

Direct Formation of Anatase (TiO₂)/Silica (SiO₂) Composite Nanoparticles with High Phase Stability of 1300 °C from Acidic Solution by Hydrolysis under Hydrothermal Condition

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Anatase (TiO₂)/silica (SiO₂) composite nanoparticles that were directly synthesized from solutions of TiOSO₄ and tetraethyl orthosilicate by hydrolysis under hydrothermal conditions at 200 °C showed far more enhanced phase stability than pure anatase-type TiO₂. By the presence of 48.2 mol % SiO₂ as mostly amorphous phase, the crystallite growth of anatase was completely suppressed to maintain the crystallite size (14–16 nm) of the as-prepared condition after heating at 1000 °C, and the anatase-to-rutile phase transformation was retarded to maintain the anatase-type structure up to 1300 °C with no trace of rutile phase. The critical crystallite size of anatase in the composite samples for the anatase-to-rutile phase transformation was suggested to be around 70–100 nm. The silica, which contained -OTi groups around tetrahedrally coordinated Si and was regarded to exist mostly as amorphous phase, was considered to play an important role in suppressing diffusion between anatase crystallites, which led to the retardation of the crystallite growth of anatase and consequently resulted in the suppression of the phase transformation.

Introduction

Titanium dioxide (titania, TiO₂) has been extensively studied because of its unique properties and used in a wide variety of technological applications (wet-type solar cells,^{1,2} sensors, catalysts³ or photocatalysts,^{4–7} pigments, etc.). In particular, recently much attention has been attracted for its applications as photocatalysts to decompose environmental pollutants such as halogenated organic compounds⁸ and nitrogen oxides⁹ and to cleave organisms and bacteria.¹⁰ The titania has three polymorphs: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The rutile phase is thermodynamically stable, but the metastable anatase phase that is generally formed at low temperature, for example, by sol–gel processing,¹¹ transforms to rutile by heating or even by mechanical grinding. Generally,

the metastable anatase-type titania shows higher photoactivity than other phases. The phase stability of anatase, that is, anatase-to-rutile phase transformation from a metastable phase to a stable one, is markedly influenced by the nature and the amount of cation impurities^{12–20} and anion impurities²¹ present in the system, grain size,²² and preparation conditions such as reaction atmosphere.²³ To control the polymorphs in the preparation of TiO₂ is practically essential for producing excellent functions. The effectiveness of the addition of SiO₂ for enhancement of the phase stability^{13,24–27} and the photocatalytic activity^{28,29} of anatase have been reported. Although, up to now, various

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methods for preparing fine powders of pure titania have been developed, most studies on the preparation of SiO₂-containing titania have been done by sol-gel methods,^{24–26,29,30} except for chemical vapor deposition (CVD),¹³ and solvothermal process in organic solvent,²⁷ etc. We have directly synthesized nanometer-sized crystalline complex oxides^{31–35} and oxide solid solutions, for example, CeO₂–ZrO₂,^{36,37} Fe₂O₃–TiO₂,¹⁷ and ZrO₂–TiO₂,^{18,19} through soft solution routes.

In the present study, anatase (TiO₂)/silica (SiO₂) composite nanoparticles containing SiO₂ up to 70.9 mol % were directly formed as nanometer-sized particles from acid precursor solutions of TiOSO₄ and tetraethyl orthosilicate (TEOS) by hydrolysis under hydrothermal conditions. The effects of the amount of SiO₂ on the crystallite growth, the anatase-to-rutile phase transformation, microstructure, and lattice parameter of anatase were investigated. Here we report the properties of anatase-type TiO₂ with improved phase stability, that is, stable at 1300 °C for 1 h in air.

Experimental Section

Aqueous solutions of reagent-grade TiOSO₄ and tetraethyl orthosilicate (TEOS) in various ratios of Ti/Si with total cation concentrations (Ti + Si) of 0.2 mol/dm³ were prepared, and 18 cm³ of each solution was placed in a 25 cm³ Teflon container held in a stainless steel vessel. After the vessel was tightly sealed, it was heated at 200 °C for 24 h with rotation at 1.5 rpm. After hydrothermal treatment, the precipitates were washed with distilled water until the pH value of the rinsed water became 7.0, separated from the solution by centrifugation, and dried in an oven at 65 °C. The powders thus prepared were heated in an alumina crucible at a heating rate of 200 °C/h, held at 600–1400 °C for 1 h in air, and then cooled to room temperature in a furnace.

The as-prepared and heated powders were examined by X-ray diffractometry (XRD; model RINT-2000, Rigaku, Tokyo, Japan) with Cu K α radiation and observed under transmission electron microscopy (TEM; model JEM-2010, JEOL, Tokyo, Japan). The anatase crystallite size was estimated from the line broadening of the 200 diffraction peak according to the Scherrer equation: $D_{\text{XRD}} = K\lambda/(\beta \cos \theta)$, where θ is the Bragg angle of the diffraction lines, K is a shape factor ($K = 0.9$ in this work), λ is the wavelength of the incident X-rays, and β is the corrected half-width given by $\beta^2 = \beta_m^2 - \beta_s^2$, where β_m is the measured half-width and β_s is the half-width of a standard sample. The lattice parameters were measured with silicon as the internal standard. The amounts of rutile phase formed in the heated samples were calculated from³⁸

$$F_R = 1/\{1 + 0.79[I_A(101)/I_R(110)]\}$$

where F_R is the mass fraction of rutile in the samples and $I_A(101)$ and $I_R(110)$ are the integrated 101 intensity of anatase

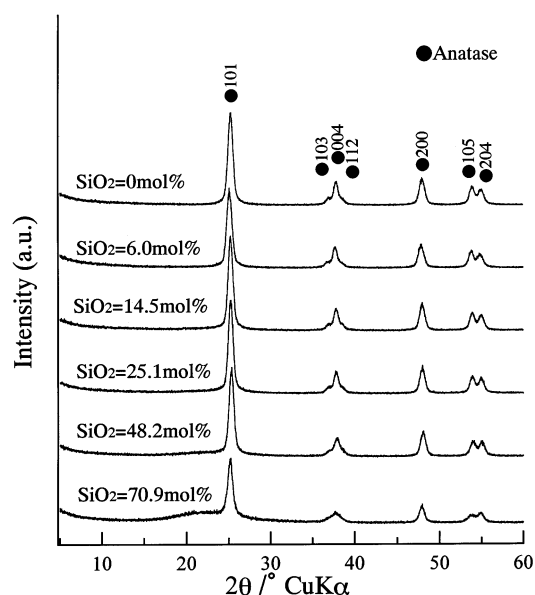


Figure 1. XRD patterns of precipitates as-prepared from solutions of TiOSO₄ and tetraethyl orthosilicate with total metal cation concentration of 0.2 mol/dm³ under hydrothermal condition at 200 °C for 24 h.

and 110 intensity of rutile, respectively, both of these lines being around 26° in 2θ .

The TiO₂/SiO₂ molar ratio (mole percent) in the samples was determined via an inductively coupled plasma emission spectrometer (ICP; model ICP575II, Nippon Jarrell-Ash, Japan). Raman spectra were obtained from a Raman spectrometer (model NRS-1000, Nihon Bunko, Tokyo, Japan) with the 532 nm line of a 10 mW green laser. The specific surface area of the prepared samples was calculated from the adsorption isotherm of nitrogen at 77 K on the basis of the Brunauer–Emmett–Teller method (BET; model Nova 1200, Yuasa Ionics, Osaka, Japan). To characterize the local structure around Si in the samples, solid-state ²⁹Si magic-angle spinning (MAS) NMR spectra were measured for the samples containing 14.5, 48.2, and 70.9 mol % SiO₂. The ²⁹Si MAS NMR spectra were obtained operating at 9.4 T on a spectrometer (model DSX400, Bruker Instruments, Karlsruhe, Germany) at 7 mm MAS probe operating at 79.49 MHz and at a spinning rate of 4.5 kHz. The spectra were accumulated by use of a 4.5 μ s pulse (45° pulse) and 0.5 min recycle delay. Spectra were referenced externally to silicone rubber at 0 ppm.

Results and Discussion

Direct Formation of TiO₂/SiO₂ Composite Nanoparticles. The hydrolyses of the precursor solutions of TiOSO₄ and TEOS having a metal cation concentration of 0.2 mol/dm³ with various compositions were carried out under hydrothermal conditions at 200 °C for 24 h. Figure 1 shows the XRD patterns of the precipitates directly formed by thermal hydrolysis. The compositions of the samples shown in the XRD patterns are analytical value of SiO₂ (mole percent). The single-crystalline-phase anatase was detected in the as-prepared solid precipitates obtained from the solutions with SiO₂ content up to 70.9 mol %. No diffraction peaks due to another crystalline phase were detected. However, there is a possibility of the existence of amorphous phase in

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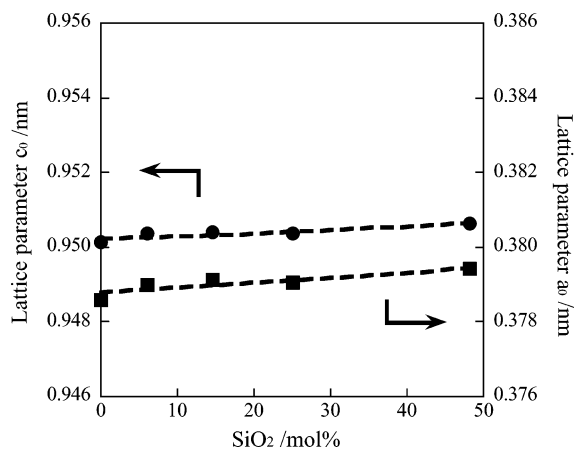


Figure 2. Lattice parameters a_0 and c_0 of anatase-type TiO_2 in as-prepared $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles versus SiO_2 content.

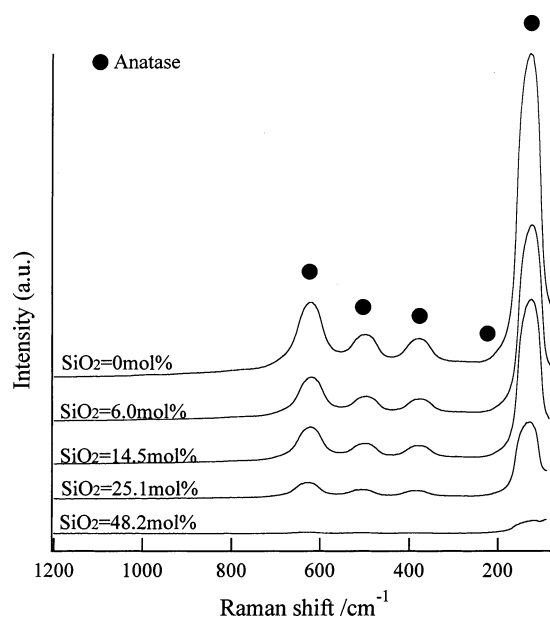


Figure 3. Raman spectra of as-prepared $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles.

the samples due to a slight change in the background of the XRD patterns around $2\theta = 20\text{--}25^\circ$. The lattice parameters a_0 and c_0 for the as-prepared anatase are plotted in Figure 2 as a function of SiO_2 content. A slight change (i.e., slight increase) in the lattice parameters a_0 and c_0 of anatase was observed with increasing SiO_2 content, although the lattice parameters a_0 and c_0 were reported to decrease.^{24,26}

The observed Raman spectra of the as-prepared powders are shown in Figure 3. The Raman spectra showed the feature of anatase.³⁹ No extra peaks corresponding to the rutile mode were observed. However, the peak intensity of the anatase mode in the Raman spectra considerably decreased with increasing SiO_2 content, although the intensity of the XRD peaks hardly changed. The Raman spectra from amorphous materials are characterized by weak intensity, extremely broadened peaks, and relatively high and featureless background. The as-prepared powder containing 48.2 mol %

SiO_2 seemed to have a certain extent of amorphous phase because its Raman spectra are considerably weaker as compared with other samples. The content of the amorphous phase in the as-prepared samples is thought to gradually increase with increasing SiO_2 content, corresponding to the decrease in intensity of the Raman spectra.

The TEM micrographs of the as-prepared pure TiO_2 and $\text{TiO}_2/\text{SiO}_2$ composite sample containing 48.2 mol % SiO_2 are shown in Figure 4, panels a and b, respectively. The TEM micrograph of the $\text{TiO}_2/\text{SiO}_2$ composite sample is out of focus due to the presence of a certain extent of amorphous phase. The electron diffraction patterns for selected regions of pure TiO_2 and $\text{TiO}_2/\text{SiO}_2$ composite samples containing 48.2 mol % SiO_2 are shown in Figure 4c–e. Figure 4c indicates relatively well-developed crystalline structure, but the electron diffraction patterns shown in Figure 4d correspond to the area out of focus and imply the existence of a certain extent of amorphous phase due to diffuse scattering electron diffraction ring. The particle sizes of the precipitates estimated from the TEM micrographs were around 10–15 nm and the difference in particle size between the samples with and without SiO_2 was hardly observed.

The crystallite sizes of anatase in the as-prepared samples containing 0 and 48.2 mol % SiO_2 determined from the 200 XRD peak of anatase were 14.1 and 14.4 nm, respectively, as shown in Figure 5. The particle sizes observed by TEM corresponded well to the crystallite sizes estimated from the line broadening of the XRD peak. The specific surface area of the as-prepared samples versus silica content is shown in Figure 6. The specific surface area increased from 109 to 277 m^2/g when the silica content was increased from 0 to 70.9 mol %, which was considered to be due to the increased amount of amorphous silica phase present in the sample.

To study the evolution of the local environment around Si atoms in the as-prepared $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles, ^{29}Si MAS NMR spectra were collected on selected samples with various SiO_2 contents (Figure 7 and Table 1). Figure 7 panels a, b, and c show the ^{29}Si MAS NMR spectra of the as-prepared samples containing 14.5, 48.2, and 70.9 mol % SiO_2 , respectively. These spectra show main resonances at about -90 , -100 , and -110 ppm, corresponding to Q_2 , Q_3 , and Q_4 structure units, respectively, all which result from tetrahedrally coordinated Si. The signal at about -93 ppm with small intensity in the sample containing 70.9 mol % SiO_2 is seen to correspond to a Q_2 structure unit that is different from the Q_2 structure unit at -90 ppm. The important point to note is that there are Si atoms that existed as polymerized Q_3 and Q_2 structure units in the as-prepared $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles, since pure SiO_2 amorphous glass shows only one single Q_4 structure unit in ^{29}Si MAS NMR spectra. The NMR signal in the Q_2 and Q_3 regions, which are thought to be equivalent to two and one $-\text{OTi}$ groups around Si, with resonances at -90 and -100 ppm, respectively, suggest the presence of $-\text{OTi}$ in the SiO_2 amorphous phase of the $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles. These measurement results indicate that the average Si in all the $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles has $-\text{OTi}$ groups around it.

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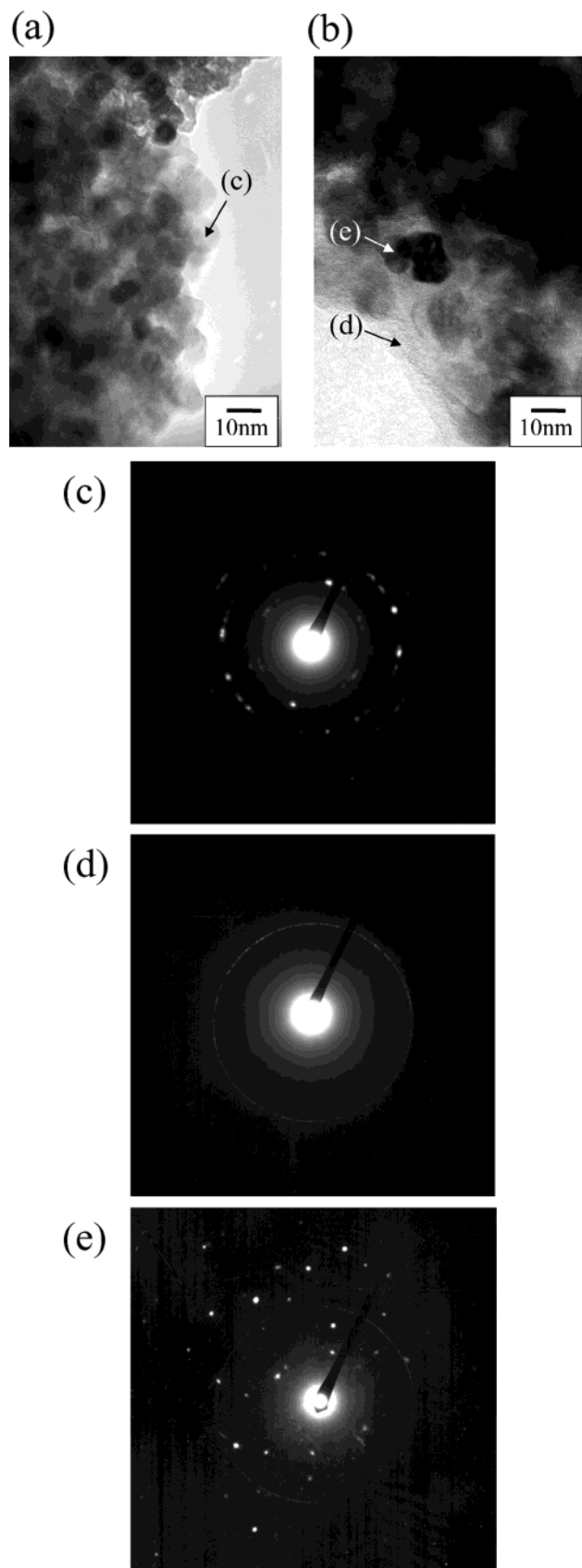


Figure 4. TEM images of as-prepared (a) pure TiO_2 and (b) $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 and electron diffraction patterns of selected regions of (c) pure TiO_2 and (d, e) $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 .

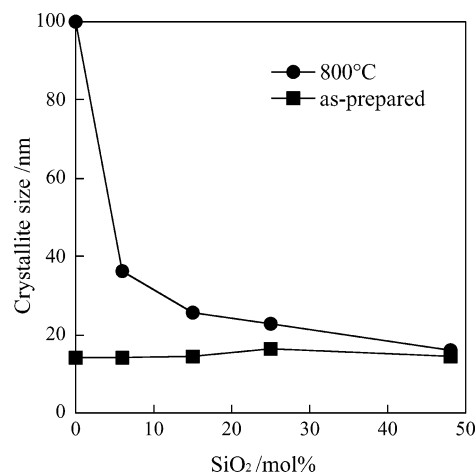


Figure 5. Crystallite size of anatase in $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles as-prepared and heat-treated at 800 °C for 1 h as a function of SiO_2 content.

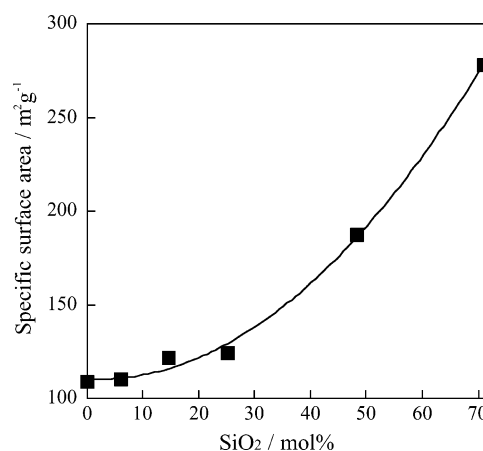


Figure 6. Specific surface area of as-prepared $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles.

Table 1. ^{29}Si MAS NMR Characterization of $\text{TiO}_2/\text{SiO}_2$ Composite Nanoparticles

sample SiO_2 (mol %)	signal intensity (%)			
	A −90 ppm	B −93 ppm	C −100 ppm	D −110 ppm
14.5	3.0	0.1	22.8	74.1
48.2	2.7	0.1	21.1	76.0
70.9	3.2	2.0	23.7	71.2

Crystallite Growth and Phase Stability of $\text{TiO}_2/\text{SiO}_2$ Composite Nanoparticles. The Raman spectra of the sample powders after being heated at 800 °C for 1 h in air are shown in Figure 8. The features of the Raman spectra were similar to those of the as-prepared samples before heating, shown in Figure 3. The anatase as crystalline phase was detected in all the samples after heating at 800 °C. No extra peaks due to another phase, such as rutile, were detected. Although the same feature (i.e., the intensity of the Raman spectra corresponding to the anatase phase gradually decreasing with increasing SiO_2 content) that appeared in Figure 3 was observed in Figure 8, the Raman spectrum intensity in the samples after heating decreased more abruptly with increased SiO_2 content than was the case in the as-prepared samples. This phenomenon is notable in the samples containing large amounts of SiO_2 , which implies a probable increase in the amorphous layer or change in the nature of the amorphous phase on the

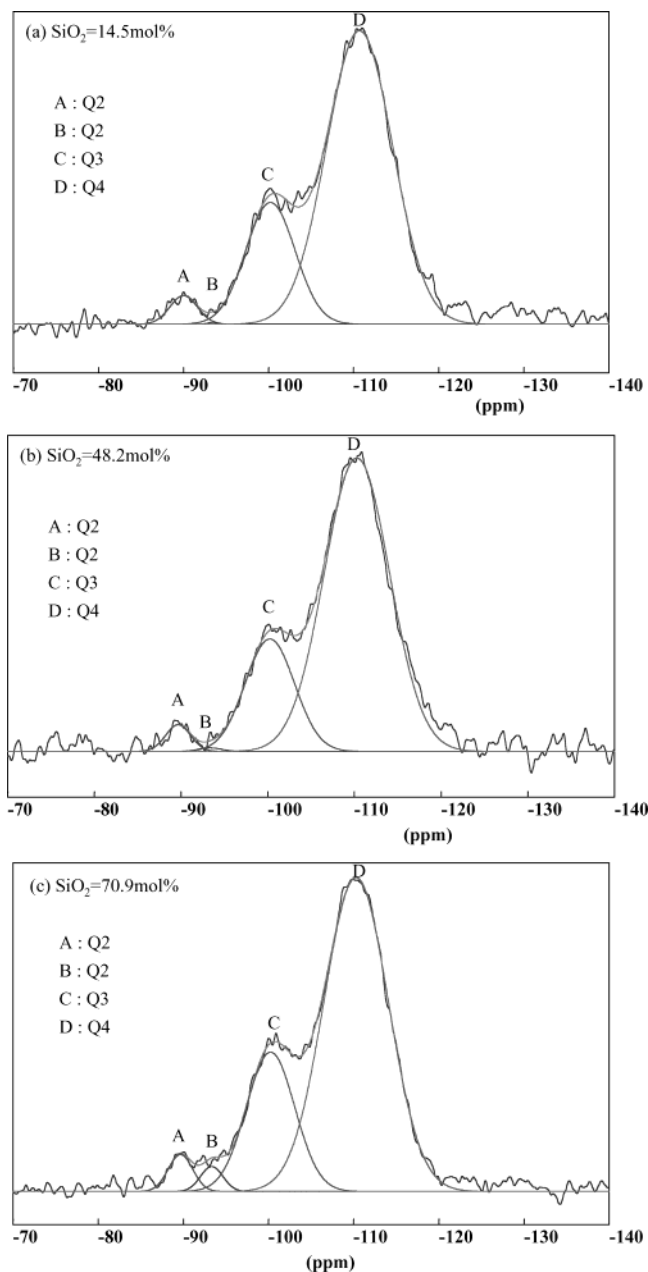


Figure 7. ^{29}Si MAS NMR spectra of as-prepared $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing (a) 14.5, (b) 48.2, and (c) 70.9 mol % SiO_2 .

surface of the anatase particles during heating. A similar phenomenon was reported for the heat-treated TiO_2 xerogels containing SiO_2 that were formed by a sol-gel method.²⁶

The XRD patterns of pure TiO_2 and $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 before and after heating at various temperatures are shown in Figure 9, panels a and b, respectively. It has been reported that anatase-type TiO_2 changes to rutile-type structure by heat treatment above 635 °C from the results of a kinetic study on the anatase-to-rutile phase transformation.^{40,41} The anatase-type pure TiO_2 hydrothermally synthesized from acidic TiOSO_4 solution by

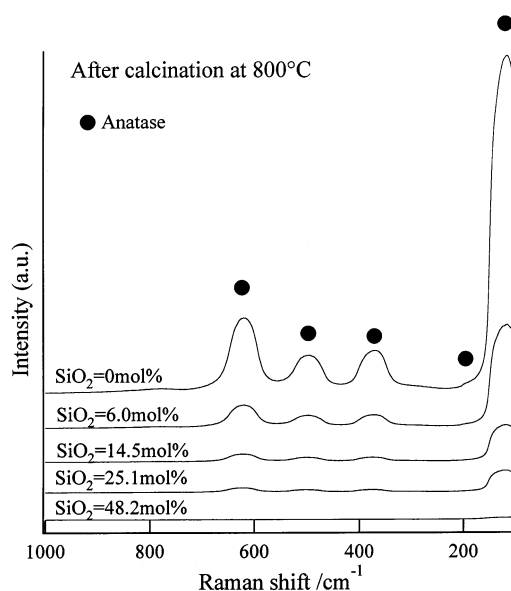


Figure 8. Raman spectra of $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles after being heated at 800 °C for 1 h.

thermal hydrolysis was confirmed to have high phase stability⁶ in comparison with other anatase-type pure TiO_2 synthesized by sol-gel method from metal alkoxides. A small amount of rutile phase is detected in the pure TiO_2 sample after heating at 900 °C, and the pure TiO_2 almost transformed to the rutile structure at 1050 °C. We have shown that the phase stability of anatase-type TiO_2 hydrothermally formed from TiOSO_4 solution is improved to maintain the structure up to 1000 °C by making solid solutions with ZrO_2 ,¹⁹ while the $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 maintained anatase structure perfectly even after heating at 1300 °C for 1 h. The crystallization of amorphous SiO_2 into cristobalite was confirmed at the samples heated above 1350 °C.

The proportion of the rutile phase (mass percent) formed by the anatase-to-rutile phase transformation is plotted as a function of heating temperature in Figure 10. The phase transformation curve for the pure TiO_2 shows that the anatase-type pure TiO_2 , which was formed by hydrolysis of TiOSO_4 , originally has higher phase stability than that obtained from titanium alkoxide. This high phase stability is thought to be due to the probable existence of residual impurity SO_4^{2-} that was not removed perfectly via washing from the precipitates. By the presence of 6.0 mol % SiO_2 , the starting and completion temperature of the phase transformation were shifted from 850 to 1050 °C and from 1050 to 1200 °C, respectively. The phase transformation was extremely delayed and the phase stability of the anatase was enhanced about 400 °C by the presence of 48.2 mol % SiO_2 .

Figure 11 shows the TEM micrographs of the anatase-type pure TiO_2 and $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 before and after heating at 800 °C. Although considerable grain growth was observed in the pure TiO_2 (Figure 11c in comparison with Figure 11a), the particle size of anatase containing 48.2 mol % SiO_2 (Figure 11d) hardly changed after heating at 800 °C compared to that before heating (Figure 11b). The compositional dependence of the anatase crystallite size after heating at 800 °C is also shown in Figure 5.

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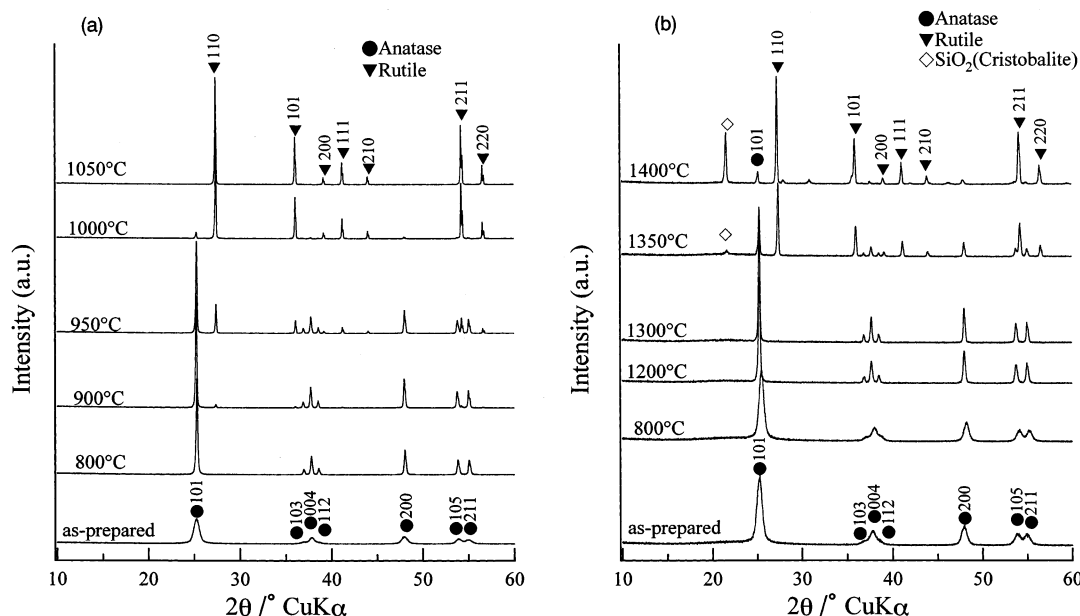


Figure 9. XRD patterns of $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing (a) 0 and (b) 48.2 mol % SiO_2 as-prepared and after being heated at various temperatures for 1 h.

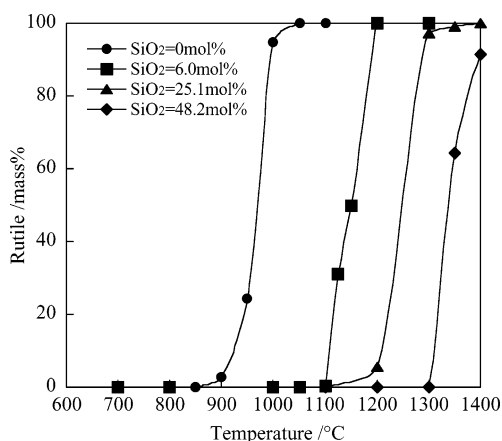


Figure 10. Phase transformation from anatase-type to rutile-type structure for $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing various amount of SiO_2 plotted against heating temperature (holding time at the heating temperature was 1 h).

The considerable suppression effect on the crystallite growth of anatase was confirmed by the presence of SiO_2 .

The crystallite growth of anatase in the $\text{TiO}_2/\text{SiO}_2$ composite samples containing 0, 6.0, 25.1, and 48.2 mol % SiO_2 is shown as a function of heating temperature in Figure 12. The crystallite growth of anatase was almost perfectly suppressed by the presence of 48.2 mol % SiO_2 up to 1000 °C, which is considered to closely relate to the shift of the phase transformation temperature more than 400 °C.

The specific surface area of the $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 after heating is plotted as a function of heating temperature in Figure 13. The high specific surface area of the sample is still maintained after heating to 1000 °C, although it decreases with increasing heating temperature. The decrease in specific surface area is suddenly accelerated when the heating temperature increases from 1000 to 1200 °C. The specific surface area of the sample after heated at 1300 °C became less than $1/100$ that before

heating. As can be seen in Figure 12, up to 1000 °C the particle size does not change for the sample with 48.2 mol % SiO_2 . Surface area, however, drops significantly already at 800 °C. This means that the surface area change is almost exclusively due to sintering of the silica matrix, not to changes in the titania part.

The suppressing effect of Nb_2O_5 and the accelerating effect of CuO , Cr_2O_3 , and Fe_2O_3 as impurities on the anatase-to-rutile phase transformation have been interpreted by the creation and reduction of oxygen vacancies, that is, in terms of a defect structure mechanism,^{14,42} since this phase transformation involves a collapse of relatively open anatase structure by about 8%.⁴³ On the other hand, the inhibiting effect of phosphate on the anatase-to-rutile transformation was explained through a mechanism that implies its chemisorption on TiO_2 as a bidentate ligand that hinders the surface ionic mobility by Criado and Real.⁴⁴ The phase transformation from metastable anatase to stable rutile phase can occur when the thermal energy is high enough to overcome the nucleation energy, which has been proposed for the similar case of the phase transformation from metastable tetragonal ZrO_2 to stable monoclinic phase.^{45,46} The larger-grained microstructure may have had a smaller nucleation barrier for transformation because of the increase in microstructural defects, for example, dislocations and residual stresses generated locally by the thermal expansion anisotropy within the grain, as in the case of metastable tetragonal ZrO_2 .^{47,48} An increase in grain (crystallite) size means a decrease in the intrinsic phase stability of a metastable anatase grain. By comparing the crystallite size data in Figure 12 with the phase transformation tem-

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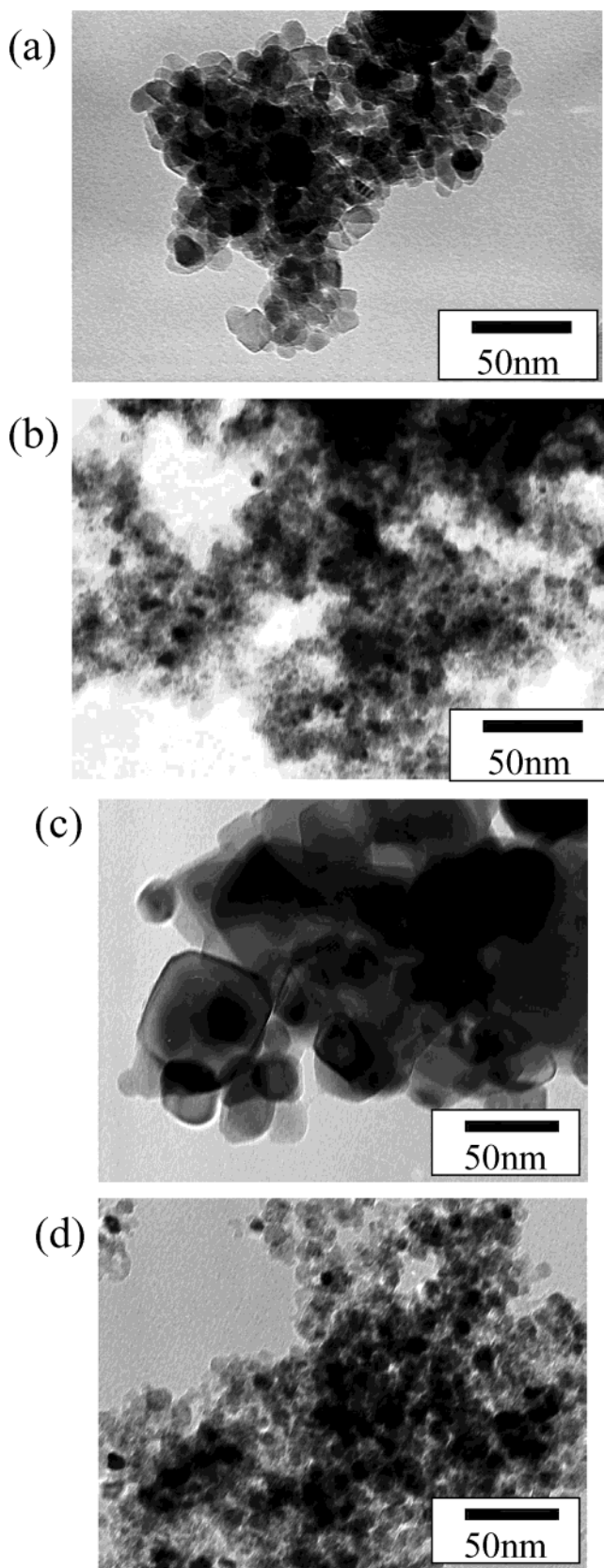


Figure 11. TEM micrographs of $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing (a) 0 and (b) 48.2 mol % SiO_2 as-prepared and those containing (c) 0 and (d) 48.2 mol % SiO_2 after being heated at 800 °C for 1 h.

perature in Figure 10, the anatase–rutile phase transformation begins to occur when the crystallite size reaches around 70–100 nm by heating in the cases for

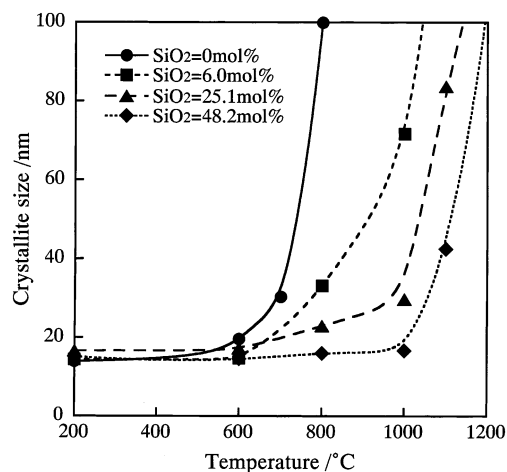


Figure 12. Crystallite size of anatase-type TiO_2 in composites containing various amount of SiO_2 plotted against heating temperature.

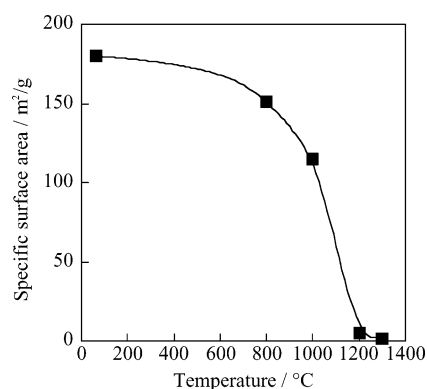


Figure 13. Specific surface area of $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles containing 48.2 mol % SiO_2 plotted against heating temperature.

the $\text{TiO}_2/\text{SiO}_2$ composite samples containing 6.0, 25.1, and 48.2 mol % SiO_2 , which value “around 70–100 nm” may be the critical crystallite size for the transformation of the composite samples. Although we already reported that the critical crystallite size for the transformation in the zirconium-doped anatase-type TiO_2 formed by thermal hydrolysis under hydrothermal conditions was about 70 nm,¹⁹ this critical crystallite size for the transformation is supposed to depend on the nature of metastable anatase, e.g., contained impurities, the nature and the amount of dopant, crystallinity, surroundings, and so on. In the present study, the enhanced stabilization of the anatase phase is due to the existence of the surrounding amorphous SiO_2 phase through the TiOSi interface, which is supported from the ^{29}Si MAS NMR spectral data (Figure 7). At the interface, Ti atoms are substituted into the tetrahedral SiO_2 lattice, forming tetrahedral Ti sites. The interaction between the tetrahedral Ti species and the octahedral Ti sites in the anatase was thought to prevent the transformation to rutile.^{28,49} The existence of the surrounding amorphous SiO_2 phase through the TiOSi interface and the SiO_2 lattice locking the Ti–O species at the interface with the TiO_2 domains is considered to prevent the diffusion between anatase crystallites and the nucleation that is

(49) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic Press: Boston, 1990.

necessary for the phase transformation to rutile, which may have led to the retardation of the crystallite growth and consequently the anatase-to-rutile phase transformation, because heating at higher temperature was necessary to reach the critical anatase grain (crystallite) size for the transformation in the $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles than that in the pure TiO_2 .

The $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles with a unique microstructure in this study, i.e., nanometer-sized anatase crystallites, existed relatively separated from each other via $\text{TiO}_2/\text{SiO}_2$ interface by the existence of photopervious amorphous silica phase and showed far more improved photocatalytic activity for the decomposition of methylene blue in its aqueous solution and NO gas.⁵⁰

Conclusions

(1) $\text{TiO}_2/\text{SiO}_2$ composite nanoparticles were directly formed as nanometer-sized particles from the acid precursor solutions of TiOSO_4 and TEOS by thermal

hydrolysis under hydrothermal conditions at 200 °C. A certain amount of SiO_2 is regarded to exist on the surface of the anatase crystallite as amorphous phase due to low Raman spectrum intensity, out of focus transmission electron micrograph, and diffused electron diffraction ring.

(2) The crystallite growth of anatase was almost perfectly suppressed up to 1000 °C, and the starting temperature of the anatase-to-rutile phase transformation was retarded from 850 to 1300 °C by the presence of 48.2 mol % SiO_2 . The diffusion between anatase crystallites was considered to be fairly suppressed by the presence of amorphous SiO_2 and TiOSi interface on the surface of the anatase crystallite, which led to the retardation of crystallite growth and, as a consequence, led to suppression of the phase transformation.

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