Nanomaterials

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Synthesis of Nanostructured Reduced Titanium Oxide: Crystal Structure Transformation Maintaining Nanomorphology**

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There is an increasing need for the synthesis of nanostructured reduced oxides because of their attractive properties; for example, compared with titanium dioxide (TiO_2), reduced titanium oxides are attractive for photovoltaics, photocatalysts, and fuel cells owing to their narrow band gap enabling absorption of visible light,[1,2] chemical stability, and relatively high electrical conductivity, comparable to that of graphite.[3] Generally, reduced titanium oxides have been synthesized by 1) thermal reduction of TiO_2 at about 1000 °C with H_2 gas or Ti powder,[4,5] 2) photochemical reduction of TiO_2 with UV laser irradiation,[6,7] or 3) direct synthesis from unique precursors or using laser ablation techniques.[2,8] These reductive techniques in turn cause particle growth or compositional inhomogeneity,[7,9] making it difficult to obtain high-quality nanostructures. Ti_4O_7 and Ti_8O_{15} nanowires were synthesized by annealing $H_2Ti_3O_7$ nanowires in a hydrogen atmosphere.[2] These nanostructures seem the most sophisticated reported so far; however, particle growth is inevitable and the method seems to be inapplicable to other nanostructures. Since nanostructures are of significant importance for exploiting reduced titanium oxides,[10] development of novel techniques for synthesizing them on the nanoscale is needed. Herein we report a novel method for synthesizing nanostructured reduced titanium oxides by reducing nanostructured TiO_2 with a strong reducing agent at much lower temperatures than in conventional techniques. Interestingly, nanostructured reduced titanium oxide with the same morphology as its precursor was obtained, though its crystal structure was transformed from the tetragonal to the hexagonal system. The synthesis is applicable to other nanostructured titanium dioxides, and thus opens up fascinating possibilities for designing nanostructures of reduced titanium oxides for a wide range of applications.

We chose TiO_2 nanoparticles with rutile structure (tetragonal, $P4_2/mnm$), which is a high-temperature phase obtained above about 800 °C and irreversibly stable at room temperature, as precursor. The as-received TiO_2 nanoparticles were thoroughly mixed with a fourfold molar excess of CaH_2 powder, and then heated at 350 °C for 15 d. Low-temperature reduction with binary metal hydrides was first demonstrated by Hayward et al., who used solid NaH as a reducing agent to topotactically synthesize infinite-layer $LaNiO_2$ from perovskite $LaNiO_3$.[11] Since then, alkali and alkaline earth metal hydrides such as CaH_2 and LiH have been employed by Hayward et al. and others to obtain unprecedented reduced phases inaccessible by conventional reduction techniques.[12] The powerful reducing activity even at low temperatures of such binary metal hydrides was expected to enable us to synthesize nanostructured reduced titanium oxides from nanostructured TiO_2. The final product was a black powder (see Figure 3), which is typical for reduced titanium oxides.[5]

Figure 1 compares the synchrotron powder X-ray diffraction (SXRD) patterns of the rutile TiO_2 precursor and the reduced product. After reduction, SXRD patterns significantly changed; all major peaks of the product were readily

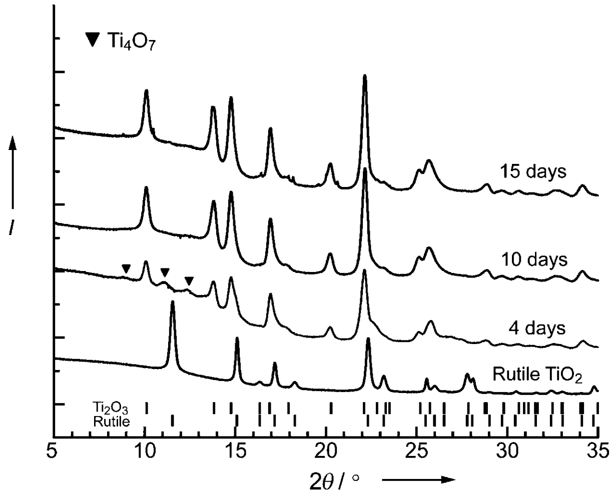

Figure 1. SXRD patterns of the TiO_2 nanoparticles reduced at 350 °C for 4, 10, or 15 d. Vertical marks represent the allowed Bragg peak positions for Ti_2O_3 (top) and rutile TiO_2 (bottom).

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indexed in the hexagonal system with lattice constants of $a=5.0745(4)$, $c=13.7516(12)$ Å, and $V=306.67(4)$ Å^3, which correspond to the corundum Ti_2O_3 phase (hexagonal, $R\bar{3}c$; see Figure 2b). Compared with the values of bulk Ti_2O_3 ($a=5.1570(4)$, $c=13.610(1)$ Å, $V=313.46(2)$ Å^3), the a axis has contracted and the c axis expanded, probably because the low-temperature reaction could not relieve the stress caused by lattice transformation; moreover, such lattice strain may provide different properties.[13] This reduced titanium oxide with corundum structure is reported to be a semiconductor that absorbs visible light and has a relatively high conductivity of about 0.1 kS cm^{-1} at room temperature.[14] Several weak reflections assignable to a Magnéli phase of Ti_4O_7 (triclinic, $I\bar{1}$; see Figure 2c) were also visible as a minor phase after reduction for 4 d, but completely disappeared after further reduction for at least 6 d.

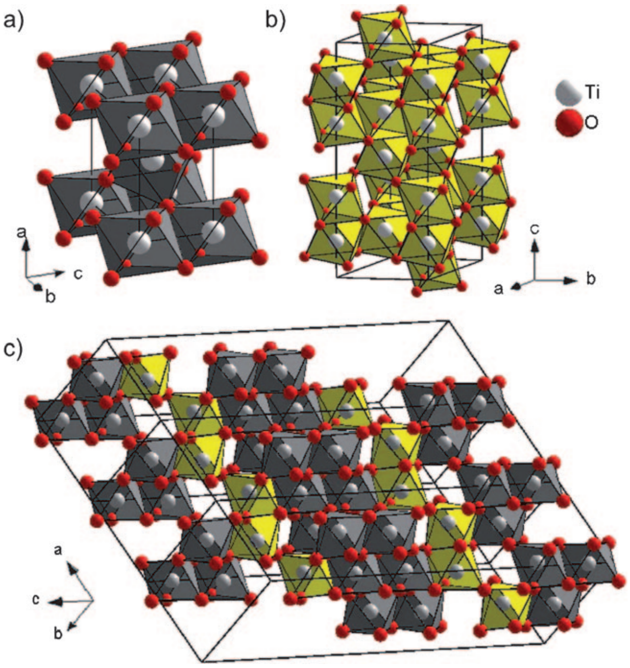

Figure 2. Schematic illustrations of crystal structures of titanium oxides. a) TiO_2 of rutile structure. b) Ti_2O_3 of corundum structure. c) Ti_4O_7 Magnéli phase. The black octahedra indicate edge-sharing sites, and the yellow ones face-sharing sites.

The above results show that the TiO_2 precursor was successfully reduced to Ti_2O_3, and the crystal structure transformed from the tetragonal to the hexagonal system. Interestingly, possible intermediates, namely, Magnéli phases Ti_nO_{2n-1} ($n>4$), were not observed, and both the crystallinity and the homogeneity of the product seemed high, given the low temperature used and the small particles. Since the intermediates are reported to have approximately ten times larger entropies than TiO_2, Ti_4O_7, and Ti_2O_3,[15] the absence of such entropically favored Magnéli phases means that enthalpies dominated the Gibbs energy of the system. That is, the use of the strong reducing agent CaH_2 not only enhanced the reaction rate but also made the reduction reaction more enthalpically favorable, that is, decreased the amount of intermediates. Thus, low-temperature reduction resulted in such relatively homogeneous Ti_2O_3 products, and this feature is also an important aspect of low-temperature reduction with a strong reducing agent.

To investigate the influence of crystal structure change on the morphology, the microstructure was observed by SEM and TEM. As shown in Figure 3a and b, the reduced powder was composed of ricelike nanoparticles of about 20 nm in width and about 50 nm in length. Interestingly, this morphology is exactly the same as that of the precursor, that is, reduction removed oxygen atoms without changing the morphology of the particles. Nanobeam electron diffraction (ED) patterns (Figure 4) revealed that each individual particle consists of a single crystal domain of tetragonal ED pattern for TiO_2 or trigonal ED pattern for Ti_2O_3. These results support the transformation from TiO_2 of rutile structure to Ti_2O_3 of corundum structure, as determined by SXRD. Thus, low-temperature reduction yields well-crystallized Ti_2O_3 nanoparticles with exactly the same morphology as the precursor.

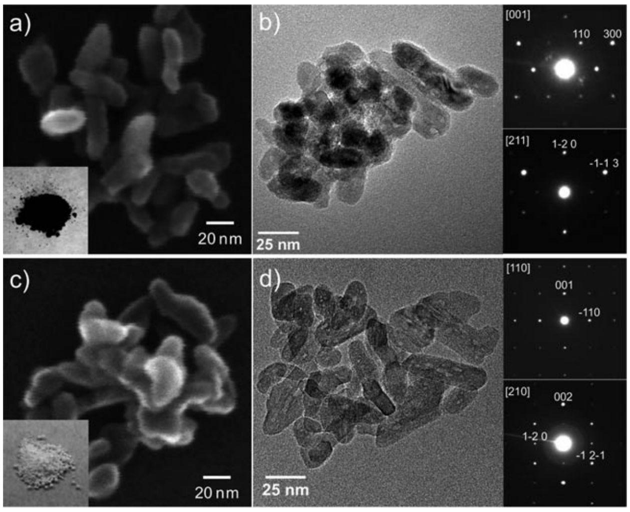

Figure 3. Electron microscopy analyses of the reduced TiO_2 nanoparticles (a,b) and the rutile TiO_2 precursor (c,d). a,c) SEM images. The insets are photographs of the powders. b,d) TEM images and nanobeam electron diffraction patterns of one particle.

In the mechanism of reduction maintaining nanomorphology, we consider that formation of Ti_4O_7 as an intermediate phase is of primary importance on the basis of SXRD measurements. As illustrated in Figure 2, rutile TiO_2 consists of edge-sharing octahedral chains linked to each other by corner sharing while corundum Ti_2O_3 consists of face-sharing Ti_2O_9 octahedral dimers linked to each other by corner and edge sharing. Ti_4O_7 is a member of the homologous series of Ti_nO_{2n-1} ($n\geq 4$), which has rutile blocks interleaved with corundum-like layers (see Figure 2). The presence of this dual-structure intermediate should play a crucial role in maintaining the nanomorphology during the reduction reaction. This consideration is supported by the results obtained for the reduction of crystalline-oriented TiO_2 thin film and anatase TiO_2 nanoparticles (see the Supporting Information).

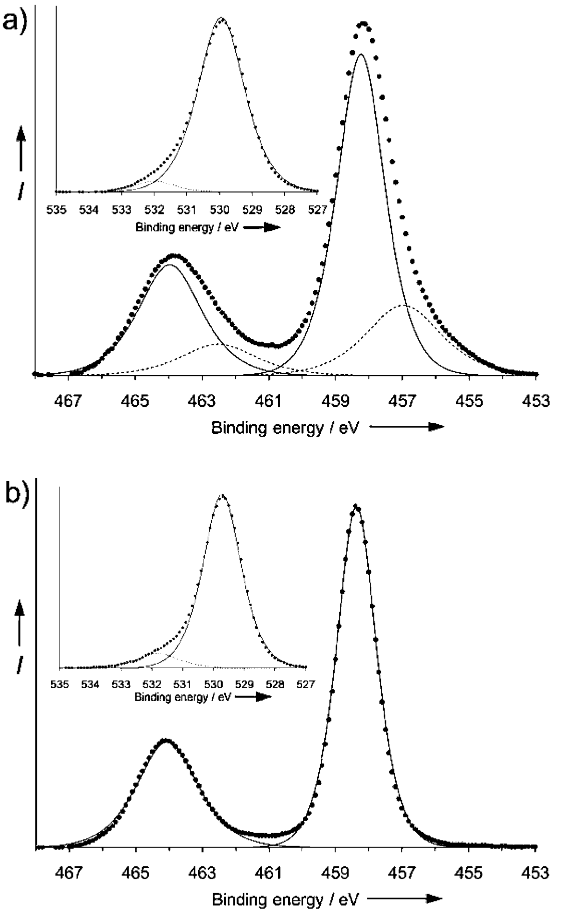

Figure 4. Core-level XP Ti 2p spectra of reduced TiO_2 (a) and rutile TiO_2 precursor (b). The insets are O 1s spectra. The circular dots show the experimental spectra, and the curves fitted data.

A {100}-oriented TiO_2 thin film of rutile structure, with rutile chains aligned parallel to the substrate, was reduced to a {110}-oriented Ti_2O_3 thin film of corundum structure. Since the face-sharing sites in a corundum structure exist along the *c*-axis direction, such sites were formed parallel to the substrate. This is consistent with the consideration that the frameworks of rutile chains were maintained by stepwise reduction via Magnéli phases (see Figures S1 and S2 of the Supporting Information). Anatase TiO_2 powder was also reduced to Ti_2O_3 with a corundum structure, but the morphology was not maintained (Figures S3–S5 of the Supporting Information). This again confirms the importance of stepwise reduction via Magnéli phases.

Since the native surface TiO_2 layer on titanium metal was reported to be about 8 nm thick,[16] there was concern that the nanoparticles of Ti_2O_3 were oxidized to TiO_2. Thus, the surface elemental states were analyzed by X-ray photoelectron spectroscopy (XPS). Figure 4 shows XP spectra of the Ti 2p doublet region and the O 1s peak with peak deconvolution after background removal by the Shirley method and charge collection assuming the C 1s peak to be located at 284.8 eV. Comparing the spectrum of the reduced titanium oxide to that of TiO_2 revealed that the 2p doublet peaks of the former have tails in the region of lower binding energy, which indicate the presence of lower valence states. The peak deconvolution clearly attributed the trails to the presence of Ti^{3+} of Ti_2O_3, which exhibited a small peak located at 457.0 eV for Ti $2p_{3/2}$. In addition, the main sharp peak of Ti $2p_{3/2}$ was located at 458.2 eV, which is assignable to Ti^{4+} as observed in the TiO_2 spectrum (458.4 eV), that is, a native surface TiO_2 layer of less than 2 nm thickness is present (considering the resolution depth of XPS of about 2.1 nm in this case).[17] The Ti^{3+}/Ti^{4+} ratio was determined to be about 34 % from the peak areas. Thus, a surface TiO_2 layer protected the Ti_2O_3 phase of the nanoparticles from further oxidation by air. The O 1s spectra of the reduced titanium oxide and the precursor were quite similar and consisted of a large peak located at about 530 eV, assignable to O atoms in titanium oxide, and a small peak around 532 eV, attributable to surface OH species, probably originating from surface defect sites.[17]

In summary, reduction of rutile TiO_2 nanoparticles by CaH_2 powder at a low temperature of 350 °C yielded corundum Ti_2O_3 nanoparticles with the same morphology. This is of great promise for synthesizing nanostructured reduced titanium oxides, for example, mesoporous ones from mesoporous titania, and will contribute to exploiting reduced titanium oxides in photovoltaics, fuel cells, and so on. In future, we will comprehensively evaluate physical properties important for applications (e.g., absorption wavelength and conductivity) and apply this technique also to other nanostructured titanias (e.g., TiO_2 nanowires) and other oxides.

Experimental Section

As-received TiO_2 nanoparticles (Ishihara Sangyo Kaisha, 10–30 nm) were thoroughly mixed with a fourfold molar excess of CaH_2 powder (Aldrich, 90 %) in an Ar-filled glove box, and then heated at 350 °C for 15 d in an evacuated glass tube with intermediate grinding. Residual CaH_2 and byproduct CaO were removed with a 0.1 M solution of NH_4Cl in methanol. The final product thus obtained was dried in air.

The SXRD patterns were collected on the NIMS beamline at SPring-8 ($\lambda = 0.65298$ Å). The microstructure was observed by SEM (S4800 from Hitachi) and TEM (JEM2100F from JEOL). The surface elemental states were analyzed by XPS (Theta Probe from Thermo Electron) by applying $Al_{K\alpha1}$ radiation.

Further details are available in the Supporting Information.

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