃ phase.

Table 1. Rietveld Refinement of the Structural Parameters of the High-Energy Synchrotron XRD Pattern

| atom   | site | x   | y   | z     | occupancy | Biso   |
|--------|------|-----|-----|-------|-----------|--------|
| Ba     | 1a   | 0   | 0   | 0     | 1         | 0.331  |
| Ti     | 1b   | 1/2 | 1/2 | 0.4699| 1         | 0.056  |
| O1     | 1b   | 1/2 | 1/2 | 0.9890| 1         | 0.212  |
| O2     | 2c   | 1/2 | 0   | 0.4654| 2         | 0.088  |
| a/Å    |      | 3.98592 | 7 | |
| c/Å    |      | 4.02376 | 8 | |
| Rwp/%  |      | 5.876 |   | |
| Rp/%   |      | 4.112 |   | |

Figure 15. PDF analysis of the XRD pattern obtained by means of high-energy synchrotron X-rays as shown in Figure 14. Concerning the PDF analysis, the recorded spectrum is shown as a black solid line and red circles are the fit to recorded spectrum. The black solid line, red circle marks, and blue solid lines represent observed, calculated, and differing intensities, respectively.

Figure 19 shows an observation of a BaTiO₃ nanocube in the direction of [110] incidence. The nanocube was confirmed to be a single crystal of BaTiO₃ on the basis of its TEM image (Figure 19a) and its corresponding nanobeam diffraction pattern (Figure 20b).
middle of the array shows broad views of the BaTiO₃ nanocube. The direction of [110] incidence shows a contrast on the nanocube that indicates that this incidence is taken through a corner. The brighter section indicates more atoms, and the darker sections indicate less atoms. On the other hand, an image that has little contrast indicates a face on incidence, for example, Figure 18. Figure 20b-1,b-2,d-1,d-2,g-1,g-2 shows images of the corners of the BaTiO₃ nanocube. Figure 20c-1,c-2,e-1,e-2,f-1,f-2 shows images of the top, right, and bottom sides of the BaTiO₃ nanocube, respectively. A Cs-corrected HAADF-STEM image and ABF-STEM image of the atomic column arrangement and surface reconstruction were used to observe the sides of the BaTiO₃ nanocube. Notably, one of the atomic positions of O is overlapped with the atomic position of Ti in the direction of [001] incidence (Figure 18). On the other hand, a different O atom position is overlapped with the atomic position of Ba in the direction of [110] incidence (Figure 20). Therefore, all the atomic positions of the O atoms are clearly observed using the images in both the directions of [001] and [110].

We tried to examine the surface of BaTiO₃ nanocube; however, the electron beam could not transmit through the BaTiO₃ nanocube well, so the surface reconstruction of cube-like BaTiO₃ nanoparticles with facets was examined through elemental analysis. Figure S14 shows observations of cube-like BaTiO₃ in the direction of [001] incidence. From the TEM results, a single crystal of BaTiO₃ nanocube was clarified (Figure S14a), with the corresponding nanobeam diffraction pattern (Figure S14b). Figure S15 shows HAADF-STEM observations and EELS analysis of a cube-like BaTiO₃ in the direction of [001] incidence, as is visible in the corresponding same sample in Figure S14. Here, the constituent element of BaTiO₃ is three (Ba, Ti, and O), and analysis of Ba and O can be performed using energy dispersive X-ray spectroscopy, although analysis of Ti is more difficult due to the Lα lines of Ba overlapping the Kα lines of Ti. On the other hand, electron energy-loss spectroscopy (EELS) allows for the elemental analysis of Ti.
analysis of Ti because Ti peaks do not overlap Ba peaks in EELS spectra. Accordingly, elemental analysis of a BaTiO3 nanocube surface was performed using EELS. Ba and Ti are indicated by green and red, respectively. Elemental analyses of Ba and Ti were carried out on the basis of the EELS peaks for Ti and Ba. Observation of the atomic column of HAADF-STEM and their EELS analyses were conducted on the top and left side of the cube-like BaTiO3 nanoparticle. A regular arrangement of Ba and Ti columns was clearly observed inside the cube-like BaTiO3 nanoparticle, as well as with surface reconstruction made up of Ti columns with no Ba columns at the outermost surface on every side of the cube-like BaTiO3 nanoparticles. As a result, the surface reconstruction of the cube-like BaTiO3 nanoparticles was confirmed from Figure S14.

A three-dimensional (3D) moving image (Supporting Information 3D-1), which is constructed from HAADF-STEM images of Figure S16, shows electron tomography results for the BaTiO3 nanocubes, as constructed by acquiring HAADF-STEM images at various angles and subsequently rendering the volume and isosurface, which can provide information about the interior and surface of substances, respectively (Figure 21).31 Clearly, the BaTiO3 nanocubes exhibit a 3D cubic morphology with defined edges and facets clearly exposed. In addition, the interior of the BaTiO3 nanocubes was observed from a slice image along the intersection of the x, y, and z axes. Using electron tomography, we confirmed that BaTiO3 nanocubes were obtained without voids. In addition, 3D analysis of other BaTiO3 nanocubes is shown in Figure S17. Supporting Information 3D-2 shows a 3D moving image of the BaTiO3 nanocubes as constructed from HAADF-STEM images of Figure S18. The voidless BaTiO3 nanocubes were indicated from Figures S17 and S18.

■ CONCLUSIONS

We synthesized BaTiO3 with an average particle size of less than 25 nm using a hydrothermal method using water as a reaction medium with fine TiO2 particles as a raw material. A key point for the morphology control of BaTiO3 is the particle size and particle size distribution of the TiO2. Highly dispersed TiO2 nanoparticles with a particle size less than 25 nm are difficult to obtain from commercial sources. We therefore synthesized highly dispersed TiO2 below 25 nm using a hydrothermal method. In addition, we controlled the structure of the TiO2 as anatase, rutile, or brookite depending on the water-soluble Ti complex and the hydrothermal conditions used for the in situ synthesis of TiO2.
We subsequently hydrothermally synthesized highly dispersed BaTiO₃ nanocubes with a narrow size distribution using the previously synthesized TiO₂ as the raw material. The particle size of the BaTiO₃ was confirmed to be 117 nm on the basis of measurements of its particle size distribution. The size of the BaTiO₃ crystallites was consistent with its average particle size. The key to synthesizing highly dispersed BaTiO₃ nanocubes with a narrow size distribution is the size of the TiO₂ particles, not their structure. In addition, surface reconstruction of the obtained BaTiO₃ nanocube was confirmed via electron microscopy observations, which identified the outermost surface as being composed of a Ti layer.

Given the aforementioned results, the present study clarified that the particle size of BaTiO₃ nanocubes depends on the particle size of TiO₂ used as the raw material and that BaTiO₃ particles with a narrow size distribution are obtained when TiO₂ raw-material particles have a narrow size distribution.

### EXPERIMENTAL SECTION

**Raw Materials.** The following raw materials were used for the synthesis of BaTiO₃: titanium (Ti; 99.9% purity; Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan); nitric acid (HNO₃; 60.0–61.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan); ammonia solution (NH₃; 28.0–30.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan); hydrogen peroxide (H₂O₂; 30.0–35.5% purity; Kanto Chemical Co., Inc., Tokyo, Japan); lactic acid [CH₃CH(OH)COOH; 85.0–92.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan]; glycolic acid (HOCH₂COOH; >99.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan); citric acid [HOOCCH₂COOH·H₂O; >99.0% purity; Kanto Chemical Co., Inc., Tokyo, Japan]; anatase-type TiO₂ (particle size <25 nm; 99.7% purity; Sigma-Aldrich, St Louis, MO, U.S.A.); anatase-type TiO₂ (99.8% purity; Sigma-Aldrich, St Louis, MO, U.S.A.); barium hydroxide octahydrate [Ba(OH)₂·8H₂O; 99% purity; Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan]; acetic acid (CH₃COOH; 99.7% purity; Kanto Chemical Co., Inc., Tokyo, Japan); and ethanol (C₂H₅OH; 99.5% purity; Kanto Chemical Co., Inc., Tokyo, Japan).

**Synthesis of Water-Soluble Ti Complexes.** Figure S19a shows the flowchart of the synthesis of water-soluble Ti complex. Ti metal powder (10 mmol) was placed in a beaker followed by the sequential addition of 40 mL of acetic acid aqueous solution and 10 mL of ammonia solution to the beaker. The beaker was stored in an ice bath, and the Ti metal was dissolved in the mixture solution of H₂O₂ and ammonia. After Ti metal was dissolved, a yellow transparent solution containing the Ti-peroxo complex was obtained. Thereafter, a complexing agent [lactic acid, glycolic acid, citric acid, d(-)-tartaric acid, or l(+)-tartaric acid] was added to the solution. The amount of ligand was 30 mmol lactic acid, 27 mmol glycolic acid, 10 mmol citric acid, 10 mmol d(-)-tartaric acid, or 10 mmol l(+)-tartaric acid, respectively. To remove excess H₂O₂ and NH₃, the solution was left at room temperature overnight and then heated to 80 °C until a gel-like solid substance had formed. The gel-like solid substance was dissolved in water, and an aqueous solution of the Ti complex was obtained.

**Hydrothermal Synthesis of TiO₂ Nanoparticles.** Figure S19b shows the flowchart of hydrothermal synthesis of TiO₂ nanoparticles. The TiO₂ nanoparticles were synthesized via a hydrothermal method. A water-soluble Ti-complex aqueous solution (40 mL) was added to a Teflon reactor that was subsequently put into a stainless-steel autoclave that had 100 mL of internal volume. Then, the hydrothermal reaction was carried out at 200 °C for 12 h. Thereafter, we cooled the autoclave to room temperature. We collected the resultant powder by centrifugation at 10,000 rpm and rinsed it with water for three cycles and ethanol for two cycles. Finally, the resultant powder was dried at 80 °C in a drying oven.

**Hydrothermal Synthesis of BaTiO₃ Nanocubes.** Figure S19c shows the flowchart of the hydrothermal synthesis of BaTiO₃ nanocubes. BaTiO₃ nanocubes were synthesized using a hydrothermal method. TiO₂·Ba(OH)₂·8H₂O and a reaction medium of water, nitric acid solution, or ammonia water were added to a Teflon reactor. The raw materials and reaction media were stirred at 350 rpm for 5 min; the resultant mixture was placed into a stainless-steel autoclave that had 100 mL of internal volume. The hydrothermal reaction was then carried out at 200 °C for 72 h. Thereafter, the autoclave was cooled to room temperature. We collected the resultant powder by centrifugation at 10,000 rpm, rinsed it with water for three cycles and ethanol for two cycles, and then dried it at 80 °C in a drying oven.

**Acetic Acid Treatment.** To remove the barium carbonate (BaCO₃) byproduct, an acetic acid treatment was performed. First, the concentration of the acetic acid aqueous solution was adjusted to 0.69 mol·dm⁻³; then 50 mL of this solution was combined with 2 g of the product, and the resultant mixture was stirred at 350 rpm for 5 min. The product was collected by means of a centrifugal separator at 10,000 rpm, rinsed with water for three cycles and ethanol for two cycles, and then dried overnight at 80 °C in a drying oven.

**Characterization of the Obtained Powders.** XRD measurements were conducted by means of an Ultima IV diffractometer (Rigaku Co., Tokyo, Japan) equipped with a Cu Kα radiation source (wavelength: 0.15418 nm) operating at 40 kV and 30 mA. Samples were scanned at room temperature over the 2θ range from 10 to 80°. The products of anatase-type TiO₂, rutile-type TiO₂, and brookite-type TiO₂ were then assigned using JCPDS cards 21-1272, 1-1292, and 29-1360, respectively. High-energy synchrotron XRD measurements were performed at SPring-8 (Hyogo, Japan). The data were obtained in transmission mode at the SPring-8 BL22XU beamline by means of high-energy X-rays with a wavelength of 0.020615 nm. Short- and long-range structural parameters were refined by means of the Rietveld technique and the RIETAN-FP program. SE images of the powders were acquired with SEM using an instrument (SU-4800; Hitachi High-Tech Corporation, Tokyo, Japan) operating at an accelerating voltage of 3 kV. STEM was performed with SE, bright-field (BF), and HAADF detectors by means of an instrument (HD-2700; Hitachi High-Tech Corporation, Tokyo, Japan) operating at a 200 kV acceleration voltage. In addition, TEM observations and its nanobeam diffraction patterns as well as HAADF-STEM and ABF-STEM observations were conducted by means of a JEM-ARM200CF (JEOL Ltd., Tokyo, Japan) operating at an accelerating voltage of 200 kV and equipped with a cold field emission gun and a Cs corrector to view the atomic columns of BaTiO₃. Elemental analysis was performed using a JEOl JEM-ARM200CF equipped with an EELS. In regard to the accelerating voltage, 200 kV has high resolution for the observation of the atomic
columns in contrast with 80 kV, whereas 80 kV is suitable for EELS elemental mapping as it can be conducted over a long duration of time. A long duration observation can damage the BaTiO₃ nanoparticle if seen at an accelerating voltage of 200 kV. Accordingly, in the STEM observations including the EELS elemental mapping, 80 kV was used with an accelerating voltage due to the lower risk of damage to the BaTiO₃ nanoparticle.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04013.

- XRD patterns, STEM images, and EELS analyses of BaTiO₃ (PDF)
- 3D moving image constructed from HAADF-STEM images of Figure S16 (MP4)
- 3D moving image constructed from HAADF-STEM images of Figure S18 (MP4)

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**Author Contributions**
Kouichi Nakashima conceived and designed the overall project. Samples were synthesized and characterized by Kouta Hironaka, Kazuma Oouchi, and Mao Ajioka. Synchrotron XRD pattern was measured and Rietveld refinement was carried out by Yasuhiro Yoneda. Yoshio Kobayashi, Shu Yin, Masato Kakihana, and Tohru Sekino contributed to discussions and developed the concept of the present research.

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The authors declare no competing financial interest.

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