

NOTE

Low-temperature hydrothermal synthesis and characterization of SrTiO₃ photocatalysts for NO_x degradation

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SrTiO₃ is an excellent photocatalyst due to its high photocorrosion resistance and thermal stability. In this study, we synthesized SrTiO₃ nanoparticles with high specific surface areas by the hydrothermal method at reduced temperature. Titanium(IV) bis(ammonium lactato)dihydroxide (TALH) solution and strontium hydroxide octahydrate [Sr(OH)₂·8H₂O] were used as starting materials. SrTiO₃ nanoparticles were directly synthesized by hydrothermal heating at 150°C for 72–120 h. The synthesized nanoparticles had diameters of 20–40 nm, and the SrTiO₃ powder heated for 72 h exhibited the highest specific surface area of 33.1 m²/g. This sample also showed the highest degradation rate for NO gas.

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Photocatalysts have been drawing widespread attention as environmental purification materials for removing organic pollutants. Since the pioneering study of the Honda-Fujishima effect,¹⁾ the photocatalytic activity of titanium dioxide (TiO₂) and other oxides has been extensively investigated. Among these, strontium titanate (SrTiO₃), is an excellent photocatalyst due to its high photocorrosion resistance and thermal stability. A number of studies report the application of SrTiO₃ to the degradation of organic pollutants^{2)–6)} and to the hydrogen evolution.^{7)–9)}

SrTiO₃ is commonly synthesized by solid-state reaction, but this method requires a high temperature to promote the reaction, and ends up producing particles with large particle sizes, serious agglomeration and low specific surface areas. Yu et al.¹⁰⁾ and Garcia-Lopez et al.¹¹⁾ have pointed out that the synthesis of nanoparticles with high crystallinity and high specific surface areas is effective for improving photocatalytic activities. Various liquid-phase synthesis methods have been reported to satisfy these conditions in recent years. Puangpetch et al.⁴⁾ reported a sol-gel method for the synthesis of mesoporous-assembled SrTiO₃ with the aid of a structure-directing surfactant. Wang et al.¹²⁾ successfully synthesized SrTiO₃ nanoparticles by the solvothermal method with metatitanic acid, and obtained uniform particles with high crystallinity.

The hydrothermal reaction method is also effective in synthesizing nanoparticles with uniform sizes and high crystallinity. The reaction can be promoted at a lower temperature compared to the solid-state method, and the particle sizes and morphologies can be easily controlled by changing the reaction temperature, time, pH and concentration of the precursors. Zhang et al.¹³⁾ proposed a single-step direct hydrothermal synthesis at 220°C, for example, by employing P25 TiO₂ as a titanium precursor without calcination.

Here, we report the hydrothermal synthesis of SrTiO₃ nanoparticles at the much lower temperature of 150°C with titanium(IV) bis(ammonium lactato)dihydroxide (TALH) and strontium hydroxide octahydrate [Sr(OH)₂·8H₂O] as the titanium and strontium sources, as well as an investigation of their photocatalytic activities focusing on the degradation of NO_x gas.

Titanium(IV) bis(ammonium lactato)dihydroxide solution (TALH, Sigma-Aldrich Chemistry Co. LLC) and strontium hydroxide octahydrate [Sr(OH)₂·8H₂O, Wako Pure Chemical Industries, Ltd.] were used as starting materials. They were mixed at an equimolar ratio. 50 mL of 5 M NaOH solution was then added to the mixture, and the obtained suspension was stirred for 30 min. The reaction mixture was then transferred to a Teflon-lined autoclave and heated at 150°C for 72, 96 and 120 h, respectively. After cooling to room temperature, the contents were taken out and washed with distilled water and ethanol several times to remove residual Na⁺ ions. The final products were

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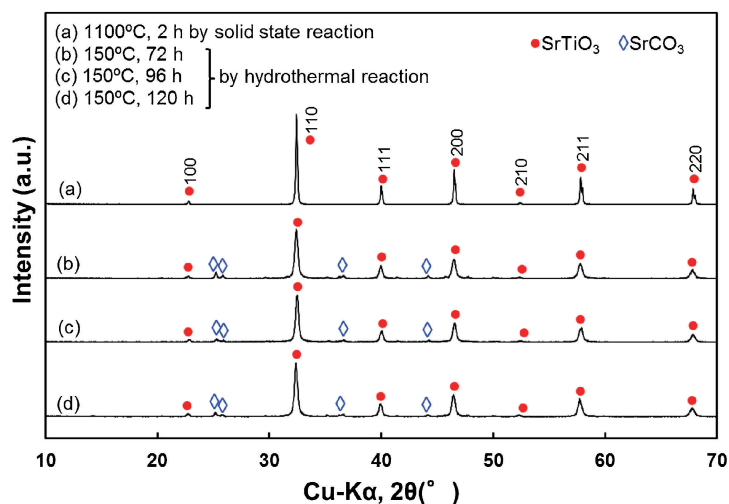


Fig. 1. XRD patterns of SrTiO₃ powders synthesized by (a) solid-state reaction at 1100°C for 2 h, and (b)–(d) hydrothermal reaction at 150°C for: (b) 72 h, (c) 96 h, and (d) 120 h.

obtained by centrifugation and dried in an oven at 80°C for 12 h. For comparison, SrTiO₃ powder was also synthesized by solid-state reaction with strontium carbonate (SrCO₃, Wako Pure Chemical) and TiO₂ anatase (Kojundo Chemical Laboratory Co. Ltd.) at 1100°C for 2 h in an alumina crucible in air.

The crystal structures of the obtained powders were analyzed by X-ray diffraction (XRD, Multiflex, Cu-K α , 40 kV and 40 mA, Rigaku) at a scanning rate of 4°/min in the 2 θ range of 10–70°. The microstructures of the synthesized samples were observed by field-emission scanning electron microscopy (FE-SEM, SU9000, Hitachi High-Technologies). Nitrogen adsorption/desorption isotherms at 77 K of the powders were measured using a gas sorption analyzer (Autosorb-3-AG, Quantachrome).

The photocatalytic activity of the obtained powders was investigated by degradation of NO gas in a flow reactor under irradiation with a 450-W high-pressure mercury lamp.¹⁴⁾ The sample was spread and filled into a hollow (20 mm \times 15 mm \times 0.5 mm) of a glass plate and then placed at the center of the reactor (373 cm³) while 1 ppm NO 50 vol.% air-mixed gas was flowed at a rate of 200 cm³/min. Prior to the light irradiation, NO gas was flowed for ca. 15 min to satisfy the adsorption equilibrium and stabilize the gas concentration. The wavelengths of the lamp were controlled by two filters: a 510-nm cut-off filter (Fuji, triacetyl cellulose) and a 400-nm cut-off filter (Kenko, L41 Super Pro (W)). The measuring time under each wavelength was maintained at 10 min. The concentration of NO was checked with a NO_x analyzer (Yanaco, ECL-88A).

Figure 1 shows the XRD patterns of synthesized SrTiO₃ powders. All the samples exhibited a perovskite-type structure of SrTiO₃ (JCPDS Card No. 35-0734). As shown in Fig. 1(a), single-phase SrTiO₃ with no detectable impurities was obtained by the solid-state reaction. SrTiO₃ with trace SrCO₃ was obtained by the hydrothermal reaction. To analyze this result quantitatively, we calculated the weight ratio of the residual SrCO₃ in each sample by

the two-component calibration curve method. The integrated intensities of the SrTiO₃ 110 and the SrCO₃ 111 peaks were measured by analyzing the XRD patterns of mixed powders of commercial SrTiO₃ and SrCO₃ (SrTiO₃: SrCO₃ = 10:0, 8:2, 6:4, 4:6 and 2:8), and the calibration curve was prepared. As a result, 12.0, 10.6 and 10.1 vol.% of SrCO₃ were estimated to remain in samples (b)–(d), respectively. Although a slight residual SrCO₃ phase remained, we succeeded in synthesizing \sim 90% SrTiO₃ powders, even at 150°C. The crystallite sizes of (b)–(d) estimated from Scherrer's equation were 27.0, 31.2 and 41.7 nm, respectively. Note that the bandgap of the SrCO₃ phase was reported to be 3.17 eV,¹⁵⁾ similar to that of the SrTiO₃ main phase.

Figure 2 shows the microstructure of synthesized SrTiO₃ powders. The particle sizes of SrTiO₃ powder synthesized by solid-state reaction [Fig. 2(a)] were 200–300 nm, whereas those for the hydrothermal reaction [Figs. 2(b)–2(d)] had diameters of 20–40 nm, which were in good agreement with the values from XRD analysis. The hydrothermal method inhibited grain growth remarkably, and the particle sizes clearly became smaller. There was no significant difference in particle size or morphology among the three samples, despite changes in the heating time [Figs. 2(b)–2(d)].

Figure 3 represents the N₂ adsorption/desorption isotherms and BET plots of synthesized SrTiO₃ powders. No samples had mesopores, and it was found that multi-layer adsorption took place, as determined by the International Union of Pure and Applied Chemistry (IUPAC) type-III hysteresis loop. The specific surface area (SSA) calculated by the BET method of the powder synthesized by solid-state reaction was relatively small, 2.88 m²/g [Fig. 3(a)]. Those of powders synthesized by the hydrothermal reaction, on the other hand, had much higher SSAs of 33.1, 27.7 and 26.0 m²/g [Figs. 3(b)–3(d)].

Figure 4 shows NO degradation rates for the powders at wavelengths λ of >510 , >400 and >290 nm. As

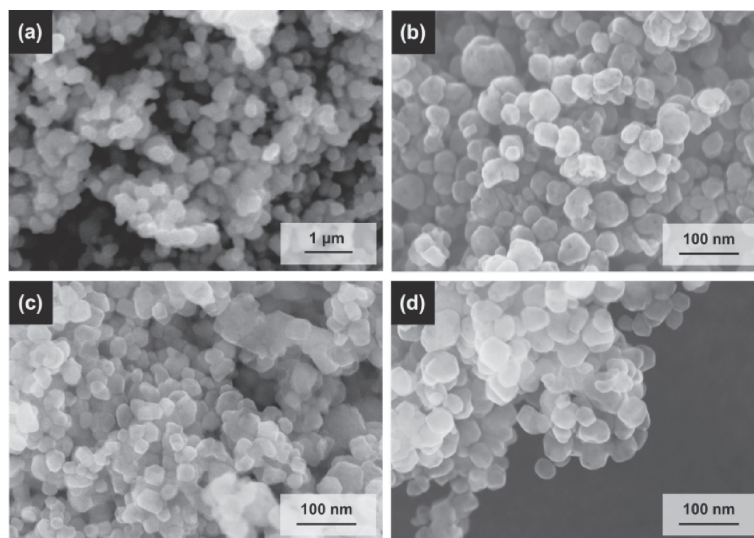


Fig. 2. SEM micrographs of SrTiO₃ powders synthesized by (a) solid-state reaction at 1100°C for 2 h, and (b)–(d) hydrothermal reaction at 150°C for: (b) 72 h, (c) 96 h, and (d) 120 h.

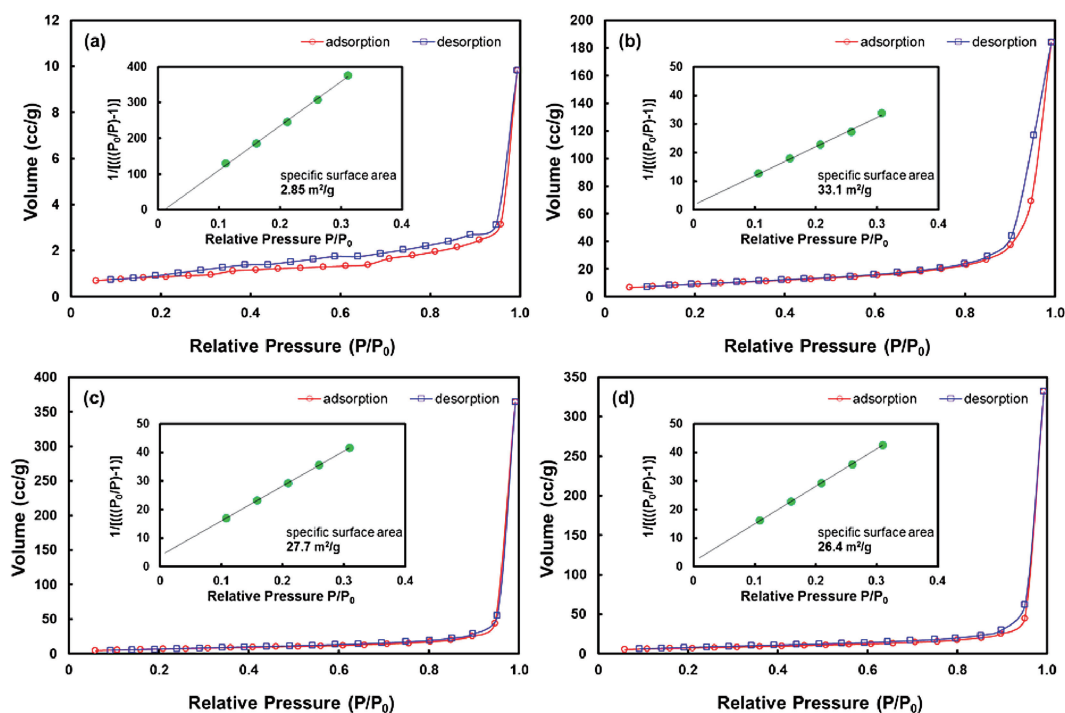


Fig. 3. Nitrogen adsorption/desorption isotherms and BET plots (inserts) of SrTiO₃ powders synthesized by (a) solid-state reaction at 1100°C for 2 h, and (b)–(d) hydrothermal reaction at 150°C for: (b) 72 h, (c) 96 h, and (d) 120 h.

expected from the bandgap of 3.2 eV, the photocatalytic activities of all the samples were insufficient in the visible light regions (>510 and >400 nm). However, the photocatalytic activities of the solid-state sample (a) and the hydrothermal reaction sample (b) became much higher in the UV-containing region (>290 nm). Sample (b), which had lower crystallinity but a larger surface area, showed similar photocatalytic activity to that of sample (a). It is worthy of note that NO gas was flowed for ca. 15 min to satisfy the adsorption equilibrium and to stabilize the gas concentration prior to light irradiation. The decrease in

the NO gas concentration was thus not caused by further adsorption of NO gas on the particle surface but by photodegradation.

In order to verify the effect of remnant SrCO₃, the photocatalytic activity of pure SrCO₃ (using a commercial powder, Wako Chemical) was evaluated (see Fig. S1). The evaluation clearly showed that pure SrCO₃ evidenced little activity in the visible light region and showed much weaker activity than SrTiO₃ in the UV light region.

In conclusions, SrTiO₃ nanoparticles were successfully synthesized by hydrothermal reaction, even at 150°C for

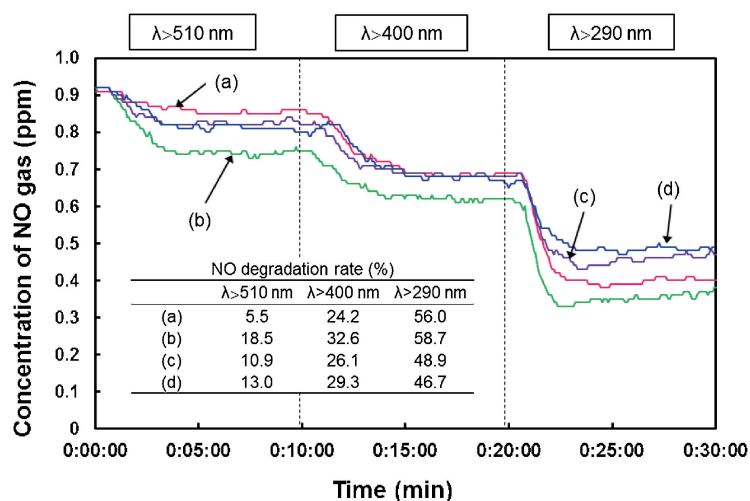


Fig. 4. NO gas degradation of SrTiO₃ powders synthesized by (a) solid-state reaction at 1100°C for 2 h, and (b)–(d) hydrothermal reaction at 150°C for: (b) 72 h, (c) 96 h, and (d) 120 h.

72–120 h, which was a much lower temperature compared to those of conventional methods. The synthesized nanoparticles had diameters of 20–40 nm, and the SrTiO₃ powder heated for 72 h exhibited the highest specific surface area of 33.1 m²/g. This sample also showed the highest degradation rate for NO gas.

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References

- 1) A. Fujishima and K. Honda, *Nature*, **238**, 37–38 (1972).
- 2) M. Miyauchi, M. Takashio and H. Tobimatsu, *Langmuir*, **20**, 232–236 (2004).
- 3) T. Ohno, T. Tsubota, Y. Nakamura and K. Sayama, *Appl. Catal. A-Gen.*, **288**, 74–79 (2005).
- 4) T. Puangpetch, T. Sreethawong, S. Yoshikawa and S. Chavadej, *J. Mol. Catal. A-Chem.*, **287**, 70–79 (2008).
- 5) J. Xu, Y. Wei, Y. Huang, J. Wang, X. Zheng, Z. Sun, L. Fan and J. Wu, *Ceram. Int.*, **40**, 10583–10591 (2014).
- 6) G. Wu, P. Li, D. Xu, B. Luo, Y. Hong, W. Shi and C. Liu, *Appl. Surf. Sci.*, **333**, 39–47 (2015).
- 7) H. Kato and A. Kudo, *J. Phys. Chem. B*, **106**, 5029–5034 (2002).
- 8) R. Konta, T. Ishii, H. Kato and A. Kudo, *J. Phys. Chem. B*, **108**, 8992–8995 (2004).
- 9) T. Puangpetch, S. Chavadej and T. Sreethawong, *Energ. Convers. Manage.*, **52**, 2256–2261 (2011).
- 10) H. Yu, S. Ouyang, S. Yan, Z. Li, T. Yu and Z. Zou, *J. Mater. Chem.*, **21**, 11347–11351 (2011).
- 11) E. Garcia-Lopez, G. Marci, B. Megna, F. Parisi, L. Armelao, A. Trovarelli, M. Boaro and L. Palmisano, *J. Catal.*, **321**, 13–22 (2015).
- 12) N. Wang, D. Kong and H. He, *Powder Technol.*, **207**, 470–473 (2011).
- 13) Y. Zhang, L. Zhong and D. Duan, *J. Mater. Sci.*, **51**, 1142–1152 (2016).
- 14) S. Yin, D. Maeda, M. Ishitsuka, J. Wu and T. Sato, *Solid State Ionics*, **151**, 377–383 (2002).
- 15) S. Ni, X. Yang and T. Li, *Mater. Lett.*, **65**, 766–768 (2011).