FULL PAPER

Low-temperature synthesis of strontium titanate particles with high specific surface area

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Strontium titanate (SrTiO₃) particles are expected to be applied to various catalysts, and many kinds of synthesis procedures of SrTiO₃ particles with a high specific surface area have been proposed. This study investigates a synthesis procedure of preparing SrTiO₃ particles with a high specific surface area by minimizing the crystallization temperature to the least possible value. The SrTiO₃ particles are prepared by maintaining spherical hydrous titania particles with smooth or porous surfaces in highly concentrated strontium hydroxide solutions at ≤120 °C. When porous hydrous titania particles are used as the raw material and the Sr/Ti ratio in the reaction solution is set at 10, spherical protrusions of SrTiO₃ develop on the surface of the original hydrous titania, even at a low temperature (25 °C). Single-phase SrTiO₃ particles with spherical protrusions composed of very fine crystallites are obtained by treatment at 40 °C for 24 h. These particles have a high BET specific surface area of 237 m² g^{−1}. The process developed herein is eco-friendly and effective for fabricating various perovskite-type compounds with a high specific surface area.

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1. Introduction

Strontium titanate (SrTiO₃) is used in various applications, such as electronic devices,^{1)–4)} gas sensors,^{5),6)} thermoelectric conversion materials,^{7)–9)} and pigments,¹⁰⁾ because of its thermal and chemical stabilities, ferroelectricity, semiconductivity, and thermoelectric properties. In the recent years, the application of SrTiO₃ as catalysts^{11),12)} and photocatalysts^{13),14)} has widely progressed, especially in water-splitting photocatalysts according to the Z-scheme,¹⁵⁾ owing to the ease in doping of dissimilar metals and the appropriate band structure. A high specific surface area is generally required to utilize solid materials as catalysts. Therefore, numerous synthesis methods for preparing SrTiO₃ nanoparticles with a high specific surface have been reported.^{16)–20)} For example, Zhang et al. obtained SrTiO₃ nanoparticles with a Brunauer–Emmett–Teller specific surface area (S_{BET}) of 42 m² g^{−1} using a hydrothermal method.²¹⁾ Sulaeman et al. and Silva et al. obtained such nanoparticles using a microwave-assisted solvothermal reaction (S_{BET} : 65 m² g^{−1})²²⁾ and a modified polymeric precursor method (S_{BET} : 83 m² g^{−1} using),²³⁾ respectively. However, nanoparticles are difficult to handle and obtain uniform dispersions in solvents, and recovering these particles from suspensions as an as-prepared powder

is challenging. Furthermore, there have been some concerns about the toxicity of nanomaterials.^{24),25)} On the contrary, particles with both sub-micron to micron diameters and high specific surface area have been realized by constructing porous^{26)–30)} or hierarchical structures^{27),31)–33)} on the particle surface. Such structures can be achieved using templates,²⁶⁾ solvothermal,^{31),32)} molten salt,²⁹⁾ or hydrothermal methods.^{27),28),30),33)} Liu et al. synthesized porous particles with a sub-micron diameter and a maximum S_{BET} of 434 m² g^{−1} via a molten salt method (however, holding at 205 °C for 7 days in molten salt was required).²⁹⁾ Using water, the simplest solvent, Pan et al. synthesized particles with an S_{BET} of 170 m² g^{−1} and an average diameter of approximately 450 nm through a 4 h hydrothermal treatment involving hydrous titania particles at 140 °C.³⁰⁾ This study aims to develop a synthesis procedure for achieving micron-sized SrTiO₃ particles with a high specific surface area.

The low-temperature crystallization of SrTiO₃ particles has been tried to suppress the decrease in the specific surface area. Using an ionic liquid as the solvent, Alammari et al. synthesized SrTiO₃ particles with an S_{BET} of 62 m² g^{−1} using ultrasound irradiation without a thermal treatment.³⁴⁾ In addition, Yamaguchi et al. reported that SrTiO₃ can be crystallized at room temperature by leaving the mixture of “the hydrous titania gel having more OH groups” with strontium hydroxide powder (S_{BET} was not reported).³⁵⁾ Thus, in the present study, we focused on the

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effect of concentrated strontium hydroxide when obtaining SrTiO_3 at low temperatures. In our previous work, we reported a preparation method that achieves uniformly sized hydrous titania particles via titanium butoxide hydrolysis using ammonia and water in a mixed solution of butanol and acetonitrile.^{36,37)} Hydrous titania particles, especially those prepared with low ammonia and water concentrations, have low chemical stability and become porous when soaked in ethanol by the partial dissolution of the surface part.³⁸⁾ Porous hydrous titania particles are highly reactive and can convert to SrTiO_3 particles at 90 °C in a strontium hydroxide solution, maintaining the particle size and shape of the raw material particles.³⁹⁾ However, the effect of the Sr^{2+} to Ti^{4+} ratio (Sr/Ti) in the reaction system was not examined in our previous study; instead, the concentration ratio was fixed at 1. Moreover, the core part of the particles was not completely converted to SrTiO_3 .

In this study, hydrous titania particles with a spherical shape having smooth or porous surfaces were prepared as the starting materials for the SrTiO_3 conversion. Their conversion conditions to SrTiO_3 by hot water (<100 °C) or hydrothermal treatment (≥ 100 °C) in strontium hydroxide solutions were widely examined. We refer herein to the treatment lower than 100 °C as the “hot water treatment.” The difference between hydrothermal and hot water treatment in this study is the variation in temperature from 25 to 120 °C and pressure due to the vapor pressure of water (1.96 atm at 120 °C) and the operation is exactly the same. However, treatments below 100 °C cannot be called “hydrothermal,” so we individually distinguished the treatment as “hot water” treatment. An important advantage of the “hot water treatment” (compared with hydrothermal treatments) is that we can perform the treatment without a costly pressure-resistant container. Moreover, crystallization at low temperatures is beneficial in terms of the environment and cost. We particularly focused on the effect of the concentrated strontium hydroxide for obtaining particles of single-phase SrTiO_3 with a high specific surface area by lowering the crystallization temperature to the least possible temperature.

2. Material and methods

2.1 Synthesis of the SrTiO_3 particles

The reagents used in this study were titanium *n*-butoxide, *n*-butanol, acetonitrile, ammonia water (28 wt.%), strontium hydroxide octahydrate [$\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$],

and nitric acid (0.1 M; FUJIFILM Wako Pure Chemical Industries Ltd., Japan). The water used for the synthesis and washing of the particles was prepared by reverse osmosis and electrodeionization (Elix System; Millipore Corp., USA). Two kinds of hydrous titania particles, namely, spherical particles with a smooth surface (hereafter referred to as spherical particles) and those with a porous surface (hereafter referred to as porous particles), were prepared by hydrolyzing titanium butoxide following a published procedure.³⁸⁾ First, two batches of 50 vol % acetonitrile and 50 vol % *n*-butanol mixed solvents were prepared. Titanium butoxide was added to one of the mixed solvent systems under a dry N_2 atmosphere. Subsequently, ammonia water was added to the other mixed solvent. Both prepared solutions were preheated at 80 °C using a water bath before initiating the reaction. These two solutions were then mixed and kept at 80 °C for 30 min while stirring. Upon mixing, the hydrolysis product precipitated immediately, forming a white suspension. After 30 min of stirring, the precipitates were centrifuged and the supernatant was removed. The remaining precipitates were washed by re-dispersion in ethanol and centrifuged thrice to dissolve the insufficiently polycondensed parts of the particles. The particles were then rinsed thrice in the same manner with water to wash the remaining alcohol. After washing, the particles were dried at 75 °C. Spherical particles with a uniform size were obtained when the concentrations of the starting materials after mixing were set at 0.05 M titanium butoxide, 0.10 M ammonia, and 0.50 M water [Fig. 1(a)]. Meanwhile, a porous structure was constructed at the washing stage with ethanol [Fig. 1(b)] when the concentrations of ammonia and water were changed to 0.02 and 0.31 M, respectively.

SrTiO_3 particles were prepared by hot water or hydrothermal conversion of the hydrous titania particles. Hydrous titania particles and strontium hydroxide octahydrate were added to water and dispersed ultrasonically. Titanium concentration in the suspension was set to 0.02 M. The amount of hydrous titania particles was adjusted according to the water content estimated using thermogravimetry.⁴⁰⁾ The suspensions were placed in a PTFE-lined autoclave and either hot water treated or hydrothermally treated. After the treatment, the particles were centrifuged and washed once with dilute nitric acid (approximately 0.1 M)³⁹⁾ and twice with water to remove the unreacted strontium hydroxide.

Fig. 1. SEM images of the (a) spherical and (b) porous hydrous titania particles.

2.2 Characterization

The crystalline phases were identified with X-ray diffractometry (XRD; MiniFlex, Rigaku Co. and MXP3; MacScience) using Cu K α radiation. The sample morphologies were observed using scanning electron microscopy (SEM; JSM-6510, JEOL, Ltd.) and transmission electron microscopy (TEM; H-7650A, HITACHI, Ltd.). The water content of the hydrous titania particles was determined using thermogravimetry (TG8120; Rigaku Co.). The S_{BET} and the N₂ adsorption-desorption isotherms of the samples were measured using an automatic specific surface area/pore size distribution analyzer (BELSORP-max; MicrotracBEL Co.).

3. Result and discussion

In a previous study, we fixed the concentration ratio (Sr/Ti) to 1. In this condition, we needed 120 °C for 24 h to form the SrTiO₃ phase on the spherical hydrous titania particles. Moreover, a small amount of hydrous titania remained in the central part of the particles treated under this condition.³⁹⁾ **Figures 2 and 3** show the XRD patterns and the SEM images of the hydrothermally treated spherical hydrous titania particles, respectively, in aqueous solutions with various strontium hydroxide concentrations. The hydrothermal treatment condition was set at 120 °C for 24 h. After the hydrothermal treatment, the SrTiO₃ phase formation was confirmed, regardless of the Sr/Ti ratio.

The SEM images showed that the particles hydrothermally treated under the Sr/Ti = 1 condition maintained the size and the shape of the original spherical hydrous titania particles. However, with the increasing Sr/Ti ratio, the particle shape tended to collapse, and the particles prepared under the Sr/Ti = 10 condition could not maintain the diameter of the original hydrous titania particles. Two

types of reaction mechanisms were proposed for converting titania particles to perovskite-type compounds in aqueous solution systems.^{41)–43)} The first type is the in situ reaction mechanism, in which alkaline-earth metal ions react on the titania surface, and the crystallization continues with diffusion of the alkaline-earth metal ions inside the particles. The diffused Sr ions react with the titanium source and converted to the SrTiO₃ inside of the particle. The second type is the dissolution-precipitation reaction mechanism, in which hydrous titania particles are first dissolved in the solvent (aqueous solution of Sr ions), and the dissolved Ti species react with alkaline-earth metal ions and the crystals of a perovskite-type compound are formed by homogeneous nucleation or heterogeneous nucleation on titania particles. In the present case, the in situ reaction mechanism was dominant when the Sr/Ti ratio was set at 1 because the original shape of hydrous titania was

Fig. 2. XRD patterns of the spherical particles after hydrothermal treatment at 120 °C for 24 h with various Sr/Ti ratios (Sr/Ti = 1–10).

Fig. 3. SEM images of the spherical particles after hydrothermal treatment at 120 °C for 24 h with various Sr/Ti ratios: (a) Sr/Ti = 1, (b) Sr/Ti = 3, (c) Sr/Ti = 4, and (d) Sr/Ti = 10.

maintained. When the Sr/Ti ratio in the reaction system was set at a high value, a heterogeneous nucleation of the SrTiO_3 microcrystals must have occurred on the original hydrous titania particles because of the high Sr ion concentration, even though the amount of titanium species dissolved in the aqueous solution was very small.

When porous hydrous particles were employed as the starting materials, and the concentration ratio (Sr/Ti) was set at 1, we needed the hot water treatment condition of 90 °C for 48 h to obtain the SrTiO_3 phase.³⁹⁾ **Figures 4** and **5** show the XRD patterns and the SEM images of the hot water-treated porous hydrous titania particles, respectively, in aqueous solutions with various strontium hydroxide concentrations. The hot water treatment condition was set at 90 °C for 48 h. After the treatment, the SrTiO_3 formation was confirmed, regardless of the Sr/Ti ratio. The SEM observation confirmed that after the hot water treatment,

Fig. 4. XRD patterns of the porous particles after hot water treatment at 90 °C for 48 h with various Sr/Ti ratios (Sr/Ti = 1–10).

the particles almost kept the original morphology of the porous hydrous titania particles used as the starting materials when the Sr/Ti ratio in the reaction system was set at 1. On the contrary, when the Sr/Ti ratio was set at a higher value, the particle morphology was drastically changed. Small spherical protrusions were newly formed, surrounding the original particles.

Figures 6 and **7** show the XRD patterns and the SEM images of the hot water-treated porous hydrous titania particles, respectively, at 90 °C for various treatment times. The Sr/Ti ratio in the reaction system was set at 10. In this case, the porous hydrous particles were converted to SrTiO_3 even with the short treatment time of 2 h. The half-widths of the XRD peaks became narrower with a prolonged treatment time. The SEM image illustrated small spherical protrusions forming on the particles treated for 2 h. Their appearance did not change much even after 48 h treatment. These results showed that the protrusions formed at the initial crystallization stage and only the SrTiO_3 crystallites grew with the treatment time without changing the outer shape of the protrusions.

The SrTiO_3 phase was obtained at a short treatment time when the Sr/Ti ratio was set at 10; thus, we tried low-temperature crystallization as the next step. **Figures 8(a)** and **9** show the XRD patterns and SEM images of the hot water-treated porous hydrous titania particles at various temperatures for 24 h. **Figure 8(b)** presents the XRD patterns of the particles additionally annealed at 600 °C for 2 h after the hydrothermal treatment. In this case, at 40 °C and lower, strontium hydroxide did not dissolve completely in the aqueous solution, and the precipitations of the solid strontium hydroxide remained in a saturated aqueous solution of the Sr ion. When the porous hydrous titania particles were treated in a saturated aqueous solution of the Sr ion, the SrTiO_3 phase was formed, even

Fig. 5. SEM images of the porous particles after hot water treatment at 90 °C for 48 h with various Sr/Ti ratios: (a) Sr/Ti = 1, (b) Sr/Ti = 3, (c) Sr/Ti = 4, and (d) Sr/Ti = 10.

Fig. 6. XRD patterns of the porous particles after hot water treatment at 90 °C for various times (Sr/Ti = 10).

at the low temperature of 25 °C. The treatment in this temperature range cannot be called hot water treatment; hydrous titania particles were merely soaked in the Sr ion aqueous solution. The half-widths of the XRD peaks became narrower with the increasing treatment temperature. After the annealing at 600 °C for 2 h, the anatase phase was newly formed on the particles treated at 25 °C. This result indicates that the hydrous titania remained in the particles and was crystallized to anatase by the annealing. The particles treated at 40 °C and higher were single-phase SrTiO_3 , even after the annealing. This proved that the Sr ions were sufficiently diffused to the center of the particles. The SEM image depicted that the particles treated at 40 and 80 °C have a similar morphology; that is, small spherical protrusions surrounded the original particles. Although solid strontium hydroxide co-existed in the reaction system at the reaction temperature of 40 °C, their existence did not affect the particle morphology.

Fig. 7. SEM images of the porous particles after hot water treatment at 90 °C for (a) 2 h, (b) 6 h, (c) 24 h, and (d) 48 h (Sr/Ti = 10).

Fig. 8. XRD patterns of the porous particles (a) after hot water treatment at various temperatures for 24 h and (b) with additional annealing at 600 °C for 2 h (Sr/Ti = 10).

Fig. 9. SEM images of the porous particles after hot water treatment for 24 h (Sr/Ti = 10) at (a) 25 °C, (b) 40 °C, and (c) 80 °C.

Fig. 10. TEM images of the porous particles (a) hydrous titania, after hot water treatment for 24 h (Sr/Ti = 10) (b) at 40 °C and (c) 80 °C.

Meanwhile, on the particles treated at 25 °C, the spherical protrusions were only locally formed, and the structure of the original particles remained considerably porous. Although the reason for the local formation of the protrusions was not clear, it may be attributable to the variation in the chemical stability and microstructure of the surface of the porous hydrous titania because the dissolution of titanium species at the ethanol washing stage was not uniform. The protrusions seemed to be formed only at the low-stability part.

Figure 10 shows the TEM images of the spherical protrusions formed on the porous hydrous titania particles after hot water treatment at 40 or 80 °C for 24 h. The Sr/Ti ratio in the reaction system was set at 10. The spherical protrusions were composed of fine primary crystallites. The surface of the particles treated at 40 °C had an aggregate structure of fine primary particles similar to the surface of the hydrous titania particles. The crystallites prepared at 80 °C were slightly larger than those prepared at 40 °C. This result is consistent with the crystallite growth expected from the half-width of the XRD peaks.

Figure 11 shows the N₂ adsorption–desorption isotherms of the single-phase SrTiO₃ particles with spherical protrusions around them prepared with a high Sr/Ti ratio of 10. The treatment conditions were at 40 °C for 24 h. The isotherms of the non-treated porous hydrous titania particles and the porous SrTiO₃ particles prepared by hot water treatment at 90 °C for 48 h with the Sr/Ti ratio of 1³⁹⁾ were also shown for comparison. The S_{BET} of the SrTiO₃ particles with spherical protrusions estimated from the isotherm

Fig. 11. N₂ adsorption–desorption isotherms of (a) porous hydrous titania,³⁹⁾ (b) SrTiO₃ particles prepared at 40 °C for 24 h with the Sr/Ti ratio of 10, and (c) SrTiO₃ particles prepared at 90 °C for 48 h with the Sr/Ti ratio of 1³⁹⁾ (closed symbols = adsorption; open symbols = desorption).

was 237 m² g^{−1}. Although this value was lower than that of the porous hydrous titania (357 m² g^{−1}),³⁹⁾ they had approximately twice the value of the porous SrTiO₃ particles prepared at 90 °C for 48 h with the Sr/Ti ratio of 1 (115 m² g^{−1}).³⁹⁾ The specific surface area of the particles treated at 40 °C is lower than that of the particles prepared

using the molten salt method.²⁹⁾ However, as mentioned in the Introduction, this area is quite large for micron-sized single-phase SrTiO₃ particles. Furthermore, the particles were obtained at a temperature of 40 °C without the use of special solvents or ultrasound techniques. On the nitrogen adsorption–desorption isotherms of the SrTiO₃ particles with spherical protrusions [Fig. 11(b)], the rapid increase in the adsorption amount at a low relative pressure region indicated the existence of micropores. Although this rapid increase in the adsorption amount was smaller than that of the porous hydrous titania [Fig. 11(a)], it was much larger than that of the porous SrTiO₃ particles prepared at 90 °C for 48 h. This difference in the porous structure affected the specific surface area of the particles. The TEM image [Fig. 10(b)] depicted those spherical protrusions were constructed with ultrafine primary crystallites. The spaces between these ultrafine crystallites must correspond to the micropores.

From the obtained results, the formation process of small spherical protrusions is discussed as follows: spherical protrusions observed when the Sr/Ti ratio in the reaction system was set at high values cannot be formed via the in situ reaction mechanism. In the initial reaction stage, the top surface parts of the hydrous titania particles would dissolve in the Sr ion solution to some extent. This amount of dissolution is expected to be larger for porous particles with a low chemical stability and a larger surface area in contact with the aqueous solution than that for the spherical ones. The titanium species produced by the dissolution will immediately react with the high Sr ion concentration and lead to a rapid heterogeneous nucleation in or around the macropores of the porous particles with a rough surface. This rapid heterogeneous nucleation all around the porous hydrous titania particles should result in the formation of spherical protrusions consisting of fine crystallites.

The SrTiO₃ particles with a high specific surface area prepared herein could be utilized for various catalysis by incorporating trace metal ion doping⁴⁴⁾ or co-catalyst deposition.¹¹⁾ Moreover, this process is expected to be applied for the low-temperature synthesis of various composite oxide particles with a high specific surface area.

4. Conclusions

Single-phase SrTiO₃ particles with a high S_{BET} of 237 m²g^{−1} were obtained at a low temperature of 40 °C by soaking porous hydrous titania particles in a concentrated Sr ion aqueous solution. In the presence of highly concentrated Sr ions, the porous hydrous titania particles were converted to particles with a characteristic structure, in which small spherical protrusions surrounded the original particles. This method is advantageous for obtaining micron-sized composite oxide particles with high specific surface area at low temperatures without requiring special equipment such as pressure resistant containers or ultrasound-irradiation devices.

Conflict of interests The authors declare that there is no conflict of interest.

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