SPECIAL ARTICLE

*The 70th CerSJ Awards for Advancements in Ceramic Science and Technology: Review***Low-temperature solid-state reduction approach to highly reduced titanium oxide nanocrystals**Yoshihiro TSUJIMOTO^{1,†}¹Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Considerable attention has been paid to reduced transition metal nanomaterials because they exhibit attractive properties for practical applications in fuel cells, memory or thermoelectric devices, and photocatalysts. In particular, a series of oxygen-nonstoichiometric titanium oxides has advantages such as abundance of the elements, non-toxicity, corrosion resistance, and high electrical conductivity. However, the control of nanostructures is not straightforward because a high-temperature reductive condition is required for the synthesis of highly reduced metal oxides. Recently, it has been demonstrated that the novel low-temperature reduction technique can afford highly reduced titania nanoparticles with different particle sizes ranging from 20 to 300 nm diameter. This review article is focused on the synthesis of corundum-type Ti_2O_3 nanoparticles, the reaction mechanism, and the correlation between structure and physical properties.

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Key-words : Transition metal oxides, Nanocrystals, Low-temperature reduction, Ti_2O_3 , Metal-insulator transition

[Received March 3, 2018; Accepted May 10, 2018]

I. Scope and policy

1. Introduction

Band gap insulators based on early transition metals, such as TiO_2 and WO_3 , are of great interest because of their practical applications in photocatalysts, Li-ion battery anodes, pigments, and dielectric devices.^{1)–3)} Interestingly, oxygen removal from these insulators, which involves complex structure modification, drastically changes the physical properties. One of the most important examples is the family of $\text{Ti}_n\text{O}_{2n-1}$ ($2 \leq n$), which has been extensively investigated over the last half century.^{4)–6)} The phase with $4 \leq n \leq 10$ is termed the Magnéli phase. Ti_2O_3 ($n = 2$) is isostructural with corundum $\alpha\text{-Al}_2\text{O}_3$. As shown in **Fig. 1**, the rutile structure is built up with one-dimensional chains of edge-sharing TiO_6 octahedra linked with another chains by sharing corners. In the corundum structure, each Ti-centered octahedron shares one face along the c axis and three edges in the ab plane with each other. $\text{Ti}_n\text{O}_{2n-1}$ ($4 \leq n \leq 10$) has rutile-like slabs with n octahedral thickness, each of which is connected by corner- and face-sharing. These oxygen-deficient phases exhibit high electrical conductivity at room temperature, which provides good opportunities for a new class of titania-based electronic devices, such as electrodes of fuel cells and resis-

Fig. 1. Crystal structure of TiO_2 , Ti_4O_7 , and Ti_2O_3 .

tance random access memory.^{7)–9)} For their practical applications, it is crucial to control the nanostructures of reduced titania. However, high-temperature reducing conditions are required to prepare highly reduced titania, which results in breaking of the nanostructures.

In this review paper, a novel approach to nanostructured reduced titania is presented: a low-temperature reduction method using binary metal hydride as a reducing agent. This reaction method was employed for the first time by Hayward and Rosseinsky in 1999 to synthesize LaNiO_2 with a square planar NiO_4 .¹⁰⁾ Metal hydrides such as NaH and CaH_2 exhibit strong reducing power even at temperatures as low as 500°C , which allows us to design in a topotactic manner complex metal oxides with unusual coordination environments. I successfully synthesized Ti_2O_3 of nanoparticles and nanorods by the reaction of TiO_2 nanocrystals with CaH_2 and systematically investigated the effects of size reduction on their structural and physical properties.^{11),12)}

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2. Low-temperature reduction for oxygen-deficient titanium oxide nanoparticles

Commercially available TiO_2 nanoparticles (average diameter: 20 nm) with rutile structure (space group, $P4_2/mnm$) were reduced to Ti_2O_3 with corundum structure ($R3-c$) by reaction with CaH_2 powder, maintaining the nanomorphology.¹¹ TiO_2 , which was preheated at 200°C for several hours, was thoroughly mixed with CaH_2 in a molar ratio of 1:4 in an Ar-filled glovebox. The mixture was pressed into a pellet, sealed in a Pyrex tube under vacuum without exposure to air, and then heated at 350°C in a tubular furnace for several days with intermediate grindings. Finally, the samples were washed with a 0.1 M solution of NH_4Cl in methanol to remove residual CaH_2 and the byproduct CaO . After filtration, bluish black powders were obtained (see Fig. 2). Note that ‘bulk’ Ti_2O_3 prepared at elevated temperatures is dark brown. Complete removal of calcium species was confirmed by energy dispersive X-ray analysis.

Figure 3 shows the room-temperature synchrotron X-ray diffraction (SXRD) patterns of the rutile TiO_2 precursor and the product reduced for 4 or 10 days, measured using a Debye–Scherrer camera installed on BL15XU at SPring-8 at a wavelength of 0.65298 Å. After reaction for 4 days, the SXRD patterns drastically changed: the rutile phase fully disappeared and new peaks appeared. The major peaks of the product can be readily indexed to a hexagonal cell [$a = 5.0826(3)$ Å, $c = 13.6864(14)$ Å, $V = 306.19(4)$ Å³] with the space group $R3-c$, which is similar to Ti_2O_3 structure.⁶ Compared with the lattice constants of bulk Ti_2O_3 [$a = 5.15443(1)$ Å, $c = 13.60810(2)$ Å, $V = 313.1051(7)$ Å³], the a axis is contracted and the c axis is

Fig. 2. Photographs of the pellets of 20-nm-diameter TiO_2 , 20-nm-diameter Ti_2O_3 , and sintered Ti_2O_3 .¹²⁾

Fig. 3. Synchrotron X-ray powder diffraction patterns of rutile TiO_2 nanoparticle and samples reduced for 4 or 10 days at 350°C.¹¹⁾

elongated. Several weak reflections could be assigned to Ti_4O_7 (space group $P-1$), a member of the Magnéli phase. The volume reduction involving the anisotropic volume change is attributed to the surface strain effects caused by particle-size reduction to a nanometric scale. In fact, transmission electron microscopy (TEM) observation revealed that no apparent particle growth occurred after the reduction [Figs. 4(a) and 4(c)]. In addition, the Brunauer–Emmett–Teller (BET) measurements revealed that the product retained 80% of the specific surface area of the precursor (80.72 m²/g). The high-resolution TEM (HRTEM) images of TiO_2 and Ti_2O_3 nanoparticles are shown in Figs. 4(b) and 4(d), respectively, and the insets show selected area electron diffraction (SAED) patterns. The SAED patterns of the samples are consistent with the diffraction patterns expected from the rutile and corundum structures. The HRTEM images exhibit good crystallinity and uniformly spaced lattice fringes in each particle, indicating that each particle maintains the single-domain structure even after the reduction. These results are very surprising because the reductive reaction proceeds in a non-topotactic manner involving displacement of titanium atoms.

Next, the consequence of using anatase nanoparticles with 20 nm diameter and the surface area of 61.72 m²/g as a precursor was explored. Figure 5 shows the SXRD data of the products reduced at 350°C for 4, 8, or 12 days. As in the case of rutile, anatase reduced into Ti_2O_3 after 4 days, but the precursor remained in the products even after 8 days. No intermediate phases such as Ti_4O_7 are observed; however, the brookite phase formed together with Ti_2O_3 , retaining the ratio of relative intensities. It is worth noting that the reduction of anatase with CaH_2 involves particle growth. The specific surface areas reduced with increasing reaction time, for example, by 40% with respect to the original surface area after 12 days. This result suggests that not only the low-temperature treatment, but also the structural framework of the precursor are important factors for

Fig. 4. TEM and HRTEM images of (a, b) TiO_2 and (c, d) Ti_2O_3 nanoparticles. The insets of (b) and (d) are selected-area electron diffraction patterns.¹²⁾

Fig. 5. Synchrotron X-ray powder diffraction patterns of anatase TiO_2 nanoparticle and its reduced products.

Fig. 6. X-ray powder diffraction patterns of Ti_2O_3 nanoparticles with different sizes.¹²⁾

maintaining the nanomorphology. As described above, Ti_4O_7 , which is observed as an intermediate phase in the reaction of rutile with CaH_2 , has structural features common to both rutile and corundum structures. Thus, the formation of this phase plays a crucial role in suppressing the displacement of Ti atoms during the reductive reaction. Attempts were made to obtain Ti_4O_7 as a single phase by controlling the reaction time and temperature; however, mixed phases were always obtained with the precursor or corundum phase.

3. Nanoparticles and nanorods with different sizes

The low-temperature reduction is applicable to the synthesis of Ti_2O_3 nanoparticles and nanorods with different sizes.¹²⁾ Figure 6 shows the XRD patterns ($\text{Cu K}\alpha$) of the reduced products, which exhibit a broadening of the diffraction peaks with decreasing particle size. For nanoparticles with 70 and 300 nm diameters, the corundum phase is also obtained as the main phase; however, some low-intensity uncharacterized peaks appeared as minor phases for nanoparticles with 300 nm diameter. It should be noted that the reaction time increases with increasing particle size or surface area. Reduction with CaH_2 proceeds through a solid-solid reaction between the reductant and precursors,

Fig. 7. TEM and HRTEM images of (a, b) 300-nm-diameter TiO_2 nanoparticles and (c, d) their reduced samples.¹²⁾

Fig. 8. SEM images of (a) TiO_2 nanorods and (b) Ti_2O_3 nanorods. (c), (d) TEM and HRTEM images of the reduced nanorods.

and thus the physical contact between them is the key to promoting the reductive reaction. Indeed, TiO_2 nanoparticles with 20 and 70 nm diameters and high surface areas were completely reduced to Ti_2O_3 within 8 days. However, the nanoparticles with 300 nm diameter and a much lower surface area ($6.36 \text{ m}^2/\text{g}$) required 20 days.

Figure 7 shows the TEM and HRTEM images of TiO_2 and Ti_2O_3 nanoparticles with 300 nm diameter, which reveals that the nanomorphology and particle size are no longer maintained. The TiO_2 nanoparticles possess uniform size, spherical morphology, and a single-domain structure, while the nanoparticles after reduction broke into pieces, resulting in 21% increase in surface area. The HRTEM images of the reduced phase exhibit lattice fringes running in different directions between each other. These results are in marked contrast to those of 20-nm-diameter nanoparticles. The observed multi-domain formation can be accounted for by considering the drastic structural rearrangement. In relatively large particles, the stress from the

Fig. 9. Size dependence of volume and Ti-Ti bond lengths of Ti_2O_3 nanoparticles and bulk Ti_2O_3 .¹²⁾

displacement of Ti atoms and shearing motion is too great to maintain the single-domain structure of the precursor. The formation of multi-domain structures and broken particles results from the release of this stress energy.

Ti_2O_3 nanorods with 100 nm diameter and $\sim 1 \mu\text{m}$ length can also be obtained as a single phase by the low-temperature reduction. **Figures 8(a) and 8(b)** show the scanning electron microscopy (SEM) images of TiO_2 and Ti_2O_3 nanorods, and **Figs. 8(c) and 8(d)** show the TEM and HRTEM images, respectively. These TEM images reveal that the single domain structure is maintained; however, the size and morphology are not maintained. As seen in the SEM images, the precursor is greater than $1 \mu\text{m}$ in length, but the reductive reaction results in the breaking of the rods and roughing of the surfaces. The BET measurements reveal an increase in specific surface area from 10.6 to $13.2 \text{ m}^2/\text{g}$. These results are very similar to those of 300-nm-diameter nanoparticles. It should be noted that the morphological degradation observed in nanorods is caused by non-topotactic structural transformation, not by the grinding of TiO_2 nanorods with CaH_2 powders.

4. Size dependence of structural and physical properties

The successful synthesis of Ti_2O_3 nanoparticles with different sizes enables us to systematically investigate the effects of particle size on structural and physical properties.¹²⁾ Bulk Ti_2O_3 exhibits an unusual metal-to-insulator transition (MIT) in a wide temperature range from 420 ($= T_{\text{MIT}}$) to 550 K.^{6,13,14)} The sluggish transition of Ti_2O_3 is in sharp contrast to an abrupt MIT observed in Ti_4O_7 involving the charge ordering of $\text{Ti}^{3+}/\text{Ti}^{4+}$.¹⁵⁾ Each TiO_6 octahedron in Ti_2O_3 is subjected to a slight trigonal distortion, which results in the splitting of the three-fold degenerate t_{2g} orbitals into a low-lying a_{1g} orbital directed along the c axis and two e_g^π orbitals directed toward the next-nearest neighbor Ti ions in the basal plane.^{16,17)} The MIT involves a gradual elongation of the Ti-Ti dimer along the c axis upon heating, which results in the narrowing of the energy gap between the bonding a_{1g} and anti-bonding a_{1g}^* bands. Because the e_g^π and $e_g^{*\pi}$ bands are located between the a_{1g} and a_{1g}^* bands, the semiconducting gap between the a_{1g} and e_g^π bands is closed across the MIT.¹⁶⁾

Given the strong correlation between the structure and

Fig. 10. UV-vis-NIR spectra of Ti_2O_3 nanoparticles and the bulk Ti_2O_3 .¹²⁾

the electronic properties of Ti_2O_3 , the particle-size reduction can be expected to affect the MIT. **Figure 9** shows the particle-size dependence of the volume, and the bond lengths of the Ti(1)-Ti(3) dimers in the basal plane and the Ti(1)-Ti(2) dimer along the c axis. The volume and the intradimer distances monotonically shrunk with decreasing particle size. It is worth noting that the shrinkage of the Ti(1)-Ti(2) bond increases the bandwidth of the Ti 3d bands. This is confirmed from the ultraviolet visible near infrared (UV-vis-NIR) spectra shown in **Fig. 10**, where two peaks centered at 378 and 514 nm corresponding to the $a_{1g}-a_{1g}^*$ and $a_{1g}-e_g^{*\pi}$ interband transitions,¹⁸⁾ respectively, broadened with decreasing particle size. The increasing bandwidth leads to narrowing of the semiconducting gap. **Figure 11** shows the temperature dependence of the electrical resistivity (ρ) of 20-nm-diameter sample and bulk Ti_2O_3 . Although the ρ of bulk Ti_2O_3 does not show any anomaly up to 400 K,¹⁹⁾ the ρ vs T curve for the nanoparticles exhibits a steep drop at 350 K, which results from the onset of MIT. The reduction in T_{MI} by particle-size reduction is the first observation for Ti_2O_3 .

5. Summary

Corundum Ti_2O_3 nanoparticles and nanorods with different sizes have been successfully synthesized by low-temperature reduction using CaH_2 . The crystal structure, particle type and size of the parent materials play important roles in yielding homogeneous, high-quality Ti_2O_3 nanocrystals because of kinetics. Recently, similar tech-

Fig. 11. Temperature dependence of the resistivity of Ti_2O_3 nanoparticles and bulk Ti_2O_3 .¹²⁾

niques have been applied not only to nanoparticles, but also to thin films and core-shell structures.^{20)–22)} We expect that the low-temperature reduction will open up the possibility of designing nanostructures of highly reduced phases, leading to new functional properties that cannot emerge in the bulk form.

Acknowledgement The author thanks all the collaborators for contributing to his studies. A part of our work was supported by JSPS KAKENHI (15K17837, 25289233, 50584075, 16H0648, 17K14466, 17H05493, 16H04501)

References

- 1) J. Pan, G. Liu, G. Q. Lu and H.-M. Cheng, *Angew. Chem. Int. Edit.*, **50**, 2133–2137 (2011).
- 2) D.-D. Qin, C.-L. Tao, S. A. Friesen, T.-H. Wang, O. K. Varghese, N.-Z. Bao, Z.-Y. Yang, T. E. Mallouk and C. A. Grimes, *Chem. Commun.*, **48**, 729–731 (2012).
- 3) K. J. Griffith, A. C. Forse, J. M. Griffin and C. P. Grey, *J. Am. Chem. Soc.*, **138**, 8888–8899 (2016).
- 4) L. A. Bursill and B. G. Hyde, *Prog. Solid State Ch.*, **7**, 177–253 (1972).
- 5) S. Andersson, A. Sundholm and Magnéli, *Acta Chem. Scand.*, **13**, 989–997 (1959).
- 6) C. E. Rice and W. R. Robinson, *Acta Crystallogr. B*, **33**, 1342–1348 (1977).
- 7) S. Ohkoshi, Y. Tsunobuchi, T. Matsuda, K. Hashimoto, A. Namai, F. Hakoe and H. Tokoro, *Nat. Chem.*, **2**, 539–545 (2010).
- 8) C. Yao, F. Li, X. Li and D. Xia, *J. Mater. Chem.*, **22**, 16560–16565 (2012).
- 9) D.-H. Kwon, K. M. Kim, J. H. Jang, J. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim and C. S. Hwang, *Nat. Nanotechnol.*, **5**, 148–153 (2010).
- 10) M. A. Hayward, M. A. Green, M. J. Rosseinsky and J. Sloan, *J. Am. Chem. Soc.*, **121**, 8843–8854 (1999).
- 11) S. Tominaka, Y. Tsujimoto, Y. Matsushita and K. Yamaura, *Angew. Chem. Int. Edit.*, **50**, 7418–7421 (2011).
- 12) Y. Tsujimoto, Y. Matsushita, S. Yu, K. Yamaura and T. Uchikoshi, *J. Asian Ceram. Soc.*, **3**, 325–333 (2015).
- 13) C. E. Rice and R. Robinson, *Mater. Res. Bull.*, **11**, 1355–1360 (1976).
- 14) J. M. Honig and T. B. Reed, *Phys. Rev.*, **174**, 1020–1026 (1968).
- 15) M. Taguchi, A. Chainani, M. Matsunami, R. Eguchi, Y. Tanaka, M. Yabashi, K. Tamasaku, Y. Nishino, T. Ishikawa, S. Tsuda, S. Watanabe, C.-T. Chen, Y. Senba, H. Ohashi, K. Fujiwara, Y. Nakaura, H. Takagi and S. Shin, *Phys. Rev. Lett.*, **104**, 106401 (2010).
- 16) L. L. Van Zandt, J. M. Honig and J. B. Goodenough, *J. Appl. Phys.*, **39**, 594–595 (1968).
- 17) A. Mooradian and P. M. Raccach, *Phys. Rev. B*, **3**, 4253–4256 (1971).
- 18) M. Uchida, J. Fujioka, Y. Onose and Y. Tokura, *Phys. Rev. Lett.*, **101**, 066406 (2008).
- 19) C. N. R. Rao, R. E. Loehman and J. M. Honig, *Phys. Lett.*, **27A**, 271–272 (1968).
- 20) A. Kitada, S. Kasahara, T. Terashima, K. Yoshimura, Y. Kobayashi and H. Kageyama, *APEX*, **4**, 035801 (2011).
- 21) L. Seinberg, S. Yamamoto, R. Gallage, M. Tsujimoto, Y. Kobayashi, S. Isoda, M. Takano and H. Kageyama, *Chem. Commun.*, **48**, 8237–8239 (2012).
- 22) S. Yamamoto, G. Ruwan, Y. Tamada, K. Kohara, Y. Kusano, T. Sasano, K. Ohno, Y. Tsujii, H. Kageyama, T. Ono and M. Takano, *Chem. Mater.*, **23**, 1564–1569 (2011).

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