JOURNAL OF MATERIALS SCIENCE **37** (2002) 4683 – 4689

Preparation of spherical SnO_2 particles by W/O type emulsion method

H. SHIOMI, C. TANAKA
Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
E-mail: Shiomi@ipc.kit.ac.jp

An attempt to prepare spherical particles was made using a W/O type emulsion as a reaction field. The effects of surfactant content, W/O ratio and stirring conditions for the preparation of emulsions, which determined the size of water drops in the emulsions, were investigated on the size and morphology of the obtained SnO_2 particles. The size and morphology of the obtained particles were largely influenced by a water/surfactant molar ratio (R-value) for the preparation of the emulsions. Particles having relatively high sphericity were obtained at an R-value below 1500. In order to obtain mono-sized SnO_2 particles with narrow distributions, R-value should be adjusted to the narrow range from 250 to 500. Spherical SnO_2 particles showing narrow particle size distributions were obtained at W/O ratio of 1/1 and surfactant content of 11.2×10^{-2} mol/l or 22.4×10^{-2} mol/l. Furthermore, the particle size and morphology of SnO_2 depended on the revolution rate of an emulsifier for emulsification. Mono-dispersed spherical particles having narrow size distributions formed at revolution rates of 3000 and 4000 rpm. At extremely low and high revolution rate of the emulsifier, particles showing high sphericity were not obtained, but agglomerates of un-spherical fine particles. The interfacial reaction time determined the internal structures of spherical particles. The reaction for short time yielded hollow spherical SnO_2 particles, and the internal structure of the particles became denser with increasing reaction time.

1. Introduction

Preparation processes of ceramic powders are broadly divided into two categories, that is "*Breaking down process*", in which coarse grains are used as starting materials and pulverized with various grinding machines, and "*Building up process*", in which particles are usually prepared in gas or liquid phase [1]. For example, a colloidal process is one of the most typical building up methods and applied to preparation of various ceramic powders and pigments [2]. This process includes precipitation of inorganic salts [3], hydrolysis of alkoxides [4] and so on, and makes it possible to precisely control the size, morphology, and chemical compositions of final products [5]. Therefore, the colloidal process is often used for the preparation of micrometer-sized and submicrometer-sized spherical particles having narrow particle size distributions [6–8].

Various preparation methods of mono-dispersed particles has been proposed by many researches, such as hydrolysis of inorganic salt aqueous solutions at high temperatures [9], which was established by Matijevic, homogeneous precipitation using urea and formaldehyde as precipitants [10, 11], hydrolysis and condensation of metal alkoxides [12–14] etc.

The powder synthesis by a W/O type micro-emulsion method was developed in the early 80s and has been applied to preparation of many kinds of mono-dispersed particles [15, 16]. In addition, a wide variety of studies on the fabrication of inorganic micro-capsules by the micro-emulsion method has been carried out for the last two decades, and possibility for the synthesis of functional hybrid particles has been reported [17–19].

SnO_2, which is focused on in the present research, has been put to practical use as a starting material of various gas sensing elements [20–26] and conductive components of glass composites, such as hybrid IC thick film resistors [27–29], because of its excellent thermodynamic and electrochemical stability. In order to satisfy the desired electrical properties of these electronic devices, it is necessary to accurately control microstructure of them. For this purpose, it is essential to synthesize SnO_2 particles having well-controlled size and morphology.

In this study, an attempt to prepare spherical SnO_2 particles was made using a W/O type emulsion as a reaction field. The size and morphology of water drops in the emulsions are thought to largely influence those of the obtained SnO_2 particles. Therefore, in the present study, the effects of surfactant content, W/O ratio and stirring conditions for the preparation of the W/O type emulsions, which determined the size and morphology of water drops in the emulsions [30, 31], were investigated on the size and morphology of the SnO_2 particles.

0022–2461 © *2002 Kluwer Academic Publishers*

2. Experimental

Fig. 1 shows preparation procedure of spherical SnO_2 particles by a W/O emulsion method. The 1.0 mol/l aqueous solutions of sodium stannic acid (Na_2SnO_3) were mixed with benzene containing a surfactant (sorbitan monooleate, Span80) of fixed amount so that the total volume of the mixed solution was 100 ml. The mixed solutions were stirred with an emulsifier for 3 min at a fixed revolution rate to obtain W/O type emulsions. In this study, the effects of the preparation conditions of W/O type emulsions, including the amount of surfactant, W/O ratio and the revolution rates of the emulsifier, were investigated on the size and morphology of obtained SnO_2 particles.

The details of the preparation conditions of the emulsions are summarized in Table I. The effects of the amount of the surfactant and W/O ratio were investigated for the emulsions prepared by stirring at 3000 rpm for 3 min. Also, the W/O type emulsions were prepared at the various revolution rates of the emulsifier. In this case, the surfactant concentration and W/O ratio were kept constant at 11.2×10^{-2} mol/l and 1/1, respectively.

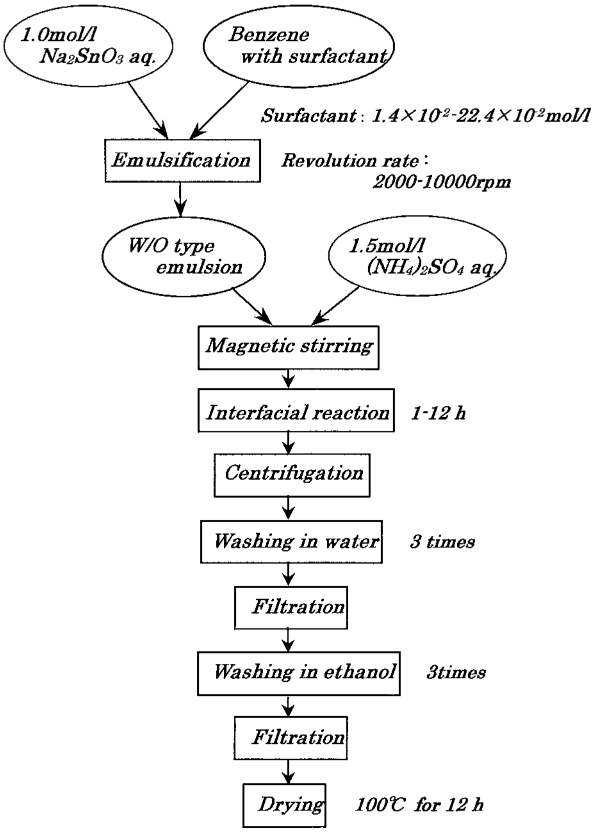

Figure 1 Preparation procedure of spherical SnO_2 particles by W/O emulsion method.

The obtained W/O type emulsions were added to 1.5 mol/l $(NH_4)_2SO_4$ aqueous solution of fixed amount with stirring to obtained SnO_2 hydrates according to the following chemical reaction. Although the chemical reaction shown in Equation 1 is equivalent when an $Na_2SnO_3/(NH_4)_2SO_4$ molar ratio is 1/1, it was adjusted to 1/3, which is an adequate preparation condition for spherical SnO_2 particles, according to the results of preparatory experiments.

$$Na_2SnO_3 \cdot xH_2O + (NH_4)_2SO_4 \rightarrow SnO_2 \cdot xH_2O + 2NH_3 + Na_2SO_4 \qquad (1)$$

Although the time of interfacial reaction was commonly 1 h in sires of experiments, the samples for observation of the microstructure in the spherical SnO_2 particles were also prepared by the reaction for 12 h. Both the preparation of emulsions and interfacial reaction were conducted at a constant temperature of 30°C at all times, because the stability of emulsions, which influences the morphology and size of final products, would be changed by temperature [32].

After centrifuging precipitates obtained by the interfacial reaction from mother liquor, they were washed in ion-exchanged water in order to remove Na_2SO_4 generated during the interfacial reaction. For some application, especially for electrical application, the sodium contamination is critical. In our preliminary experiment, the change of the amount of sodium contamination with the number of washing in ion-exchanged water had been examined with an inductively coupled plasma spectroscope (ICP, Seiko Electronics: SPS-4000). After washing above three times, the amount of the sodium contamination had been almost constant from 30 to 40 ppm. Therefore, the washing of the precipitates in ion-exchanged water was carried out three times in the present study. After filtrating the precipitates washed in ion-exchanged water, they were ultrasonically redispersed in ethanol in order to remove residual organic compounds. The washing in ethanol was also conducted three times. After washing, the precipitation was collected by suction filtration, and then dried at 100°C in air for 12 h.

The characterization of the obtained SnO_2 particles involved SEM observation and the measurement of particle size distributions. After sputtering C or Au as a conductive film, the morphology of the SnO_2 particles was observed using a field-emission type scanning electron microscope. For 500 spherical particles selected in SEM images, diameters of the circle of equal projected area (Heywood's diameter) were determined by a computer assisted image analysis, and then average particle diameters were calculated.

TABLE I Preparation conditions of W/O type emulsions. R-values enclosed within parentheses for each surfactant concentration indicates water/surfactant molar ratios at W/O ratios of 1/3, 1/1 and 3/1, respectively

Surfactant concentration (mol/l)	W/O ratio	Revolution rate of emulsifier (rpm)
1.4×10^{-2} ($R = 1330, 4000, 12000$) 2.8×10^{-2} ($R = 670, 2000, 6000$) 5.6×10^{-2} ($R = 330, 1000, 3000$) 11.2×10^{-2} ($R = 170, 500, 1500$) 22.4×10^{-2} ($R = 83, 250, 750$)	1/3, 1/1, 3/1	3000
11.2×10^{-2} ($R = 500$)	1/1	2000, 3000, 4000, 5000, 10000

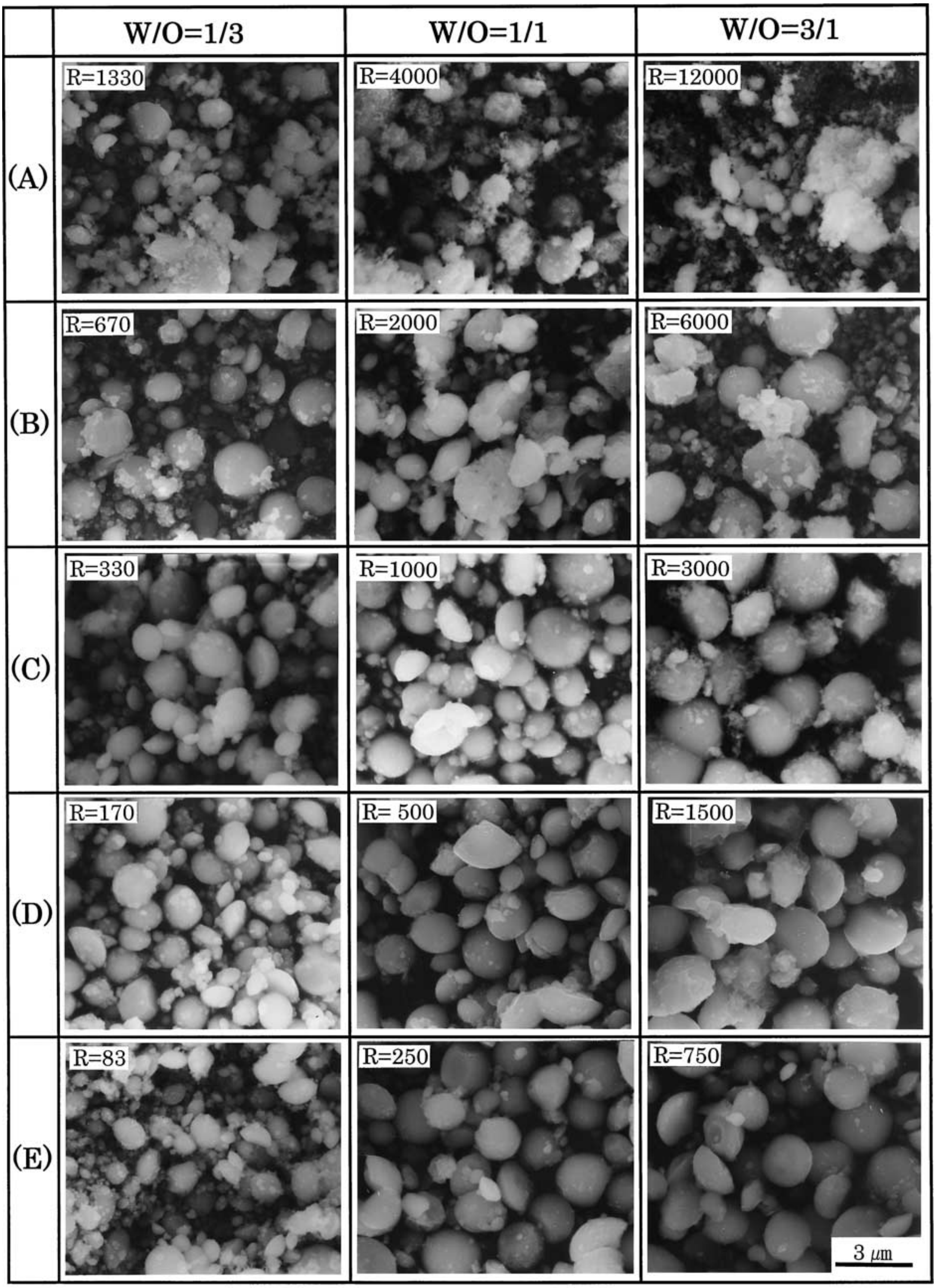

Figure 2 SEM photographs for SnO_2 particles prepared at various surfactant concentrations and W/O ratios. *R*-value in each photograph indicates surfactant/water molar ratio for preparation of W/O type emulsion. Surfactant concentration: (A) 1.4×10^{-2}, (B) 2.8×10^{-2}, (C) 5.6×10^{-2}, (D) 11.2×10^{-2}, (E) 22.4×10^{-2} mol/l.

In order to observe the internal structure of a spherical particle, the samples ultrasonically fractured at 250 W after firing at 900°C were observed by the scanning electron microscope.

The particle size distributions of the obtained SnO_2 particles were measured by a laser light scattering method using 0.2 mol/l sodium hexametaphosphate aqueous solution as a dispersing medium after ultrasonication at 60 W and 40 W for 2 min and 3 min, respectively.

3. Results and discussion

3.1. Effects of surfactant concentration and W/O ratio

Fig. 2 shows SEM observation results for spherical SnO_2 particles prepared at various surfactant concentrations and W/O ratios. R-value indicated in each photograph means water/surfactant molar ratio for the preparation of emulsions.

For W/O ratio = 1/3, although spherical particles were formed at a surfactant concentration as low as 1.4×10^{-2} mol/l, the sphericity of particles was still lower even at high surfactant concentrations than that of particles prepared at W/O ratio = 1/1. Especially, spherical particles were not formed, but agglomerates of fine particles at 22.4×10^{-2} mol/l. For W/O ratio = 1/1, the formation of spherical particles was confirmed at above 2.8×10^{-2} mol/l, whereas, for W/O ratio = 3/1, the sphericity of particles was low even at surfactant content of 5.6×10^{-2} mol/l.

Fig. 3 shows particle size distributions for the samples prepared using emulsions containing 5.6×10^{-2}, 11.2×10^{-2} and 22.4×10^{-2} mol/l surfactant at W/O ratio = 1/1. Fig. 4 shows the change in particle size distributions for the samples containing 11.2×10^{-2} mol/l surfactant with W/O ratio.

From both figures, it was clarified that almost mono-dispersed spherical SnO_2 particles having narrow particle size distributions were obtained from the emulsions containing 11.2×10^{-2} mol/l ($R = 500$) and 22.4×10^{-2} mol/l ($R = 250$) at W/O ratio = 1/1 although spherical particles were formed under all preparation conditions presented in Figs 3 and 4. In other cases, particle size distributions were broad.

From the above-mentioned results, it is clear that the emulsion should be prepared at an R-value below 1500 in order to obtain particles with relatively high sphericity. Furthermore, it is desirable to adjust R-value in a restricted range from 250 to 500 for the preparation of mono-dispersed spherical particles having narrow particle size distribution.

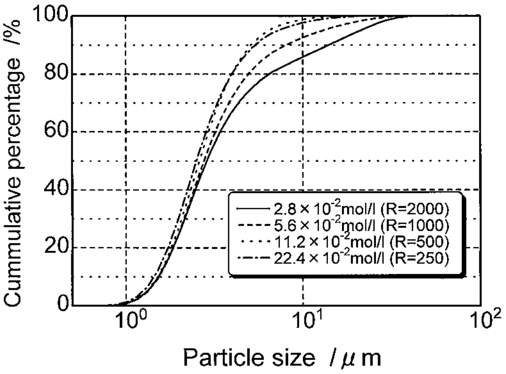

Figure 3 Change in the particle size distributions with surfactant concentration. R-values indicate water/surfactant molar ratios for preparation of W/O type emulsion (W/O ratio: 1/1, Stirring speed : 3000 rpm).

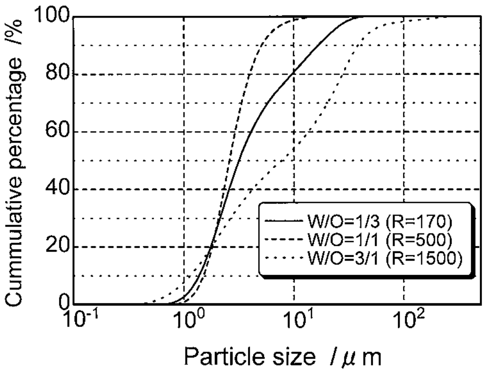

Figure 4 Change in the particle size distributions with W/O ratio. R-values indicate water/surfactant molar ratios for preparation of W/O type emulsion (surfactant concentration: 11.2×10^{-2} mol/l, Stirring speed: 3000 rpm).

At higher R-values, which means higher water contents, the amount of surfactant is not enough to stabilize water drops in organic media, so the emulsions are unstable [29]. When the chemical reaction occur at the unstable water/oil interface, the water drop would collapse before SnO_2 spherical particles fully develop. Moreover, if water/surfactant molar ratio (R-value) for preparation of the emulsion is high, the water drops in the emulsion would coalesce each other to reduce water/oil interfacial area [33]. In this case, it is thought that large water drops are collapsed by shear stress generated during stirring in an interfacial reaction step. Consequently, the particles with homogeneous morphology are difficult to be obtained, but the agglomerates of fine particles are formed. Large cohesive force of fine particles makes it difficult for the agglomerates to be disintegrated into primary particles even by ultrasonication, and thus the particle size distribution is broad. On the other hand, at low R-values, the size of the water drops in the emulsions is reduced, and water molecules in a reversed micelle are strongly constrained by hydrophilic groups in surfactant molecules [33]. Furthermore, the excess surfactant molecules is attracted around the micelles by van der Waals force between hydro-carbon chains, and form bi-molecular layers at the outside of water drops, i.e., hemi-micelles [34]. Therefore, the formation of spherical SnO_2 by an interfacial reaction would be prevented.

Figs 5 and 6 show the dependences of the average size for 500 spherical SnO_2 particles randomly selected in SEM images, which is measured by a computer assisted image analysis, on the surfactant content at W/O ratio = 1/1 and W/O ratio at 11.2×10^{-2} mol/l surfactant, respectively.

As seen from Fig. 5, at constant W/O ratio, the particle size decreased with increasing surfactant content. In addition, from Fig. 6, it was clarified that the higher W/O ratio, the larger the particle size, at constant surfactant content. Moreover, from both figures, it was seen that the lower R-values led to smaller particle size of spherical particles.

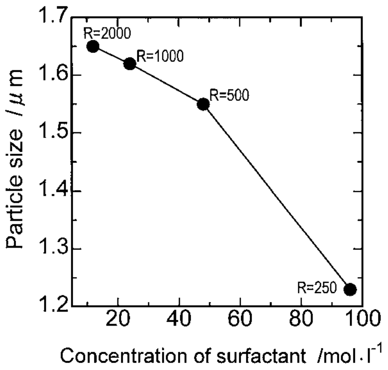

Figure 5 Effect of surfactant concentration on the size of spherical SnO_2 particles. *R*-values indicate water/surfactant molar ratios for preparation of W/O type emulsion (W/O ratio: 1/1, Stirring speed : 3000 rpm).

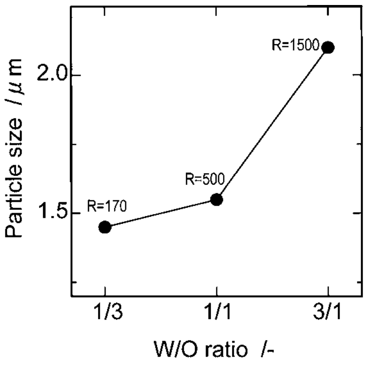

Figure 6 Effect of W/O ratio on the size of spherical SnO_2 particles. *R*-values indicate water/surfactant molar ratios for preparation of W/O type emulsion (surfactant concentration: 11.2×10^{-2} mol/l, Stirring speed: 3000 rpm).

In general, the following facts have been known: The size of water drops in W/O type emulsions decreases with increasing surfactant concentration at constant W/O ratio [33]. In case of constant surfactant concentration, high W/O ratio leads large size of water drops in the emulsions because the amount of surfactant adsorbed in a unit area on the water/oil interface is considered constant. Therefore, the size of SnO_2 spherical particles obtained by an emulsion method increases with decreasing surfactant content and increasing W/O ratio.

As mentioned above, in this study, the sphericity and size of obtained SnO_2 particles would be controlled by the stability and size of water drops in the emulsions as reaction fields, which is generally accepted for the preparation of spherical particles by the emulsion method.

3.2. Effect of revolution rate of emulsifier

Fig. 7 shows SEM photographs of SnO_2 particles obtained using emulsions prepared at various revolution rates of an emulsifier. In this case, the concentration of a surfactant and a W/O volume ratio were kept constant at 11.2×10^{-2} mol/l and 1/1, respectively. Fig. 8 shows the effect of the revolution rate of the emulsifier on the size of spherical particles randomly selected in SEM photographs, which is evaluated by a computer assisted image analysis.

As seen from Fig. 7, it was confirmed that spherical particles were obtained at all conditions except 1000 rpm, and that the highest sphericity was achieved

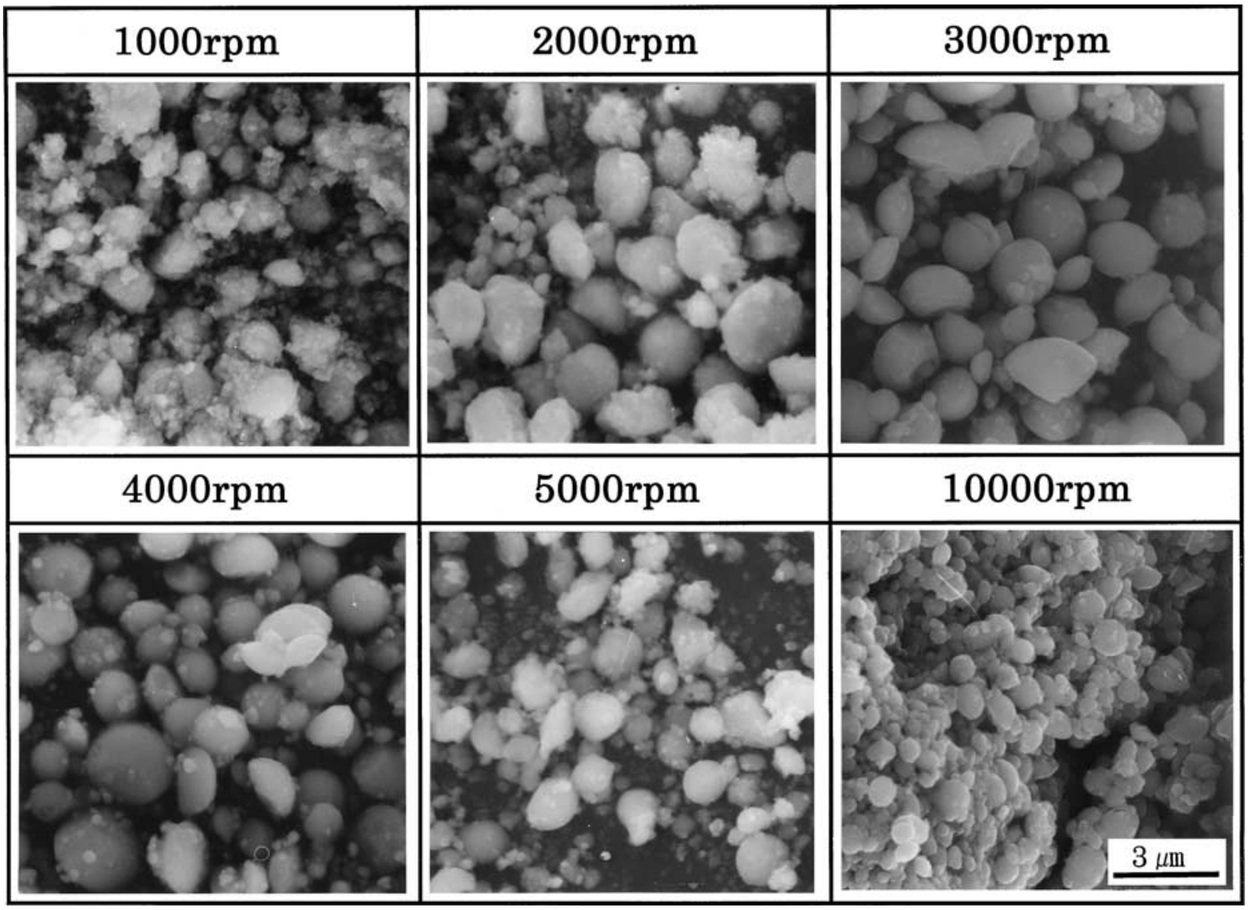

Figure 7 SEM photographs of SnO_2 particles obtained using W/O type emulsions prepared at various revolution rates of an emulsifier.

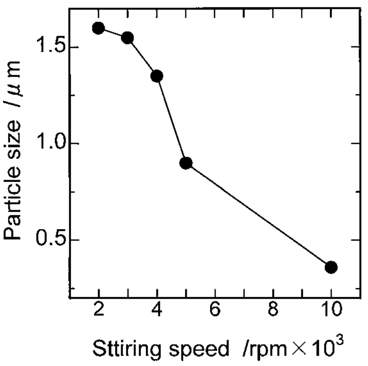

Figure 8 Effect of stirring speed for preparation of W/O type emulsion on the size of spherical SnO_2 particles (surfactant concentration: 11.2×10^{-2} mol/l, W/O ratio: 1/1, $R = 500$).

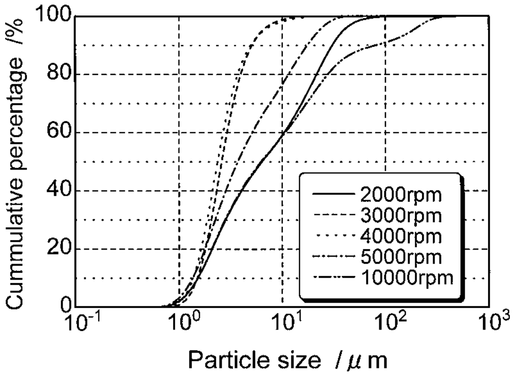

Figure 9 Change in the particle size distributions with revolution rate of an emulsifier (surfactant concentration: 11.2×10^{-2} mol/l, W/O ratio: 1/1, $R = 500$).

at 3000 rpm. Below 2000 rpm and above 5000 rpm, however, un-spherical fine particles increased. Especially, large amount of agglomerates of un-spherical and spherical fine particles were observed at 10000 rpm. From Figs 7 and 8, it was found that the size of spherical particles decreased with increasing revolution rate of the emulsifier.

Fig. 9 shows particle size distributions for the particles obtained using emulsions prepared at 3000, 4000 and 5000 rpm. At 4000 and 3000 rpm, at which spherical particles with relatively high sphericity were obtained, narrow particle size distributions almost near mono-sized particle dispersion were observed. On the other hand, in cases of 2000, 5000 and 10000 rpm, the particle size distributions were quite broad. Although the experimental results have not been shown, the samples of 2000 and 10000 rpm showed quite broad particle size distributions similar to that of 5000 rpm. Fine particles as shown in SEM photographs would form hard agglomerates due to their strong adhesive force, and thus the particle dispersion for measurement of particle size distribution would be unsatisfactory.

At low revolution rates, the broad size distribution for water drops in emulsions due to inhomogeneous mixing of water and oil is thought to be responsible for the multi-sized dispersion of obtained SnO_2 particles. In addition, in case of heterogeneous mixing, a stable emulsions are not obtained because the adsorption of the surfactant is ununiform on the interface between water and oil. When a chemical reaction occurs at the unstable interface, water drops would collapse before spherical particles form, and thus a large amount of un-spherical fine particles generate and agglomerate.

It is generally known that the size of water drop in the W/O emulsion decreases with increasing shear stress generated during emusification [31, 35]. Therefore, in this study, the reduction in size of water drops in emulsions at high revolution rates of the emulsifier is thought to be responsible for the smaller size of SnO_2 spherical particles as shown in Fig. 7. However, further increase of a stirring rate is predicted to make the emulsions unstable because excessive disintegration of water drops into smaller ones causes depletion of surfactant molecules on W/O interfaces [31, 35]. In this case, unstable water drops would collapse during interfacial reaction, resulting in the generation of un-spherical fine particles as well as the case of lower stirring rates. In addition, it is supposed that if the water drops are integrated during the stage of particle growth, nearly spherical fine particles are highly agglomerated as shown in the SEM photograph of a 10000 rpm stirred sample in Fig. 7.

From the above mentioned results, it is found that the revolution rate of the emulsifier must be adjusted to the optimal range at a fixed surfactant concentration and W/O ratio to obtain spherical particles having nearly mono-sized distribution. In order to obtain mono-sized spherical particles, it is necessary to prepare stable

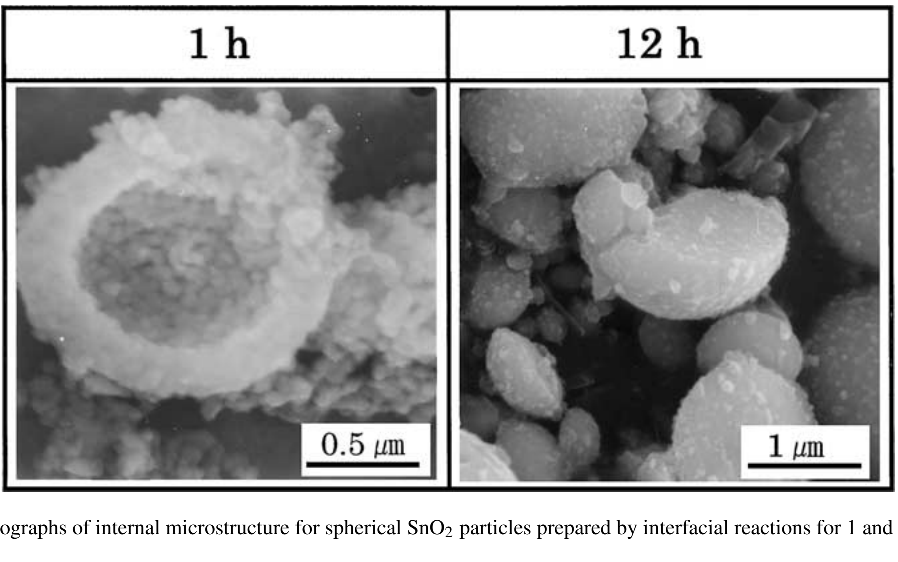

Figure 10 SEM photographs of internal microstructure for spherical SnO_2 particles prepared by interfacial reactions for 1 and 12 h.

reversed micelles composed of a single molecular layer of the surfactant. Therefore, the size of water drops in the W/O type emulsions should be controlled to suitable values for the formation of surfactant monolayers on a W/O interface at a fixed surfactant concentration and W/O ratio because the number of surfactant molecules adsorbed on a unit area of the interface is regarded as constant.

3.3. Internal structure of a spherical SnO_2 particle

Fig. 10 shows SEM photographs of spherical particles, which were prepared by interfacial reactions for 1 and 12 h, fractured by ultrasonication at 250 W in order to observe internal structure after firing at 900°C. For the interfacial reaction for 1 h, hollow spherical particles were obtained, and the increase of the reaction time made the particles dense. These results show that hydrated SnO_2 shells, which form at W/O/W interface after mixing a W/O type emulsion including dispersing phase of a Na_2SnO_3 aqueous solution with a $(NH_4)_2SO_4$ aqueous solution, grow toward inside with increasing reaction time. Therefore, it is supposed to be possible to prepare hollow spherical SnO_2 particles having various wall thicknesses by suitable selection of interfacial reaction time.

4. Conclusion

An attempt to prepare spherical particles was made using a W/O type emulsion as a reaction field. The effects of surfactant content, W/O ratio and stirring conditions for the preparation of emulsions, which determined the size of water drops in the emulsions, were investigated on the size and morphology of the obtained SnO_2 particles. The results are summarized as follows.

1. Spherical SnO_2 particles showing narrow particle size distributions were obtained at W/O ratio of 1/1 and surfactant content of 11.2×10^{-2} mol/l or 22.4×10^{-2} mol/l. The size and morphology of the obtained particles were largely influenced by a water/surfactant molar ratio (R-value) for the preparation of the emulsions. Particles having relatively high sphericity were obtained at an R-value below 1500. Especially, it was found that, in order to obtain mono-sized SnO_2 particles with narrow distributions, R-value should be adjusted to the narrow range from 250 to 500.
2. At constant surfactant concentration, the size of spherical SnO_2 particles increased with increasing W/O ratio. At constant W/O ratio, the higher the surfactant concentration, the smaller the size of SnO_2 particles.
3. The particle size of SnO_2 decreased with increasing revolution rate of an emulsifier for emulsification. At extremely low and high revolution rate of the emulsifier, particles showing high sphericity were not obtained, but agglomerates of un-spherical fine particles. Within the limits of this experiment, mono-dispersed spherical particles having narrow size distributions formed at revolution rates of 3000 and 4000 rpm.
4. The internal structure of a spherical particle depended on interfacial reaction time. An interfacial reaction for short time yielded hollow spherical SnO_2 particles, and the internal structure of the particles became denser with increasing reaction time.

References

1. M. KOISHI, in "Biryu-shi sekkei" (Kogyo-chosakai, Tokyo, 1988) p. 23.
2. T. SUGIMOTO, *Hyo-men* **22** (1984) 177.
3. J. TAKAHASHI, *J. Soc. Powder Tech. Jpn.* **29** (1992) 286.
4. N. MIZUTANI, *ibid.* **26** (1989) 183.
5. S. HIRANO, *Ceramics* **22** (1987) 1052.
6. E. MATIJEVIC, *J. Colloid Interface Sci.* **58** (1976) 374.
7. B. J. INGEBRETHEN and E. MATIJEVIC, *J. Aerosol Sci.* **11** (1979) 271.
8. T. SUGIMOTO and E. MATIJEVIC, *J. Colloid Interface Sci.* **74** (1980) 227.
9. D. L. CATONE and E. MATIJEVIC, *ibid.* **48** (1974) 291.
10. M. D. SACKS, T. Y. TSENG and S. Y. LEE, *Am. Ceram. Soc. Bull.* **63** (1984) 301.
11. J. E. BLENDELL, H. K. BOWEN and R. L. COBLE, *ibid.* **63** (1984) 797.
12. B. FEGLEY JR, P. WHITE and H. K. BOWEN, *ibid.* **64** (1985) 1115.
13. T. OGIHARA, T. IKEMOTO, N. MIZUTANI and M. KATO, *J. Mater. Sci.* **21** (1986) 2771.
14. K. UCHYAMA, T. OGIHARA, T. IKEMOTO, N. MIZUTANI and M. KATO, *ibid.* **22** (1987) 4343.
15. T. OGIHARA and N. MIZUTANI, *Inorganic Mater.* **3** (1996) 194.
16. T. IMAI, *Shikizai* **71** (1998) 194.
17. Y. NAKAHARA, *ibid.* **59** (1986) 543.
18. S. KIDA, *J. Soc. Powder Tech. Jpn.* **24** (1987) 474.
19. M. JEFELICCI JR, M. R. DAVOLOS, F. J. D. SANTOS and S. J ANDRADE, *J. Non-Cryst. Solids* **247** (1999) 98.
20. J. F. MACALEER, P. T. MOSELEY, J. O. W. NORRIS and D. E. WILLIAMS, *J. Chem. Soc., Faraday Trans. 1* **83** (1987) 1323.
21. V. LANTTO and P. ROMPPAINEN, *J. Electrochem. Soc.* **135** (1988) 2550.
22. K. H. SONG and S. J. PARK, *J. Mater. Sci.: Mater. in Electronics* **4** (1993) 249.
23. N. L. WU, S. Y. WANG and I. A. RUSOKAVA, *Science* **285** (1999) 1375.
24. C. NAYRAL, T. O. ELY, A. MAISONNAT, B. CHAUDRET, P. FAU, L. LESCOUZERES and A. P. LAVGNE, *Adv. Mater.* **11** (1999) 61.
25. A. K. MUKHOPADHYAY, P. MITRA, A. P. CHATTERJEE and H. S. MATI, *Ceram. Int.* **26** (2000) 123.
26. E. R. LEITE, I. T. WEBER, E. LONGO and J. A. VARELA, *Adv. Mater.* **12** (2000) 965.
27. H. SHIOMI, H. KOBAYASHI, T. KIMURA and M. NAKAMURA, *J. Mater. Sci.: Mater. in Electronics* **7** (1996) 437.
28. H. SHIOMI, H. KOBAYASHI and M. NAKAMURA, *J. Ceram. Soc. Jpn.* **106** (1998) 213.
29. H. SHIOMI and H. FURUKAWA, *J. Mater. Sci.: Mater. in Electronics* **11** (2000) 31.
30. M. ABE, *Shikizai* **67** (1994) 263.
31. H. NAKAJIMA, *ibid.* **71** (1998) 526.
32. J. BOYD, C. PARKINSON and P. SHERMAN, *J. Colloid Interface Sci.* **41** (1972) 359.
33. T. KAWAI, *Shikizai* **71** (1998) 449.
34. A. KITAHARA and K. FURUSAWA, in "Saishin Koroidoka-gaku" (Koudan-sya, Tokyo, 1993) p. 41.
35. H. NAKAJIMA, *Hyo-men* **36** (1998) 39.

Received 19 April 2001
and accepted 22 July 2002