

The effect of calcination temperature on the crystallinity of TiO₂ nanopowders

Yung-Fang Chen^{a,b,*}, Chi-Young Lee^{c,d}, Ming-Yu Yeng^a, Hsin-Tien Chiu^a

^a Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan, ROC

^b Department of Chemical Engineering, Ta-Hwa Institute of Technology, Chung-Lin, Hsinchu 307, Taiwan, ROC

^c Materials Science Center, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

^d Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung 811, Taiwan, ROC

Received 20 January 2002; accepted 9 September 2002

Communicated by M. Roth

Abstract

TiO₂ nanopowders have been prepared using 0.1 M titanium tetraisopropoxide (TTIP) in varied pH aqueous solution containing TMC and NP-204 surfactants. Only the powder acquired from a solution of pH=2 has a regular particle size distribution. Anatase phase powders are obtained by calcination in nitrogen in the 250–500°C temperature range. When calcined at 400°C, the diameter of the nanoparticles is approximately 10 nm with a specific surface area of 106.9 m²/g. As the calcination temperature is increased, the particle size increases. Rutile phase powders are formed at calcination temperatures above 600°C.

© 2002 Elsevier Science B.V. All rights reserved.

PACS: 81.20.Fw; 81.05.Ys; 61.46.+w

Keywords: A1. Crystallinity; A1. Microstructure; B1. Nanomaterials; B1. Titanium oxide

1. Introduction

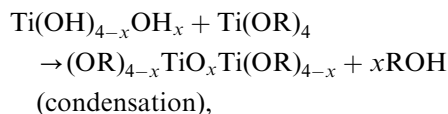
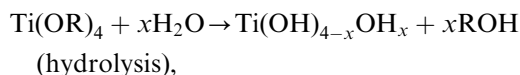
Titanium dioxide (TiO₂) is one of the most interesting nanostructured materials at the present time, since it possess excellent optical, dielectric and catalytic properties. It is therefore commonly used in industry as a component of pigments [1],

gas sensors [2–4], photocatalysts [5,6], etc. Increasing the surface area or decreasing the primary particles size can improve the performance of TiO₂ in most of the applications. In the photocatalytic reactions, the anatase phase of TiO₂ functions better than that of rutile TiO₂.

There are many methods of producing TiO₂ nanopowders, such as chemical vapor deposition (CVD) [7], the sol–gel technique [8], hydrolysis [9] and the microemulsion method [10]. Hydrolysis of alkoxides is the most common method of producing TiO₂ nanopowders. The reactions can be schematically represented as follows [11]:

*Corresponding author. Department of Chemical Engineering, Ta-Hwa Institute of Technology, Chung-Lin, Hsinchu 307, Taiwan, ROC. Tel.: +886-35-592-3551; fax: +886-35-592-7310.

E-mail address: yfchen@thit.edu.tw (Y.-F. Chen).



where R is ethyl, propyl, *i*-propyl, *n*-butyl, etc.

In these reactions, there are many factors influencing the size and morphology of the formed TiO₂ particles. These factors include the alkoxy groups of alkoxides, the concentration of reactants, the pH of solution, the temperature of hydrolysis and the addition of electrolytes [12–14]. There have been records showing that the reactivity of hydrolysis decreases as the alkoxy chain length is increased [12]. Look and Zukoski [14] have shown that the higher is the concentration of HCl used, the smaller are the particles obtained. In this case, the concentration of titanium tetraethoxide (TEOT) is 0.2 M, and the final particles are approximately $(0.35 \pm 0.04) \mu\text{m}$ in diameter for $0.6 \text{ M} < [\text{H}_2\text{O}] < 1 \text{ M}$ and $5 \times 10^{-4} \text{ M} < [\text{HCl}] < 7 \times 10^{-4} \text{ M}$.

Hereby we report on the preparation of TiO₂ nanopowders using titanium tetraisopropoxide in varied pH aqueous solutions with cationic and nonionic surfactants. When calcined in a N₂ atmosphere at a temperature of 400°C, nanopowders of the TiO₂ anatase phase are obtained. The primary particles are approximately 10 nm in diameter and the specific surface area is 106.9 m²/g.

2. Experimental procedure

Titanium tetraisopropoxide, TTIP (supplied by Aldrich), was used as a starting material without further purification. A TTIP isopropanol solution (0.1 M) was slowly dripped into an aqueous solution containing surfactants of TMC (Cetyl Trimethyl Ammonium Chloride, from Taiwan Surfactant Company) and NP-204 (Polyoxyethylene Nonyl Phenyl Ether, from En How Polymer Chemical Company). The desired pH value of the solution was adjusted by adding HCl or NaOH. Hydrolysis of TTIP offered a turbid solution.

After centrifugation, TiO₂ particles were precipitated. The solids were collected and dried at 100°C for 2 h in a vacuum system to remove water and IPA (*i*-propanol). Finally, the dried particles were calcined at temperatures of 250°C, 300°C, 400°C, 500°C, 600°C, 700°C and 900°C in a N₂ atmosphere.

Several techniques were used for characterization of the powders. Distribution of the particles size in the solution was measured by means of light scattering using a Honeywell UPA150. Thermogravimetric analysis (TGA) was performed using a Du-Point TGA 51 instrument in the temperature range of 50–800°C in nitrogen atmosphere at a heating rate of 10°C/min. A Fourier-transform infrared absorption spectrophotometer (FT-IR) Perkin-Elmer System 2000 was used to determine the specific functional groups. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to estimate the particle sizes and study their morphology. The SEM images were taken using a HITACHI S-4000 equipped with a field emission gun at 25 kV. The transmission electron micrographs were obtained by using a JEOL JEM-2000 FX II microscope at 15 kV. Samples for TEM were prepared by placing a drop of suspension solution on a copper grid coated with carbon film and dried in a vacuum system. Powder X-ray diffraction (XRD) was measured on a MAC MO3S diffractometer (at 40 kV and 30 mA) with nickel filtered CuK α radiation. The particle size was approximated from the X-ray line broadening, using the Debye–Scherrer equation. The specific surface area of the powders was measured via the Brunauer–Emmett–Teller (BET) method with nitrogen absorption (FISION Sorpty 750). The Ti/O ratio was determined by a JEOL JXA-8800M electron probe X-ray microanalyzer (EPMA). An elemental analyzer (EA, Heraeus CHN-O Rapid) was used to determine the amount of carbon in the powder.

3. Results and discussion

The hydrolysis of TTIP has been performed under the conditions of varied pH aqueous solutions and using TMC and NP-204 as surfactants to

obtain turbid solutions. When the pH level of the solution is higher than 2, the gel precipitants are formed immediately as the hydrolysis reactions occur. Otherwise, when the pH level of the solution is lower than 2, there is good dispersion. According to the particle size analyzer measurements, the particle size distribution is uniform only when the solution has a pH of 2 (Fig. 1) and the particle size is approximately 16 nm.

After being centrifuged and dried at 100°C in a vacuum system for 2 h, a yellow-white powder is obtained. Fig. 2 depicts the thermogravimetric characteristics measured for these particles. The thermal analysis has been performed in a dried nitrogen flow to minimize oxidation effects. Obviously, the weight loss proceeds in stages with increasing temperature, while the most significant loss occurs between 100°C and 400°C. The total weight loss monitored up to 600°C is 33.07% for the as-prepared powder. The TGA measurements for the TMC and NP-204 surfactants indicate that the organic surfactants decompose at temperatures below 300°C. From the TGA data of the as-prepared powders, we presume that the additional weight loss above 400°C is probably caused by a residual decomposition product that forms a sheath over the titania particles [11].

In Fig. 3 we show the IR transmission spectra of TiO₂ powders produced under various calcination temperatures. The IR spectrum (Fig. 3a) of the particles dried at 100°C for 2 h under vacuum shows broad bands at 3365 and 1623 cm⁻¹. These bands can be assigned to the Ti–OH stretching modes [15]. Additionally, two bands at 2917, 2843 cm⁻¹ and one band at around 1507 cm⁻¹ are assigned to the asymmetric stretching, symmetric stretching and bending C–H vibrations.

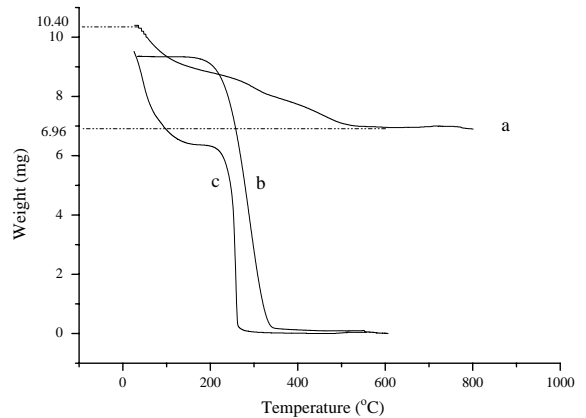


Fig. 2. TG measurements of (a) as-prepared powder, dried at 100°C under vacuum for 2 h, (b) NP-204, (c) TMC.

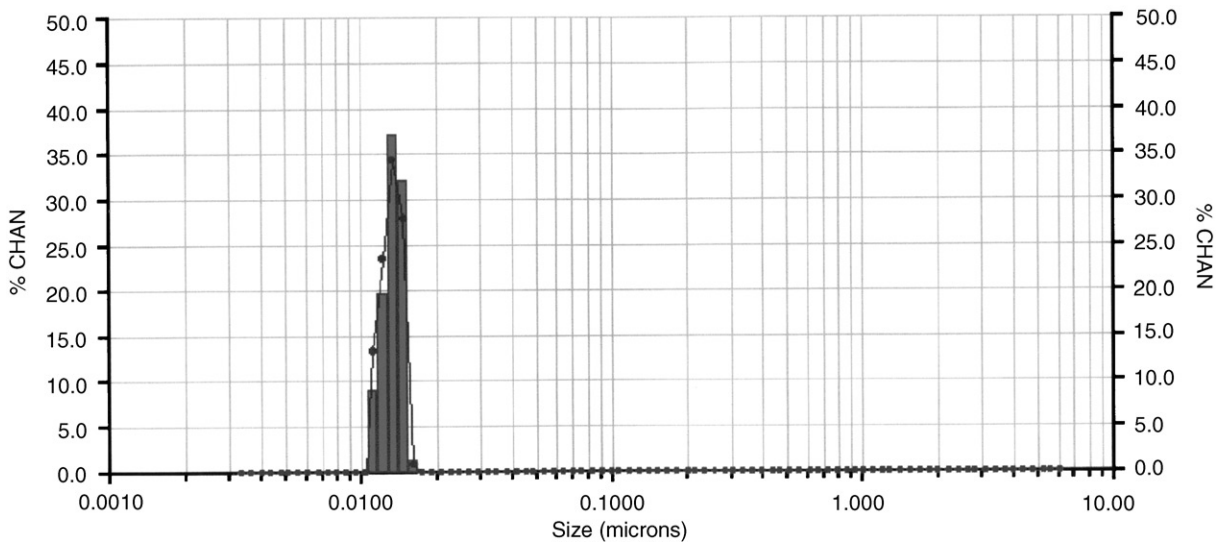


Fig. 1. Particle size distribution at pH=2 in the solution.

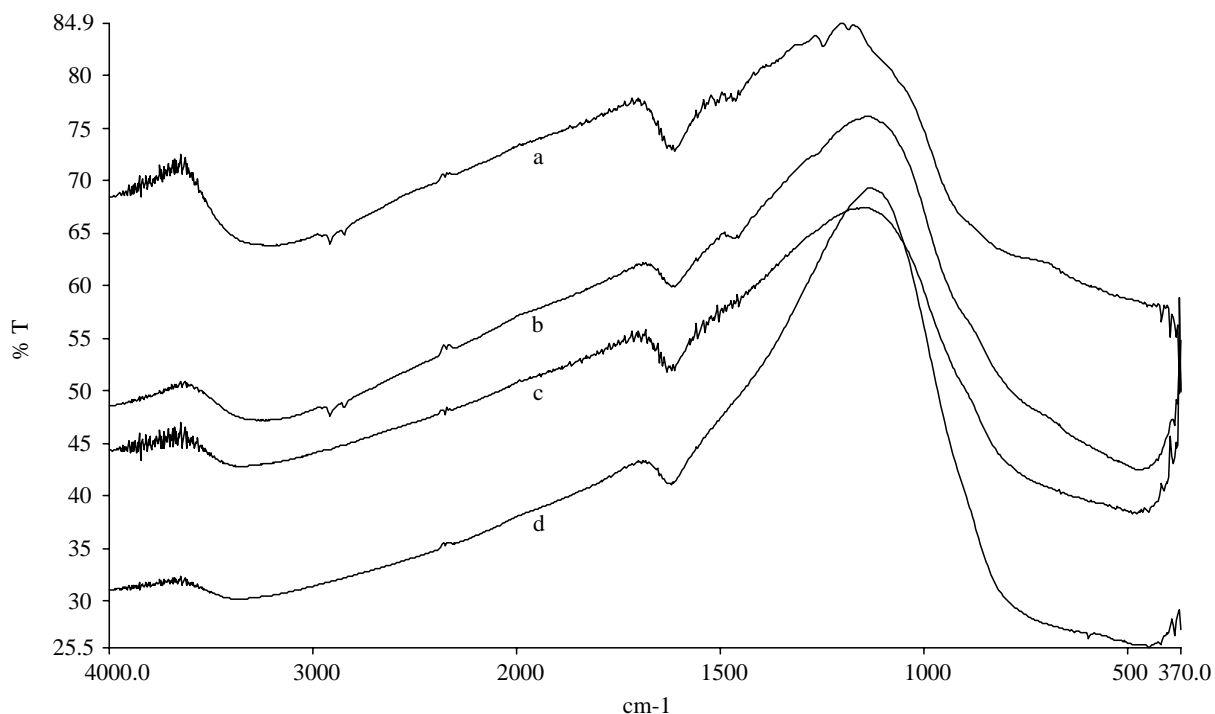


Fig. 3. IR spectra of powders prepared at various temperatures: (a) dried at 100°C, (b) calcined at 250°C, (c) 300°C, (d) 400°C.

The C–H vibrations can be attributed to the organic part of the surfactants that remain incorporated even after the drying process. After calcination at higher temperatures, the Ti–OH vibration bands become much weaker. This shows that a certain amount of OH groups in TiO₂ are removed during the calcination. After a heat treatment at temperatures above 300°C, the spectra (Fig. 3c and d) show the disappearance of the peaks of the Ti–OH and C–H vibrational modes, indicating that the elimination of hydroxy groups, and the decomposition of organic surfactants is complete. All spectra show the Ti–O–Ti absorption peaks at 400–600 cm⁻¹ [15].

In Fig. 4 we show the XRD patterns of TiO₂ powders calcined at various temperatures in flowing nitrogen atmosphere for 2 h. All samples are crystalline. The XRD pattern of the powder formed at 250°C (Fig. 4a) is characteristic of anatase TiO₂. The temperature observed in our result is much lower than that achieved by Kim et al. at 500°C [10]. The XRD peaks become sharper as the calcination temperature is increased.

When the calcination temperature is above 600°C, rutile phase peaks appear. This suggests that there is a phase transition from anatase to rutile at about 600°C which agrees with previous experiments [16]. Residual anatase phase still exists in the samples up to 700°C. At 900°C, the transition to the rutile phase is complete.

Crystallinity of the titania powders calcined at various temperatures has been studied. The crystallite size of the particles has been estimated from the Debye–Scherrer's equation [17] using the XRD line broadening. The (1 0 1) plane diffraction peak is used for anatase and the (1 1 0) peak for rutile. The specific surface area has been measured using the BET method. The effect of the calcination temperature on the crystallinity of TiO₂ is reported in Table 1. As seen in Table 1, the smallest crystallites are obtained from the hydrolysis of TTIP in the solution with pH=2 and a calcination temperature of 250°C. At higher calcination temperatures, the crystallites formed are larger in size, which can be attributed to the thermally promoted crystallite growth. The size of

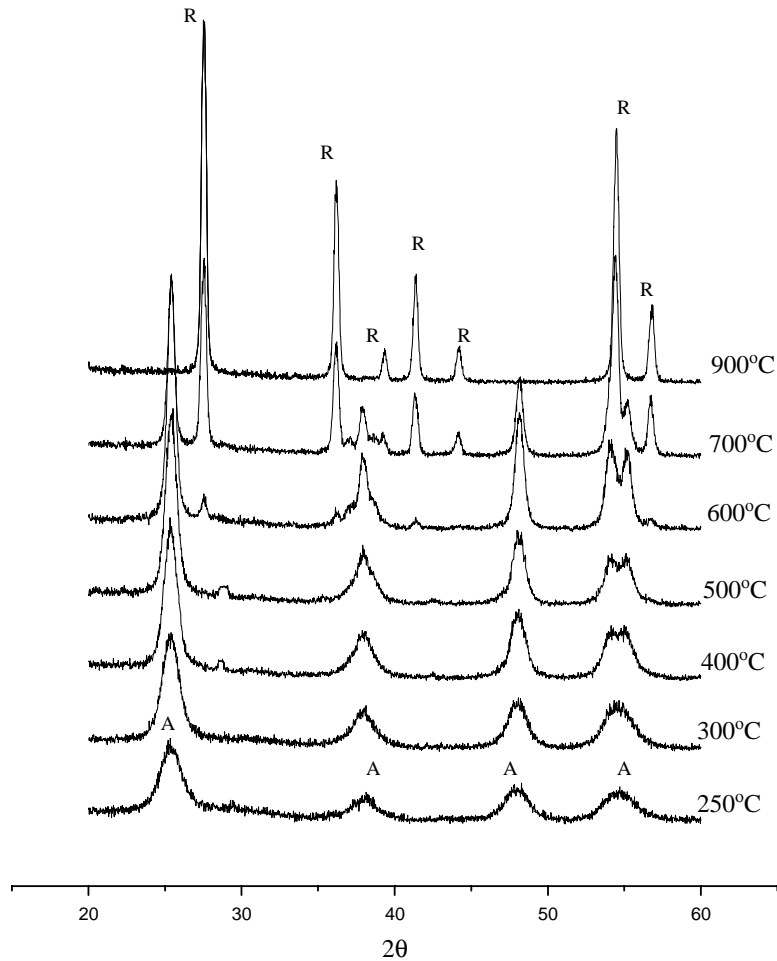


Fig. 4. XRD patterns of powders prepared at different calcination temperatures (A: Anatase, R: Rutile).

the anatase crystallites increases from 6.8 to 17.7 nm when the calcination temperature is raised from 250°C to 700°C. The rutile phase shows a different result. The crystallite size is 20.5 nm at 600°C, while it increases only slightly to 22.7 nm at 900°C. The change in the specific surface areas of the samples is also listed in Table 1. As expected, the sample prepared at 250°C has the highest surface area, 145.8 m²/g. Apparently, the surface areas can be correlated to the crystallite sizes, i.e. smaller size crystallites have larger specific surface areas. As the temperature of calcinations is raised to 700°C, the surface area decreases to 26.85 m²/g.

Table 1

XRD and specific surface area results for TiO₂ particles calcined at various temperatures for 2 h in N₂ atmosphere

Calcined temp. (°C)	Crystallite size (nm) ^a		Specific surface area (m ² /g)
	Anatase	Rutile	
250	6.8	—	145.8
300	7.3	—	120.1
400	8.9	—	106.9
500	11.3	—	100.7
600	15.1	20.5	64.88
700	17.7	20.5	26.85
900	—	22.7	—

^a Calculated by (101) for anatase, (110) for rutile.

Fig. 5 shows the SEM micrographs of TiO_2 particles prepared at different calcination temperatures. As shown in Fig. 5a, the as-prepared powders consist of ~ 10 nm spherical particles, and aggregation takes place during the particle formation process (see Figs. 5a and b). It is observed that, the higher is the calcination temperature, the larger particle size is obtained. For the sample calcined at 700°C (Fig. 5c), the particle size is 50 nm. Grain boundaries are clearly observed in the SEM micrographs of the samples calcined at high temperatures. The TEM image and the select-area electron diffraction (SAED) pattern of a sample calcined at 400°C are shown in Figs. 6(a) and (b), respectively. The calcined TiO_2 particles are aggregated into clusters in the range of several hundred nanometers. Because of the poor contrast in the micrograph, it is difficult to measure the size of the primary spherical particles accurately. From the micrograph, their diameter is estimated to be below 10 nm. In Fig. 6(b), the

SAED pattern of TiO_2 calcined at 400°C is shown. The first four rings are assigned to the (101), (004), (200), (005) reflections of the anatase phase. Fig. 7 shows the SAED pattern of the sample calcined at 250°C in a N_2 atmosphere for 2 h. The ring pattern is assignable to the anatase phase too. The SAED studies are in good agreement with the XRD measurements.

Elemental analysis has been performed on the sample calcined at 400°C in an atmosphere of flowing nitrogen. The result shows that the residual carbon content is 1.07 wt%. It is consistent with the TGA results of the as-prepared sample shown in Fig. 2a. The residual carbon is the result of the incomplete decomposition of the surfactants. The chemical composition of the powder has been determined by EPMA. The stoichiometry of the titanium oxide is $\text{TiO}_{2.1}$, which indicates that the sample does not lose oxygen after calcination in the atmosphere of flowing nitrogen.

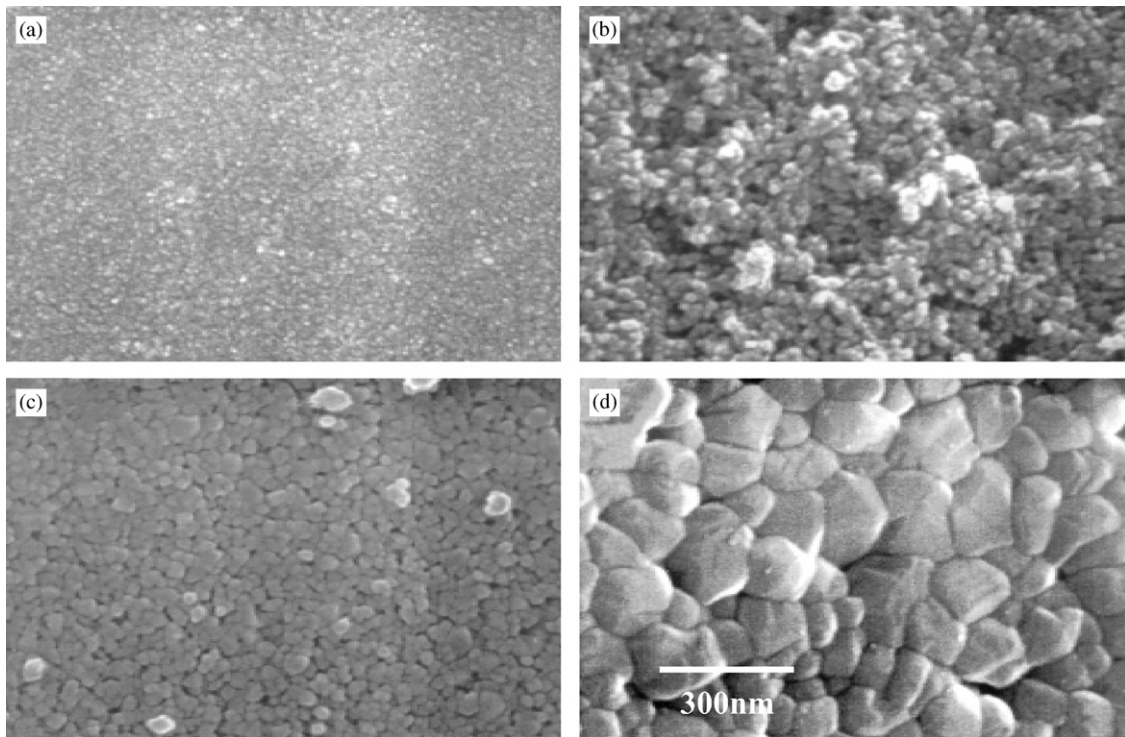


Fig. 5. SEM micrographs of powders prepared at different temperatures: (a) solution, (b) calcined at 400°C , (c) 700°C , (d) 900°C .

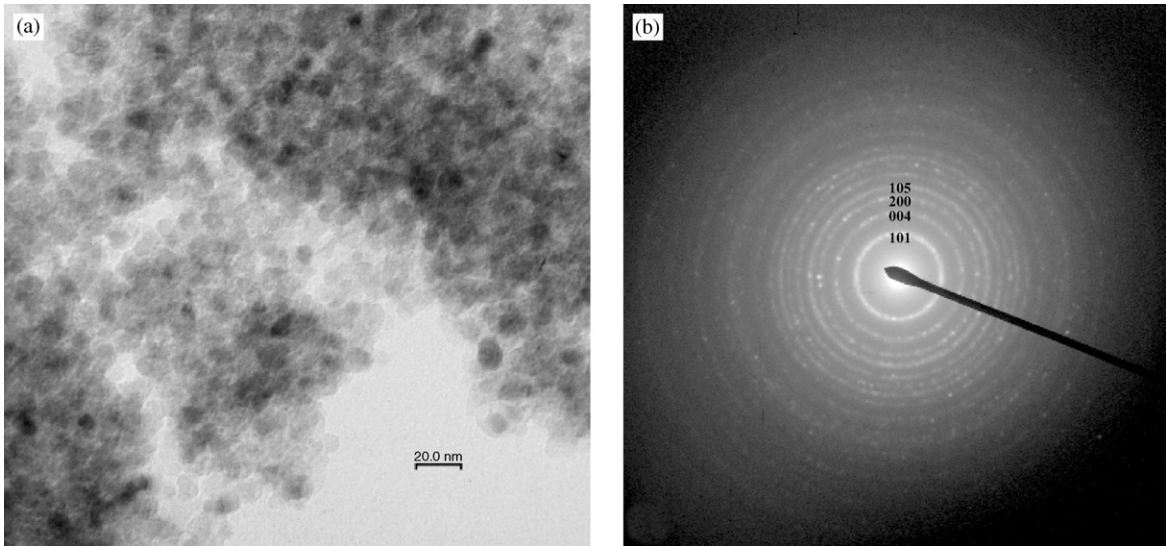


Fig. 6. (a) TEM and (b) SEAD of powder calcined at 400°C.

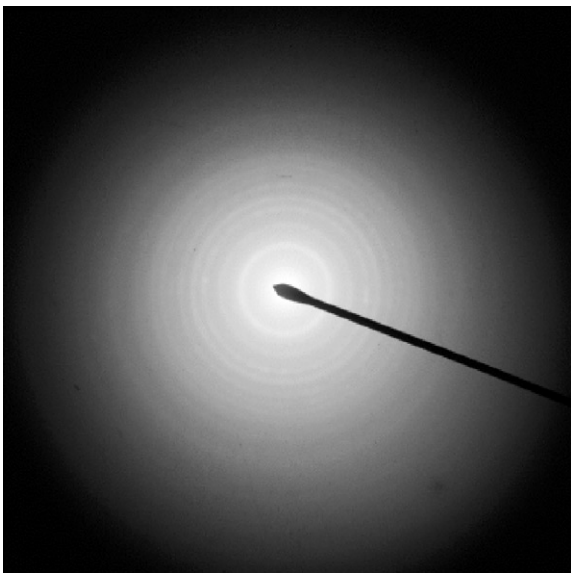


Fig. 7. SEAD of powder calcined at 250°C in N₂ atmosphere for 2 h.

4. Conclusions

Nanocrystalline TiO₂ powders can be easily prepared by the hydrolysis of titanium tetraisopropoxide (TTIP) in the presence of the TMC and NP-204 surfactants. According to the particle size

analysis measurements, only the powder obtained from a solution of pH = 2 has a uniform particle distribution. Anatase phase powders are obtained at the calcinations temperature of 250–500°C in N₂. When calcined at 400°C, the diameter of nanoparticles is approximately 10 nm with a specific surface area of 106.9 m²/g. As the calcinations temperature is increased, the particle size increases. Rutile phase powders are formed at calcinations temperatures above 600°C.

Acknowledgements

We thank the National Science Council of the Republic of China for support (NSC-89-2113-M-007-061 and NSC-89-2113-M-009-013).

References

- [1] M.J. Hird, J. Coatings Tech. 48 (1976) 75.
- [2] L. Zheng, M. Xu, T. Xu, Sensors and Actuators B 66 (2000) 28.
- [3] M. Ferroni, V. Guidi, G. Martinelli, G. Faglia, P. Nelli, G. Sberveglieri, Nanostructured Mater. 7 (1996) 709.
- [4] Y. Takao, K. Fukuda, Y. Shimizu, M. Egashira, Sensors and Actuators B 10 (1993) 235.

- [5] D.M. Blake, J. Webb, C. Turchi, K. Magrini, *Sol. Energy Mater.* 24 (1991) 584.
- [6] N.N. Rao, S. Dube, *J. Mol. Catal. A* 104 (1996) L197.
- [7] J.A. Ayllon, A. Figueras, S. Garelik, L. Spirkova, J. Durand, L. Cot, *J. Mater. Sci. Lett.* 18 (1999) 1319.
- [8] E. Haro-Poniatowski, R. Rodriguez-Talavera, M. de la Cruz Heredia, O. Cano-Corona, R. Arroyo-Murillo, *J. Mater. Res.* 9 (1994) 2102.
- [9] H.K. Park, D.K. Kim, C.H. Kim, *J. Am. Ceram. Soc.* 80 (1997) 743.
- [10] E.J. Kim, S.-H. Hahn, *Mater. Lett.* 49 (2001) 244.
- [11] D.C. Hague, M.J. Mayo, *J. Am. Ceram. Soc.* 77 (1994) 1957.
- [12] D. Vorkapic, T. Matsoukas, *J. Am. Ceram. Soc.* 81 (1998) 2815.
- [13] J.-L. Look, C.F. Zukoski, *J. Am. Ceram. Soc.* 78 (1995) 21.
- [14] J.-L. Look, C.F. Zukoski, *J. Am. Ceram. Soc.* 75 (1992) 1587.
- [15] T. Lopez, R. Gomez, E. Sanchez, F. Tzompantzi, L. Vera, *J. Sol-Gel Sci. Tech.* 22 (2001) 99.
- [16] K.P. Kumar, K. Keizer, A.J. Burggraaf, *J. Mater. Chem.* 3 (1993) 1141.
- [17] A.R. West, *Solid State Chemistry and its Applications*, Wiley, New York, 1986, p. 174.