Journal of the European Ceramic Society 23 (2003) 691–696
www.elsevier.com/locate/jeurceramsoc

Effect of brookite phase on the anatase–rutile transition in titania nanoparticles

Yi Hu*, H.-L. Tsai, C.-L. Huang

Department of Materials Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, 104 Taipei, Taiwan

Received 8 May 2001; received in revised form 27 May 2002; accepted 16 June 2002

Abstract

Nanosized TiO_2 powders were prepared from the precipitation in the $TiCl_4$ precursor under various pH values. The prepared titania existed in the form of nanocrystalline anatase with some brookite, which was evidenced by X-ray diffraction analysis and Raman spectroscopy. The average crystallite sizes of the TiO_2 particles heat treated at 450 °C for 2 h are in the range of 7–9 nm. The lattice constant c of anatase increased with increasing the synthesized pH value, whereas the volume fraction of the brookite phase increased with decreasing the synthesized pH value. The beginning and ending temperatures for the anatase–rutile transformation were found to decrease with increasing the volume fraction of the brookite phase. The brookite phase in the powder is responsible for enhancing the anatase–rutile transition.

Keywords: Anatase; Brookite; Phase transitions; Powders-chemical preparation; Rutile; TiO_2

1. Introduction

Phase transformation in titania (TiO_2) has been widely studied from the point of view of both scientific interest and technological applications.[1–5] It is well known that titania has three polymorphs in nature: rutile (tetragonal, space group P42/mmm), anatase (tetragonal, space group I41/amd), and brookite (orthorhombic, space Pcab). Rutile is the only stable phase, whereas anatase and brookite are metastable at all temperatures and transfer to rutile when they are heated.

Many researchers attempted to understand and control the anatase–rutile (A–R) transition, since that the TiO_2 phase, i.e., anatase or rutile, is one of the most critical parameters determining the properties of the material such as photocatalytic properties. The effect of particle size on the A–R transformation has been well investigated through thermodynamics or kinetics.[6–8] On the other hand, the A–R transformation has been proved to be dependent on the fabrication conditions.[9–11] However, the parameters in the fabrication process are complicated. It is essential to investigate and control the fabrication parameters for the titania transformation.

Most of TiO_2 systems are composed of several phases, while anatase or rutile is typically the major product of inorganic syntheses and is the main constituent of nanocrystalline materials. Recently, nanosized anatase accompanied brookite phase has been obtained in some preparing processes.[12,13] However, little information on the effect of brookite on the titania transformation may be found in the literature.[8] This would be different from many similar investigations that considered only the conversion scheme of A–R. The role of the brookite phase in the A–R transition becomes much interest to study. In this paper, the relationship between the synthesizing pH values and the thermal transformation of the precipitated TiO_2 powders, which was a mixture of anatase and brookite, was investigated.

2. Experimental

Hydrous TiO_2 powders were obtained from the $TiCl_4$ precursor precipitated under different pH values by adding aqueous ammonia. First, titanium tetrachloride

---

* Corresponding author. Tel.: +886-2-25925252; fax: +886-2-25936897.

E-mail address: huyi@ttu.edu.tw (Y. Hu).

0955-2219/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(02)00194-2

(98% $TiCl_4$) was dissolved in distilled water in an ice-water bath and in a glove box with argon atmosphere. Then isopropanol and HCl were added into the solution. The volume ratio of H_2O and isopropanol was 1:3. The concentrations of both $TiCl_4$ and HCl were adjusted to 0.1 M. The precursor showed to be very clear and transparent without any precipitation. The precursor was then cooled to 5 °C.

White precipitates were obtained by adding aqueous ammonia into the precursor, of which the pH value was adjusted to a range from 2 to 9. The solution was further heated to 50 °C for 1 h. The precipitates were separated with centrifugal separator and washed with a deionized water. The washing procedure was preformed three times. Finally, the collected powders were dried in an electric oven at 100 °C for 24 h. The dried powders were then heated at different temperatures for 2 h for the study of phase transformation.

The phase evolution of the TiO_2 powders under heat treatment was examined by powder X-ray diffraction (XRD) using a Siemens D-5000 instrument with CuK_α radiation. The volume fractions of anatase and rutile were calculated from the (101) reflection of anatase and the (110) reflection of rutile. The volume fraction of rutile present in the composites after various heat treatment were calculated using the following equation:[14]

$$\%\ \text{transformation of rutile} = W_R = \frac{1}{1+0.8(I_A/I_R)}$$

I_A and I_R are the X-ray integrated intensity of (101) reflection of anatase and (110) reflection of rutile respectively. The integrated intensity was calculated after correcting for instrumental and wavelength related broadening. The mean crystallite size of anatase was evaluated from X-ray diffraction of (101) plane of anatase based on Scherrer's equation.

Raman spectra analysis was conducted on the samples from 300 to 1000 cm^{-1} using a Renishaw system 2000 spectrometer and an He–Ne laser operating at 632.8 nm with incident power of 17 mW.

3. Results and discussion

Fig. 1 shows XRD patterns of the powders heat treated at 450 °C for 2 h via the synthesized pH value. These powders were identified as a mixture of anatase, as the predominant phase, and brookite ($2\theta \sim 30.8°$). The average crystallite size of anatase was calculated from the (101) plane in the XRD pattern in the range of 7–9 nm. No apparent difference in the average crystallite size has been found in these powders. The appearance of brookite was further confirmed by the analysis of Raman spectra.

Fig. 2 shows Raman spectra of the powders heat treated at 450 °C for 2 h via the synthesized pH value.

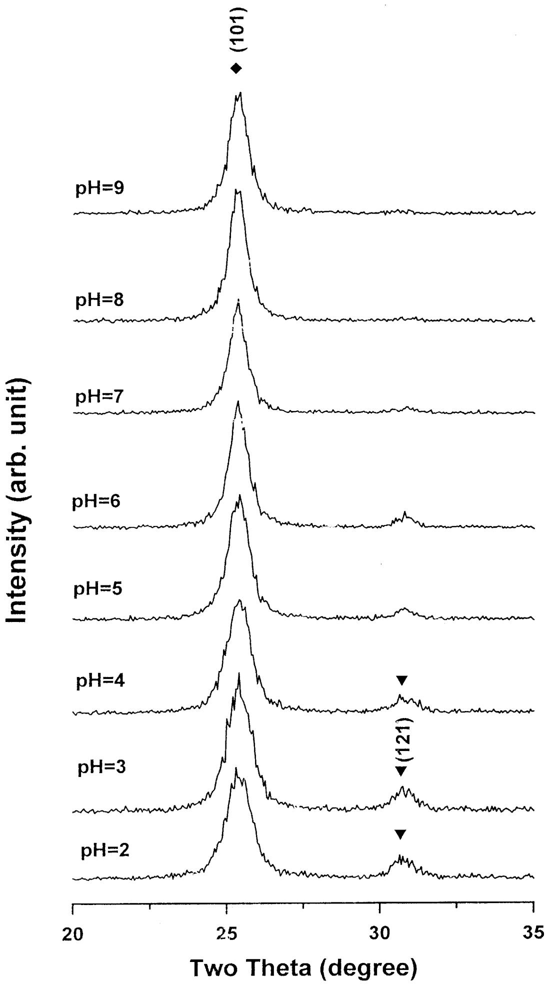

Fig. 1. XRD patterns of the powders heat treated at 450 °C for 2 h via the synthesized pH values. ◆: anatase, ▼: brookite.

The Raman spectrum for anatase has been investigated to show the six characteristic bands at 144, 197, 399, 513, 519, and 639 cm^{-1}.[15] The characteristic bands for brookite are reported at 128, 135, 153, 172, 195, 214, 247, 288, 322, 366, 396, 412, 454, 461, 502, 545, 585, 636 cm^{-1}.[16] The existence of the brookite phase as in Fig. 2 is evidenced from the Raman spectra at 216, 245, 320, 364, 449 cm^{-1} with relative stronger intensity. It was also found that the intensity of the shift bands of bookite phase became weaker with increasing the synthesized pH value. This is consistent with the observation that the relative XRD intensity of brookite decreased with increasing the synthesized pH value. Fig. 3 shows the relative X-ray integrated intensity of (121) reflection of brookite and (101) reflection of anatase respectively. It was found that the relative intensity of brookite decreased with increasing the pH value. Besides, the bands at 430 and 707 cm^{-1} in Raman spectra were ascribed to the sample holder.

Fig. 4 shows the variation in the lattice parameters of anatase versus the synthesized pH values. It was found that the *c* parameter increased and the *a* parameter

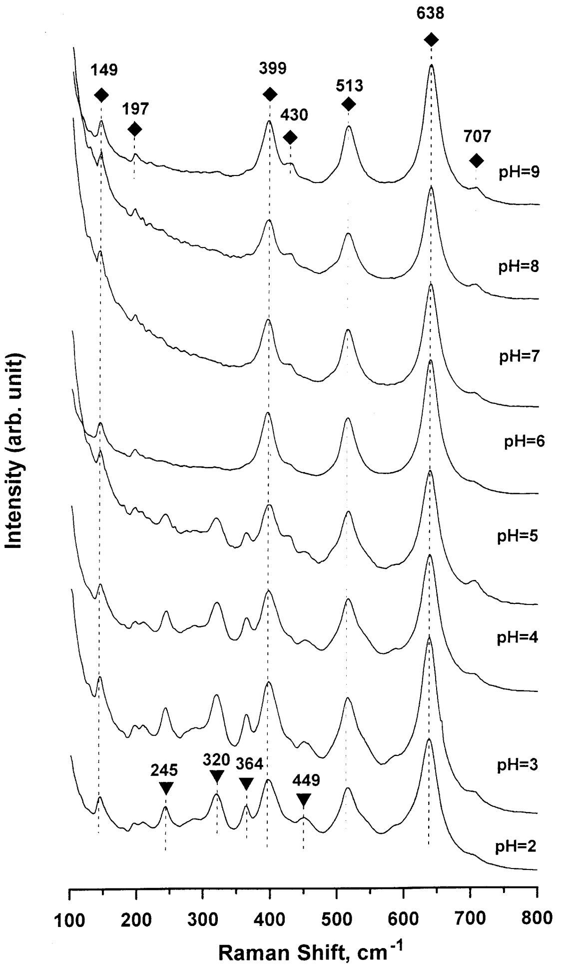

Fig. 2. Raman spectra of the powders heat treated at 450 °C for 2 h via the synthesized pH values. ◆: anatase, ▼: brookite.

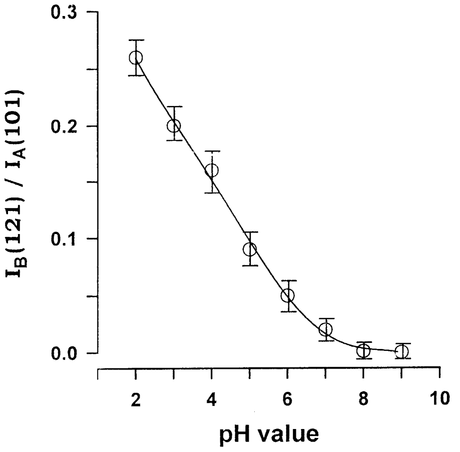

Fig. 3. The relative intensity of the XRD peaks of brookite and rutile. I_B (121) and I_A (101) are the X-ray integrated intensities of (121) reflection of brookite and the (101) reflection of anatase, respectively.

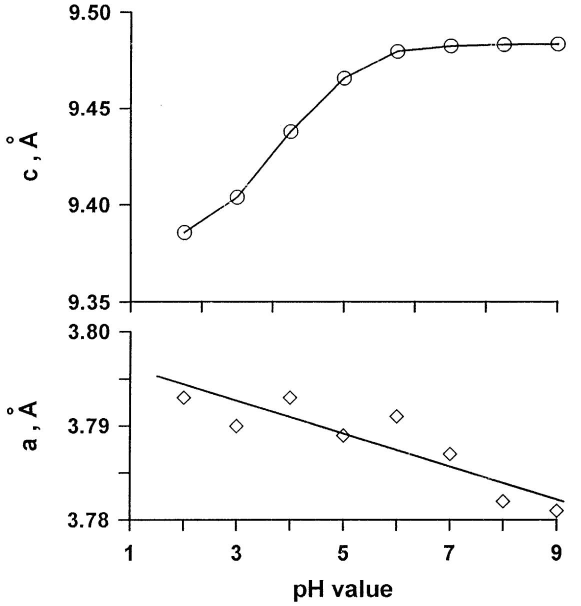

Fig. 4. Lattice parameters of anatase calculated form the XRD patterns of the powders heat treated at 450 °C for 2 h via the synthesized pH values.

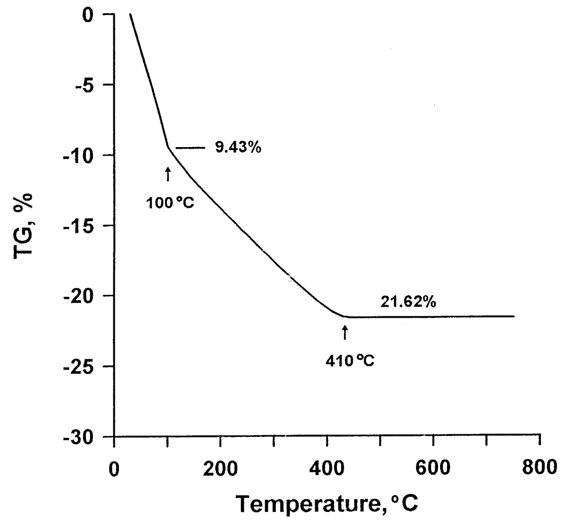

Fig. 5. The TG curve for the sample with synthesized pH of 2 under a heating rate of 10 °C/min in air.

slightly decreased with increasing the pH value. The changes in the lattice constants of anatase are thought to be from the microstrains induced from oxygen vacancy, hydrostatic pressure or specific cations. Fig. 5 shows the weight change of the powders under heating. The 12% weight loss between 100 and 400 °C was attributed to the decomposition of the hydroxyl group. No weight gain in the powders has been observed under heating at a temperature higher than 410 °C from TGA result as in Fig. 5. This indicates that there were no changes in composition when the powders were heat treated higher than 450 °C. The most possible explanation for the changes in lattices of anatase, therefore, is ascribed to the strain under hydrostatic pressure. In the nanophase of TiO_2, the size-induced radial pressure may act in a manner similar to the effect of hydrostatic pressure on single crystals.[17] In addition, microstrains depend also on the coherent structure of between two phases with different crystal structures. It was found that the *c* lattice parameter increased with the decreases of the volume fraction of brookite (Figs. 3 and 4). It seems that the variation in the lattice parameters of anatase is ascribed to the presence of brookite. The attachment of brookite on anatase has be recently reported [18] and possibly results in the microstrain in anatase.

Figs. 6 and 7 show the typical XRD patterns of the powders with synthesizing pH value of 2 and 9 under the heat treatment at different temperatures, respectively. It was found that the anatase-rutile transition seemed to start ahead of the brookite–anatase transition in Fig. 6. Fig. 8 shows the volume fraction of rutile under various heat treatments. When the heat-treated temperature increased, the anatase–rutile transformation preceded predominantly in the powders with lowest synthesized pH value. The anatase–rutile transformation was almost completed for all the samples under the 900 °C heat treatment (Figs. 6 and 7). It was also found that the beginning and ending temperatures for anatase–rutile transformation increased with increasing the synthesizing pH value as in Fig. 9. In addition, phase transition for brookite completed ahead of the A–R transition.

The factors affecting the reaction rate of A–R transition have been reported in the literature.[6,7,17] Particle size as suggested is one of the most important factors to control the phase stability of TiO_2 nanoparticles. Recently, Zhang and Bandfield reported that if particle size of the three nanocrystalline phase are equal, anatase is most thermodynamically stable at sizes less than 11 nm, brookite is most stable for crystal size between 11 and 35 nm, and rutile is most stable at sizes greater than 35 nm.[19] Therefore, brookite would transform directly to rutile and anatase may either transform directly to rutile or brookite and then to rutile. From the variation of intensities of anatase and brookite under heat treatment as seen in Figs. 6 and 7, anatase seems to transform to rutile directly since the intensity of brookite does not increase due to the volume lessening of anatase. Fig. 9 shows the most possible mechanism that brookite directly transforms into rutile along with anatase.

It was reported that the rate of B–R transformation is much faster than A–R transformation. The A–R transformation, therefore, is suggested to be enhanced by the

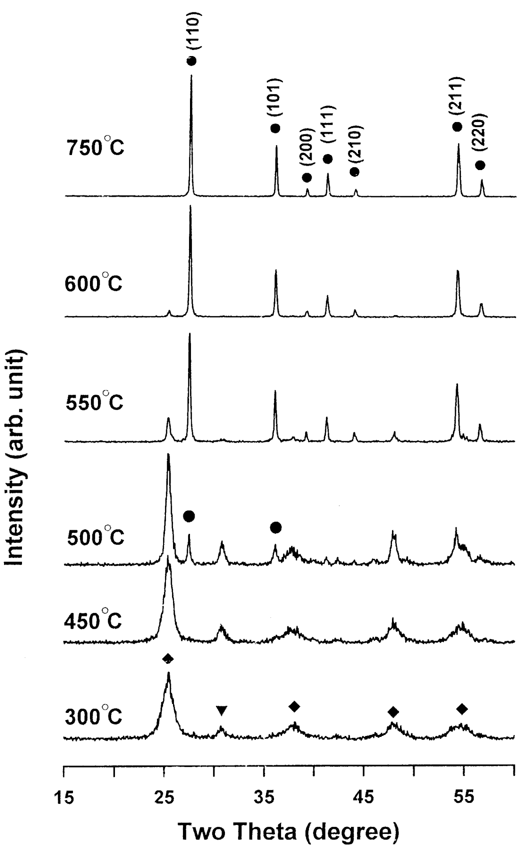

Fig. 6. XRD patterns of the powders with various synthesized pH values of 2 via the temperatures of heat treatment for 2 h. ☐: anatase, ▼: brookite, •: rutile.

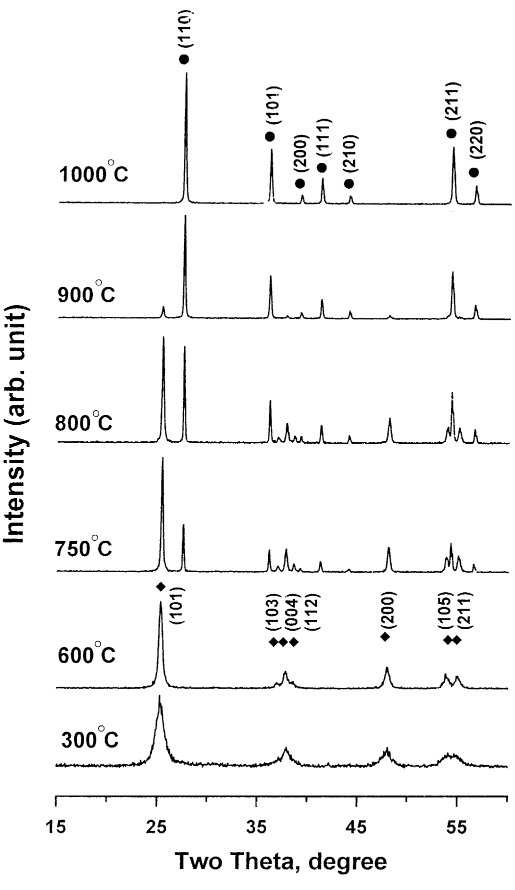

Fig. 7. XRD patterns of the powders with various synthesized pH values of 9 ia the temperatures of heat treatment for 2 h. ☐: anatase, •: rutile.

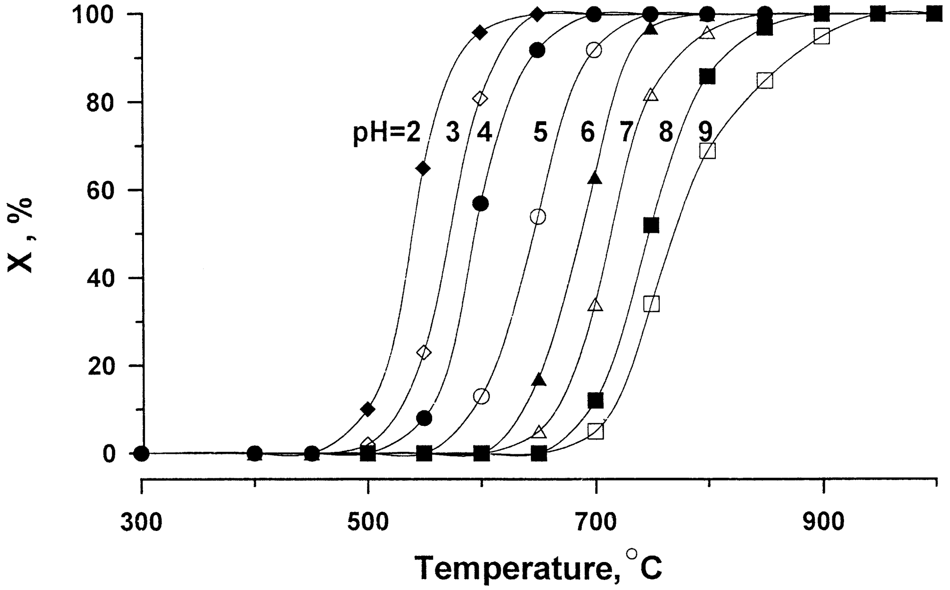

Fig. 8. Correlation between the anatase-rutile transformation fraction and the temperatures of heat treatment for the precipitated powders.

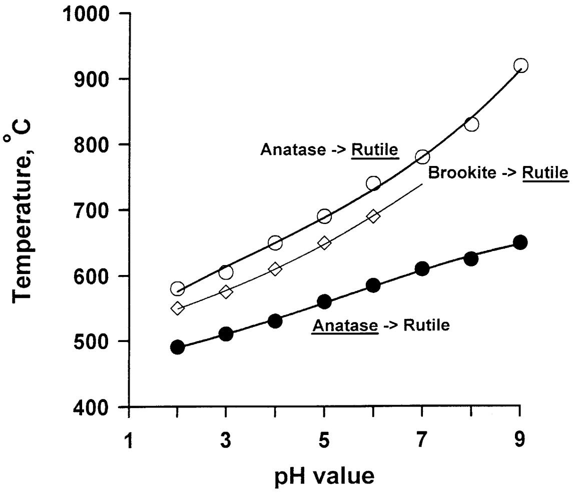

Fig. 9. The beginning and ending temperature of the anatase–rutile transition. •: The beginning temperature of the anatase–rutile transition; ○:the ending temperature of the anatase–rutile transition; ◇: the ending temperature of the brookite transition.

B–R transformation. This may be explained by the higher volume of the nucleation site with brookite phase. Gribb and Banfield suggested that the number of potential nucleation sites is the rate-limiting factor in the anatase–rutile transformation. In addition, pressure on small anatase crystallites may also promote reaction rate by reducing the strain energy accompanying the formation of a rutile nucleus.[7] As mentioned before, the pressure induced from the surface curvature would not result in the large variance in the transition temperatures of A–R transition as in Fig. 9 since the crystallite sizes of the powders have little difference. Additional pressure formed from the attachment of brookite on anatase, therefore, as thought to enhance the rate of A–R transition. On the other hand, the interface between brookite and anatase with high interfacial energy would provide potential nucleation sites for A–R transition. The powders with larger volume fraction of brookite would have larger amount of nucleation sites and thus have higher reaction rate and lower transition temperatures. The existence of brookite, therefore, is responsible for the enhancement of the A–R transition.

4. Conclusions

Nanosized TiO_2 powders with a mixture of anatase and brookite were obtained from the $TiCl_4$ precursor precipitated under controlling pH values by adding aqueous ammonia. The volume fraction of brookite increased with decreasing the synthesized pH value. The average crystallite sizes of the TiO_2 particles heat treated at 450 °C for 2 h are in the range of 7~9 nm. The powders heat treated at 450° for 2 h showed that the *c* parameter of anatase increased with the increase of the pH value and the decrease of the volume fraction of brookie. The beginning and ending temperatures for anatase–rutile transition increased with the increase of the volume fraction of brookite. The enhancement of anatase–rutile transformation in the powders with lower synthesized pH value is ascribed to the formation of the brookite phase.

Acknowledgements

Financial support for this research by National Science Council, Taiwan, ROC, under the grant NSC 88-2216-E-036-014 is gratefully acknowledged.

References

1. Suresh, C., Biju, V., Mukundan, P. and Warrier, K. G. K., Anatase to rutile transformation in sol-gel titania by modification of precursor. *Polyhedron*, 1998, **17**, 3131–3135.
2. Park, S. D., Cho, Y. H., Kim, W. W. and Kim, S.-J., Understanding of homogeneous spontaneous precipitation for monodispersed TiO_2 ultrafine powders with rutile phase around room temperature. *J. Solid State Chem.*, 1999, **146**, 230–238.
3. Zhang, Q., Gao, L. and Guo, J., Effects of calcination on the photocatalytic properties of nanosized TiO2 powders prepared by TiCl4 hydrolysis. *Appl. Catalysis B: Environmental*, 2000, **26**, 207–215.
4. Gennari, F. C. and Pasquevich, D. M., Enhancing effect of iron on the anatase–rutile transition in titanium dioxide. *J. Am. Ceram. Soc.*, 1999, **82**, 1915–1921.
5. Chan, C. K., Porter, J. F., Li, Y.-G., Guo, W. and Chan, C.-M., Effects of calcination on the microstructures and photocatalytic properties of nanosized titanium dioxide powders prepared by vapor hydrolysis. *J. Am. Ceram. Soc.*, 1999, **82**, 566–572.
6. Kumar, K.-N. P., Growth of rutile crystallites during the initial stage of anatase-to-rutile transformation in pure titania and in titanina–alumina nanocomposites. *Scripta Metallurgica et Materilia*, 1995, **32**, 873–877.
7. Gribb, A. A. and Banfield, J. F., Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO_2. *Am. Mineral.*, 1997, **82**, 717–728.
8. Zhang, H. and Banfield, J. F., Thermodynamic analysis of phase stability of nanocrystalline titania. *J. Mater. Chem.*, 1998, **8**, 2073–2076.
9. Ha, P. S., Youn, H.-J., Jung, H. S., Hong, K. S., Park, Y. H. and Ko, K. H., Anatase–rutile transition of precipitated titanium oxide with alcohol rising. *J. Colloid and Interface Sci.*, 2000, **223**, 16–20.
10. Ding, X.-Z. and Liu, X.-H., Grain growth enhanced by anatase-to-rutile transformation in gel-derived nanocrystalline titania powders. *J. Alloys and Compounds*, 1997, **248**, 143–145.
11. Sasmoto, T., Enomoto, S., Shimoda, Z. and Saeki, Y., Effect of hydrolysis conditions on thermal transformation of alkoxide-derived titanium dioxide. *J. Ceram. Soc. Jpn.*, 1993, **101**, 230–232.
12. Gotic, M., Ivanda, M., Sekulic, A., Music, S., Popovic, S. and Turkovic, A., Microstructure of nanozised TiO_2 obtained by sol-gel synthesis. *Mater. Lett.*, 1996, **28**, 225–229.
13. Music, S., Gotic, M., Ivanda, M., Popovic, S., Turkovic, A., Trojko, R. and Sekulic, A., Chemical and microstructueal properties of TiO_2 synthesized by sol-gel procedure. *Mater. Sci. Eng.*, 1997, **B47**, 33–40.
14. Spurr, R. A. and Myers, H., Quantitative analysis of anatase–rutile mixture with an X-ray diffractometer. *Anal. Chem. Res.*, 1957, **29**, 760–762.
15. Ohsaka, T., Temperature dependence of the raman spectrum in anatase TiO_2. *J. Phys. Soc. Jpn.*, 1980, **48**, 1661–1668.
16. Tompsett, G. A., Bowmaker, G. A., Cooney, R. P., Metson, J. B., Rodgers, K. A. and Seakins, J. M., The raman spectrum of brookite, TiO_2 (Pbca, $Z=8$). *J. Raman Spectro.*, 1995, **26**, 57–62.
17. Depero, L. E., Sangaletti, L., Atlierc, B., Bontempi, E., Marino, A. and Zocehi, M., Correlation between crystallite size and microstrains in TiO2 nanopowders. *J. Cryst. Growth*, 1999, **198/199**, 516–520.
18. Penn, R. L. and Banfield, J. F., Oriented attachment and growth, twinning, polytypism, and formation of metastable phases: insights from nanocrystalline TiO2. *Am. Mineral.*, 1998, **83**, 1077–1082.
19. Zhang, H. and Banfield, J. F., Understanding polymorphic transformation behavior during growth of nanocrystalline aggregates: insights from TiO_2. *J. Phys. Chem. B*, 2000, **104**, 3481–3487.